Symmetry

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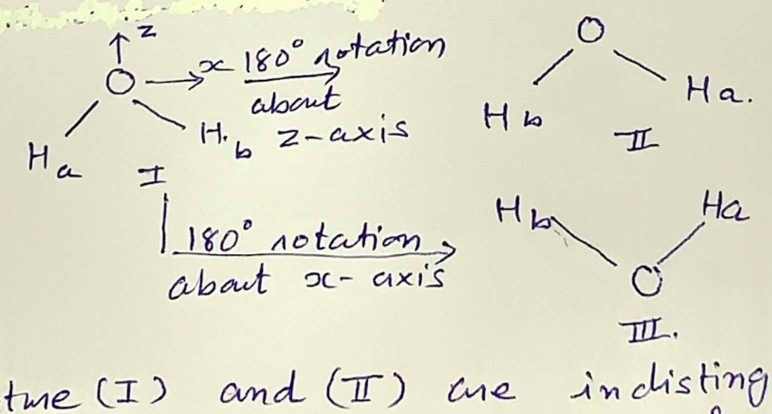
⊛ Introduction:-

Symmetry is a widely distributed property in nature. The human body, each wing of butterfly is symmetric, the left hand side is the mirror image of the right hand side. Thus a plane of symmetry divides the two halves and a reflection in this plane transfers the left hand side to the right hand side and vice-versa. Symmetry of molecule and solid is very powerful tool for developing and understanding of bonding and physical properties symmetry is very important tools in theoritical and inorganic chemist also to predict the nature of molecular orbitals, to predict whether electronic and vibration spectroscopic transitions can be observed.

⊛ Symmetry Operation:-

Symmetry operation is the process carried out on the molecule which bring it from the original orientation to another equivalent orientation.

e.g.



Structure (I) and (II) are indistinguishable (equivalent) therefore rotation of water molecule about z-axis is sym. operation but (I) & (III) are unequivalent. ∴ rotation about x-axis is not sym. operation.

Elements of symmetry:-

symmetry operation in a molecule are carried out with respect to some fixed plane, axis one point, these features are called elements of symmetry.

e.g. In above example rotation of water molecule about z-axis gives indistinguishable molecule therefore z-axis is an sym. element but rotation of water molecule about x-axis gives distinguishable orientation therefore x-axis is not the sym. element.

Various Types Of Symmetry Operations:-

By examination of different molecules there are four types of symmetry operations: (i) Rotation (ii) Reflection (iii) Improper rotation and (iv) Inversion.

(i) Rotations:- C_n [n-fold axis of symmetry]

A rotation through $2\pi/n$ radians or $360/n$ about an axis is called C_n or n-fold axis of symmetry.

where n = any integral value = 1, 2, 3 .....

If angle of rotation = θ then $n = 360/\theta$.

C_n: This is an imaginary axis passing through the molecule, over which rotation can be carried out to take the molecule from one orientation to another equivalent orientation.

$C_1 \rightarrow$ $n = 1$ = Rotation through an angle 2π radians
= $360°$ Rotation

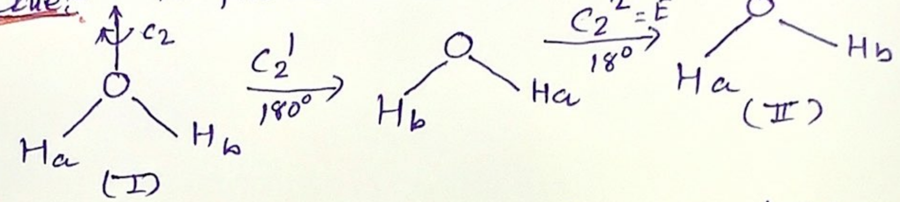
→ Identity Operation (E):- Doing no change on the object or any molecule is called identity operation

→ or Rotation of molecule about $360°$ is called Identity operation. (E).

* C_2 - Two fold axis of symmetry :-

The z-axis in water molecule is a two fold axis of e symmetry, rotation through C_2-axis about 180° is gives equivalant Oriention and two times rotation gives identity E and One time rotation about 180° called C_2' and anticlockwise rotation called C_2^{-1}.

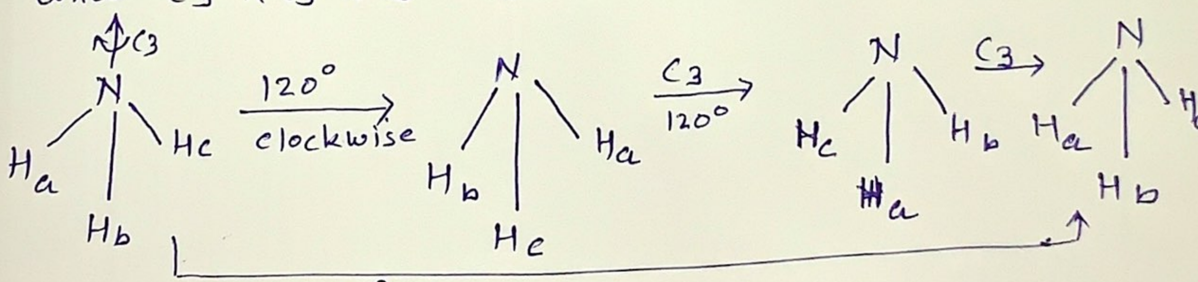
(*) Que:- To prove $C_2^2 = E$.



* C_3 : Three fold axis of symmetry :

In the triangular planer and triangular pyramidal shaped molecules contain three-fold axis of symmetry. In these molecules $C_3^3 = E$ & $C_3^2 = C_3^{-1}$.

C_3 operation performed twiece i.e. $C_3' \times C_3' = C_3^2$ and $C_3' \times C_3' \times C_3' = C_3^3 = E$. Also $C_3^2 = C_3^{-1}$



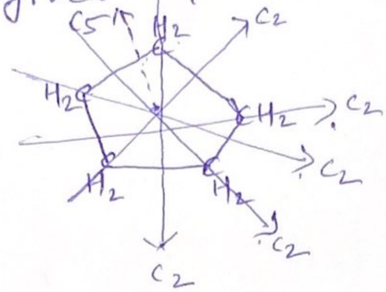
$C_3^3 = E$.

* C_4 - Four fold axis of symmetry :-

A rotation through $2\pi/4$ radian or 90° ~~is~~ about the principle axis of rotation is called four fold axis of symmetry. In the C_4 operation three types of operations possible, C_4', C_4^2 and C_4^3, $C_4^4 = E$.

⊛ C_5 : Five fold axis of symmetry:-

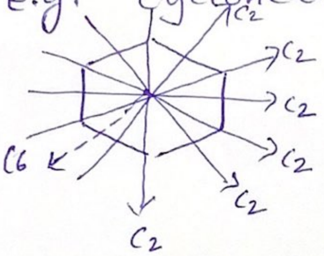
Rotation of molecule about 72° through C_5 axis of gives equivalent orientation. e.g. Cyclopentane.



$C_5 \perp 5C_2 \rightarrow D_5$

⊛ C_6 :- Six-fold axis of symmetry:-

Rotation of molecule about 60° through C_6 axis,
e.g. Cyclohexane.



$C_6 \perp 6C_2 \rightarrow D_6$

Possible operation $C_6^1, C_6^2, C_6^3, C_6^4$ & C_6^5,
Also $C_6^6 = E$

⊛ C_∞ ! An axis of infinite fold symmetry :-

Linear molecues, such as acetylene, HCl, CO_2, etc. have an infinite fold axis of symmetry.
A rotation through an idefinitely small angle θ about the internuclear axis gives equivalent orientation.

$H - Cl \xrightarrow{\theta} C_\infty$ $\quad$ $H - C \equiv C - H \xrightarrow{\theta} C_\infty$

∞C_2 $\quad$ $C_\infty + \infty C_2 \rightarrow D_\infty$

[2] Reflection : Plane Of Symmetry : 6

It is defined as: An imaginary plane within the molecule which ~~is~~ devides it into two parts which are mirror images of each other. If reflection carried out over the plane of symmetry new orientation will be equivalent to the original orientation.

The plane is the element of symmetry and process of reflection is sym. operation. If double reflection is carried out it gives the original orientation. $\therefore \sigma^2 = E$

This can be classified into three types.

(i) Vertical Plane (σv) : It is an imaginary plane passing through principal axis of rotation and one of the subsidary axis (if present) is called vertical plane (σv).

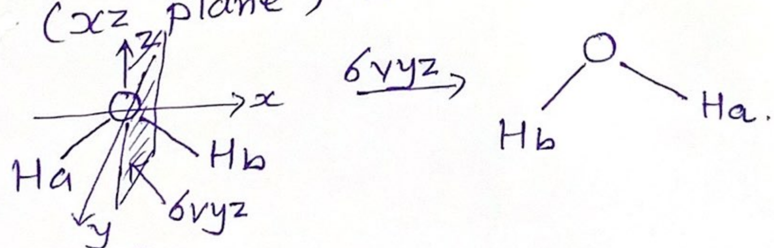
(ii) Horizontal Plane (σh): The plane perpendicular to the principal axis of rotation is called σh.

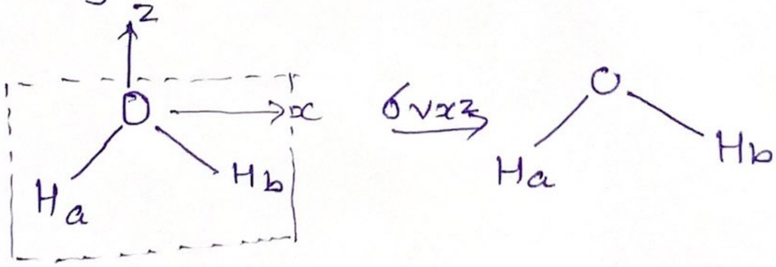
(iii) Dihedral Plane (σd) The plane passing through the principal axis but passing in between two subsidary axis is called dihedral Plane σd

(*) Vertical Plane Of Symmetry :-

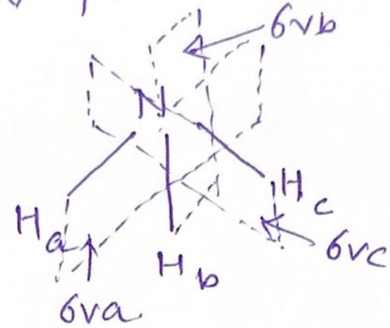
→ Water molecule, SO_2 etc. (V shaped) has two σv, one passing throug O and in betn two H atoms (yz plane) is $\sigma v yz$ and other is the molecular plane (whole molecule) is called $\sigma v xz$.

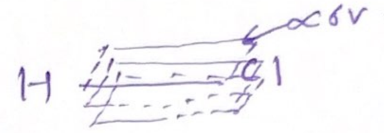
(xz plane) is called





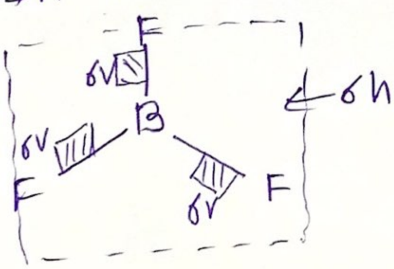
→ In ammonia molecule there are three σ_v present passing through N atom and one of the H-atom. HCl, H_2, O_2, Cl_2 etc. molecules contain $\infty\sigma_v$ planes.

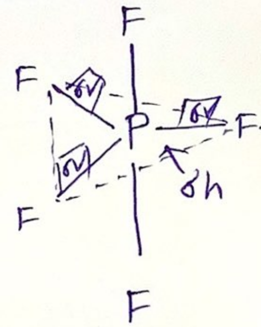


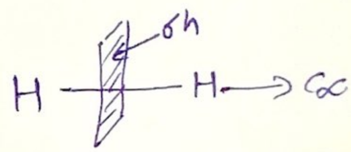


* Horizontal Plane Of Symmetry (σ_h):—

The plane perpendicular to the principal axis of rotation is called horizontal plane (σ_h). In BF_3 molecule $3\sigma_v$ and one σ_h plane present. In PF_5 triangular bipyramidal molecule there are $3\sigma_v$ and one σ_h plane present. In H_2, Cl_2 ... molecule $\infty\sigma_v$ and σ_h plane present.

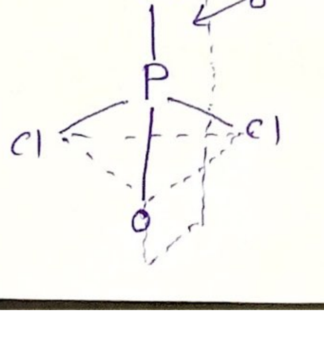






There are some molecules with no axis of symmetry but have plane of sym.

e.g.



Dihedral Plane: (σd):

The plane passing through principal axis of rotation and in between to subsidary axes of rotation is called dihedral plane (σd).
e.g. Allene molecule contain 3 C_2 axes, perpendicular to each other 2 dihedral planes passing through one of the C_2 axis and in between two C_2 axes.

[3] Improper rotation (S_n):-

It is an imaginary axis on which the molecule has to be rotated and then reflected on a plane perpendicular to the rotation axis to attain an equivalent orientation.

$$S_n = C_n \times \sigma h = \sigma h \times C_n$$

order of operation does not affect the resut.

When n is even number:

$$S_n^n = C_n^n \times \sigma h^n = E \times E = E.$$
$$S_6^6 = C_6^6 \times \sigma h^6 = E \times E = E.$$

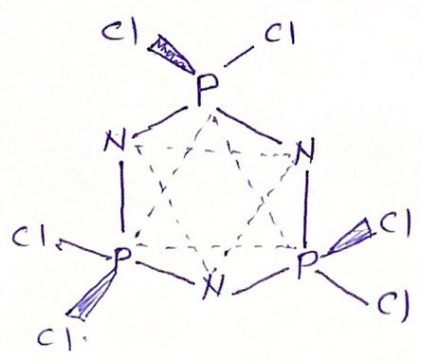
& n = odd numbers:

$$S_n^n = C_n^n \times \sigma h^n = E \times \sigma h = \sigma h$$
$$S_n^{2n} = C_n^{2n} \times \sigma h^{2n} = E \times E = E.$$

e.g. $S_3^3 = C_3^3 \times \sigma h^3 = E \times \sigma h = h$

$S_3^6 = C_3^6 \times \sigma h^6 = E \times E = E$

e.g. $(PNCl_2)_3$: S_3 axis present.

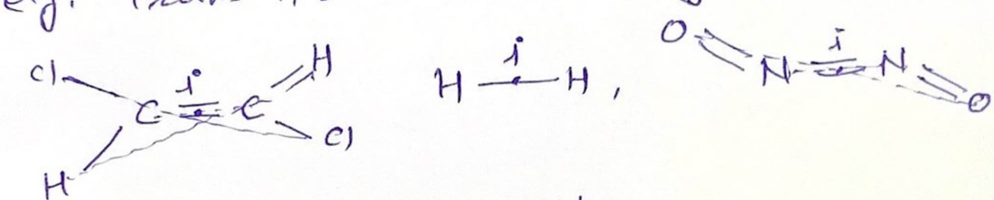


[4] Inversion Centre (i) [Centre of Symmetry].

This is an imaginary point in the centre of the molecule, through which the reflection of each atom can be carried out to result in its coincidence with an equivalent atom.

or If any atom in the molecule is connected with the centre of sym. and extended equally on the other side, it meets another equivalent point.

e.g. Trans 1, 2 di chloro ethylene, N_2O_4, H_2 --



$i = S_2 = C_2 \times \sigma h.$

* Point Groups *

A molecule may have different elements of symmetry such as axes of sym., planes of sym., centre of sym. etc. A collection of these elements of sym. constitute a sym. group.

If in an object of finite dimensions or in molecules at least one point of the object remains fixed when any of these sym. operations is carried out, then the sym. group is called the point group.

* Point Group :— Rules must obey

1. Each group contains the identity element E, called the unit element of the group.
2. The product of any two elements of a group is also an element of that group.
3. If A, B and C are elements in a group then they follow associative multiplication.

$A(BC) = (AB)C$

If for all elements $A \times B = B \times A$, the group is said to be Abelian.

(4). For each element A and A^{-1} are carried out in succession the net effect is the identity E.

i.e. $A \times A^{-1} = A^{-1} \times A = E$.

* Important Point Groups :

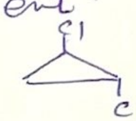
[1]. Cn - Groups : [Cyclic group] :

In the Cn group only n-fold axis and identity operation E present. group contains $C_n, C_n^2, \cdots C_n^n = E$

* C_1 : without any sym. operation only E present.
  e.g. SbOCl, CHClBrI ..

C_2 : E, C_2^1 ~~operation~~ elements present.

e.g. 1, 2 dichloro cyclo propane ,



All elements in a cyclic group commute with each other hence cyclic group is Abelian.

[2] Cnv groups :- ($C_n + n\sigma_v$)

These group obtained from Cn group by adding vertical plane of symmetry σ_v.

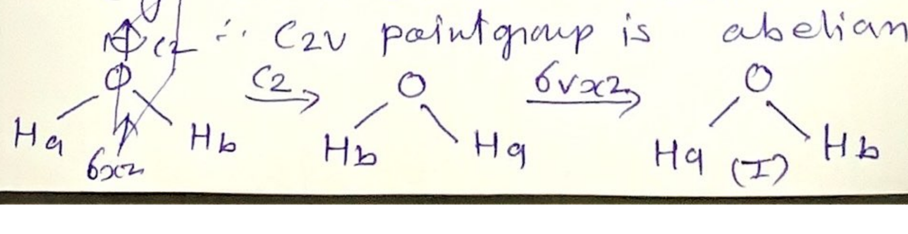
e.g. C_{2v} point group :- C_{2v} pointgroup contain E, C_2, σ_{vxz} and σ_{vyz} elements.

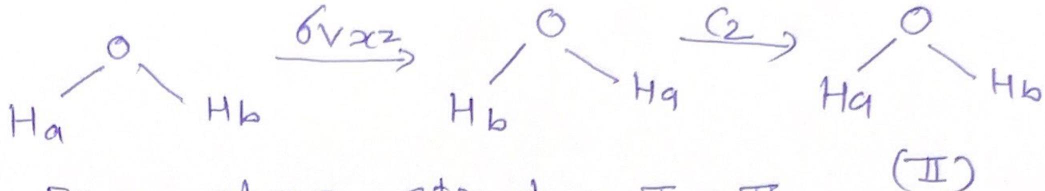
que: Prove that C_{2v} pointgroup is Abelian pointg

⇒ For the C_{2v} pointgroup the result is independent of the order in which the two operations are carried out.

e.g. $C_2 \times \sigma_{vxz} = \sigma_{vxz} \times C_2$ ∴ $A \times B = B \times A$

∴ C_{2v} pointgroup is abelian point group.



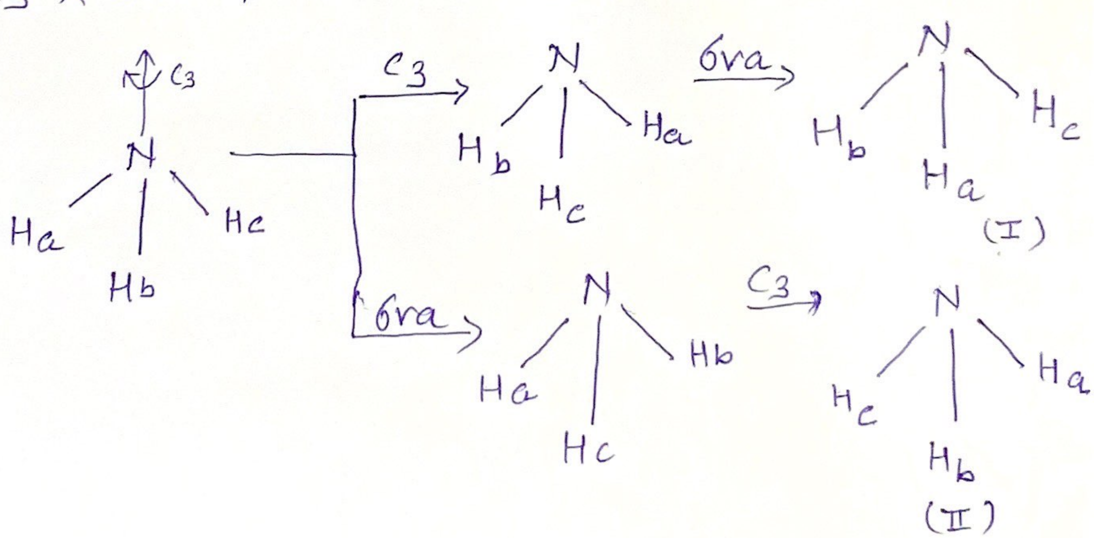


From above structure I = II
∴ We can ~~sa~~ say that C_{2v} is Abelian point gr

(*) V – Shaped molecules like H_2O, SO_2, H_2S, & H_2Se
NH_2, BCl_2^- ....etc. contain C_{2v} point group.

C_{2v}	E	$C_{2(z)}$	$\sigma_{v(xz)}$	$\sigma'_{v(yz)}$
E	E	C_2	σ_v	σ'_v
$C_{2(z)}$	C_2	E	σ'_v	σ_v
$\sigma_{v(xz)}$	σ_v	σ'_v	E	C_2
$\sigma'_{v(yz)}$	σ'_v	σ_v	C_2	E

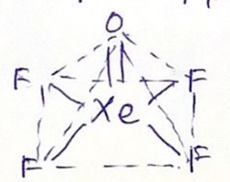
(*) Non Abelian C_{3v} point group: E, C_3 + $3\sigma_v$
C_{3v} point gr. contain: E, C_3^1, C_3^2, σ_{va}, σ_{vb} & σ_{vc}
e.g. Triangular pyramidal shaped molecules
NH_3, PH_3, CH_3^- etc.
C_{3v} is non abelian point group because $AB \neq BA$
$C_3 \times \sigma_{va} \neq \sigma_{va} \times C_3$ (∵ I ≠ II)



Multiplication table for C_{3v} point groups:-

C_{3v} ↓ second operation	First	Operation →				
	E	C_3^1	C_3^2	σ_{va}	σ_{vb}	σ_{vc}
E	E	C_3^1	C_3^2	σ_{va}	σ_{vb}	σ_{vc}
C_3^1	C_3^1	C_3^2	E	σ_{vc}	σ_{va}	σ_{vb}
C_3^2	C_3^2	E	C_3^1	σ_{vb}	σ_{vc}	σ_{va}
σ_{va}	σ_{va}	σ_{vb}	σ_{vc}	E	C_3^1	C_3^2
σ_{vb}	σ_{vb}	σ_{vc}	σ_{va}	C_3^2	E	C_3^1
σ_{vc}	σ_{vc}	σ_{va}	σ_{vb}	C_3	C_3^2	E

* C_{4v} Point group:- E, $C_4 + 4\sigma_v$
  e.g. Square pyramidal molecules, $XeOF_4$, IF_5...



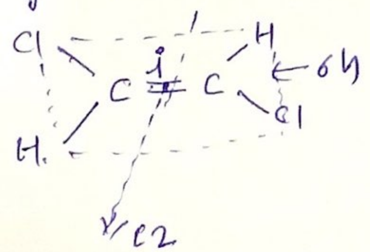
Sym. operations: $E, C_4^1, C_4^2, C_4^3, 4\sigma_v$.

* $C_{\infty v}$:- e.g. heteronuclear diatomic molecules, HCl, HF ---

H —— Cl ⇄ C_∞ Sym. elements: E, C_∞, $\infty\sigma_v$.

* C_{nh} group:-
  This group contain E, C_n, σ_h and $C_n \times \sigma_h = S_n$.

e.g. C_{2h}:- E, C_2, σ_h, i
When n is even number i is present.
Trans 1,2-dichloro ethylene is the example and this group is an abelian point group.



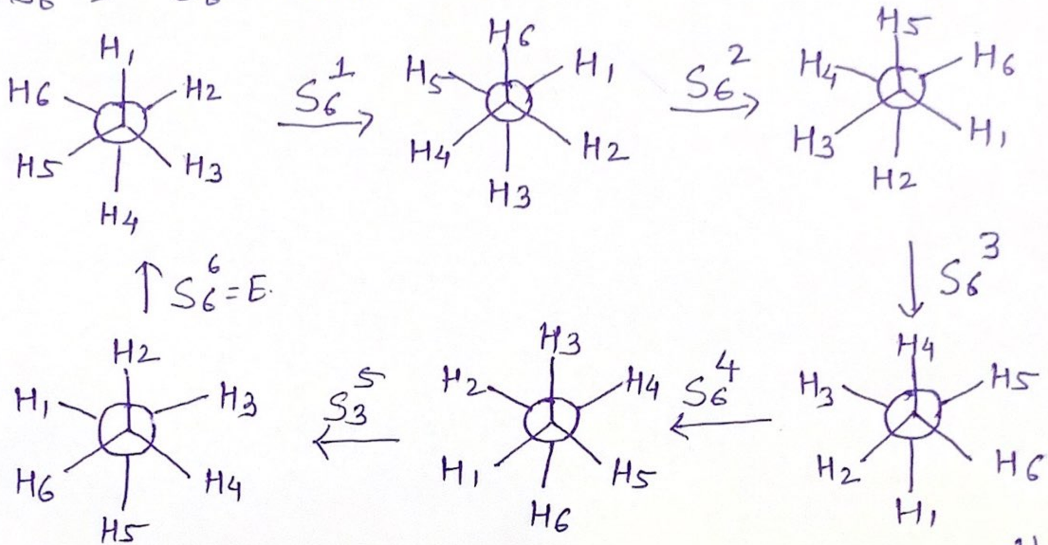
$C_2 \times i = i \times C_2$
When n is odd number at that time inversion centre i absent

Sn groups :- [Presence of Sn axis].

Q: Prove that $S_n^n = E$ for n = even number with proper example.

e.g. Staggared ethane contain S_6 axis.

$S_6^6 = C_6^6 \times \sigma h^6 = E \times E = E.$



From the above structures we can say that $S_6^6 = E$ & $n = 6$ (even number.).

Que:- Prove than $S_n^{2n} = E$ for n = odd number.

⇒ e.g. Eclipsed ethane contain S_3 axis.

$\therefore S_3^3 = C_3^3 \times \sigma h^3 = E \times \sigma h = \sigma h$

$S_3^6 = C_3^6 \times \sigma h^6 = C_3^3 \times C_3^3 \times \sigma h^6 = E \times E \times E = E$

$S_3^2 = C_3^2 \times \sigma h^2 = C_3^2$

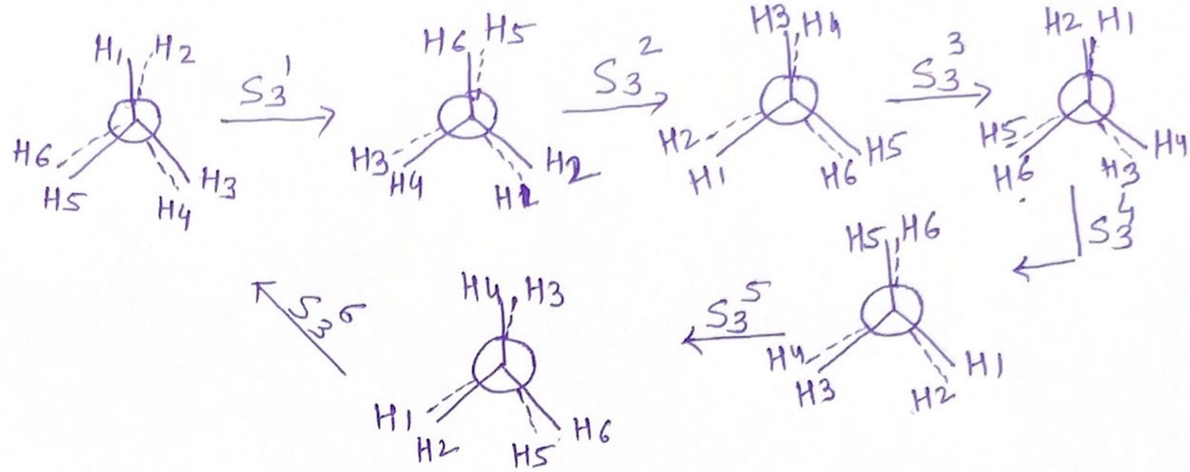
$S_3^4 = C_3^4 \times \sigma h^4 = C_3^3 \times C_3^1 \times \sigma h^4 = E \times C_3^1 \times E = C_3^1$

$S_3^5 = C_3^5 \times \sigma h^5 = C_3^3 \times C_3^2 \times \sigma h$

$= E \times C_3^2 \times \sigma h$

$= C_3^2 \times \sigma h.$

Eclipsed ethane.



Dn Groups [Dihedral Groups] :- $C_n \perp nC_2$

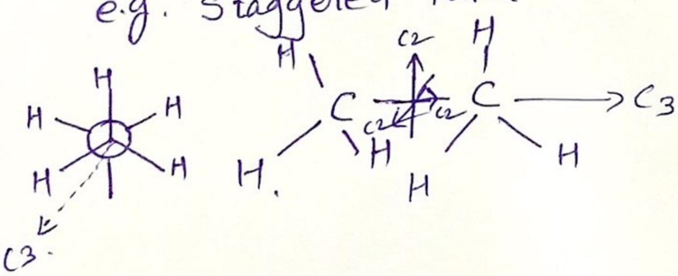
This groups have n-two fold axes, perpendicular to principal n-fold axis. There is no plane of symmetry.

D1 group: Identical with C_2 group because it contains E and C_2.

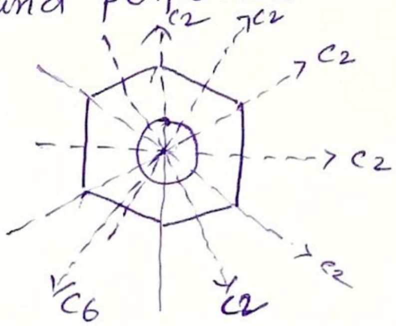
D2 :- E, $C_2^{(x)}$, $C_2^{(y)}$, $C_2^{(z)}$

D3 :- E, $2C_3$ (C_3^1, C_3^2), $3C_2 \perp C_3$

e.g. Staggered form of ethane contain $C_3 \perp 3C_2$

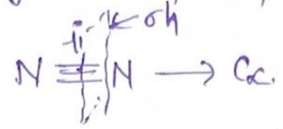


D6 : Benzene molecule contain C_6 principal axis and perpendicular $6C_2$ axes present



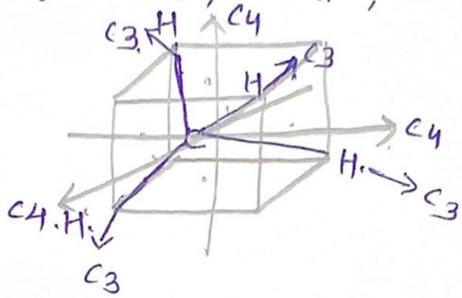
(21) $D_{\infty h}$:- $E, C_\infty \perp \infty C_2, \sigma_h, \infty \sigma_v, i$

e.g. N_2, H_2, Cl_2, CO_2, Cl_2, Acetylene...



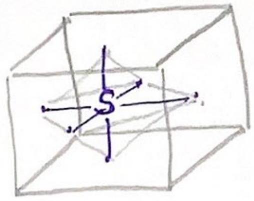
(22) T_d (Tetrahedral point group) :- $E, 3C_4, 4C_3, 6\sigma_d$ $(3S_4)$

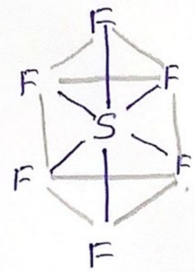
e.g. CH_4, ClO_4^{-1}, CCl_4



(23) O_h (octahedral Pointgroup): $E, 3C_4(S_4), 4C_3(S_3)$,
$3\sigma_h, 6C_2, 6\sigma_v, i$

e.g. SF_6, SiF_6, $Mo(CO)_6$





* Reference book:
Introductory Quantum Chemistry fourth edition
– A.K. Chandra.

⇒ **Dnd Groups :-** $D_n + n\sigma_d$

The addition of σ_d operation to D_n groups.

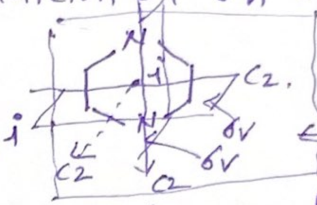
e.g. In Allene ($H_2C=C=CH_2$)

D_{2d}: $E, C_2(S_4) \perp 2C_2, 2\sigma_d$

⇒ **Dnh Groups :-** The addition of σ_h to D_n group.

e.g. Pyrazine molecule

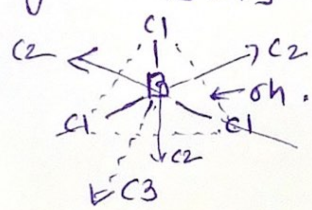
D_{2h}: $E, C_2 \perp 2C_2, \sigma_h, 2\sigma_v, i$



When n = even numbers inversion centre i present and n = odd numbers i absent.

D_{3h} :- $E, C_3 \perp 3C_2, \sigma_h, 3\sigma_v$

e.g. BCl_3 (Triangle planar molecules).



$D_{\infty h}$:- $E, C_\infty \perp \infty C_2, \sigma_h, \infty\sigma_v$

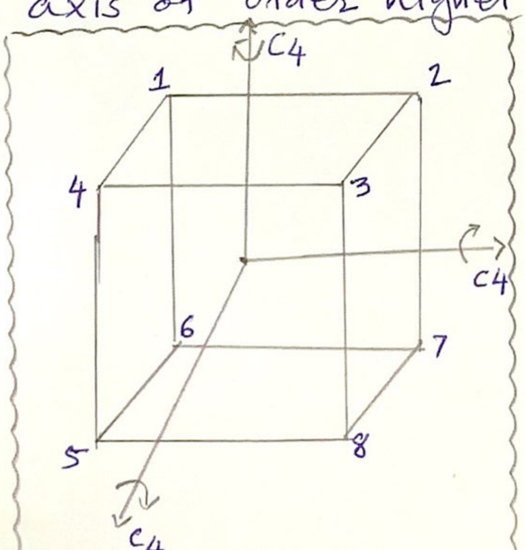
e.g. H_2, Cl_2, N_2 ....

Cubic Point Groups :-

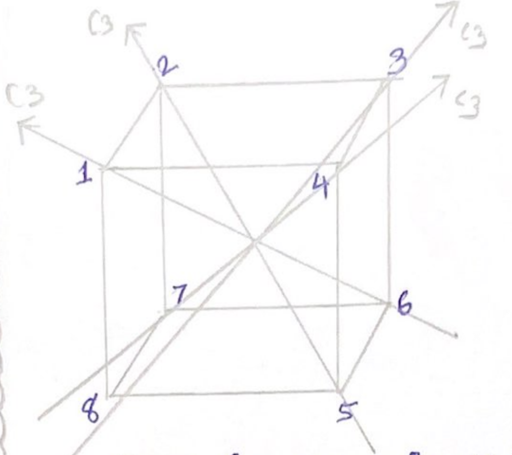
In the cubic point groups always more than one axis of order higher than two. For example, a cube has three C_4 and four C_3 axes present. Three C_4 axes are perpendicular to each other and four C_3 axes are:

$C_3^{(1)}$ passes through point 1 & 6
$C_3^{(2)}$ passes through point 2 & 5
$C_3^{(3)}$ passes through point 3 & 8
$C_3^{(4)}$ passes through point 4 & 7

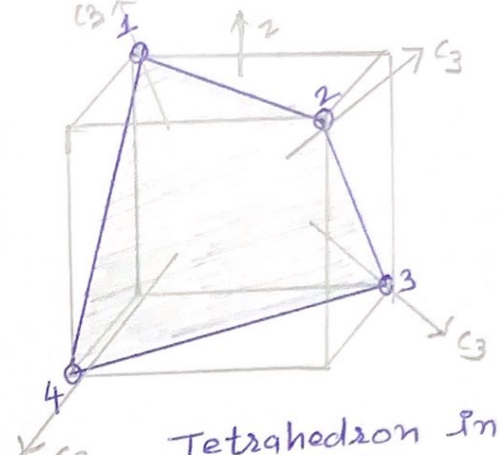
There are two types of point group in cubic symmetry. Tetrahedral (T) and octahedral (O) groups.



Three C_4 axes in Cube



Four C_3 axes in a cube

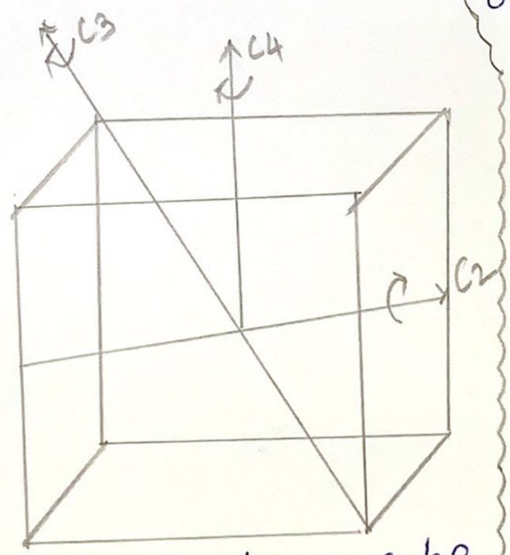


Tetrahedron in a cube

* **Td groups:** The addition of a σd plane to T group is Td. (Tetrahedral). e.g. Methane

* Ti (Th) Groups:- Addition of center of sym. to T group

* **O group** :→ There are ~~four~~ three C_4 axes passing through the centers of the opposing faces. Four C_3 axes passing through opossite corners. There are six C_2 axes passing through midpoint of opposite edges.



C_4, C_3 & C_2 axes in a cube

There are 24 different operations in O group.

$E, [C_4^1, C_4^2, C_4^3] \times 3 = 9$,

$[C_3^1, C_3^2] \times 4 = 8$ and

$6C_2$ operation possible.

Oh groups:- Addition of center of symmetry to O group gives Oh groups. In this point group E, $3C_4$, $4C_3(S_3)$, $3\sigma h$, $6\sigma v$, $9C_2$, $4S_6$, i elements present and total 48 operations are possible

e.g. SF_6, SiF_6^{-2}, $PbCl_6^{-2}$, $Fe(CN)_6^{-4}$, $Mo(CO)_6$.

How to Determine the Pointgroup of a molecule?

Following rules are important.

(1) Three special groups which do not have any unique axis of high symmetry.

(a). Tetrahedron (T_d) (b) Octahedron (O_h) and

(c) Icosahedron (I_h).

(2) If molecule contain only a mirror plane $\rightarrow C_s$

If it has no symmetry at all $\rightarrow C_1$

(3) If molecule contain C_n principal axis of rotation and also perpendicular to nC_2 axis present.

(a) D_n group.

(b) σ_h present D_{nh}

(c) σ_d present D_{nd}.

(4). If molecule contain C_n principal axis of rotation but perpendicular nC_2 absent.

(a) No plane of symmetry C_n

(b) $n\sigma_v$ planes present. C_{nv}

(c) σ_h plane present C_{nh}.

(5) If molecule is linear

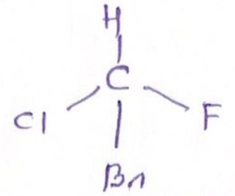
(a) σ_h present :- $D_{\infty h}$

(b) σ_h absent : $C_{\infty v}$.

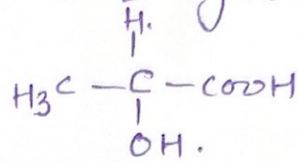
① C_1 point group:

Symmetry element :- E (only)

(a)

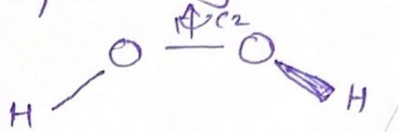


(b) 2-hydroxy propanoic acid.



② C_2 point group: symmetry elements :- E, C_2

H_2O_2 (Trans)

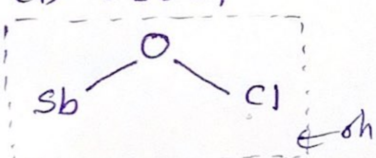


③ C_3 Point group:- Sym. elements :- E, C_3

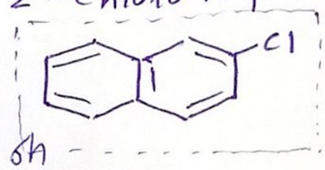
Dimethyl ethane (Crouch) :-

④ C_s point group:- sym. elements: E, C_1, σh (only σ)

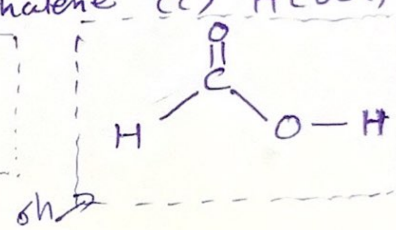
(a) SbOCl



(b) 2-Chloro Naphthalene



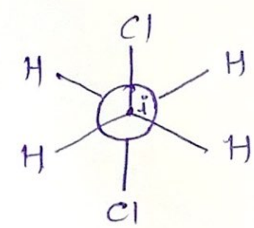
(c) HCOOH



(d) CH_2ClBr.

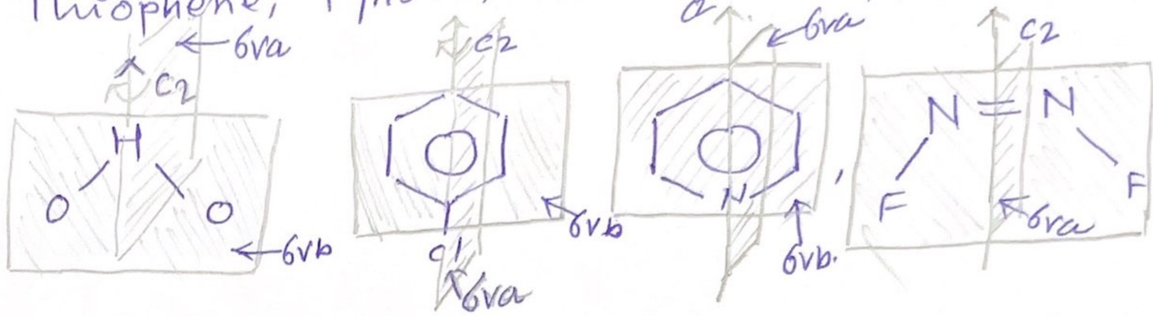
⑤ C_i point group :- E, C_1, i (only i present except E)

e.g. 1,2 di chloro ethane
(Staggered)



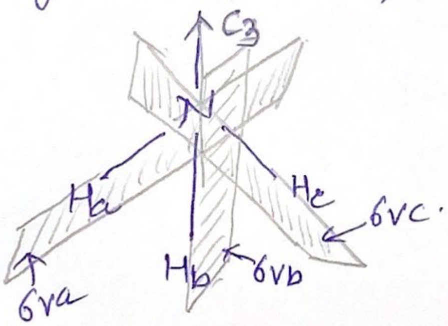
(6) **C_{2v} Point group** :- $E, C_2, \sigma_{v xz}, \sigma_{v yz}$

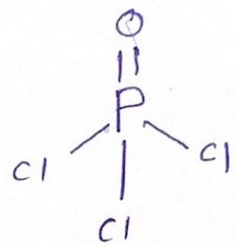
e.g. H_2O, SO_2 H_2Se, Chlorobenzene, furan, Thiophene, Pyrrole, phenanthrene, N_2F_2 (cis)..

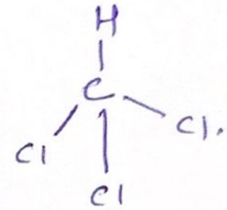


(7) **C_{3v} Point group** :- $E, C_3^1, C_3^2, \sigma_{va}, \sigma_{vb}, \sigma_{vc}$.

e.g. NH_3, NF_3, PH_3, CH_3Cl, $CHCl_3$, $POCl_3$

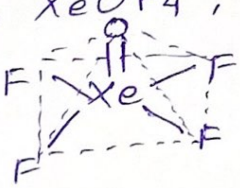


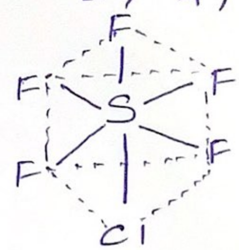




(8) **C_{4v} Point group** :- $E, C_4^1, C_4^2, C_4^3, 4\sigma_v$

e.g. $XeOF_4$, SF_5-Cl





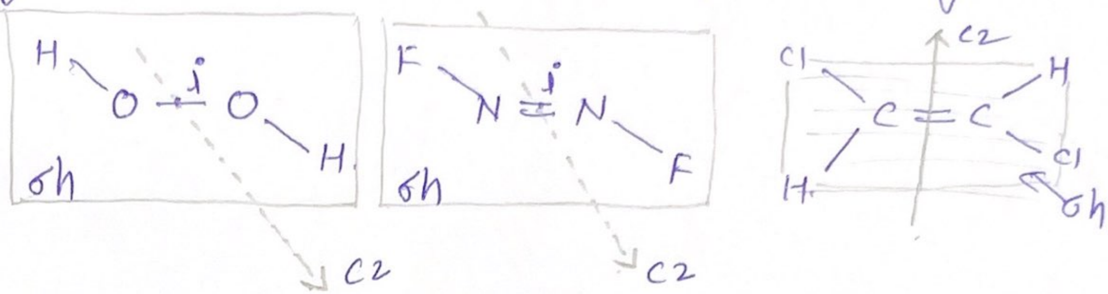
(9) **$C_{\infty v}$ Point group** :- $E, C_\infty, \infty\sigma_v$

e.g. HCl, HCN, HF, N_2O, HBr

$H — Cl \xrightarrow{} C_\infty$

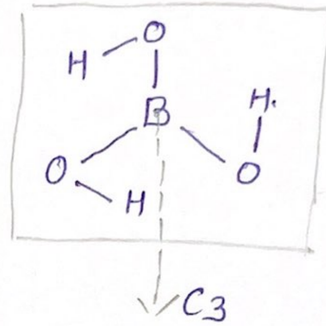
(10) **C_{2h}** :- E, C_2, σ_h, i

e.g. H_2O_2 (trans), N_2F_2 (trans), trans ethylene dichloride



(11) **C_{3h}** :- $E, C_3 (S_3), \sigma_h$

e.g. H_3BO_3

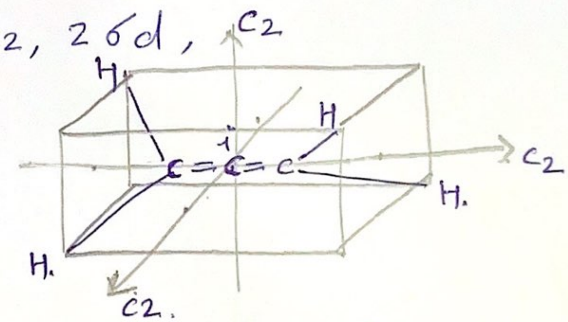


(12) **C_{4h}** :- $E, C_4(S_4), \sigma_h, i$

e.g. Swastik.

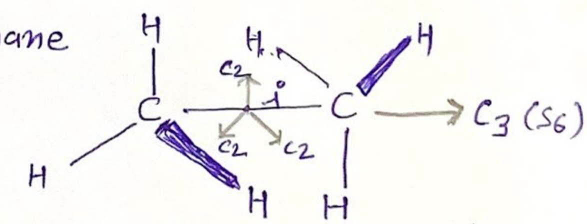
(13) **D_{2d}** :- $E, C_2 (S_4), \perp 2C_2, 2\sigma_d$,

e.g. Allene (C_3H_4)



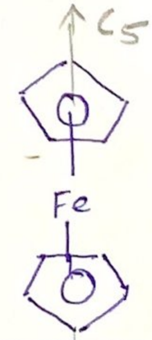
(14) **D_{3d}** :- $E, C_3 (S_6), \perp 3C_2, 3\sigma_d, i$

e.g. Staggered ethane



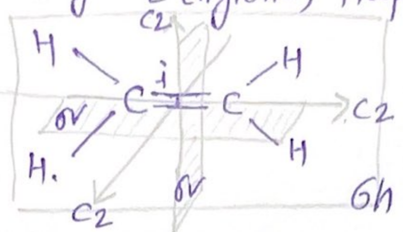
(15) **D_{5d}** :- $E, C_5 (S_{10}), \perp 5C_2, 5\sigma_d$

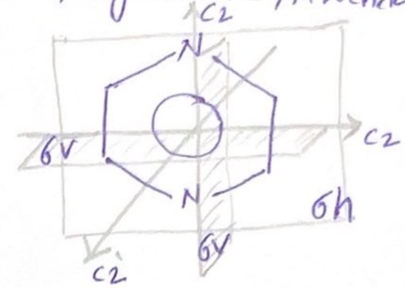
e.g. Ferrocene staggered.



(16) **D_{2h}** :- $E, C_2 \perp 2C_2, \sigma h, 2\sigma v, i$

e.g. Ethylene, Naphthalene, Pyrazine, Anthracene ....

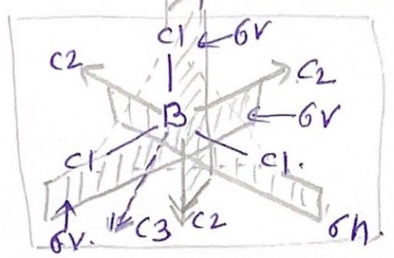


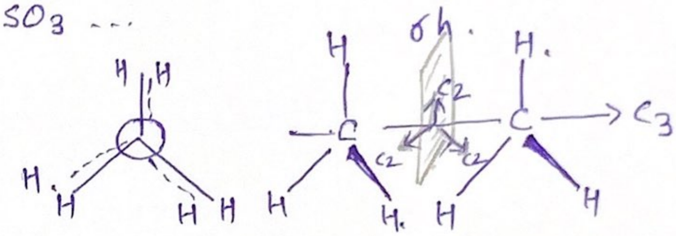


(17) **D_{3h}** :- $E, C_3, \perp 3C_2, \sigma h, 2\sigma v$.

e.g. BCl_3, BF_3, PCl_5, CO_3^{-2}, NO_3^{-1}, 1,3,5, trichlorobenzene.

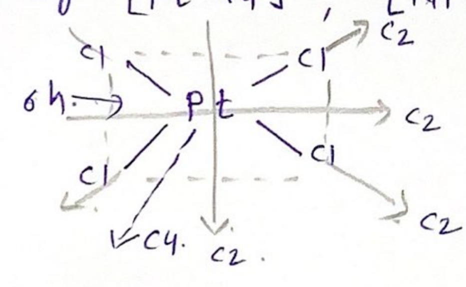
eclipsed ethane, SO_3 ...





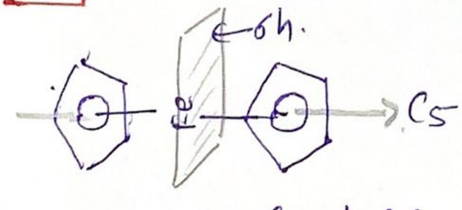
(18) **D_{4h}** :- $E, C_4 \perp 4C_2, \sigma h, 4\sigma v, i$

e.g. $[PtCl_4]^{-2}$, $[Ni(CN)_4]^{-2}$, cyclobutane ...



(19) **D_{5h}** :- $E, C_5 (S_5) \perp 5C_2, \sigma h, 5\sigma v$.

e.g. Eclipsed ferrocene.



(20) **D_{6h}** :- $E, C_6 (S_6) \perp 6C_2, \sigma h, 6\sigma v, i$

e.g. Benzene