GROUP THEORY

Symmetry Elements,
Symmetry Operations,
Point Groups.

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SYMMETRY ELEMENTS & SYMMETRY OPERATIONS :

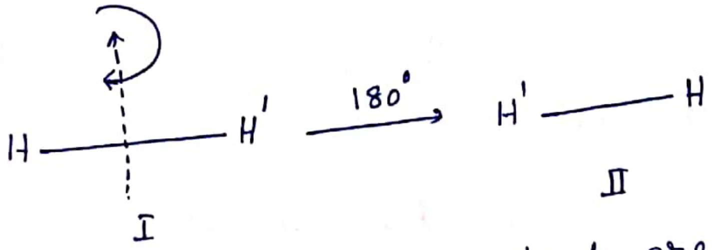
Symmetry implies as a geometrical property of the substance in which a part is in harmony with other, as well as to whole structure

The word symmetry is used in one of two ways

- Mutual relation of the parts of something in respect of position and magnitude, relative arrangement of parts, relative measurement of parts ; proportion.
- Harmony of parts with each other and the whole, fitting, regular & balanced arrangement and relation of parts or elements ; the condition or quality of being well proportioned or well balanced.

"Scientifically, an object is said to be symmetrical, if it can take up more than one equivalent (indisintinguishable) orientations"

For example :



Strutture I & II of H_2 molecule are indistinguishable. though structure I is rotated by an angle 180°.

- The term symmetry become synonymous to beauty. Because nature made most of the things symmetrical.

Symmetry operations :-

The process carried out on the molecule, which brings it from the original orientation to another equivalent orientation (indistinguishable from original) is called symmetry operation.

Symmetry elements:

The symmetry operation over which indistinguishable structure is obtained, called symmetry elements.

Thereare following symmetry elements

1. Identity 2. Centre of Symmetry or Inversion centre
3. Axis of symmetry or Proper axis 4. Plane of symmetry
5. Rotation reflexation axis or, Axis of improper rotation or Improper axis.

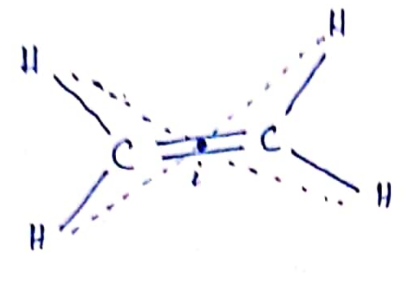
1. Identity :

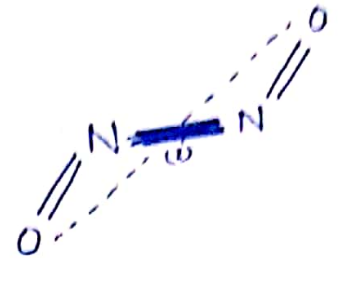
The operation which brings back the molecule to the original orientation is called identity operation It is represented by 'E' from the German word 'Einheit' meaning unity.

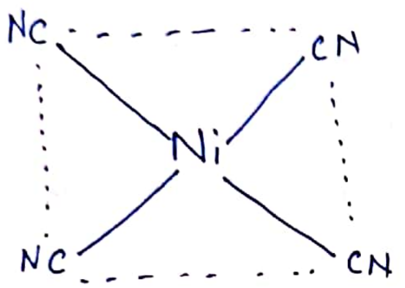
The identity operation infact means that doing nothing on the molecule. Hence each molecule has 'E' operation.

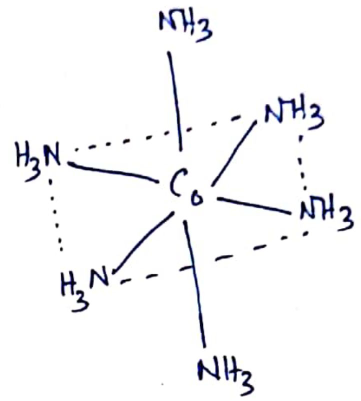
2. Centre of Symmetry or Inversion Centre:

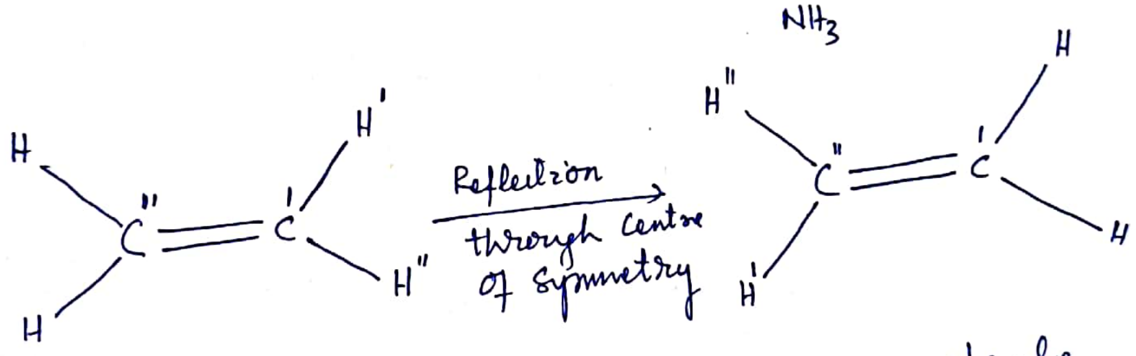
The imaginary point mirror at the centre of molecule which makes reflection of each atom and gives indistinguishable structure is called centre of symmetry or Inversion centre. It is denoted by 'i'







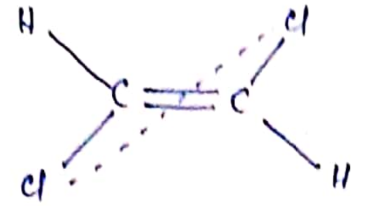




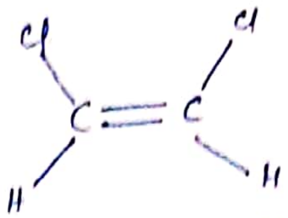
Thus as a result of this operation the molecule is completely inverted to an equivalent orientation

→ Only one inversion is possible. Because second inversion gives back the original orientation

→ ~~Tetraed~~ Tetrahedral molecule (CH_4 ...) has no centre of symmetry.



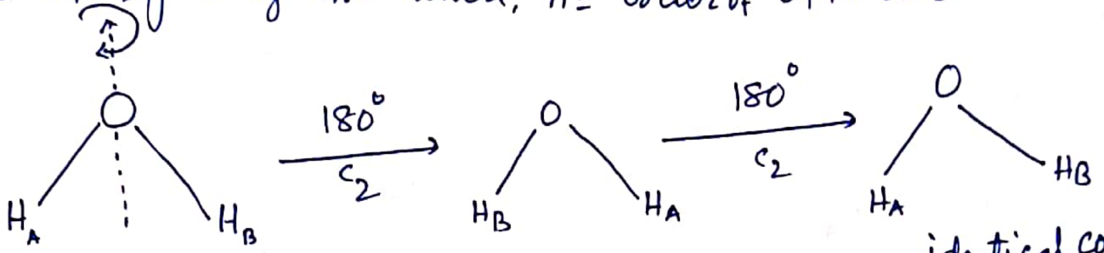
trans-form.



(No centre of symm.)

3. Axis of Symmetry or, Proper axis:

The imaginary axis passing through the molecule, rotation around which clockwise/anticlockwise makes indistinguishable structure is called axis of symmetry. It is represented by C_n. where, n = order of the axis



identical configuration

Equivalent configuration

C_n = Proper axis of highest order

$$n = \frac{360^\circ}{\theta}$$

$$\theta = 180^\circ \quad \therefore \quad C_n = \frac{360^\circ}{180^\circ} = 2 = C_2 : \text{Two fold axis}$$

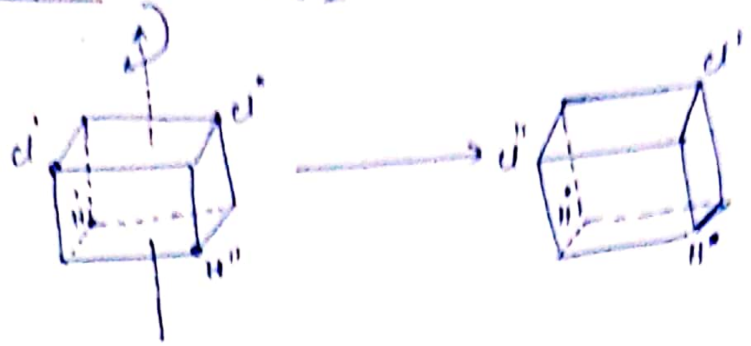
$$\boxed{C_2 \cdot C_2 = C_2^2 = \text{Identical configuration} = E}$$

$$C_n^n = E$$

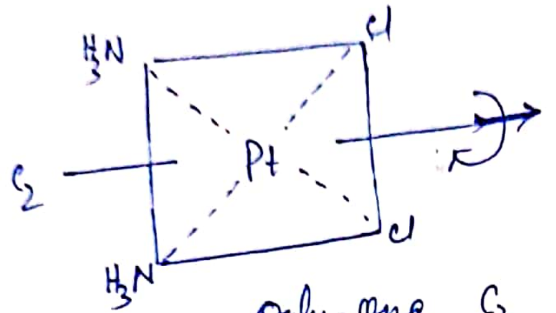
→ All V-shaped molecules have C_2-axis

e.g.: H_2O, H_2S, H_2Se, H_2Te, NO_2, SO_2, $SnCl_2$ etc

CH_2Cl_2 , $Co(Py)_2Cl_2$.

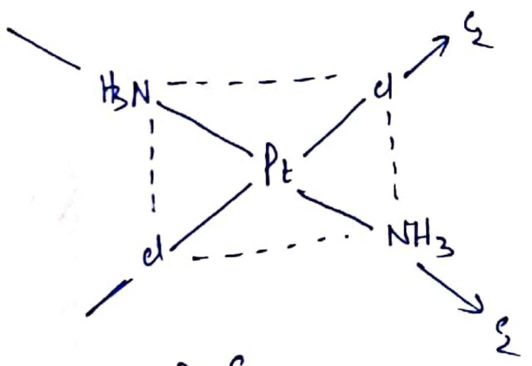


cis- $Pt(NH_3)_2Cl_2$



only one C_2

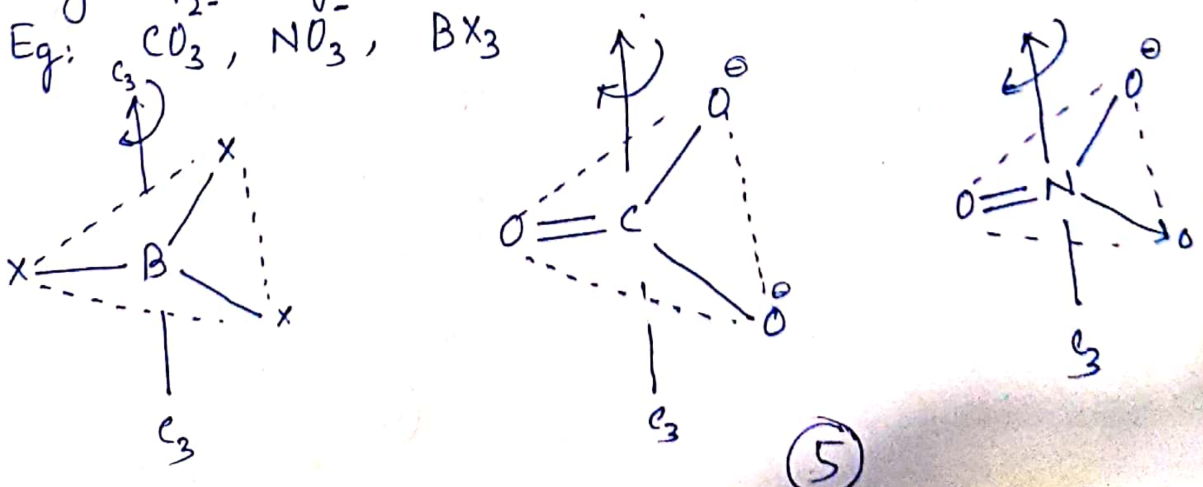
trans-$[Pt(NH_3)_2Cl_2]$



2 C_2

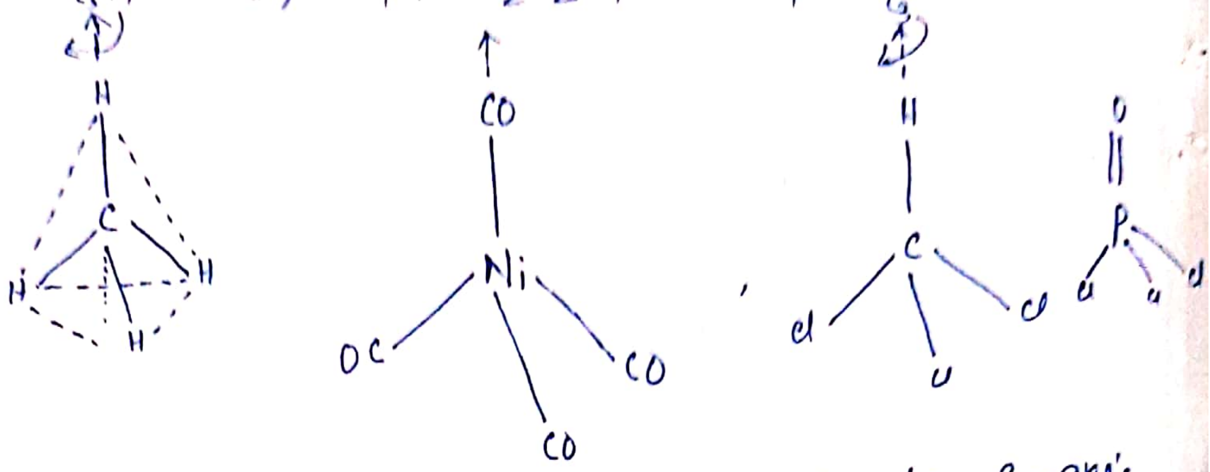
→ Trigonal planar geometry has C_3-axis ($\theta = 120°$)

Eg: CO_3^{2-}, NO_3^-, BX_3



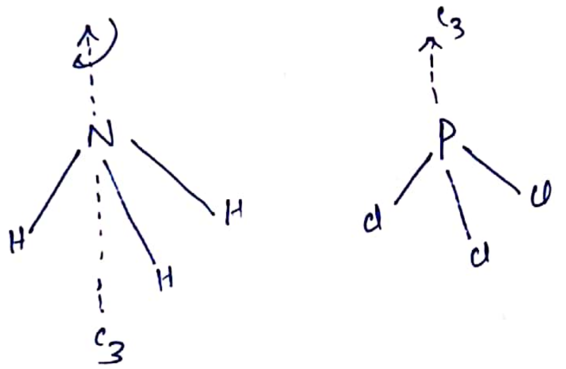
- Tetrahedral structure has C_3-axis.

CH_4, $CHCl_3$, CCl_4, CH_2Cl_2, $Ni(CO)_4$, $POCl_3$



- sp^3 hybridised conical pyramidal structure has C_3-axis

Eg: NH_3, NX_3, PX_3, PH_3

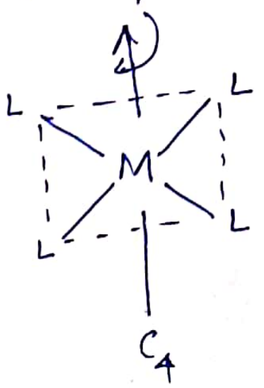


C_4 - axis

$\theta = 90^\circ$

$n = \frac{360^\circ}{90^\circ} = 4 = C_4$

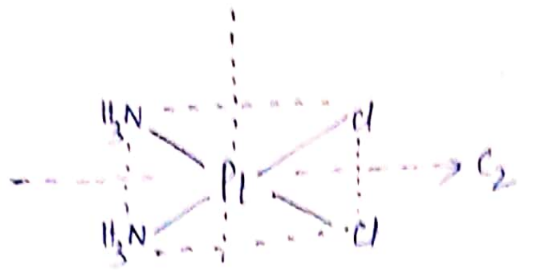
Square planar complexes has C_4- axis.



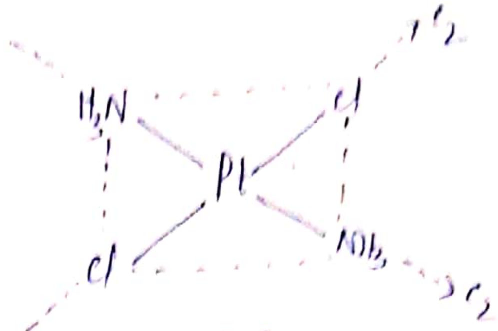
$[Pt(NH_3)_4]^{2+}$, $[Cu(NH_3)_4]^{2+}$,

$[Cu(CN)_4]^{2-}$, $[PdCl_4]^{2-}$

Cis-$[Pt(NH_3)_2Cl_2]$

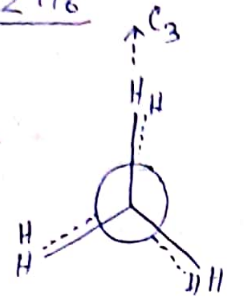


Cis-dipyridine dichloro Pt(II)
1 C_2

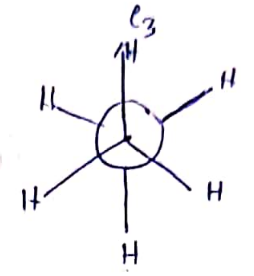


2 C_2

C_2H_6



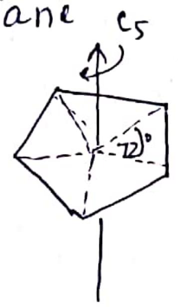
eclipsed



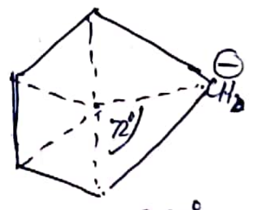
staggered.

C_5 - axis

Cyclopentane

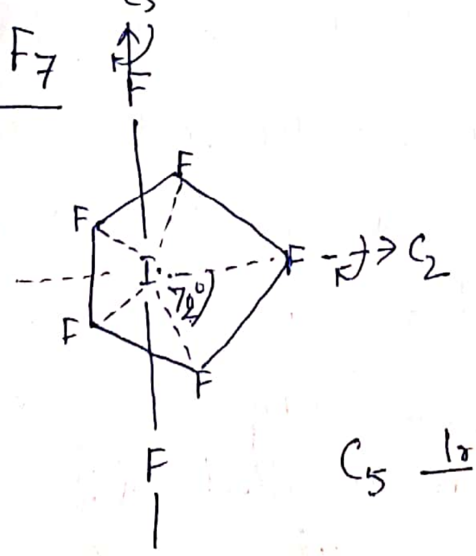


Cyclopentadiene ion



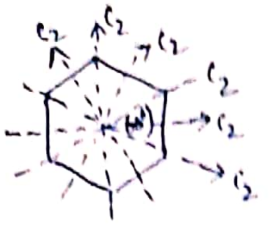
$C_n = \frac{360°}{72} = 5 = C_5$

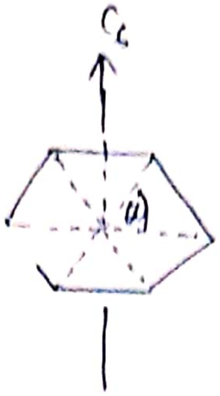
IF_7



$C_5 \perp 5C_2$

C_6-axis





$$C_n = \frac{360^\circ}{60^\circ} = 6 = C_6$$

$C_6 \perp r$ $6C_2$

Note: Axis of the highest order is known as the principal axis and, other lower order axes are called subsidiary axis.

4. PLane of Symmetry/Reflection at a plane:-

The imaginary mirror plane passing through the molecule makes indistinguishable structure is called plane of symmetry.

It is three types

(a) Vertical plane of symmetry

(b) Horizontal plane of symmetry

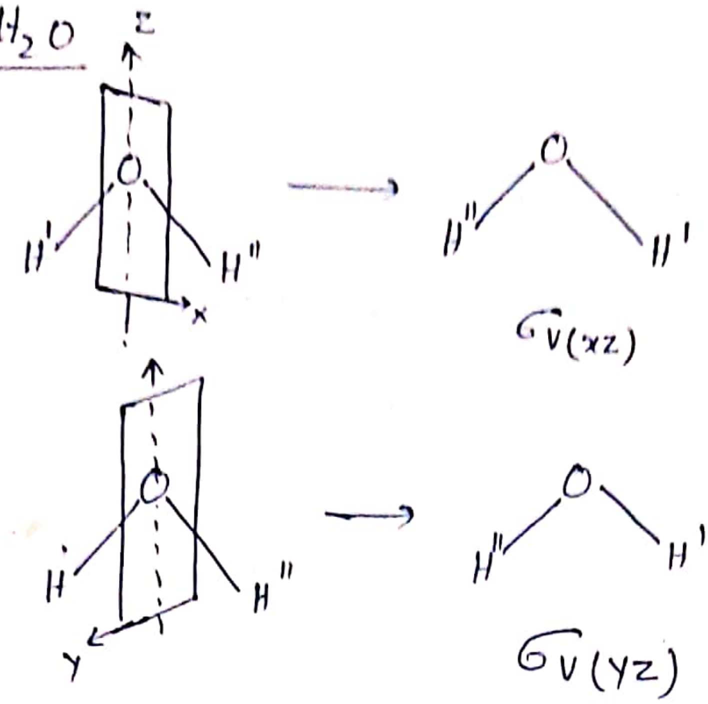
(c) Dihedral plane of symmetry

(a) Vertical plane of symmetry (σ_v):—

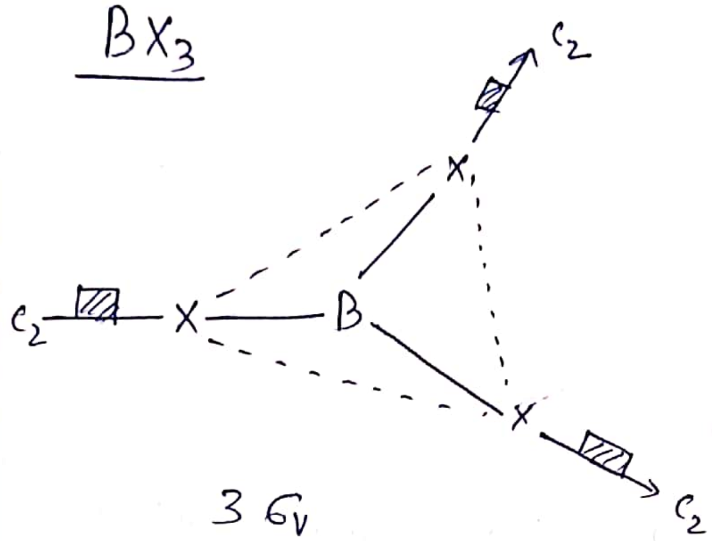
Plane passing through the vertical axis is called vertical plane of symmetry. It is denoted by σ_v.

→ Any plane containing the z-axis (vertical axis) is called σ_v.

H_2O

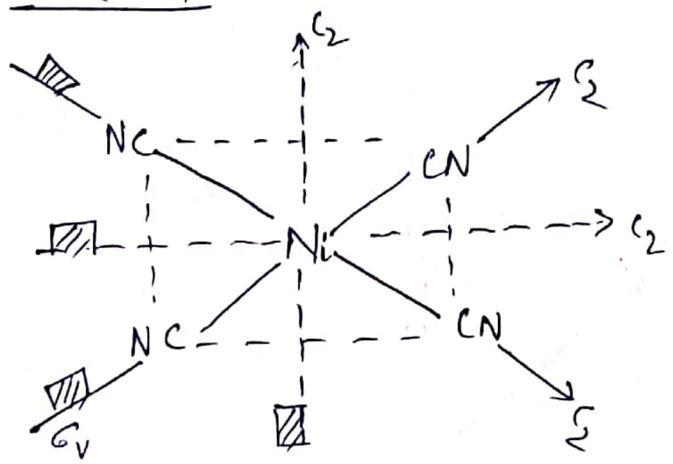


BX_3



$3\sigma_v$

$Ni(CN)_4$



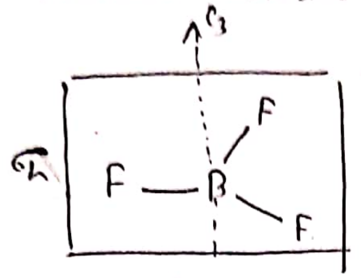
$\Rightarrow 4\sigma_v$

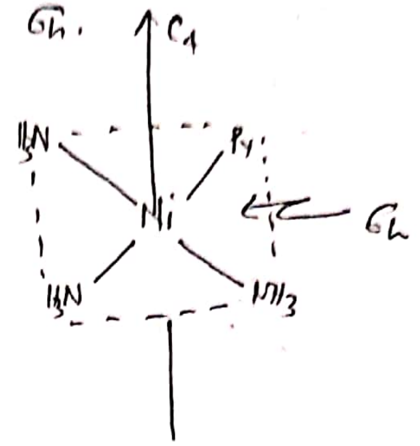
Note: All planar molecules can have σ_v.

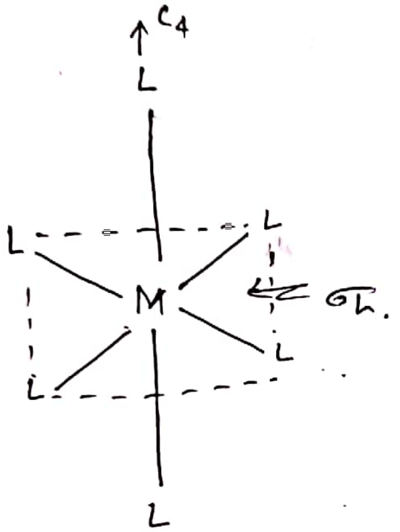
(b) HORIZONTAL PLANE OF SYMMETRY (σ_h)

The plane perpendicular to proper axis is called horizontal plane of symmetry (σ_h)

→ PLanar molecule Contains σ_h.

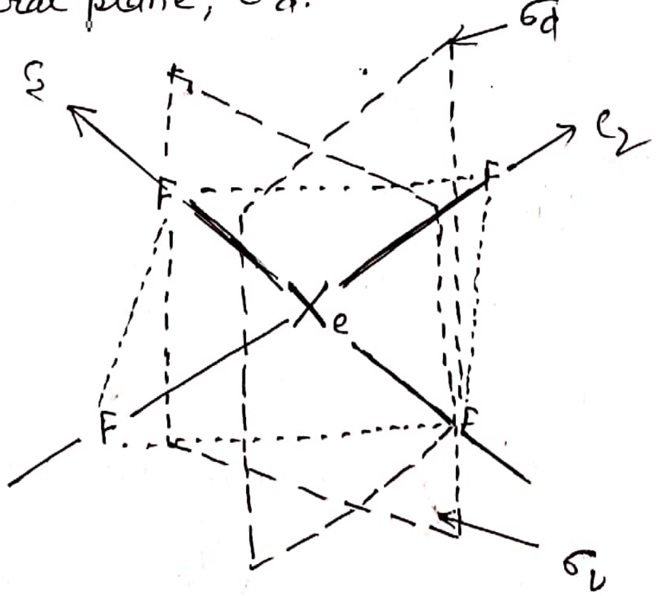




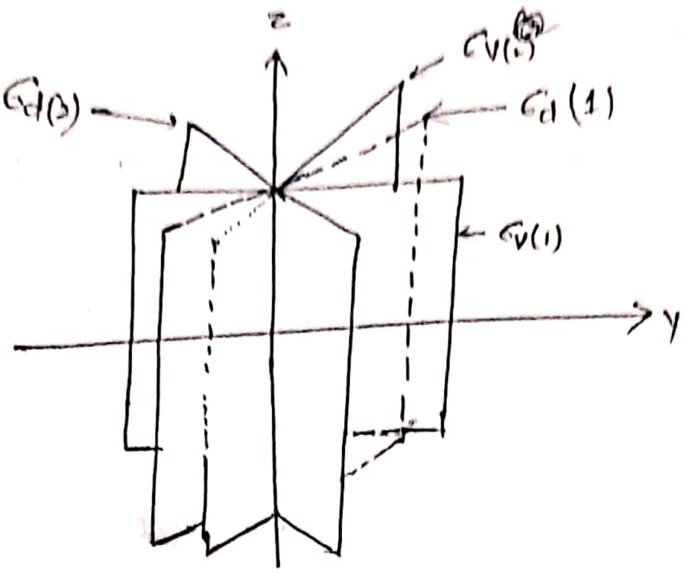


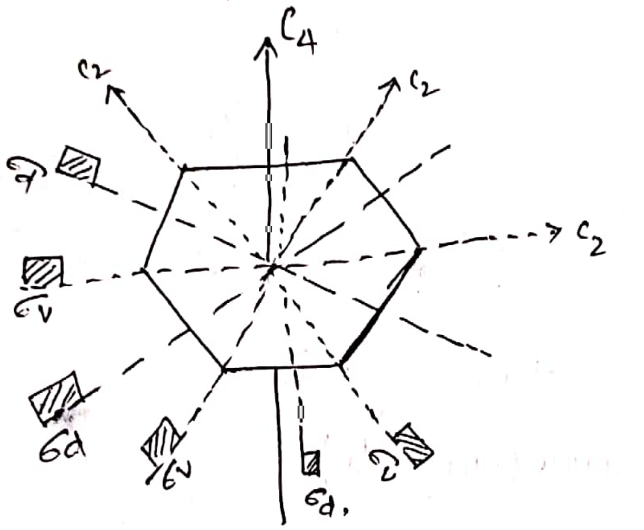
(c) DIHEDRAL PLANE (σ_d)

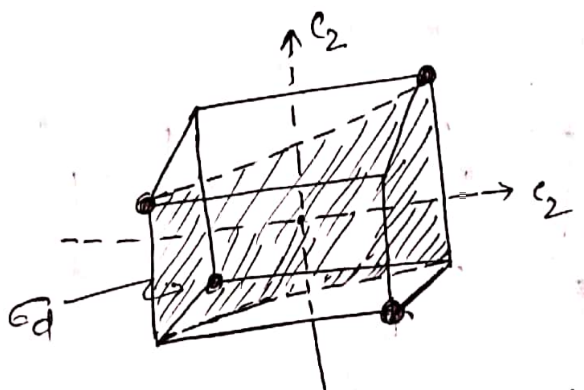
Vertical plane bisecting two C_2- axes and passing through the minimum number of atoms is called dihedral plane, σ_d.



→ Bisector of two σ_v is also called σ_d.







There are σ_d in tetrahedral geometry passing through parallel diagonal of opposite faces.

5. Roation-reflection or Improper axis

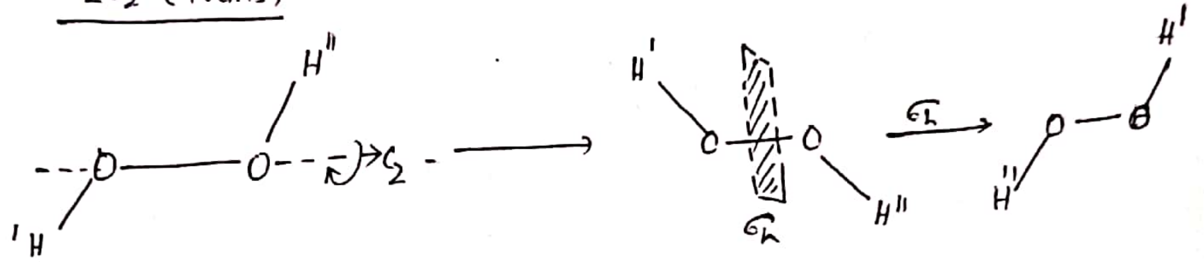
The ~~op~~ symmetry operation is combination of Proper axis (C_n) with a reflection in a plane perpendicular to the rotation axis (σ_h) is called improper axis. It is denoted by S_n.

$$\boxed{S_n = C_n \perp \sigma_h}$$

$$C_n + \sigma_h = S_n$$

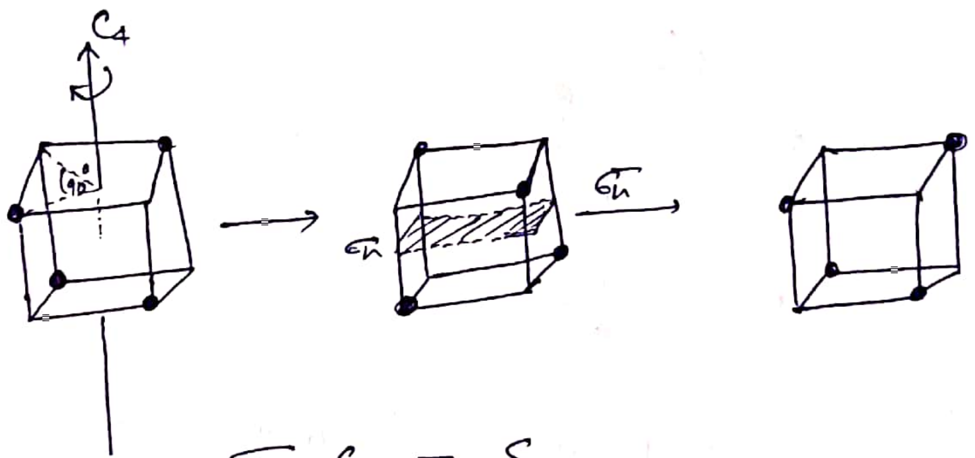
Examples:

H_2O_2 (Trans)



$$C_2 + \sigma_h = S_2$$

Tetrahedral structure (CH_4, CCl_4)



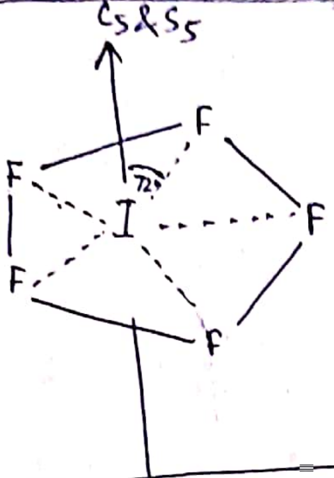
$$\sigma_h \cdot C_4 = S_4$$

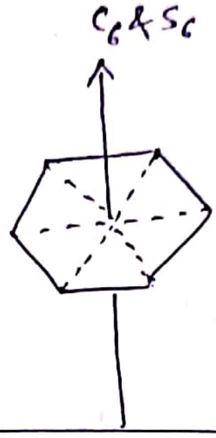
→ Here S_4 is Coincident with C_2

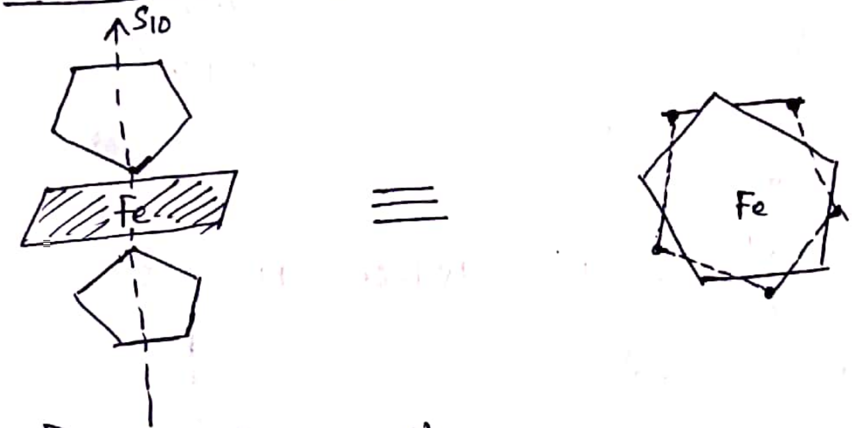
$$C_2 = S_4$$

$$C_3 \cdot \sigma_h = S_3$$

Here, S_3 coincident with S_3

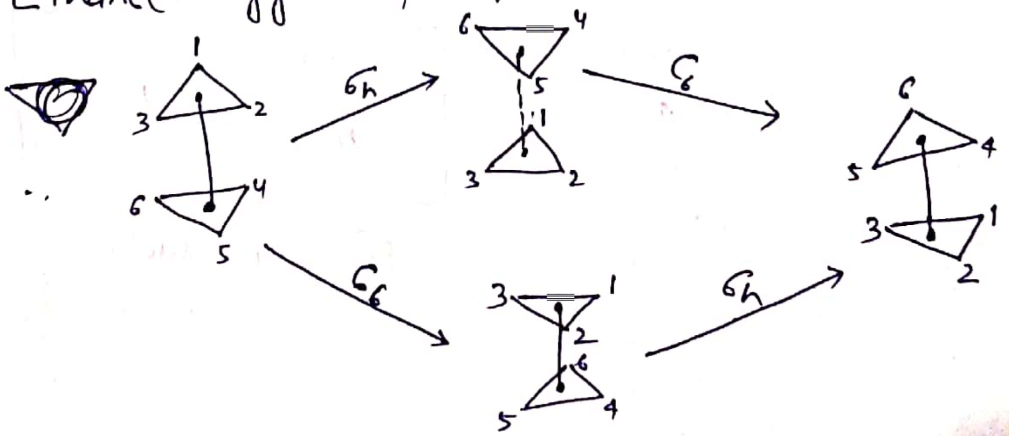






Ferrocene (staggered)

Ethane(staggered form)



- The symmetry element S_n in general generates a set of operations S_n : S_n^2, S_n^3 ...
- The important features of S_n.

(a) If n is even

S_6^1 = C_6^1 followed by σ^1

S_6^2 = C_6^2 followed by σ^2 = C_3 followed by σ^2 = C_3

S_6^3 = C_6^3 " " σ^3 = C_2 followed by σ^3 =

S_6^4 = C_4^6 " " σ^4 ≡ C_3^2 followed by σ^2 ≡ C_3^2

S_6^5 = C_6^5 " " σ^5 ≡ C_6^5 followed by σ

S_6^6 = C_6^6 followed by σ^6 = Identity followed by identity = E

$$S_6^6 = E$$

$\Rightarrow S_n^n = E$ when n = even.

(b) If n is odd:

$S_5 = C_5 \;\&\; \sigma$

$S_5^2 = C_5^2$

$S_5^3 = C_5^3 \;\&\; \sigma$

$S_5^4 = C_5^4$

$S_5^5 = \sigma$

$S_5^6 = C_5$

$S_5^7 = C_5^2 \;\&\; \sigma$

$S_5^8 = C_5^3 \;\cancel{\&\;\sigma}$

$S_5^9 = C_5^4 \;\&\; \sigma$

$S_5^{10} = \cancel{E}\; E$

$$\boxed{S_n^{2n} = E}$$

When n = odd.

Group Theory : A Mathematical group:

A set of elements having the following defining properties is said to be a mathematical group.

1. The product of any two elements or the square of the element must be an element of the group.

   - multiplication means any operation.
   - Multiplication may obey commutative law or not
     - → If obeys commutative law, the group is called <u>'abelian group'</u>

$$AB = BA$$
$$5+3 = 3+5$$
$$5\times 3 = 3\times 5$$

→ If multiplication does not obey commutative law, the group is called non-abelian group

$$AB \neq BA$$

2. A group must contain an element which commutes with all other ~~group~~ elements and leaves them unchange. It is called identity element (E)

$$AE = EA = A$$
$$BE = EB = B$$

3. Every element must have an inverse, which also be an member of the group. Such that

$$A A^{-1} = A^{-1}\cdot A = E$$

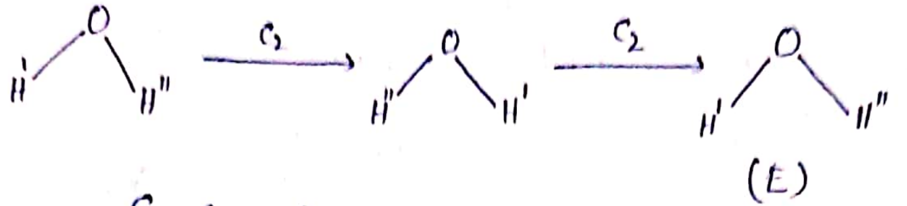
4. Associative law must ~~be~~ holds good.

$$A(BC) = (AB)C$$

Note: Product AB means that, we perform the operation B first & then operation A.

- Inverse of an element A is denoted by A^{-1} (this does not mean $\frac{1}{A}$). It is the element of the group such that $A^{-1} \cdot A = E$. i.e A^{-1} means that annuls the effect of operation A.

For example.



$C_2 \cdot C_2 = E$.

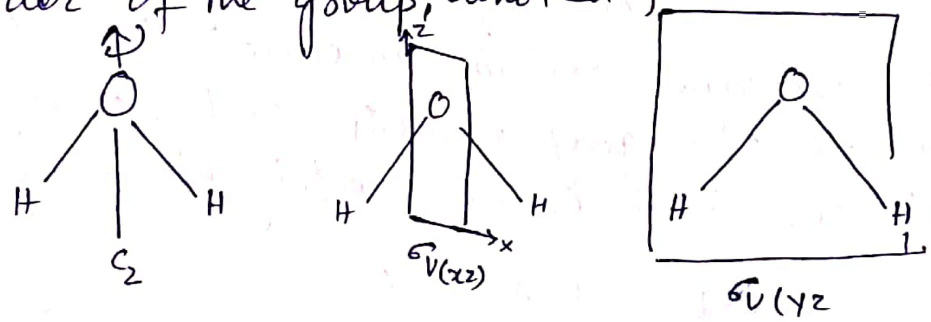
Therefore $C_2^{-1} = C_2$ i.e C_2 is its own inverse.

This rule is not general. For example

$C_6^2 = C_3 \neq E$. Hence C_6^{-1} is not C_6

Order of the group :-

The elements statisfying all rules (1 to 4) of group theory and total number of elements is called order of the group, denoted by h.



$C_{2v} = E, C_2, \sigma_{v(xz)}, \sigma_{v(yz}$

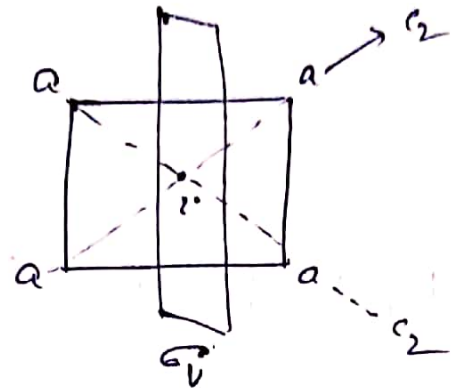
Order of group, h = 4

Sub group: A set of elements of a point group constituting a group in mathematical sense is said to be a ~~grout~~ sub-group.

Eg: C_2 is a sub-group of the point group C_{2v}. & C_{2h}.

→ A molecule contains 2-elements of symmetry, it may require a third element of symmetry.

→ A molecule has plane of symmetry and also an axis of symmetry (C_2) perpendicular to the plane, the molecule must have a centre of symmetry.

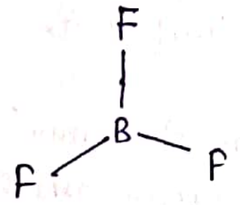


→ A molecule has two C_2-axis perpendicular to each other, it must have a third C_2-axis ⊥r to the plane

Symmetry elements present in the compounds:

(i) 

: E, C_2, $\sigma_v(xz)$, $\sigma_v(yz)$

(ii) 

: E, $2C_3$ (clockwise & anticlockwise), $3C_2 \perp^r C_3$, $3\sigma_v$, σ_h, S_3

(iii) --H—Cl→ C_∞ --C≡O→ C_∞

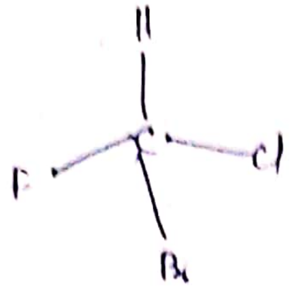
E, C_∞, $\infty\sigma_v$.

(iv) CO_2, C_2H_2, BeX_2

---O=C=O→ C_∞

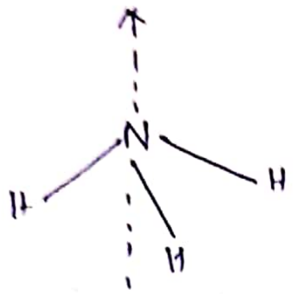
E, C_∞, $\infty C_2 \perp^r C_\infty$, $\infty \sigma_v$, σ_h, i, ∞S_2

(v) CHClBrF & Lactic acid



: E, C_1

(vi) NH_3, NX_3



$E,\ 2C_3\ (C_3^+, C_3^-),\ 3\sigma_v$

Symmetry operations and elements

Symmetry operation	Symmetry element
(i) No change (E)	Identity (E
(ii) Rotation by $2\pi/\theta$ about an axis of symmetry (C_n)	A n-fold axis of rotation (C_n)
(iii) Reflection in plane of symmetry perpendicular to principal axis of symmetry (σ_h)	A plane of symmetry $\perp$r the principal axis (σ_h)
(iv) Reflection in plane of symmetry containing principal axis (σ_v)	A plane of symmetry containing the principal axis of symmetry (σ_v.)
(v) Reflection in a plane of symmetry containing principal axis and bisecting two C_2- axes of symmetry (σ_d	σ_d.
(vi) Rotation by $2\pi/\theta$ about an axis followed by reflection in a plane perpendicular to that axis	S_n : Improper axis
(vii) Inversion in a centre of symmetry, centre of symmetry (i)	Centre of symmetry (i)

- The order of the sub-group of a group is divisor of of the order of that group.
  - → If order of a group is 6.

    Probability of a order of sub-group = 2, 3

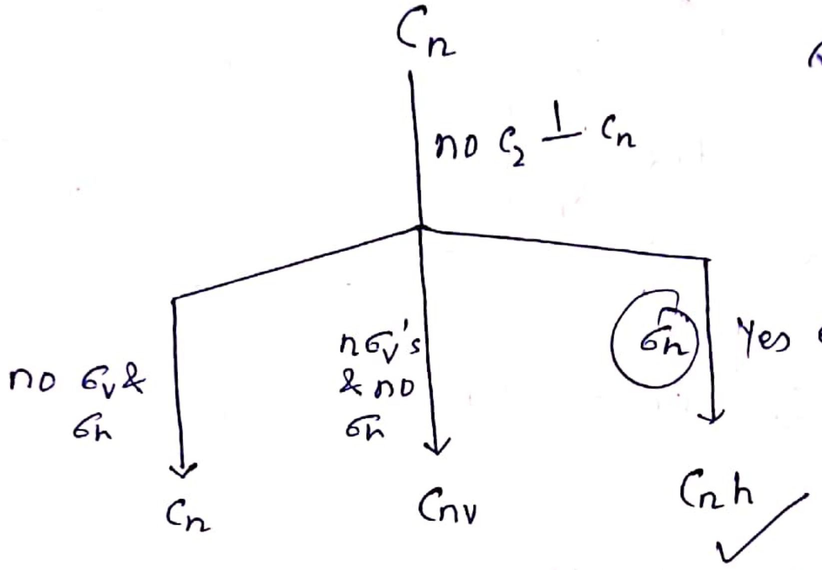
Point group and classification of point groups :-

The molecules are classified in the following point groups according to the generator elements present in it.

[A] Rotational point group (C_n) → These group contains C_n but not $C_2 \perp C_n$.

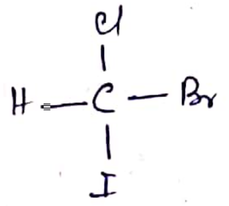
$\sigma_v < \sigma_h < \sigma_d$

Priority →



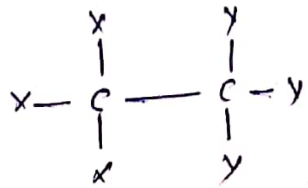
(i) C_1 groups : E, C_1

Here, $C_1 = E$



C_2 - groups : E, C_2.

C_3 - groups : E, C_3

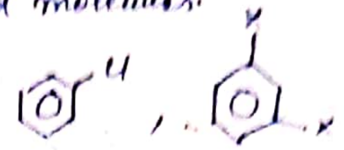


(ii) C_nV group

E, C_n, $n\sigma_v$.

C_{2V}: E, C_2, $2\sigma_v$; All V-shaped molecules.

Eg: H_2O, H_2S, NO_2, SO_2,

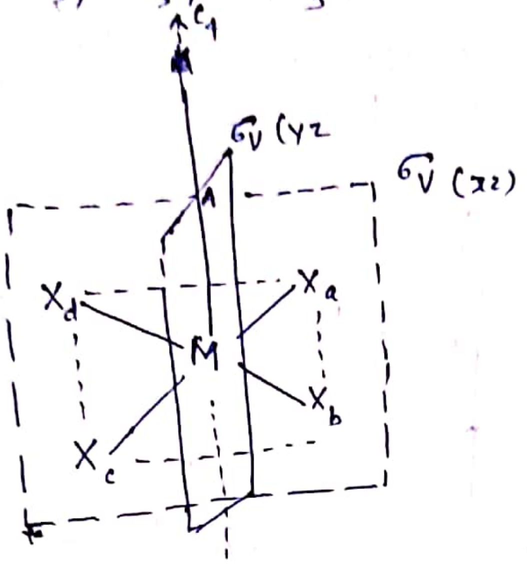


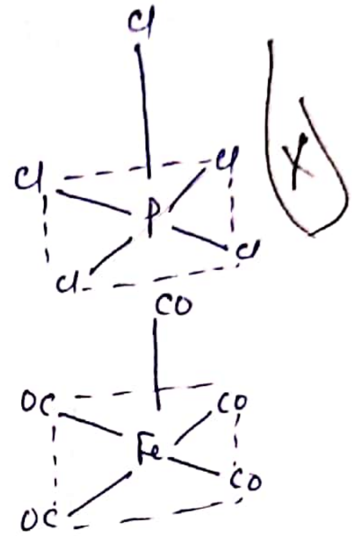
C_{3V}: E, $2C_3$, $3\sigma_v$.

All trigonal pyramidal molecules like

NH_3, PH_3, $CHCl_3$, NCl_3

C_4V :





E, C_4, $2\sigma_v \equiv 2\sigma_d$,

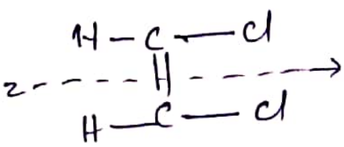
$C_{\infty}V$: E, C_{∞}, $\infty\sigma_v$

N_2H_2, CO HCl, HCN O=C=S

(III) C_nh : E, C_n, $\sigma_h \perp C_n$-axis

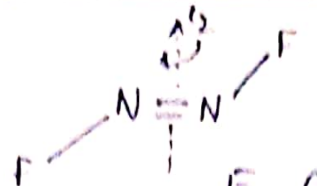
- In n = even, there is centre of Symmetry (i)

C_2h :



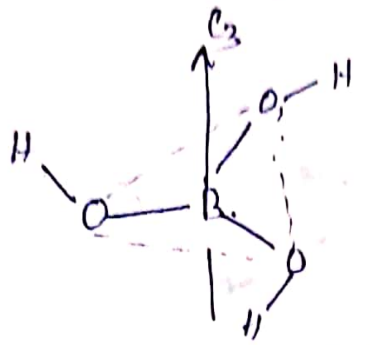
C_2 & xy plane is σ_h

N_2F_2, H_2O_2

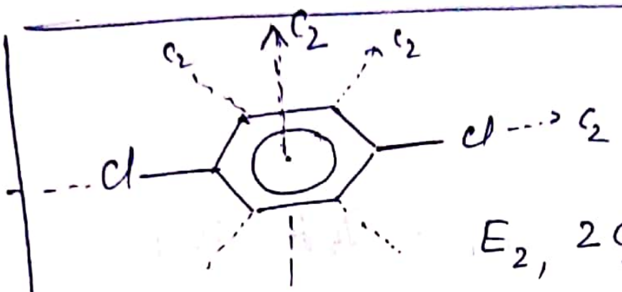


E, C_2, σ_h, i

<u>C_{3h}</u> : $B(OH)_3$



$E, 2C_3, \sigma_h, S_3$

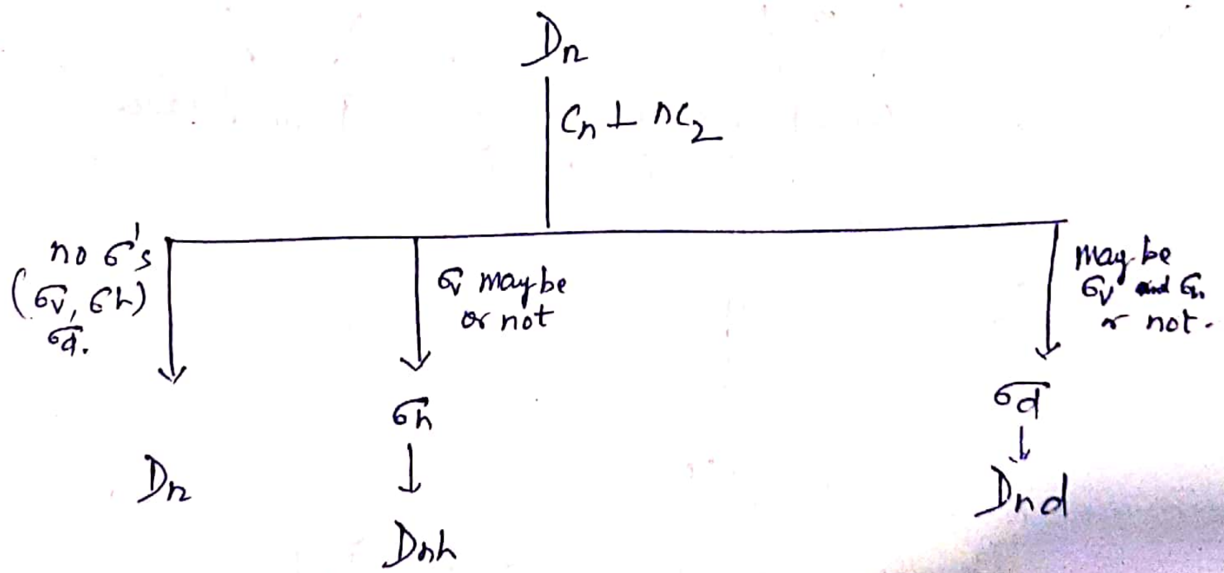


$E_2, 2C_2 \perp 2C_2, 2\sigma_v, \sigma_h$

(D_{2h})

[B] D_n : Pont group

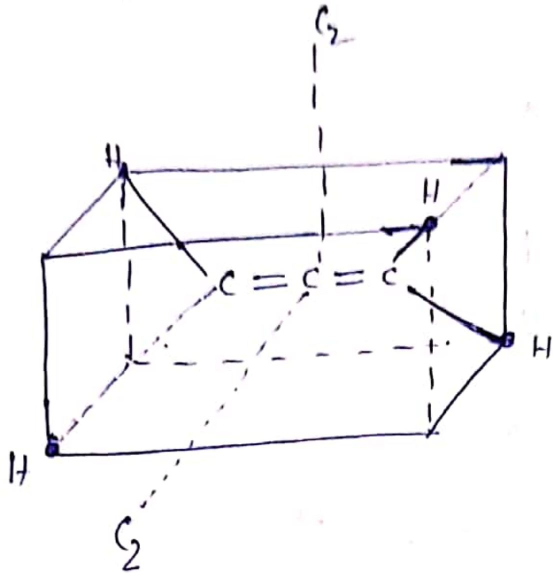
$E, C_n \perp nC_2 = D_n$



D_n - group : E, C_n, nC_2,

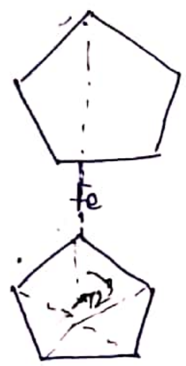
(i) D_2 :

(ii) D_2d :



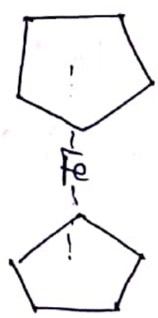
E, $2C_2$, σ_d = $\cancel{D_{2h}}$ D_{2d}

(iii)



D_5h.

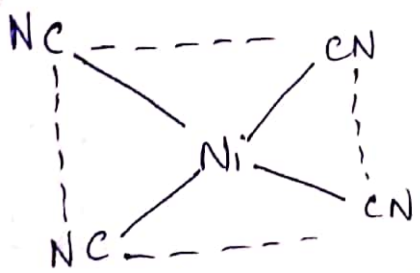
Cis-Ferrocene



:

Trans ferrocen.

E, C_5, C_2, $5\sigma_v$, σ_h = D_{5h}



E, C_4, $4C_2$, $4\sigma_v$, σ_h = D_4h

Special group:

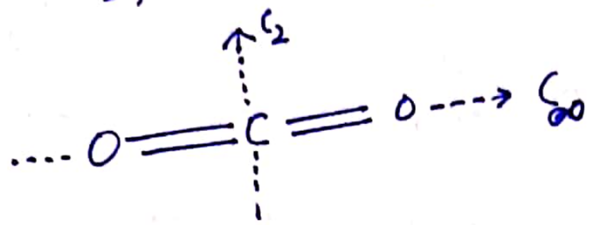
(A) Linear molecules : (i) CO, HCl ... unsymmetrical molecules
CO_2, H_2 N_2 ..

= $C_{\infty v}$. point group.

... H —— Cl. C_∞, σ_v = $C_{\infty v}$.

(ii) Symmetrical linear molecules:

CO_2, CS_2, C_2H_2, BeX_2



$C_\infty \perp C_2$, σ_h, σ_v = $D_{\infty h}$.

[B] Molecules having multiple high order axis.

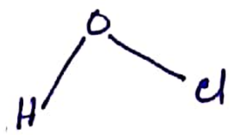
T_h, T_d, O, O_h, I

T_d-point group: CH_4, CCl_4, $NiCl_4^{2-}$, $CuCl_4^{2-}$, $Ni(CO)_4$

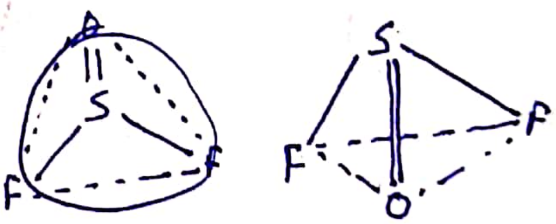
O_h-point group: Octahedral geometry & point of inversion (i)

Eg: SF_6, $[Co(NH_3)_6]^{2+}$

[C] C_s-point group: $E + \sigma = C_s$



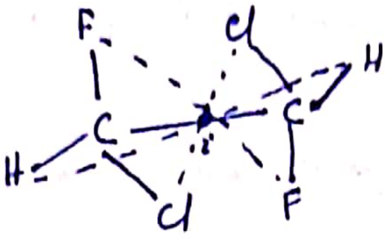
E, σ_h = C_s



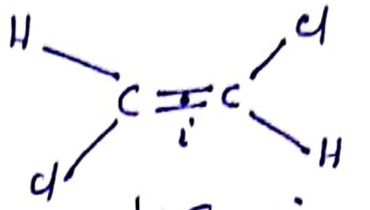
E, σ_v = C_s

[D] Ci - point group

$E + i = C_i$



$E,\ i = C_i$



$C_2 \perp \sigma_h,\ i = S_2$

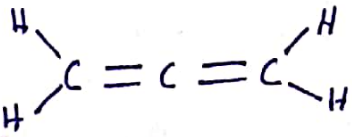
(E) Molecules containing only Sn-axis, where, n = even ($S_2, S_4, S_6, S_8 \cdots S_n$)

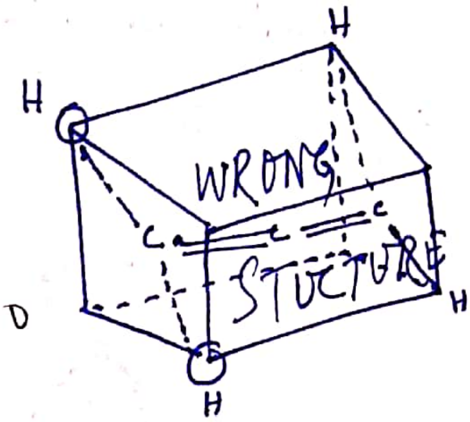
Eg: Spirane ~~contains S_4 & C_2~~

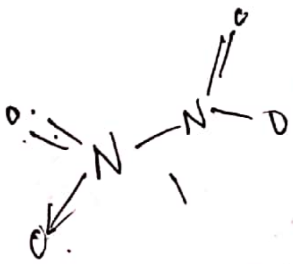
(i) S_4 contains a C_2-axis

(ii) S_6 contains a C_3 and a C_2-axis.

Allene:





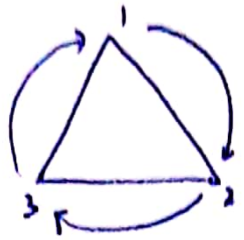


SOME COMMON POINT GROUPS WITH SYMMETRY ELEMENTS & EXAMPLES

Point group	Symmetry elements	Examples
C_1	E	$SiBrClF,I$, $SOFCl$
C_{2h}	E, $C_2 \perp \sigma_h$	trans-$C_2H_2Cl_2$, trans-planar H_2O_2
C_{2v}	E, C_2, $2\sigma_v$	H_2O, H_2S, SO_2,
C_{3v}	E, $2C_3$, $3\sigma_v$	NH_3, NX_3, CH_3Cl, $POCl_3$, PF_3, SiH_3Cl
C_{4v}	E, $3C_4$, $4\sigma_v$	$XeOF_4$.
D_{2h}	E, $3C_2 \perp C_2$, $2\sigma_v$, $1\sigma_h$, i	N_2O_4, $C_2O_4^{2-}$
D_{3h}	E $1C_3 \perp 3C_2$, $3\sigma_v$, $1\sigma_h$	BCl_3, BF_3, PCl_5, SO_3
D_{5h}	E, $C_5 \perp C_2$, σ_h	Eclipse ferrocene
D_{6h}	E, $C_6 \perp C_2$	Eclipse $Cr(C_6H_6)_2$
D_{4h}	E, $C_4 \perp 4C_2$, i σ_h, $4\sigma_v$	$PtCl_4^{2-}$, $[Ni(CN)_4]^{2-}$
D_{2d}	$3C_2$-axis, two σ_d & one S_4 (coinsident with one C_2)	$H_2C=C=CH_2$
D_{4d}		$Mn_2(CO)_{10}$
D_{3d}		Staggered Si_2H_6, C_2H_6
T_d	$3C_2 \perp$ to each other, four C_3, 6σ & $3S_4$ containing C_2	CH_4, $SiCl_4$, ClO_4^-
O_h		octahedral complexes
$C_{\infty v}$		H_2, CO_2, HCl
$D_{\infty v}$		

Cyclic group : A cyclic group contains an element and all powers of x upto $x^n = E$.

C_{3v} : E : $2C_3$, $3\sigma_v$



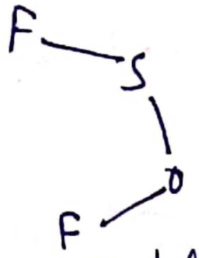
$C_3^3 = E$

C_3	E	C_3^+	C_3^-
E	E	C_3^+	C_3^-
$C_3 = C_3^+$	C_3^+	C_3^-	E
$C_3^2 = C_3^-$	C_3^-	E	C_3^+

$$C_3^+ \cdot C_3^+ = C_3^2 = C_3^-$$

$$C_3^3 = E$$

SOF_2



(C_s - point group)

Group multiplication table:- For C_{2v} point group

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$
E	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz$
C_2	C_2	E	$\sigma_v(yz)$	$\sigma_v(xz)$
$\sigma_v(xz)$	$\sigma_v(xz)$	$\sigma_v(yz)$	E	C_2
$\sigma_v(yz$	$\sigma_v(yz)$	$\sigma_v(xz)$	C_2	E

(i) An element E (identity) commute to any element left them unchange.

(ii) Every element is its own inverse

$$C_2 \cdot C_2 = E, \quad \sigma_{v(xz)} \cdot \sigma_{v(xz)} = E$$

(iii) $C_2 \cdot \sigma_{v(xz)} = \sigma_v \cdot C_2$

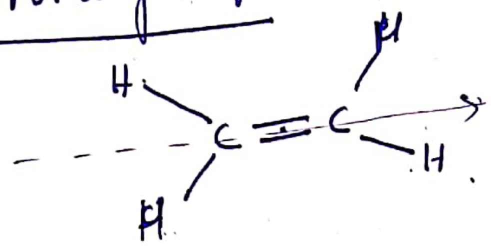
It is abelian group.

(iv) $C_2 [\sigma_{v(xz)} \cdot \sigma_{v(yz)}] = C_2 \cdot C_2 = E$

$[C_2 \ \sigma_{v(xz)}] \ \sigma_{v(yz)} = \sigma_{v(yz)} \cdot \sigma_{v(yz)} = E$

$\therefore$ Associative law holds good.

C_{2h} Point group



$E, 2C_2, i, \sigma_h$

C_{2h}	E	C_2	i	σ_h
E	E	C_2	i	σ_h
C_2	C_2	E	σ_h	i
i	i	σ_h	E	C_2
σ_h	σ_h	i	C_2	E

(i) Every element is its own inverse

(ii) C_2 is a sub-group of point group C_{2h}

(iii) $\left.\begin{aligned} \sigma_h \cdot C_2 &= i \\ C_2 \cdot \sigma_h &= i \end{aligned}\right\}$ Commutative law holds good = Abelian.