GROUP THEORY

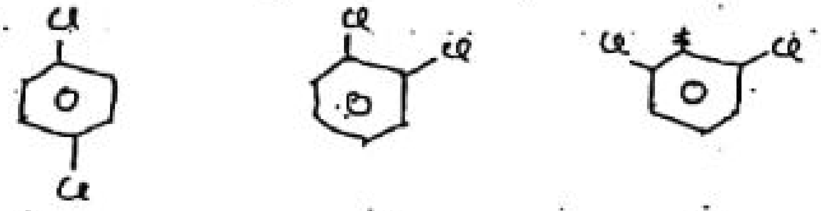
10-14 Marks

* **Books:-**
  (i) F.A. Cotton
  (ii) K. Veera Reddy.
  (iii) S.F.A. Keltie
  (iv) K.C. Molley
  (v) M. Arthur

Symmetry:- Regular arrangements of atoms or groups in a molecule or an object is called symmetry.
⇒ Quantitative

Mathematical study of symmetry is Group Theory.

e.g.



(I) (II) (III)

Symmetry order: I > II = III

$$\boxed{\text{Symmetry} \propto \text{No. of Operation}}$$

→ To quantify the amount of symmetry in an object or a molecule, we need to describe:
(i) Elements of symmetry (ii) operation

Elements of symmetry:- Geometrical entities like axis, point, plane that can be used as a tool to analyse the symmetric properties of an object or a molecule.

Operation:- The process that used upon elements of sym. is defined as operation.

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Elements of symmetry	Operation
1.) Axis of symmetry (C_n)	Rotation
2.) Plane of symmetry (σ)	Reflection / Bisection
3.) Improper axis (S_n), $n = 3, 4, \ldots$	Roto-reflection
4.) Inversion ($i = S_2$)	Invert (complete rotation)
5.) Identity (E)	Nothing

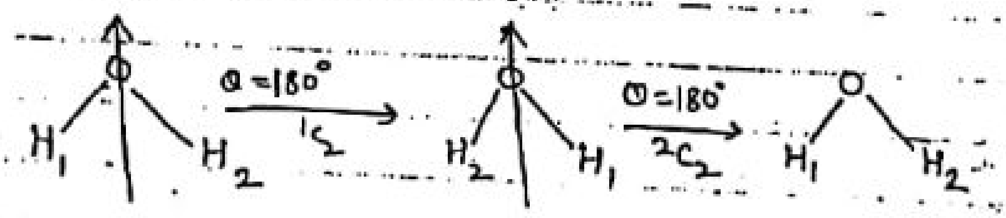
1.) Axis of Symmetry: Imaginary axis passing through an object or molecule rotation on which by θ degree produces equivalent orientation.
It is denoted by C_n where n is order of axis.

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

(a) $\theta = 360^\circ$, $n = 1$
(b) $\theta = 180^\circ$, $n = 2$
(c) $\theta = 120^\circ$, $n = 3$
(d) $\theta = 90^\circ$, $n = 4$

Examples:

→ (a) H_2O



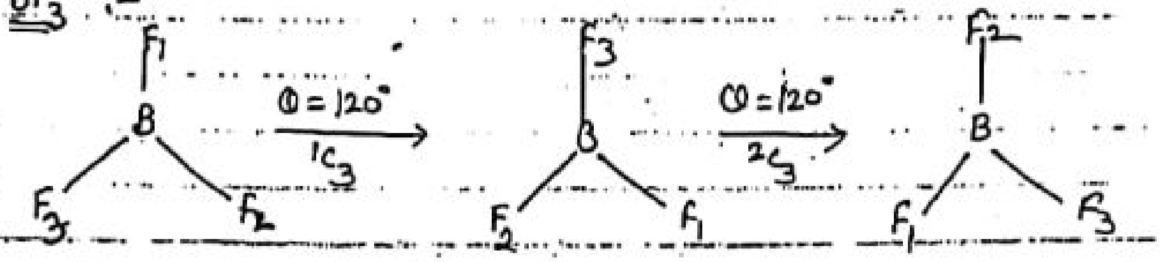
Initial orientation | Equivalent orientation | Identical Orientation

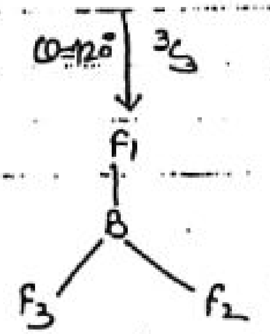
→ No. of operation / No. of equivalent orientation $= n - 1$

→ Water molecule contains 1 C_2 axis passing through oxygen atom & interchanging H_1 & H_2.

$^{M}C_n \rightarrow$ 'M' times 'n'- fold rotation

(b) $\underline{BF_3}$:-

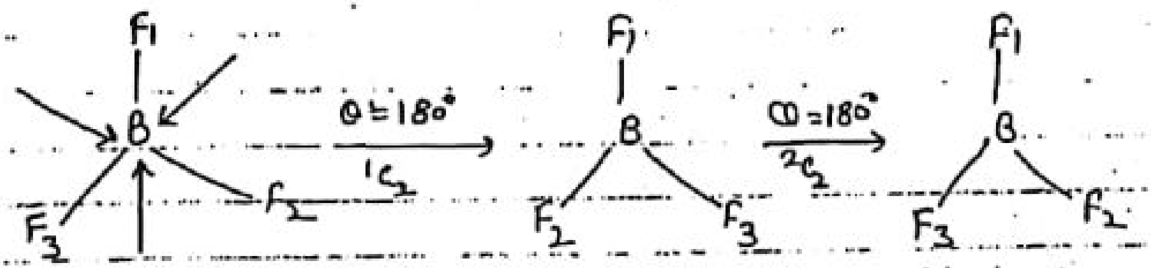




$C_3 = 3-1 = 2$

No. of operations / No. of equivalent orientations = 2

→ BF_3 molecule contains one C_3 axis passing through B-atom ⊥ to triangular plane & interchanging all three 'F' i.e. F_1, F_2, F_3 with each other.



Initial orientation — equivalent — identical

→ BF_3 molecule contains three C_2-axis passing through each B-F bond & interchanging other two F's with each other.

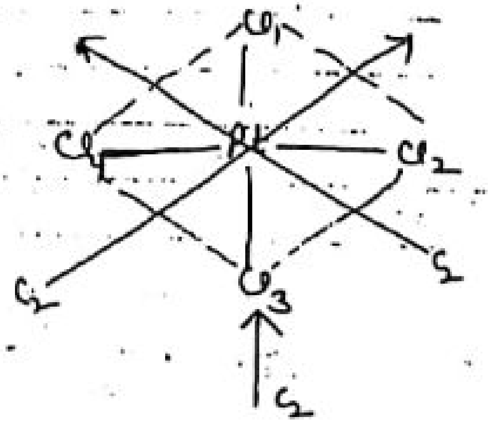
No. of operations w.r.t axis in BF_3

$C_3 \approx 2$

$3C_2 \approx 3(2-1) = 3$

∴ Total operations = 2+3 = 5

(c) $[PtCl_4]^{2-}$:- square planar.



(i) one C_4 axis passing through 'Pt' atom, ⊥ to square plane and interchanging Cl_1, Cl_2, Cl_3, Cl_4 with each other

(ii) Ist C_2 passing through $Cl_1-Pt-Cl_3$ bond & interchanging Cl_2 with Cl_4.

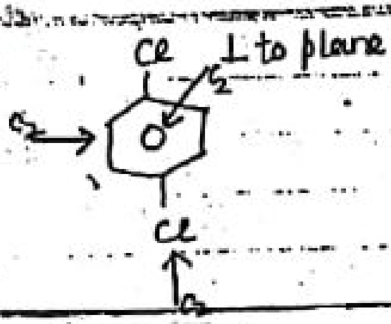
(iii) 2nd C_2 passing through $Cl_2-Pt-Cl_4$ bond & interchanging Cl_1 & Cl_3.

(iv) 3rd C_2 passing through 'Pt' & interchanging Cl_1 with Cl_2 & Cl_3 with Cl_4.

(v) 4th C_2 passing through 'Pt' & interchanging Cl_1 with Cl_4 & Cl_2 with Cl_3.

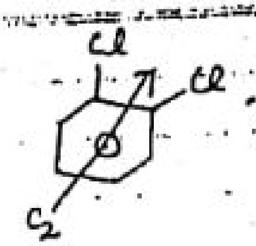
* No. of Operations w.r.t. axis in $PtCl_4$ are 7.
[∵ $^1C_4$, $^2C_4$, $^3C_4$, C_2, $^2C_2$, $^3C_2$, $^4C_2$ as $^4C_4$ is identity]

(i)



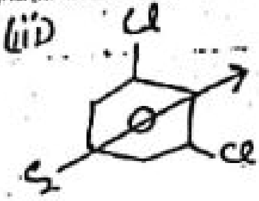
$\boxed{3C_2}$

(ii)



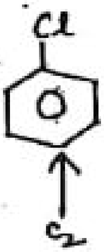
$\boxed{1C_2}$

(iii)



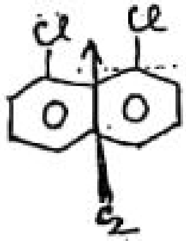
$\boxed{1C_2}$

(iv)



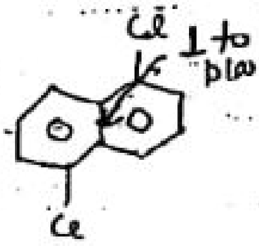
$\boxed{1C_2}$

(v)



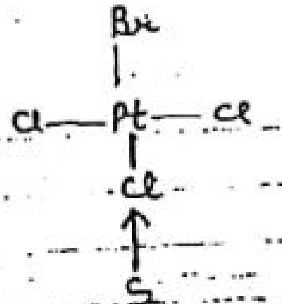
$\boxed{1C_2}$

(vi)



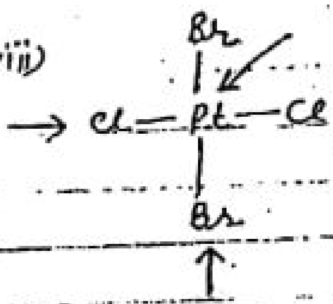
$\boxed{1C_2}$

(vii)



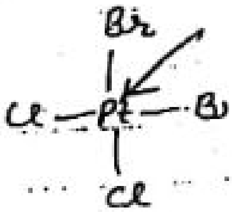
$\boxed{1C_2}$

(viii)



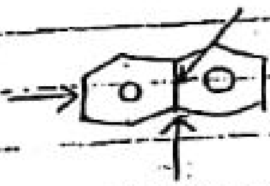
$\boxed{3C_2}$

(ix)



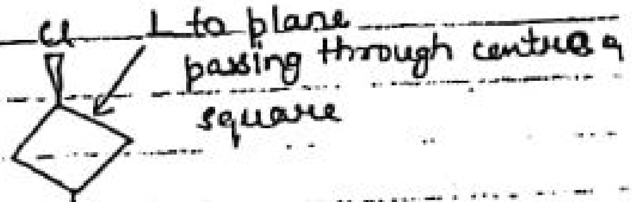
$\boxed{1C_2}$

(x)



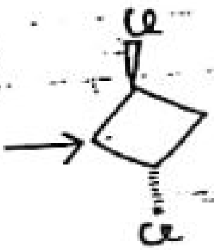
$\boxed{3C_2}$

(xi)



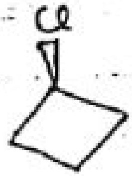
$\boxed{1C_2}$

(xii)

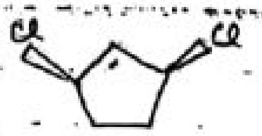


$\boxed{1C_2}$

(xiii)



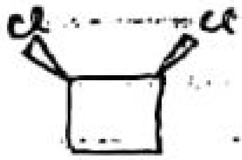
$\boxed{=0}$

(xiv) 

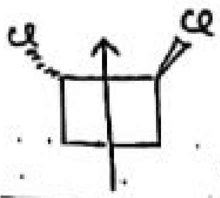
$\boxed{=0}$

(xv) 

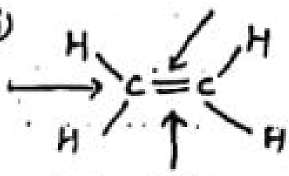
$\boxed{=0}$

(xvi) 

$\boxed{=0}$

(xvii) 

$\boxed{1C_2}$

(xviii) 

$\boxed{3C_2}$

(xix)

$O=C=O$

0°

$(C_\infty + \infty C_2)$

$\frac{360}{0} = \infty = n$

(xx) $O=C=S$

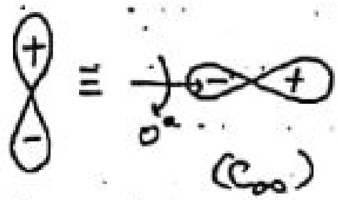
0°

(C_∞)

NOTE :- If we introduce O^{18} in CO_2 [one 'O' atom], then what will be required axis of rotation ?

→ Only C_∞, C_2 axis will vanish.

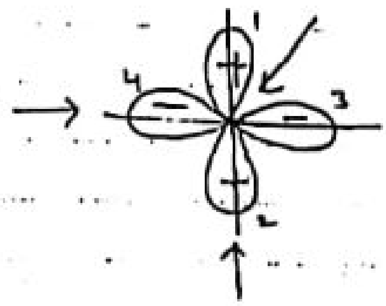
(xi) p-orbital :-



(C_∞)

[∵ On applying C_2 axis, +ve lobe change to -ve lobe]

(xxii) $d_{x^2-y^2}$:



$\boxed{3C_2\text{-axis}}$

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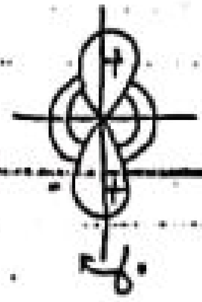
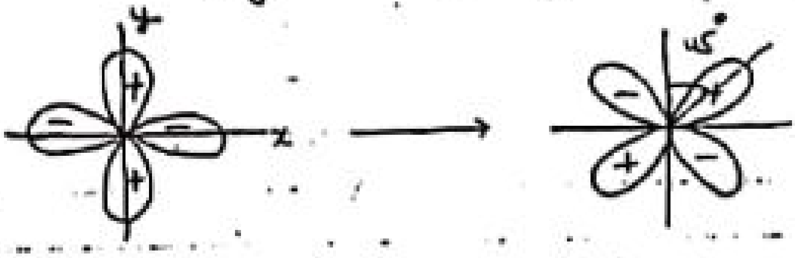
(xiii) d_{z^2} :-



$(C_\infty + \infty C_2)$

Q:- No. of operations w.r.t. C_n axis are ______

$d_{x^2-y^2} \xrightarrow{C_n} d_{xy}$



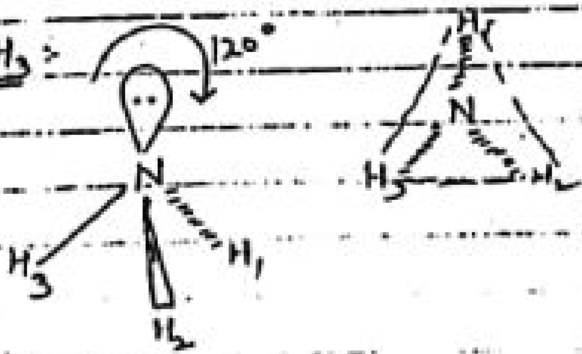
i.e. $\theta = 45°$

$n = \frac{360°}{45} = 8$

$d_{x^2-y^2}$ d_{xy}

No. of operations $= 8 - 1 = 7$

(xiv) NH_3 :-



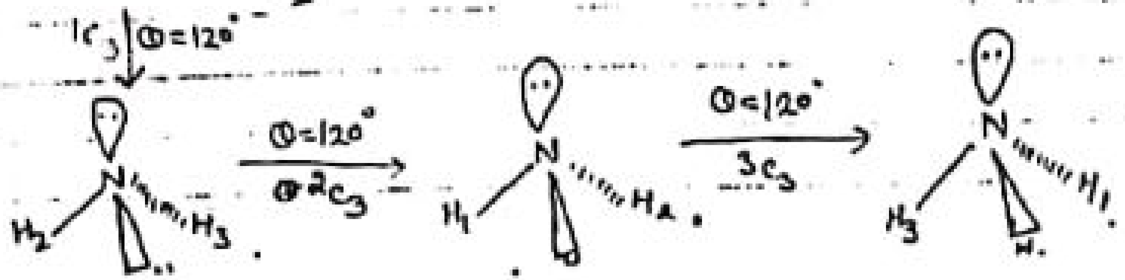
Bond angle in $NH_3 = 107$

But angle of rot^n = 120

2 equivalent orientation

$\therefore n = 3$

$\boxed{NH_3 \text{ has one } C_3 \text{ axis}}$



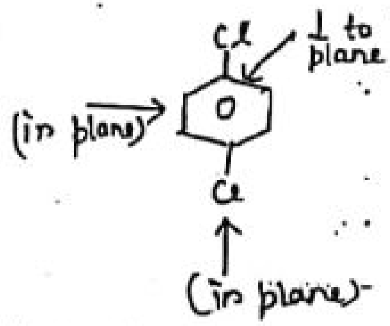
★ Classification of axis :-

1) Principal axis :- Axis of highest order is defined as principal axis.

2.) Subsidiary axis :- Axis other than principal axis is defined as subsidiary axis.

Note :- If order of all axis are same, then axis which appears distinct from others will be P.A.

e.g.



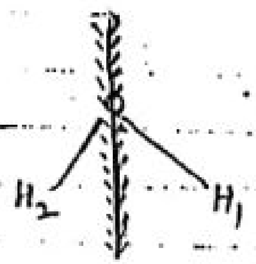
→ appears distinct (∴ This axis is P.A.)

★ PLANE OF SYMMETRY :-

Imaginary plane passing through an object or a molecule which bisects the molecule in two equal halves is called 'Plane of symmetry'.

e.g.

1)



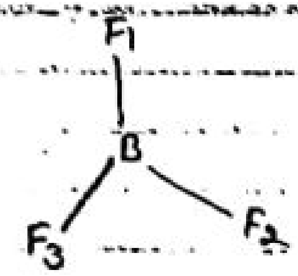
2σ

⇒ Plane bisects O & replaces H_1 & H_2

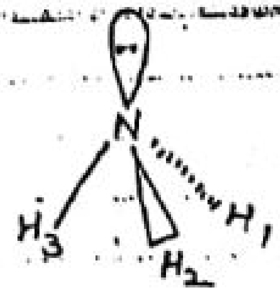
⇒ Plane bisecting the molecule.

1

2.)



(3)

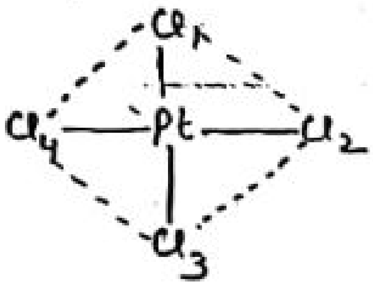


$\boxed{4\sigma}$

$\boxed{3\sigma}$

No molecular plane

4.)



→ Plane bisecting Cl_1-Pt-Cl_3 & reflecting Cl_2 with Cl_4

→ " " Cl_2—Pt—Cl_4 & reflecting Cl_1 with Cl_3.

→ Plane bisecting Pt only & reflecting Cl_1 with Cl_4 & Cl_2 with Cl_3.

→ Plane bisecting Pt only & reflecting Cl_1 with Cl_2 and Cl_3 with Cl_4.

→ Molecular plane.

⇒ Classification of Plane :- Planes are classified on the basis of principal axis.

1.) Vertical Plane (σ_v) :- The plane which is $\parallel$ to principal axis is called vertical plane.

2.) Horizontal Plane (σ_h) :- The plane which is $\perp$ to principal axis is called Horizontal plane.

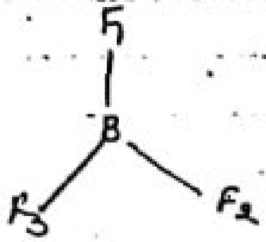
3.) Dihedral Plane (σ_d) :- It is $\parallel$ to principal axis] mu

* Plane bisecting minimum no. of atoms.
* Plane bisecting angle b/w two C_2-axis.

e.g. (1) H_2O

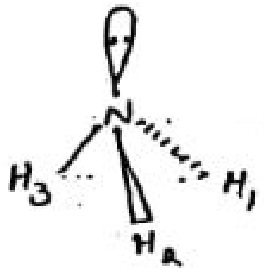
$(C_2 + 2\sigma_v)$

(2) BF_3



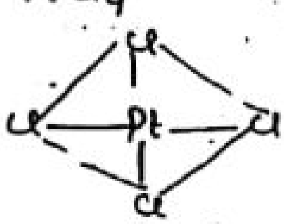
$(C_3 + 3C_2 + 3\sigma_v + 1\sigma_h)$

(3) NH_3



$(C_3 + 3\sigma_v)$

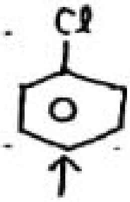
(4) $PtCl_4$



P.A. = C_4

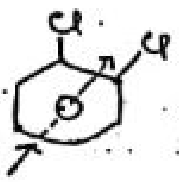
$(C_4 + 4C_2 + 4\sigma_v + \sigma_h)$

(5)



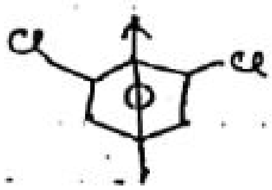
$(C_2 + 2\sigma_v)$

(6)



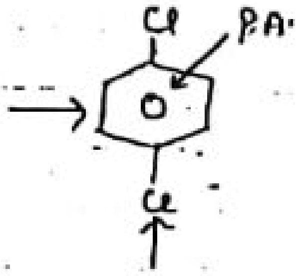
$(C_2 + 2\sigma_v)$

(7)



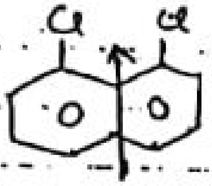
$(C_2 + 2\sigma_v)$

(8)



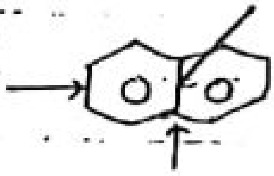
$(C_2 + 2C_2 + 2\sigma_v + 1\sigma_h)$

(9)



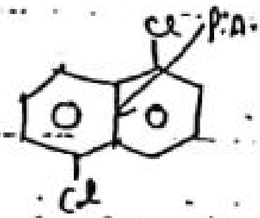
$(C_2 + 2\sigma_v)$

(10)



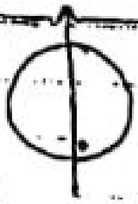
$(C_2 + 2C_2 + 2\sigma_v + 1\sigma_h)$

(11)



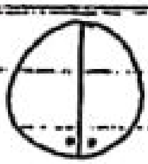
$(C_2 + 1\sigma_h)$

(12)



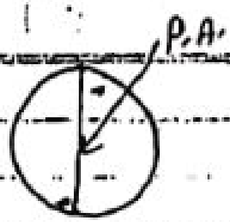
($C_2 + 2\sigma_v$)

(13)



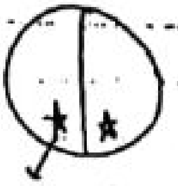
($C_2 + 2\sigma_v$)

(14)



($C_2 + 1\sigma_h$)

(15)



Projecting outwards

(σ)

(16)

Projecting outwards

(C_2)

(17)

O=C=O

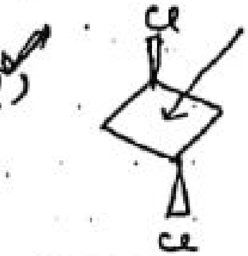
($C_\infty + \infty C_2 + \infty\sigma_v + \ldots$

(18)

O=C=S

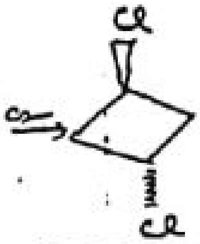
($C_\infty + \infty C_v$)

(19)



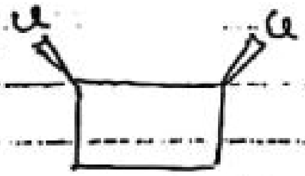
$\boxed{C_2 + 2\sigma_v}$

(20)



$\boxed{C_2 + 1\sigma_h}$

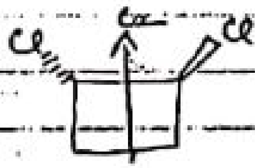
(21)



No axis

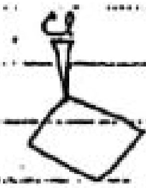
(σ)

(22)



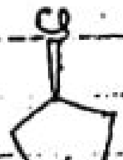
(C_2)

(23)



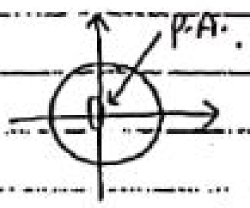
(σ)

(24)



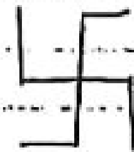
(σ)

(25)



($1C_2 + 2C_2 + 2\sigma_v + 1\sigma_h$)

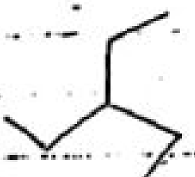
(26)



E = ${}^1C_4$ ${}^2C_4$ ${}^3C_4$ ${}^4C_4$

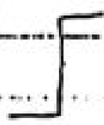
($C_4 + 1\sigma_h$)

(27)



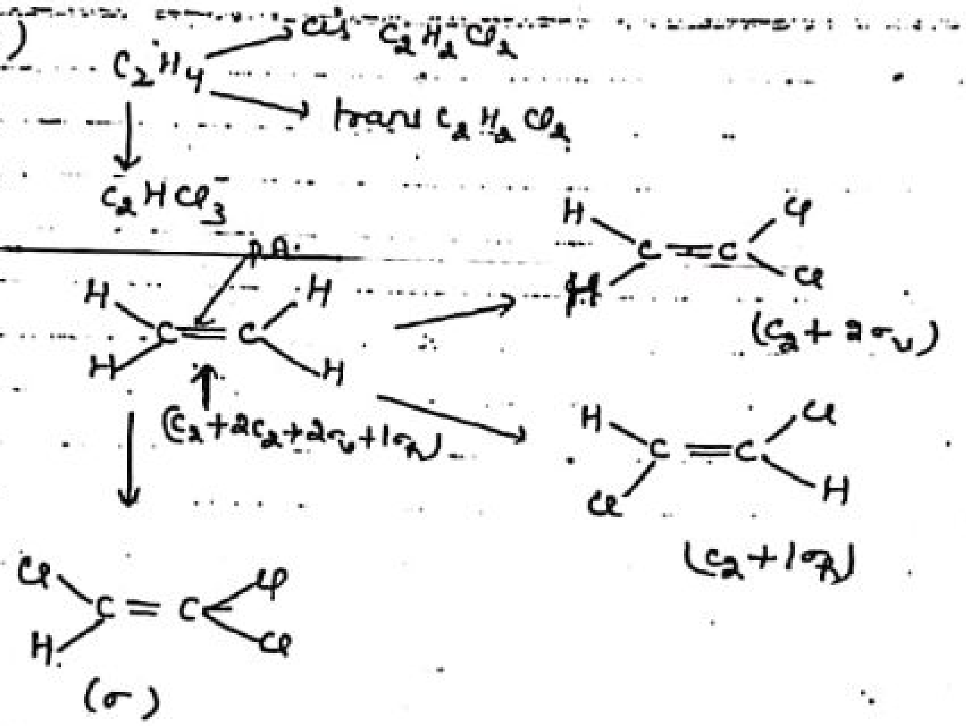
($C_2 + 1\sigma_h$)

(28)



($C_2 + 1\sigma_h$)

(29)



Q30:- $CH\equiv CH \xrightarrow[\text{reagent}]{\text{1 mole}} H-C\equiv \overset{\ominus}{C}\overset{\oplus}{Na} \xrightarrow[\text{reagent}]{\text{1 mole}} \overset{\oplus}{Na}\overset{\ominus}{C}\equiv\overset{\ominus}{C}-\overset{\oplus}{Na}$

$(C_\infty+\infty C_2+\infty\sigma_v+1\sigma_h)$ $\quad$ $(C_\infty+\infty\sigma_v)$ $\quad$ $(C_\infty+\infty C_2+\infty\sigma_v+1\sigma_h)$

Q31:- $NH_3 \longrightarrow NH_2Cl \longrightarrow NHCl_2 \longrightarrow NCl_3$

$(C_3+3\sigma_v)$ $\quad$ (σ) $\quad$ (σ) $\quad$ $(C_3+3\sigma_v)$

Plane bisecting N–Cl & reflecting H_1 & H_2

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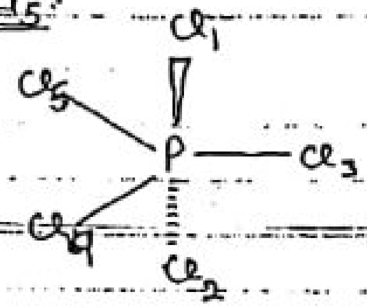
(30) PCl_5:



⇒ 1 C_3 axis passing through Cl_1-P-Cl_2 bond and interchanging Cl_3, Cl_4, Cl_5 among themselves.

⇒ 1st C_2 axis passing through PCl_3 bond and interchanging C_4 with C_5 & Cl_1 with Cl_2.

⇒ 2nd C_2 axis passing through P-Cl_4 bond & interchanging Cl_3 with Cl_5 & Cl_1 with Cl_2

⇒ 3rd C_2 axis passing through P-Cl_5 bond & interchanging Cl_3 with Cl_4 & Cl_1 with Cl_2.

⇒ 1st σ_v Plane bisecting P, Cl_1, Cl_2, Cl_3 and reflecting Cl_4 with Cl_5.

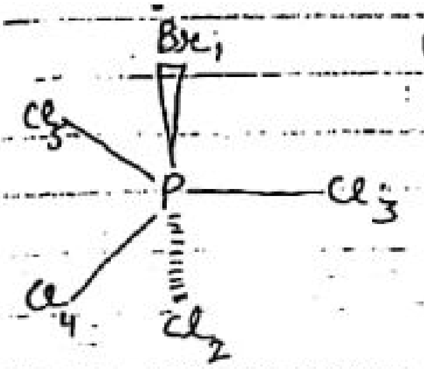
⇒ 2nd σ_v bisecting P, Cl_1, Cl_2, Cl_4 & reflecting Cl_3 with Cl_5.

⇒ 3rd σ_v bisecting P, Cl_1, Cl_2, Cl_5 & reflecting Cl_3 with Cl_4.

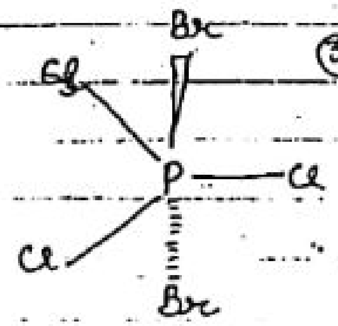
⇒ 4th σ_h bisecting P, Cl_3, Cl_4, Cl_5 & reflecting Cl_1 with Cl_2.

$$\boxed{C_3 + 3C_2 + 3\sigma_v + 1\sigma_h}$$

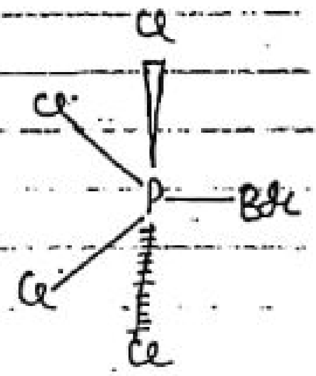
(31)



(32)



(33)



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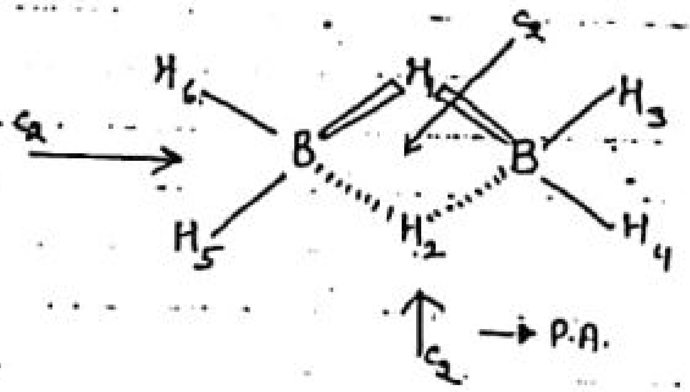
Substitution	Elements remain	Elements vanished
1. One axial Cl in PCl_5 is replaced by Br.	$C_3 + 3\sigma_v$	$3C_2 + 1\sigma_h$
2. Both axial Cl are replaced by Br.	$C_3 + 3C_2 + 3\sigma_v + 1\sigma_h$	Nothing
3. One equitorial Cl is replaced by Br.	(P.A.) $C_2 + \sigma_v + \sigma_v$ ($\because \sigma_h \to \sigma_v$)	$C_3 + 2C_2 + 2\sigma_v$
4. One axial Cl is replaced by Br & one equitorial Cl is replaced by Br.	σ	$C_3 + 3C_2 + 2\sigma_v + 1\sigma_h$
5. One axial Cl is replaced F and one equitorial Cl is replaced By Br.	σ	$C_3 + 3C_2 + 2\sigma_v + 1\sigma_h$

10: Draw the structure of B_2H_6 and find out all axis and plane of symmetry.

Ans:

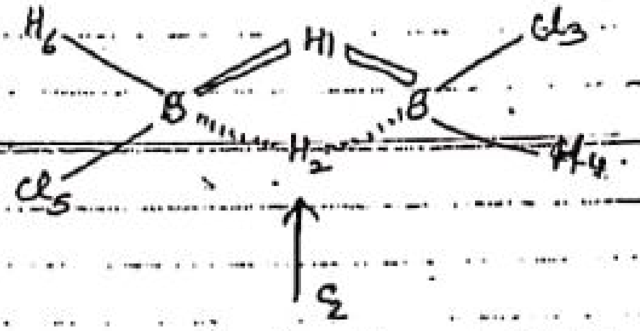


σ_v via H_1 & H_2

σ_v via B, B

$$\boxed{C_2 + 2C_2 + 2\sigma_v + 1\sigma_h}$$

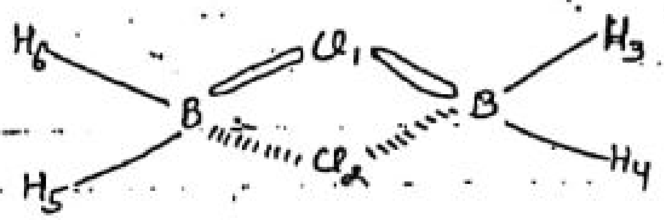
1. ⇒ H_3 is replaced by Cl_3 & H_5 with Cl_5.



$: \boxed{C_2 + 1\sigma_h}$

passing through H_1 & H_2

2. ⇒ H_1 & H_2 are replaced by Cl.



$\boxed{C_2 + 2C_2 + 2\sigma_v + 1\sigma_h}$

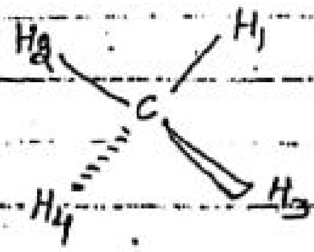
★✓ <u>IMPROPER AXIS</u> :- (S_n) :- $n = 3, 4, 5, \ldots$

Imaginary axis rotation on which by θ degree followed by ⊥ reflection produces equivalent orientation.

$S_3 = C_3 + \perp$ plane

$S_4 = C_4 + \perp$ plane

⇒ $\boxed{S_4}$:- CH_4



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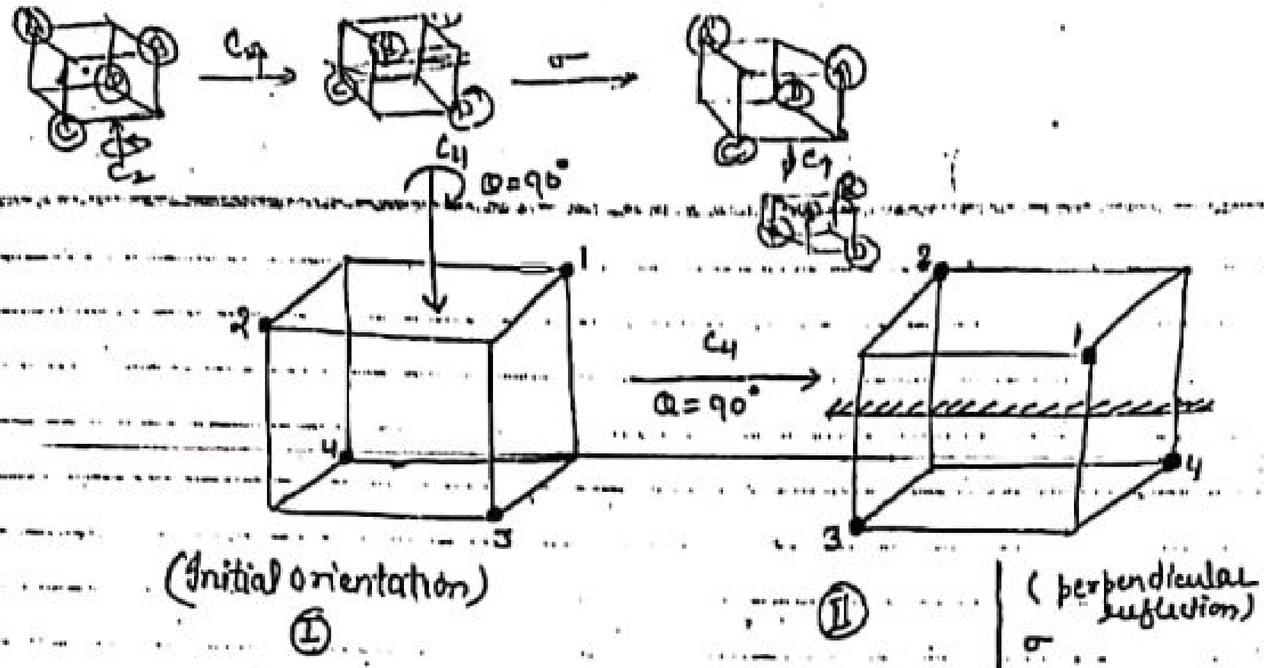
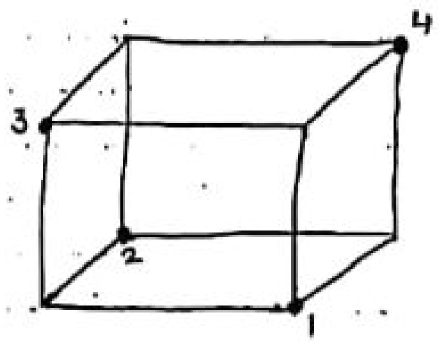
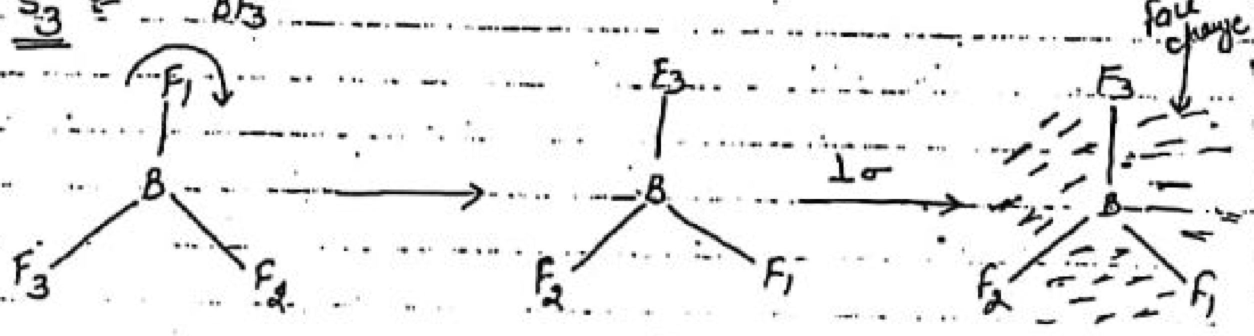




III
(Equivalent orientation)

I & III are equivalent orientation.

⇒ S_3 :- BF_3



(Equivalent orientation)

★ <u>INVERSION CENTRE</u> :- $(i \approx S_2)$

Imaginary point within the molecule which can invert all the atoms to