CHAPTER-2

POINT GROUP

AIM:-

(1) To calculate total no. of elements/operations
(2) To generate point group

(1.) **C_{nh} Point group :-**

$$C_{nh} = C_n + 1\sigma_h$$

Total no. of elements/operations = $2n$

C_{2h} :- $4 = C_{2h} = \underset{1}{C_2} + \underset{1}{1\sigma_h} + \underset{1}{E} + \underset{1}{S_2}$ ← no. of operations

C_{3h} :- $6 = C_{3h} = \underset{2}{C_3} + \underset{1}{1\sigma_h} + \underset{1}{E} + \underset{2}{S_3}$

C_{4h} :- $8 = C_{4h} = \underset{3}{C_4} + \underset{1}{1\sigma_h} + \underset{1}{E} + \underset{2}{S_4} + \underset{1}{S_2}$

C_{5h} :- $10 = C_{5h} = \underset{4}{C_5} + \underset{1}{1\sigma_h} + \underset{1}{E} + \underset{4}{S_5}$

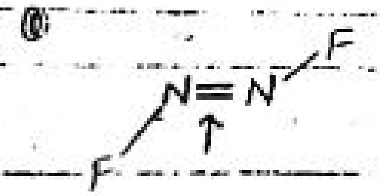
Note 1:- In case of C_{nh} point group, we will try improper axis (S_n).

If n = even $\xrightarrow{\text{no. of operation}}$ S_n and/or $\frac{S_n}{2}$

If n = odd $\longrightarrow$ S_n

Note 2:- No. of operations in improper axis
If n = even, then no. of operation = $\frac{n}{2}$
If n = odd, " " " " = $n-1$

(1)



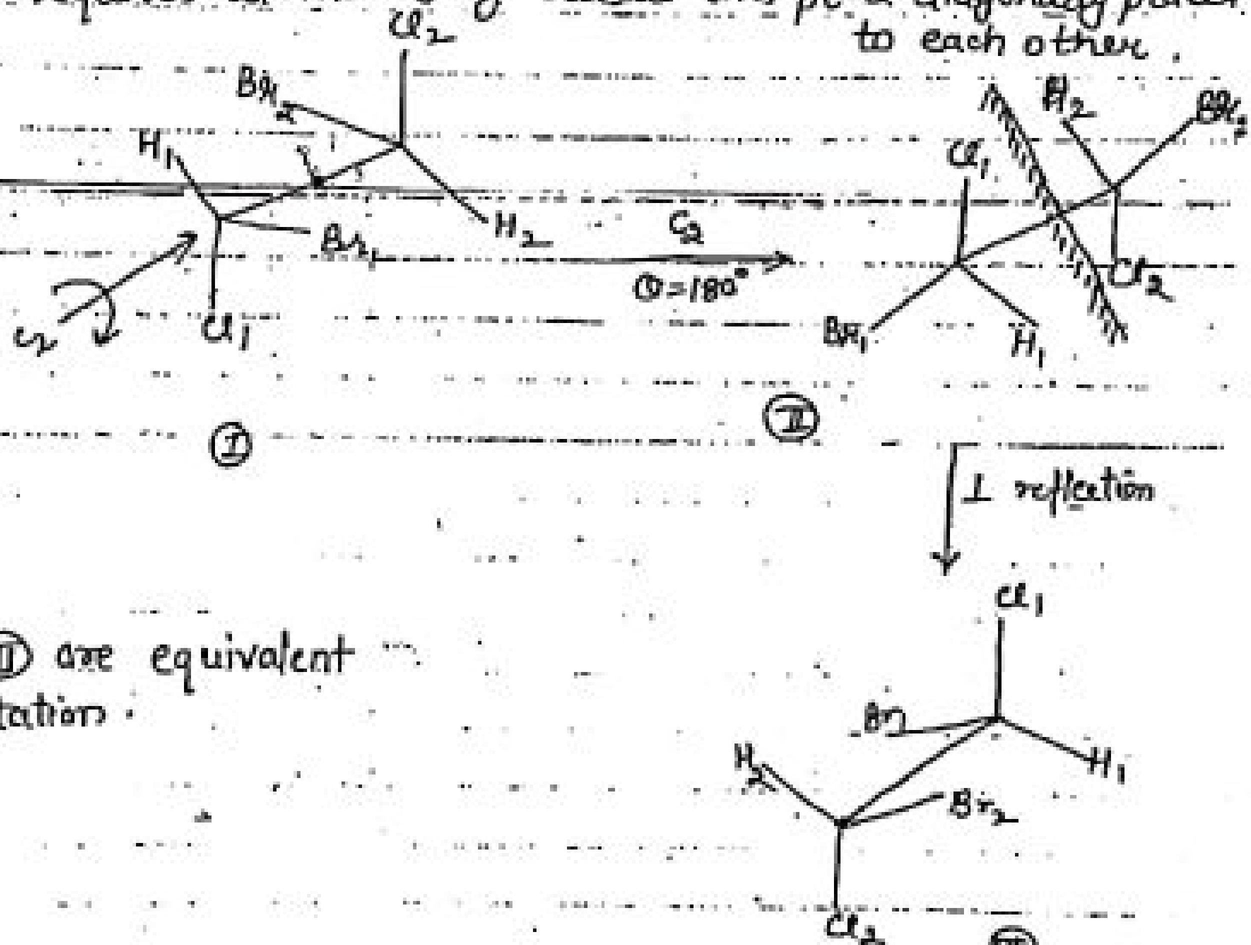
(2)

C_{2h}

$S_2 = C_2 + \perp$ plane

$\bullet = C_2 + \perp$ plane

produce equivalent orientation Molecules having this type of symmetry requires atoms lying outside this pt. are diagonally placed to each other.



I

II

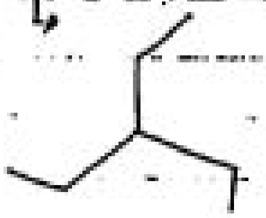
III

I & III are equivalent orientation.

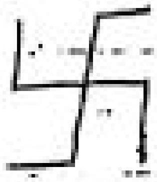
★ **IDENTITY (E)** :-

Nothing

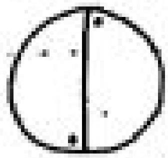
Gate-2011

③ 

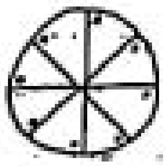
C_{2h}

④ 

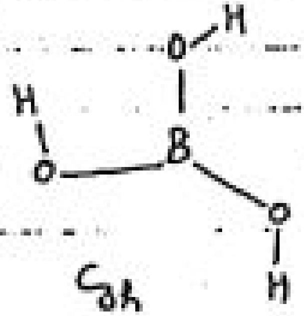
C_{4h}

⑤ 

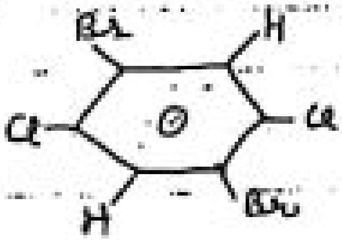
C_{2h}

⑥ 

C_{8h}

⑦ 

C_{3h}

⑧ 

C_{2h}

⑨ S

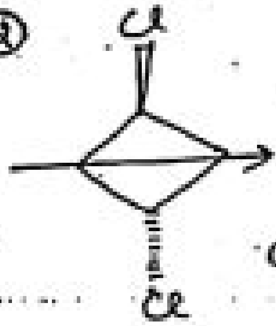
C_{2h}

⑩ N

C_{2h}

⑪ Z

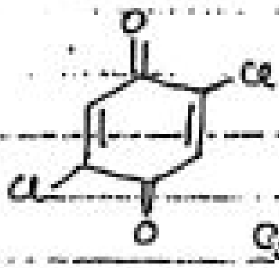
C_{2h}

⑫ 

C_{2h}

⑬ 

C_{2h}

⑭ 

C_{2h}

(2) Cnv Point group:-

$$C_{nv} = C_n + n\sigma_v$$

No. of operations = $2n$

C_{2v}: $4 = C_2 + 2\sigma_v$: $1+2$

C_{3v}: $6 = C_3 + 3\sigma_v$

C_{4v}: $8 = C_4 + 4\sigma_v$

C_{5v}: $10 = C_5 + 5\sigma_v$

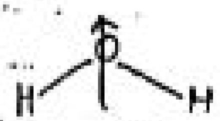
$4 = C_{2v} = \underset{1}{C_2} + \underset{2}{2\sigma_v} + \underset{1}{E}$

$6 = C_{3v} = \underset{2}{C_3} + \underset{3}{3\sigma_v} + \underset{1}{E}$

$8 = C_{4v} = \underset{3}{C_4} + \underset{4}{4\sigma_v} + \underset{1}{E}$

$10 = C_{5v} = \underset{4}{C_5} + \underset{5}{5\sigma_v} + \underset{1}{E}$

(1) H_2O

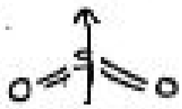


C_{2v}

(2) HCl

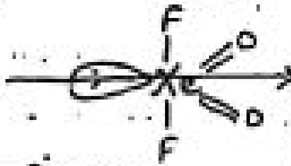
$C_{\infty v}$

(3) SO_2



C_{2v}

(4) XeO_2F_2



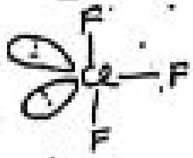
(See-saw)

C_{2v}

(5) XeO_3

C_{3v}

(6) ClF_3



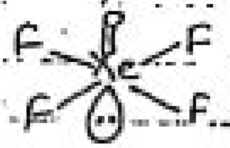
C_{2v}

(7) SF_4

(See-saw)

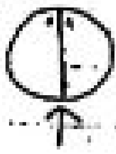
C_{2v}

(8) $XeOF_4$



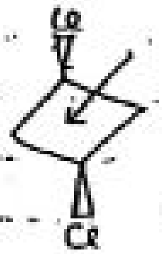
C_{4v}

(9)



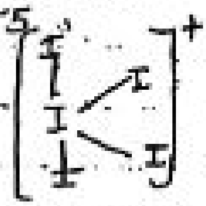
C_{2v}

(10)



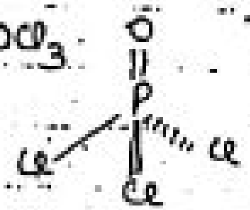
C_{2v}

(11) $I_5^{\oplus}$



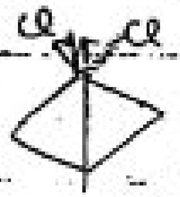
C_{2v}

(12) $POCl_3$



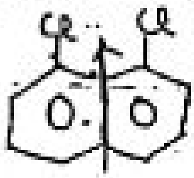
C_{3v}

(13)



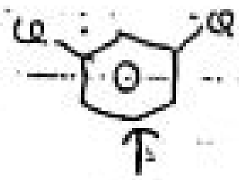
C_{2v}

(14)



C_{2v}

(15)

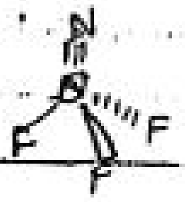


C_{2v}

(16) Propyne

C_{3v}

(17) NSF_3



C_{3v}

(18) $H_3O^{\oplus}$

C_{3v}

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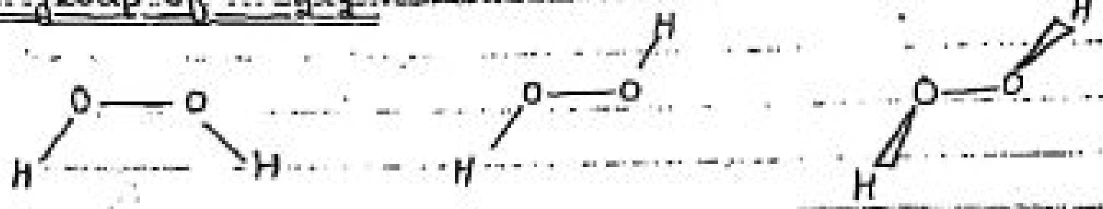
★ **Point group of H_2O_2 :-**



cis- H_2O_2 — C_{2v}

trans- H_2O_2 — C_{2h}

Open book — C_2

Qo:- Point group of H_2O_2 is _____

i) C_{2v} ii) C_{2h} iii) ✓ C_2 iv) D_{2h}

Qo:- Which one of the following is not point group of H_2O_2 → D_{2h}

Qo:- Point group of trans- H_2O_2 → C_{2h}

Qo:- " " " cis- " → C_{2v}

(3) **D_{nh} Point group :-**

Formula : $\boxed{C_n + nC_2 + n\sigma_v + 1\sigma_h}$

No. of operations = $4n$

$8 = D_{2h} = \underset{1}{C_2} + \underset{2}{2C_2} + \underset{2}{2\sigma_v} + \underset{1}{1\sigma_h} + \underset{1}{E} + \underset{1}{S_2}$

$12 = D_{3h} = \underset{2}{C_3} + \underset{3}{3C_2} + \underset{3}{3\sigma_v} + \underset{1}{1\sigma_h} + \underset{1}{E} + \underset{2}{S_3}$

$16 = D_{4h} = \underset{3}{C_4} + \underset{4}{4C_2} + \underset{4}{4\sigma_v} + \underset{1}{1\sigma_h} + \underset{1}{E} + \underset{2}{S_4} + \underset{1}{S_2}$

$20 = D_{5h} = \underset{4}{C_5} + \underset{5}{5C_2} + \underset{5}{5\sigma_v} + \underset{1}{1\sigma_h} + \underset{1}{E} + \underset{4}{S_5}$

Note:- ③ In case of D_{nh} pt. group, we will try S_n operation

If n = even then S_n and $S_{n/2}$ operations

n = odd " S_n operations = S_{n-1}

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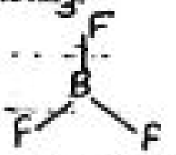
Note-4 No. of operations in improper axis

if n = even — $\frac{n}{2}$ formula

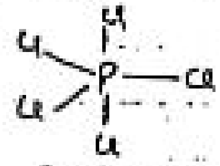
n = odd — $n-1$ formula

(1) BF_3



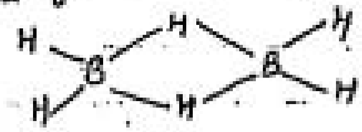
$C_3+3\sigma_v+1\sigma_h+3C_2 = D_{3h}$

(2) PCl_5



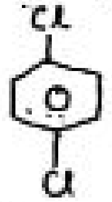
$C_3+3\sigma_v+3C_2+1\sigma_h = D_{3h}$

(3) B_2H_6



$C_2+2C_2+2C_2+1\sigma_h = D_{2h}$

(4)

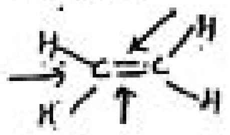


$C_2+2\sigma_v+2C_2+1\sigma_h = D_{2h}$

(5) Ethyne

$C_\infty+\infty\sigma_v+\infty C_2+1\sigma_h = D_{\infty h}$

(6) Ethene



D_{2h}

(7) H_2

H—H

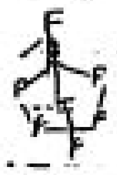
$D_{\infty h}$

(8) CO_2

O=C=O

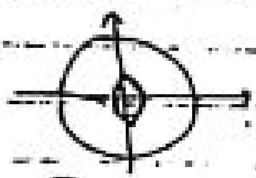
$D_{\infty h}$

(9) IF_7 (Grade 2015)



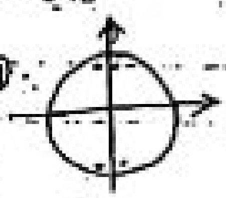
D_{5h}

(10)



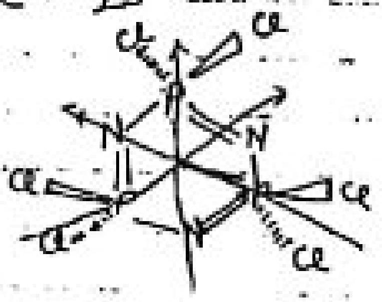
D_{2h}

(11)



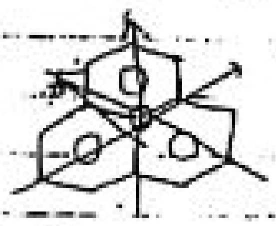
D_{2h}

(12) $(NPCl_2)_3$



D_{3h}

(13)

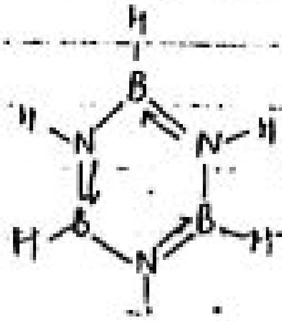


D_{3h}

(14)

D_{2h}

(15) $B_3N_3H_6$ (Borazine)



D_{3h}

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⇒ **Finding out no of operations in improper axis :-**

Prove

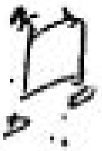
(a) When n = even , no. of operation $= \frac{n}{2}$

(i) S_2 :- $n = 2$ $= \frac{2}{2} = 1$

$C_2^1 \cdot \sigma^1 = S^1$

$C_2^2 \cdot \sigma^2 = E \cdot E = E$] No. of operation = 1.

(ii) S_4 :-



$C_4^1 \cdot \sigma^1 = S_4^1$

$C_4^2 \cdot \sigma^2 = C_2^1 \cdot E = C_2^1$

$C_4^3 \cdot \sigma^3 = C_4^3 \cdot \sigma = S_4^3$

$C_4^4 \cdot \sigma^4 = E \cdot E = E$] No. of operation = 2

(iii) S_6 :-

$C_6^1 \cdot \sigma^1 = S_6^1$

$C_6^2 \cdot \sigma^2 = C_3^1 \cdot E = C_3^1$

$C_6^3 \cdot \sigma^3 = C_2^1 \cdot \sigma = S_2^1 (i)$ No. of operations = 3

$C_6^4 \cdot \sigma^4 = C_3^2 \cdot E = C_3^2$

$C_6^5 \cdot \sigma^5 = C_6^5 \cdot \sigma = S_6^5$

$C_6^6 \cdot \sigma^6 = E \cdot E = E$

Note:- If n is even, repeatition of sequence occurs from $S_n^{n\text{th}}$

(b) If n = odd , no. of operations = $n-1$

(i) S_3 :-

$C_3^1 \cdot \sigma^1 = S_3^1$

$C_3^2 \cdot \sigma^2 = C_3^2 \cdot E = C_3^2$

$C_3^3 \cdot \sigma^3 = E \cdot \sigma = \sigma$

$C_3^4 \cdot \sigma^4 = C_3^1 \cdot E = C_3^1$

$C_3^5 \cdot \sigma^5 = C_3^2 \cdot \sigma = S_3^2$

$C_3^6 \cdot \sigma^6 = E \cdot E = E$

No. of operation = 2

(ii) S_5 :-

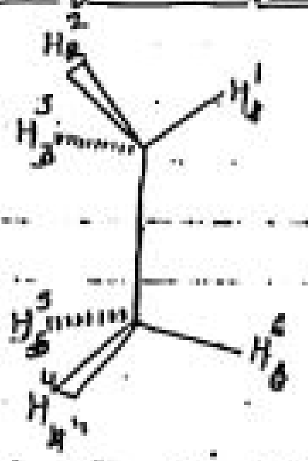
$$C_5^1 \cdot \sigma^1 = S_5^1$$
$$C_5^2 \cdot \sigma^2 = C_5^2 \cdot E$$
$$C_5^3 \cdot \sigma^3 = C_5^3 \cdot \sigma = S_5^3$$
$$C_5^4 \cdot \sigma^4 = C_5^4 \cdot E = C_5^4$$
$$C_5^5 \cdot \sigma^5 = E \cdot \sigma = \sigma$$
$$C_5^6 \cdot \sigma^6 = C_5^1 \cdot E = C_5^1$$
$$C_5^7 \cdot \sigma^7 = C_5^2 \cdot \sigma = S_5^2$$
$$C_5^8 \cdot \sigma^8 = C_5^3 \cdot E = C_5^3$$
$$C_5^9 \cdot \sigma^9 = C_5^4 \cdot \sigma = S_5^4$$
$$C_5^{10} \cdot \sigma^{10} = E \cdot E = E$$

No. of operations = 4

Note:-

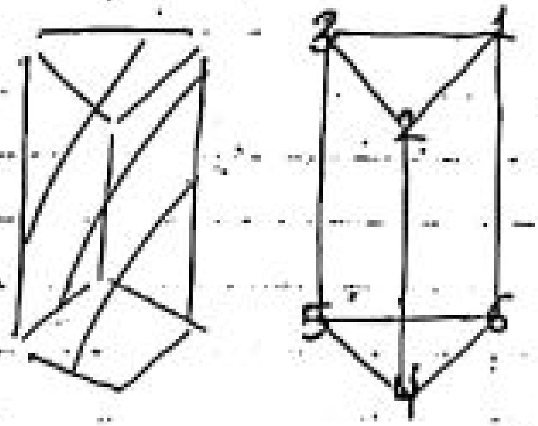
If n odd, Repeatition of Sequence occurs from S_n^{2n+1}

⇒ <u>Point group of eclipsed ethane</u> :- D_{3h}



⇒ H^1 is eclipsed H^6.
H^2 " " H^4
H^3 " " H^5

⇒ 1 C_3 axis passing through C–C bond and interchanging $H^1 \to H^2 \to H^3$ & $H^4 \to H^5 \to H^6$



⇒ 1st C_2 axis passing through middle of C–C bond (H_1–H_6 edge) and interchanging H^1 with H^6, H^2 with H^5 and H^3 with H^4.

→ 2nd C_2 axis passing through the middle of C–C bond (H_2–H_4 edge) and interchanging H^2 with H^4, H^1 with H^5 & H^3 with H^6.

⇒ 3rd C_2-axis passing through middle of C–C bond (H^3-H^5 edge) and interchanging H^3 with H^5, H^1 with H^4 & H^2 with H^6.

⇒ 1st vertical plane (σ_v) bisecting H^1–C–C–H^6 & reflecting H^2 with H^3 & H^4 with H^5.

⇒ 2nd σ_v bisecting H^2–C–C–H^4 & reflecting H^1 with H^3 & H^5 with H^6.

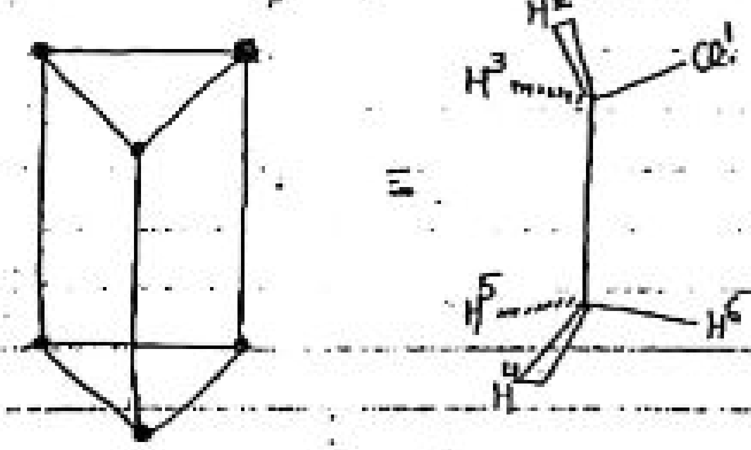
⇒ 3rd σ_v bisecting H^3–C–C–H^5 & reflecting H^1 with H^2 & H^4 with H^6.

⇒ 1 σ_h bisecting C–C bond & reflecting H^1 with H^6, H^2 with H^4 & H^3 with H^5.

$$C_3 + 3C_2 + 3\sigma_v + 1\sigma_h = D_{3h}$$

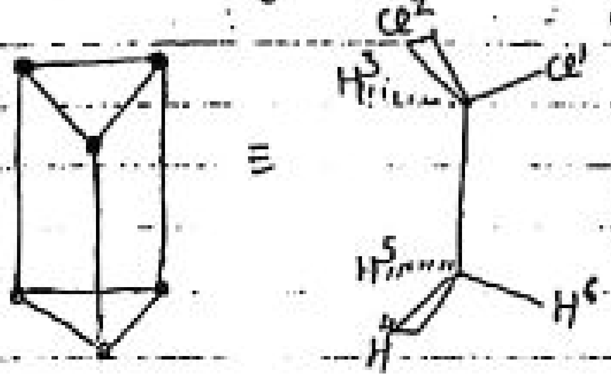
No. of operation $= 4n = 4 \times 3 = 12$

(a) H^1 is replaced by Cl^1.



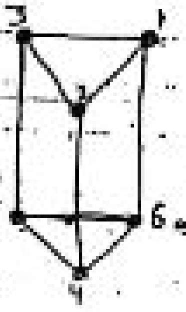
$\sigma \Rightarrow C_s$

(b) H^1 is replaced by Cl^1 & H^2 with Cl^2:



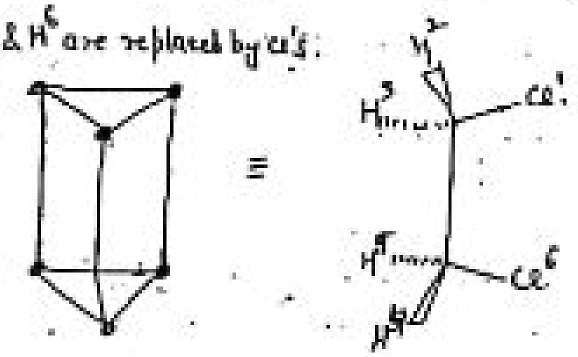
$\sigma \Rightarrow C_s$

Ⓒ H^3 is also replaced by Cl^3:-



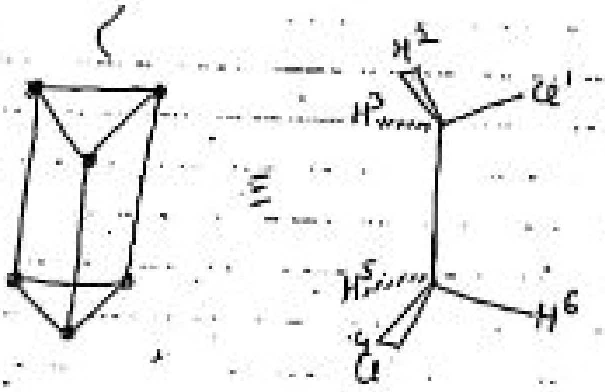
$$C_3 + 3\sigma_v = \boxed{C_{3v}}$$

ⓓ H^1 & H^6 are replaced by Cl's:



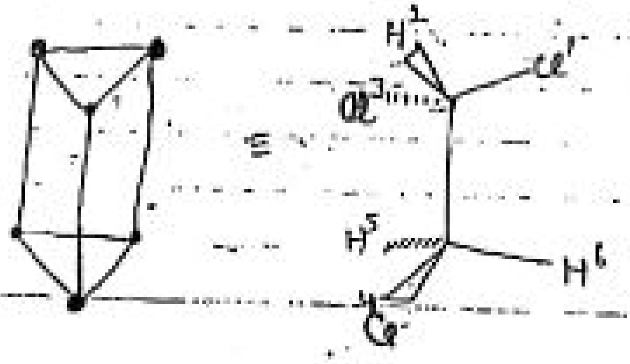
$$C_2 + 2\sigma_v = \boxed{C_{2v}}$$

ⓔ



$$\boxed{C_2}$$

(f)



$$\boxed{C_s}$$

Eclipsed Ethane

If one substitution = C_s

two " of same Carbon = C_s

three " " = C_{3v}

two " different C of same edge = C_{2v}

" " " " different = C_2

(4.) D_{nd} Point group :-

$$C_n + nC_2 + n\sigma_d$$

No. of operations = $4n$

$8 = D_{2d} = \underset{1}{C_2} + \underset{2}{2C_2} + \underset{2}{2\sigma_d} + \underset{1}{E} + \underset{2}{S_4}$

$12 = D_{3d} = \underset{2}{C_3} + \underset{3}{3C_2} + \underset{3}{3\sigma_d} + \underset{1}{E} + \underset{2}{S_6} + \cancel{i}$

(excluding i)

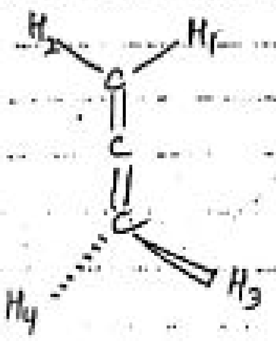
$16 = D_{4d} = \underset{3}{C_4} + \underset{4}{4C_2} + \underset{4}{4\sigma_d} + \underset{1}{E} + \underset{4}{S_8}$

Note :- In case of D_{nd} point group, we will try S_{2n} operations

Examples :

Allene :-

⇒ Point group of Allene :- $D_{2d} = C_2 + 2C_2 + 2\sigma_d$



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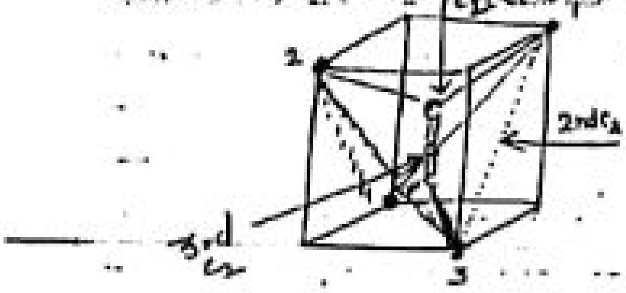
upper & lower faces are square's.
other side faces are rectangle.

1^{st} C_2 (Principle axis) b/c passing through max^m no. of

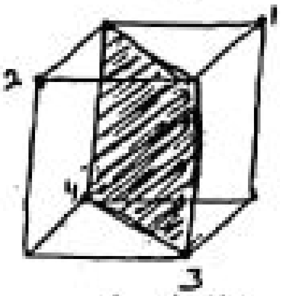


(entering)
(i) Ist C_2 axis passing through (1-2) diagonal and outgoing through (3-4) diagonal & inter-changing H_1 with H_2 & H_3 with H_4.

(ii) 2nd C_2-axis entering through (1-3) diagonal and outgoing through (2-4) diagonal & interchanging H_1 with H_3 & H_2 with H_4.

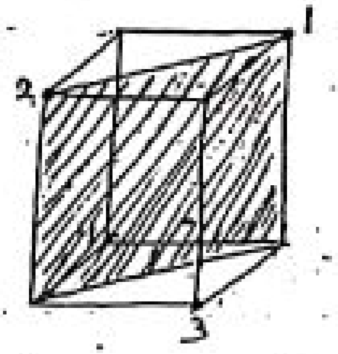
(iii) 3rd C_2-axis entering through (2-3) diagonal and outgoing through (1-4) diagonal & interchanging H_2 with H_3 & H_1 with H_4.

(iv)



Ist dihedral plane (σ_d) bisecting H_3 and H_4 and 3 carbon atoms and reflecting H_1 with H_2.

(v)

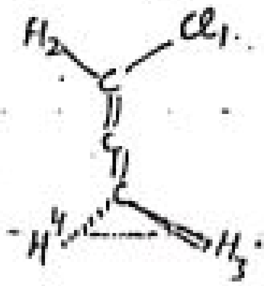


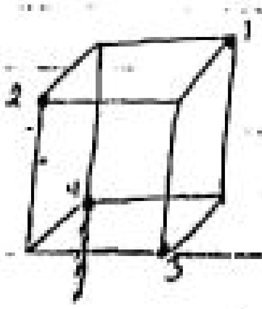
2nd σ_d bisecting H_1 & H_2 and 3 carbon atoms and reflecting H_3 with H_4.

$\boxed{C_2 + 2C_2 + 2\sigma_d} \rightarrow D_{2d}$

Only one plane (σ)

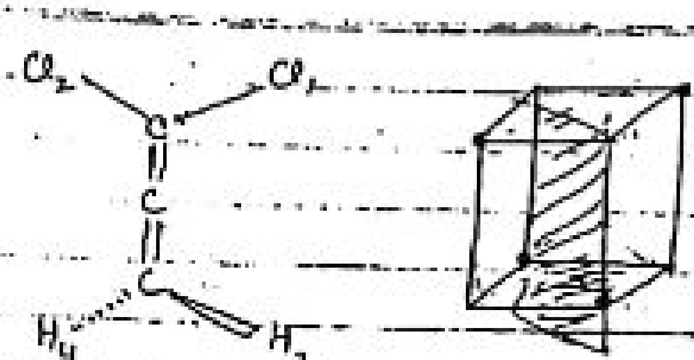
(a)





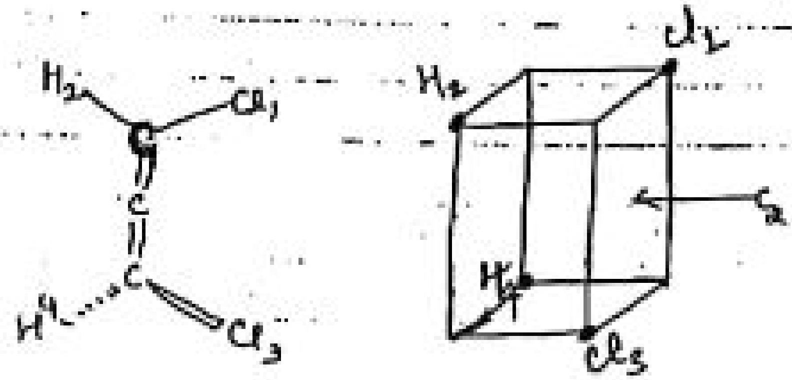
$\boxed{C_s}$

(b)



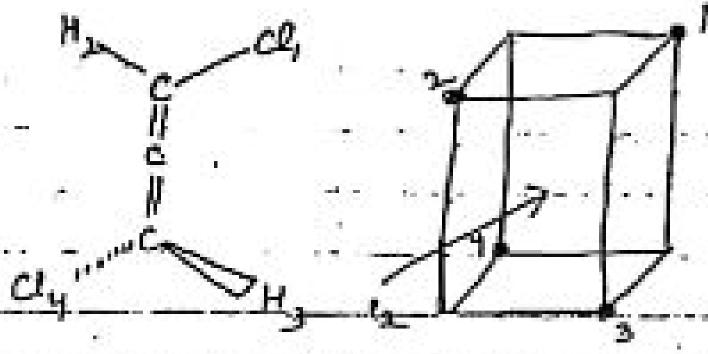
$C_2 + 2\sigma_v = \boxed{C_{2v}}$

(c)



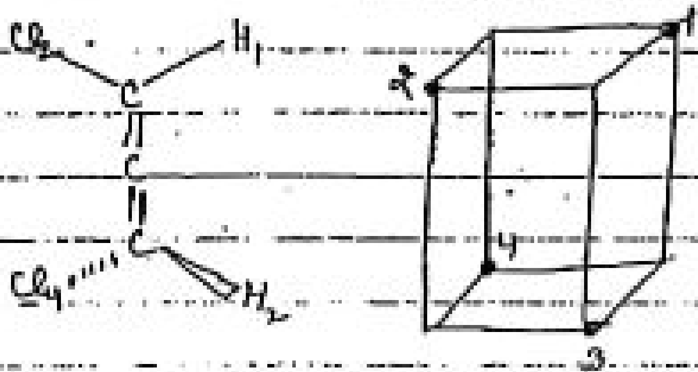
$\boxed{C_2}$

(d)



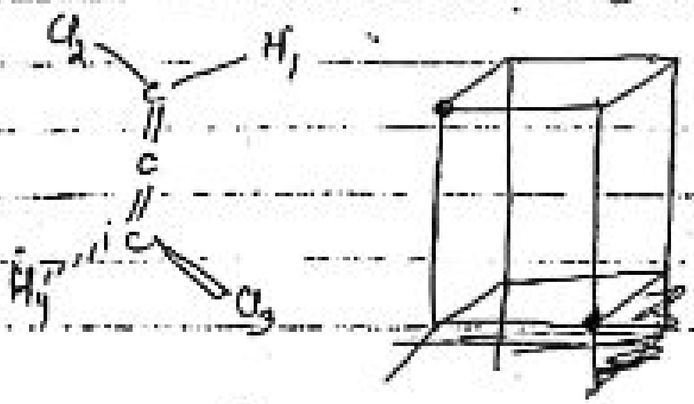
$\boxed{C_2}$

(e)



$\boxed{C_2}$

(f)



$\boxed{C_2}$

★ Conclusion ⇒ * If one H of allene is substituted by Cl, Point gp. is C_s.

* If 2 H's of same carbon is substituted → C_{2v}
* " " " " different " → C_2
*

Qo:- For this molecule $CH_2=(C)_x=CH_2$, $x = 1, 2, 3, \ldots n$.

(a) No. of operations does not depend upon value of x → $\boxed{\text{True}}$

Reason:- If x = odd (behave like allene)

$D_{2d} = 4n = 8$

If x = even (behave like ethene).

$D_{2h} = 4n = 8$

(b) Improper axis present is same for all values of x. $\boxed{\text{False}}$

If x = odd, $D_{2d} = S_4$

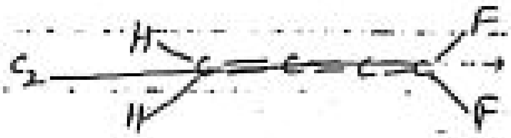
" x = even $D_{2h} = S_4$

(c) There is no change in no. of operations if 2 H's of same carbon is replaced by F for all values of x. $\boxed{\text{True}}$

If x = odd (Allene)

C_{2v} & No. of operations = 4

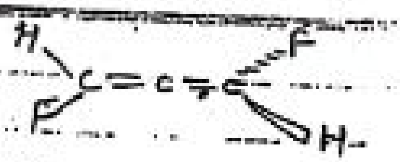
If x = even (alkene)



C_{2v} & No. of operations = 4

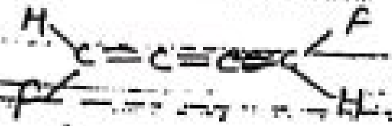
(d) There is no change in no. of operations if two H's of different carbon are substituted by F for all values of x. $\boxed{\text{False}}$

If x = odd.



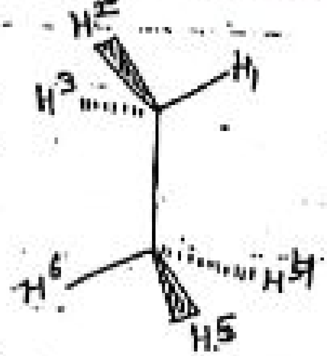
⇒ C_2 & No. of operations = 2

If x = even



→ C_{2h} & No. of operations = 4

⇒ <u>Staggered Ethane</u> :- $\boxed{D_{3d}}$ ⇒ $C_3 + 3C_2 + 3\sigma_d$.



H^1 is anti-staggered to H^6.
H^2 " " " H^4
H^3 " " " H^5

Figure-1.

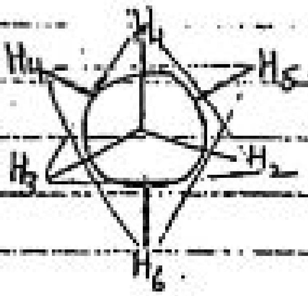


Figure-2

≡

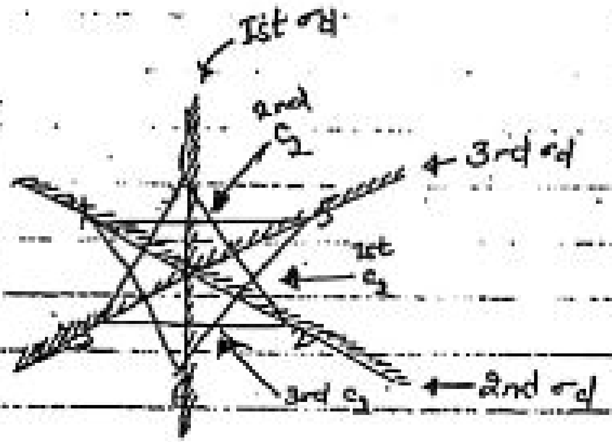


Figure-3

(i) C_3 axis passing through C–C bond and interchanging $H^1 \to H^2 \to H^3$ & $H^4 \to H^5 \to H^6$.

(ii) 1st C_2-axis interchanging : H^1 with H^6, H^2 with H^5 & H^3 with H

(iii) 2nd " " " H^1 with H^5, H^2 with H^4 & H^3 with H^6.

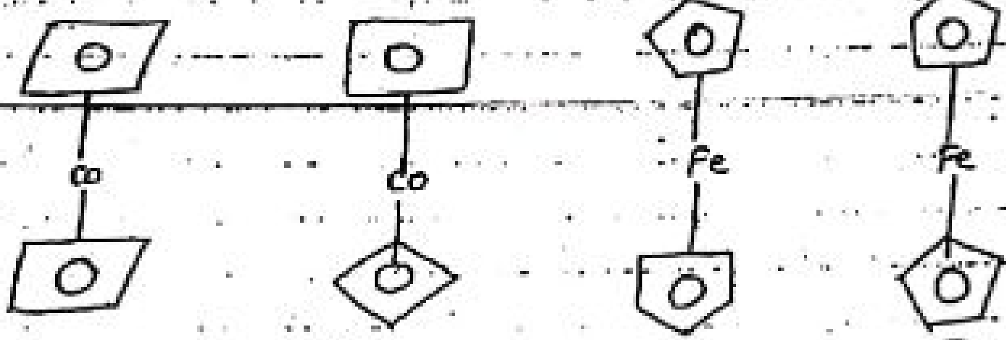
(iv) 3rd " " " H^2 with H^6, H^3 with H^5 & H^1 with H^4.

(v) 1st σ_d bisecting H^1–C–C–H^6 & reflecting H^2 with H^3 & H^4 with H^5.

(vi) 2nd " " H^2–C–C–H^4 & " H^1 with H^3 & H^5 with H^6.

(vii) 3rd " " H^3–C–C–H^5 & " H^1 with H^2 & H^4 with H^6.

Point group of substituted staggered Ethane :-



D_{4h} D_{4d} D_{5d} D_{5h}

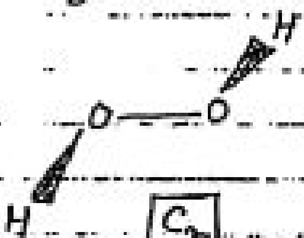
(5) **C_n Point group** :- $C_n + E$

No. of operations $= n$

$C_2 = C_2 + E = 2$

$C_3 = C_3 + E = 3$

(i) H_2O_2

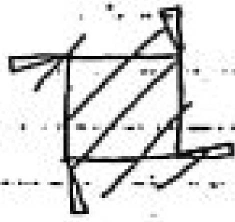


$\boxed{C_2}$

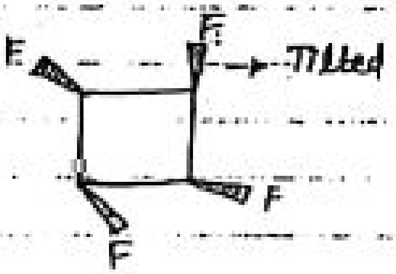
(ii) PPh_3

$\boxed{C_3}$

(iii)



(iii)



$\boxed{C_4}$

(6) **S_{2n} Point Group :-** $\boxed{S_{2n} + C_n + E}$

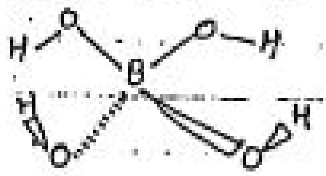
$n = 1, 2, 3, \ldots$

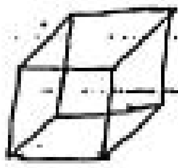
No. of operations $= 2n$

S_4 :- $S_4 + C_2 + E$ No. of operation

$2 \quad 1 \quad 1 = 4$

(a) $B(OH)_4^{\ominus}$:-





(7) **D_n Point group :-** $\boxed{C_n + nC_2}$

No. of operations $= 2n$

$6 = D_3 \Rightarrow C_3 + 3C_2 + E$

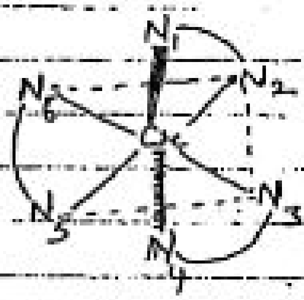
$\quad\quad 2 \quad 3 \quad 1$

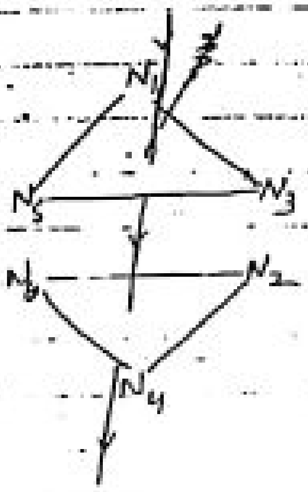
$8 = D_4 \Rightarrow C_4 + 4C_2 + E$

$\quad\quad 3 \quad 4 \quad 1$

(a) $D_3 \Rightarrow M(AA)_3$ $[C_3 + 3C_2]$

i.e. $Co(en)_3 \Rightarrow D_3$





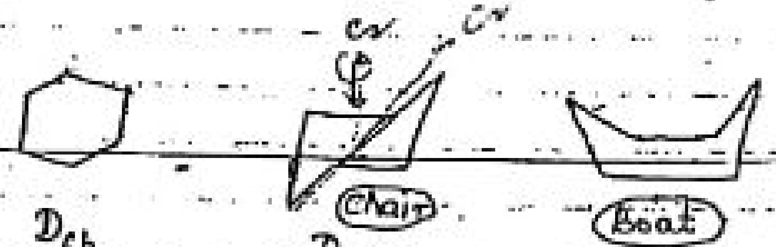
(1) C_3 axis entering through Ist triangle & outgoing through lower triangle

(2) Ist C_2 entering through $N^5 - N^6$ relation and interchanging $N_1 - N_2$ with $N_4 - N_3$.

(3) IInd " " " $N_3 - N_4$ & interchanging $N_1 - N_6$ with $N_2 - N_5$.

(4) IIIrd " " " $N_5 - N_2$ & interchanging $N_1 - N_4$ with $N_5 - N_6$.

⇒ Example of D_2 :- Twisted boat form of cyclohexane.

⇒ 

D_{6h} D_{3d} (Just like staggered ethane) C_{2v}

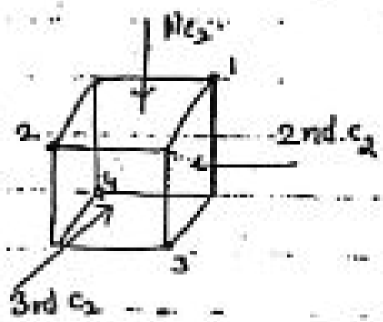
★ Tetrahedral Point group :- CH_4

① 4 corners ② 6 Edges ③ 4 triangular faces

Total no. of operations = 24. $(8+3+6+6+1=24)$

(1.) $4\ C_3$-axis passing through each C–H bond through each corner. ⇒ 8 operations.

(2.) $3\ C_2$-axis passing through opposite edge or faces of cube. ⇒ 3 operations.

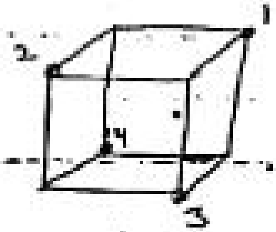


(3.) 3- S_4 along each C_2-axis ⇒ 6 operations

(4.) $6 - \sigma_d$ (dihedral plane) ⇒ 6 operation

(5.) Identity (E) ⇒ 1 operation.

⇒ How there are 6 dihedral Planes :-



Bisecting	Reflecting
1, 2	[illegible] 4
1, 3	2 – 4
1, 4	2 – 3
2, 3	1 – 4
2, 4	1 – 3
– ,,	1 – 2

9+8+6+6+8+3+6+1+1 = 48

⇒ Octahedral Point group :- SF_6 [No-of operations = 48]

6 corners, 12 edges, 8 triangular faces ⇒ 9

1. 3 - C_4 axis passing through opposite corners ⇒ 9
2. 4 - C_3 axis passing through opposite triangular faces ⇒ 8
3. ~~6 - C_2 axis passing through opposite edges ⇒ 6~~
4. 3 - S_4 axis along each C_4 axis ⇒ 6
5. 4 - S_6 axis along each C_3 - axis ⇒ 12 - 4 ⇒ 8 (Excluding i)
6. 3 - σ_h perpendicular to each C_4 - axis ⇒ 3
7. 6 - σ_d (dihedral planes) ⇒ 6
8. 1 - i (Inversion centre) ⇒ 1
9. 1 - E (identity) ⇒ 1

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