P.G. Sem. IInd
Inorg. Chem.
Core course - VI
Unit III

Point Symmetry of molecules :-

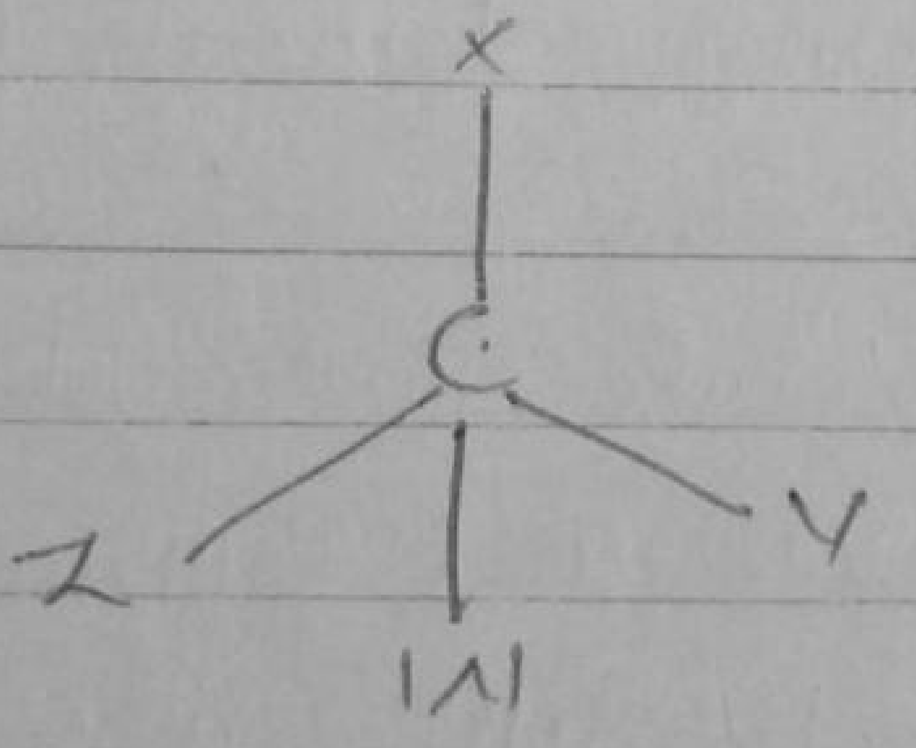
A number of symm. operations can be carried out on a molecule. A short hand notation which gives information about the number of symm. operations possible on the molecule is called point symmetry. The term point symmetry is used, because in carrying out all these operations, the centre of the symm. of the molecule, or in its absence, the centre of gravity of the molecule remains unaffected.

For obtaining point symm. of a ~~molecule~~ a molecule the following points are necessary →.

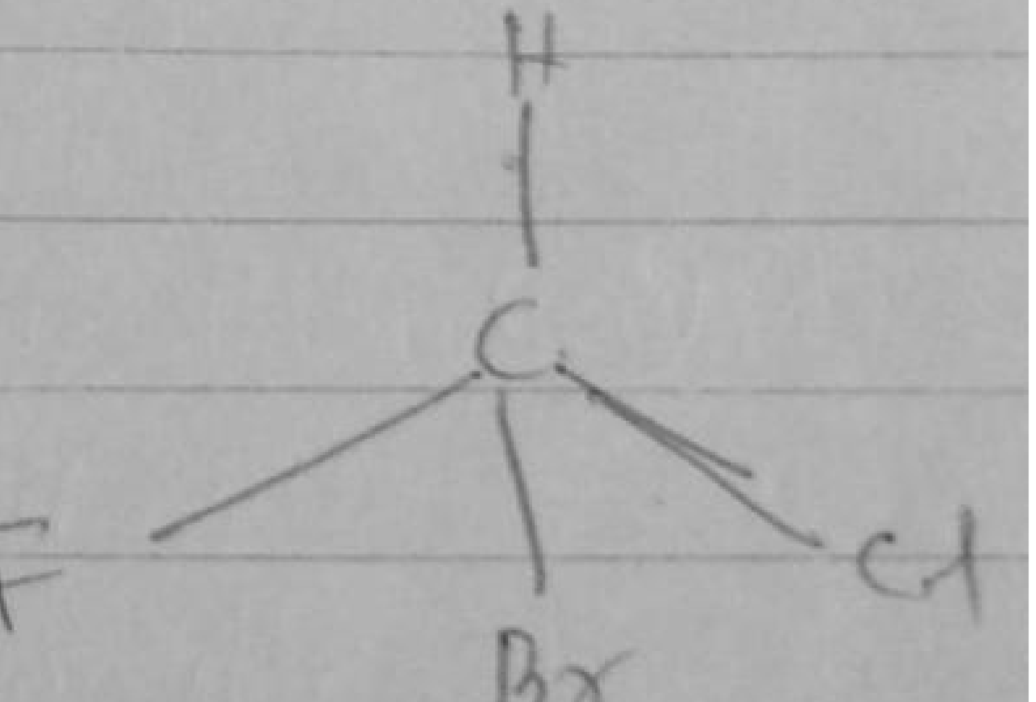
(1) First see whether the molecule belongs to the special point symmetries $C_{\infty v}$, $D_{\infty h}$, Td, Oh. or icosahedron.

(2) If the molecule is completely unsymmetrical and has only identity, it can be said to have an axis of one fold symmetry. Any unsymm. molecule on being rotated by 360° on any axis (C_1) will give the original orientation. Thus C_1 is an identi[ty] operation. Such molecules are assigned point symm[etry] C_1.

Example — example of such ~~molecule~~ is a case is Tetrasubstituted methane molecule.



i.e



Point group C_1

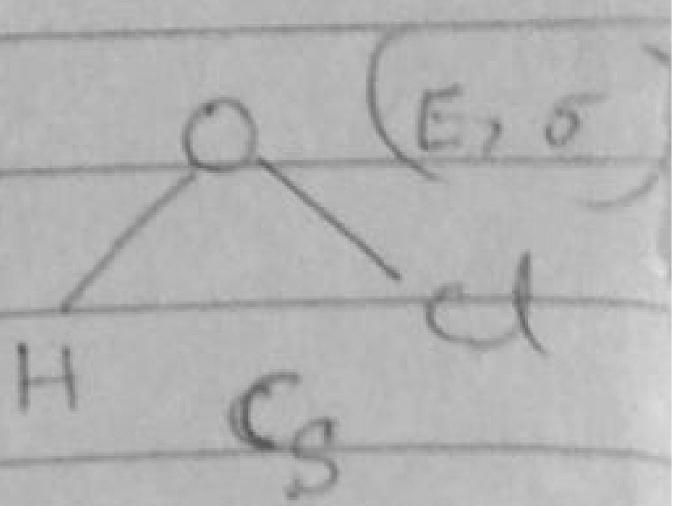
Symm. operation E (C_1)

Example →

SiBrClFI

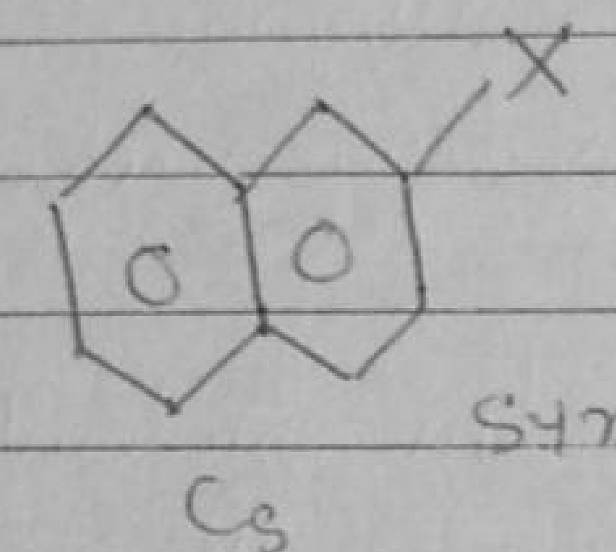
(3) If the molecule has only a plane of symm. the notation used for the point symmetry is C_s.

Example → (i) HOCl



(ii) Monosubstituted naphthalene molecule → It has only molecular plane as the plane of symmetry. There is no other element of symmetry. hence it has C_s point symm.

C_s

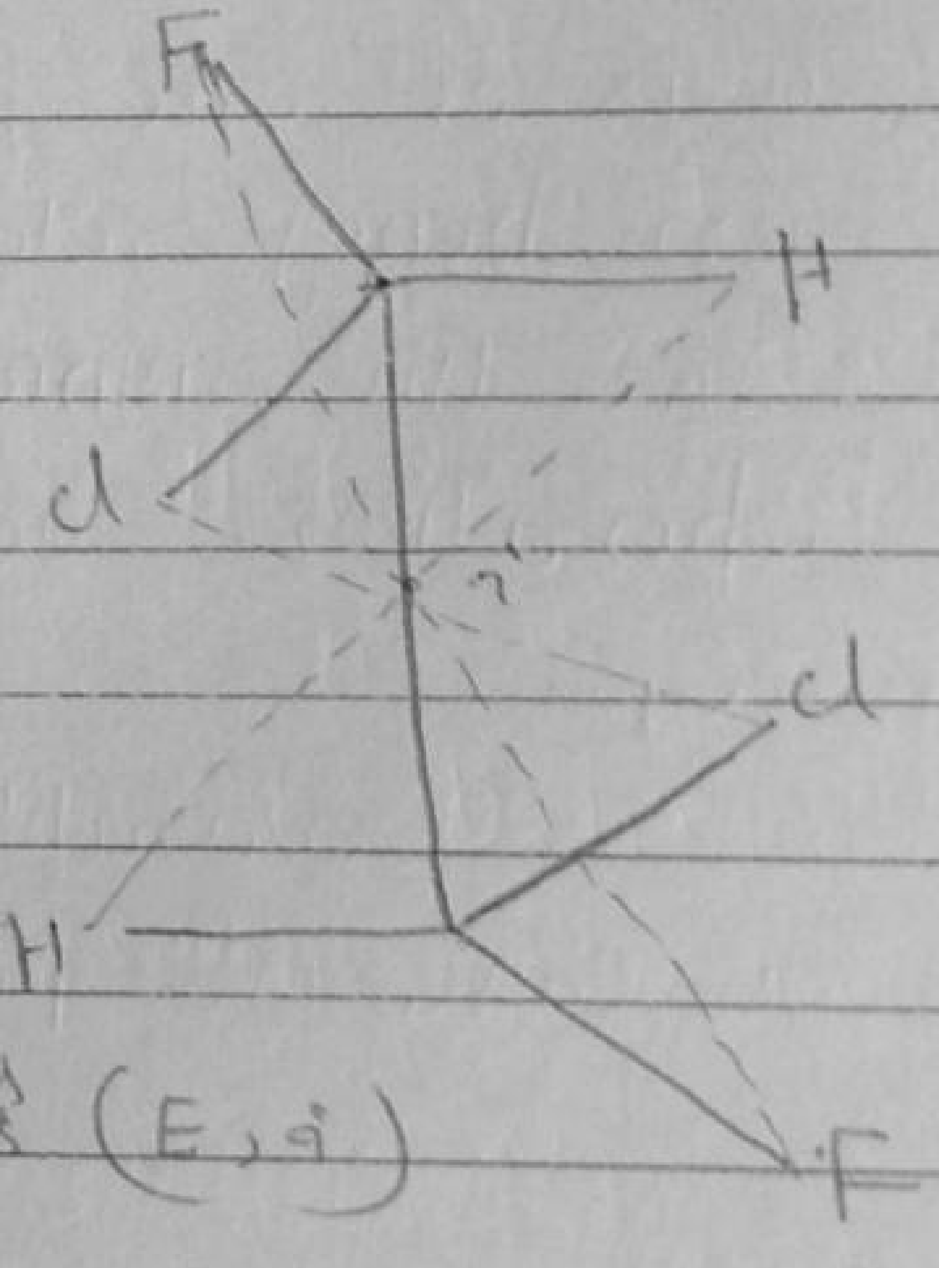


symm. operation E, σ

(4) If the molecule has only centre of symmetry and no other operation is possible, point symm. assigned is C_i.

Example → 1,2-dichloro-1,2-difluoro ethane molecule in staggered form.

C_i



symm. ~~elements~~ operations (E, i)

(5) If the molecule has only one axis of n-fold symm the point symm. assigned is C_n. The symm. operations possible are E and n-1 rotation.

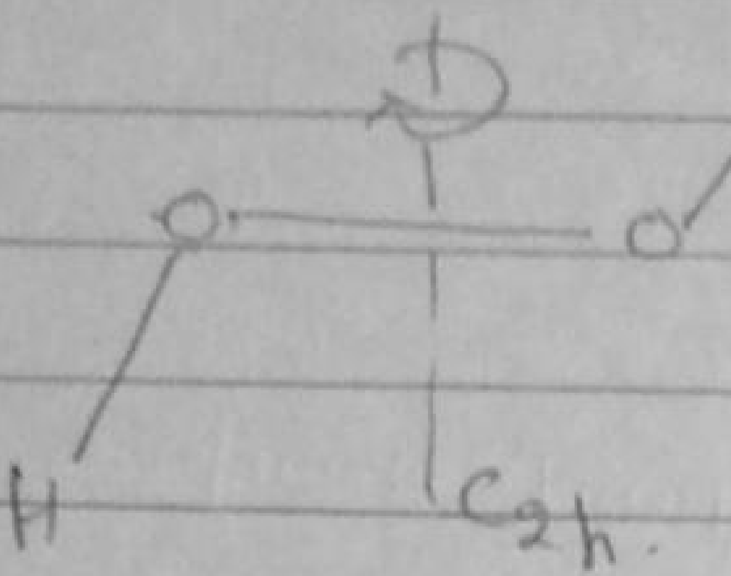
(6) If the molecule has an axis of improper rotation of n-fold symm., it is assigned ~~as~~ point symm. S_n. In such molecules symm. operation possible are E and n-1 improper rotation

(7) If the molecule has a C_n axis and a horizontal plane, it is assigned point symm. C_{nh}.

Example →

Trans H_2O_2

C_{2h}



There is an axis C_2 ⊥r to the molecular plane. The plane of molecule is plane of symm. and is ⊥r to principal axis

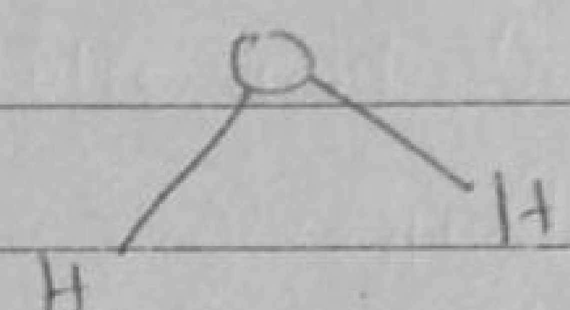
Symm. operations — E, C_2^1, σ_h, i = 4

(8) If the molecule has a C_n axis and n vertical plane of symmetry, it is assigned point group C_{nv}.

Example →

(i) H_2O →

C_{2v}



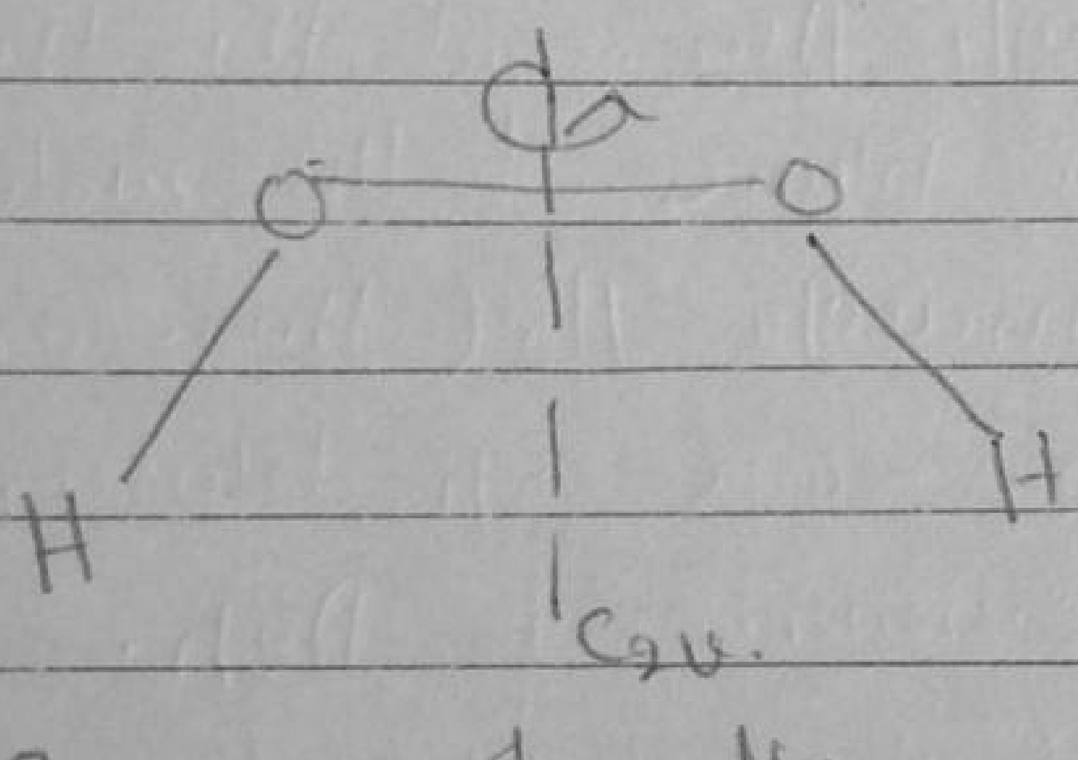
It has one C_2 axis and two σ_v plane ~~C_{2v} grp.~~

point group C_{2v}.

Symm. operations — $C_2^1, \sigma_{xy}, \sigma_{yz}, E = 4$

(ii) cis H_2O_2 →

C_{2v}

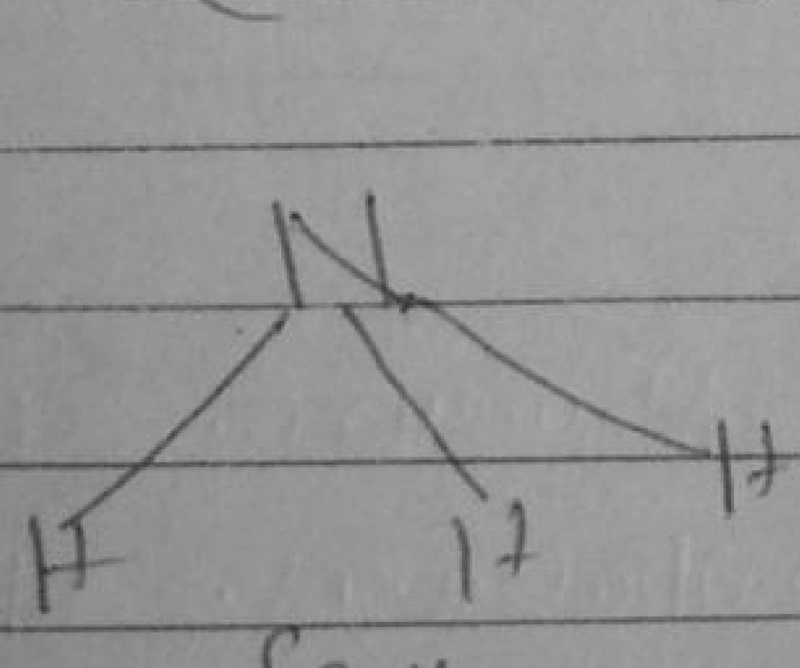


cis H_2O_2 has one C_2^1 axis and two σ_v plane and belong C_{2v} point group.

Symm. operations — $E, C_2, \sigma_{xz}, \sigma_{yz} = 4$

(iii) NH_3 → It has an axis of three-fold symm and three vertical planes. The point symm. is C_{3v}. There are six symm. operations.

C_{3v}



C_{3v}.

Symm. operations — $E, C_3^1, C_3^2, 3\sigma_v$ =

Example →. $POCl_3$, CH_3Cl.

other example of C_{2v} group →. SO_2Cl_2, $SiCl_2.Br_2$.

PF_5 → The molecule has a trigonal bipyramidle but the symm. operations possible are as in BF_3 and hence point symm. is D_{3h}.

D_{3h}

Square Planar Structure :→ (AB_4)

It has principal axis C_4. This is also an axis of improper rotation S_4. There are four subsidiary axes C_2, four vertical plane σ_v and one horizontal plane σ_h. The point symm. is D_{4h}.

D_{4h}

Symm. operations possible are —

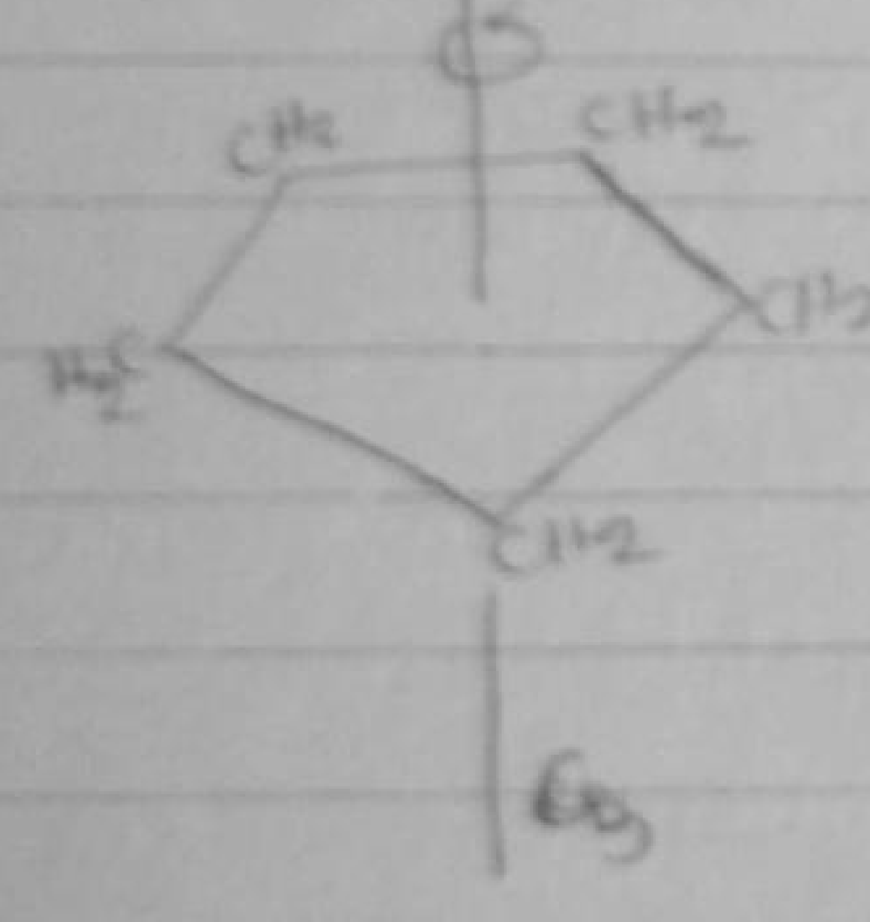
$E, C_4^1, C_4^2, C_4^3, S_4^1, S_4^3, 4C_2^1, 4\sigma_v, \sigma_h, i = \underline{16}$

$[Ni(NH_3)_4]^{2+}$ and $[Ni(CN)_4]^{2-}$ has D_{4h} point group

Cyclopentane →

It has principal axis perpendicular to the plane of the molecule C_5. It has also five C_2 subsidiary axes each passing through one C-atom and centre of the opposite edge.

D_{5h}



C_5 axis is also S_5. There are five vertical plane and one σ_h. point symm. is D_{5h}.

Symm. operations $= E, C_5^1, C_5^2, C_5^3, C_5^4$
$5C_2^1, 5\sigma_v, \sigma_h, S_5^1, S_5^3, S_5^7$
$S_5^9 = \underline{20}$

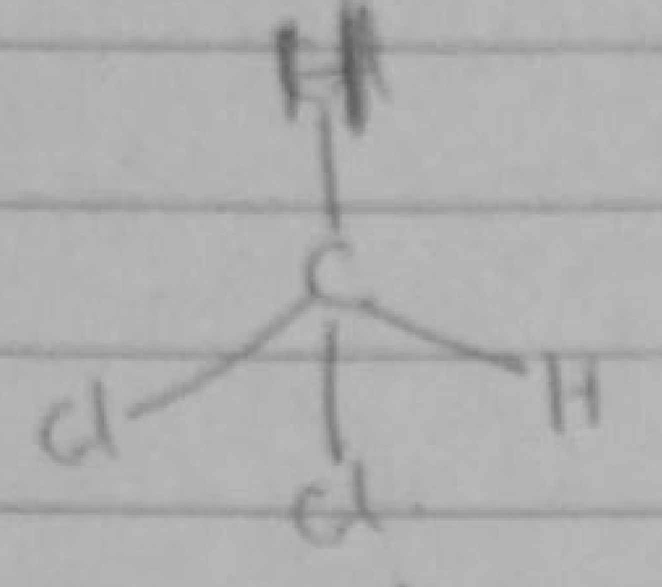
Benzene (C_6H_6) →

It has C_6 principal axis $\perp^r$ to molecular plane. There are also six subsidiary axes C_2. six σ_v, one σ_h. point symm. is D_{6h}.

D_{6h}

The possible symm operations $= E, C_6^1, C_6^2, C_6^3, C_6^4$
$C_6^5, 6C_2, S_6^1, S_6^5, 6\sigma_v, \sigma_h, i, S_3^1, S_3^2$

(ii) $CH_2Cl_2 \rightarrow C_{2v}$



(i) It has one C_2-axis.

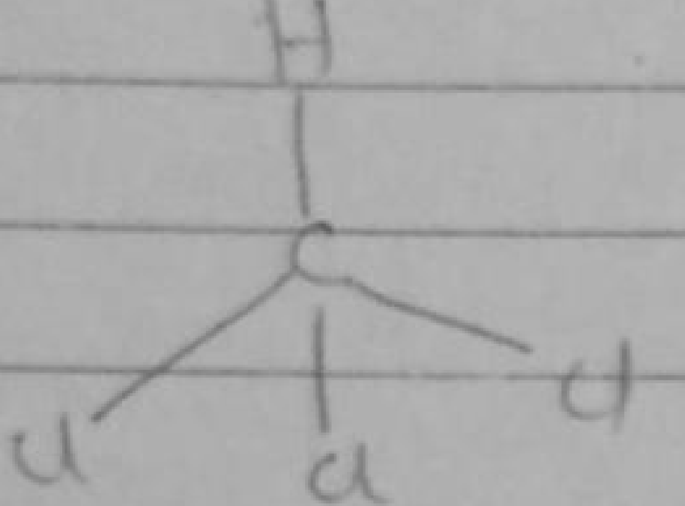
(ii) It has two σ_v plane.

Hence symm. point group = C_{2v}.

Possible operations →

$E, C_2, 2\sigma_v = 4$

(iii) $CHCl_3 \rightarrow C_{3v}$



(i) It has C_3^1, C_3^2 axis

(ii) It has $3\sigma_v$ plane

Hence it has symm. point group = C_{3v}

Possible symm. operations -

$E, C_3^1, C_3^2, 3\sigma_v = 6$

Find the point group of the following -

(1) ICl_4^- (2) C_2H_4 (3) C_4H_8 (4) C_5H_5N (5) CCl_4

(6) 1, 3, 5 trichloro benzene

(1) $ICl_4^- \rightarrow D_{4h}$

(i) It has C_4 - axis of rotation as a principal axis

(ii) It has four subsidiary axis.

(iii) It has S_4 axis of improper rotation S_4^1, S_4^3.

(iv) It has four σ_v plane and one σ_h plane.

Symm. operation possible

$E, C_4^1, C_4^2, C_4^3, 4C_2, 4\sigma_v, \sigma_h, S_4^1, S_4^3, i$

$= 16$