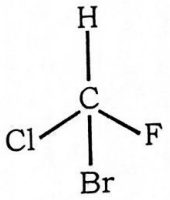
4.7 PointGroups and Classifications

Molecule may be of high symmetry or may be of low symmetry. Symmetry of the molecule can be judged using the symmetry elements and symmetry operations present in them. All the symmetry operations present in a molecule form a group. A molecular group is called as a point group. The symmetry group or a point group of a molecule is denoted by a specific symbol. This symbol was introduced by Schoenflies. Several molecules have the same set of operations and hence, belong to the same point group but different set of operations belong to the different point group.

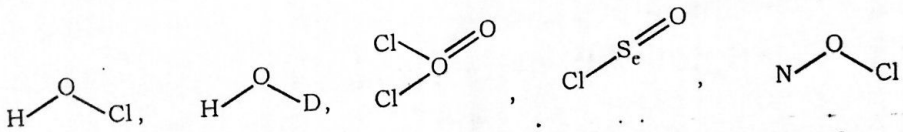
Classification : Molecules are classified into different groups.

Type 1 : Molecules with low symmetry.

(i) **Point group C_1**—Molecule having no other symmetry elements except identity (E) belong to this group. This group has a onefold proper axis of rotation (C_1) and includes all molecule possessing one assymetric atom.

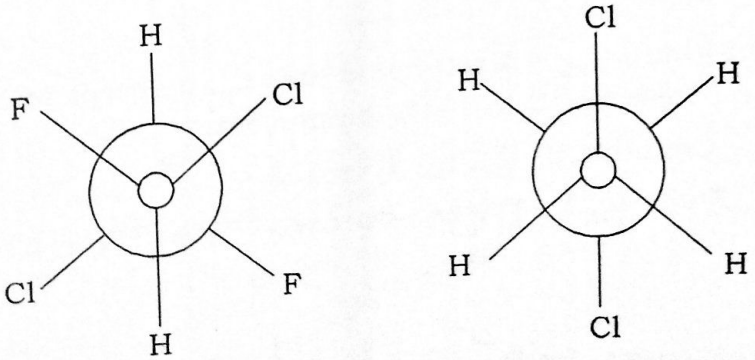


(ii) **Point group C_s**—This group has only two elements of symmetry i.e., E (identity) and σ (plane of symmetry) e.g.,



(iii) **Point group C_i**—This group has only two elements of symmetry i.e., E and i (point of symmetry)

i.e., 1, 2–dichloro dibromoethane



(iv) Point group C_n – This group has only a n–fold proper rotational axis e.g., 1, 2–Dichloroethane–point group C_2, 1, 3–Dichloroallene – point group C_3.

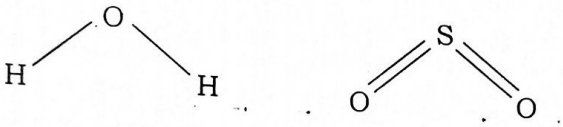
Type–2 : Molecules with intermediate symmetry.

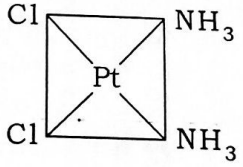
Characteristic for this type of symmetry group is the presence of rotational axis (C_n) along with plane of symmetry (σ), subsidiary rotational axis (C_2), point of symmetry (i).

(i) **Point group C_{nv}**—The assocation of a rotational axis (C_n) with *n* vertical reflection planes ($n\sigma_v$) generates C_{nv} point group. There are so many molecules which have C_{nv} point group.

(a) C_{2v} – contains E, C_2 and $2\sigma_v$

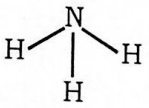
e.g., H_2O, SO_2, CH_2Cl_2, ClF_3, SO_2Cl_2, $SiCl_2Br_2$, $BClF_2$, C_6H_5X, $C_6H_4X_2$(0 & m), *Cis*–$[Pt(NH_3)_4Cl_2]^{--}$, *Cis*–$[Pt(NH_3)_2Cl_2]$, *Cis*–H_2O_2.





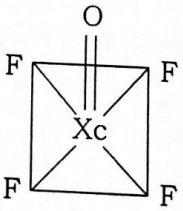
(b) C_{3v} – Contains E, $2C_3$ and $3\sigma_v$

e.g., NH_3, PH_3, PCl_3, $CHCl_3$, $POCl_3$, CH_3Cl



(c) C_{4v} – Contains E, $3C_4$ and $4\sigma_v$

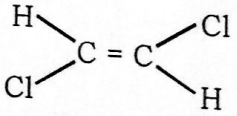
e.g., $[Co(NH_3)_4ClH_2O]^+$, SF_5Cl (octahedral), $XeOF_4$, ClF_5



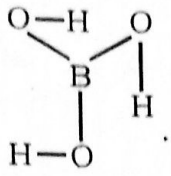
(ii) Point group C_{nh} – A rotational axis C_n, σ_h perpendicular to C_n gives rise to C_{nh} group. Here Sn ($C_n.\sigma^h$) also be present.

(a) C_{2h} – Contains E, C_2, σ_h, S_2 (≡ i)

e.g., *Trans*–H_2O_2, *Trans*–2–butene, *Trans*–CHCl = CHCl, *Trans*–N_2F_2

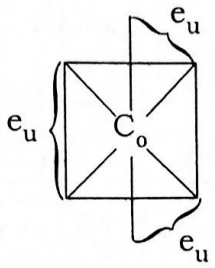


(b) C_{3h} – Contains E, $2C_3$, σ_h, $2S_3$
e.g., H_3BO_3 (Planar)



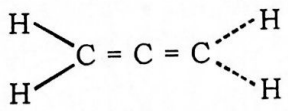
(iii) **Point group D_n**—A D_n group is generated by high order rotational axis C_n ($n = \geq 2$) and nC_2 axes pependicular to it. This group has only a few molecular species.

(a) D_3 – e.g., $[Co(en)_3]^{+++}$, Gauche conformation of ethane.

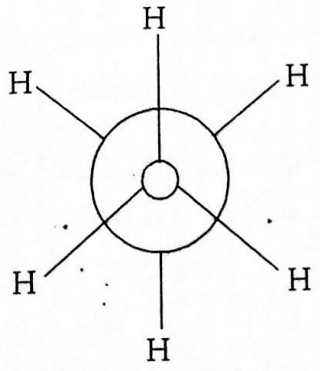


(iv) **Point group D_{nd}**—The D_{nd} groups are generated by the association of the D_n ($C_n + nC_2$) elements with n dihedral planes ($n\sigma_d$).

(a) D_{2d} – Contains E, $3C_2$ (mutually perpendicular), S_4 e.g., Allene, cyclooctatetroene.

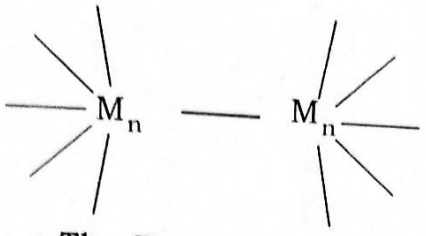


(b) D_{3d} – Contains E, $2C_3$, $3C_2$, S_6, i, $3\sigma_d$
e.g., staggered ethane, cyclohexane



(c) D_{5d} – Contains E, $4C_5$, $5C_2$, $5\sigma_d$

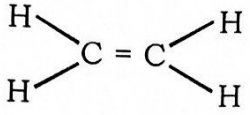
e.g., $Mn_2(Co)_{10}$, staggered ferrocene



(v) Point group D_{nh} – The D_{nh} groups are generated by the association of D_n (C_n + nC_2) with σ_n and improper axes also.

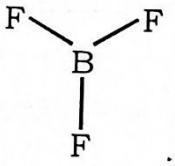
(a) D_{2h} – Contains E, C_2, $2C_2$, $2\sigma_v$, σ_n, i

e.g., C_2H_4, N_2O_4 (planar), $C_2O_4^{--}$, $Pt(NH_3)_2Cl_2$ *trans*, *para*–$C_6H_4X_2$, Naphthalene.



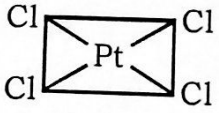
(b) D_{3h} – Contains E, $2C_3$, $3C_2$, $3\sigma_v$, σ_h, $2S_3$

e.g., BF_3, PF_5, PCl_5, SO_3, BCl_3, CO_3^{--}, NO_3^-, C_2H_6 (eclipsed), planar–tribromobenzene.



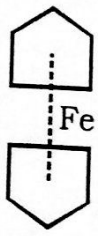
(c) D_{4h} – E, $3C_4$, $4C_2$, $4\sigma_v$, σ_h, i, $2S_4$

e.g., $[PtCl_4]^{--}$, $[Ni(CN)_4]^{--}$, trans–SF_4Cl_2, *trans* MA_4B_2 coplanar cyclobutane.



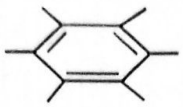
(d) D_{5h} – E, $4C_5$, $5C_2$, $5\sigma_v$, σ_h, $2S_5$

e.g., cyclopentane, eclipsed ferrocene



(e) D_{6h} – E, $5C_6$, $6C_2$, $6\sigma_v$, σ_h, $2S_6$, i .

e.g., Benzene, Eclipsed C_v $(C_6H_6)_2$

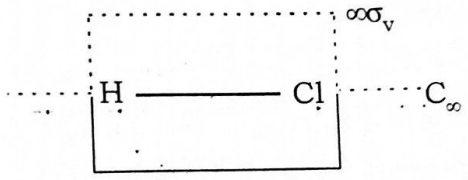


Type – 3 : Molecules of high symmetry.

[A] Linear Molecules :

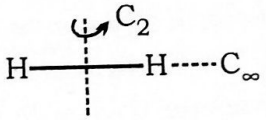
(i) Point group $C_{\infty v}$ – The linear molecules have infinite rotational axis (C_∞) and infinite no. of vertical plane ($\infty\sigma_v$) $C_{\infty v}$ – E, C_∞, $\infty\sigma_v$

e.g., HCl, HCN, CO, OC, HBr, NO



(ii) $D_{\infty h}$ – Contains E, C_∞, ∞C_2, $\infty\sigma_v$, σ_h, i

e.g., H_2, Br_2, Cl_2, CH ≡ CH, CO_2, $BeCl_2$, XeF_2



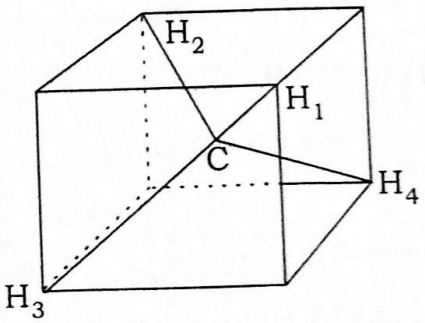
[B] Molecules having regular geometric bodies i.e., tetrahedral octahedral, icosahedron

(i) Point group T_d : Regular tetrahedra molecules have T_d point group.

e.g., CH_4, CCl_4, $Ni(Co)_4$, $SiCl_4$, $[Zn(CN)_4]^{2-}$

Total symmetry operations in T_d – E, $8C_3$, $3C_2$, $6S_4$, $6\sigma_d$ = 24

Symmetry operations are illustrated as follows :



(a) There are four axes of three fold symmetry each passing through C–atom and one H–atom. i.e., $4C_3^1$, $4C_3^2$.

(b) There are three axes of two fold symmetry each passing through centres of opposite edges. i.e., H_1, H_2 and H_3H_4, H_2H_3 and H_1H_4 H_2H_4 and H_1H_3.

(c) Each of the C_2 axis is also S_4 and S_4 is S_4^1, $2S_4^2$ hence $6S_4$ are present.

(d) There are sin planes of symmetry each passing through one edge and centre of opposite edges.

(ii) Point group Oh – Regular octahedral molecules have Oh point group.

e.g., SF_6, $[PtCl_6]^{--}$, $[Co(NH_3)_6]^{+++}$, octahedral complex of MA_6 Total symmetry operations in Oh – E, $6C_4$, $3C_2(C_4^2)$, $8C_3$, $6C_2$, $6S_4$, $8S_6$, $6\sigma_v$, $3\sigma_h$, i = 48

(iii) Point group I_n – Regular icosahedral molecule have I_n point group.

e.g., Dodecaborane $(B_{12}H_{12})^{2-}$, $[Mo(CN)_8]^{4-}$

Total symmetry operations – E, $24C_5$, $24S_{10}$, $20C_3$, $20S_6$, $15C_2$, 15σ, i = 120.