B. Sc. Part-I Hons, Paper-IB (Inorganic Chemistry)

Group-C, Unit-2: Elements of Symmetry/Symmetry elements

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⟹ Elements of Symmetry

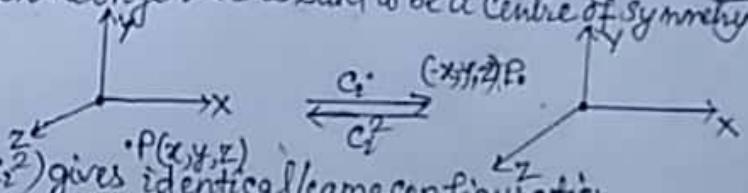
Elements of Symmetry offer a simple device to decide whether a molecule is chiral/asymmetrical or Achiral/symmetrical. A element of symmetry is a geometrical entity such as a line or axis, a plane or a point or centre, with respect to which one or more symmetry operations may be carried out. When a molecule has a plane/centre/n-fold alternating axis of symmetry, it is superimposable on its mirror image, and is achiral/symmetrical. The existance of a symmetry element can be demonstrated only by showing that the appropriate symmetry operation exist.

⟹ Types of Symmetry elements: There are main three types of symmetry elements in molecular chemistry. These are:

1. Centre of Symmetry or Inversion centre (C_i or i)
2. Plane of Symmetry (σ) 3. n-fold alternating axis of symmetry.

1. Centre of Symmetry or Inversion Centre: The Centre of symmetry is an imaginary point in a molecule from which if lines are drawn on one side and extended an equal distance on the other side meet the same atoms/groups. In other words, this is an imaginary point in the centre of the molecule through which the reflection of each atom can be carried out, to result out its concidence with an equivalent atom.

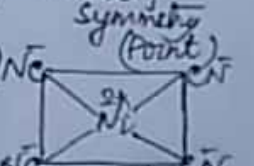
If a molecule can be brought into an equivalent configuration by changing the coordinates (x, y, z) of every atom and origin lie at a point within the molecule into $(-x, -y, -z)$, then the point at which the origin lie is said to be a centre of symmetry. It is denoted by symbol C_i or i.



* Repeat of inversion operation (C_i^2) gives identical/same configuration.
* If n is even, $C_i^n = E$ (Identity); If n is odd, $C_i^n = C_i$.

Examples: (i) Carbondioxide has centre of symmetry (i).

(ii) $[Ni(CN)_4]^{2-}$: In $[Ni(CN)_4]^{2-}$ ion, Ni^{2+} is at inversion centre (i). Two CN (cyano) ligands lie at equal distance, but opposite sides of square plane.

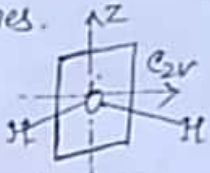


2. Plane of Symmetry: The plane which divides a molecule into two equal halves which are related as object and mirror image is known as plane of symmetry. It is denoted by symbol σ (Sigma, comes from German word Siegel, meaning mirror).

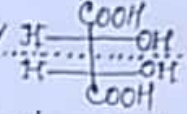
The molecules having a plane of symmetry are achiral/symmetrical. A plane of symmetry is equivalent to a one-fold alternating axis of symmetry.

* Repeat reflection(σ^2) operation gives identical configuration, i.e; $\sigma_v^2 = E$(Identity)
* If n is even, $\sigma^n = E$(Identity); If n is odd, $\sigma^n = \sigma$.
* In a molecule following planes may exist: (a) Vertical plane (σ_v) which passing/containing vertical/principal axis (b) Horizontal plane (σ_h) which is perpendicular to principal axis's (c) Dihedral plane (σ_d) which is bisecting the dihedral angle between σ_v planes.
* All planar molecules have at least one plane of symmetry, identical with the molecular plane. Linear molecules have an infinite numbers of σ-planes.

Examples: (i) H_2O molecule has a plane passing through O-atom and between two H-atoms, i.e; C_2-axis's perpendicular to the molecular plane.



(ii) Meso-tartaric acid molecule has a plane of symmetry Since one half is mirror image of other.



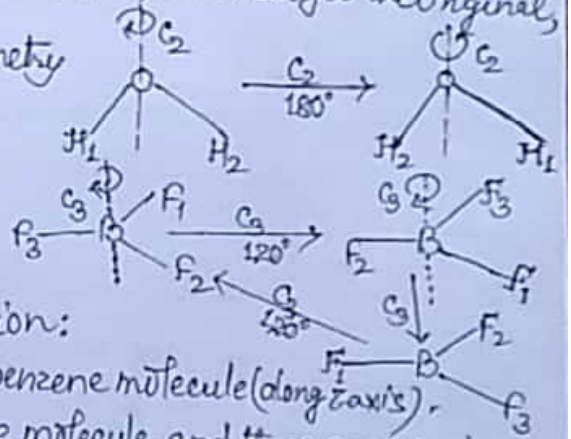
3. Axis of symmetry: A molecule is said to have a simple or proper axis of symmetry multiplicity n or n-fold axis of symmetry if a rotation of $360°/n$ around this axis leads to an arrangement which is indistinguishable from the original.

$$\text{Multiplicity}(n) = \frac{360^\circ}{\theta}$$ (where θ = angle of rotation (in degree) required for superimposition on original. It is represented by C_n.

* All linear molecules have C_∞ axis's of symmetry as in O=C=O, an equivalent arrangement is always obtained whatever be the angle of rotation.
* All molecules have an infinite number of C_1-axis, hence, the C_1-axis is never considered.
* If C_2 operation perform twice for a linear molecule (A_1-A_2), we will get the original, i.e; $C_2^2 = E$ (Identity).

Examples: (i) H_2O molecule: It has C_2-axis of symmetry passes through O-atom in the plane of the paper.

(ii) BF_3 molecule: It has C_3 axis passes through boron atom and is perpendicular to the plane of trigonal BF_3 molecule.



(iii) Benzene (C_6H_6): It has two main axis's of rotation:

(a) C_6-axis's of rotation perpendicular to the plane of benzene molecule (along z axis's).

(b) C_2-axis's of rotation lie in the plane of the benzene molecule, and these are six in numbers, Viz. AD, BE, CF, PQ, RS & MN.