M.Sc. Semester-II, CC-6 (Inorganic Chemistry)

Unit-2 Symmetry in Chemistry (By Dr. Birendra Kumar, Maharaja College.)

Elements of Symmetry?

Elements of Symmetry offer a simple device to decide whether a molecule is chiral (Symmetrical) or Achiral (unsymmetrical). 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 (unsymmetrical).

Symmetry elements and symmetry operations are so closely interrelated because the operation can be defined only with respect to the element.

The existance of a symmetry element can be demonstrated only by showing that the appropriate symmetry operation exist. There are four types of symmetry elements in molecular chemistry. These are—

Symmetry element	Symmetry operation(s)
1. Centre of Symmetry or Inversion Centre (C_i)	Inversion of all atoms through the centre. e.g. O=C=O
2. Plane of Symmetry (σ)	Reflection in the plane. e.g. COOH, H-C-OH, H-C-OH, COOH
3. Proper Axis of Symmetry (C_n)	One or more rotations about the axis. e.g. O (H, H), 180°, C_2
4. Improper Axis of Symmetry (S_n)	Reflection in a plane perpendicular to the rotation axis. e.g. BF_3 or B (F, F, F) has $3\sigma_v$, $1\sigma_h$

Symmetry operations?

A symmetry operation is a movement of a molecule such that, after the movement has been carried out, every point (element) of the molecule is coincident with an equivalent or same point (element) of the molecule in its original orientation. It can be defined as—"The geometrical operation such as reflection, rotation, inversion etc. which leads to a configuration/structure indistinguishable from the original configuration/structure."

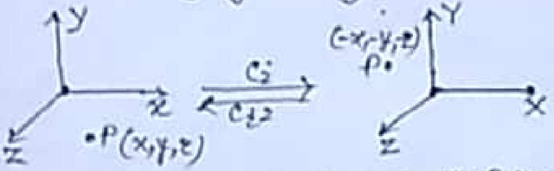
It must be emphasised that the two configurations/structures are not exactly identical, but they look like in all respects.

Different types of Symmetry elements/operations:

1. Identity (E): It is the operation of doing nothing. When we donot do anything and leave the molecule unchanged and identical to the original molecule in all respects, the operation is called Identity. It is denoted by 'E'. All systems (Molecules/Ions) except tautomers/resonating structures have identity.
2. Centre of Symmetry or Inversion Centre (C_i or i): 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 in its coincidence with an equivalent atom.

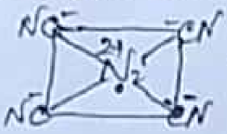
If a molecule can be brought into an equivalent configuration by changing the coordinates (x, y, z) of every atom and origin lie at a point within the molecule into $(-x, -y, -z)$, then the point at which the origin lie is said to be a centre of symmetry. It is denoted by 'C_i' or 'i'.



* 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: $O=C=O$ It has centre of symmetry (C_i) with respect to C, two O-atoms lie at equal distance, but opposite sides.

(ii) $[Ni(CN)_4]^{2-}$:



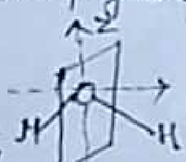
Here Ni^{2+} is at inversion centre (i) two CN^- (ligands) lie at equal distance, but opposite sides of square plane.

3. Plane of Symmetry:

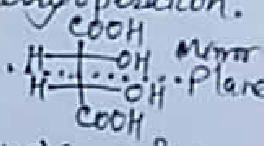
The plane which divides a molecule into two equal halves which are related as object and mirror image is known as plane of symmetry. It is denoted by σ (Sigma, comes from German word Spiegel, meaning mirror).

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

Examples: (i) H_2O molecule, has a plane passing through the C_2-axis perpendicular to the molecular plane (i.e., through O-atom & between two H-atoms) If a reflection is carried out over the plane of symmetry and the new positions of the atoms are noted, the new orientation will be equivalent to the original orientation. Therefore, σ is a symmetry operation.



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



* Repeat reflection (σ^2) operation gives identical configuration, i.e., $\sigma_v^2 = E$.
* If n is even, $\sigma^n = E$ (Identity); If n is odd, $\sigma^n = \sigma$.

In a molecule following planes may exist:

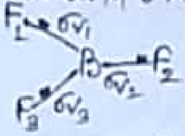
(a) Vertical Plane (σ_v): The plane containing principal (vertical) axis

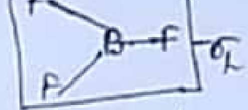
(b) Horizontal plane (σ_h): The plane perpendicular to principal axis.

(c) Dihedral Plane (σ_d): The plane 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 no. of σ planes which intersect along C_∞.

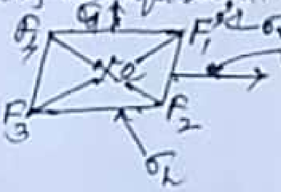
Other examples, (i) BF_3 molecule: It is a trigonal molecule. It consists of three σ_v each passing through the B-atom and one F-atom. It also consists of one σ_h lying in the plane of the molecule.





(ii) XeF_4 molecule: It is square planar molecule. It consists of one σ_h, lying in the plane of the molecule, two σ_v lying in the diagonal of the square and two σ_d passing through the intersection of σ_v planes.

Here, two σ_v through XeF_1F_3 & XeF_2F_4; two σ_d between two F-atoms (F_1, F_2 or F_3, F_4 & F_1, F_4 or $F_2 F_3$).



4. Axis of Symmetry (C_n): 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. Multiplicity $(n) = \frac{360°}{\theta}$ (where θ = number of degree of rotation required for superimposition on original. It is represented by C_n.

The general conventions for specifying coordinates are as follows:

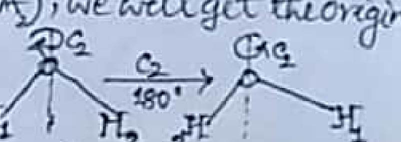
(i) The rotational axis with the highest order is the principal axis & it is z-axis.

(ii) If the rotational axes (x,y,z) are of the same order, the axis passing through the largest number of atoms must be taken as the z-axis. If one does not find such an axis z is the one passing through a large number of bonds.

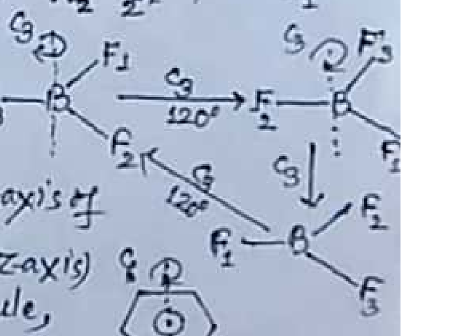
(iii) In a planar molecule, the rotational axis perpendicular to the plane of the molecule is taken as z-axis.

* All linear molecules have C_∞ axis 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 originals i.e., $C_2^2 = E$ (Identity)

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

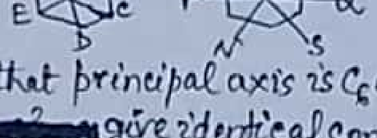


(ii) BF_3 molecule: It has C_3 axis passes through boron atom and is perpendicular to the plane of trigonal BF_3 molecule.



(iii) Benzene (C_6H_6): It has two main axis of rotation (a) C_6-axis of rotation perpendicular the plane of benzene molecule (along z-axis)

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

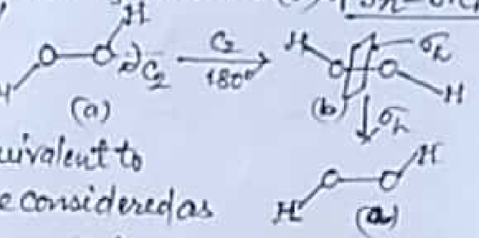


It can be noted that principal axis is C_6 axis (By conventions). C_6 axis of rotation performed twice to [redacted] give identical configuration of C_3-axis of rotation, i.e., $C_6^2 = C_3$

5. **Improper axis of Symmetry or Rotation-Reflection (S_n)**: It is an imaginary axis, passing through the molecule, on which the molecule has to be rotated by $360°/n$ angle and then reflected on a plane perpendicular to the rotation axis to attain any equivalent orientation. It is represented by S_n, where n is the order of the axis. In other words, it is a process of rotation (C_n) followed by reflection in a plane perpendicular to the axis of rotation (σ). $S_n = \sigma \cdot C_n$

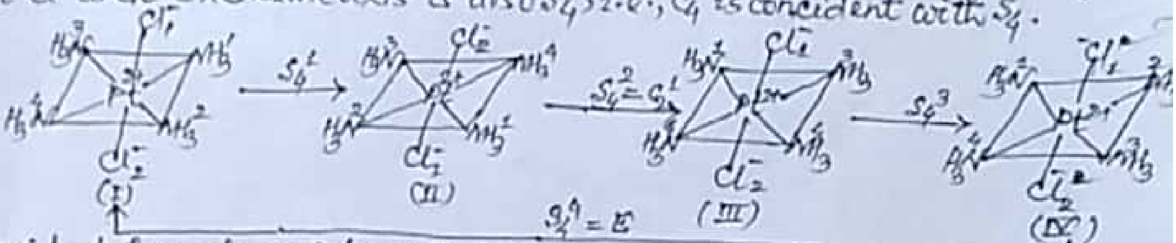
Examples: (i) H_2O_2: It has S_2 axis of rotation. $S_2 = C_2 + \sigma_h$

It is evident that S_2^2 on (a) gives the original orientation (a) and also S_2^1 operation on (a) is equivalent to inversion, i.e., $S_2^1 = i$. Hence, S_2^1 cannot be considered as a new operation.



In a molecule, an axis of improper rotation (S_n) may be concident with an axis of proper rotation (C_n). (a) $S_n^m = C_n^m \sigma_h$ (when m is odd) (b) $S_n^m = C_n^m \sigma_h^m$ (when m is even) $\sigma_h^m = E$ (identity) or, $S_n^m = C_n^m$. (c) $S_n^n = C_n^n \sigma^n = E \cdot E = E$ (when m = n = even)

For example, a distorted trans octahedral complex $[Pt(NH_3)_4Cl_2]$, the axis passing through Cl-Pt-Cl is C_n. The same axis is also S_4, i.e., C_4 is concident with S_4.



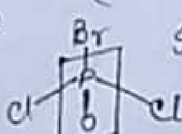
It is evident from above scheme that (a) Orientation (III) can be obtained by either performing S_4^2 on (I) or C_2^1 on (I). Hence, S_4^2 is not a new operation, i.e., $S_4^2 = C_2^1$ (b) On performing S_4^4 on (I) [four times S_4] we get (I) again. This is equivalent to identity (E), i.e., $S_4^4 = E$. (c) On S_4 axis, concident with C_4, new operations are S_4^1 and S_4^3 which give the equivalent orientations (II) & (IV) respectively.

1.Q. Indicate symmetry elements in the following: (a) N_2O_2 (b) $POBrCl_2$ (c) PF_5 (d) NH_3

Ans. (a) N_2O_2: It has centre of symmetry (i)

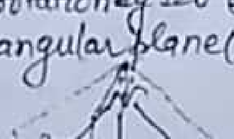
(inversion centre)

(b) $POBrCl_2$: It has plane of symmetry (σ_v). It consists of one σ_v passing through Br, P & O atoms and lying in zx plane.



(c) PF_5: It has improper axis of symmetry (S_3), since rotation by 120° ($\frac{360°}{3}$) around axis perpendicular to triangular plane (PF_3) and reflection to it gives original configuration.

(d) NH_3: It is pyramidal molecule. It consists of three σ_v planes each passing through N-atom & one of the three H-atoms.



2.Q. How symmetry elements affect stereochemistry of compounds?

Ans. Compounds having centre of symmetry (i), plane of symmetry (σ) & improper axis of symmetry (S_n) do not show enantiomerism/optical activity as they are achiral. However, compounds having C_n axis of symmetry generally show enantiomerism/optical activity as they are chiral.

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