Class---U. G. Semester II

Subject---Chemistry

Unit----   III

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MOLECULAR SYMMETRY: -

A molecule is said to have "symmetry" if part of the molecule can be interchanged without bringing about a distinguishable change in the orientation of the molecule. That means a molecule can have two or more orientation in space which are indistinguishable, then molecule have a symmetry. A body is called symmetric if any real or imaginary operation of rotation or reflection lead to a new orientation which is indistinguishable from the initial one Such operations which bring the body into coincidence with itseif, it called operation of symmetry. The geometrical elements of the body, generating symmetry operations, are called symmetry elements. Symmetry elements may be a point, an axis or a plane, with respect to which the symmetry operations are performed. The description of the symmetry of an isolated molecule is called point of symmetry. It is the set of operations transforming a system about a common point which is generally the centre of gravity of a molecule.

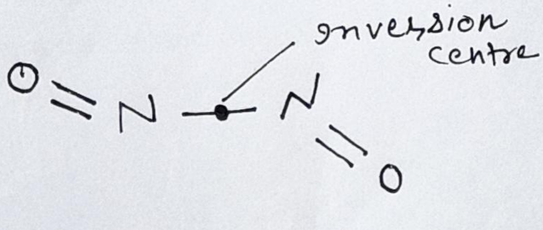
Symmetry Elements:

There are five types of symmetry elements associated with point symmetry:

Symmetry elements	Symbols	Symmetry operations
1.Centre of Symmetry or Inversion centre	i	Centre of Symmetry
2. The rotation axis	C_n	
3. The mirror plane	б	plane of reflection
4. The rotation-reflection axis	S_n	Rotation (C_n) about an axis and reflection with respect to the plane perpendicular to the rotation axis.
5.The identity	E	the rotation axis does not arise.

1. The Center of Symmetry or Inversion Center(i):

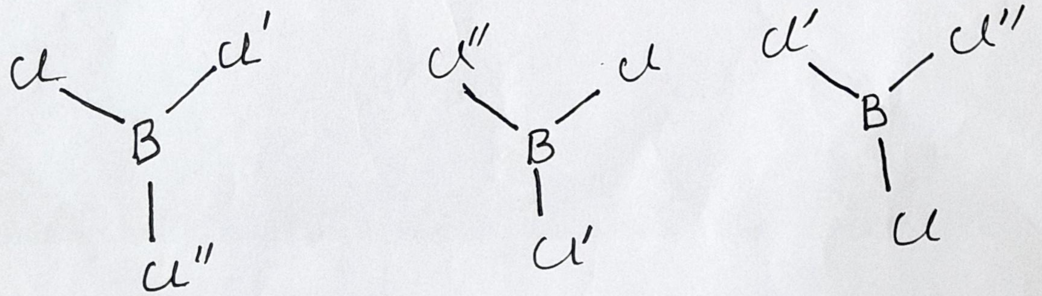
A molecule possess a center of symmetry of reflection of each of the atom in the molecule through this center results in its coming into coincidence with an identical. For example if oxygen atom A of the Hyponitrite ion (Fig.2) is moved through the inversion center an equal distance to the opposite side, it comes into coincidence with another oxygen atom. The same must apply to B and also to both nitrogen atom if the molecule is to possess a center of symmetry.



The centre of symmetry in the Hyponitrite ion.

2. The Rotation axis (C_n) or Proper rotation:

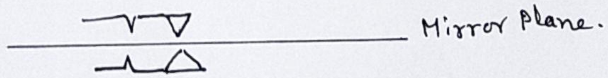
If a rotation of a molecule by $360^0/n$ results in to produce an equivalent orientation, then the molecule have n fold rotation axis. The axis about which the rotation takes place is the symmetry element. It may be possible to carry out several symmetry operation around a single rotation axis. If the molecule can occupy n-different equivalent position about this axis, the order of the axis is order n. For example, in case of Bcl_3 , let tha xis through the centre of the Boron atom perpendicular to the plane of the molecule rotation about this axis three times through an angle of 120^0 each time produces two equivalent orientations. The order n of this axis is three. Three rotations are needed to return to the original position. The molecule possess a three fold rotation axis, indicated by the symbol C_3. Rotation of the molecule through $2\pi/n$ produces equivalent orientation and n operations produces the starting configuration. The BC_3 molecule indicate the lack of centre of and the presence of the three additional two fold two fold rotation axes C_2 (Fig. 4). the highest fold rotation axis is referred to as the principal axis and is labeled as C_n. The symbol C_3^2 is employed to indicate a rotation of 240^0 around a C_3 axis. The C_3^2 operation is identical to counter clockwise rotation of 120^0 which is indicated as C_3^- . A rotation axis of order n generates operations i.e. C_n, C_n^2, C_n^3........C_n^{n-1}, C_n^n. The operation C_4^2 is equivalent to C_2 , C_6^2 is equivalent to C_3 and C_n^n is the identity. If the molecule contains several C_n rotation axes , the principal one is usually selected as the one coll inear with a unique molecular axis. If all the C_n axis are equivalent then any one may be chosen as the Principal axis.

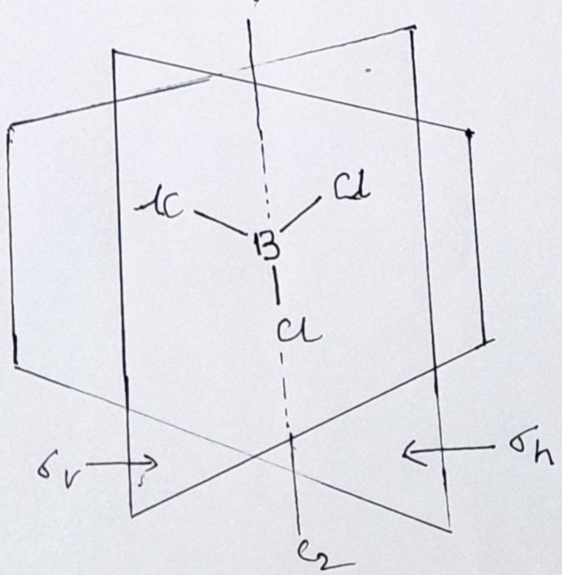


Three fold rotation axis of BCl_3.

3) The mirror plane (σ): -

If a molecule there exist a plane which separates the molecule into two halves that are mirror image of each other, the molecule possesses the symmetry element of a mirror plane. This plane can not lie outside but must pass through it. This process involves selecting a plane dropping a perpendicular from every atom in the molecule to the plane, and placing the atom at the end of the line formed by extending this line an equal distance to the opposite side of the plane. If an equivalent configuration is obtained after this is done to all the atom, the plane selected is a mirror plane in those molecule that contain more than one mirror plane the horizontal plane σ_h is taken as the one perpendicular to the principal axis. For example: in BCl_3 the plane of the paper is and there are three vertical plane perpendicular to σ_h.

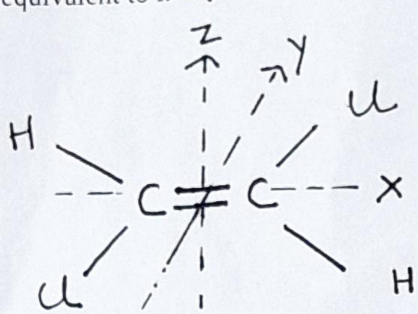




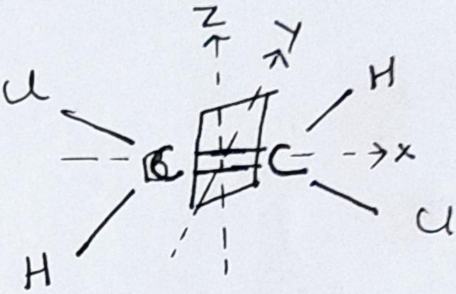
A mirror plane in BCl_3.

4. The Rotation-Reflection axis or Improper rotations(S_n):

This operation involves rotation about an axis followed by reflection through a mirror plane which is perpendicular to the rotation axis or vice versa. The result of two operations produce an equivalent structure. This operation is known as improper rotation and the rotation reflection axis is known as alternating axis. The symbol S is used to indicate this symmetry element. For example in molecule transdichloroethylene. The molecule is rotated by 180^0 followed by reflection . The improper axis are S_2 which is equivalent to i. If a molecule is rotated around an axis



(a)



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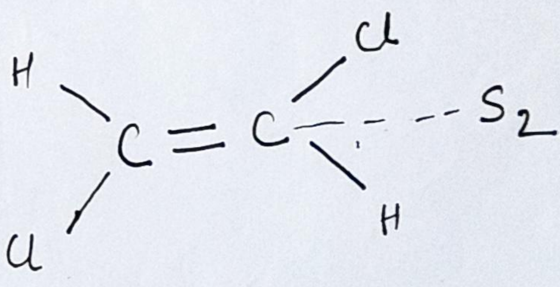

Rotation reflection axis of symmetry S_2

and the resulting ~~opre~~ orientation is reflected in a plane perpendicular to this axis and if the resulting orientation is superimposible on the original, the molecule have a rotation reflection axis.

5. Identity(E):

An identity operation results in the production of a orientation which is identical to the original orientations. All molecules when rotated by C_1 operation 360^0 results in the same molecule. The concept of identity operation involves no change in the molecule and is thus a pseudo operation. Every element has a symmetry element E. Several operations which produce configurations which are identical to the original are equivalent to the identity. For example, the rotation about the three fold rotation axis of BCl_3 gives the original configuration so C_3^3 operation which are equivalent to E.