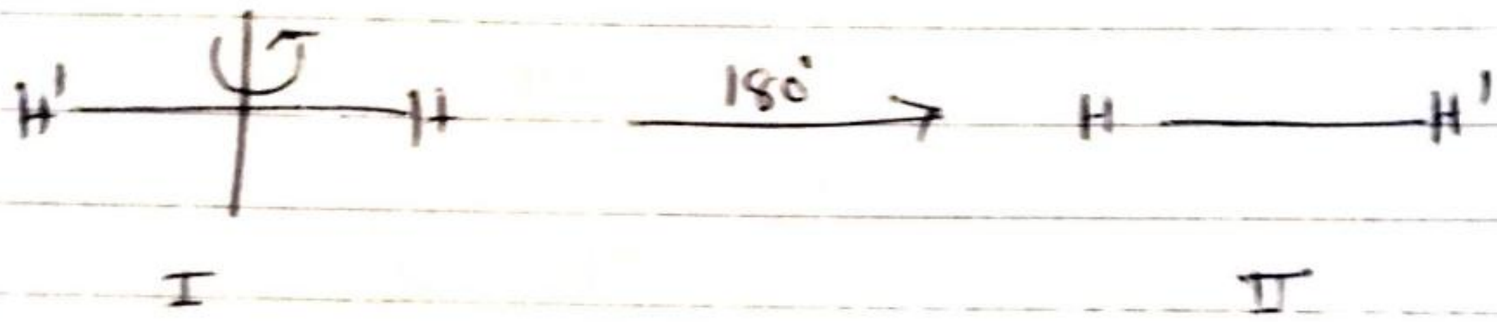
P.G. Sem. IInd
Core course - VI
Inorg. Chem.

Unit III

Group Theory.

Group theory is concerned with operations in determining Symmetry.

Symmetry :→ Symmetry means that a certain part of an object looks exactly like another part. The Sun, the planets, the human beings, animals and plants are all symmetrical. An object is said to be symmetrical if it can take up more than one equivalent (indistinguishable) orientation. For example, let us consider hydrogen molecule in orientation I (H' and H* are same). It can be rotated by 180° to the orientation II ~~(in which case~~ II can be distinguished from I ie. they are equivalent orientations.



Symmetry of an object or molecules is best described by mentioning certain operations like rotation, reflection etc. which brings the object in equivalent ~~orientation~~ position. The resulting geometric configuration is indistinguishable from the original one. Symm. arises when a molecule possess identical atom in certain part of it. For example, the H-atoms in H_2O are equivalent are cause symm. in H_2O.

Symmetry operation and Symmetry element :→

Symmetry operation :→ Symm. operation is the proce carried out on the molecule which brings it from the original orientation to another equivalent orient -tion.

Geometrical operation such as reflection, rotation, inversion etc. which produce a configuration not different from the original configuration is called symm. operation. The two configs. may or may not be exactly identical but they look alike in all respects.

Symmetry element :→ The various Symm. operations are done with respect to a geometrical entity such as straight (rotation), plane (reflection), point (inversion) ---- etc are called Symm. element.

Symm. operation	Symm. element	Symbols
(1) Doing nothing	Identity	E
(2) Rotation	Axis	C_n
(3) Reflection	plane	σ
(4) Inversion	Centre of Symm.	i
(5) Improper Rotation	Rotation about an axis followed by reflection w.r.to a plane $\perp^r$ to the rotation axis.	S_n

These operations do not change in the energy of the molecule. Also in these operations the centre of the molecule is not altered. If at least one point remain fixed in the operation, the operation is known as point group operation.

Following Symm. elements and Symm operations are possible.

(1) Identity (E) :→

This is an operation which brings back the molecule to the original orientation. Thus, it is the operation of not doing anything. In this operation system remains unchanged and identical to the original in all respects. It is a mathematical necessity.

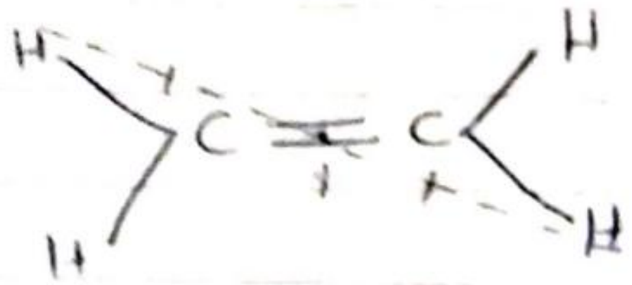
There are several different types of ~~orientations~~ operation which bring back the molecule to it original orientation. They are not considered separately but are put together as identity. For example an axis of four fold Symm., C_4^1, C_4^2 and C_4^3 are considered as rotation operation. But C_4^4 i.e. rotation by 360° is not considered as rotation operation because it is an identity operation. Over a plane of Symm. only one reflection operation is considered. If the reflection is repeated, the original orientation is obtained and hence the second reflection is an identity operation.

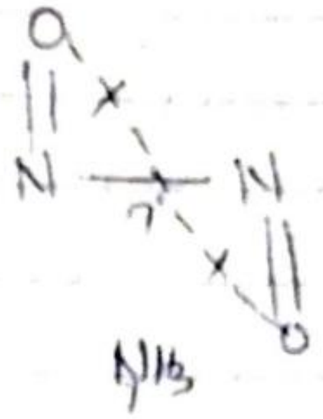
The identity operation, in effect, means doing nothing on the molecule and hence does not ~~seem~~ seem to be of much importance. But it importance lies on considering the molecules as a group and to apply the group theory to molecule

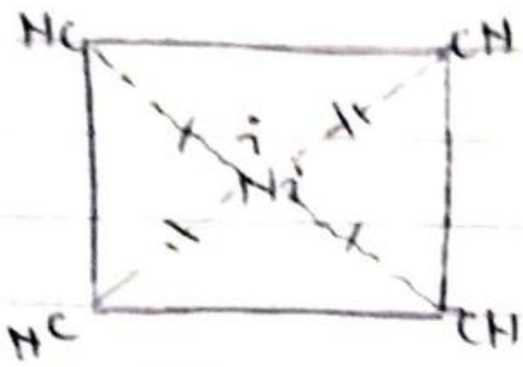
(2) Centre of Symmetry or inversion centre :-

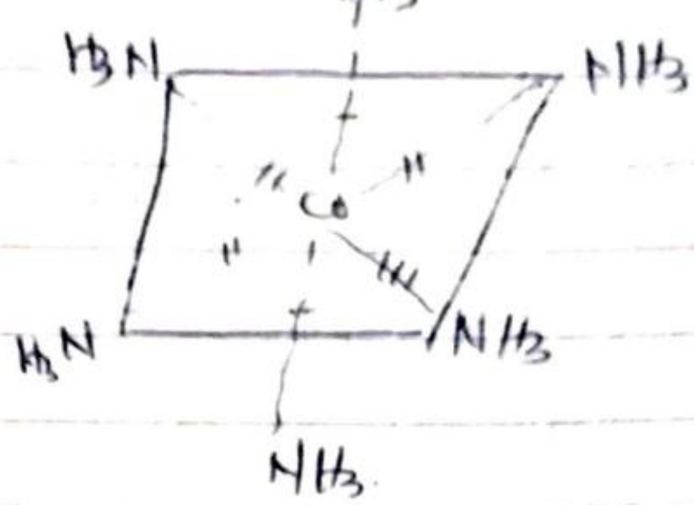
This is an imaginary point in the centre of the molecule, through which reflection of each atom can be carried out to result in its coincident with an equivalent atom. In other words if any atom in a molecule is connected with the centre of Symm. and extended equally on the other side, it meets equivalent point.

This can be illustrated by the following molecules, C_2H_4, N_2O_2, Square planar $[Ni(CN)_4]^{2-}$ and octahedral $[Co(NH_3)_6]^{3+}$ etc.

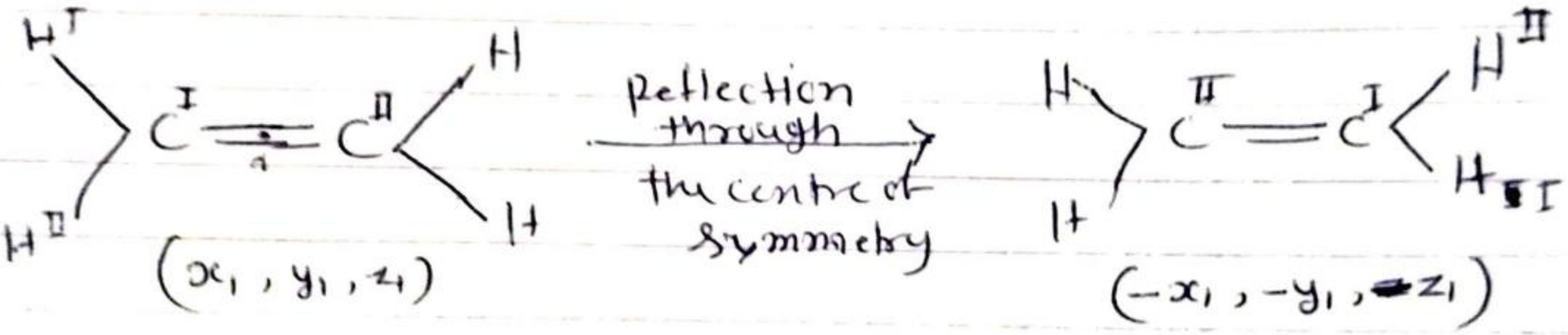






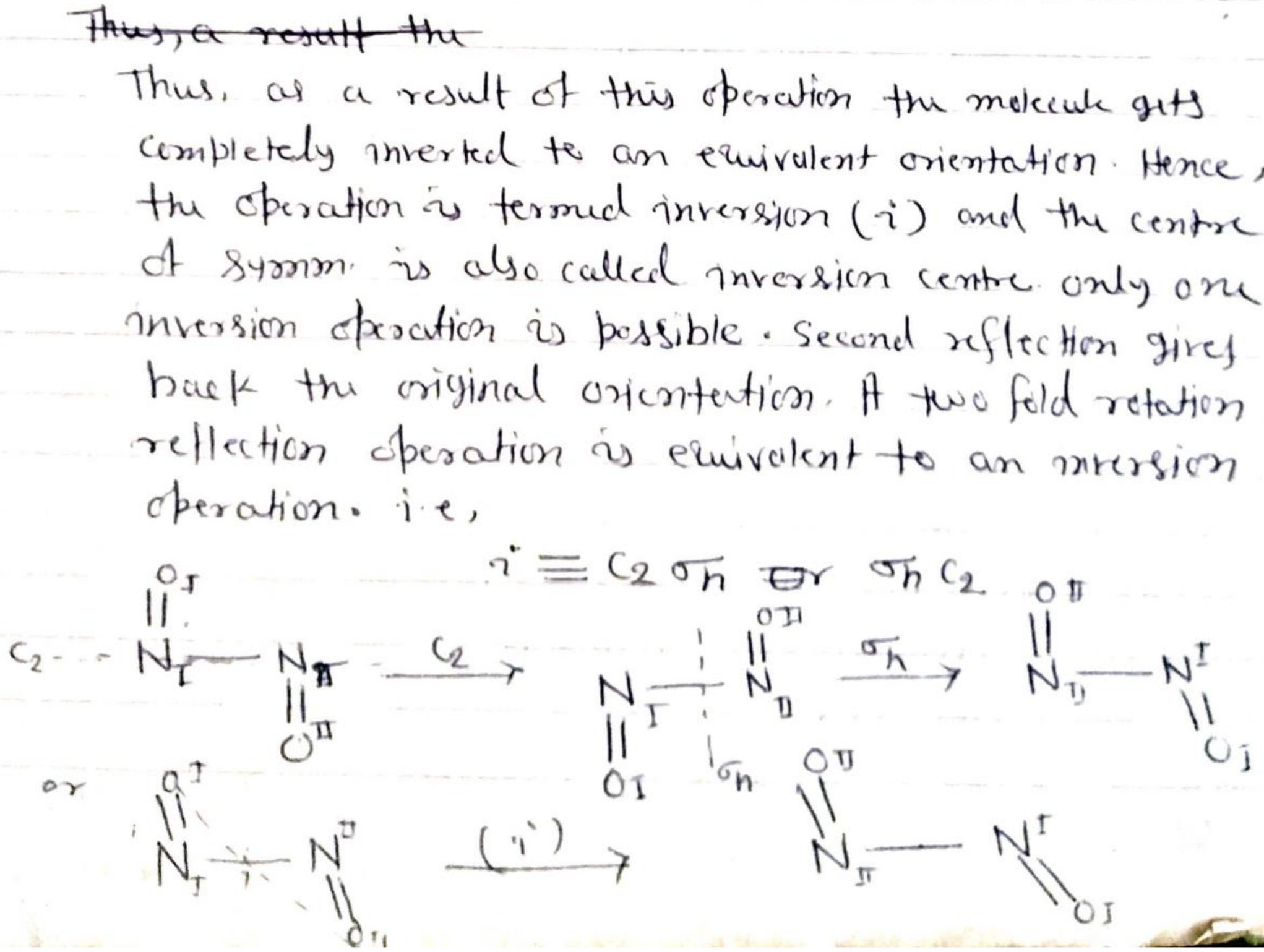


The centre of symm. is the symm. element and the process of reflection through it leading to an equivalent orientation is the symm. operation.



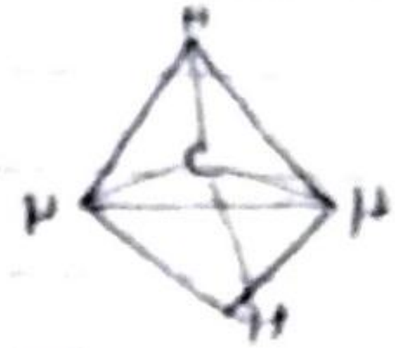
~~Thus, a result the~~

Thus, as a result of this operation the molecule gets completely inverted to an equivalent orientation. Hence, the operation is termed inversion (i) and the centre of symm. is also called inversion centre. only one inversion operation is possible. Second reflection gives back the original orientation. A two fold rotation reflection operation is equivalent to an inversion operation. i.e,

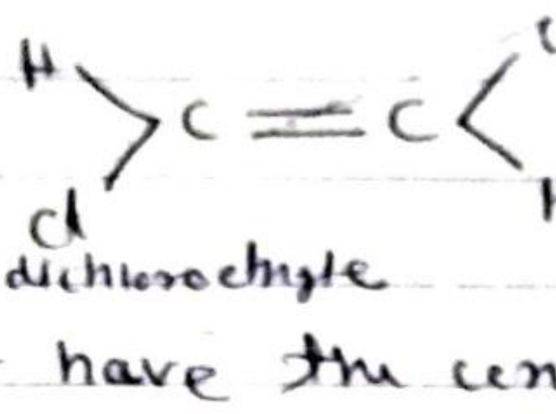


Molecules which donot have centre of symmetry

→ All tetrahydral molecule i.e CH_4 has no centre of Symm because on the opposite side of each corner there is only one face.

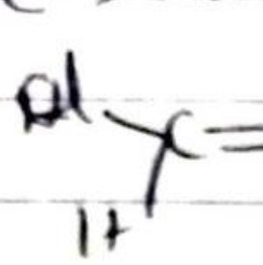


→ Transdichloroethylene has a centre of symmetry



Trans dichloroethyle

But cis dichloro ethylene do not have the centre of Symm.



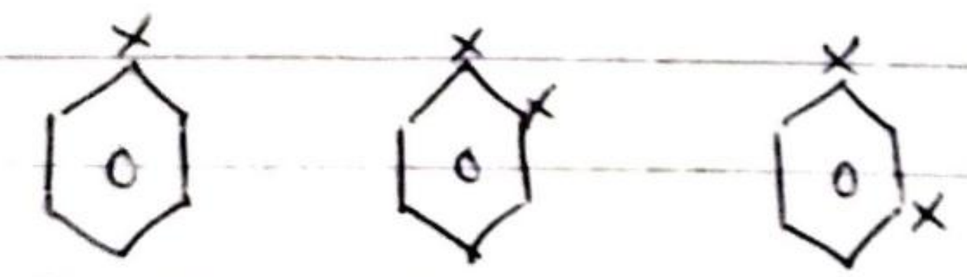
cis dichloroethylene

→ Benzene and p disubstituted benzene have centre of symm.

Benzene

p- disubstituted benzene

But monosubstituted and o, m disubstituted benzene have no centre of symmetry.



→ A molecule with more than one unpaired atom will not have centre of symm.