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UNIT-4; Part-1

Symmetry Elements and Point Groups Determination

Symmetry Elements: It is a geometrical entity (line, plane or point) with respect to which one or more symmetry operations may be carried out.

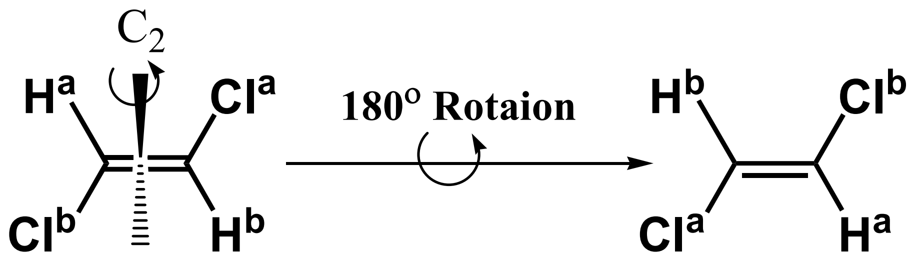
Symmetry Operation: Some operation that results a set of objects in indistinguishable configurations said to be equivalent.

Identical symmetry (E): 360 degree rotation of the molecule or object results the exactly same configuration of the initial one. It is called identical symmetry.

If there I no symmetry then also '**E**' symmetry is present, i.e., every molecule has '**E**' Symmetry.

There are four types of symmetry elements:-

1) **Simple axis or Proper axis of symmetry (C_n):** *It is an imaginary axis about which rotation of certain angle indistinguishable configurations is resulted.*



(I) **(II)**

Structure (II) is reulted due to 180 rotaion of **structure (I)** and vice versa.

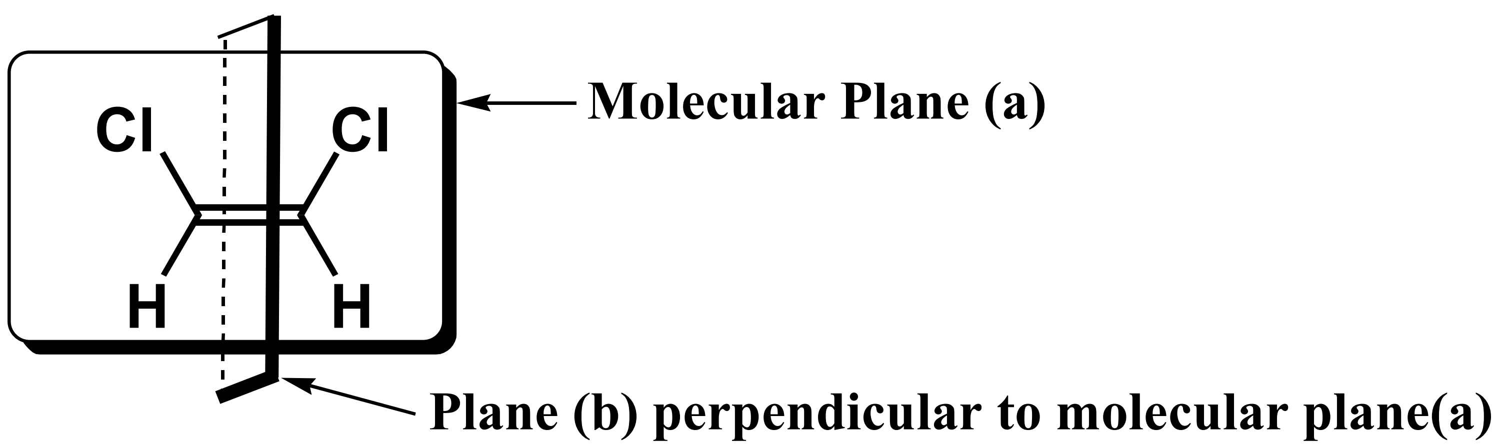
Both the structure **(I)** and **(II)** are indistinguishable. Therefore it has **C2**-imple axi of symmetry

When more than one symmetry axis present, the one with the largest value of n is called **PRINCIPLE AXIS**

2) Plane of symmetry (σ): *It is an imaginary plane that divide the molecule/object into two half that are mirror image to each other. The plane must go through the molecule, not out side the molecule.*

$\sigma_x = \sigma_{yz}$ means “reflection in a plane along the y- and z-axix, usually called the yz plane

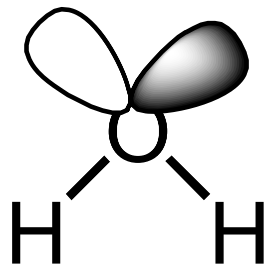
Similarly, $\sigma_y = \sigma_{xz}$ means “reflection in a plane along the x- and z-axix, usually called the yz plane ***All planar molecules*** *have at least one plane of symmetry that is molecular plane*



So, this molecule has two symmetry plane **(a)** and **(b)**

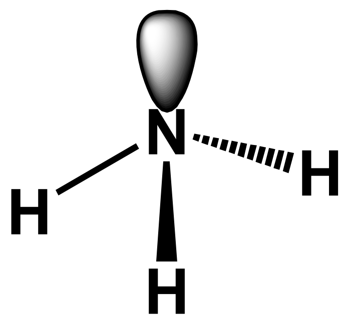
Linear molecules have infinite number of plane

H_2O: Distorted tetrahedral



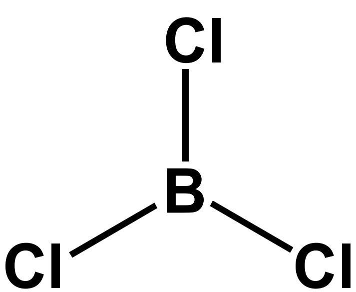
It has two planes; 1 molecular plane and other one bisecting the H-O-H angle

NH_3: Distorted tetrahedral



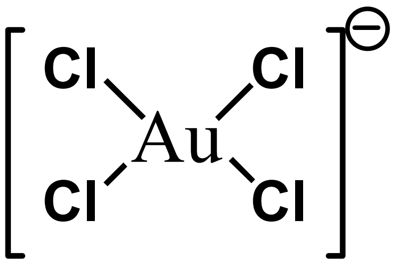
It has 3 planes containing one **N-H** bond and bisecting opposite HNH angle

BCl_3 : Trigonal planer



It has 4 planes; one molecular plane and 3 planes containing a **B-Cl** bond that bisecting the other **Cl-B-Cl** angle

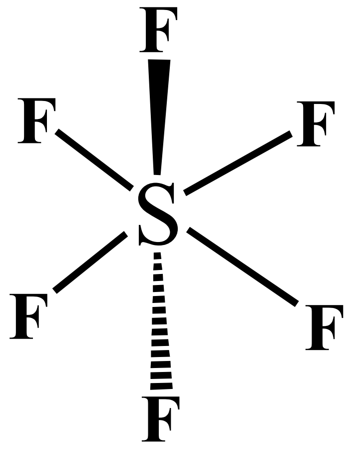
$[AuCl4]^-$: Square planar



It has 5 planes; 1 molecular plane; 2 planes containing opposite Cl-Au-Cl bond and 2 perpendicular plane bisecting the Cl-Au-Cl angles.

Octahedral molecule like SF_6 has 9 plane

(for better understanding go through the link given below)



https://chem.libretexts.org/Core/Inorganic_Chemistry/Coordination_Chemistry/Properties_of_Coordination_Compounds/Isomers/Optical_Isomers_in_Inorganic_Complexes/Identifying_Planes_of_Symmetry_in_Octahedral_Complexes

Result of multiple plane of ymmetry (σ) operation

Plane of symmetry (σ) produces an equivalent configuration.

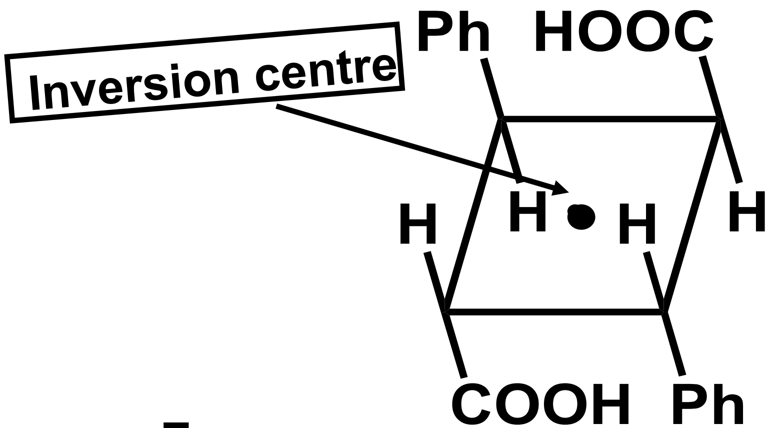
Example: σ2 = σσ produces an identical configuration with the original.

That is σ^2 = **E**

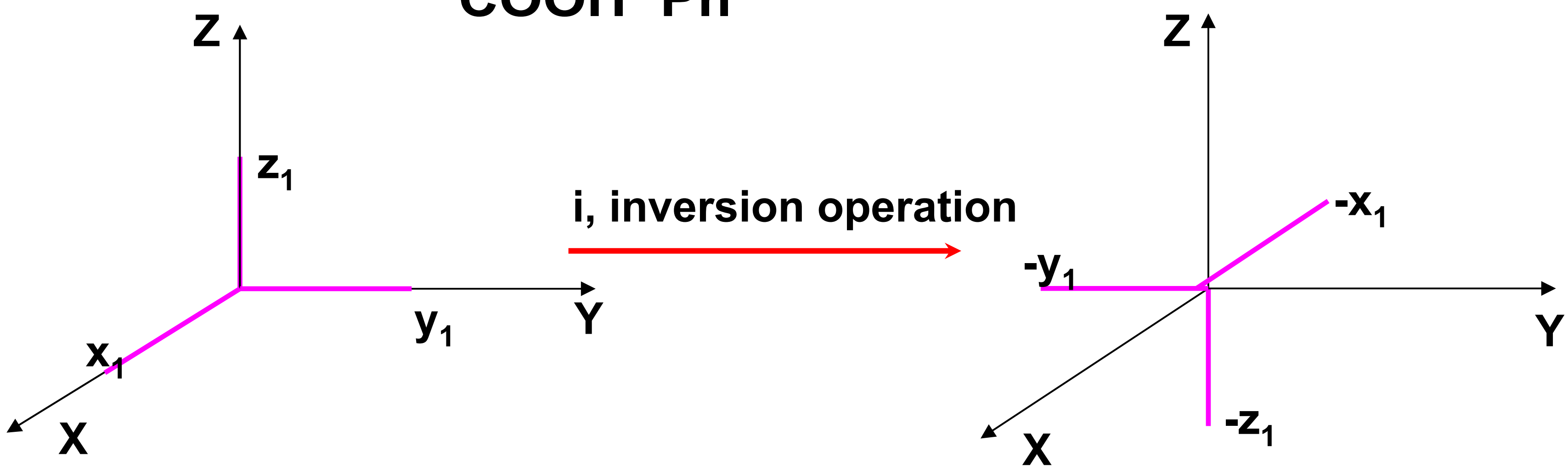
And σ^n = **E** if n is even, i.e., n = 2, 4, 6,…

σ^n = σ if n is odd, i.e., n = 3, 5, 7,…

3) Centre of symmetry or inversion centre (i): *It is an imaginary point from which in equal distances in opposite direction it will have the same atom or group of atoms.*



Here the molecule has centre of symmetry shown by bold dot at centre



Due to **inversion operation**, the coordinate of a point shifted from (x, y, z) to (-x, -y, -z)

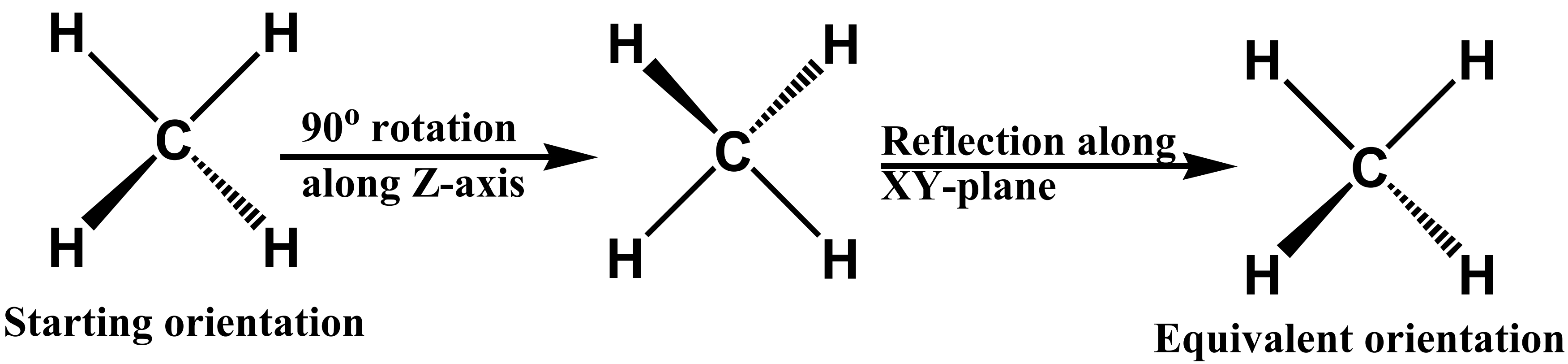
If an atom is **situated** at the **inversion centre**, then it is the **only atom** which will not move upon inversion operation. **Rest of the atoms** in the molecule present in pairs which are "twins". Therefore, there is no inversion centre for those molecules that containing an odd number of atoms.

Product of symmetry operators means: "carry out the operation successively beginning with the one on the right".

$$i^2 = ii = E$$

$$i^n = E, \text{ if } n \text{ is even}$$
$$= i, \text{ if } n \text{ is even}$$

4) Improper axis or Alternative axis of symmetry (S_n): *It is an imaginary axis about which rotation of certain angle followed by reflection on a mirror plane perpendicular to that rotational axis results indistinguishable configurations.*



Therefore, the **CH_4** molecule has **S_4** improper axis of symmetry.

Similarly PCl5 molecule has **S_3** improper axis of symmetry

The existence of an **S_n** axis requires the existence of a **$C_n/2$** axis.

If both **C_n** and **σ_h** exist, then **S_n** must exist. But **S_n** can exist although **C_n** and **σ_h** do not exit.

Products of Symmetry Operators Products of Symmetry Operation

Symmetry operators are well represented by means of a **stereogram** or **stereographic projection**. Start with a circle which is a projection of the unit sphere in configuration space (usually the **xy plane**). Take x to be parallel with the top of the page.

A point above the plane (+z-direction) is represented by a **small filled** circle.

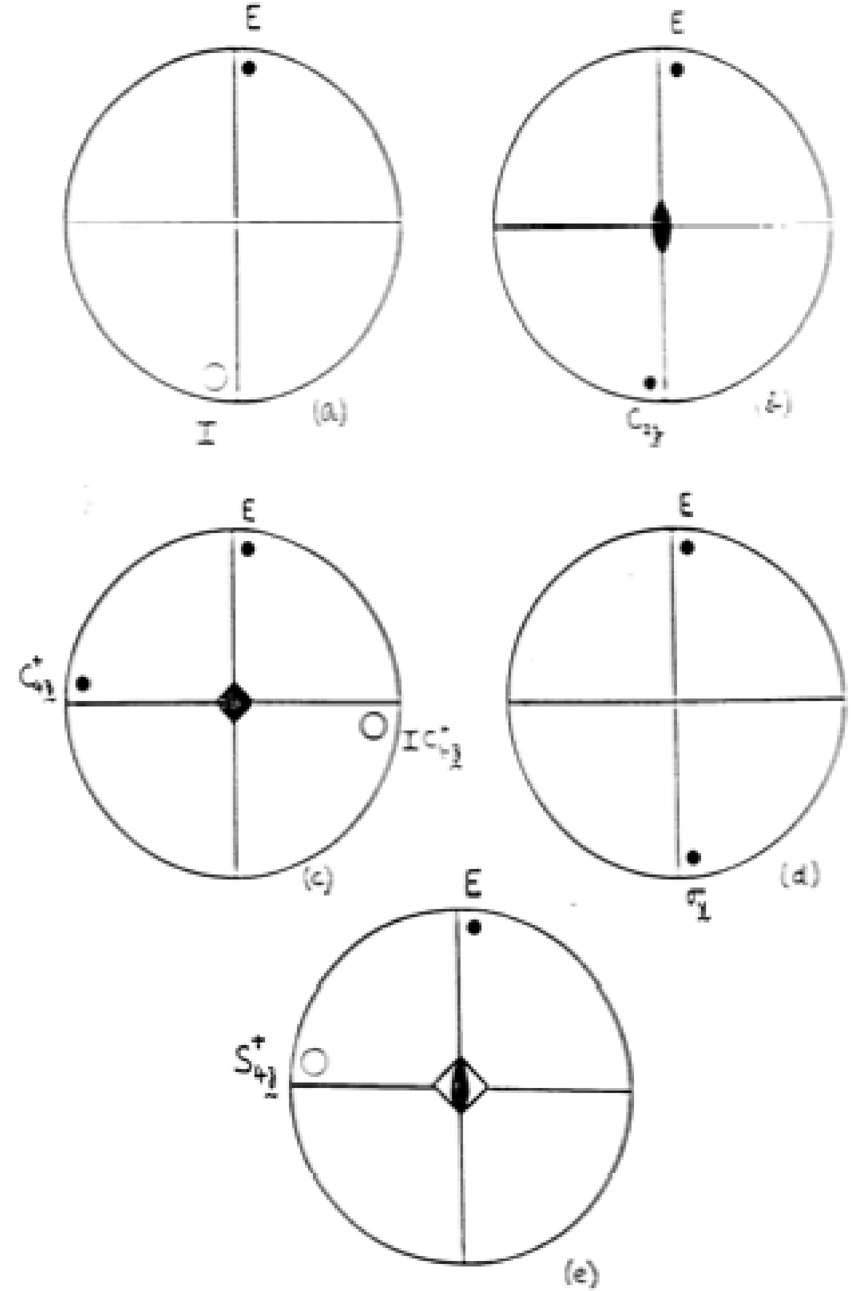
A point below the plane (-z-direction) is represented by a **larger open** circle. A general point transformed by a point symmetry operation is marked by an **E**.

Symbols used to show an n-fold proper axis. For improper axes the same geometrical symbols are used but they are not filled in. Also shown are the corresponding rotation operator and angle of rotation ϕ.

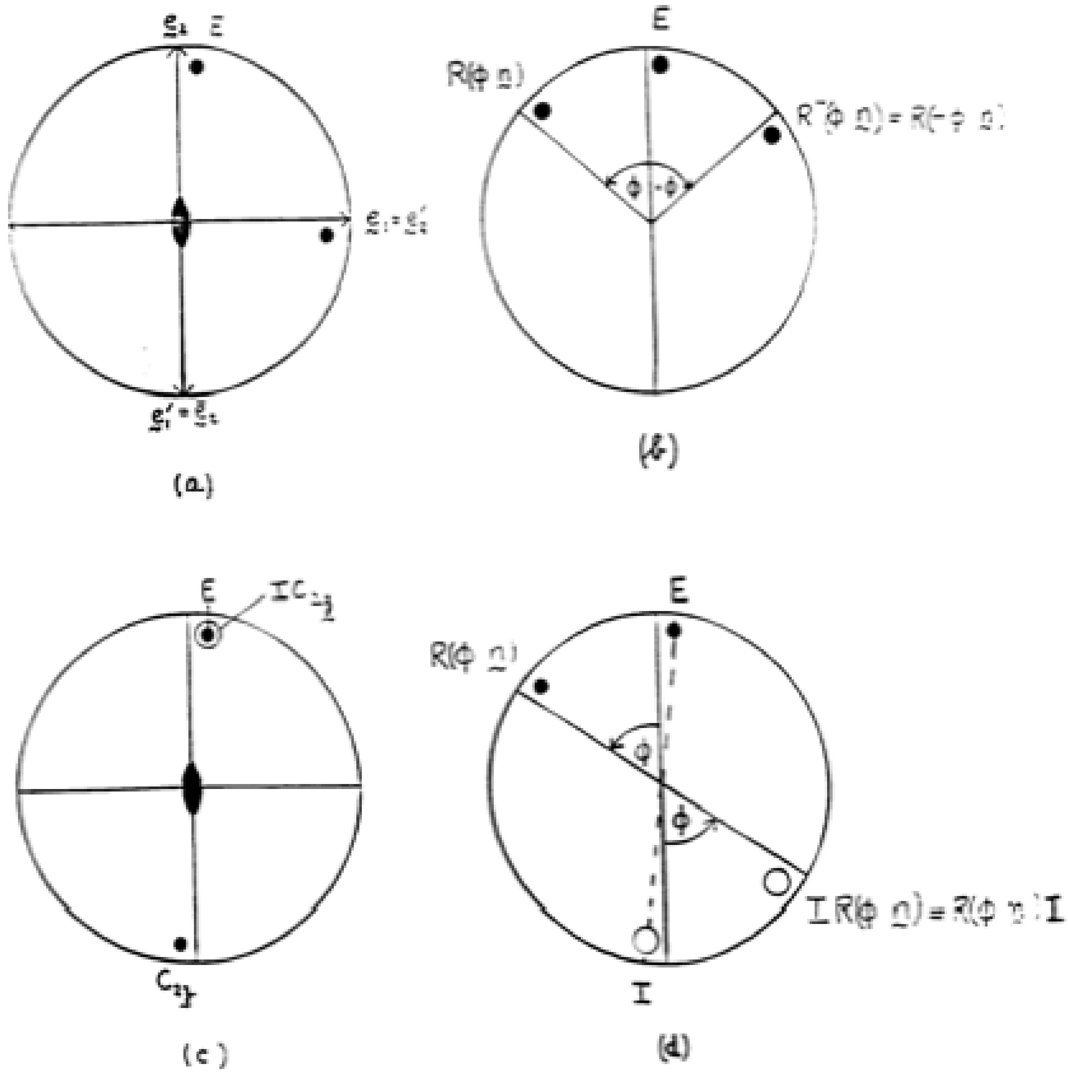
$n =$	2	3	4	5	6	etc.
	digon	triangle	rhombus	pentagon	hexagon	......
operator :	C_2	C_3	C_4	C_5	C_6	......
$\phi = 2\pi/n$	π	$2\pi/3$	$\pi/2$	$2\pi/5$	$\pi/3$	......

For improper axes the same geometrical symbols are used but are not filled in.

Stereograms showing examples of the point symmetry operators listed in Table 2.1-1. (a) I (b) C_{2y} (c) IC_{4y}^{+} (d) σ_y (e) S_{4y}^{+}.



(a) The effect of $R^{-}(\pi/2\ \mathbf{z})$ on $\{\mathbf{e}_1\ \mathbf{e}_2\ \mathbf{e}_3\}$. (b) A rotation $\mathbf{R}(-\phi\ \mathbf{n})$ means a *clockwise* rotation through an angle of magnitude ϕ about $\mathbf{n}$, that is $R^{-}(\phi\ \mathbf{n})$. (c) Proof that $I\,C_{2z} = \sigma_z$. (d) The location of the coordinate axes is arbitrary; here the plane of the stereogram is normal to $\mathbf{n}$.



The complete set of point-symmetry operators including **E** that are generated from the operators {R_1, R_2, …} that are associated with the symmetry elements {C_1, i, C_n, S_n, σ} by forming all possible products like R_2R_1 satisfy the necessary group properties:

1) Closure

2) Contains **E**

3) Satisfies associativity and

4) Each element has an inverse

Such groups of point symmetry operators are known as **Point Groups**

Problem: construct a multiplication table for the S_4 point group having the set of elements: $S_4 = \{E, S_4^+, S_4^2 = C_2, S_4^-\}$

S_4	E	S_4^+	C_2	S_4^-
E	E	S_4^+	C_2	S_4^-
S_4^+	S_4^+			
C_2	C_2			
S_4^-	S_4^-			

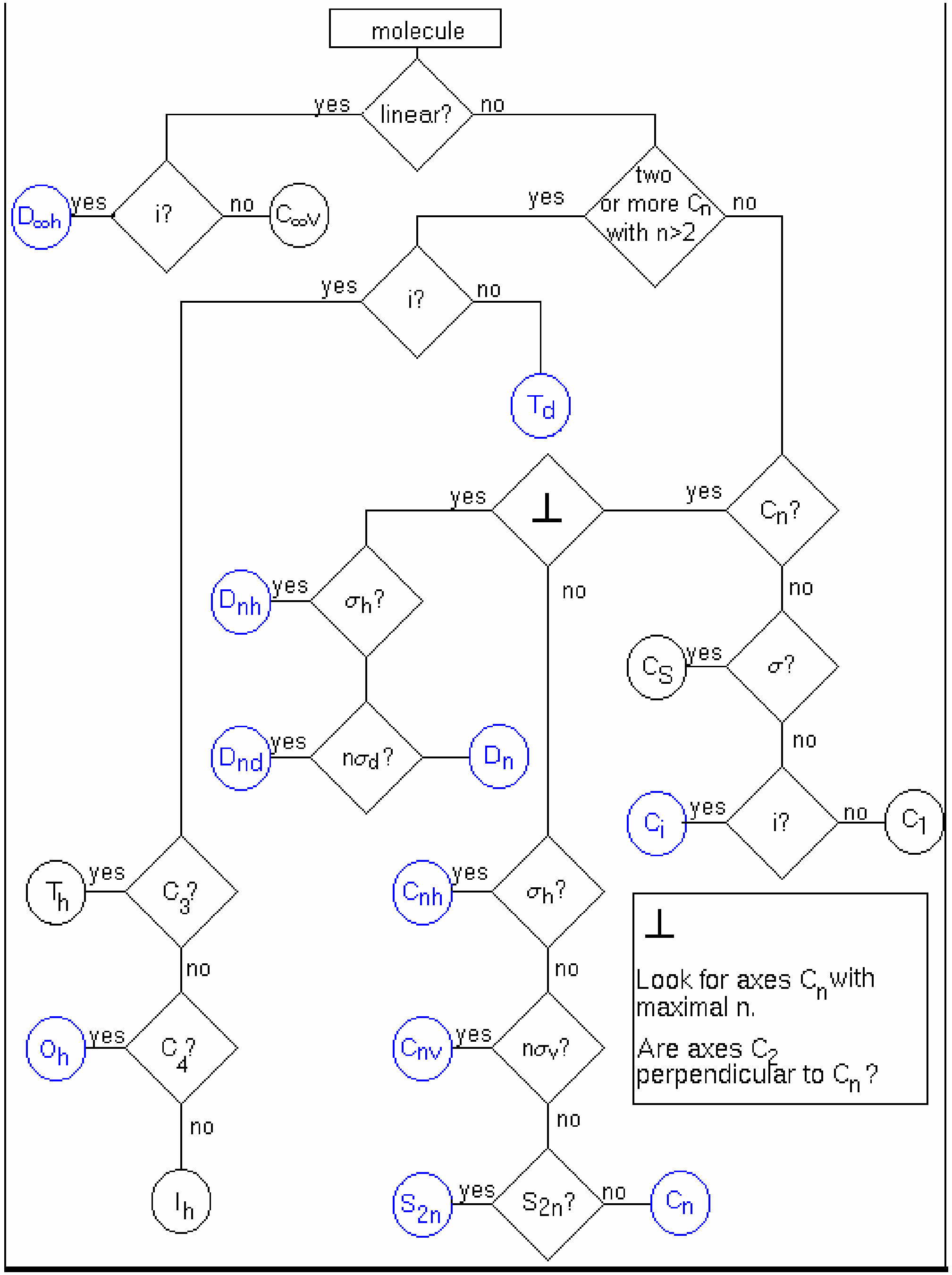
Complete row 2 using stereograms: $S_4^+S_4^+$, $C_2S_4^+$, $S_4^-S_4^+$ (column x row)

The complete table is given below

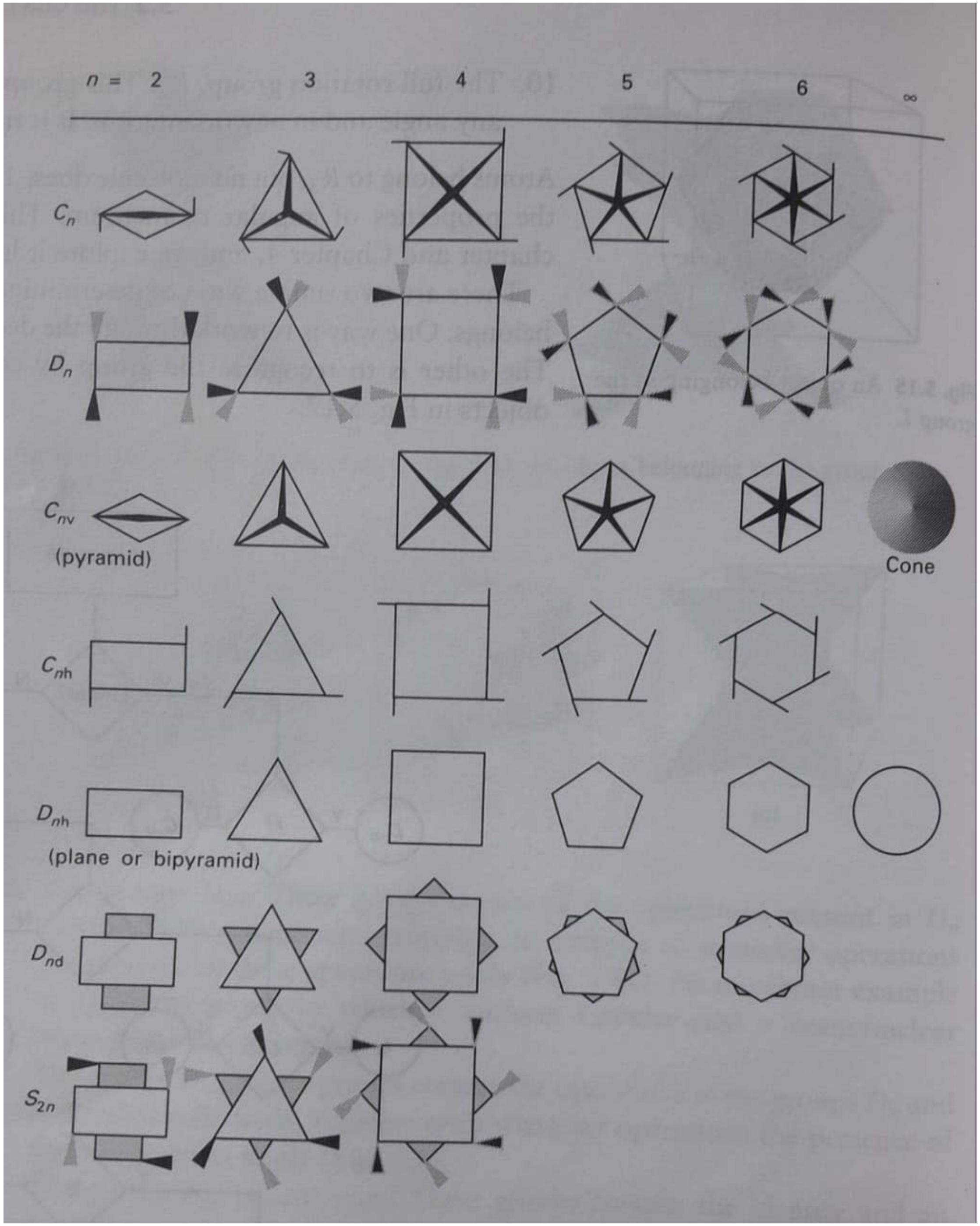
S_4	E	S_4^+	C_2	S_4^-
E	E	S_4^+	C_2	S_4^-
S_4^+	S_4^+	C_2	S_4^-	E
C_2	C_2	S_4^-	E	S_4^+
S_4^-	S_4^-	E	S_4^+	C_2

Determination of Point Group of Any molecule

- **i :** centre of inversion
- **C_2:** 2-fold rotational axis
- **C_n:** n-fold rotational axis &
- **σ_h :** horizontal (and, with respect to the principal axis perpendicular) mirror plane
- **σ_v:** vertical (and, with respect to the principal axis parallel) mirror plane
- **σ_d:** diagonal mirror plane
- **S_n:** rotatory-reflection plane



Representative hapes for various Point Groups



Few examples with Symmtry Elements and their Point Group

Point Group	Symmetry Elements	Example Molecule
C_s	E, σ	BFClBr (planar)
C_2	E, C_2	H_2O_2
C_{2v}	E, C_2, σ, σ'	H_2O
C_{3v}	$E, C_3, C_3^2, 3\sigma$	NF_3
$C_{\infty v}$	$E, C_\infty, \infty\sigma$	HCl
C_{2h}	E, C_2, σ, i	*trans*-$C_2H_2F_2$
D_{2h}	$E, C_2, C_2', C_2'', \sigma, \sigma', \sigma'', i$	C_2F_4
D_{3h}	$E, C_3, C_3^2, 3C_2, S_3, S_3^2, \sigma, 3\sigma'$	SO_3
D_{4h}	$E, C_4, C_4^3, C_2, 2C_2', 2C_2'', i, S_4, S_4^3, \sigma, 2\sigma', 2\sigma''$	XeF_4
D_{6h}	$E, C_6, C_6^5, C_3, C_3^2, C_2, 3C_2', 3C_2'', i, S_3, S_3^2, S_6, S_6^5, \sigma, 3\sigma', 3\sigma''$	C_6H_6 (benzene)
$D_{\infty h}$	$E, C_\infty, S_\infty, \infty C_2, \infty\sigma, \sigma', i$	H_2, CO_2
T_d	$E, 4C_3, 4C_3^2, 3C_2, 3S_4, 3S_4^3, 6\sigma$	CH_4
O_h	$E, 4C_3, 4C_3^2, 6C_2, 3C_4, 3C_2, i, 3S_4, 3S_4^3, 4S_6, 4S_6^5, 3\sigma, 6\sigma'$	SF_6