Chapter 2

Symmetry Point Groups

In mathematics, a ***group*** is a set of elements which satisfy certain characteristics. If we know the complete set of symmetry operations of a given system, this set of operations forms a ***symmetry point group*** if the following requirements are all met:

1) The product of any two operations is itself an operation in the group. This is called the property of ***closure***.
2) There must be an identity operation E in the set.
3) Every operation in the set must have an inverse operation that exists in the set. The inverse operation, when performed after a given operation, cancels its effect. In equation (1) the operation A^{-1} is an inverse for operation A:

$$A^{-1} \times A = E \qquad (1)$$

4) Multiplication of operations of the set must be associative, as shown in equation (2), but not necessarily commutative.

$$F \times (B \times A) = (F \times B) \times A \qquad (2)$$

Taking into account the given characteristics of symmetry groups, we can easily prove that the set of operations ($C_{2(z)}$, σ_{xz}, σ_{yz} and E) in water molecule (structure VI in Chapter 1) is a symmetry group. All requirements (1 - 4) are met here. The property of closure can be confirmed by the so-called ***symmetry multiplication table*** as shown below:

	E	$C_{2(z)}$	σ_{xz}	σ_{yz}
E	E	$C_{2(z)}$	σ_{xz}	σ_{yz}
$C_{2(z)}$	$C_{2(z)}$	E	σ_{yz}	σ_{xz}
σ_{xz}	σ_{xz}	σ_{yz}	E	$C_{2(z)}$
σ_{yz}	σ_{yz}	σ_{xz}	$C_{2(z)}$	E

Requirement (1) is met by knowing that any operation can be multiplied by any other operation to give an operation that itself is a member of the set. The presence of E satisfies requirement (2). Requirement (4) is also met in case of a triple (or higher) product. This can be subdivided in any way we like without changing the result, equation (3):

$$
\begin{array}{lllllllll}
\sigma_{xz} & \times & \sigma_{yz} & \times & C_{2(z)} & = & & & \\
(\sigma_{xz} & \times & \sigma_{yz}) & \times & C_{2(z)} & = & C_{2(z)} & \times & C_{2(z)} \\
\sigma_{xz} & \times & \sigma_{yz} & \times & C_{2(z)} & = & \sigma_{xz} & \times & \sigma_{xz} \\
 & & & & & = & E & &
\end{array} \qquad (3)
$$

Thus, the set of operations that exist in water molecule is a symmetry point group, so called $\boldsymbol{C_{2v}}$ group, as we see later. It has previously been stated that every operation must be represented by a matrix. The resulting operation must also be represented by a matrix that is a product of two (or more) representing matrices.

Classification of Symmetry Groups

Symmetry groups are classified into the following categories:

1) Simple groups of order 2:

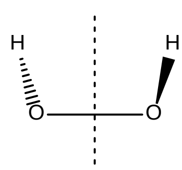
These groups contain only one operation in addition to *E*, with an order (2). This class of groups includes only three group types:

$\boldsymbol{C_s}$ group: contains *E* and one σ only.

$\boldsymbol{C_i}$ group: contains *E* and *i* only.

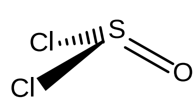
$\boldsymbol{C_2}$ group: contains *E* and C_2 only.

Examples of these symmetry groups are shown in structures I, II and III below:



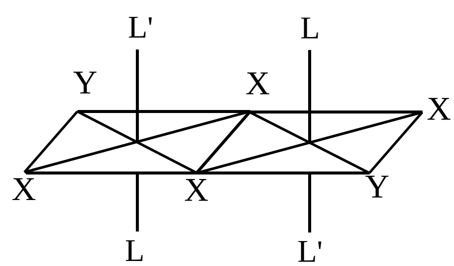
$\boldsymbol{C_2}$

I



$\boldsymbol{C_s}$

II

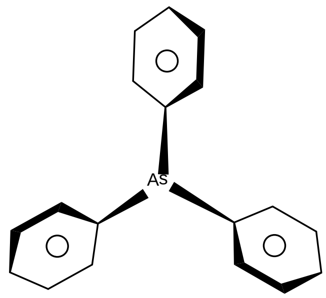


$\boldsymbol{C_i}$

III

2) C_n groups:

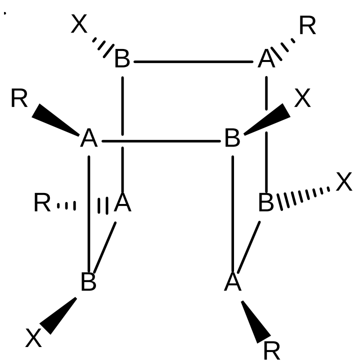
In this class, the molecule has the identity operation, together with a set of C_n^1, C_n^2, C_n^3, ... , C_n^{n-1} operations only. The order of the group is (*n*). An example of such groups is shown in structure IV below. It should be noted that the molecule IV is not a planar molecule.



C_3
IV

3) S_n groups:

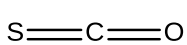
An ***S_n*** molecule has a C_n operation and a plane perpendicular to C_n , but none of these two operations exists independently. Such a group exists in molecules with even-values for *n*, and the order of the group is *n*. Structure V is an example.



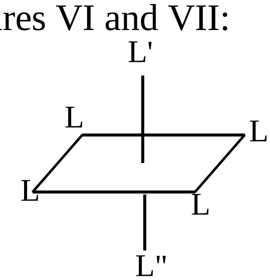
S_4
V

4) C_{nv} groups:

A ***C_{nv}*** group has a main axis of rotation (C_n), an identity (*E*) and *n* vertical reflection planes (σ_v) that intercept along the main axis. The order of such a group is 2*n*. Examples of such groups are structures VI and VII:



$C_{\infty v}$
VI



C_{4v}
VII

5) C_{nh} groups:

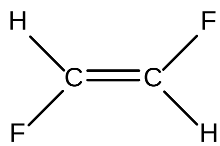
A $\boldsymbol{C_{nh}}$ group contains identity E, main axis C_n and a horizontal plane σ_h that is perpendicular to C_n. The order of such a group is $2n$, since it has:

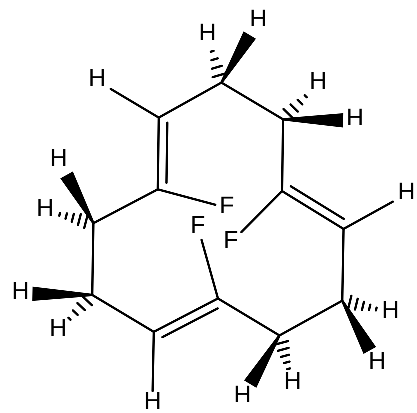
$$C_n^1 \quad , \quad C_n^2 \quad , \quad \dots\dots\dots \quad , \quad C_n^{n-1} \quad , \quad C_n^n \quad = \quad E$$

$$\sigma_h$$

$$S_n^1 \quad , \quad S_n^2 \quad , \quad \dots\dots\dots \quad , \quad S_n^{n-1} \quad , \quad S_n^n \quad = \quad E$$

examples of $\boldsymbol{C_{nh}}$ symmetry are structures VIII and IX:





$\boldsymbol{C_{2h}}$
VIII

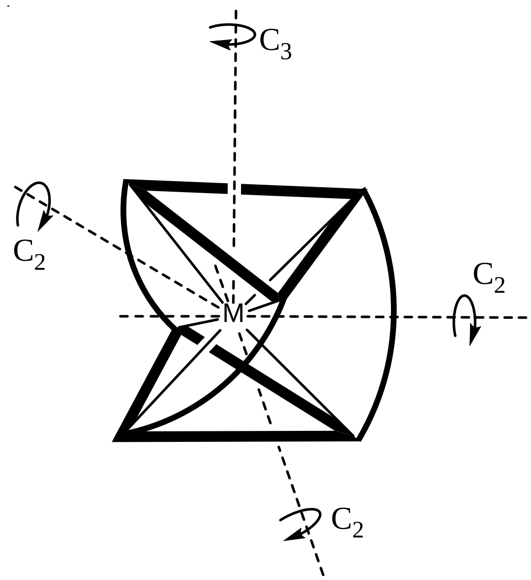
$\boldsymbol{C_{3h}}$
IX

6) D_n groups:

A $\boldsymbol{D_n}$ group has identity operation E, a C_n axis and nC_2's lying in a plane perpendicular to C_n. The order of such groups is $2n$, since they contain:

$$C_n^1 \quad , \quad C_n^2 \quad , \quad \dots\dots\dots \quad , \quad C_n^n \quad = \quad E \quad , \text{ and } nC_2$$

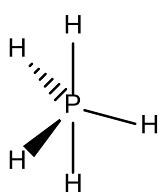
Good examples of $\boldsymbol{D_n}$ symmetry are tris-chelated complexes such as $[Co(en)_3]^{3+}$ and $[Co(acac)_3]$, structure X. These complexes have antiprismatic structure, with a vertical C_n axis of rotation, and $3C_2$ axes in a plane perpendicular to C_n.



X

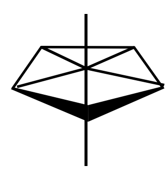
7) D_{nh} groups:

In addition to E, C_n and perpendicular nC_2, the $\boldsymbol{D_{nh}}$ group contains a horizontal plane of symmetry perpendicular to the C_n axis. The order of such a group is 4n. Examples of these groups are structures XI-XIV:



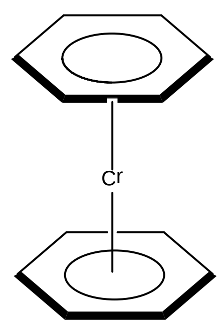
$\boldsymbol{D_{3h}}$

XI



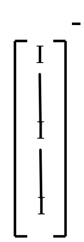
$\boldsymbol{D_{5h}}$

XII



$\boldsymbol{D_{6h}}$

XIII

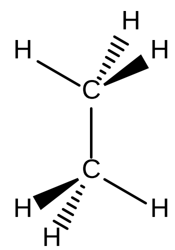


$D_{\infty h}$

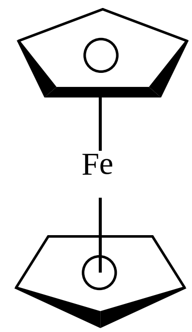
XIV

8) $\boldsymbol{D_{nd}}$ groups:

In addition to E, C_n and perpendicular nC_2, a $\boldsymbol{D_{nd}}$ group contains n vertical planes σ_d that intercept along the main axis. Note that the vertica1 planes are so called *dihedral planes* since each of them bisects the angle between two neighboring C_2's. The order of such a group is 4n. Examples of $\boldsymbol{D_{nd}}$ symmetry are ferrocene XV and ethane XVI in their staggered form.



D_{3d}
XV



D_{5d}
XVI

9) High symmetry groups:

a) The linear groups: In the previous $\boldsymbol{C_{nv}}$ and $\boldsymbol{D_{nh}}$ symmetry point groups, systems with especially high symmetries such as $\boldsymbol{C}_{\infty\mathrm{v}}$ and $\boldsymbol{D}_{\infty\mathrm{h}}$ linear species have been encountered. The $\boldsymbol{C}_{\infty\mathrm{v}}$ point group involves a C_∞ and $\infty\sigma_v$. The $\boldsymbol{D_{\infty h}}$ involves C_∞, ∞C_2 and σ_h.

b) Other common species with especially high symmetries are the *Tetrahedral* T_d and *Octahedral* O_h groups.

The tetrahedral point group **($\boldsymbol{T_d}$)**: this group has an order of (24), with symmetry operations namely as:

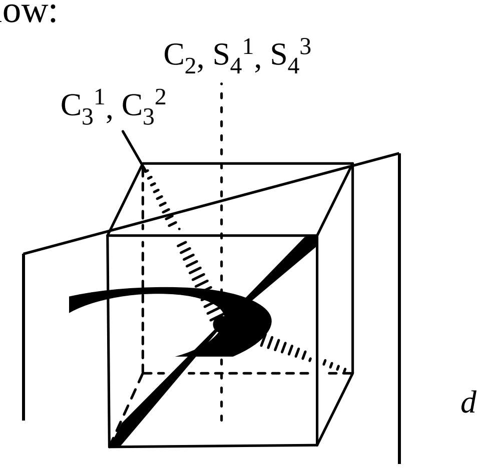
– Four × two C_3 axes (each Cartesian axis has $C_3^{\,1}$, $C_3^{\,2}$, and $C_3^{\,3} = E$)

– Six σ_d's

– Three × two S_4 axis (each Cartesian one with $S_4^{\,1}$, $S_4^{\,2} = C_2$, $S_4^{\,3}$ and $S_4^{\,4} = E$)

– Three C_2 axes

The symmetry operations for $\boldsymbol{T_d}$ point group are shown in structure XVII below:



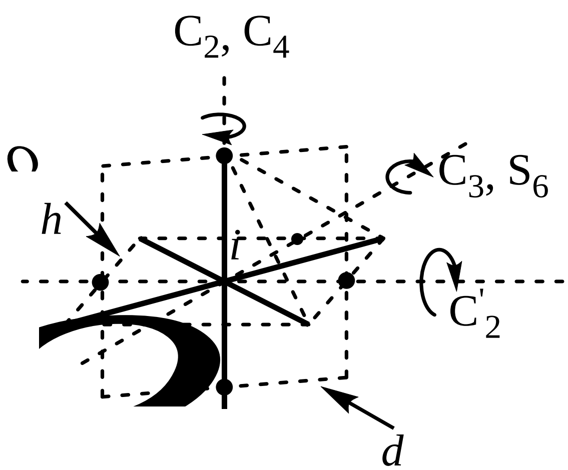
T_d
XVII

Examples of $\boldsymbol{T_d}$ symmetry are ClO_4^-, $NiCl_4^{2-}$, CH_4 and SiF_4.

The octahedral point group **($\boldsymbol{O_h}$):** This group has an order of (48), namely:

– E
– Four × two C_3 (C_3^1, C_3^2, $C_3^3 = E$)
– Three × three C_4 (C_4^1, $C_4^2 = C_2$, C_4^3, $C_4^4 = E$)
– Six C_2' (each bisecting two edges of the octahedron)
– One i
– Three × two S_4 (S_4^1, $S_4^2 = C_2$, S_4^3, $S_4^4 = E$)
– Four × two S_6
– Three σ_h (σ_{xy}, σ_{xz}, σ_{yz})
– Six σ_d

Structure XVIII below shows examples of $\boldsymbol{O_h}$ symmetry operations.



$\boldsymbol{O_h}$
XVIII

Exercises: In Exercise 1 of Chapter 1, find out the highest order symmetry point group for each species.