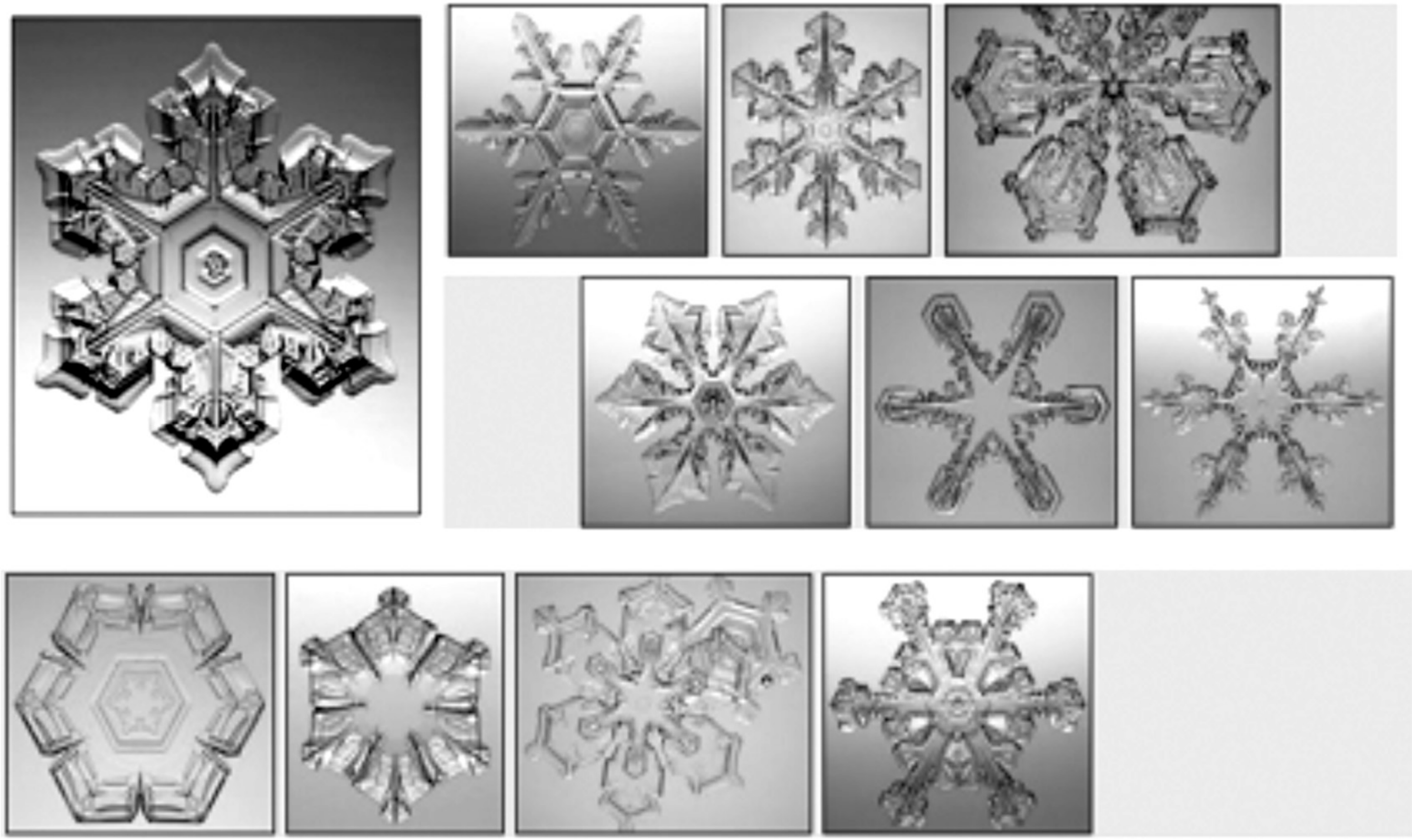
Chapter 3

Molecular symmetry and symmetry point group

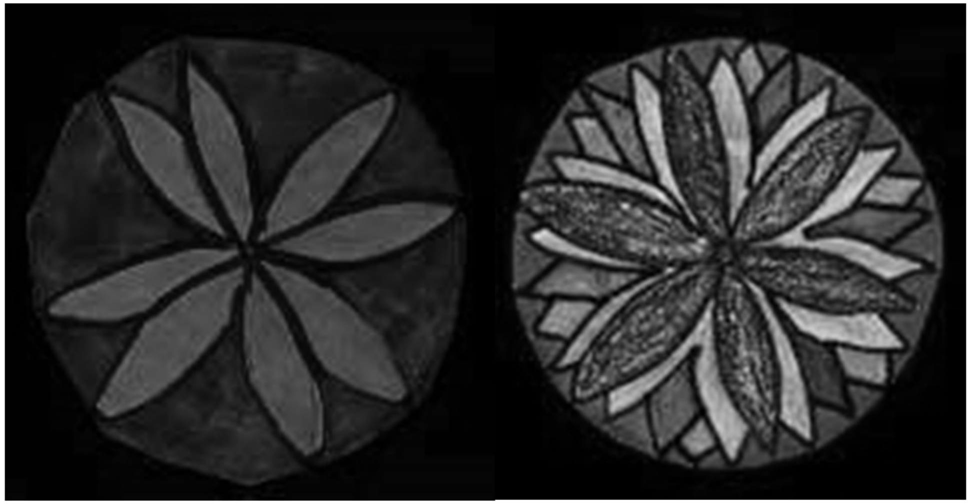


Part A

§ 3.1 Symmetry elements and symmetry operations

- **Symmetry** exists all around us and many people see it as being a thing of beauty, e.g., the snow flakes.

- A symmetrical object contains within itself some parts which are **equivalent** to one another.



What are the key symmetry elements pertaining to these objects?

Why do we study the symmetry concept?

- The molecular configuration can be expressed more simply and distinctly.

- The determination of molecular configuration is greatly simplified.

- It assists giving a better understanding of the properties of molecules.

- To direct chemical syntheses; the compatibility in symmetry is a factor to be considered in the formation and reconstruction of chemical bonds.

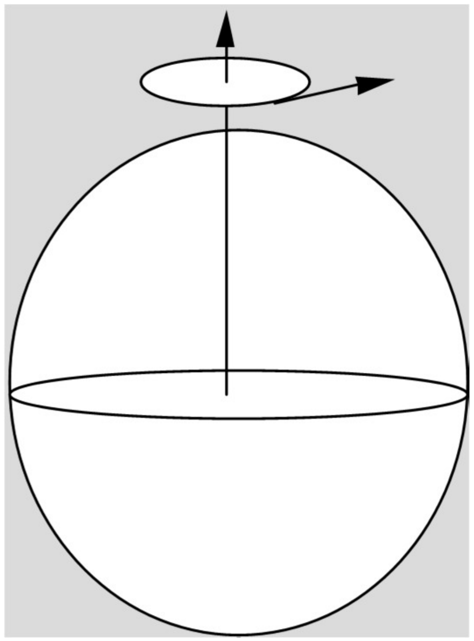
1. Symmetry elements and symmetry operations

Symmetry operation

An action that leaves an object the same after it has been carried out is called symmetry operation.

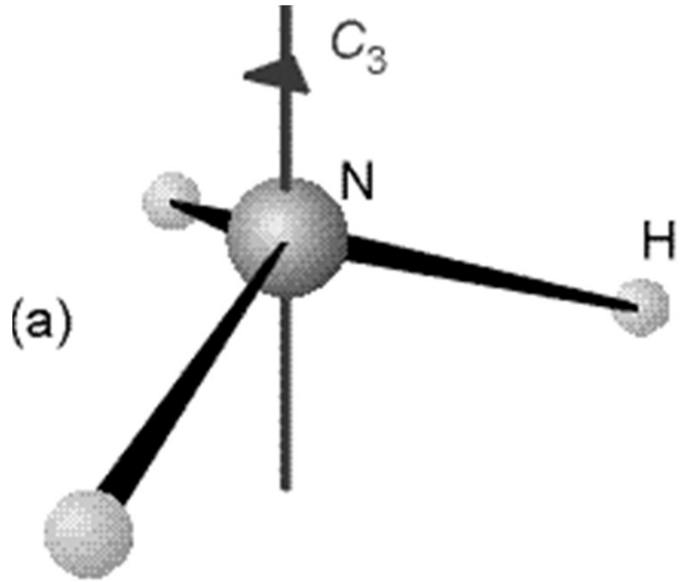
Example:

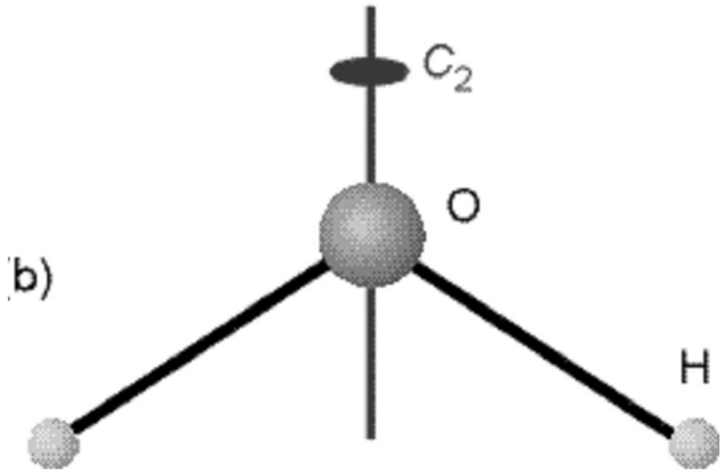
Rotation



Symmetry elements

Symmetry operations are carried out with respect to points, lines, or planes called symmetry elements.





(a) An NH_3 molecule has a threefold (C_3) axis

(b) an H_2O molecule has a twofold (C_2) axis.

Symmetry Operation

Symmetry operations are:

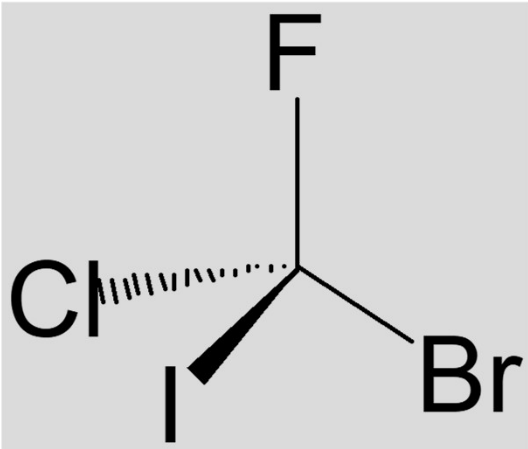
Rotation **Reflection** **Inversion**

The corresponding symmetry elements are:

a line **a plane** **a point**

1) The identity (E)

- **Operation by the identity operator leaves the molecule unchanged.**
- **All objects can be operated upon by the identity operation.**



➢Matrix representation of *an operator*

$$\hat{C}\begin{pmatrix} x_1 \\ y_1 \\ z_1 \end{pmatrix} = \begin{pmatrix} x_2 \\ y_2 \\ z_2 \end{pmatrix} \quad \Longrightarrow \quad \begin{aligned} x_2 &= c_{11}x_1 + c_{12}y_1 + c_{13}z_1 \\ y_2 &= c_{21}x_1 + c_{22}y_1 + c_{23}z_1 \\ z_2 &= c_{31}x_1 + c_{32}y_1 + c_{33}z_1 \end{aligned}$$

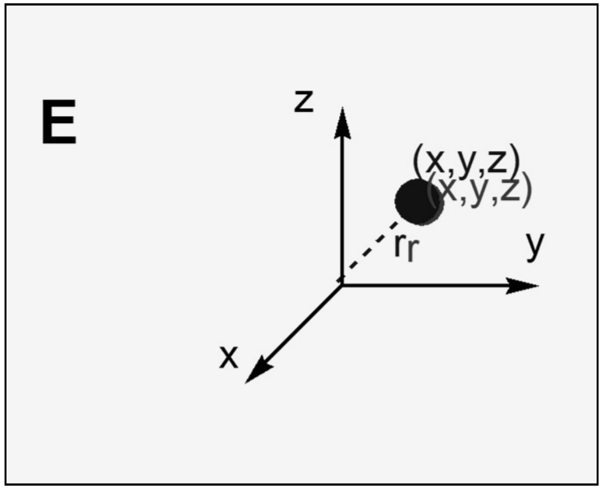
$$\begin{pmatrix} c_{11} & c_{12} & c_{13} \\ c_{21} & c_{22} & c_{23} \\ c_{31} & c_{32} & c_{33} \end{pmatrix}\begin{pmatrix} x_1 \\ y_1 \\ z_1 \end{pmatrix} = \begin{pmatrix} x_2 \\ y_2 \\ z_2 \end{pmatrix} \qquad \hat{C} = \begin{pmatrix} c_{11} & c_{12} & c_{13} \\ c_{21} & c_{22} & c_{23} \\ c_{31} & c_{32} & c_{33} \end{pmatrix}$$

➢ Matrix representation of ***E***

$$x \xrightarrow{E} x;\ y \xrightarrow{E} y;\ z \xrightarrow{E} z$$

$$x \xrightarrow{E} 1\cdot x + 0\cdot y + 0\cdot z;$$
$$y \xrightarrow{E} 0\cdot x + 1\cdot y + 0\cdot z;$$
$$z \xrightarrow{E} 0\cdot x + 0\cdot y + 1\cdot z$$

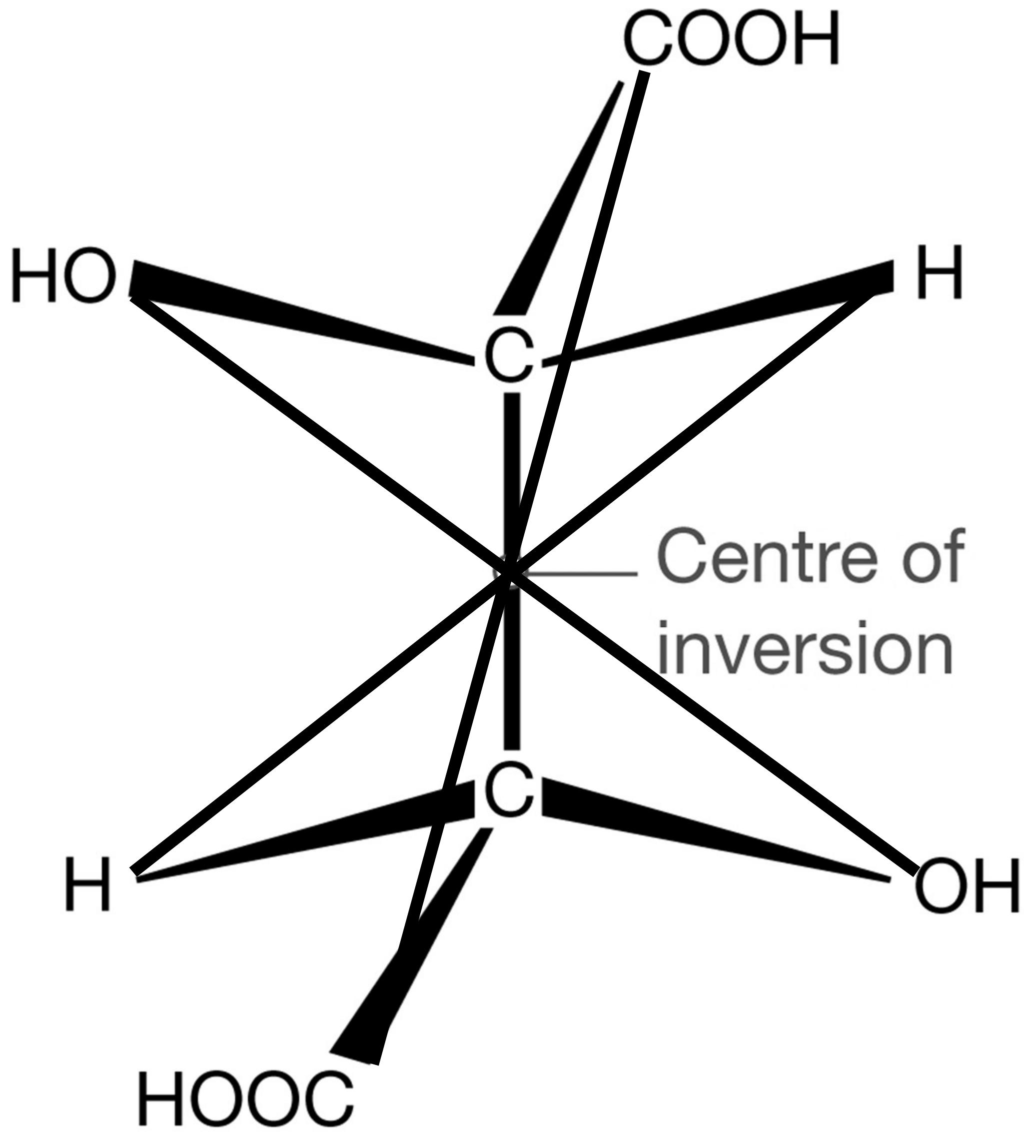
$$E\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$



$$E = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

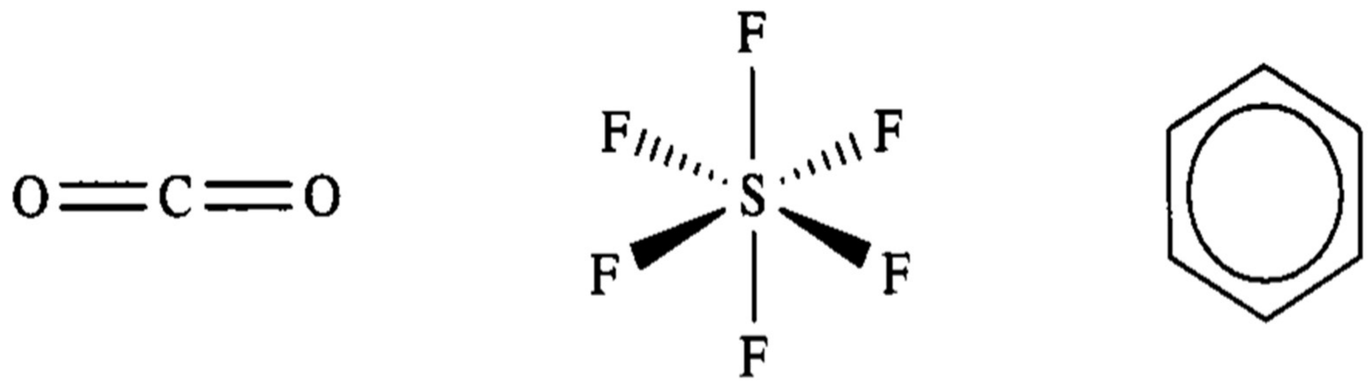
2) Inversion and the *inversion center* (*i*)

• A molecule has a ***center of symmetry***, symbolized by ***i***, if the operation of ***inverting*** all its nuclei through the center gives a configuration indistinguishable from the original one.

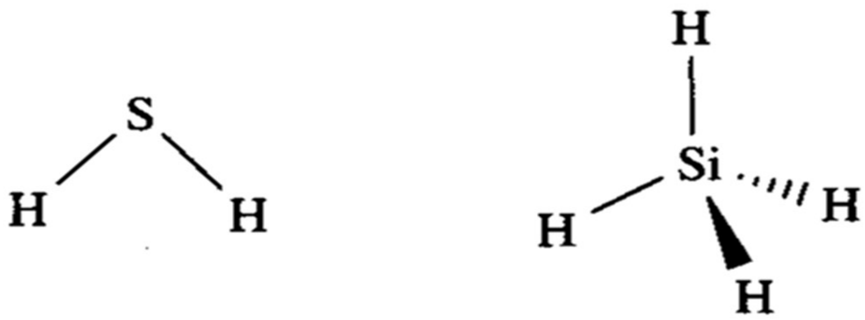


Meso-tartaric acid

For example

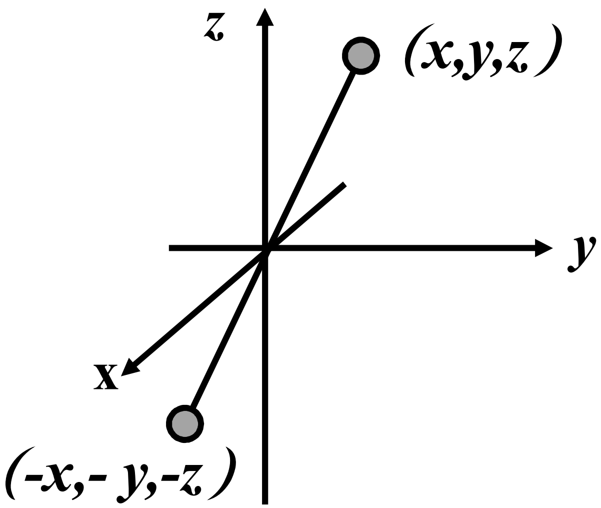


These objects have a center of inversion ***i***.



These do not have a center of inversion.

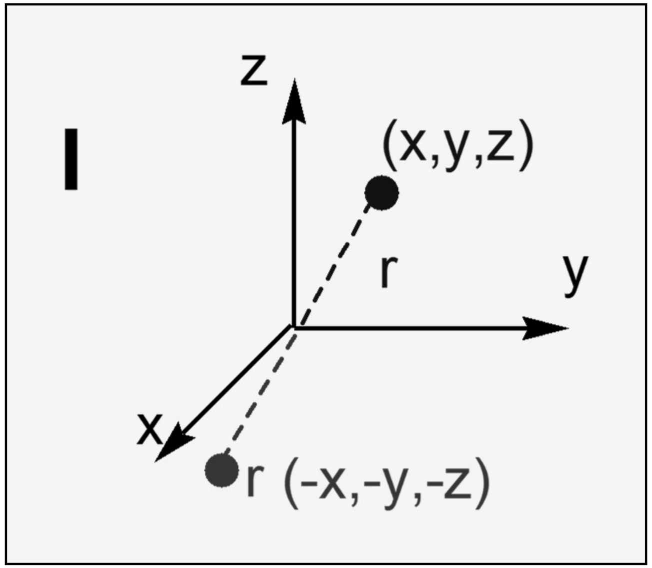
- Inverts all atoms through the centre of the object.

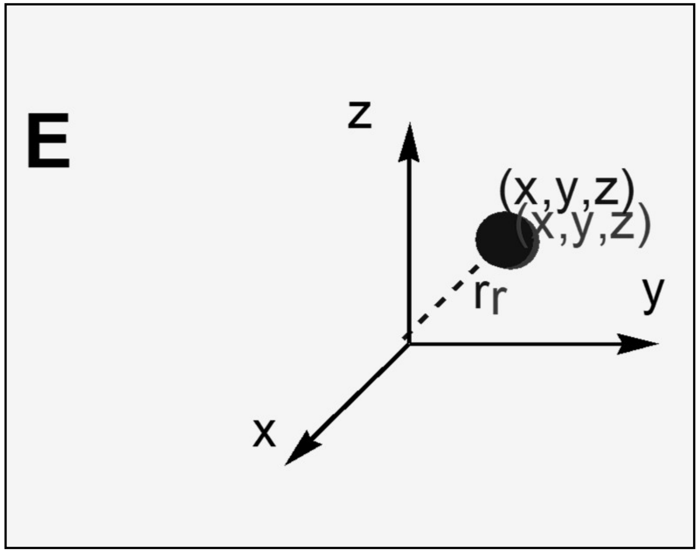


$$(x,y,z) \rightarrow (-x, -y, -z)$$

- Its matrix representation

$$I = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \qquad I\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -x \\ -y \\ -z \end{pmatrix}$$





$$I\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -x \\ -y \\ -z \end{pmatrix} \qquad I\begin{pmatrix} -x \\ -y \\ -z \end{pmatrix} = \begin{pmatrix} x \\ y \\ z \end{pmatrix} \qquad I^2\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

$$I^2 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = E$$

$$\begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \begin{pmatrix} b_{11} & b_{12} & b_{13} \\ b_{21} & b_{22} & b_{23} \\ b_{31} & b_{32} & b_{33} \end{pmatrix} = \begin{pmatrix} c_{11} & c_{12} & c_{13} \\ c_{21} & c_{22} & c_{23} \\ c_{31} & c_{32} & c_{33} \end{pmatrix}$$

$$\underline{a_{11}b_{11} + a_{12}b_{21} + a_{13}b_{31} = c_{11}} \Rightarrow \sum_{i=1}^{3} a_{1i}b_{i1} = c_{11}$$

$$\underline{a_{11}b_{12} + a_{12}b_{22} + a_{13}b_{32} = c_{12}} \Rightarrow \sum_{i=1}^{3} a_{1i}b_{i2} = c_{12}$$

$$\underline{a_{21}b_{11} + a_{22}b_{21} + a_{23}b_{31} = c_{21}} \Rightarrow \sum_{i=1}^{3} a_{2i}b_{i1} = c_{21}$$

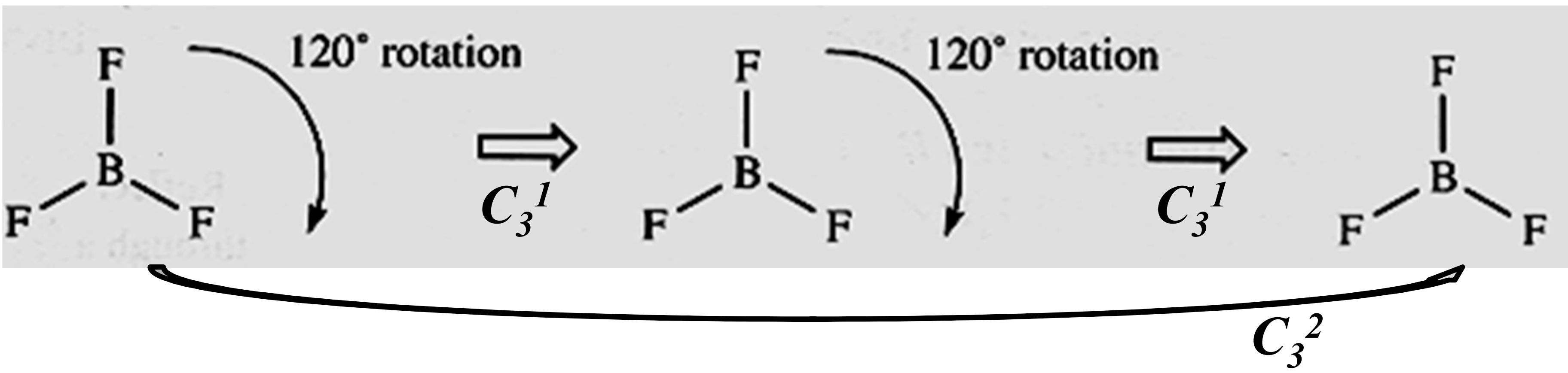
$$I^2 = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = E$$

3) Rotation and the *n*-fold rotation axis (C_n)

A body has an ***n-fold axis of symmetry*** (also called *n-fold proper axis* or *n-fold rotation axis*) if rotation about this axis by ***360/n*** degrees gives a configuration indistinguishable from the original one.

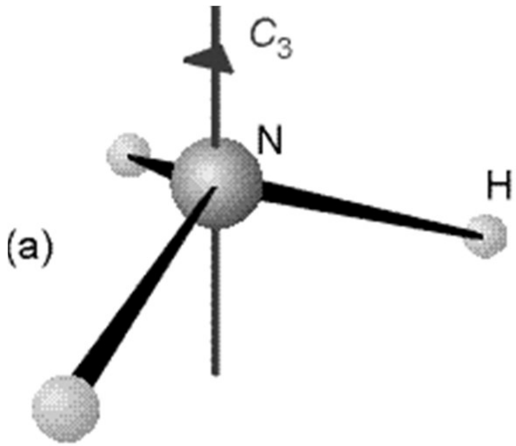
Example: Rotation of BF_3 around its C_3 axis.

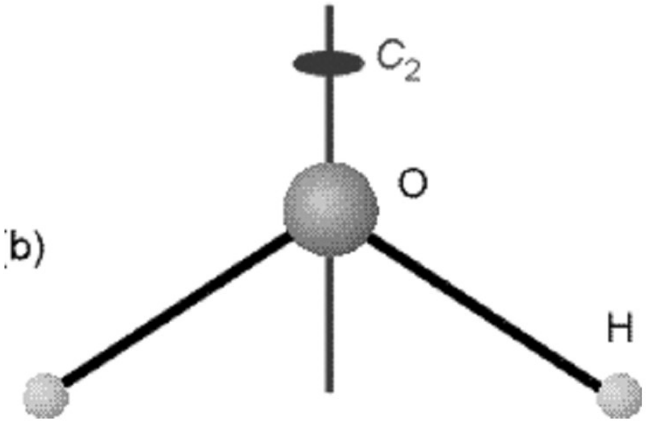
Allowed rotations: $C_3^1(\alpha=2\pi/3)$, $C_3^2(\alpha=4\pi/3)$, $C_3^3 = E$

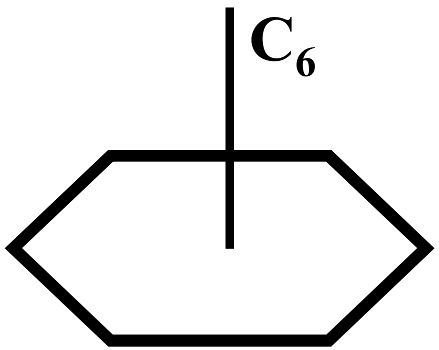


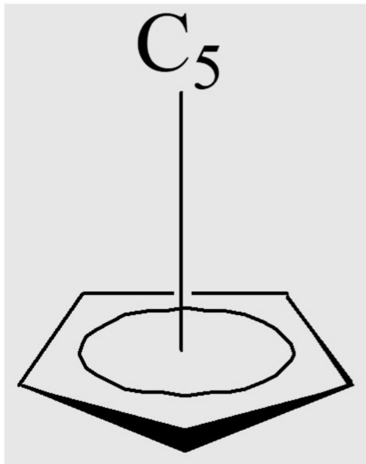
- There also exist three C_2 axes each along a B-F bond!
- The principal rotation axis is the axis of the highest fold.

The principal rotation axis is the axis of the highest fold.









The matrix representations of rotations around a C_n axis:

Conditions:

- Principal axis is aligned with the ***z***-axis

$\boldsymbol{C_n}$

A $\boldsymbol{C_n}$ axis gives rise to $\boldsymbol{n}$ unique rotational operations labeled as $\boldsymbol{C_n^m}$ ($\boldsymbol{m}$ = 1, 2,…, n).

Matrix of allowed rotations

$$C_n^{\ m} = \begin{pmatrix} \cos\alpha & -\sin\alpha & 0 \\ \sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Angle of allowed rotations:

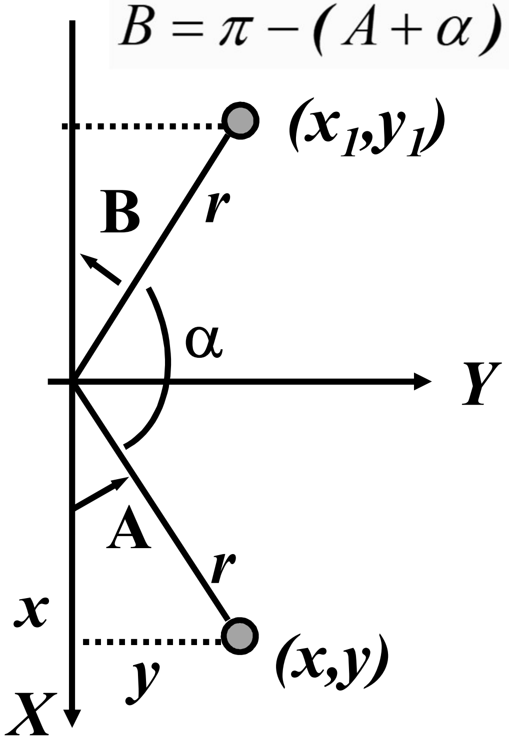
$$\alpha = \frac{2m\pi}{n}$$

($\boldsymbol{m}$ = 1,2,…,n)

The matrix representation of rotational operations: e.g., C_n^m

$C_n \parallel z$ **Allowed rotations:** $\alpha = 2m\pi/n$ (m = 1,2,…,n)

$B = \pi - (A + \alpha)$



$x = r\cos A$

$y = r\sin A$

$$x_1 = -r\cos B = r\cos(\alpha + A)$$
$$= r\cos A\cos\alpha - r\sin A\sin\alpha$$
$$= x\cos\alpha - y\sin\alpha$$

$$y_1 = r\sin B = x\sin\alpha + y\cos\alpha$$

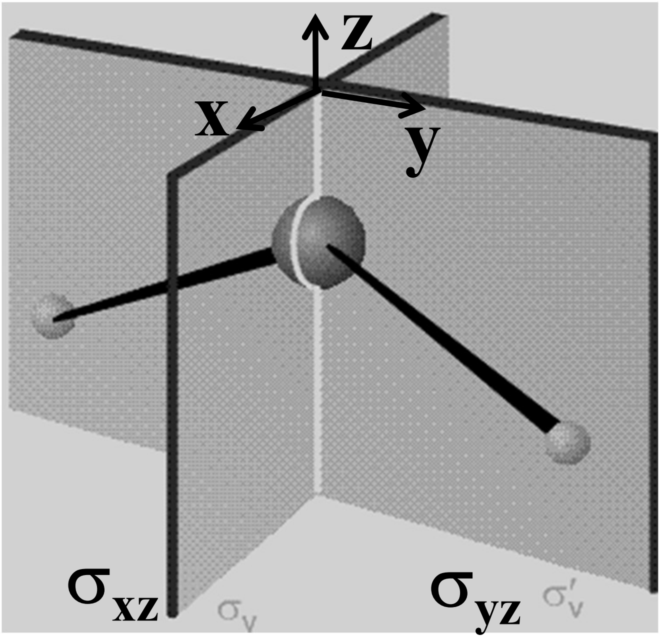
$z_1 = z$

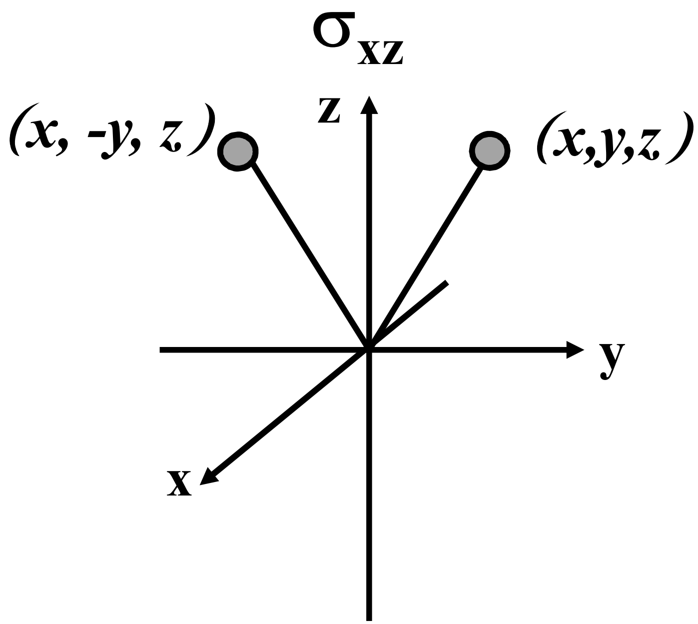
$$\begin{pmatrix} x_1 \\ y_1 \\ z_1 \end{pmatrix} = C_n^m \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} \cos\alpha & -\sin\alpha & 0 \\ \sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

$$\therefore C_n^m = \begin{pmatrix} \cos\alpha & -\sin\alpha & 0 \\ \sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

4) Reflection and the Mirror plane (σ)

➢ If reflection of an object through a plane produces an indistinguishable configuration, that plane is a plane of symmetry (mirror plane, σ).





$$\sigma_{xz}\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x \\ -y \\ z \end{pmatrix}$$

$$\sigma_{xz} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Likewise, we have

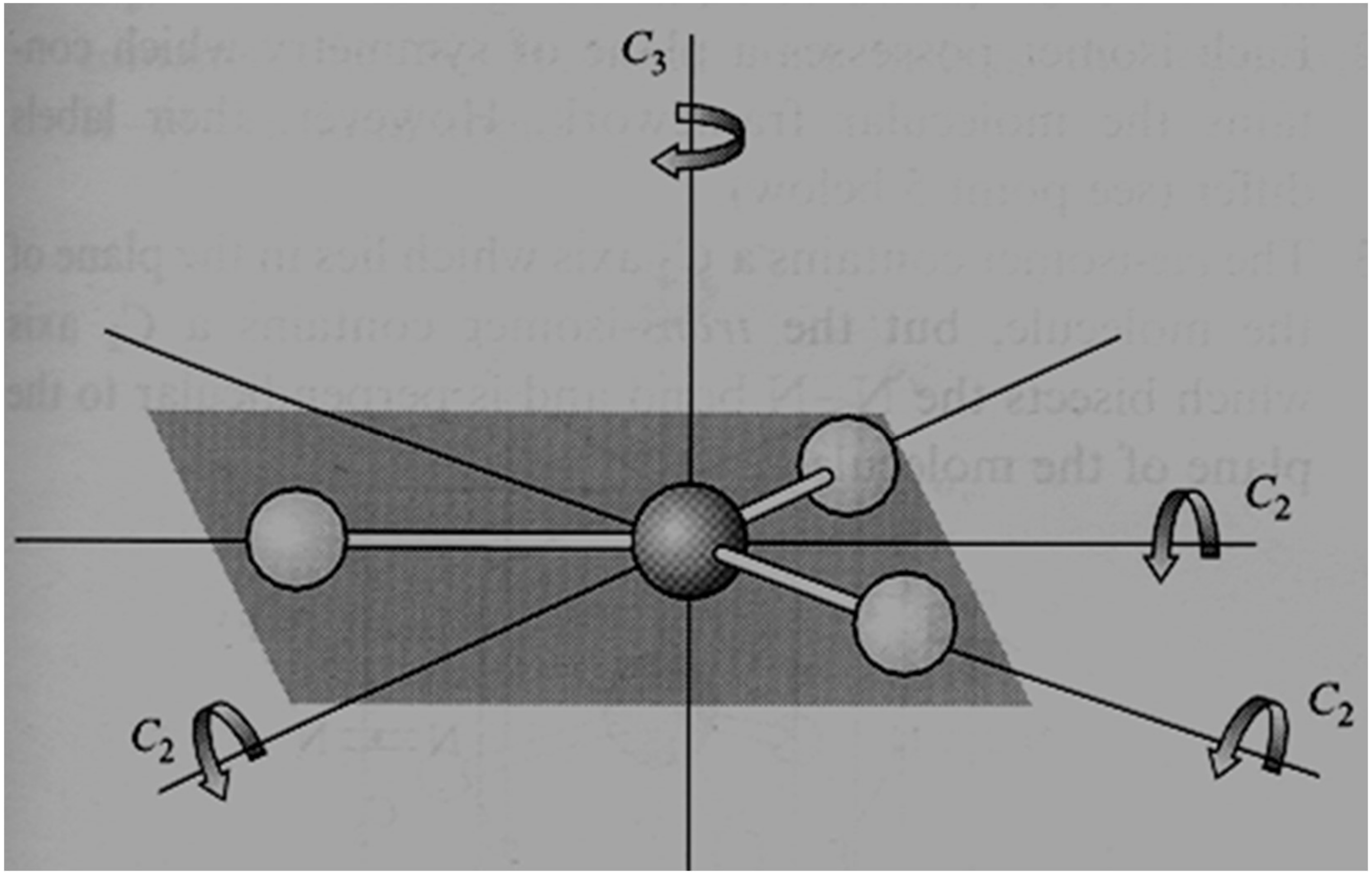
$$\sigma_{xy} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \qquad \sigma_{xy}\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x \\ y \\ -z \end{pmatrix}$$

$$\sigma_{yz} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \sigma_{yz}\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -x \\ y \\ z \end{pmatrix}$$

➢ For molecular systems, there are three types of mirror planes:

- If the plane is **perpendicular** to the vertical principal axis, it is labeled σ_h. (*h-horizontal*)
- If the plane **contains** the principal axis, it is labeled σ_v. (*v-vertical*)
- If a σ_v plane **contains** the principal axis and more specifically **bisects** the angle between two adjacent 2-fold axes, it is labeled σ_d. (*d-diagonal*)

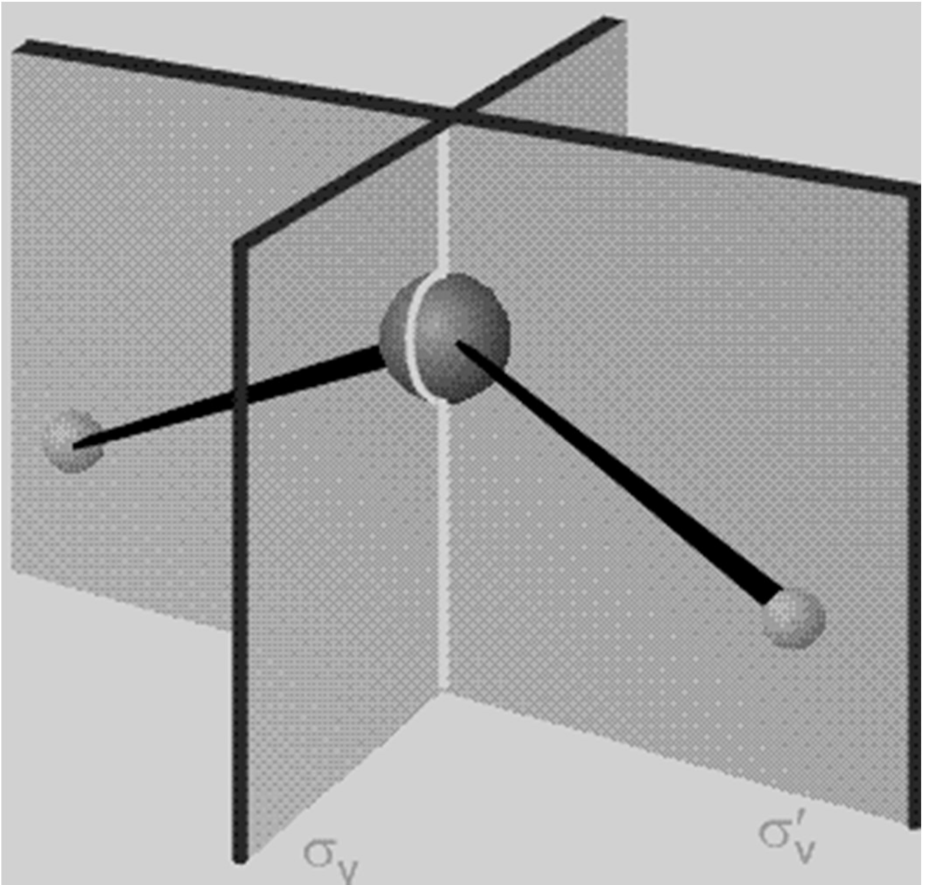
Does BF_3 have σ_h , σ_v and/or σ_d planes ?

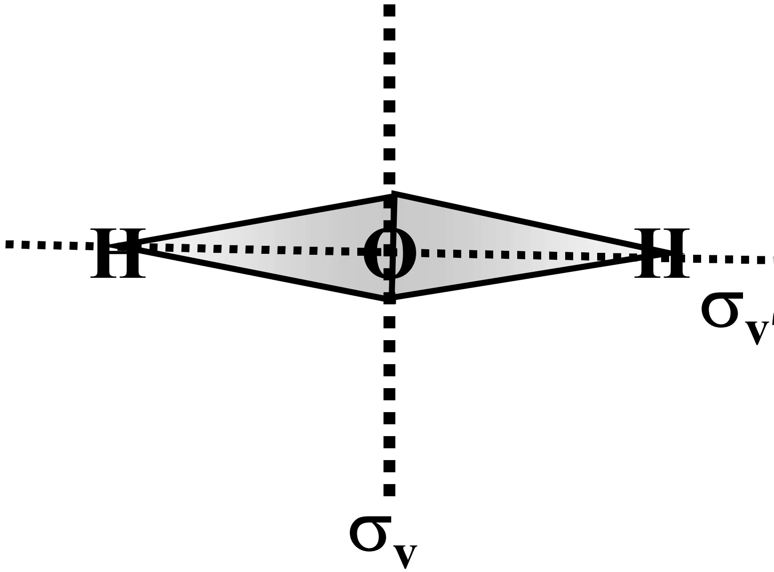


- The BF_3 plane is a σ_h plane.
- Each plane that contains a B-F bond and the C_3 axis is a σ_v and, meanwhile, a σ_d plane.

If the plane **contains** the principal axis then it is labeled σ_v.

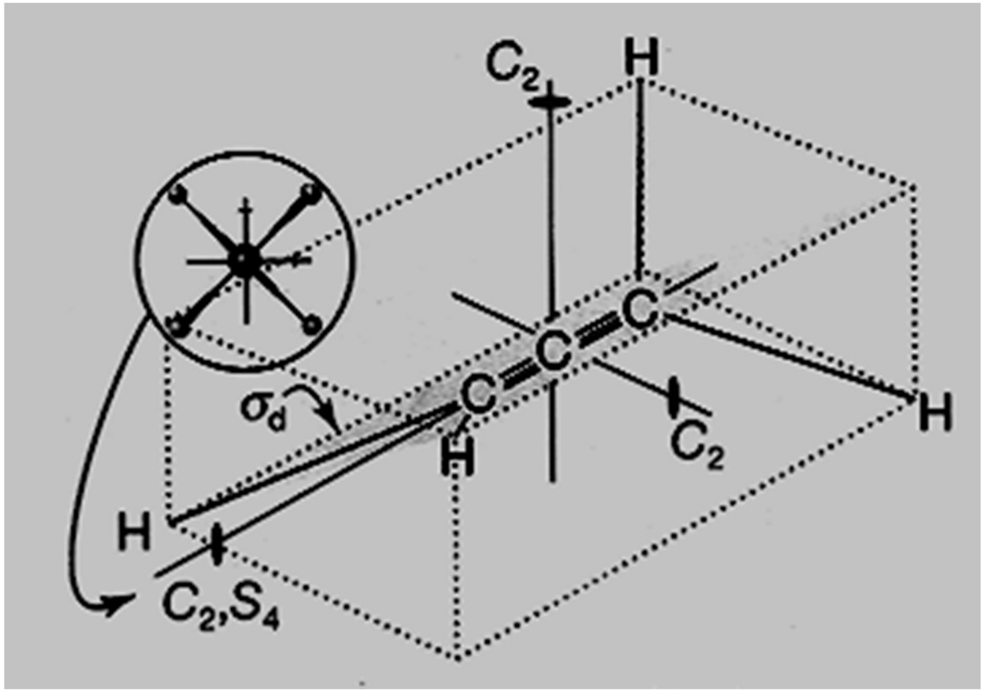
- Example: H_2O
  - Has a $\boldsymbol{C_2}$ principal axis.
  - Has two planes that contain the principal axis, σ_v and σ_v'.

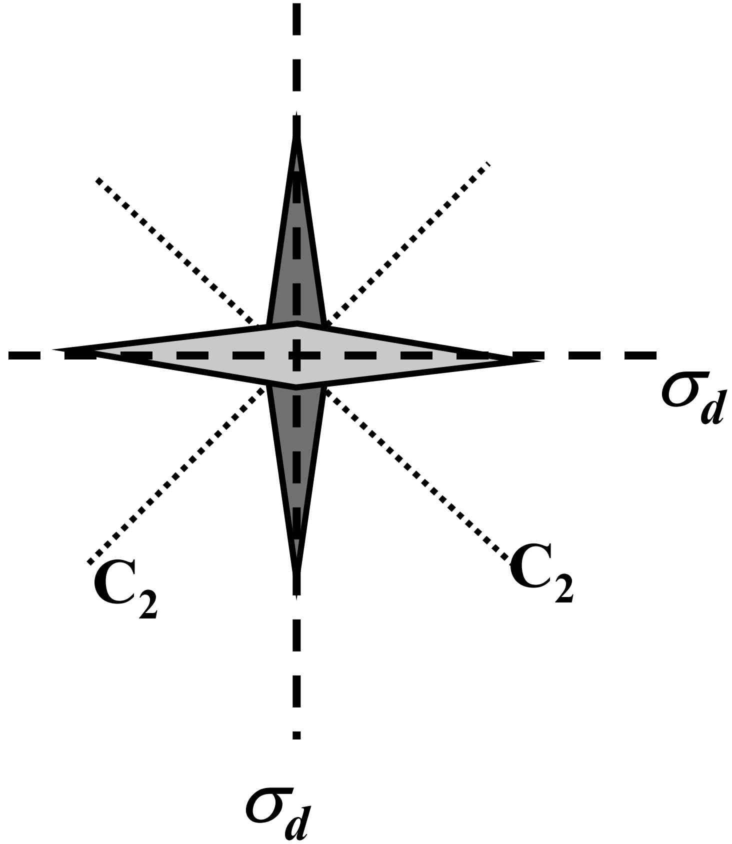




If a σ_v plane **contains** the principal axis and **bisects** the angle between two adjacent 2-fold axes, then it is a σ_d.(*Dihedral* mirror planes)

Example: $H_2C{=}C{=}CH_2$



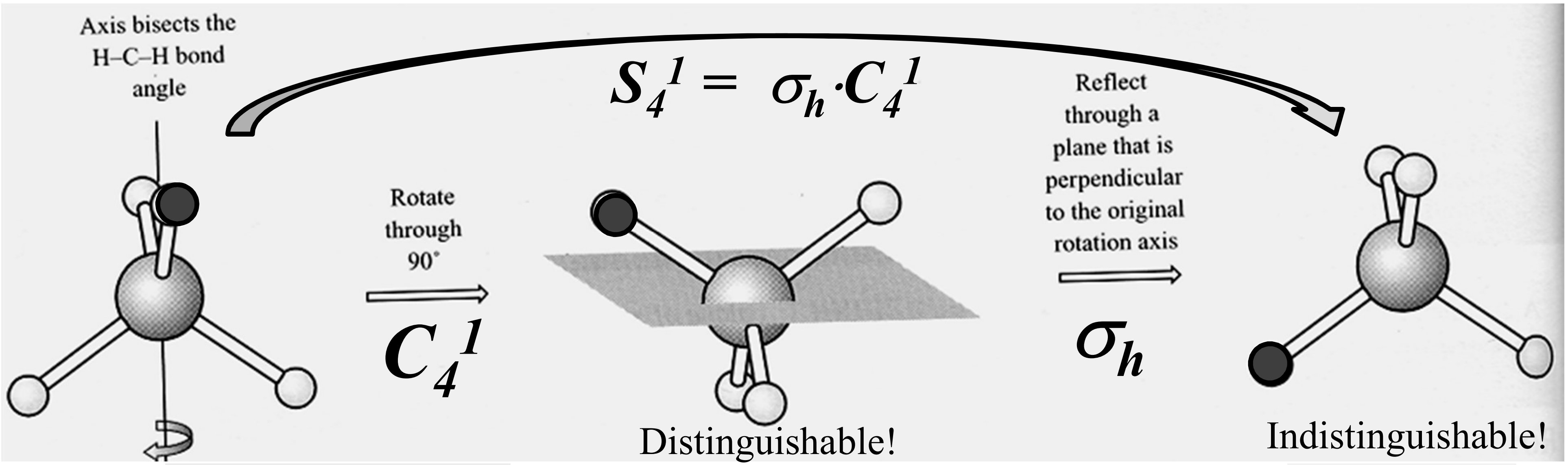


- Each HCH plane is a σ_v/σ_d plane!

5) The improper rotation axis

a. *n*-fold rotation-reflection axis of symmetry, or rotary-reflection axis (S_n)

A body has an S_n axis if rotation by *360°/n* about the axis, followed by reflection in a plane perpendicular to the axis, produces a configuration indistinguishable from the original one.

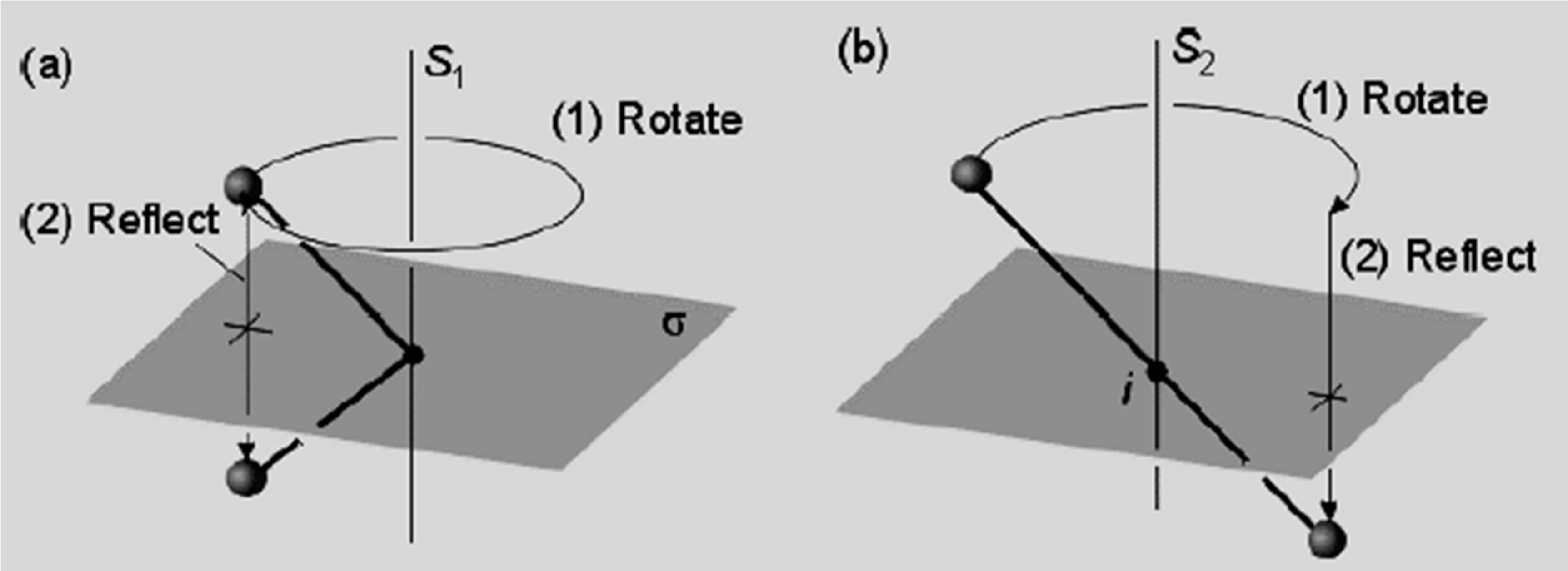


S_4

$S_4^1 = \sigma_h \cdot C_4^1$ $\quad S_4^3 = S_4^1 \cdot S_4^1 \cdot S_4^1 = \sigma_h \cdot C_4^3$ $\quad S_4^4 = E$

$$S_4^2 = S_4^1 \cdot S_4^1 = (\sigma_h \cdot C_4^1) \cdot (\sigma_h \cdot C_4^1) = (\sigma_h)^2 C_4^2 = C_2^1$$

Special Cases: S_1 and S_2

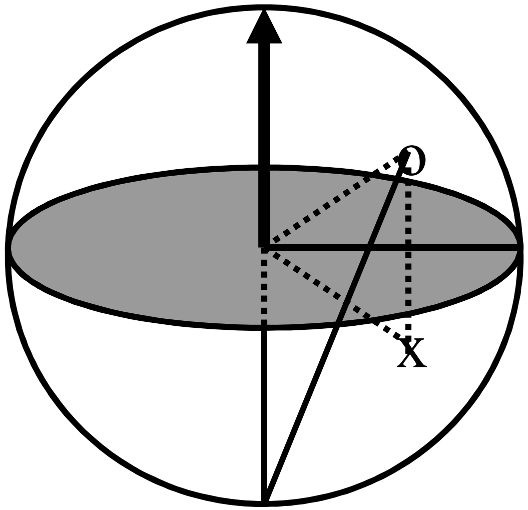


$$S_1 = \sigma_h C_1 = \sigma$$

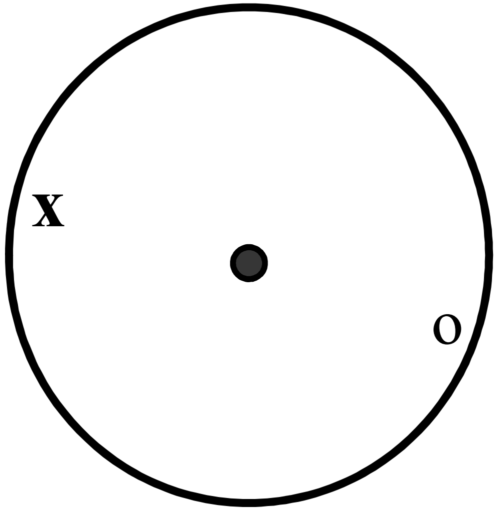
$$S_2 = \sigma_h C_2 = i$$

- **Neither S_1 nor S_2 axis is necessary!**

Stereographic Projections



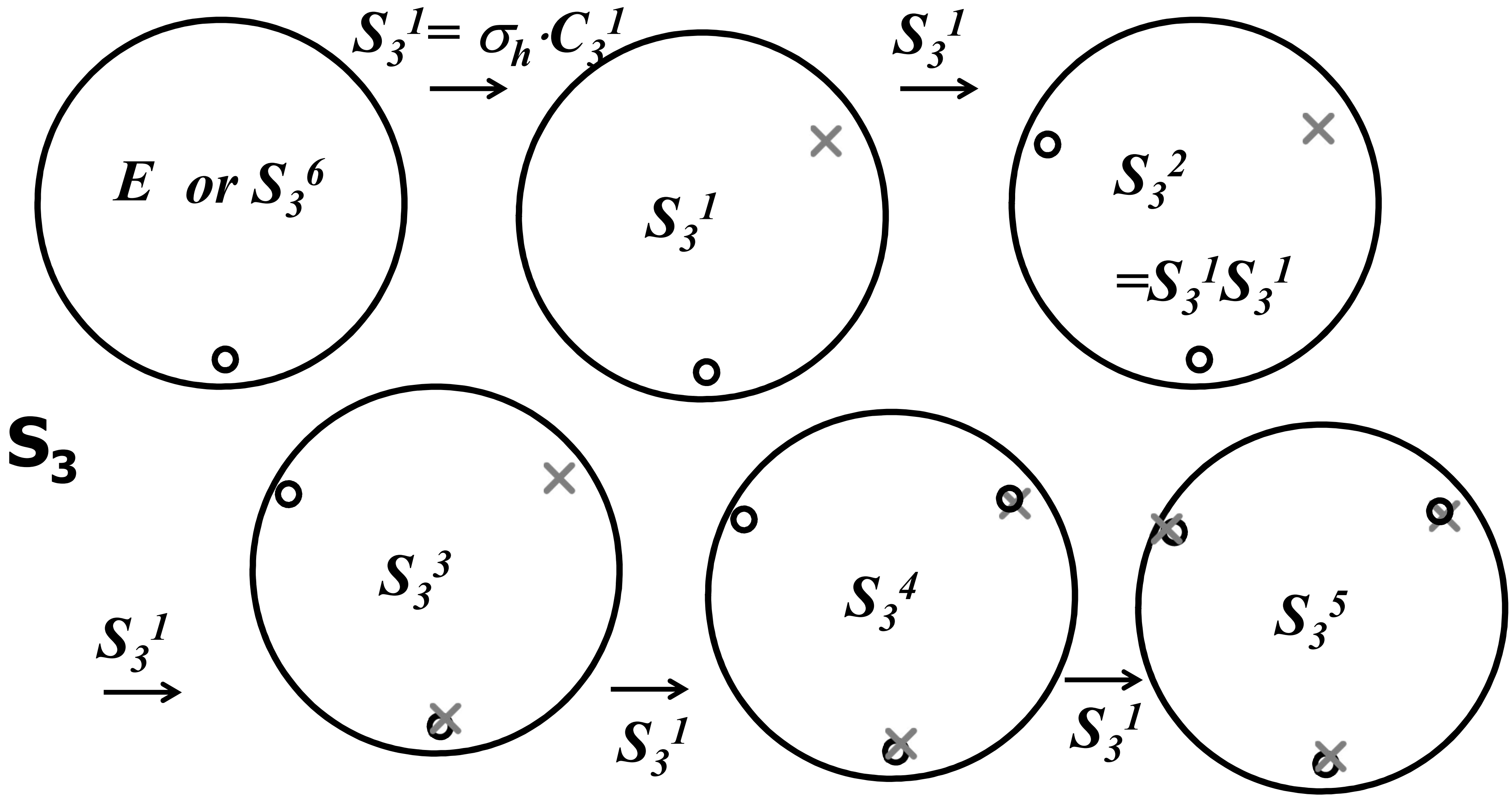
Reflection



Inversion

We will use stereographic projections to plot the perpendicular to a general face and its symmetry equivalences, to display crystal morphology

- o for upper hemisphere; x for lower

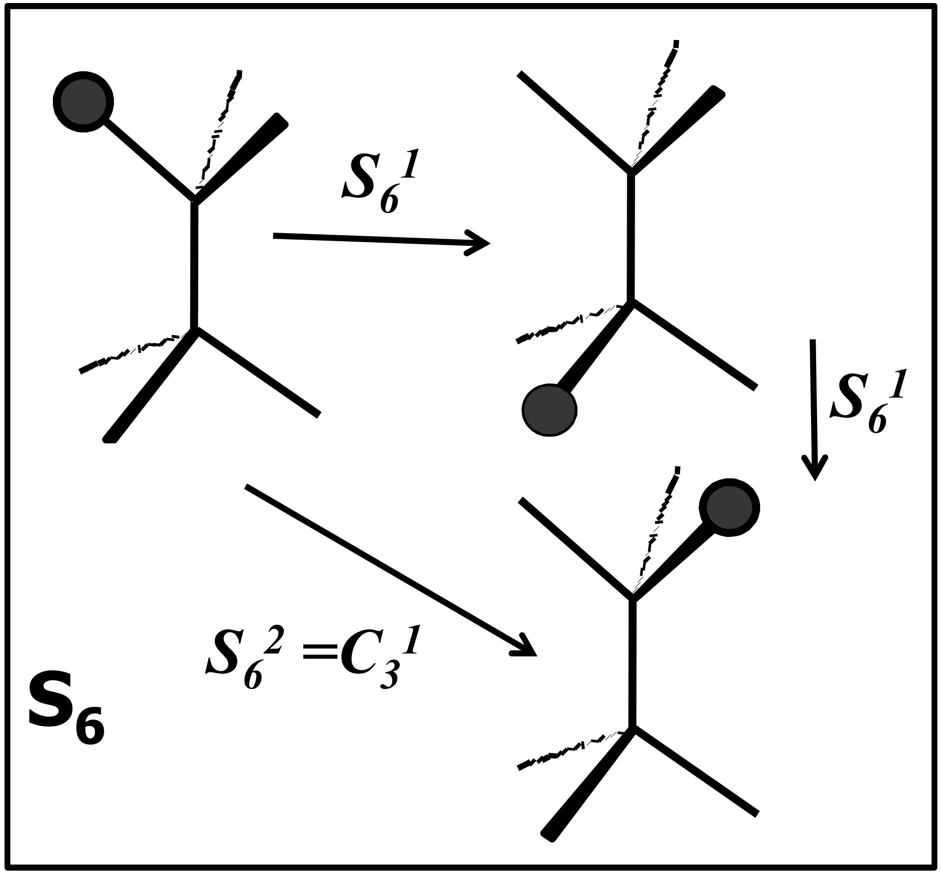


$S_3^1 = \sigma_h C_3^1$ $\quad$ $S_3^5 = \sigma_h C_3^2$ $\quad$ $S_3^3 = \sigma_h$

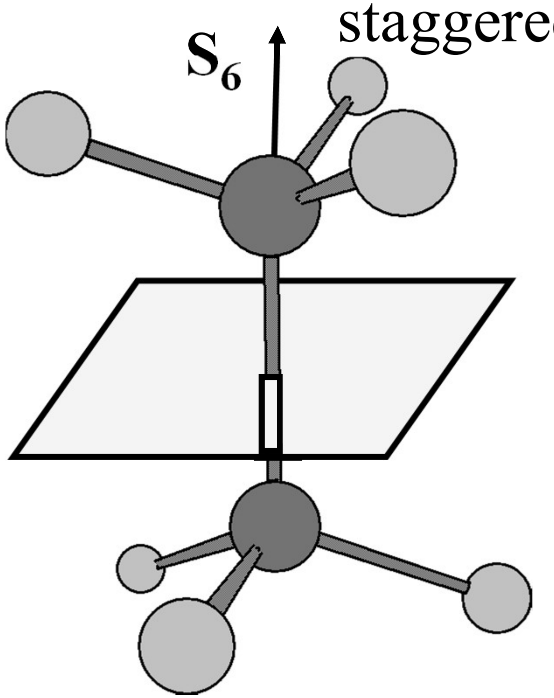
$\{ S_3^2 = C_3^2 \quad S_3^4 = C_3^1 \quad S_3^6 = E \} = C_3$

$$\therefore S_3 = C_3 + \sigma_h$$

→ S_3 is not an independent symmetry element! (no need!)



Example: $H_3C\text{-}CH_3$



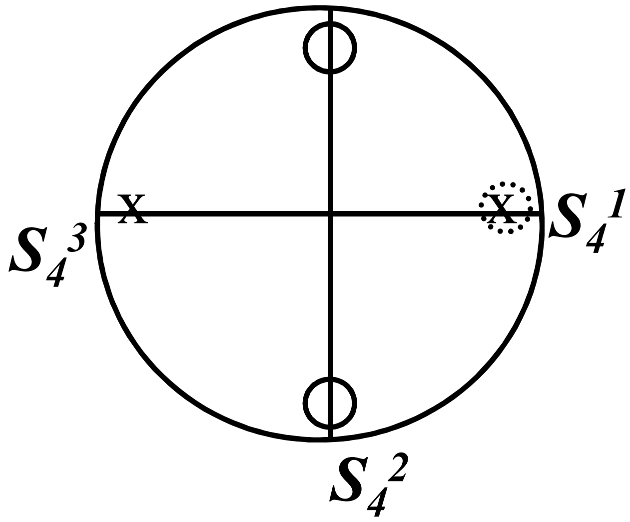
$$S_6^1 = \sigma_h \cdot C_6^1 = (i \cdot C_6^3) \cdot C_6^1 = i \cdot C_3^2 \qquad S_6^2 = C_3^1$$

$$S_6^3 = \sigma_h \cdot C_6^3 = i \qquad S_6^4 = C_3^2$$

$$S_6^5 = \sigma_h \cdot C_6^5 = (i \cdot C_6^3) \cdot C_6^2 = i \cdot C_3^1 \qquad S_6^6 = E$$

$\rightarrow$ $S_6 = C_3 + i$ * S_6 is not independent at all!

$$S_4^{\ 1} = \sigma C_4^{\ 1}; S_4^{\ 2} = C_2^{\ 1}$$
$$S_4^{\ 3} = \sigma C_4^{\ 3}; S_4^{\ 4} = E$$



- $\boldsymbol{S_4}$ is an independent sym. element!

$$S_5 = C_5 + \sigma_h$$ Not independent at all!

Possible operations pertaining to a S_5 axis:

$$S_5^{\ 1} = \sigma C_5^{\ 1}; S_5^{\ 2} = C_5^{\ 2}; S_5^{\ 3} = \sigma C_5^{\ 3}; S_5^{\ 4} = C_5^{\ 4}; S_5^{\ 5} = \sigma;$$
$$S_5^{\ 6} = C_5^{\ 1}; S_5^{\ 7} = \sigma C_5^{\ 2}; S_5^{\ 8} = C_5^{\ 3}; S_5^{\ 9} = \sigma C_5^{\ 4}; S_5^{\ 10} = E$$

- It demands the coexistence of a $\boldsymbol{C_5}$ and a σ_h, which readily produce all symmetry operations arising from $\boldsymbol{S_5}$.

Generally, the following remarks are provable,

i) A $\boldsymbol{S_n}$ improper axis with $\boldsymbol{n}$ = ***odd*** demands the coexistence of $\boldsymbol{C_n}$ and σ_h, **i.e.,** $\boldsymbol{S_n}$ **(*n* =odd)** = $\mathbf{C_n + \sigma_h}$.

ii) A $\boldsymbol{S_{2n}}$ improper axis with $\boldsymbol{n}$ = ***odd*** demands the coexistence of $\boldsymbol{C_n}$ and ***i*****, i.e.,** $\boldsymbol{S_{2n}}$ **(*n* =odd)** = $\mathbf{C_n} + \boldsymbol{i}$.

(plz prove them after class!)

→ Neither $\boldsymbol{S_n}$ nor $\boldsymbol{S_{2n}}$ with $\boldsymbol{n}$ = **odd** is independent and necessary!

In conclusion,

Only $\boldsymbol{S_4}$ and $\boldsymbol{S_8}$ ($\boldsymbol{S_{4n}}$) are independent symmetry elements.

b. *n*-fold rotation + inversion: Rotary-inversion axis (I_n)

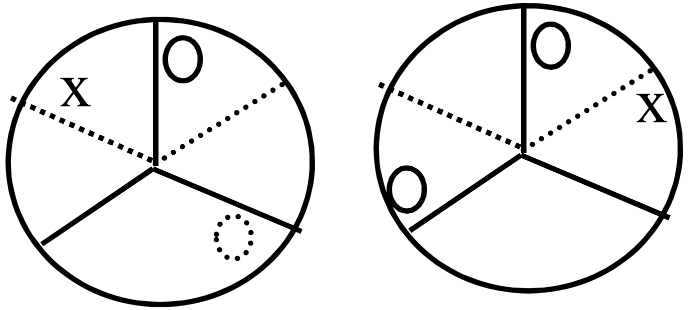
Rotation around a $\boldsymbol{C_n}$ axis followed by inversion through the center of the axis.

$$I_n^1 = iC_n^1$$

$$\because I_1 = iC_1 = i$$

$$\because I_2^1 = iC_2 = \sigma_h$$

$$\Rightarrow \quad I_1 = i \qquad I_2 = \sigma_h$$



$I_3^{\,1} = i\mathbf{C}_3^{\,1}$ $\quad I_3^{\,2} = \mathbf{C}_3^{\,2}$

$$I_3^{\,1} = iC_3^{\,1} \quad I_3^{\,2} = C_3^{\,2} \quad I_3^{\,3} = i$$

$$I_3^{\,4} = C_3^{\,1} \quad I_3^{\,5} = iC_3^{\,2} \quad I_3^{\,6} = E$$

$$\therefore I_3 = C_3 + i$$ Not independent!

Neither $\boldsymbol{I_5}$ (=$\boldsymbol{C_5}$ + $\boldsymbol{i}$) nor $\boldsymbol{I_6}$ (=$\boldsymbol{C_3}$ + σ_h) is independent!

Only $\boldsymbol{I_4}$ and $\boldsymbol{I_8}$ are independent symmetry elements!

Summary

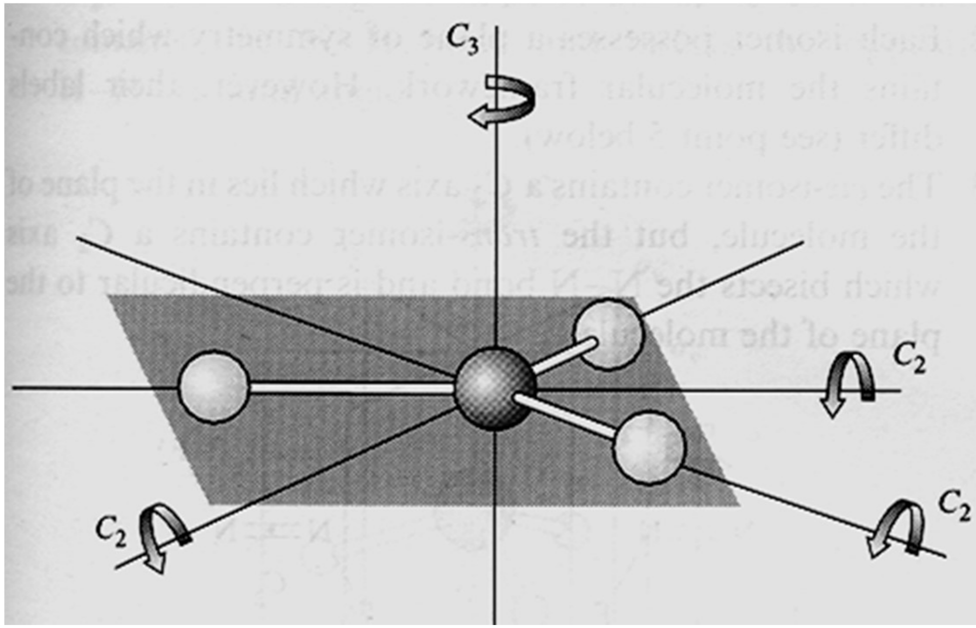
Element	Name	Operation
C_n	**n-fold rotation**	**Rotation by 360°/n**
σ	**Mirror plane**	**Reflection through a plane**
i	**Center of inversion**	**Inversion through the center**
S_n (n=4,8)	**Improper rotation axis**	**Rotation as C_n followed by reflection in perpendicular mirror plane**
E	**identity**	**Doing nothing**

2. Combination rules of symmetry elements

A. Combination of two axes of symmetry

The combination of ***two C_2 axes*** intersecting at an angle of ***$2\pi/2n$***, will create a ***C_n*** axis at the point of intersection which is perpendicular to both the C_2 axes and there are ***n*** C_2-axes in the plane perpendicular to the C_n axis.

$$C_n + C_2(\perp) \rightarrow nC_2(\perp)$$



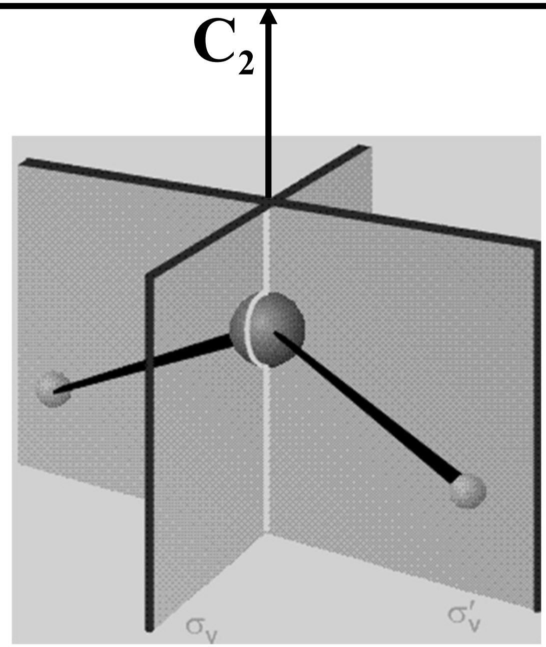
B. Combination of two planes of symmetry.

- If ***two mirrors planes*** intersect at an angle of $\boldsymbol{2\pi/2n}$, there will be a $\boldsymbol{C_n}$ axis on the line of intersection.
- Similarly, the combination of an axis $\boldsymbol{C_n}$ with *a mirror plane parallel* to and passing through the axis will produce ***n*** mirror planes intersecting at angles of $\boldsymbol{2\pi/2n}$.

$$\mathbf{C_n + \sigma_v \rightarrow n\,\sigma_v}$$

$$C_2 + \sigma_v \Rightarrow 2\sigma_v$$
$$C_3 + \sigma_v \Rightarrow 3\sigma_v$$

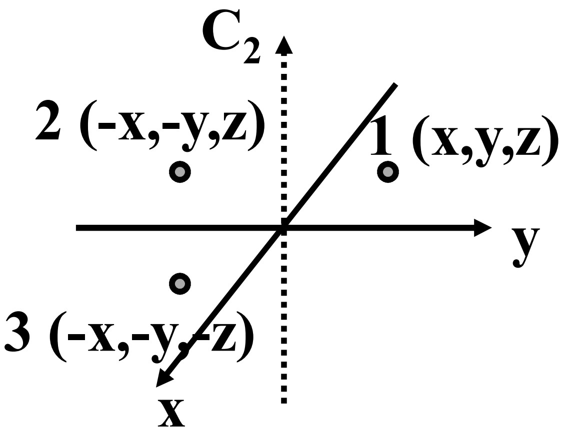
E.g., H_2O, NH_3



C. Combination of an even-order rotation axis with a mirror plane perpendicular to it.

- Combination of an ***even-order rotation axis*** with a ***mirror plane perpendicular*** to it will generate a center of symmetry at the point intersection. ($\boldsymbol{C_{2n} + \sigma_h \rightarrow i}$)
- In other words, each of the three operations σ_h, $\boldsymbol{C_{2n}}$ and $\boldsymbol{i}$ is the product of the other two operations.

$$\because C_{2n}^{n}(z) = C_2^1(z) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad \sigma_{xy} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$



$$\therefore \sigma_{xy} \cdot C_{2n}^{n}(z) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} = i$$

Similarly, $i \cdot C_{2n}^{n} = \sigma_h \quad \& \quad \sigma_h \cdot i = C_2^1$

$\boldsymbol{C_{2n} + i \rightarrow \sigma_h \quad \& \quad \sigma_h + i \rightarrow C_{2n}}$

§ 3.2 Groups and group multiplications

1. Definition: A mathematical group consists of a set of elements $\boldsymbol{G} = \{G_1, G_2, \ldots, G_i, \ldots\}$.

(a) Closure. The product of any two elements $\boldsymbol{G_i}$ and $\boldsymbol{G_j}$ in the group $\boldsymbol{G = \{G_1, \cdots, G_i \cdots\}}$, is another element in the group, i.e.,

$$G_i \cdot G_j = G_k,\ G_m^2 = G_n,\ \ldots$$

(b) Identity operation. The set includes the identity operation ***E*** such that AE = EA = A for all the operations in the set.

(c) Associative rule. If **A**, **B**, **C** are any three elements in the group, then $(\mathbf{A}\cdot\mathbf{B})\cdot\mathbf{C} = \mathbf{A}\cdot(\mathbf{B}\cdot\mathbf{C})$.

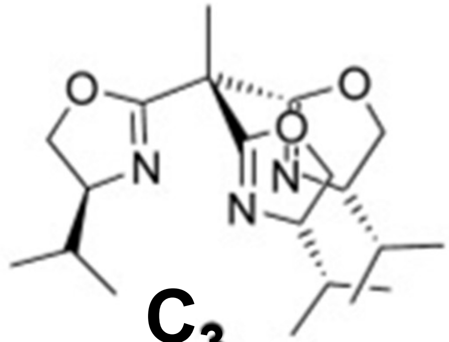
(d) Inversion. For every element **A** in ***G***, there is a unique element **X** in ***G***, such that $\boldsymbol{X\cdot A = A\cdot X = E}$. The element ***X*** is referred as the **inverse** of element ***A*** and is denoted $\boldsymbol{A^{-1}}$.

The order of a group:

The number of elements in a group!

Example: *A C_3-symmetric molecule*

- *Symmetry elements:* $(\mathrm{E}), \mathrm{C}_3$
- *Symmetry operations:* $\{\mathrm{E}, \mathrm{C}_3^1, \mathrm{C}_3^2\}$



C_3
tris(oxazoline)

$C_3^1 \cdot C_3^2 = C_3^3 = E$ $\quad C_3^1 \cdot C_3^1 = C_3^2$ $\quad C_3^2 \cdot C_3^2 = C_3^1$ Closure.

$\boldsymbol{E}$ Identity operation.

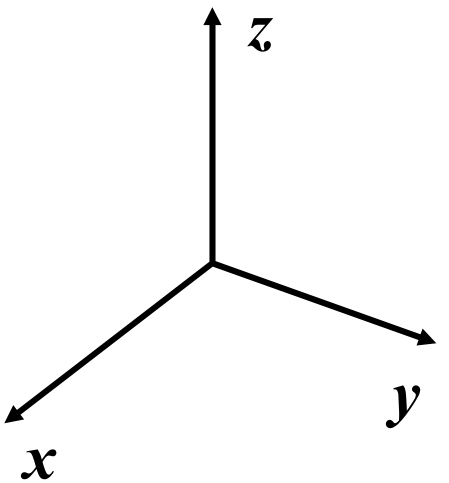
$(C_3^1 \cdot C_3^2) \cdot C_3^1 = C_3^1 (C_3^2 \cdot C_3^1)$ Associative rule.

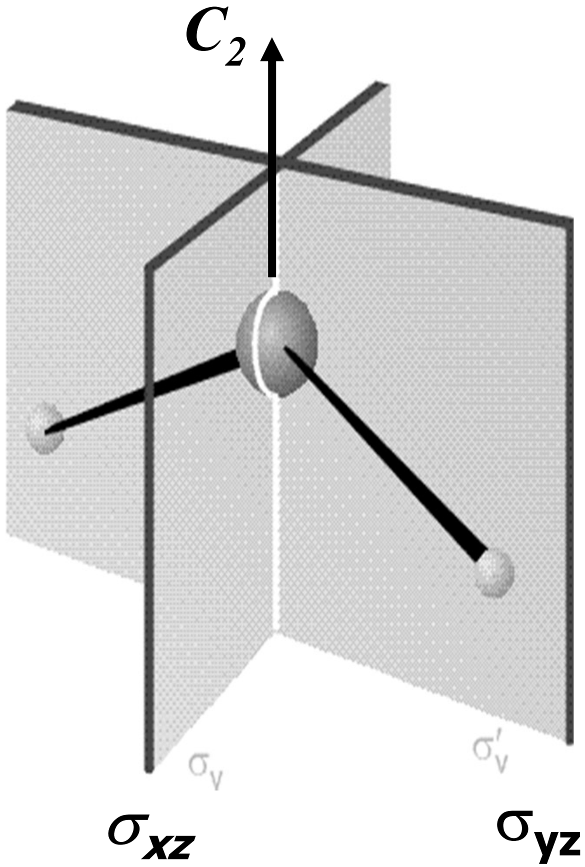
$C_3^1 \cdot C_3^2 = E$ Inversion.

- All unique symmetry operations of this molecule constitute a group, namely $\boldsymbol{C_3}$. (group order = 3)

2. Multiplication of Symmetry Operations (Group multiplication)

Example: H_2O





It has symmetry elements: $\boldsymbol{E, C_2, \sigma_{xz}, \sigma_{yz}}$

Unique symmetry operations: $\{\boldsymbol{E, C_2^{\,1}, \sigma_{xz}, \sigma_{yz}}\}$

C_{2v}

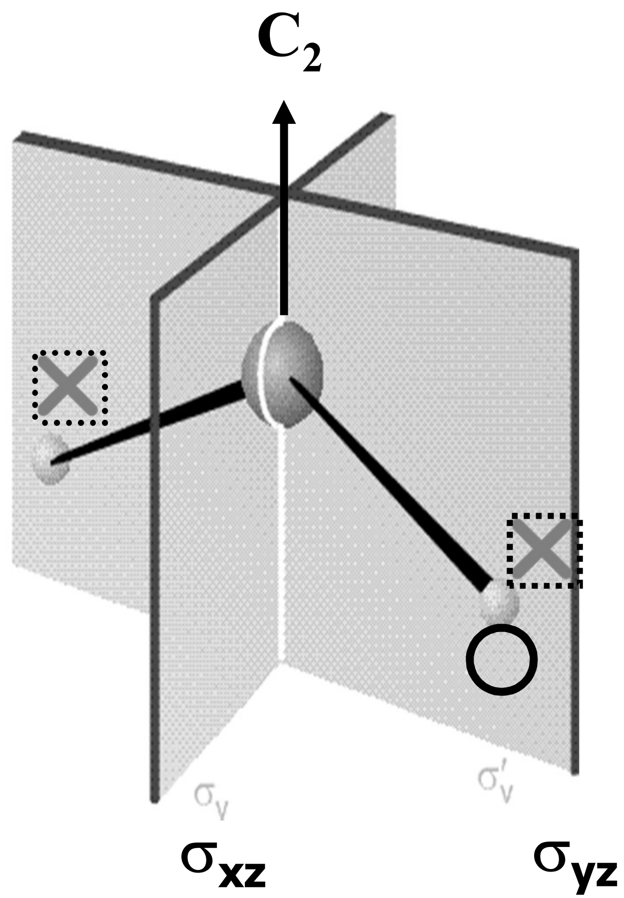
Example: H_2O

All unique symmetry operations:

$$\{E, C_2^1, \sigma_{xz}, \sigma_{yz}\}$$

Multiplication table (of C_{2v})

C_{2v}	E	C_2^1	σ_{xz}	σ_{yz}
E	E	C_2^1	σ_{xz}	σ_{yz}
C_2^1	C_2^1	E	σ_{yz}	σ_{xz}
σ_{xz}	σ_{xz}	σ_{yz}	E	C_2^1
σ_{yz}	σ_{yz}	σ_{xz}	C_2^1	E



$$C_2^1 \cdot C_2^1 = E \qquad \sigma_{xz} \cdot C_2^1 = \sigma_{yz} \qquad \sigma_{yz} \cdot C_2^1 = \sigma_{xz} \qquad \sigma_{yz} \cdot \sigma_{xz} = C_2^1$$

Note: The position of the O atom is unchanged upon any of the symmetry operations!

Multiplication table of C_{2v}

C_{2v}	E	C_2^1	σ_{xz}	σ_{yz}
E	E	C_2^1	σ_{xz}	σ_{yz}
C_2^1	C_2^1	E	σ_{yz}	σ_{xz}
σ_{xz}	σ_{xz}	σ_{yz}	E	C_2^1
σ_{yz}	σ_{yz}	σ_{xz}	C_2^1	E

Characteristics of a Multiplication table

(1). In each row or each column, each operation appears once and only once. (A group of symmetry operations!)

(2) We can identify smaller groups within the larger one. For example, ***{E,C₂}*** is a group, a ***subgroup*** of C_{2v} group. ***{E,σ}*** is another subgroup.

(3) The total number of group elements = group order.

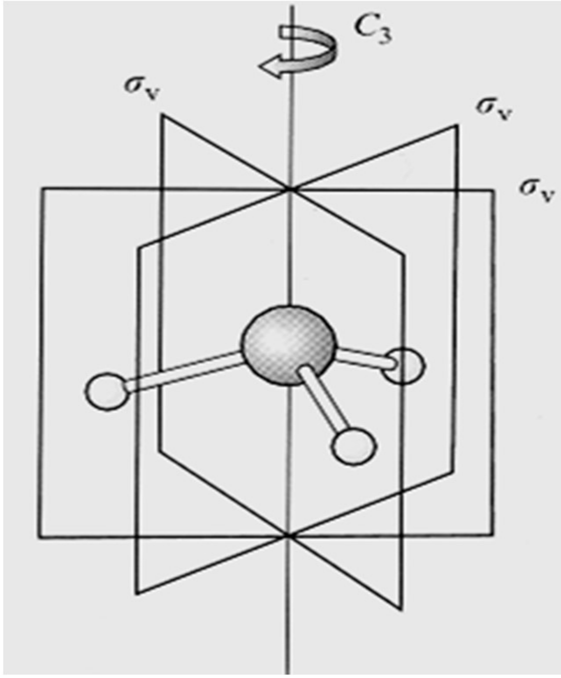
Example: NH_3

- Symmetry elements:

$$(E), C_3, 3\sigma_v(\sigma, \sigma', \sigma'')$$

- Symmetry operations:

$$\{E, C_3^1, C_3^2, \sigma, \sigma', \sigma''\}$$

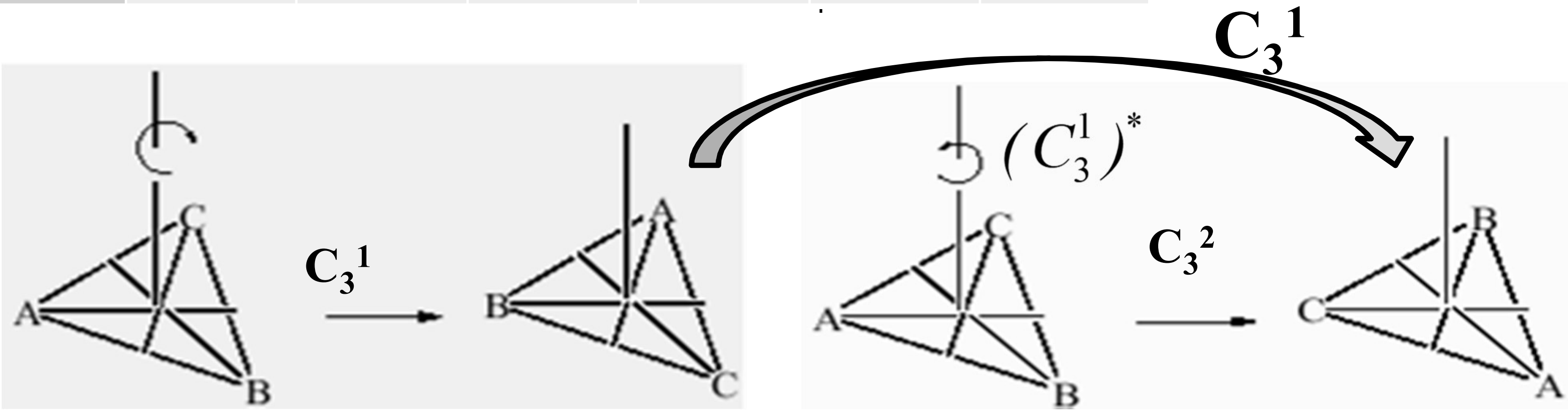


Multiplication table of C_{3v}

C_{3v}	E	C_3^1	C_3^2	σ_v	σ_v'	σ_v''
E						
C_3^1						
C_3^2						
σ_v						
σ_v'						
σ_v''						

Group Multiplication

C3v	E	C_3^1	C_3^2	σ_v	σ_v'	σ_v''
E	E	C_3^1	C_3^2	σ_v	σ_v'	σ_v''
C_3^1	C_3^1	C_3^2	E			
C_3^2	C_3^2	E	C_3^2			
σ_v	σ_v					
σ_v'	σ_v'					
σ_v''	σ_v''					



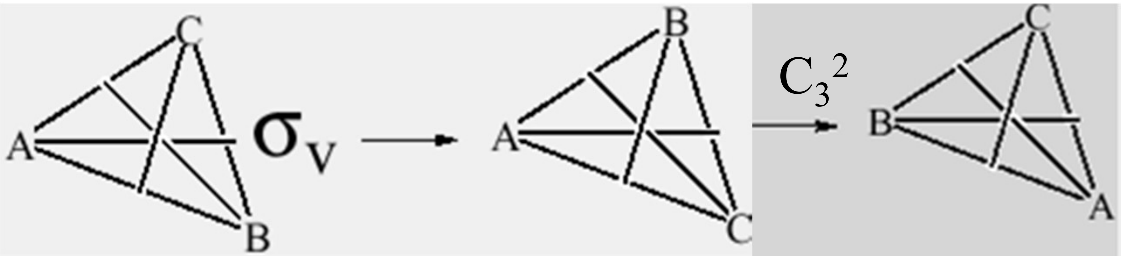
$$C_3^1 \cdot C_3^1 = C_3^2$$

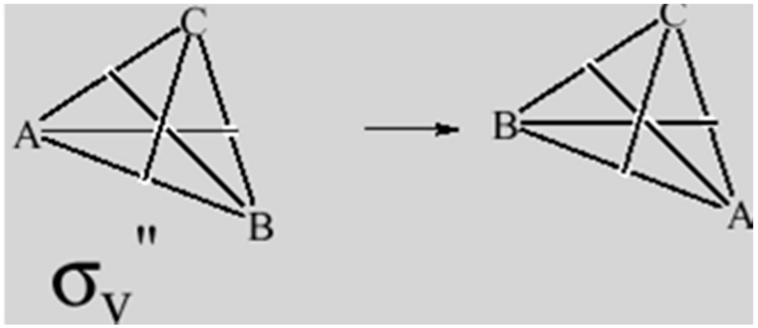
$$C_3^2 \cdot C_3^2 = C_3^1$$

$$C_3^1 \cdot C_3^2 = C_3^3 = E$$

Group Multiplication

C3v	E	C_3^1	C_3^2	σ_v	σ_v'	σ_v''
E	E	C_3^1	C_3^2	σ_v	σ_v'	σ_v''
C_3^1	C_3^1	C_3^2	E	σ_v''	σ_v	σ_v'
C_3^2	C_3^2	E	C_3^2	σ_v'	σ_v''	σ_v
σ_v	σ_v	σ_v'	σ_v''			
σ_v'	σ_v'	σ_v''	σ_v			
σ_v''	σ_v''	σ_v	σ_v'			

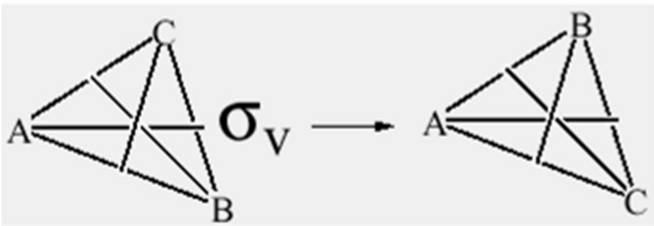


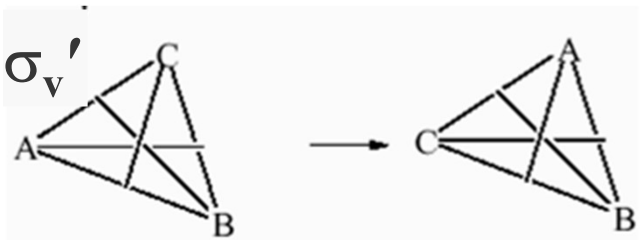


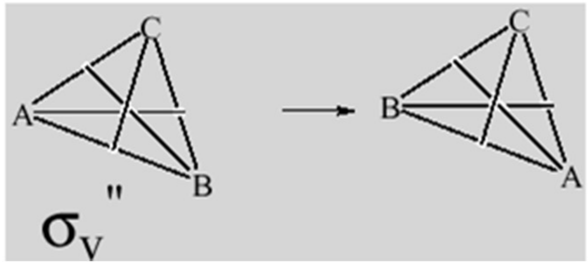
$$C_3^2\sigma_v = \sigma_v''$$

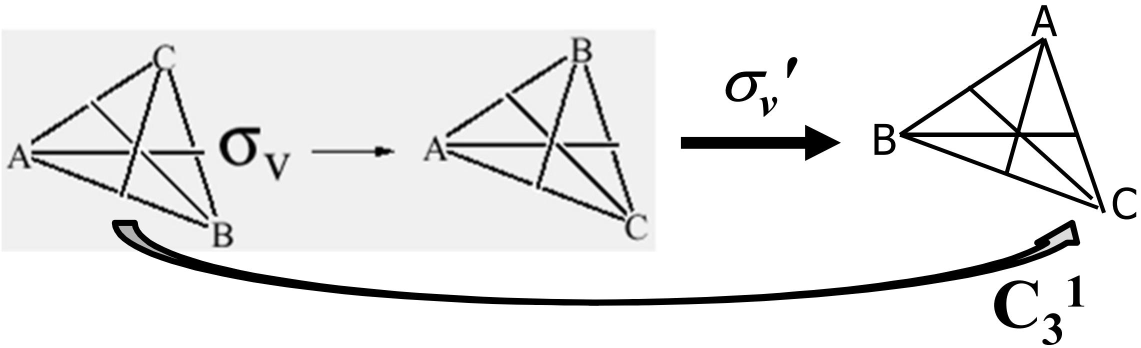
Group Multiplication

C3v	E	C_3^1	C_3^2	σ_v	σ_v'	σ_v''
E	E	C_3^1	C_3^2	σ_v	σ_v'	σ_v''
C_3^1	C_3^1	C_3^2	E	σ_v''	σ_v	σ_v'
C_3^2	C_3^2	E	C_3^2	σ_v'	σ_v''	σ_v
σ_v	σ_v	σ_v'	σ_v''	E	C_3^1	C_3^2
σ_v'	σ_v'	σ_v''	σ_v	C_3^2	E	C_3^1
σ_v''	σ_v''	σ_v	σ_v'	C_3^1	C_3^2	E









$$\sigma_v' \, \sigma_v = C_3^1$$

Multiplication table of C_{3v}

C3v	E	C_3^1	C_3^2	σ_v	σ_v'	σ_v''
E	E	C_3^1	C_3^2	σ_v	σ_v'	σ_v''
C_3^1	C_3^1	C_3^2	E	σ_v''	σ_v	σ_v'
C_3^2	C_3^2	E	C_3^2	σ_v'	σ_v''	σ_v
σ_v	σ_v	σ_v'	σ_v''	E	C_3^1	C_3^2
σ_v'	σ_v'	σ_v''	σ_v	C_3^2	E	C_3^1
σ_v''	σ_v''	σ_v	σ_v'	C_3^1	C_3^2	E

C_3 subgroup: $\{E, C_3^1, C_3^2\}$

C_S subgroup: $\{E, \sigma\}$

C_1 subgroup: $\{E\}$

§ 3.3 Point Groups, the symmetry classification of molecules

- The set of all the symmetry operations of a molecule forms a mathematical group.

- These symmetry operations have at least one common **point** unchanged (e.g., the O atom in H_2O).

- ***Such a group of symmetry operations is thus called point group.***

- Accordingly, it is quite convenient to represent the symmetry of a molecule by the very ***point group***!

The symmetry of an object(molecule) can be conveniently represented by a point group that contains all possible unique symmetry operations arising from its available symmetry elements.

Objects/ Molecules

If they have a common set of symmetry elements

They must have a common set of symmetry operations with at-least one point unchanged!

They belong to the same type of ***point group*.**

Four categories of symmetry point groups

- Groups with no $\boldsymbol{C_n}$ axis: $\boldsymbol{C_1}$ $\boldsymbol{C_s}$ $\boldsymbol{C_i}$
- Groups with a single $\boldsymbol{C_n}$ axis: $\boldsymbol{C_n}$ $\boldsymbol{C_{nh}}$ $\boldsymbol{C_{nv}}$, $\boldsymbol{S_{2n}}$
- Groups with one $\boldsymbol{C_n}$ axis and n $\boldsymbol{C_2}$ axes :

  $\boldsymbol{D_n}$ $\boldsymbol{D_{nd}}$ $\boldsymbol{D_{nh}}$ (Dihedral groups)

- Groups with more than one $\boldsymbol{C_n}$ (n >2) axis:

  $\boldsymbol{T_d}$ $\boldsymbol{T}$ $\boldsymbol{T_h}$ (Tetrahedral groups)***;***

  $\boldsymbol{O_h}$ $\boldsymbol{O}$ (Octahedral groups)***;***

  $\boldsymbol{I_h}$ $\boldsymbol{I}$ (Icohsahedral groups)***; (***$\boldsymbol{K_h}$ ***–spherical symm.)***

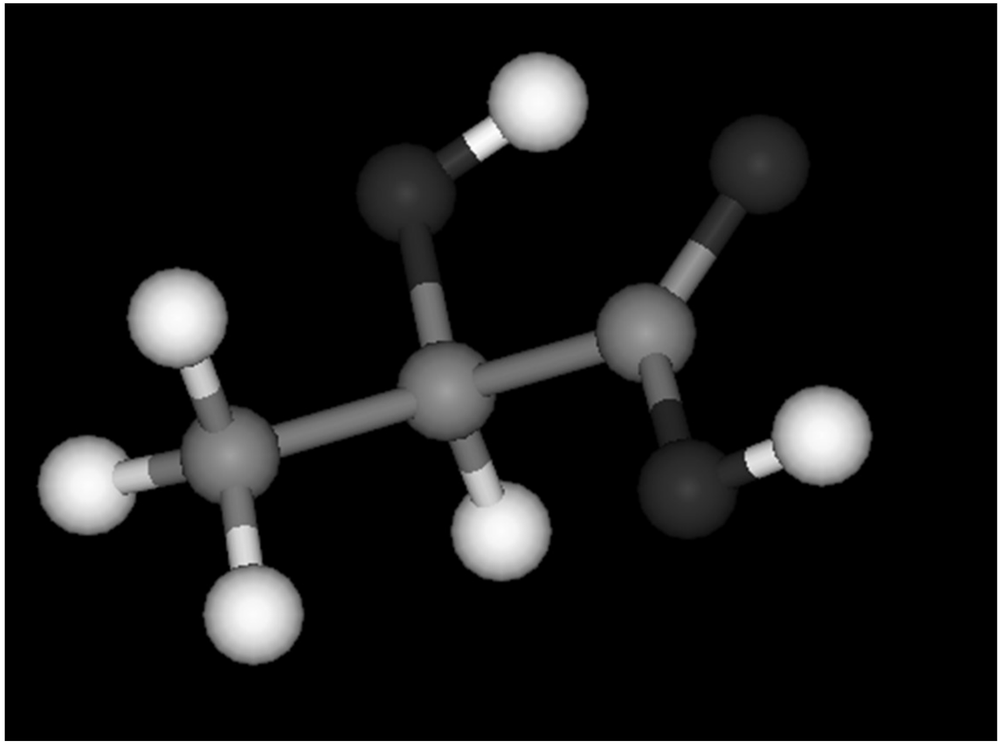
1. The groups: $\mathbf{C_1}$, $\mathbf{C_i}$, and $\mathbf{C_s}$

The group C_1

- A molecule belongs to the group $\mathbf{C_1}$ if it has no element of symmetry other than the identity.

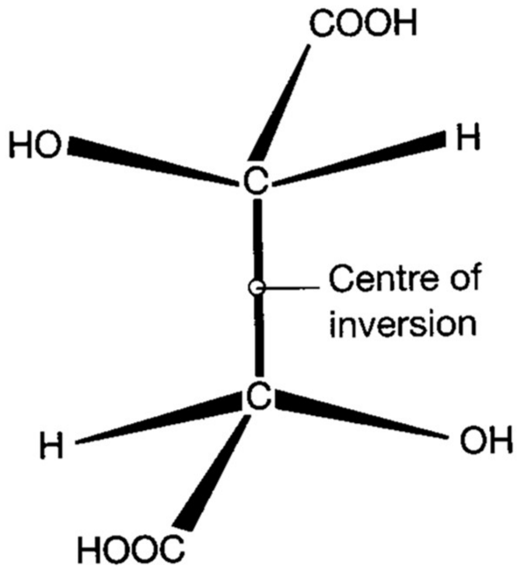
$$C_1 = \{\mathbf{E}\}$$

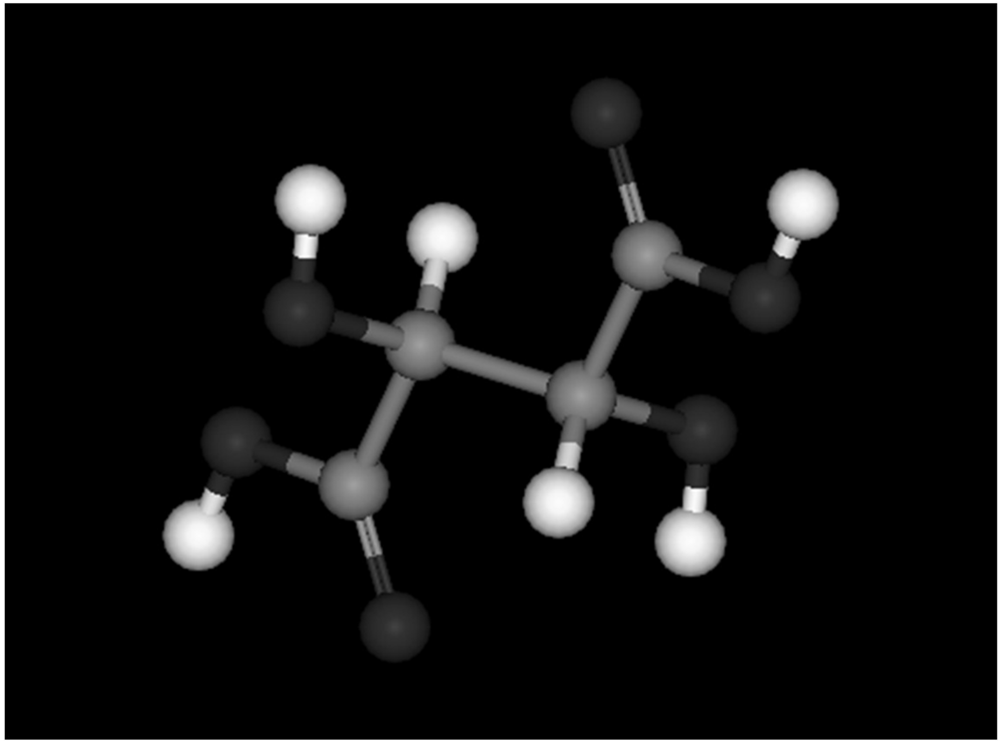
1-order group!



The group $C_i = \{E, i\}$

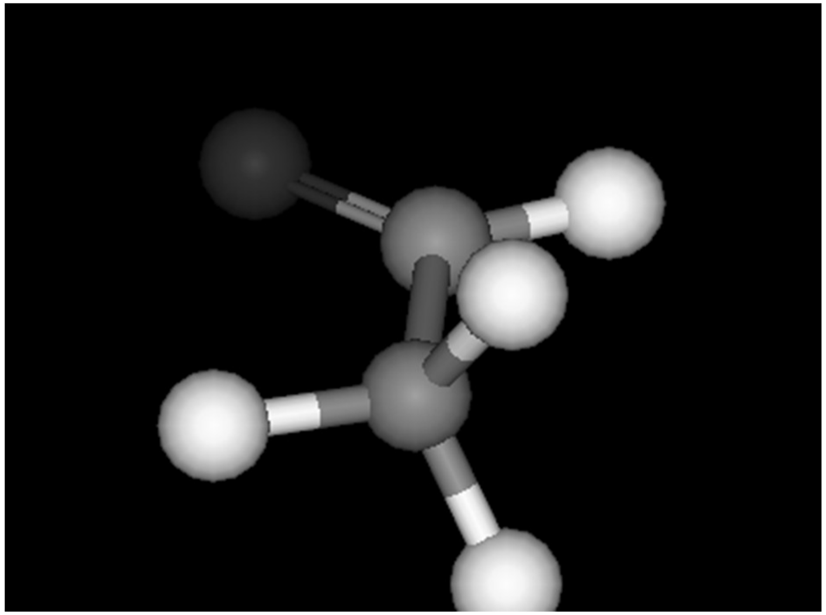
- An object belongs to C_i if it has the identity and inversion alone. $\boxed{C_i = \{E, i\}.}$
  - Examples: meso-tartaric acid, HClBrC-CHClBr

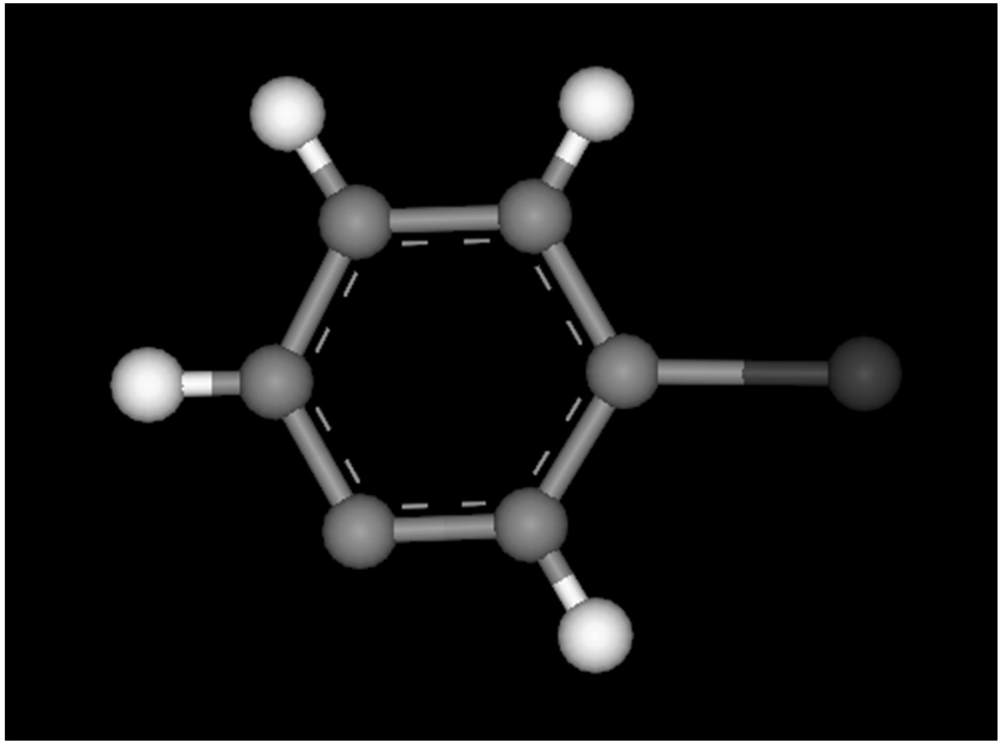




The group C_s

- An object belongs to C_s group if it has the identity $\boldsymbol{E}$ and a mirror plane σ alone.



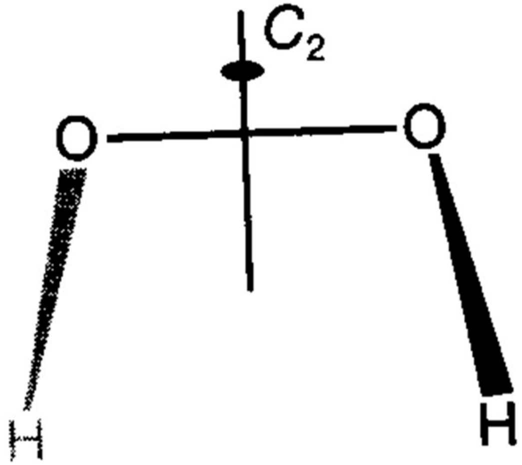


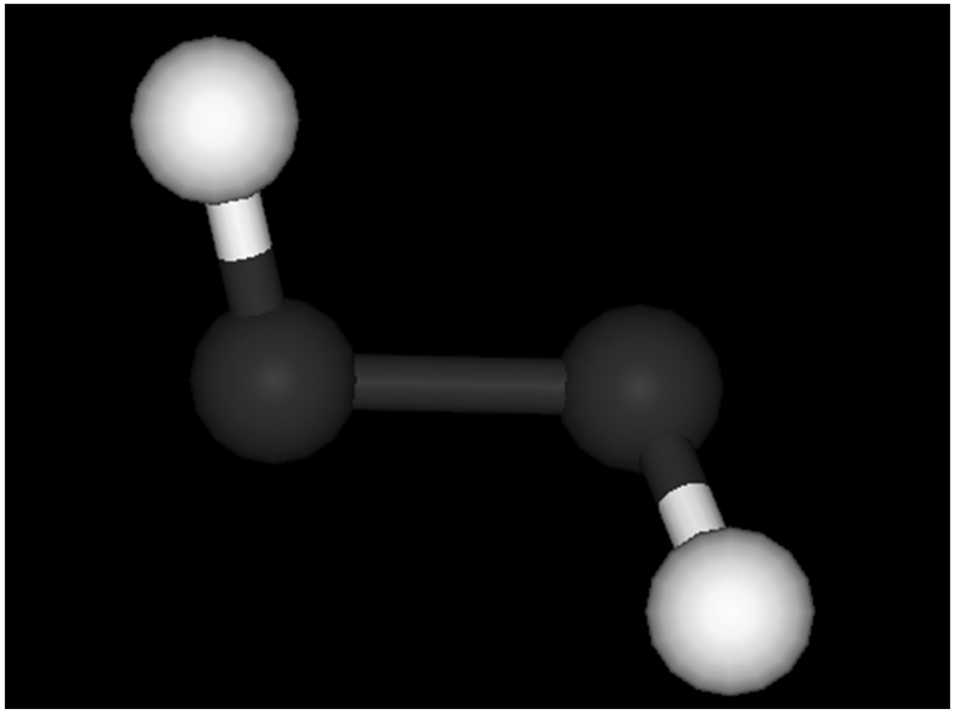
C_s group is 2-order, containing two symmetry operations $\{E, \sigma\}$.

2. The mono-axis groups C_n, C_{nv}, C_{nh} and S_n

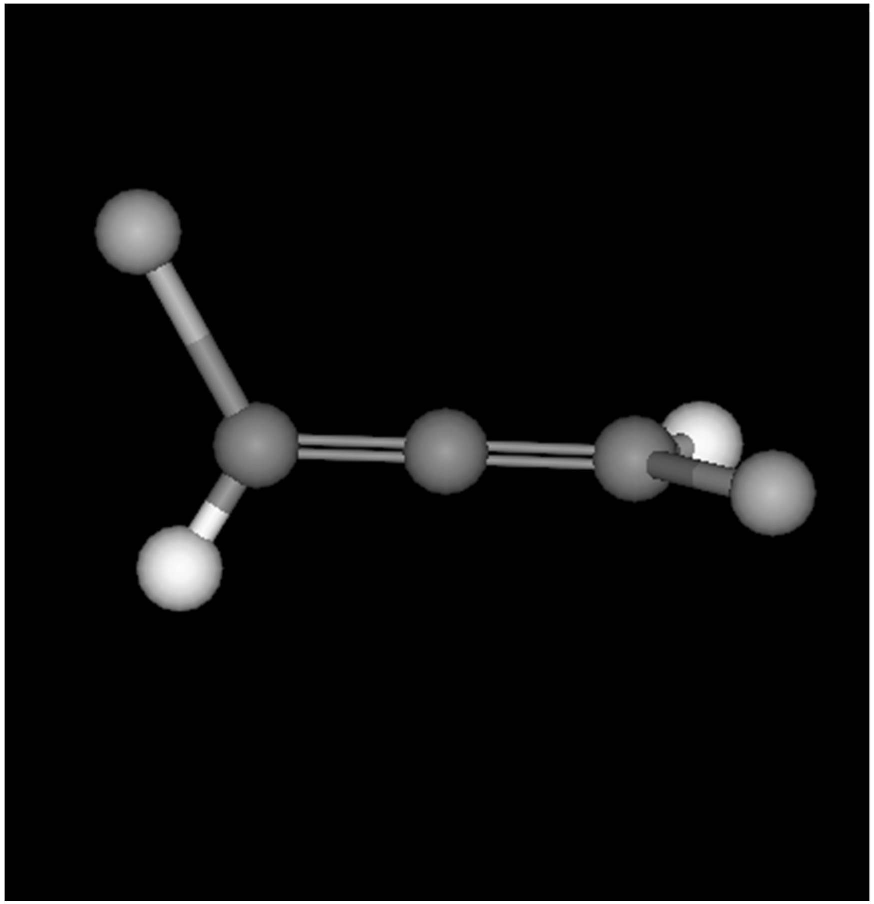
The group C_n = { E, C_n^1, …, C_n^{n-1}}

- A molecule belongs to the group C_n if it has only an *n*-fold axis.
- Example: H_2O_2

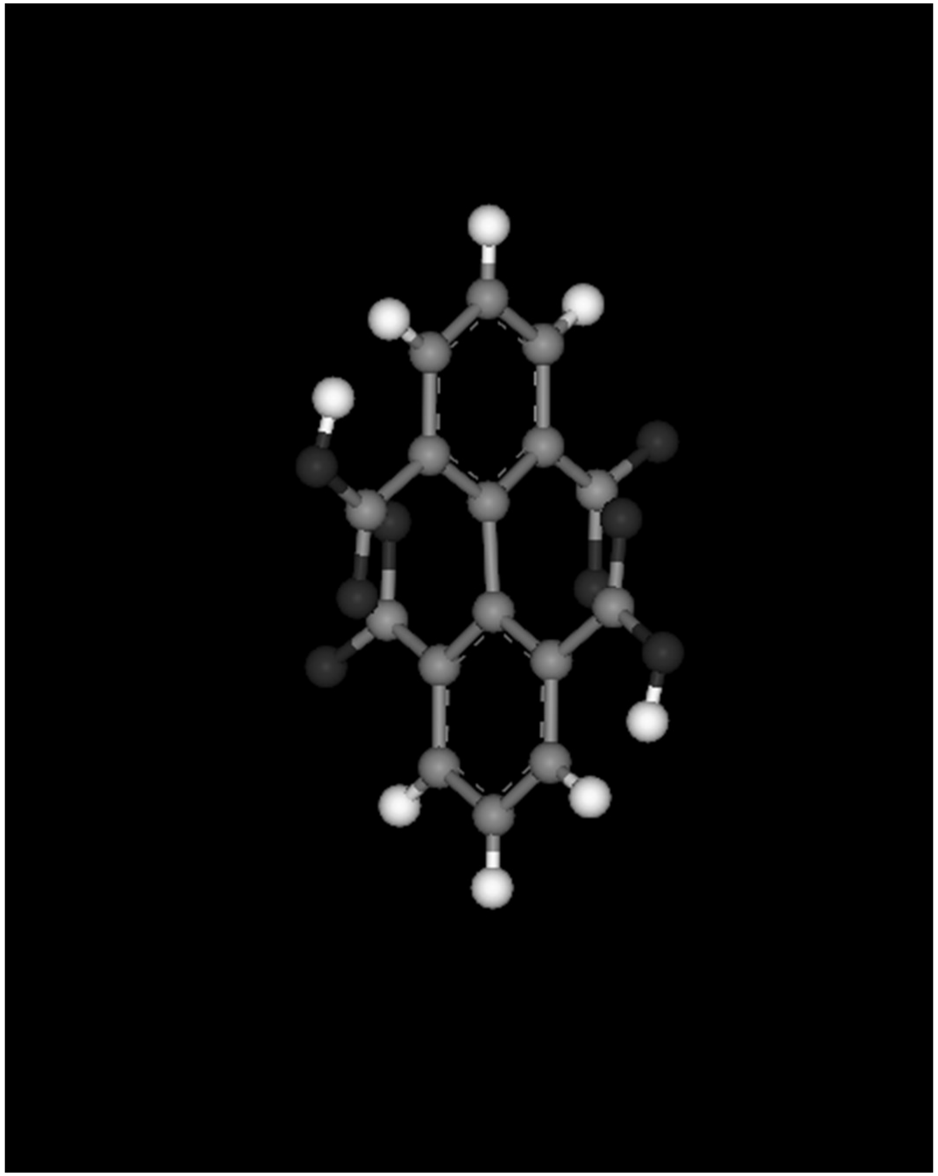




- Group order of a C_n group is ? .

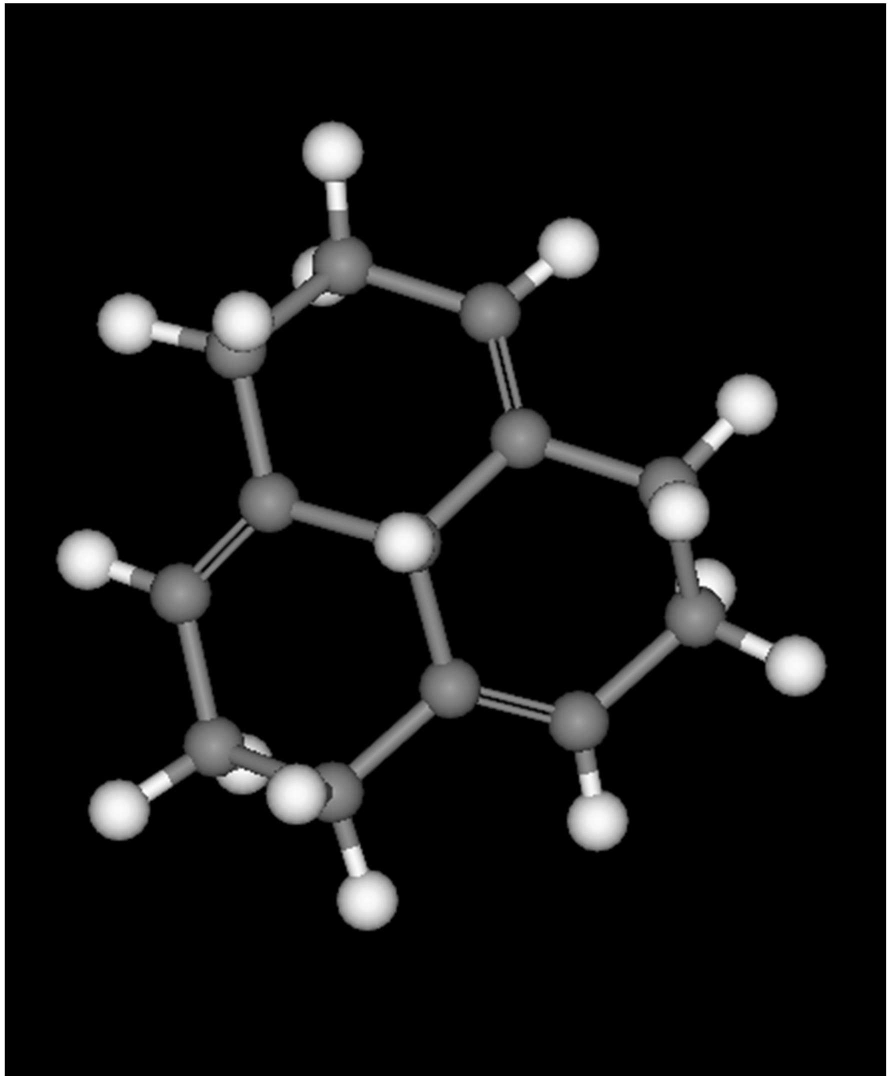


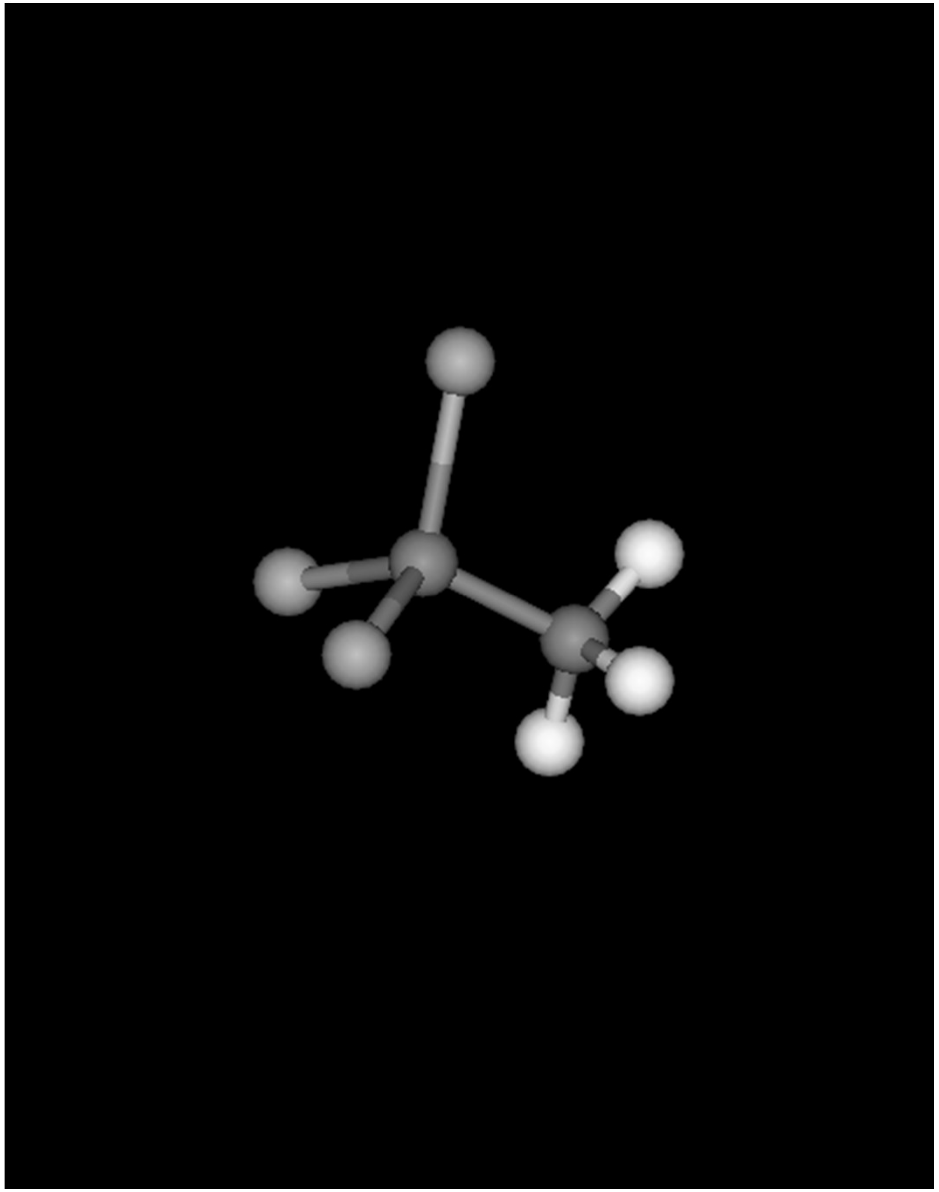
$C_2H_2Cl_2$



***C*$_2$**

C_3

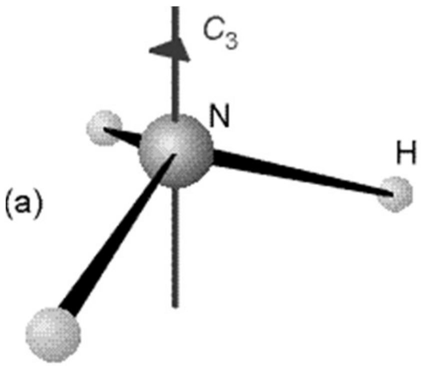




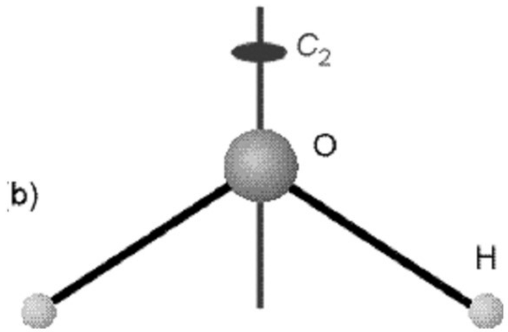
$C_2H_3Cl_3$

The group C_{nv}

- If in addition to a C_n axis an object has n vertical mirror (σ_v) planes, it belongs to the C_{nv} point group.
- $\mathbf{C_n} + \sigma_v \rightarrow n\ \sigma_v$



C_{3v}

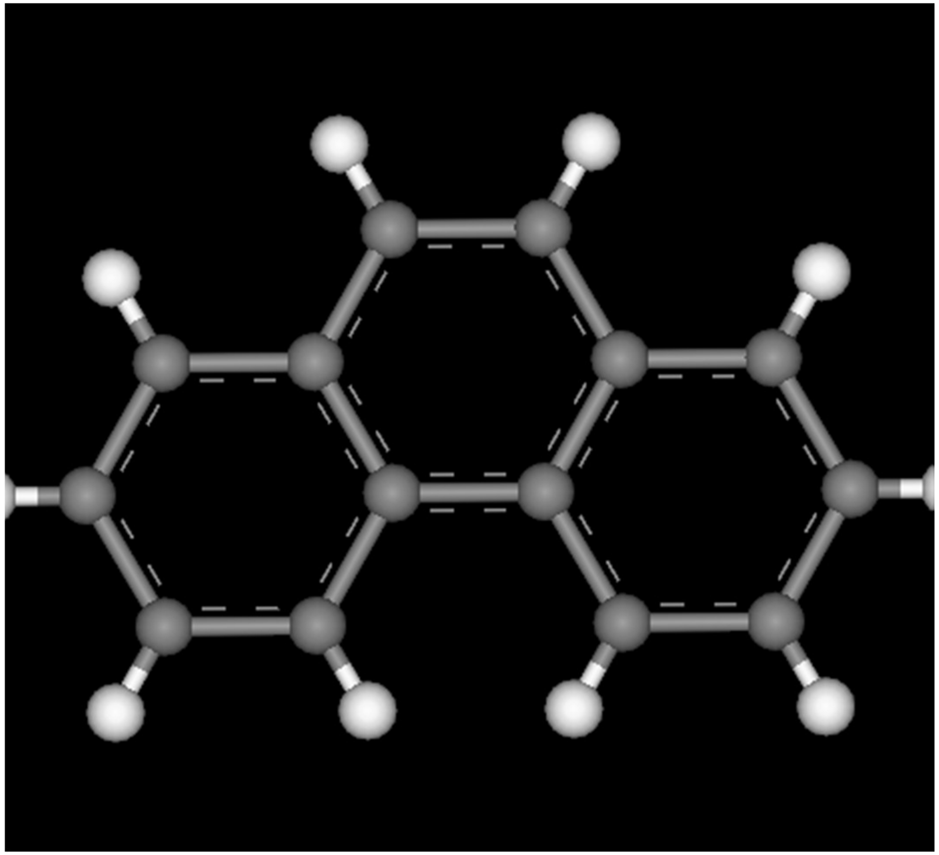


C_{2v}

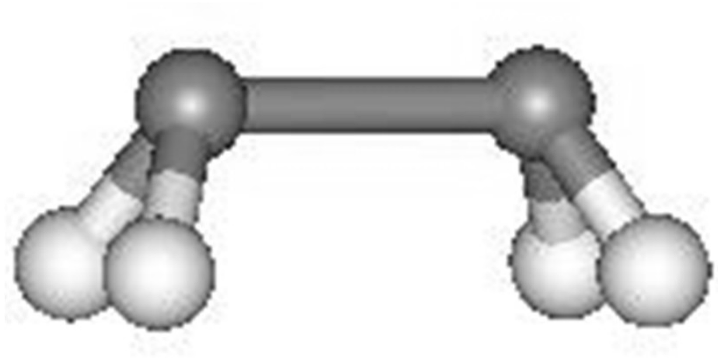
$C_{\infty v}$

- Group elements: $\{E, C_n^m\ (m = 1,\ldots,n\text{-}1),\ n\ \sigma_v\}$
- Group order: $2n$

$\boldsymbol{C_{2v}}$

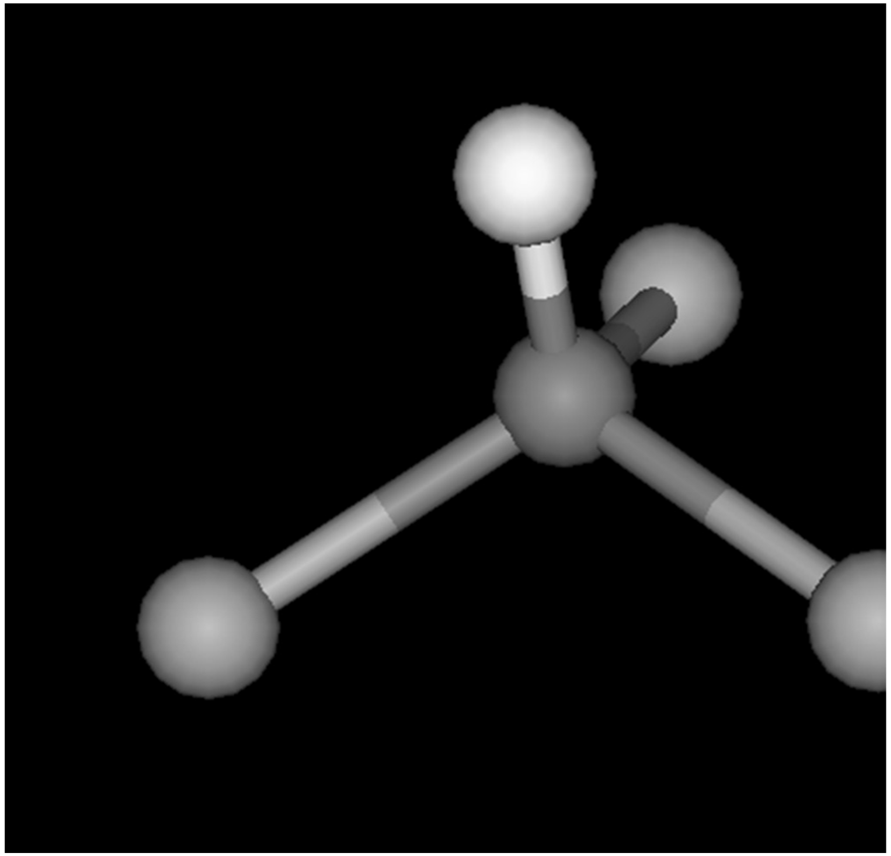


phenanthrene



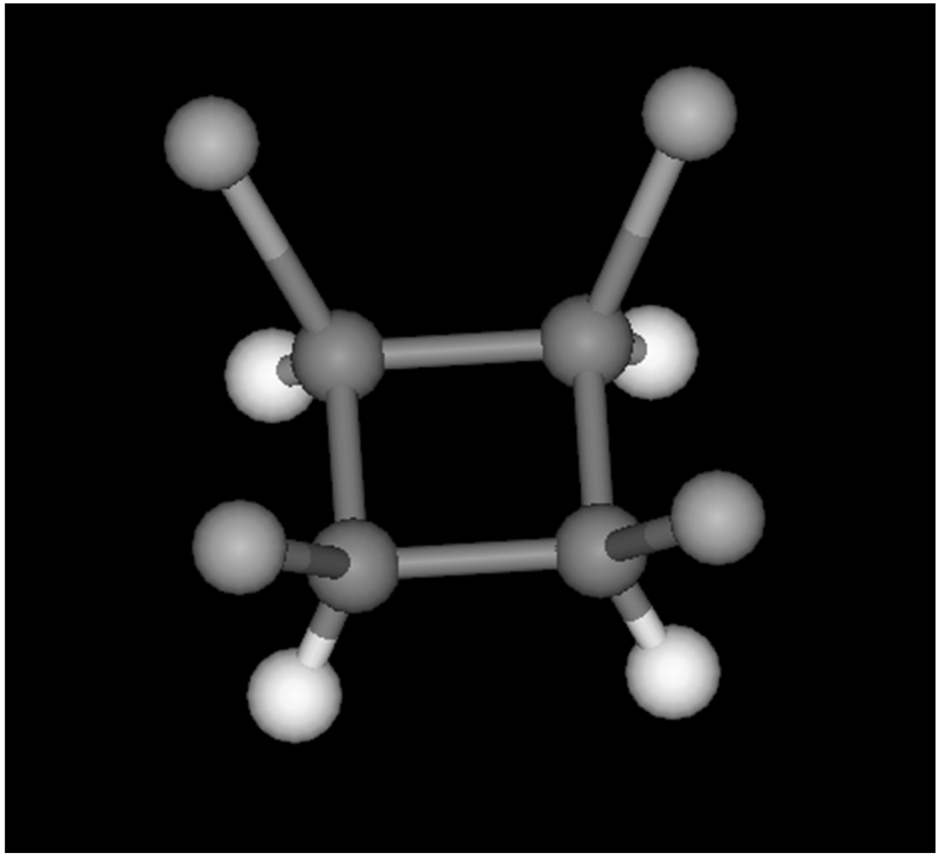
cis-N_2H_4

$HCCl_3$



$\boldsymbol{C_{3v}}$

$H_4C_4Cl_4$



$\boldsymbol{C_{4v}}$

The group C_{nh}

Objects having a C_n axis and a horizontal mirror plane σ_h belong to C_{nh}.

Symmetry elements derived from $C_n + \sigma_h$:

a) $C_n + \sigma_h \rightarrow S_n$ $\quad ((\sigma_h)^m (C_n^1)^m = S_n^m \text{ , } m = odd)$

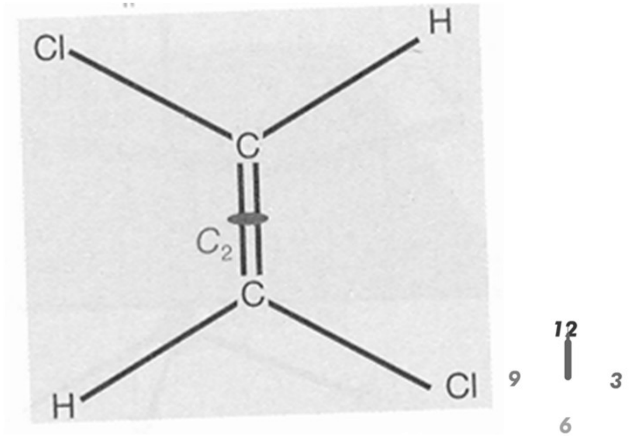
b) When $n=even$, a C_n is also a $C_{n/2}$ and a C_2.

$C_{n/2} + \sigma_h \rightarrow S_{n/2}$ $\quad ((\sigma_h)^m (C_{n/2}^1)^m = S_{n/2}^m, \ m = odd)$

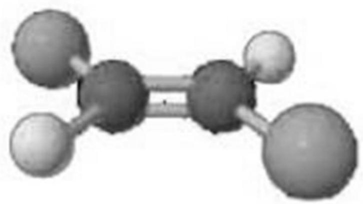
$C_2 + \sigma_h \rightarrow i$ $\quad (\sigma_h C_2^1 = i)$

C_{2h}

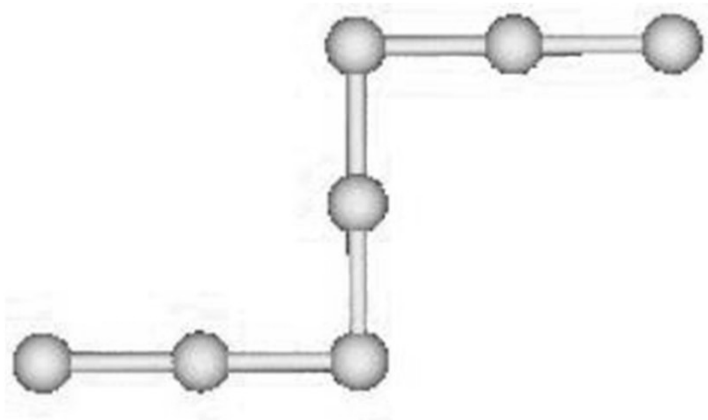
trans-CHCl=CHCl



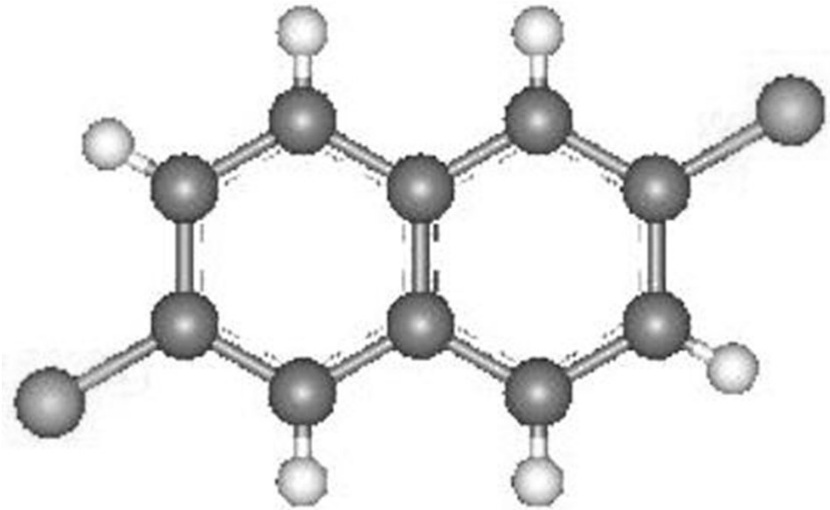
C_{2h}



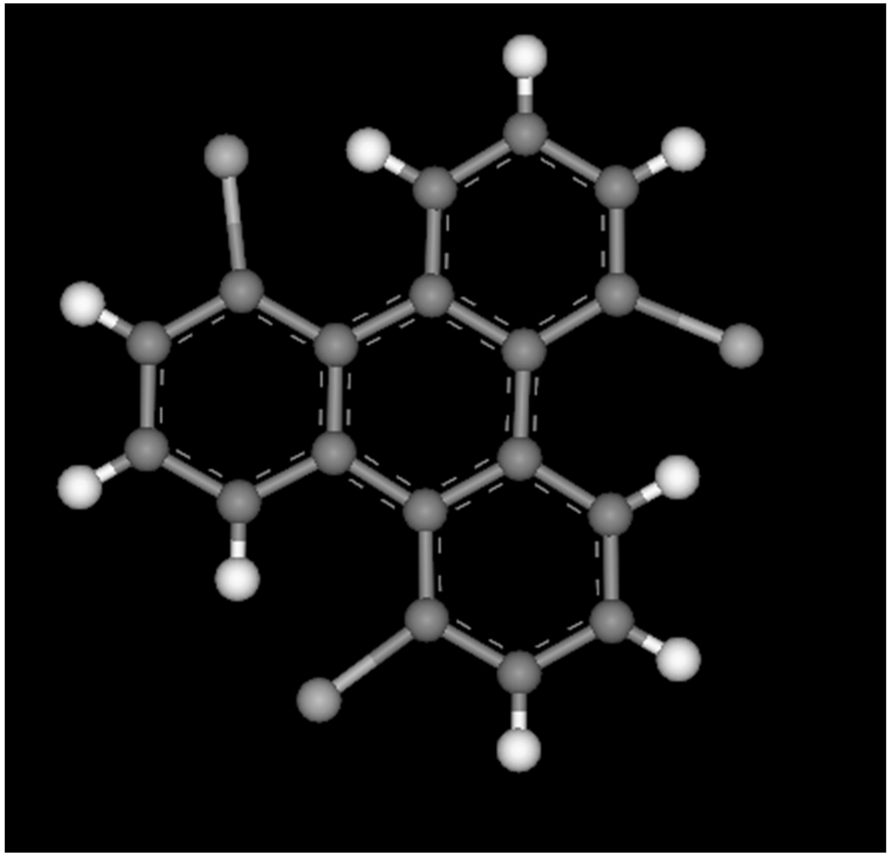
$C_2H_2Cl_2$

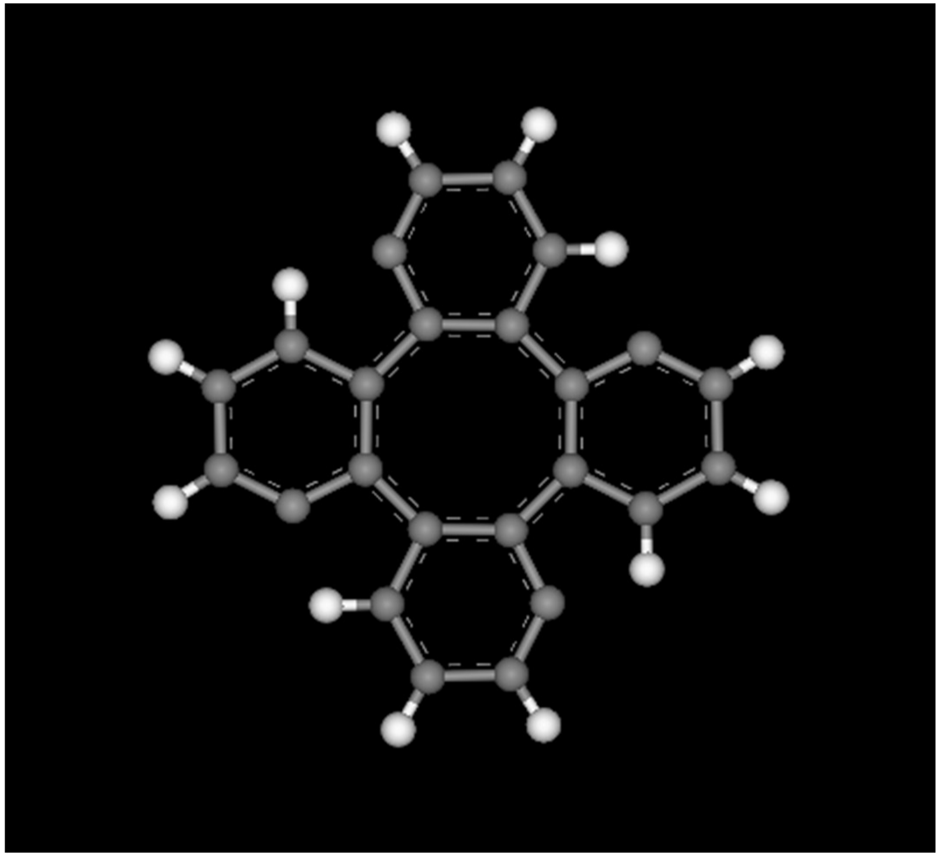


I_7^-

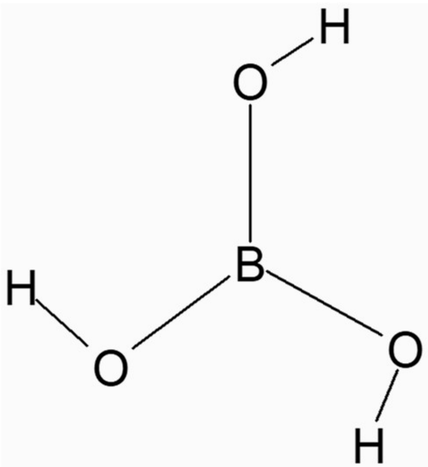


$C_{10}H_6Cl_2$



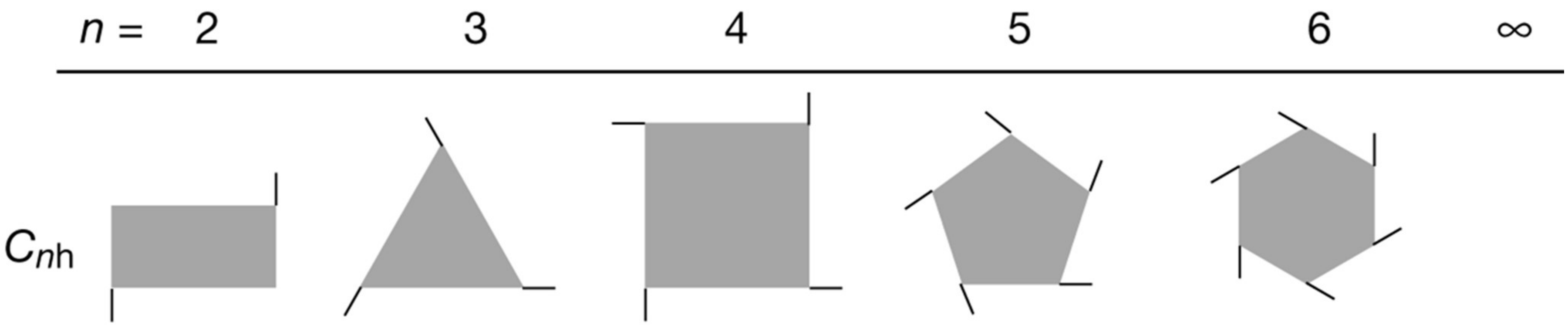


C_{3h}



$B(OH)_3$

C_{4h}



A C_{nh} point group is ***2n***-order, consisting of symmetry operations C_n^m (m=1,…,n), σ_h, and $\sigma_h C_n^m$ (m=1,…, n-1)!

Note:

i) When $n = odd$,

$$\begin{cases} m = odd, \sigma_h C_n^m = S_n^m \\ m = even, \sigma_h C_n^m = \sigma_h C_n^{n+m} = S_n^{n+m} \end{cases}$$

ii) When $n = even$,

$$\begin{cases} m = odd, \sigma_h C_n^m = S_n^m \\ m = even, \sigma_h C_n^m = \sigma_h C_{n/2}^{m/2} = S_{n/2}^{m/2} \end{cases}$$

$$with \quad \sigma_h C_n^{n/2} = \sigma_h C_2^1 = i$$

operations arising from a $S_{n/2}$!

The group S_n

- Objects having a S_n improper rotation axis belong to S_n. ($n=2m$, $m \geq 2$)

$S_1 = \sigma_h \Rightarrow C_s$

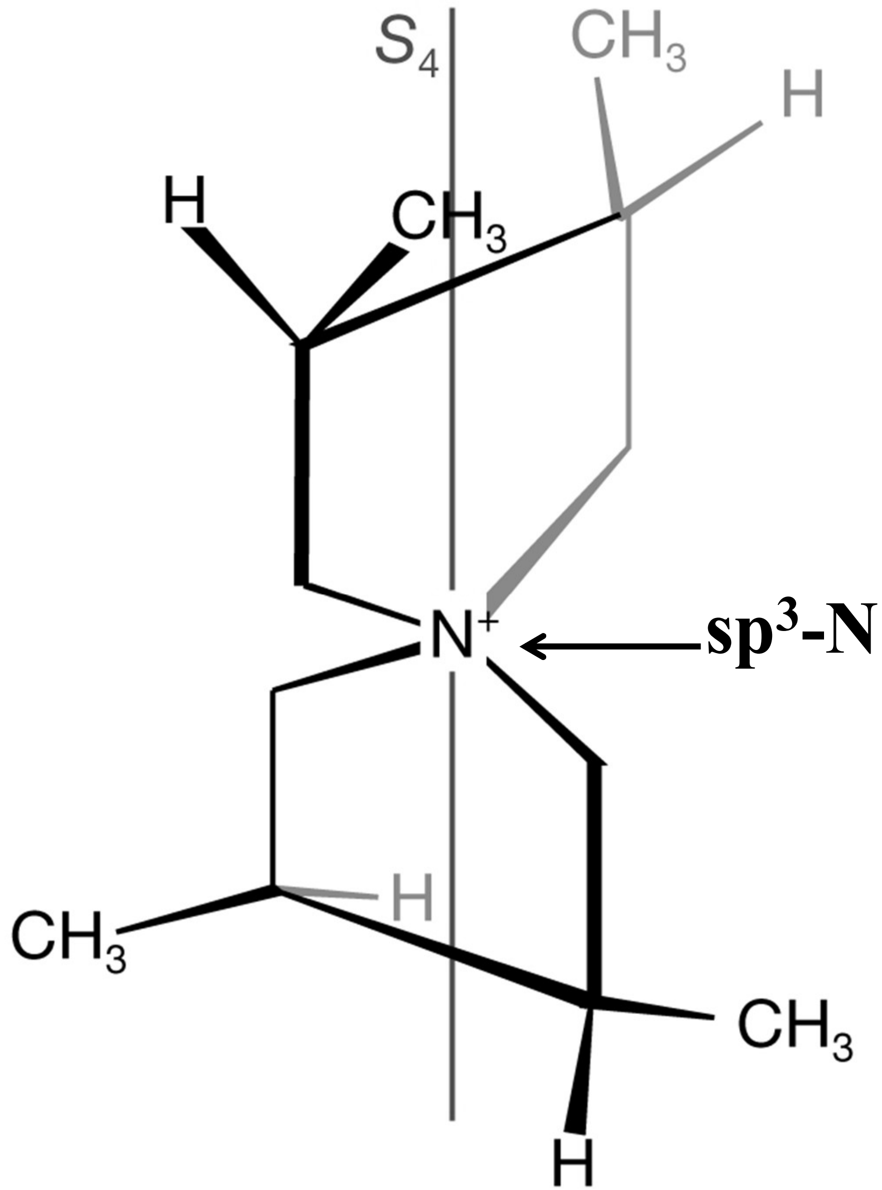
$S_2 = i \Rightarrow C_i$

$S_3 = C_3 + \sigma_h \Rightarrow C_{3h}$

$$\boxed{S_{2n+1} = C_{(2n+1)} + \sigma_h \rightarrow C_{(2n+1)h}}$$

- **S_{2n+1} does not exist!**

Group S_4



Some remarks on S_n axis and S_n group

1. Objects having an odd-fold $\mathbf{S_{2n+1}}$ axis should also have a σ_h mirror plane and a $\mathbf{C_{2n+1}}$ axis (n=1,2,…), thus actually belonging to $\mathbf{C_{(2n+1)h}}$.

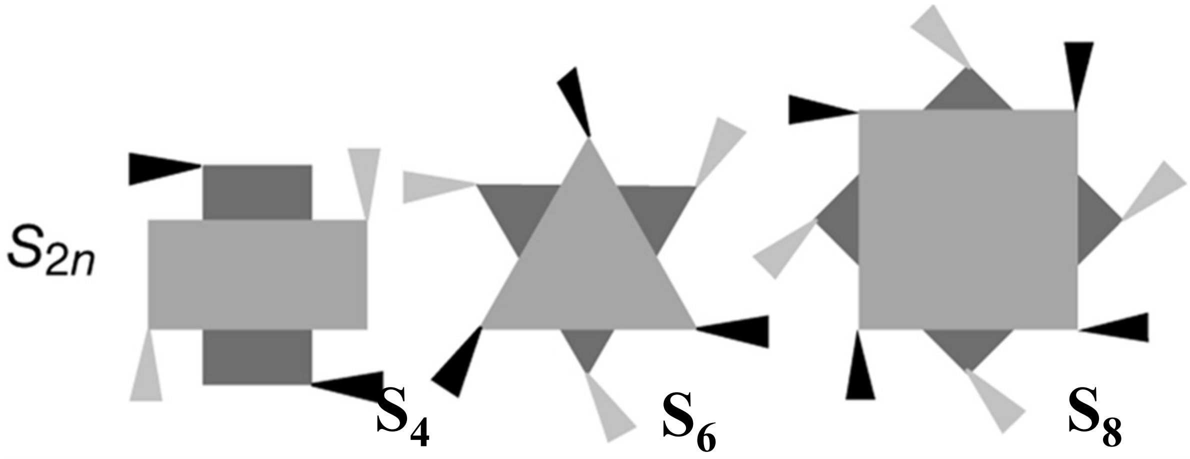
$$S_{2n+1}^{2n+1} = (C_{2n+1}^{2n+1})(\sigma_h)^{2n+1} = \sigma_h \qquad S_{2n+1} = C_{2n+1} + \sigma_h$$

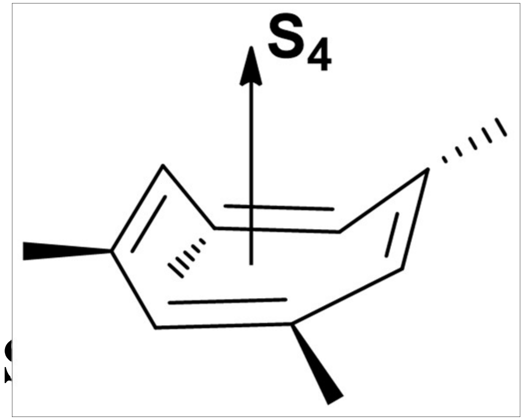
2. Objects with an $\mathbf{S_{4n+2}}$ axis have such normal symmetry elements as $\mathbf{C_{2n+1}}$ ($\mathbf{S_{4n+2}}^{\mathbf{2k}}$=$\mathbf{C_{2n+1}}^{\mathbf{2k}}$) and ***i*** ! **(n>0)**

$$S_{4n+2}^{2n+1} = (C_{4n+2}^{2n+1})(\sigma_h)^{2n+1} = i \qquad S_{4n+2} = C_{2n+1} + i$$

Namely, objects having exclusively a $\mathbf{C_{2n+1}}$ (n>0) axis and ***i*** also have an improper axis $\boldsymbol{S_{4n+2}}$, belonging to $\boldsymbol{S_{4n+2}}$ group (sometimes denoted $\boldsymbol{C_{mi}}$ group ($m=2n+1$), e.g., $\boldsymbol{S_6} = \boldsymbol{C_{3i}}$).

3. Only $\mathbf{S_{4n}}$ axes are independent ***symmetry elements***!
Objects having an $\mathbf{S_{4n}}$ axis also have a $\mathbf{C_{2n}}$ axis. (n=1,2,…)



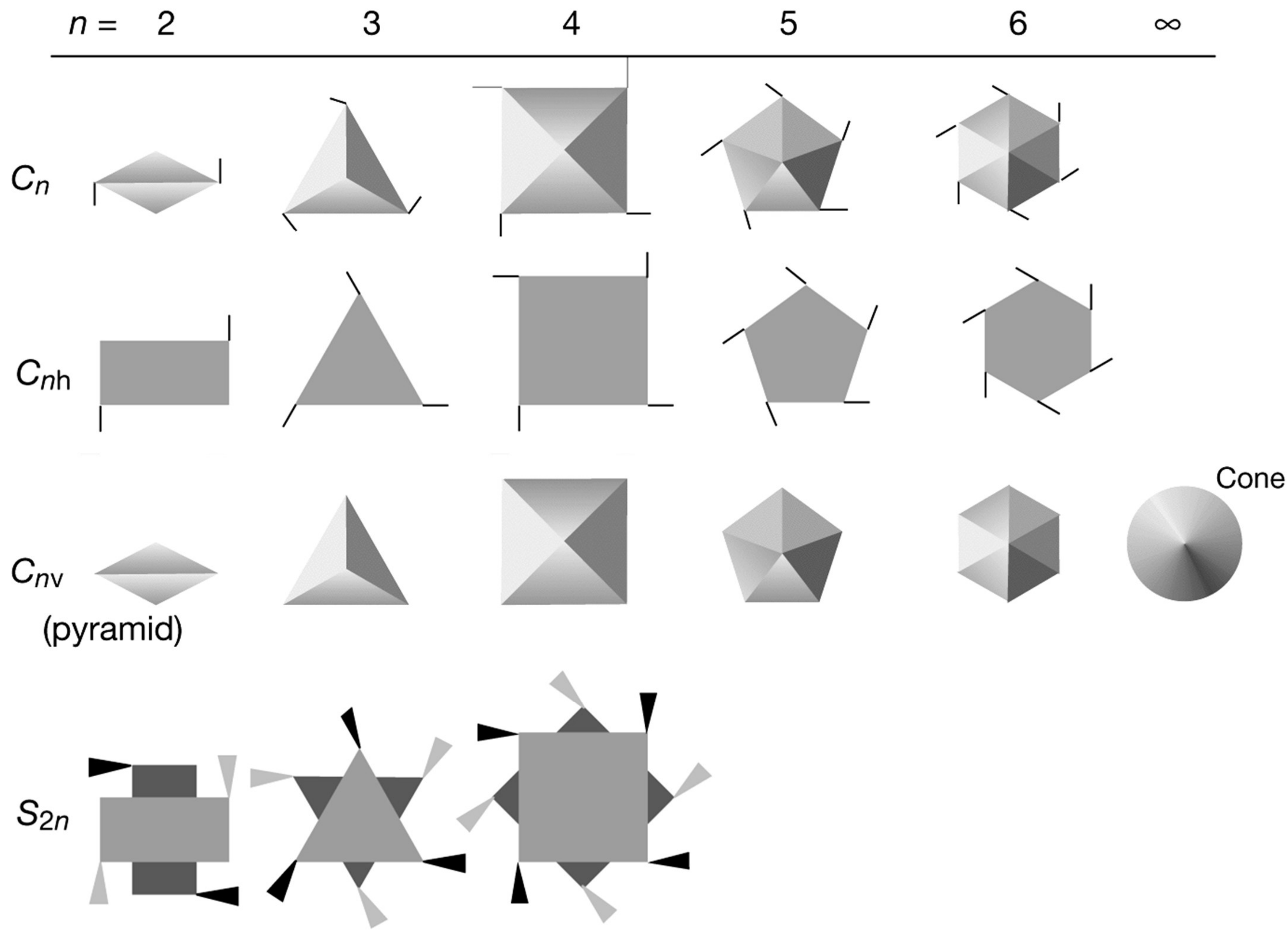


In short,

- There exist $\boldsymbol{S_n}$ groups only when $\boldsymbol{n = 2m}$ ($\boldsymbol{m}$ >1)!
- A $\boldsymbol{S_n}$ ($\boldsymbol{n = even}$) point group is $\boldsymbol{n}$-order with the elements $\{\boldsymbol{E, S_n^1, \ldots, S_n^{n-1}}\}$.

Mono-axis groups

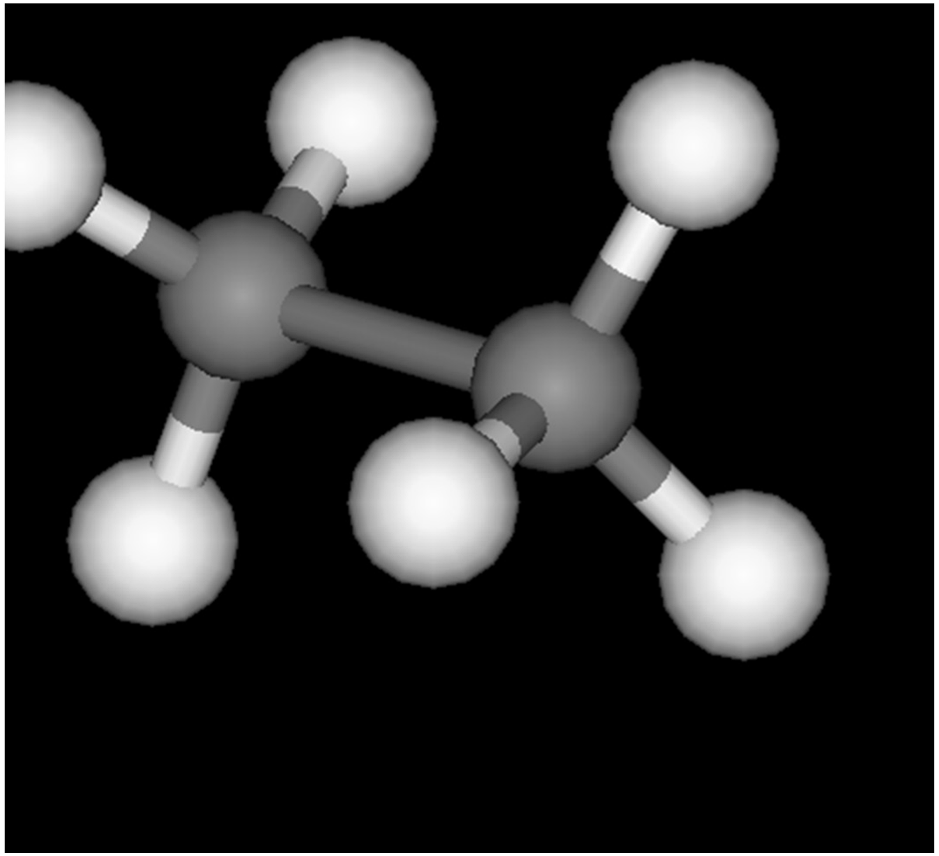
Such point groups as $\boldsymbol{C_n}$, $\boldsymbol{C_{nv}}$, $\boldsymbol{C_{nh}}$, $\boldsymbol{S_n}$ etc. having only one rotary (or improper) axis are called **mono-axis groups**.



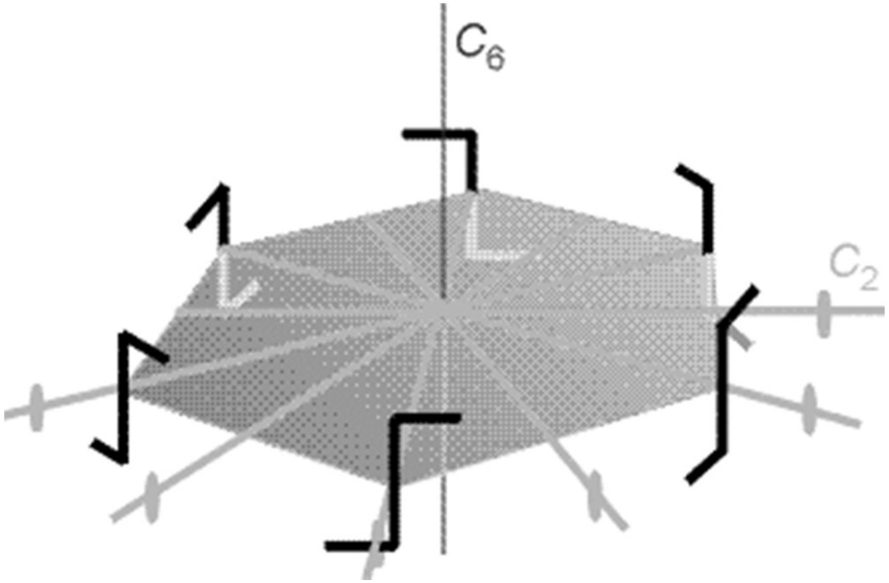
n = 2 3 4 5 6 ∞
Cn
Cnh
Cnv
(pyramid)
Cone
S2n

3. The dihedral groups: D_n, D_{nh}, D_{nd}

D_n: An object that has an n-fold principal axis (C_n) and n C_2 axes perpendicular to C_n belongs to D_n.



(Ethane in a non-equilibrium state)

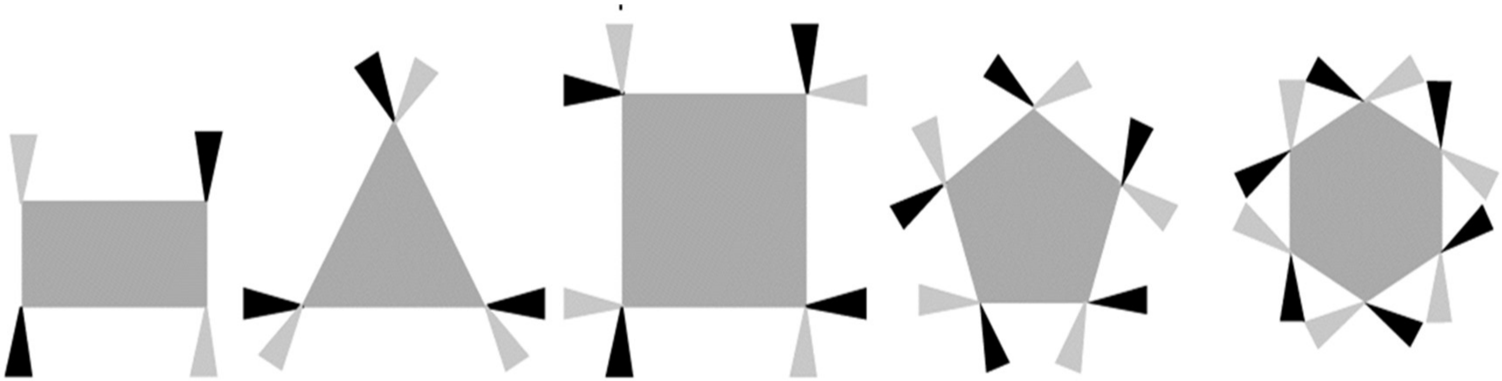


Note: $C_n + C_2(\perp) \rightarrow nC_2\ (\perp)$

$$D_n = \{\overbrace{E, C_n^{1}, \ldots, C_n^{n-1}}, nC_2\}.$$

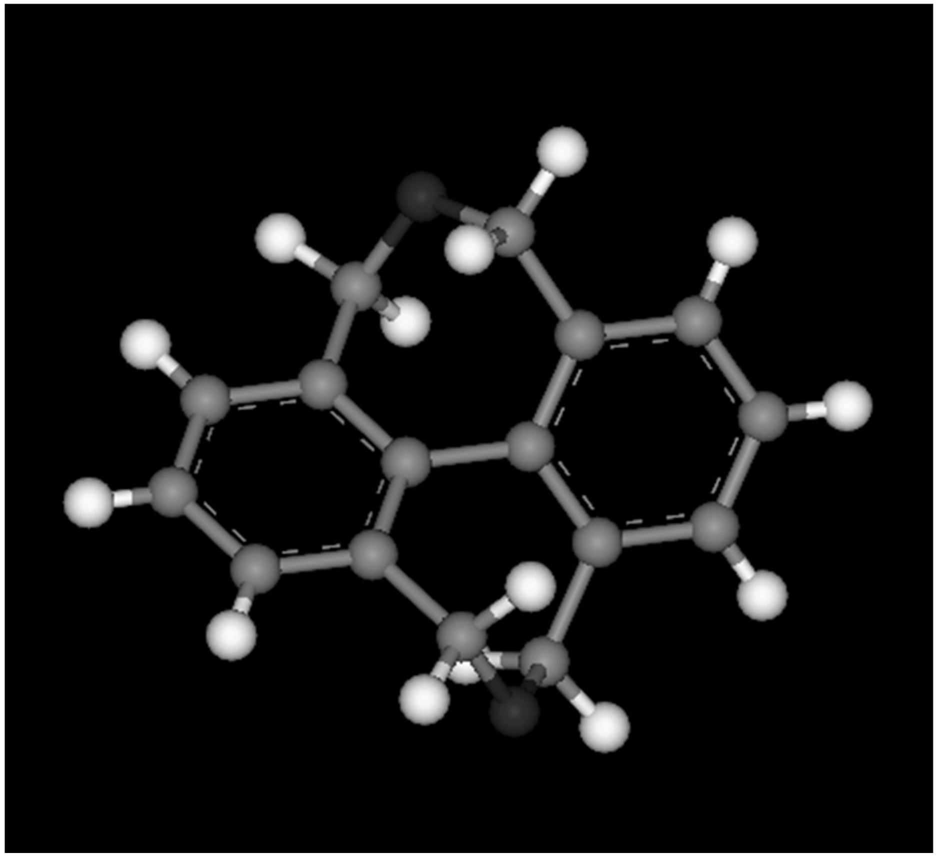
$\boxed{D_n \text{ is } 2n\text{-order.}}$

D_n



D_2 D_3 D_4 D_5 D_6

?



The group D_{nh}

A molecule having a mirror plane (σ_h) perpendicular to a $\mathbf{C_n}$ axis, and ***n*** two-fold axes ($\mathbf{C_2}$) in the plane, belongs to the group $\mathbf{D_{nh}}$.

$C_n + \sigma_h \rightarrow S_n$ or/and $S_{n/2}$

$C_n \perp C_2 \rightarrow n\,C_2$

$nC_2 \subset \sigma_h \rightarrow n\,\sigma_v$

D_{nh} is *4n*-order.

$\sigma_h = S_n^n \quad (n = \text{odd})$

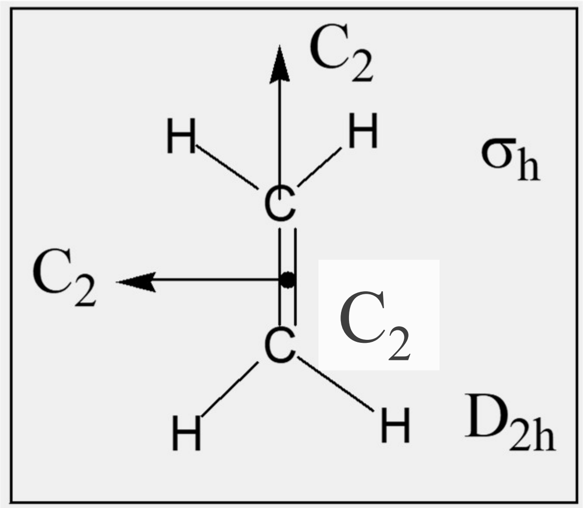
n= odd, $D_{nh} = \{E, C_n^1, \ldots, C_n^{n-1}, nC_2, n\sigma_v, \underline{S_n^1, \ldots, S_n^n \ldots, S_n^{2n-1}}\}$.

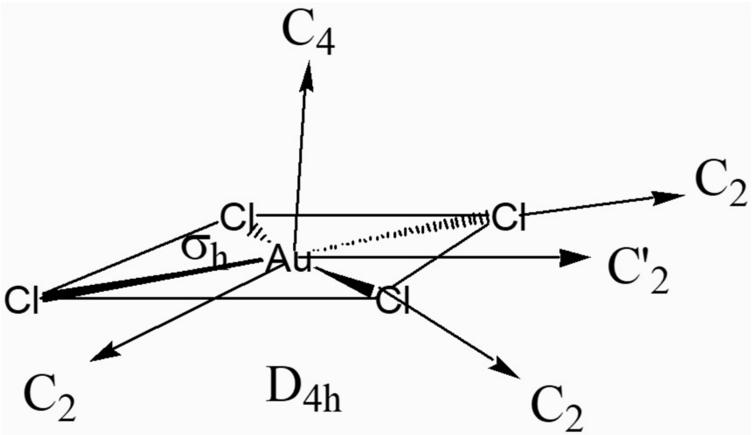
n= even, $D_{nh} = \{E, C_n^1, \ldots, C_n^{n-1}, nC_2, \sigma_h, \underbrace{i, S_n^1, S_{n/2}^1, \ldots, S_n^{n-1}, S_{n/2}^{n-1}}$, $(n/2)\sigma_v$, $(n/2)\sigma_d\}$

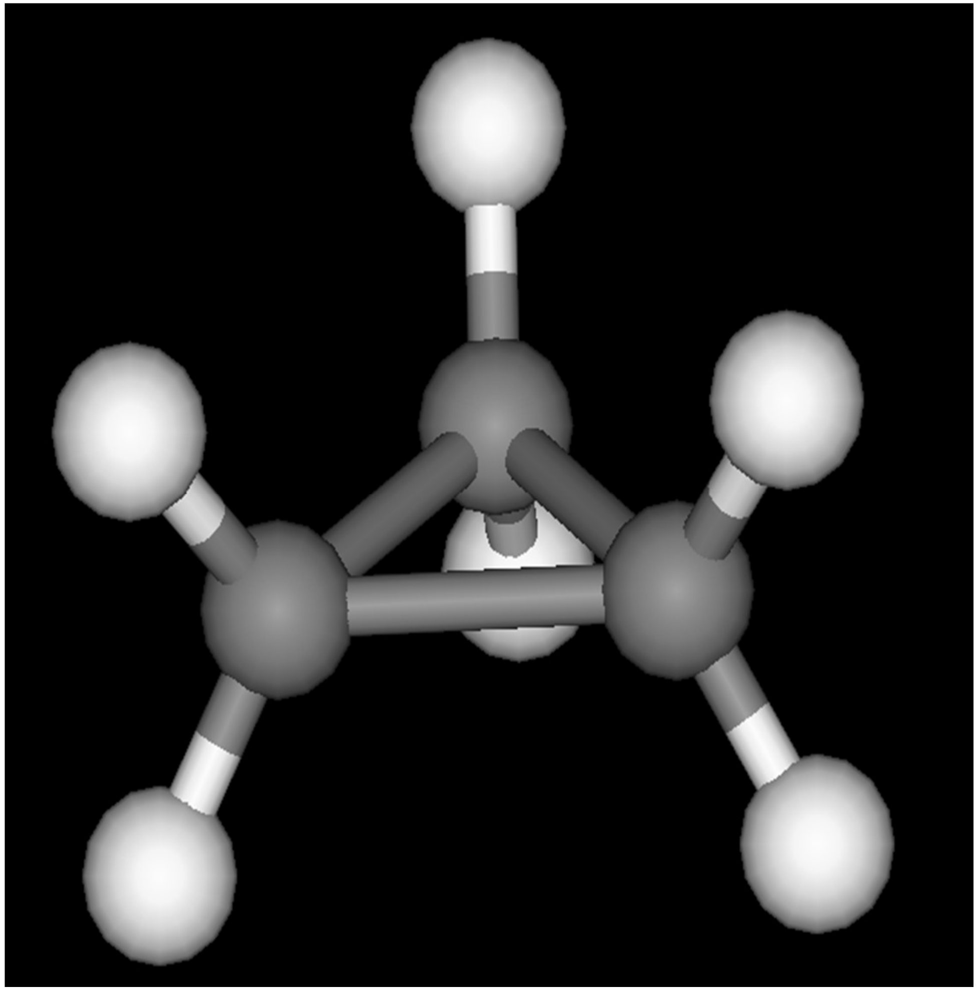
$i = S_n^{n/2}$ (n = even)

(n-1) S_n-type operations!

D_{nh}

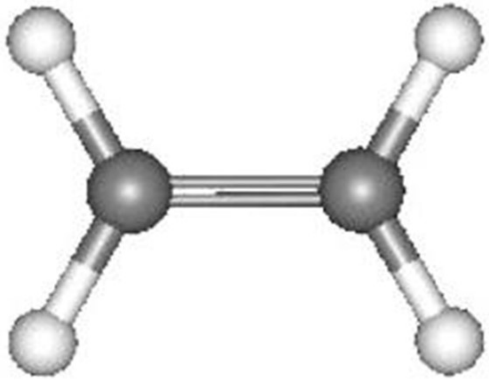




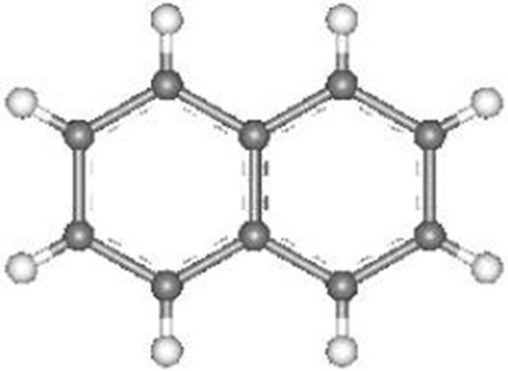


D_{3h}

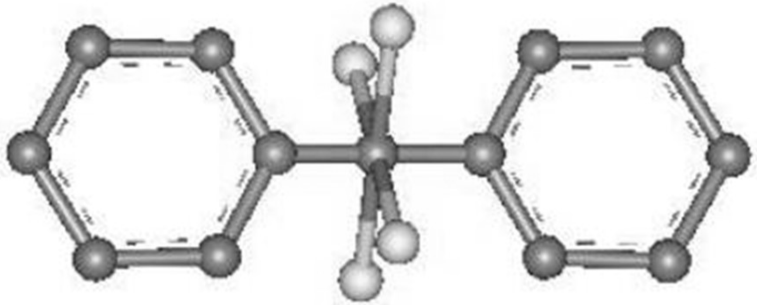
D_{2h}



C_2H_4

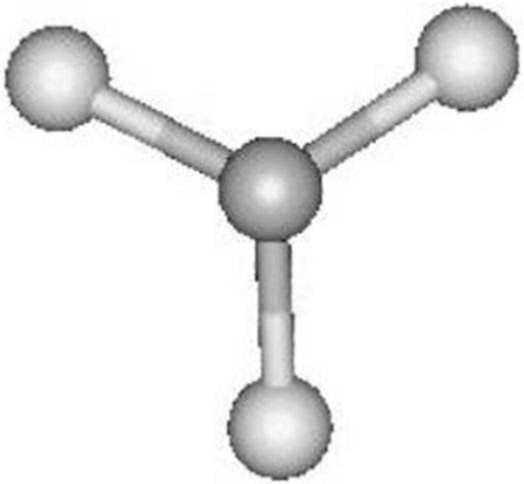


$C_{10}H_{10}$

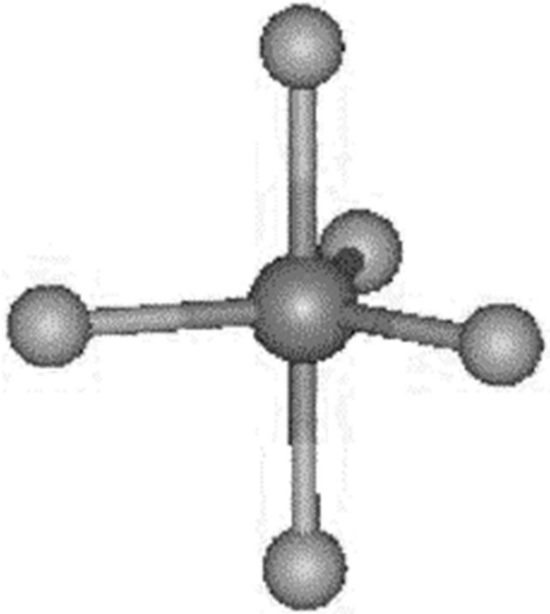


SiF_4Py_2

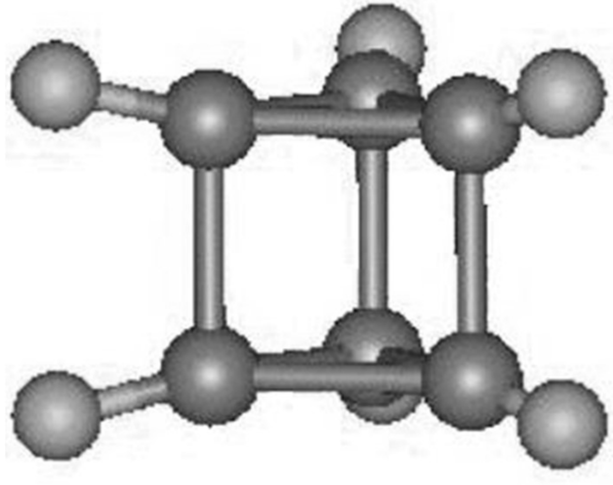
D_{3h}



BF_3

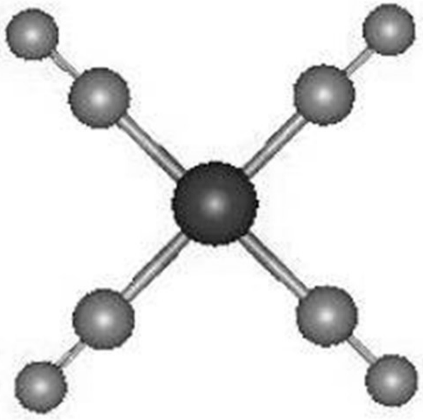


PCl_5

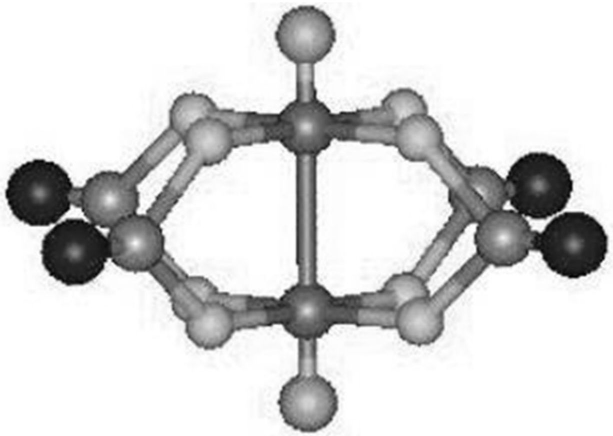


Tc_6Cl_6

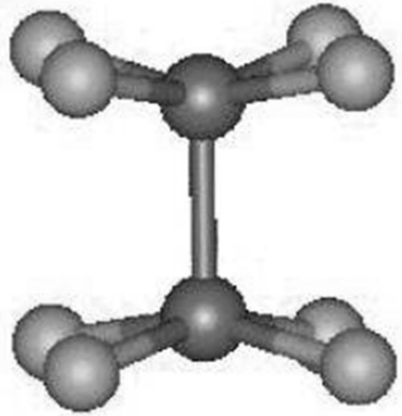
D_{4h}



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



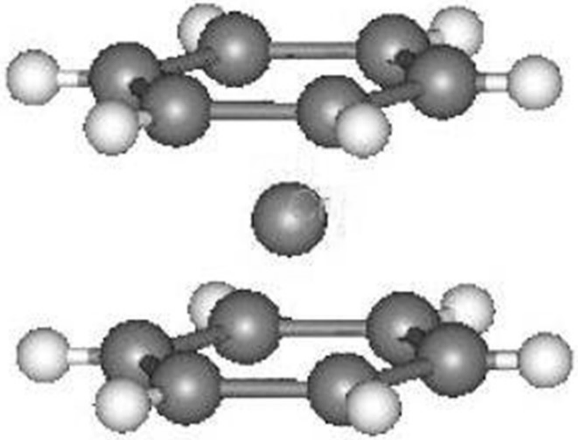
$[M_2(COOR)_4X_2]$



Re_2Cl_8

D_{6h}

C_6H_6



$Cr(C_6H_5)_2$

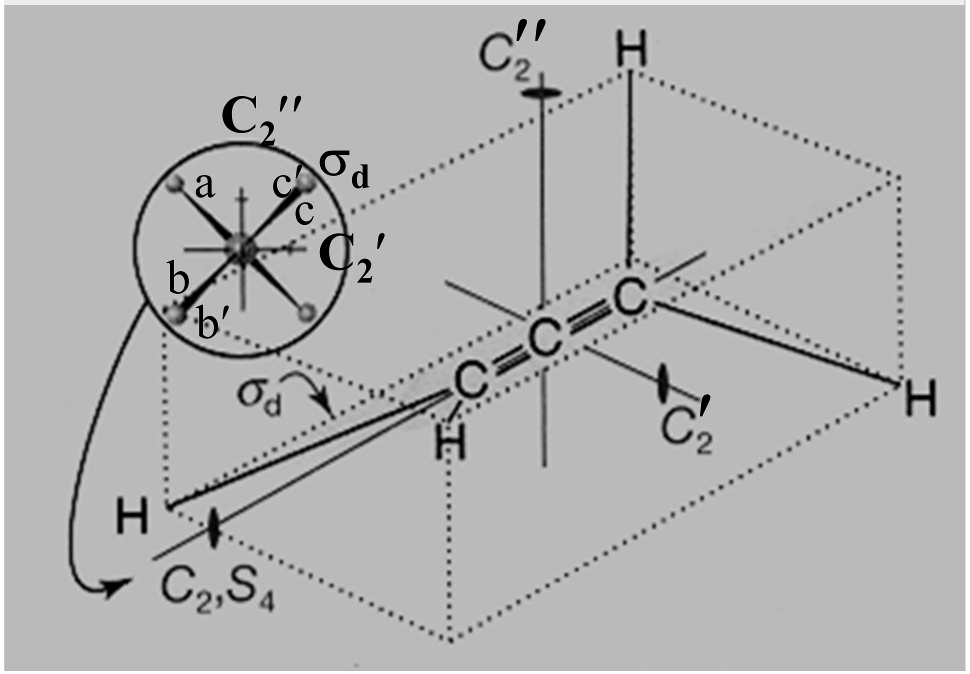
Bis(benzene)chromium

$D_{\infty h}$ O=C=O

The group D_{nd}

- A molecule that has a $\boldsymbol{C_n}$ **(n ≥2)** principle axis and n $\boldsymbol{C_2}$ axes perpendicular to $\mathbf{C}_n$ belongs to $\boldsymbol{D_{nd}}$ if it also possesses n diagonal mirror planes ($\sigma_{\mathbf{d}}$).
- *A set of operations of $\sigma_d \cdot C_2$ ($\perp C_n$) type are equivalent to $S_{2n}{}^m$, thus making the C_n being an S_{2n} axis.*

The order of group D_{nd} = 4n



For D_{2d}, $C_2 + 2C_2(\perp) + 2\sigma_{d/v}$

$$\begin{cases} \angle C_2'/C_2'' = 2\pi/2n = \pi/2 \\ \angle \sigma_d/\sigma_d' = 2\pi/2n = \pi/2 \end{cases}$$

$\mathbf{C_2'a = b', \sigma_d b' = b, \; S_4{}^1 a = b}$

⇨ $\mathbf{\sigma_d C_2' = S_4{}^1 \; (//C_2)}$

⇨ $$\begin{cases} \sigma_d C_2'' = S_4{}^3 \quad (a \rightarrow c' \rightarrow c); \\ C_2 = S_4{}^2 \; ; \; E = S_4{}^4 \end{cases}$$

∴ The C_2 axis is also a S_4!

$\mathbf{C_3H_4}$ $D_{2d} = \{E, 3C_2, 2\sigma_d, S_4{}^1, S_4{}^3\}$

D_{nd} Upon introducing σ_d, the C_n axis becomes a S_{2n} axis!

e.g., Ethane – D_{3d}.

$C_3 + 3C_2(\perp) + 3\sigma_{d/v}$

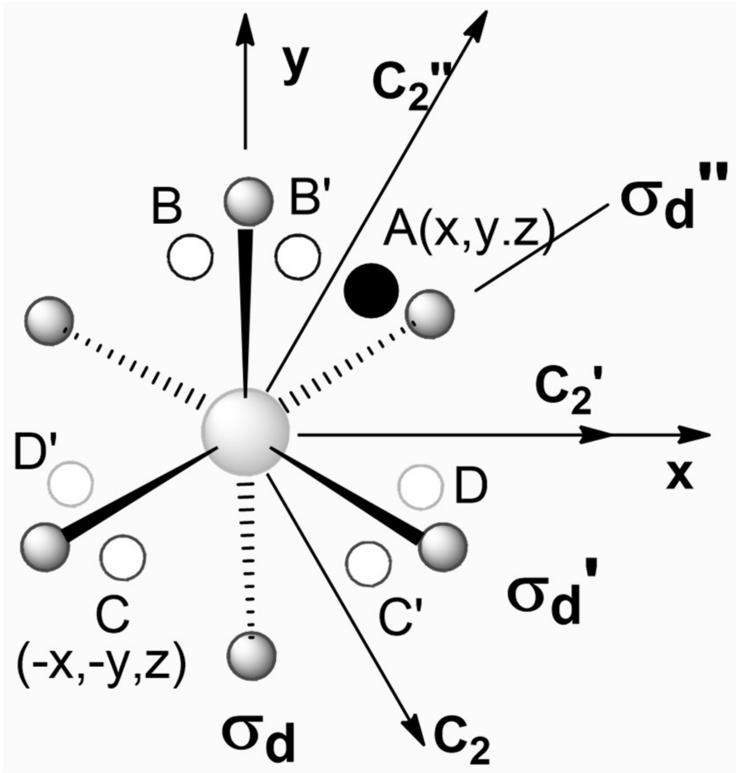
$$\begin{cases} \angle C_2/C_2'/C_2'' = 2\pi/2n = \pi/3 \\ \angle \sigma_d/\sigma_d'/\sigma_d'' = 2\pi/2n = \pi/3 \end{cases}$$

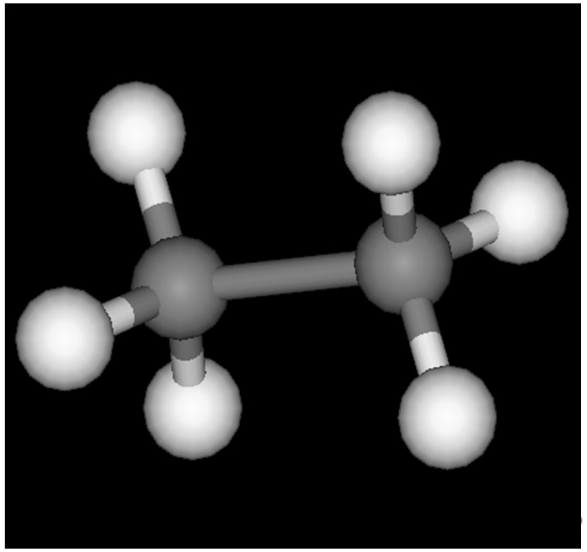
⇨ $C_2'' \perp \sigma_d', \sigma_d \perp C_2', \sigma_d'' \perp C_2$

⇨ $\sigma_d C2' = i$ or $\sigma_d' C2'' = i$

⇨ $C_3 + i = S_6$

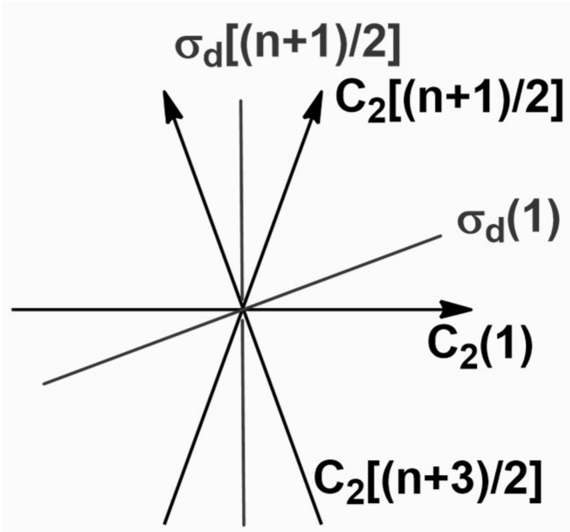
⇨ $D_{3d} = \{E, C_3^1, C_3^2, 3C_2, 3\sigma_d, i, S_6^1, S_6^5\}$





- It is provable that an object of D_{nd} (n=odd) group also has such symmetry elements i & S_{2n}.

$C_n + nC_2(\perp) + n\sigma_{d/v}$ (n=odd)



$$\angle C_2(j)/C_2(j+1) = \frac{\pi}{n} \Rightarrow \angle C_2(1)/C_2(\frac{n+1}{2}) = \frac{n-1}{2}\frac{\pi}{n}$$

$$\angle \sigma_d(j)/\sigma_d(j+1) = \frac{\pi}{n} \Rightarrow \angle \sigma_d(1)/\sigma_d(\frac{n+1}{2}) = \frac{n-1}{2}\frac{\pi}{n}$$

$$\angle C_2(j)/\sigma_d(j) = \frac{\pi}{2n}$$

$$\therefore \angle C_2(1)/\sigma_d(\frac{n+1}{2}) = \frac{\pi}{2} \Rightarrow C_2(1) \perp \sigma_d(\frac{n+1}{2})$$ $$\& \, C_2(j+\frac{n+1}{2}) \perp \sigma_d(j)$$

$$\therefore \sigma_d(\frac{n+1}{2})C_2(1) = i$$

$$C_{\mathrm{n}} + i = S_{2n} \quad (n = odd)$$

D_{nd}

$$D_{nd}=\{E, \underbrace{C_n^1,\dots,C_n^{n-1}}_{nC_n^k\ (k=1,\dots,n)}; nC_2; n\sigma_d; \underbrace{S_{2n}^1,\dots S_{2n}^{2k+1},\dots,S_{2n}^{2n-1}}_{nS_{2n}^{2k-1}\ (k=1,\dots,n)}\} \quad \text{order}=4n$$

Note:

i) Key symmetry elements:

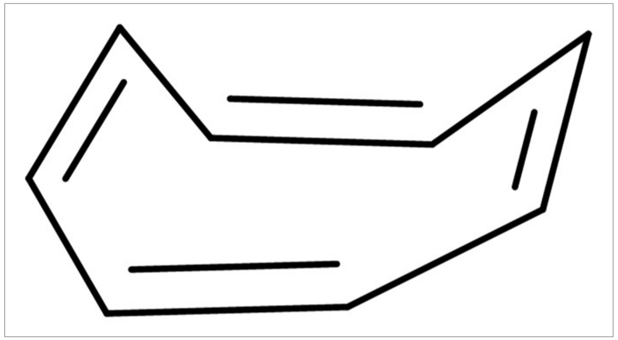
$C_n + nC_2 + n\sigma_{d/v}$ & S_{2n} (derived from $\sigma_d + C_2$)

ii) Equivalent symmetry operations: $S_{2n}^{2k} = C_n^k$ (k= 1,…, n);

iii) When *n* =odd, $S_{2n}^n = i$; $\boxed{\sigma_d \cdot C_2(\perp) = i}$

$$\boxed{\begin{aligned} &S_{2n}^n = S_{4m+2}^{2m+1} \quad (\text{n} = 2\text{m}+1) \\ &= (\sigma_h)^{2m+1}(C_{4m+2}^{2m+1}) = \sigma_h C_2^1 = i \end{aligned}}$$

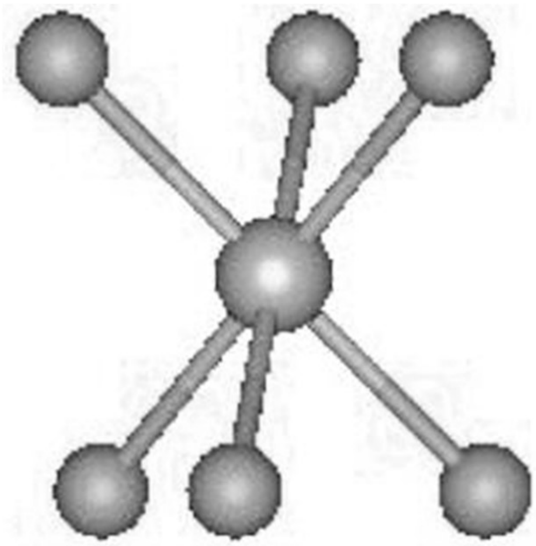
D_{2d}



Cyclooctatetraene

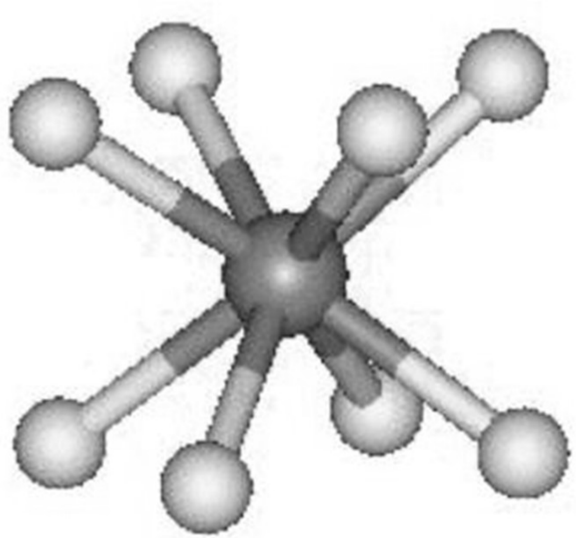
(Boat-shaped C_8H_8)

D_{3d}



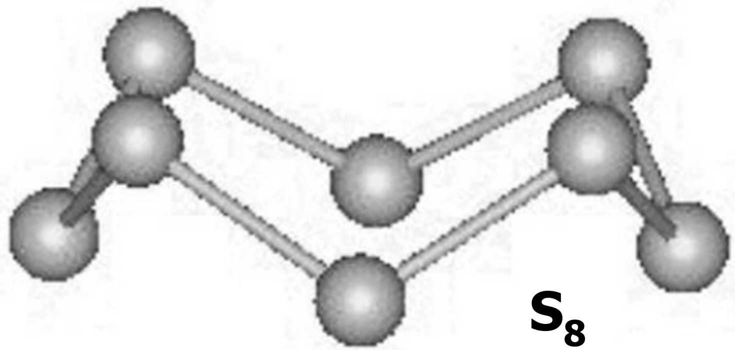
$TiCl_6^{2-}$

D_{4d}



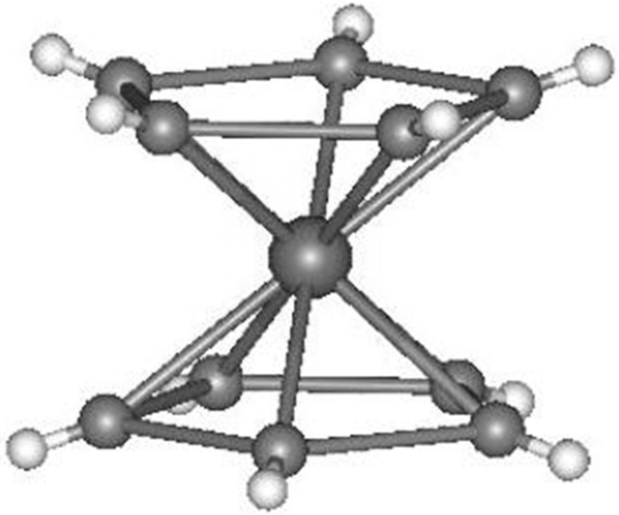
TaF_8^{3-}

D_{4d}



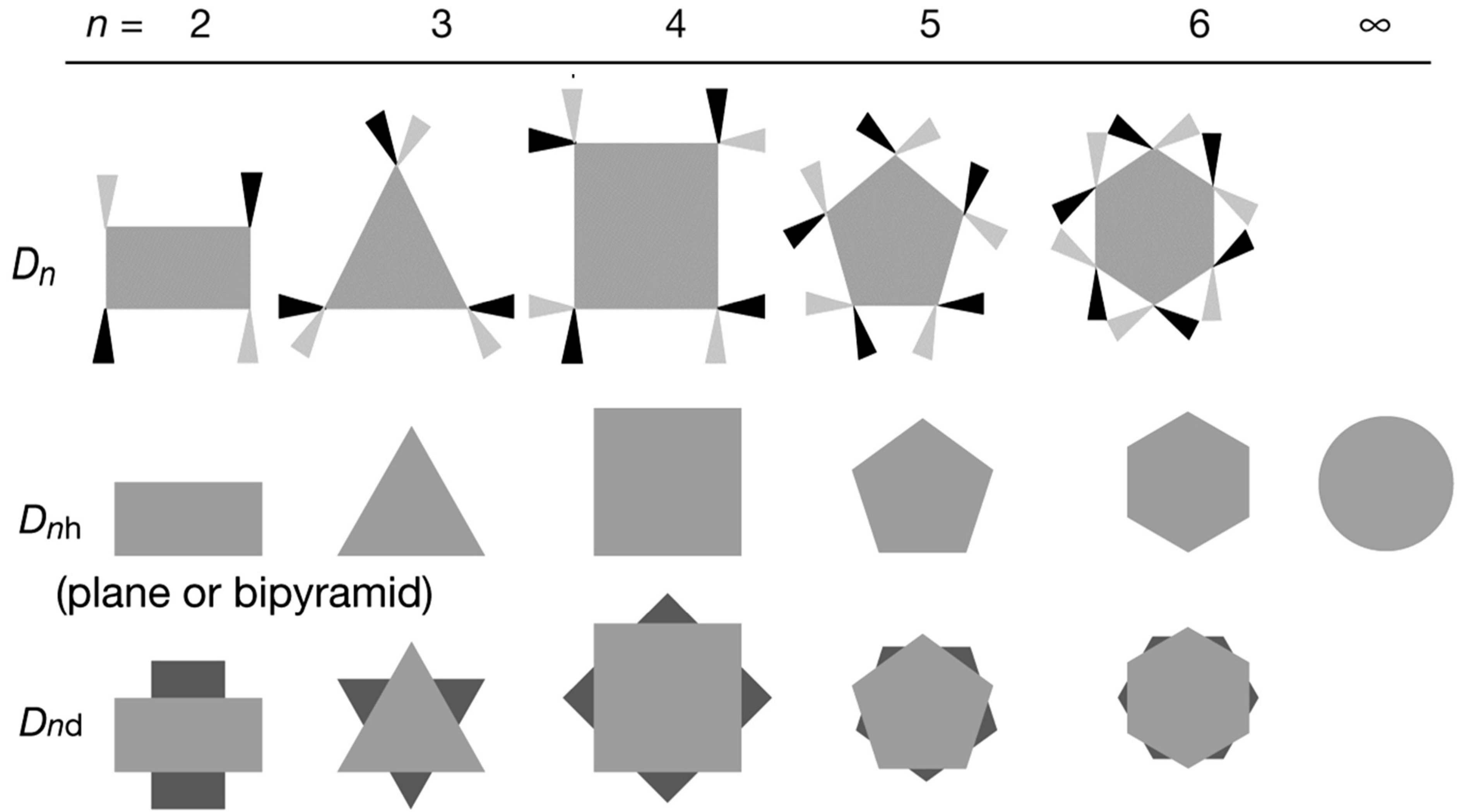
S_8

D_{5d}



Ferrocene

Dihedral Groups



4. High-order point groups (Polyhedral point groups)

- The aforementioned point groups have one axis or one ***n***-fold axis plus ***n*** 2-fold axes.
- Molecules having three or more high-order symmetry elements (several *n*-fold axes, n>2) may belong to one of the following:

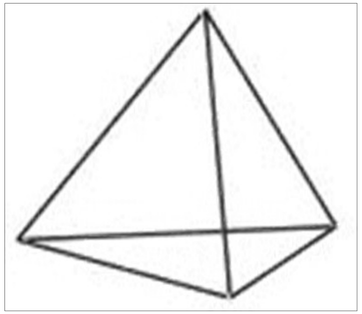
T: $4\ C_3,\ 3\ C_2$ **(T_h: $+3\sigma_h$)** **(T_d: $+3S_4$)**

O: $4\ C_3,\ 3\ C_4$ **(O_h: $+3\sigma_h$)** $\Longrightarrow$ **Cubic group**

I: $6\ C_5,\ 10\ C_3$ **(I_h: $+$ *i*)**

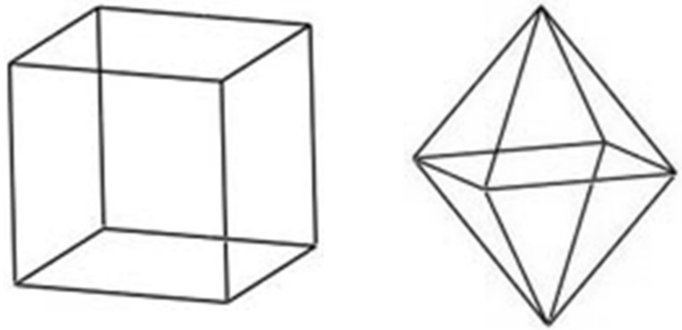
Polyhedral groups derived from Platonic Polyhedra

T_d – Species with tetrahedral symmetry

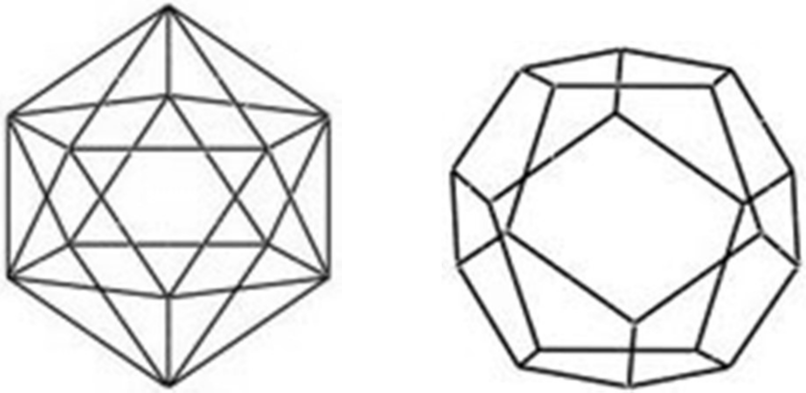


tetrahedral symmetry group

O_h – Species with octahedral symmetry (many metal complexes)



octahedral symmetry group

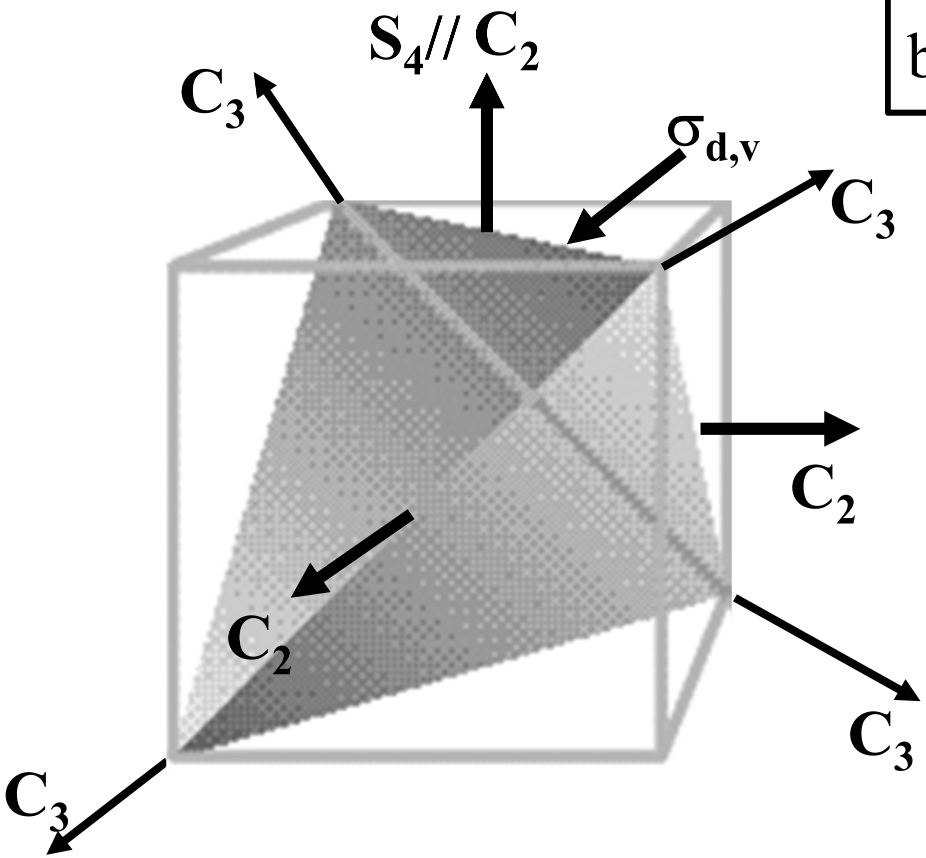


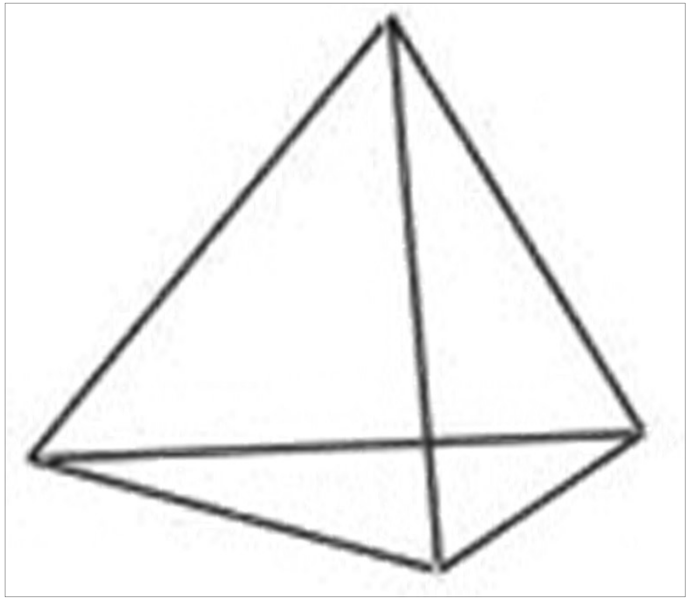
Icosahedral symmetry group

I_h – Icosahedral symmetry (Buckminster-fullerene, C_{60})

T_d $4C_3 + 3C_2 + 6\sigma_{d\,(v)}$

Upon introducing six σ_d mirror planes, the three orthogonal C_2 axes become three S_4 axes.

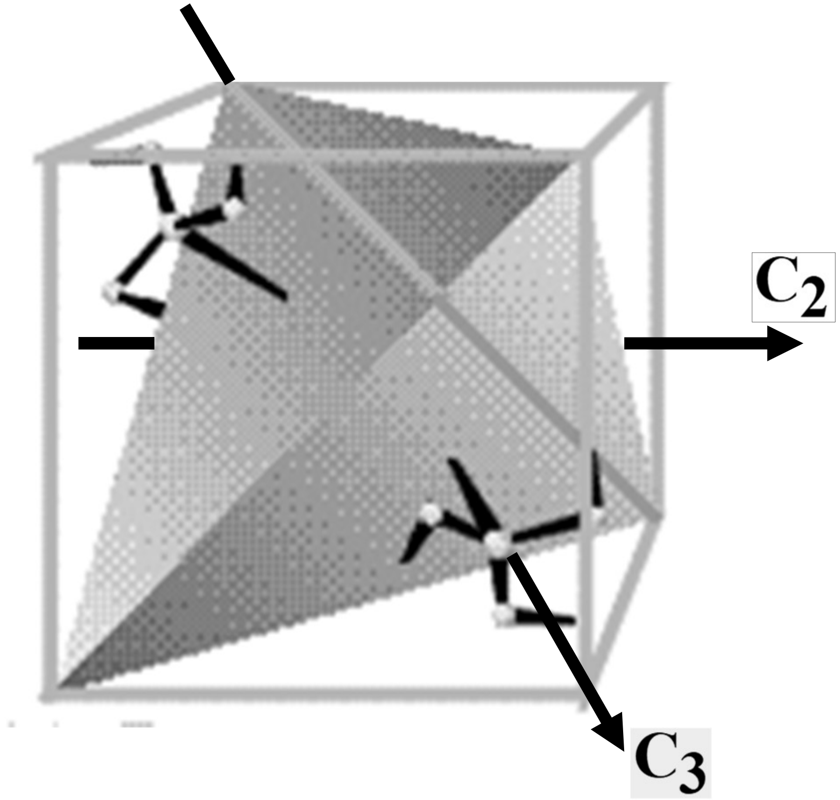




$$T_d = \{E,\ 4C_3^1,\ 4C_3^2,\ 3C_2,\ 6\sigma_d,\ 3S_4^1,\ 3S_4^3\}$$

Order =24

Note: $S_4^2 = C_2$



- **The perfectly tetrahedron-shaped object belongs to T_d point group.**
- **The windmill-like structures reduces the symmetry from T_d to T by eliminating the $\sigma_{d/v}$ planes .**

T: $4\ C_3 + 3\ C_2$ (T_d: $+ 3S_4$ or $+ 6\sigma_d$)

T = {E, $4C_3^1$, $4C_3^2$, $3C_2$} order =12

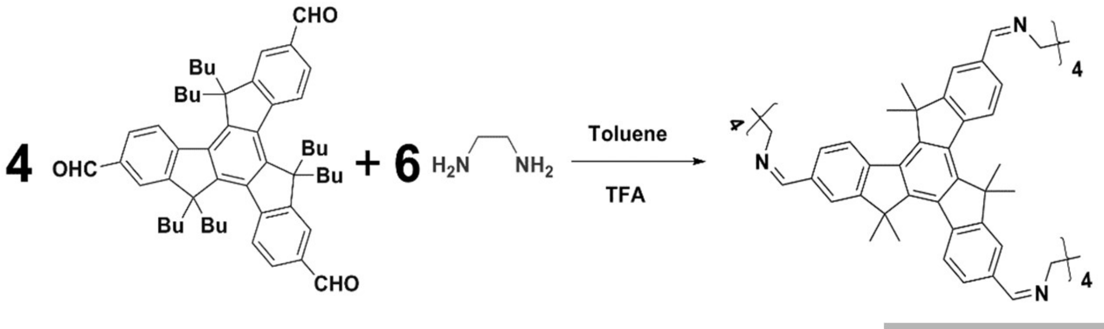
T is a pure rotation group!

Objects of T-symmetry are chiral!

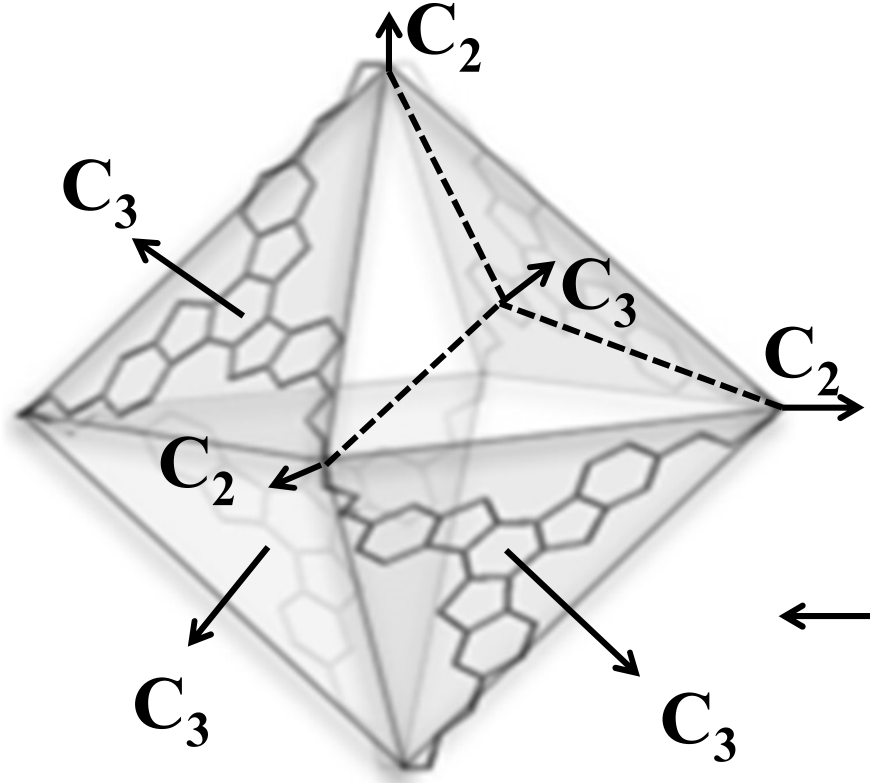
Luk Y-Y *et al*, ***Chirality***, 2008, 20, 878-884.

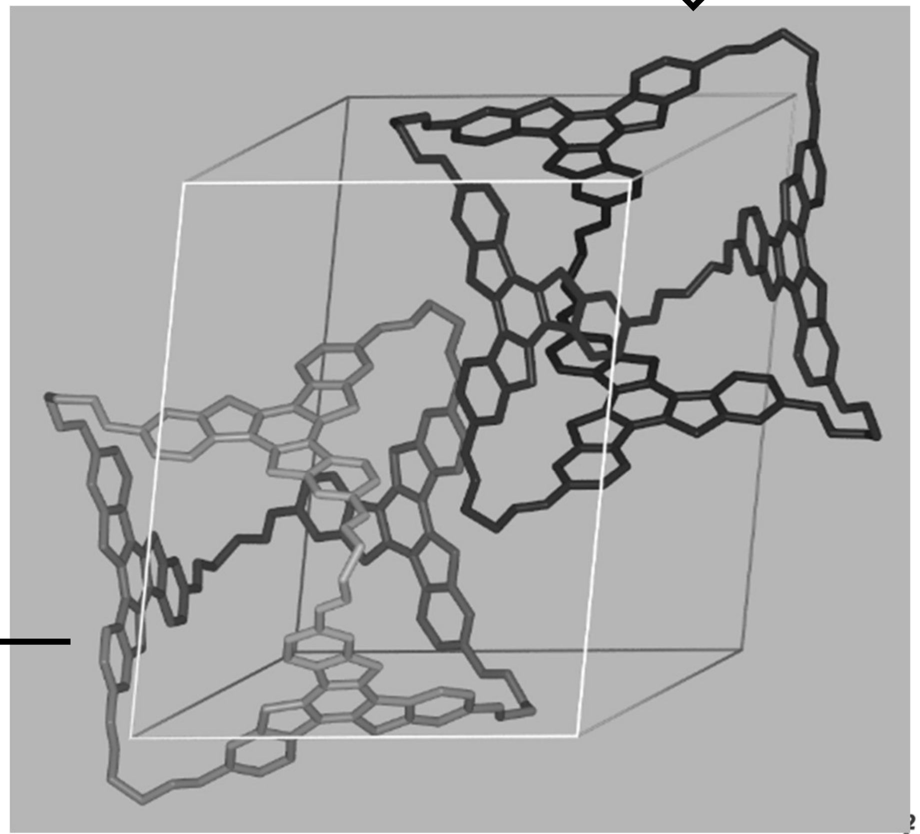
Example: **T**

Molecules of T-group symmetry are chiral!



crystallization

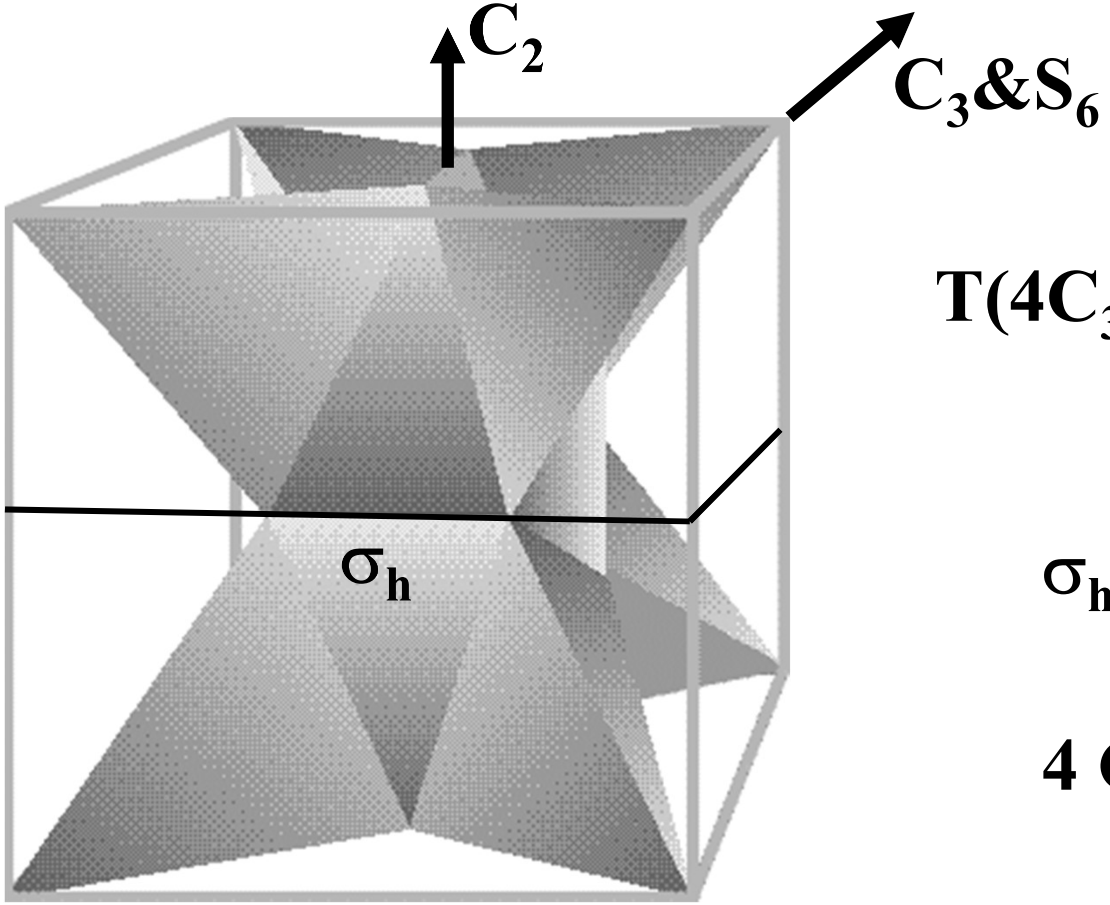




Wang XC et al. Nature Comm., 2016, 7, 12469

Cubic groups

T_h



$$T(4C_3,\ 3C_2) + 3\sigma_h\ (\perp C_2)$$
$$\downarrow$$
$$\sigma_h \perp C_2 \ \Rightarrow\ i$$

$$4\ C_3 + \ i \Rightarrow\ \ 4\ S_6\ (//C_3)$$

$$T_h = \{E,\ \ 4C_3^{\,1},\ \ 4C_3^{\,2},\ \ 3C_2,\ \ 3\sigma_h, i,\ \ 4S_6^{\,1},\ \ 4S_6^{\,5}\}$$

Order = 24

Note: $S_6^{\,2} = C_3^{\,1};\quad S_6^{\,4} = C_3^{\,2};\quad S_6^{\,3} = \ i$

$4C_3 + 3C_2$

(No C_4!)

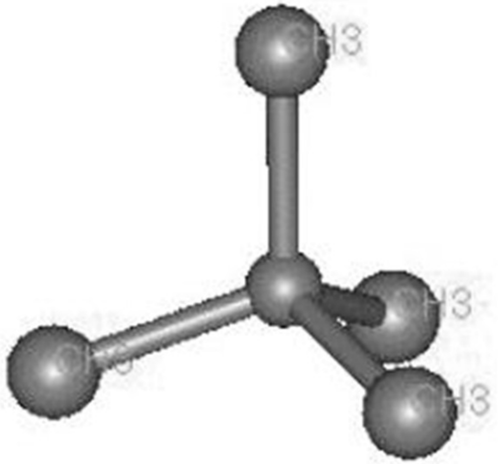
$\longrightarrow$ **T**

$\xrightarrow{\sigma_h \perp C_2 \text{ or } \boldsymbol{i}}$ $\mathbf{T_h}$

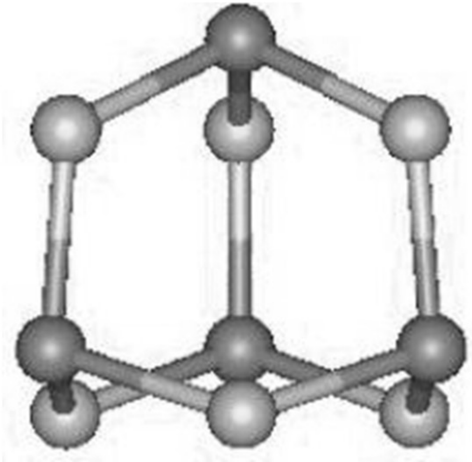
$\xrightarrow[\sigma_d\ (C_2)]{\sigma_v\ (//C_3) \text{ or}}$ $\mathbf{T_d}$

T_d T_d T_d T_h

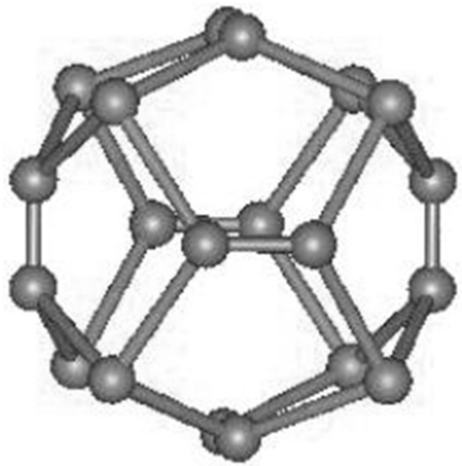
CH_4



$X(CH_3)_4$ (X=C,Si)

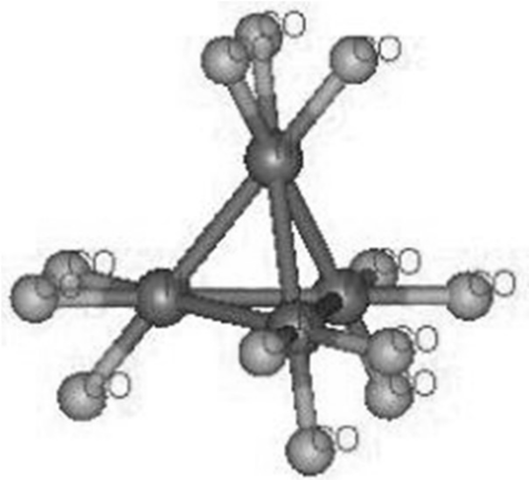


P_4O_6



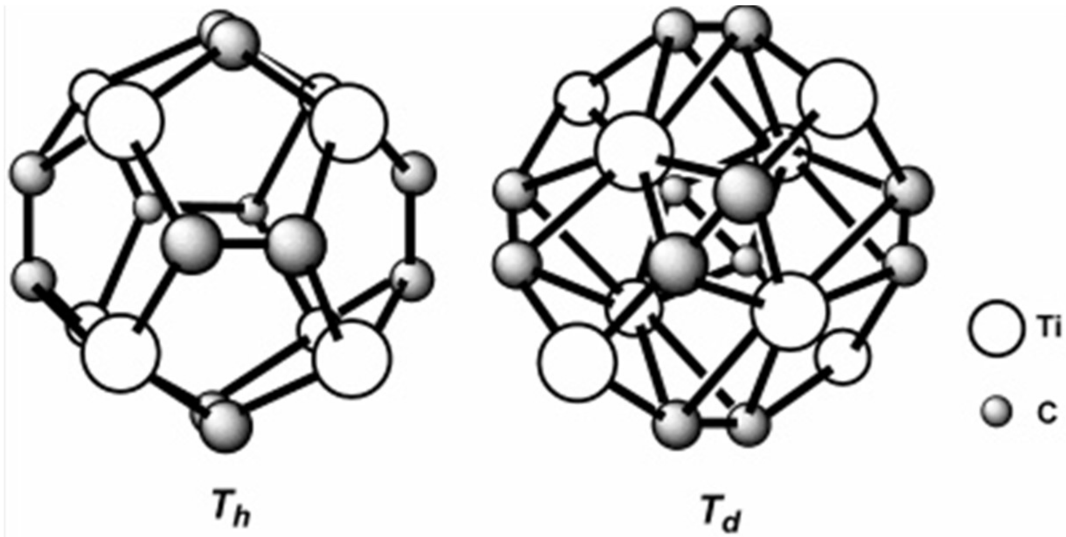
P_8C_{12}

T_d

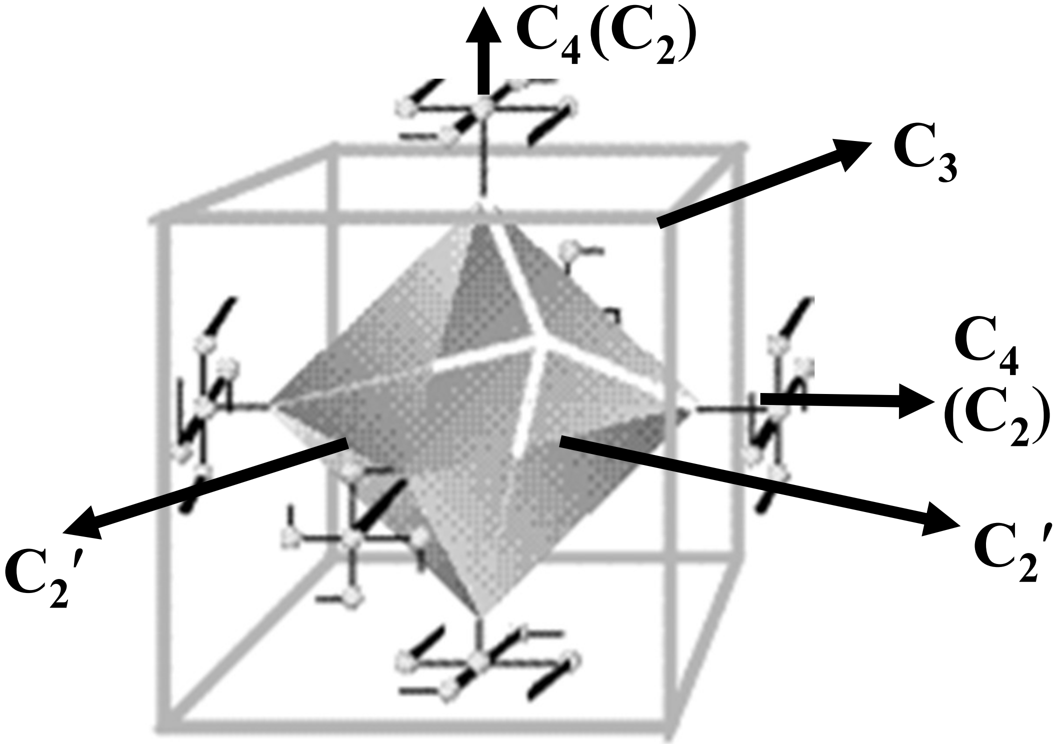


$Co_4(CO)_{12}$

Chem. Rev. 2005, 105, 3643.



Ti_8C_{12} (T_d is more stable than T_h)



O Cubic groups

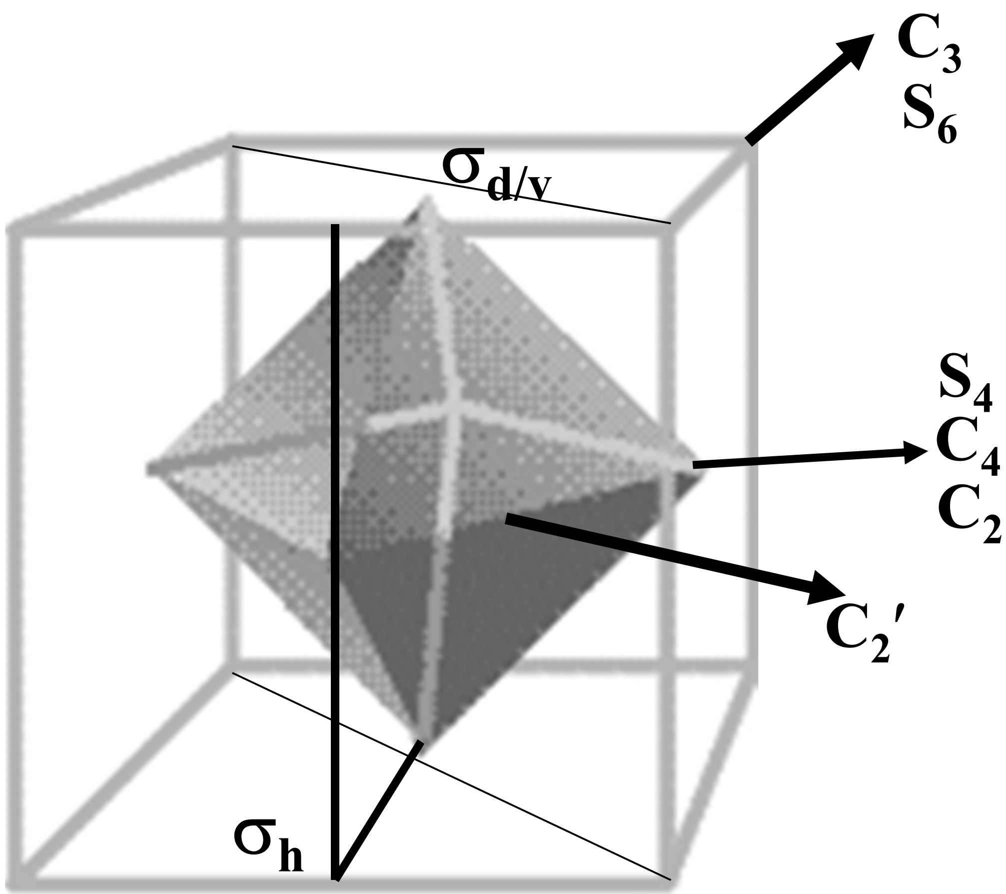
- No mirror plane is allowed due to the presence of windmill-like fragments at the apices of the octahedron!

$$\mathbf{O: 4C_3,\ 3C_4} \xrightarrow[C_4 \perp C_2 \rightarrow 4C_2\ (\perp C_4)]{} \mathbf{6C_2'}$$

$$\mathbf{O = \{ E, 4C_3^1, 4C_3^2, 3C_4^1, 3C_4^3, 3C_2, 6C_2' \}}$$

Order =24 Pure rotation group!

Molecules of O-symmetry are chiral!



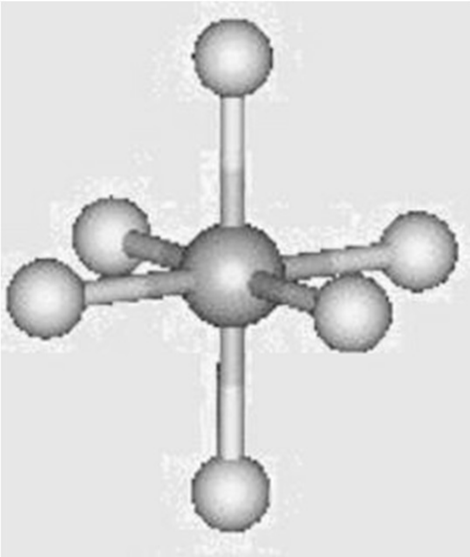
O_h **Cubic groups**

$$O(3C_4, 4C_3) + 3\sigma_h(\perp C_4)$$

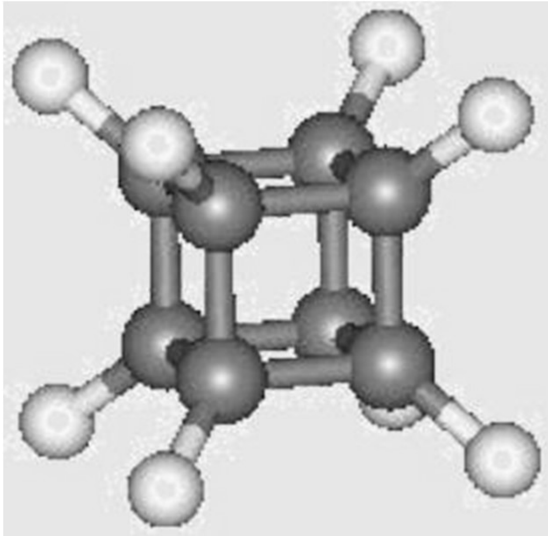
$$\boxed{\begin{array}{ll} \text{i)} & C_4 + \sigma_h \rightarrow i + S_4 \\ \textit{ii)} & i + C_3 \rightarrow S_6 \end{array}}$$

$$O_h = \{E,\ \underbrace{6C_4}_{(3C_4^1,\,3C_4^3)},\ \underbrace{3C_2}_{(3C_4^2)},\ \underbrace{8C_3}_{(4C_3^1,\,4C_3^2)},\ 6C_2',\ i,\ \overbrace{8S_6}^{(4S_6^1,\,4S_6^5)},\ \underbrace{6S_4}_{(3S_4^1,\,3S_4^3)},\ 3\sigma_h,\ 6\sigma_v\}$$

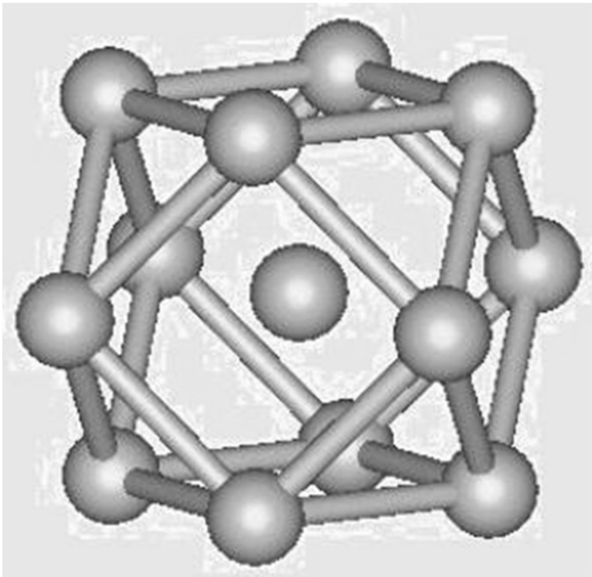
Group order= 48



SF_6



C_8H_8



Rh_{13}

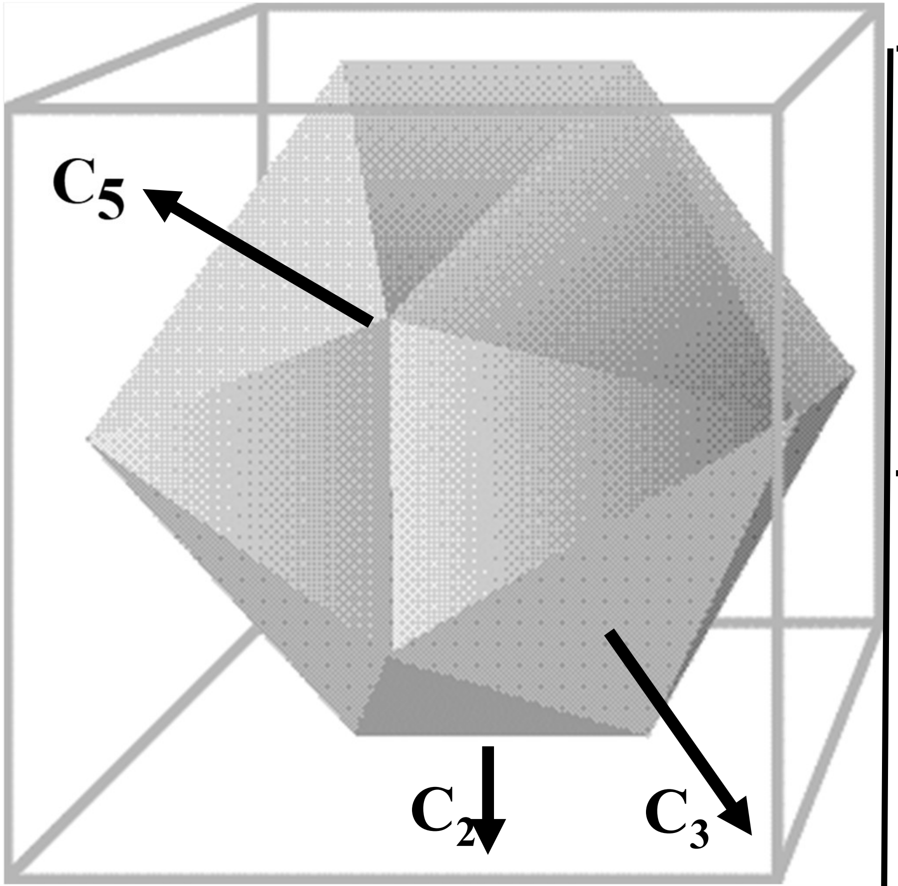
O_h

Typical subgroups of O_h

- **O** = lacks ***i*, S_4, S_6, σ_h** and **σ_d** and is called the pure rotation subgroup of O_h.
- **T_d** = lacks **C_4, i** and **σ_h** and is the group of tetrahedral molecules, e.g., CH_4.
- **T_h** = this uncommon group is derived from ***T_d*** by removing S_4 and σ_d elements.
- **T** = the pure rotation subgroup of T_d contains only C_3 and C_2 axes.

I and I_h groups

I: $6C_5$, $10C_3$, $15C_2$ (I_h: +i)



icosahedron

$A=N_{apex} = 12$, $F=N_{face}= 20$,
$E=N_{edge}= 30$

$I = \{E, 12C_5, 12C_5^2, 20C_3, 15C_2\}$

Order =60 Pure rotation group!

No i, σ, S_n -- chiral!

e.g., some virus!

I_h: ($I + i$)

$C_5 + i = S_{10}$

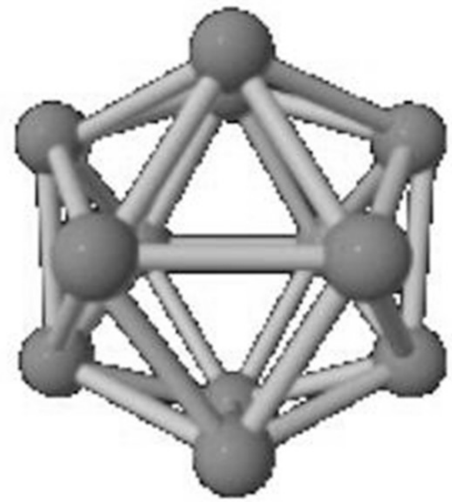
$C_3 + i = S_6$

$C_2 + i = \sigma_h$

$\{E, 12C_5, 12C_5^2, 20C_3, 15C_2, i,$
$12S_{10}, 12S_{10}^3, 20S_6, 15\sigma_h\}$

order = 120

I_h group: two long-known examples

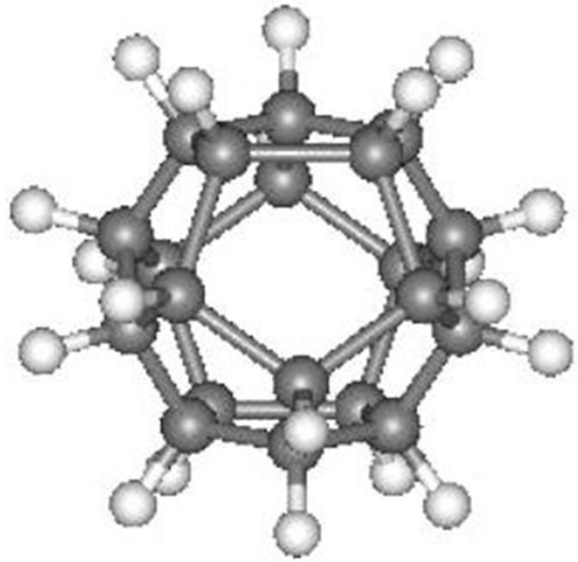


$B_{12}H_{12}^{2-}$ （hydrogen omitted）

a. $B_{12}H_{12}^{2-}$ (icosahedral borane dianion)

b. $C_{20}H_{20}$ (dodecahedrane)

- First synthesized by Paquette in 1982, three years before the discovery of C_{60}.
- It is indeed the first fullerene derivative synthesized by mankind.



$C_{20}H_{20}$

Chem. Rev. 2005, 105, 3643 and references therein.

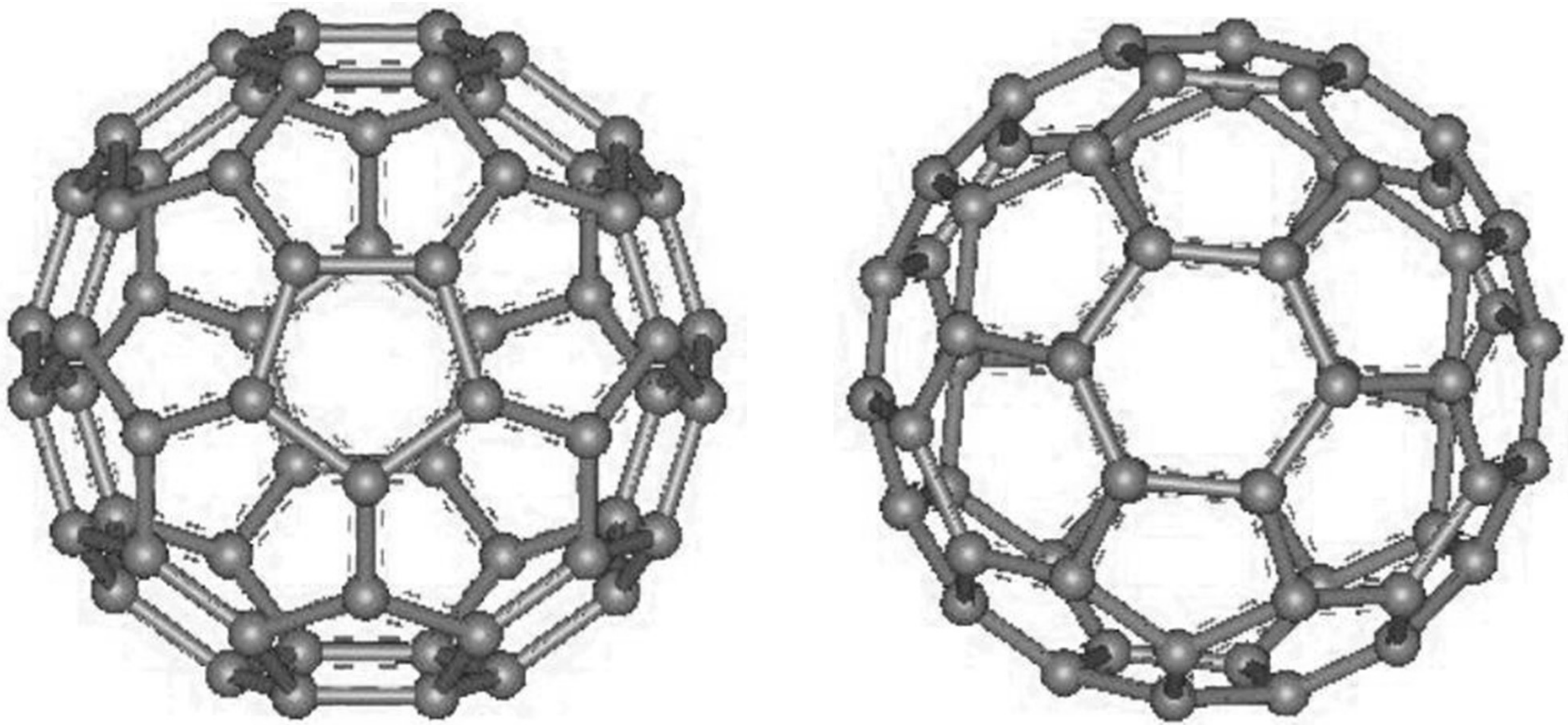
12 9 3 6

$$I_h = \{E,\ 12C_5,\ 12C_5^2,\ 20C_3,\ 15C_2,$$

I_h

$$i,\ 12S_{10},\ 12S_{10}^3,\ 20S_6,\ 15\sigma_h\}$$

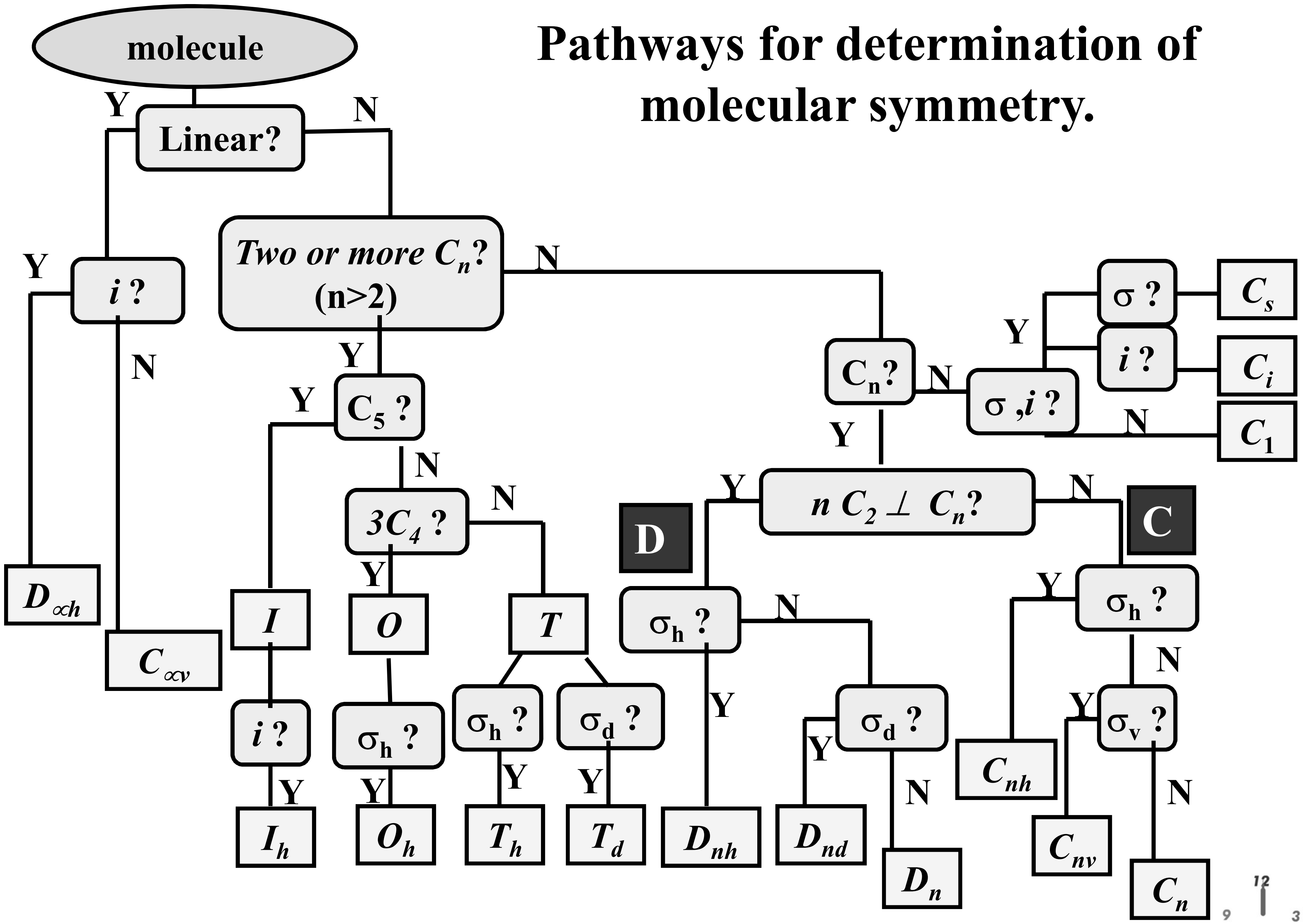
Order =120



C_{60}, bird-views from the 5-fold axis and 3-fold axis.

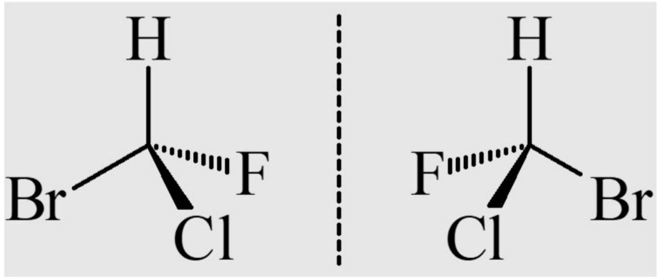
12 pentagons and 20 hexagons;

Pathways for determination of molecular symmetry.



§ 3.4 Simple Applications of symmetry

3.4.1 Chirality



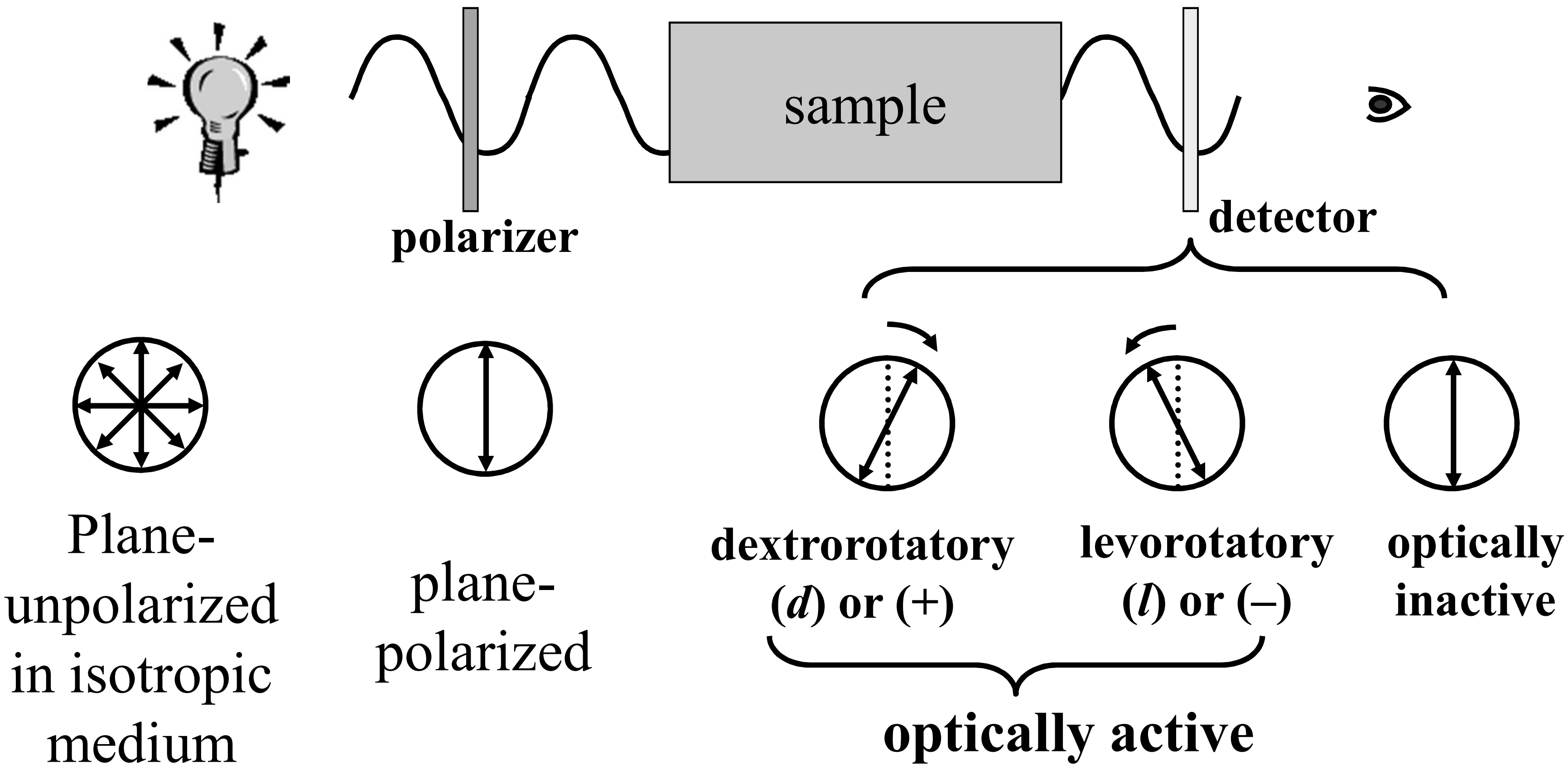
(*R*) (*S*)

A chiral molecule is a molecule that can not be superimposed on its mirror image

These molecules are:

- not superimposed on its mirror image.
- a pair of **enantiomers** (left- and right-handed isomers)
- able to rotate the plane of polarized light (**Optical activity**)
- **does not possess an axis of improper rotation, S_n (i, σ)**

Optical activity is the ability of a chiral molecule to rotate the plane of plane-polarized light.



Optical activity

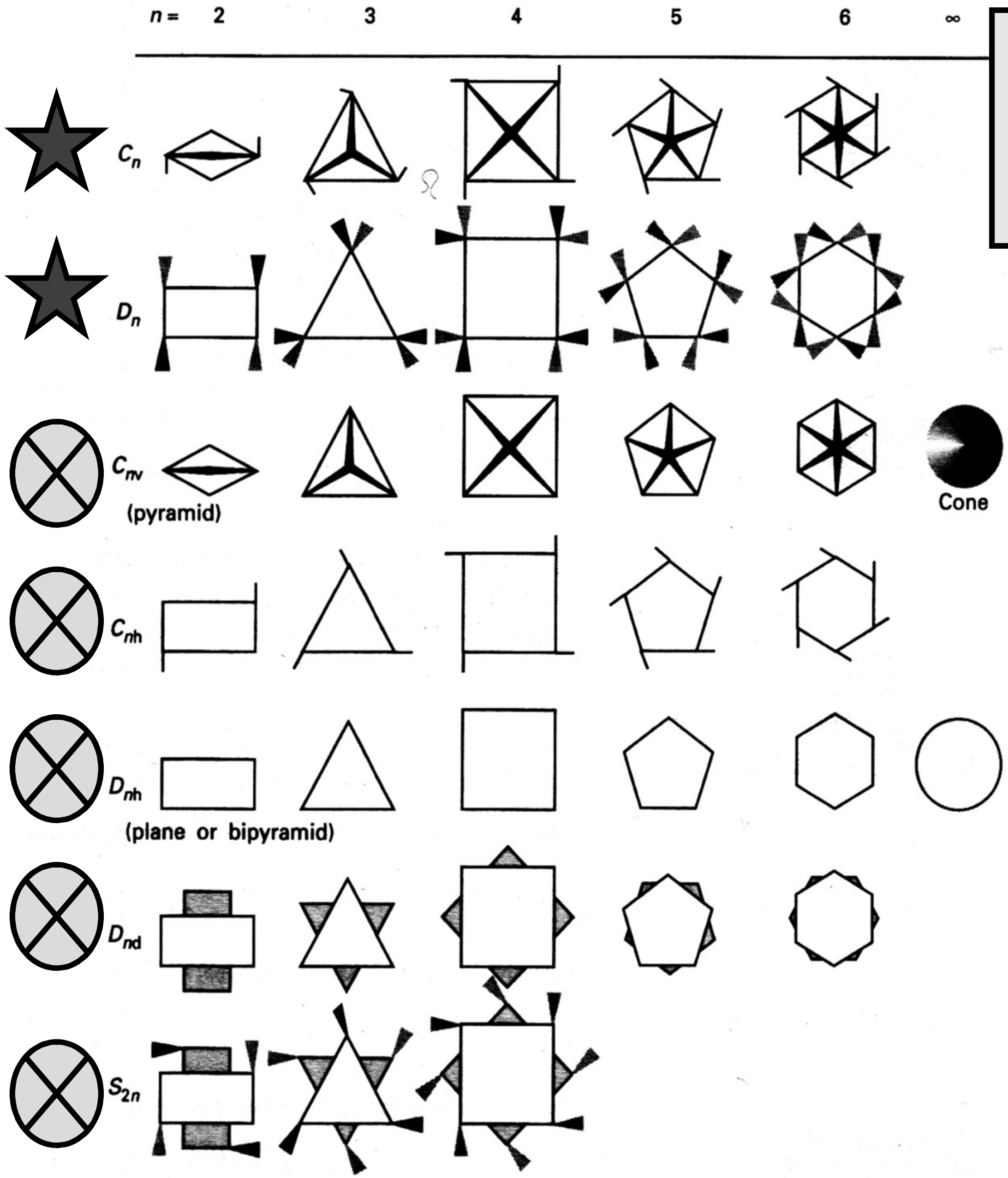
Optically inactive: **achiral molecule**
or **racemic mixture of chiral molecules**
- 50/50 mixture of two enantiomers

Optically pure: 100% of one enantiomer

Optical purity (enantiomeric excess)
= percent of one enantiomer – percent of the other

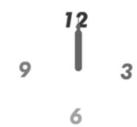
e.g., 80% one enantiomer and 20% of the other
= 60% e.e. or optical purity

- **A chiral molecule** does not possess S_n (i, σ)!



C_n and D_n may be chiral (no S_n improper axis).

Molecules of T-, O-, or I-symmetry are chiral!



- In summary, the groups that may be chiral are as follows: C_1, C_n, and D_n.
- However, not all molecules in these groups will necessarily be chiral, they are merely permitted to be.
- For example, hydrogen peroxide belongs to the group C_2, but it is **not** chiral, as free rotation about the O-O bond is possible.

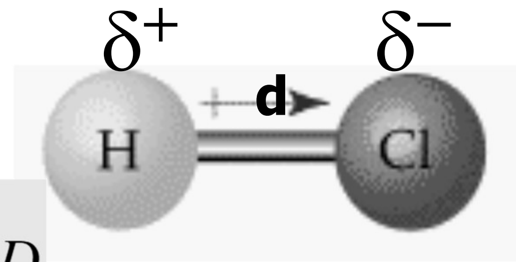
2. Polarity, Dipole Moments and molecular symmetry

A polar molecule is one with a permanent electric dipole moment.

Dipole Moments

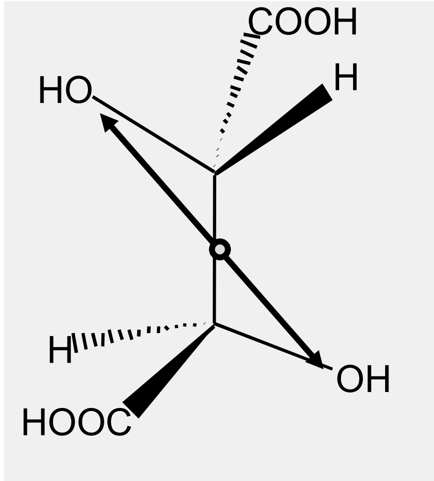
- are due to differences in atomic electronegativity
- depend on the amount of charge and distance of separation
- in Debyes (D), $\mu = \mathbf{4.8} \times \delta$ (electron charge) $\times$ **d** (angstroms)

- For one proton and one electron separated by 100 pm, the dipole moment would be:



$$\mu = (1.60\times10^{-19})(100\times10^{-12}m)\left(\frac{1D}{3.34\times10^{-30}C\cdot m}\right) = 4.80D$$

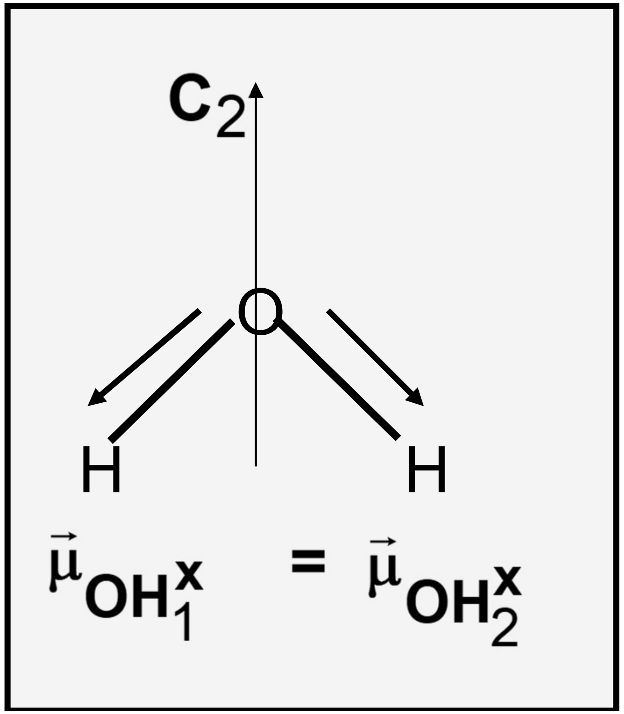
Permanent Dipole Moments



$\mu = 0$
inversion

Meso-tartaric acid

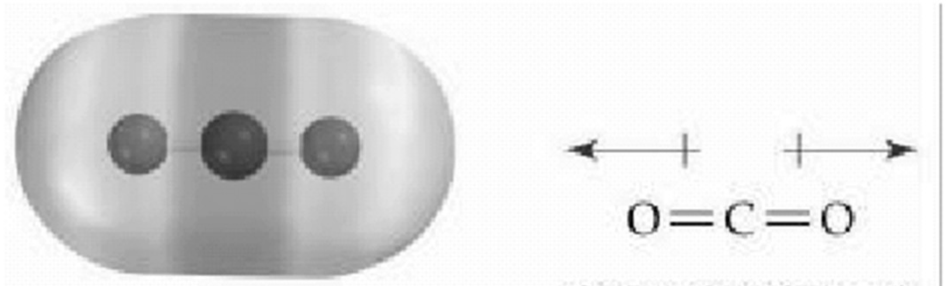
(a) Only molecules belonging to the groups C_n, C_{nv} and C_s may have an electric dipole moment.



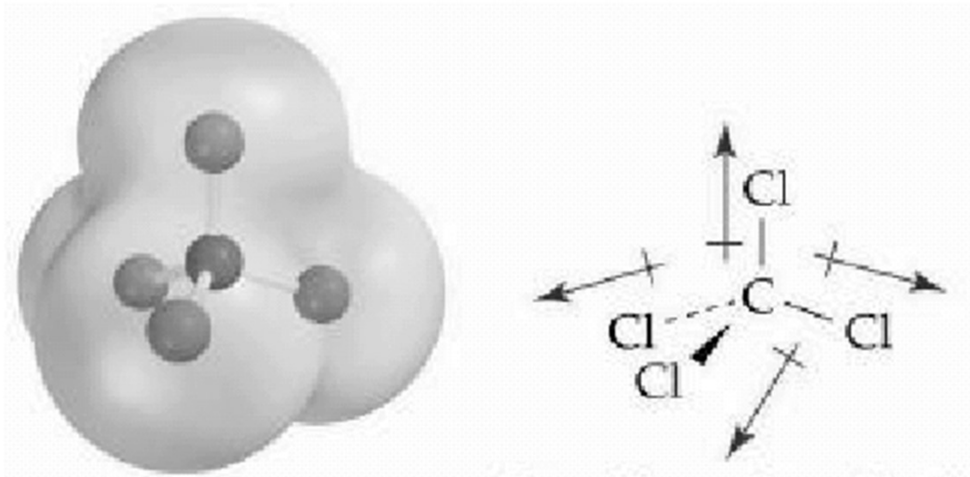
(b) Dipole moment cannot be perpendicular to any mirror plane or C_n.

Molecular Dipole Moments

Polar and Nonpolar Molecules

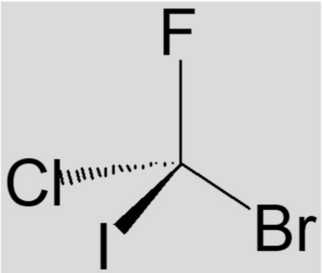


Carbon dioxide ($\mu = 0$)

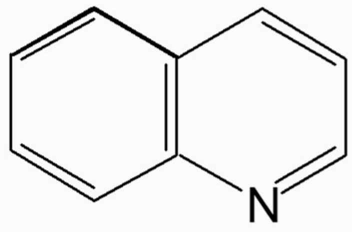


Tetrachloromethane ($\mu = 0$)

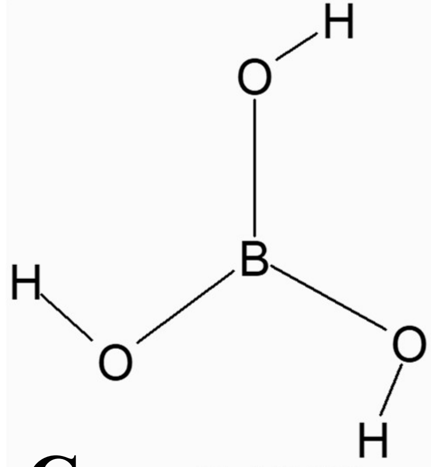
Molecular Dipole Moments and molecular symmetry



$\mathbf{C_1}$

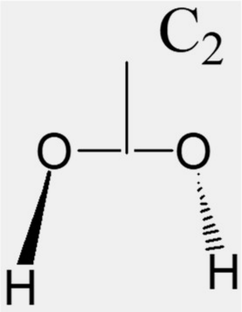


Quinoline $\mathbf{C_S}$

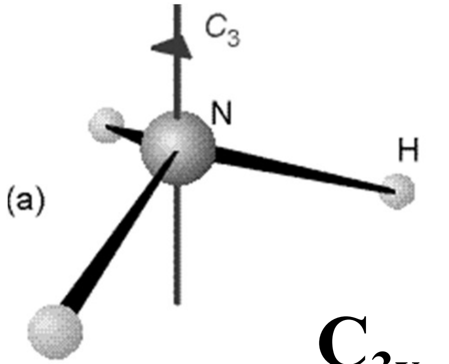


$\mathbf{C_{3h}}$ $B(OH)_3$

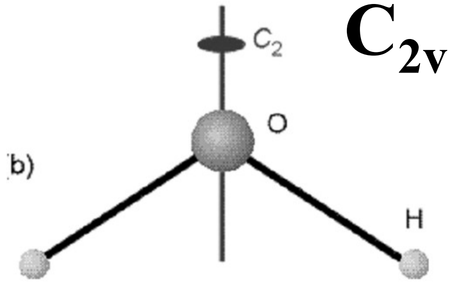
$\mu \neq 0$	$\mu \neq 0$ **in plane**	$\mu = 0$ σ_h **symmetry**



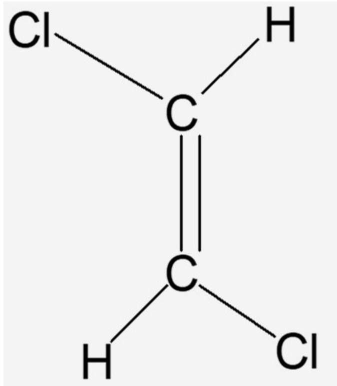
H_2O_2



$\mathbf{C_{3v}}$



$\mathbf{C_{2v}}$

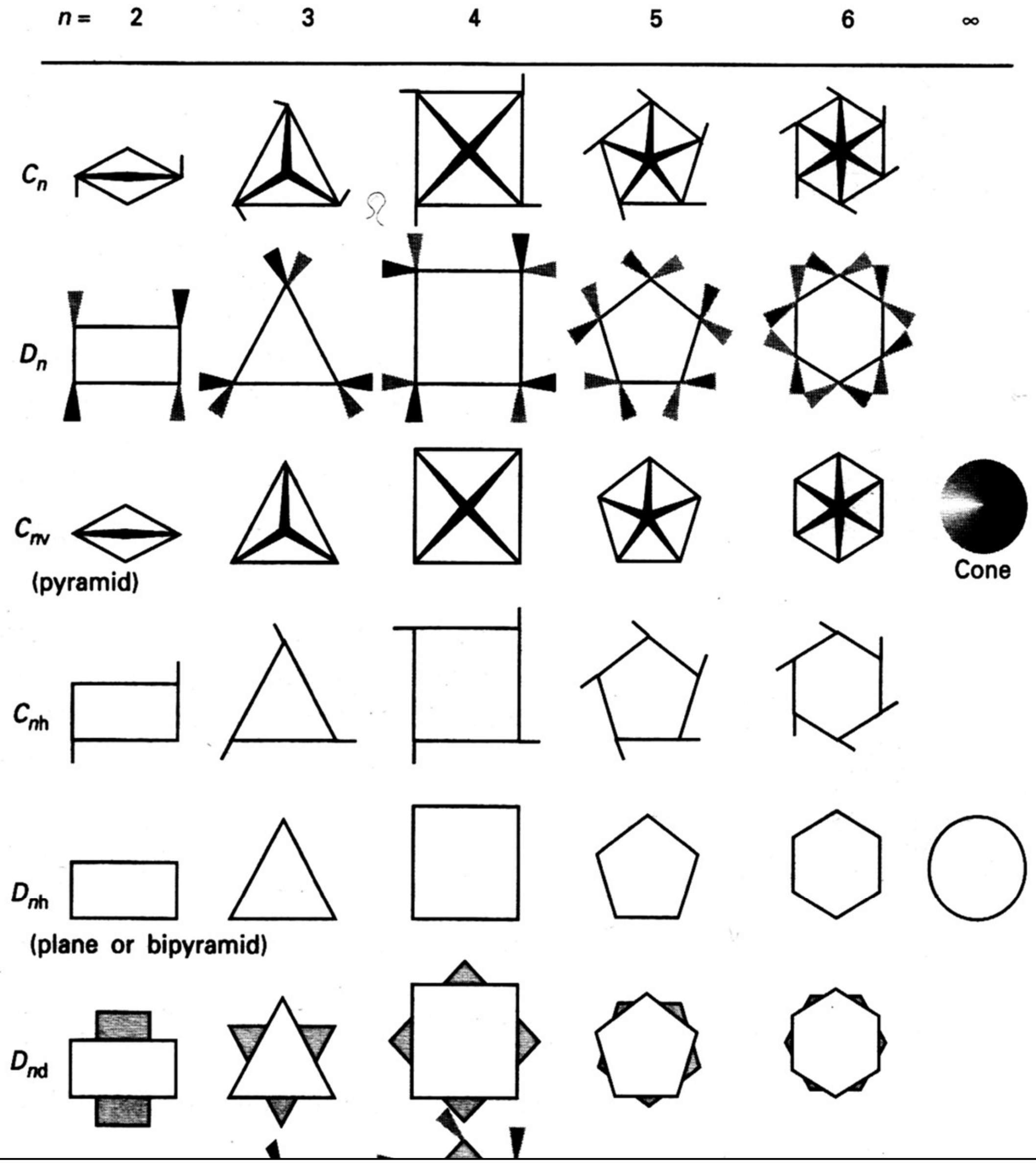


$\mathbf{C_{2h}}$

Trans CHCl=CHCl

$\mu \neq 0$ **along** $\mathbf{C_2}$	$\mu \neq 0$ **along** $\mathbf{C_3}$	$\mu \neq 0$ **along** $\mathbf{C_2}$	$\mu = 0$ **inversion**

Summary:



Groups C_1, C_i, and C_s

C_n, C_{nv} and C_s may have an electric dipole moment.

C_n and D_n may be chiral (no S_n improper axis).

Summary of this chapter

Symmetry elements & symmetry operations

Element	Name	Operation
C_n	**n-fold rotation**	**Rotate by 360° /n**
σ	**Mirror plane**	**Reflection through a plane**
i	**Center of inversion**	**Inversion through the center**
S_n	**Improper rotation axis**	**Rotation as C_n followed by reflection in perpendicular mirror plane**
E	**identity**	**Do nothing**

summary

§ 3 Point Groups, the symmetry classification of molecules

Point group:

- All symmetry operations pertaining to available symmetry elements in any molecule/object have at least one common point unchanged and constitute a group, thus called point group.
- Elements of a point group are symmetry operations.
- For a given point group, its order corresponds to the total number of symmetry operations.

(1) Point groups of low symmetry:

C_1; C_s; C_i

(2) Point groups with only one n-fold rotational axis:

C_n; C_{nh}; C_{nv}; $C_{\infty v}$

(3) The S_{2n} groups: S_4; S_6; S_8

(4) Dihedral groups containing nC_2 axes perpendicular to the principal axis C_n:

D_n; D_{nh}; D_{nd}; $D_{\infty h}$

(5) The cubic groups: T, T_h, T_d; O, O_h; I, I_h

How to discern S_n, D_n, and D_{nd} groups?

Key points:

1. S_n group exists only when n = even; objects of S_n group also have a $C_{n/2}$ axis; a S_n group is simply n-order.

2. Objects of D_n group have exclusively a C_n axis and n C_2 axes. A D_n group is 2n-order.

3. Objects of D_{nd} group have not only a C_n axis and n C_2 axes, but also ***n*** $\sigma_{d/v}$ mirror planes & a S_{2n} axis. A D_{nd} group is 4n-order.

$$\boldsymbol{S_n^{\,1} = \sigma_h C_n^{\,1} \qquad S_n^{\,m} = (S_n^{\,1})^m = (\sigma_h)^m (C_n^{\,1})^m = (\sigma_h)^m\, C_n^{\,m}}$$

i) If ***n* = *odd***,

For ***m* = *odd*=2*k*-1** (k=1,2,…, (n+1)/2), ***n* + *m* = *even***,

$\boldsymbol{S_n^{\,m} = (\sigma_h)^m C_n^{\,m} = \sigma_h C_n^{\,2k-1}}$ (when m=n, $S_n^{\,n} = \sigma_h C_n^{\,n} = \sigma_h$) &
$\boldsymbol{S_n^{\,m+n} = (\sigma_h)^{m+n}\, C_n^{\,m+n} = C_n^{\,m}}$ (when m=n, $S_n^{\,2n} = E$)

For *m* = *even*=2*k*(k=1,2,…, (n-1)/2), ***n*+*m* = *odd*,**

$$\boldsymbol{S_n^{\,m} = (\sigma_h)^m C_n^{\,m} = C_n^{\,m},\ S_n^{\,m+n} = (\sigma_h)^{m+n}\, C_n^{\,m+n} = \sigma_h C_n^{\,m}}$$

Thus, a $\boldsymbol{S_n}$ ***(n=odd)*** axis produces a set of unique operations $\{E,\ C_n^{\,m}\ (m=1,\ldots,n-1),\ \sigma_h,\ \sigma_h C_n^{\,m}\ (m=1,\ldots,n-1)\}$, that can be produced by $C_n + \sigma_h$.

ii) If n = even≠4p,

For m =even=2k (k=1,2,…,n/2), n+m =even

$\boldsymbol{S_n^{\,m} = (\sigma_h)^m C_n^{\,m} = C_n^{\,m} = C_{n/2}^{\;m/2}}$ (when m=n, $S_n^{\,n} = C_n^{\,n} = E$),

i.e., a $\boldsymbol{C_{n/2}^{\,m/2}}$ also exists!

$\boldsymbol{S_n^{\,m+n} = (\sigma_h)^{m+n}\, C_n^{\,m+n} = C_n^{\,m} = S_n^{\,m}}$ (not unique!)

For m = odd = 2k-1 (k=1,2,…,n/2), n+m = odd

when m=n/2, $S_n^{\,n/2} = \sigma_h C_n^{\,n/2} = \sigma_h C_2^{\,1} = i$, *i.e., an inversion center exists!* $S_n^{\,m} = (\sigma_h)^m C_n^{\,m} = \sigma_h C_n^{\,m} = S_n^{\,n+m} = \sigma_h C_n^{\,m} = S_n^{\,m}$ *(not unique!)*

The $\boldsymbol{S_n}$ (n=even ≠4k) is equivalent to $\boldsymbol{C_{n/2} + i}$.

- 对称操作和对称元素
- 对称元素的组合及群的概念
- 分子的点群
- 对称性与偶极矩、旋光性的关系