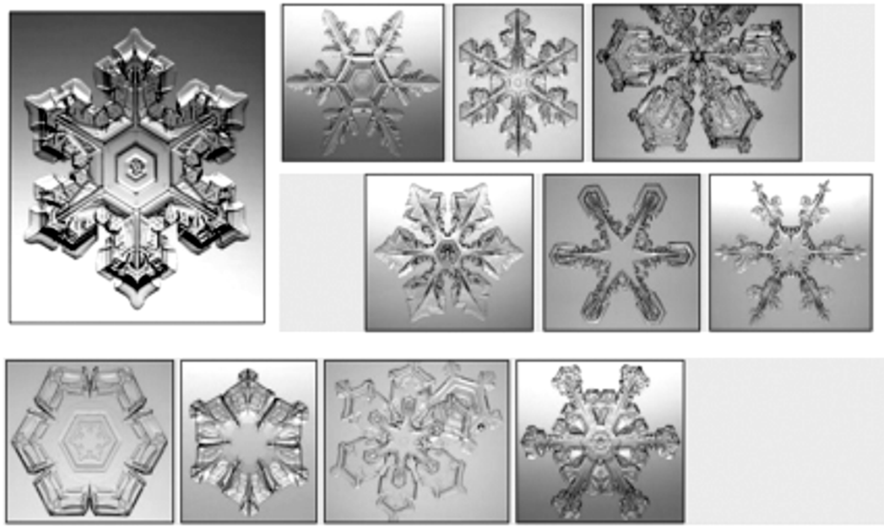
Chapter 3

Molecular symmetry and symmetry point group



Why do we study the symmetry concept?

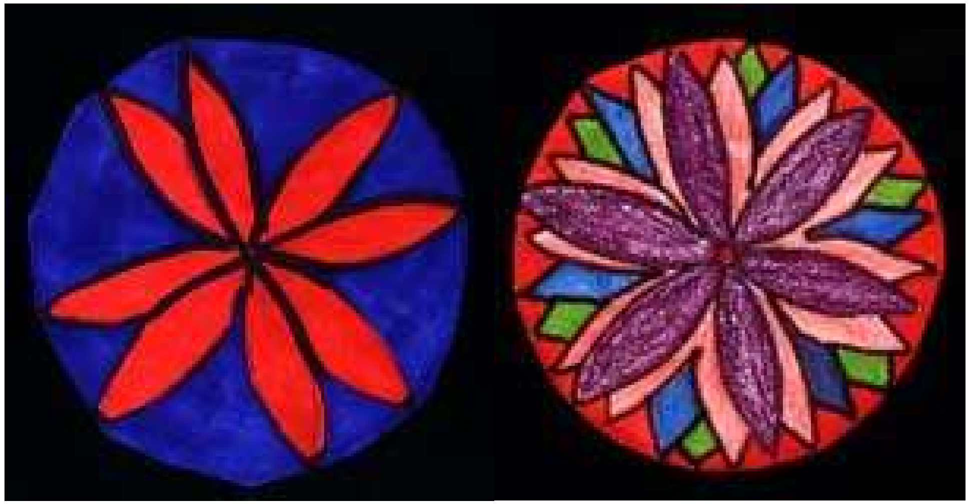
- **The molecular configuration can be expressed more simply and distinctly.**
- **The determination of molecular configuration is greatly simplified.**
- **It assists giving a better understanding of the properties of molecules.**
- **To direct chemical syntheses; the compatibility in symmetry is a factor to be considered in the formation and reconstruction of chemical bonds.**

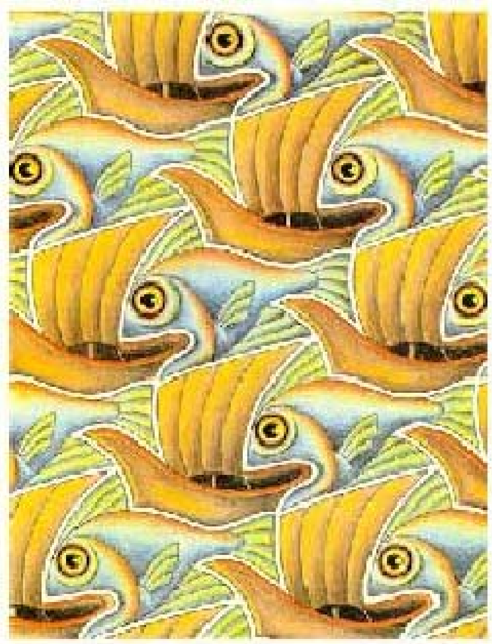
§ 1 Symmetry elements and symmetry operations

➢**Symmetry** exists all around us and many people see it as being a thing of beauty.

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

➢The systematic discussion of symmetry is called : Some objects are more symmetrical than others.



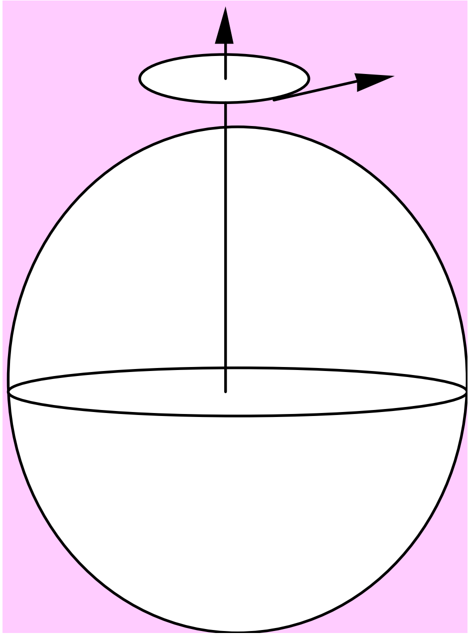


1. Symmetry elements and symmetry operations

symmetry operation

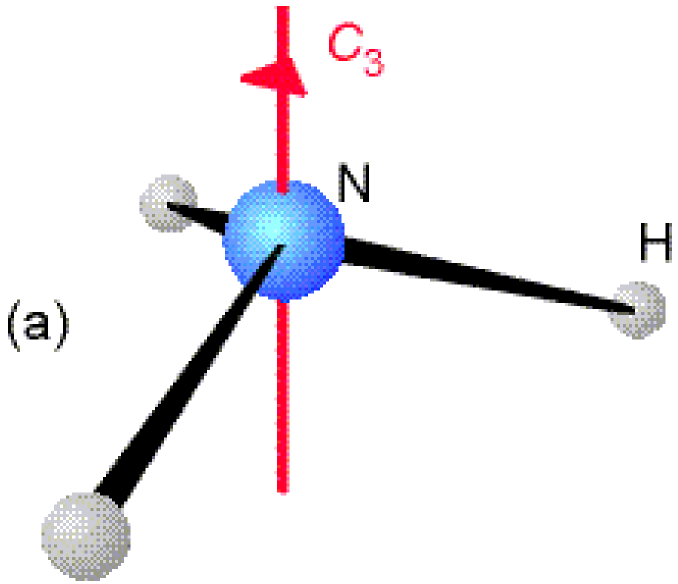
- **A action that leaves an object the same after it has been carried out is called symmetry operation.**

Example:

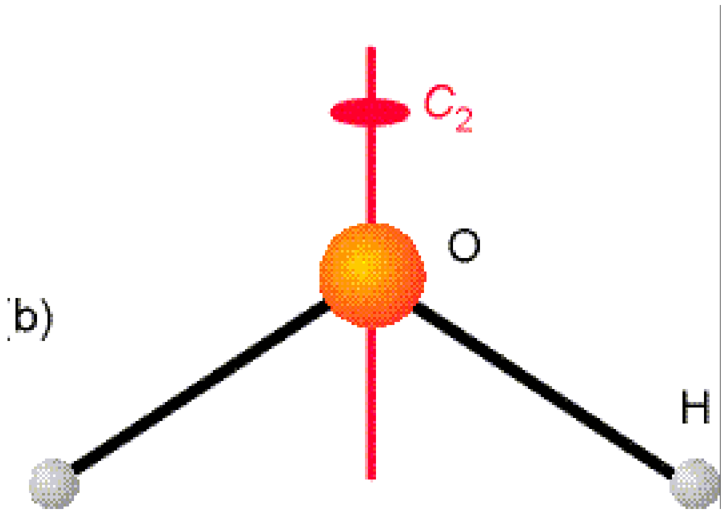


Any rotation of sphere around axis through center brings sphere over into itself

Example:



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

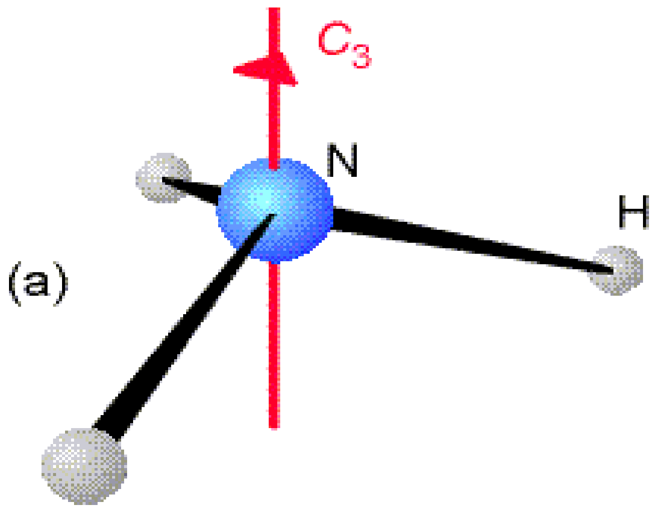


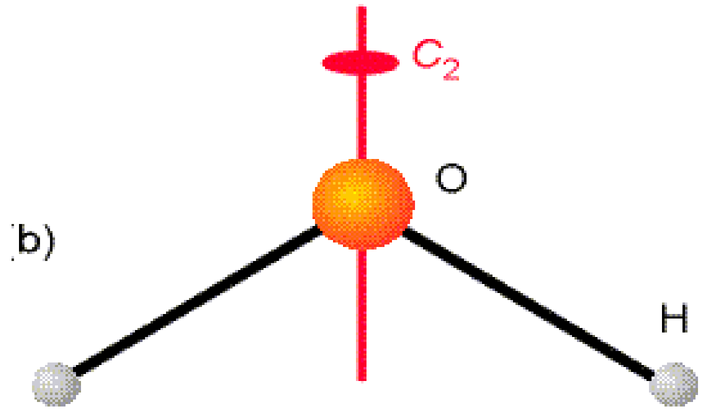
(b) an H_2O molecule has a twofold (C_2) axis.

symmetry elements

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

Example:



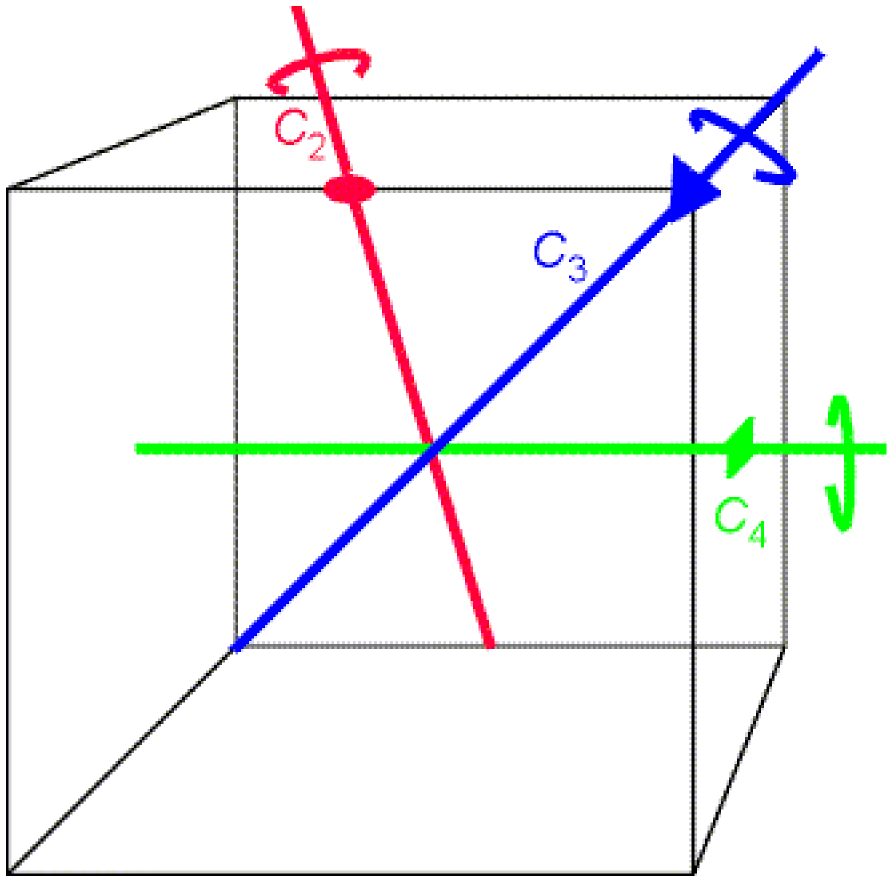


(a) An NH_3 molecule has a threefold (C_3) axis

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

NH_3 has higher rotation symmetry than H_2O

Symmetry elements



Some of the symmetry elements of a cube, the twofold, threefold, and fourfold axes.

Symmetry Operation

Symmetry operations are:

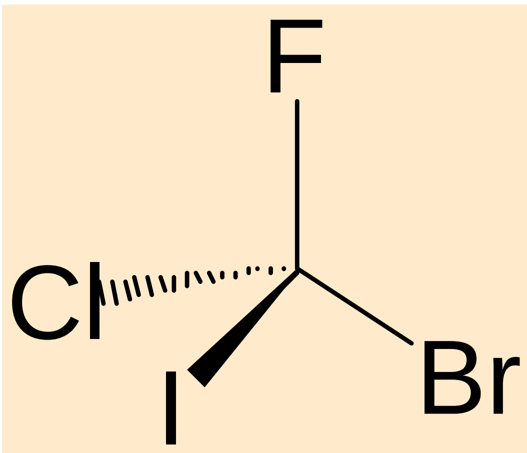
Rotation | **Reflection** | **Inversion**

The corresponding symmetry elements are:

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

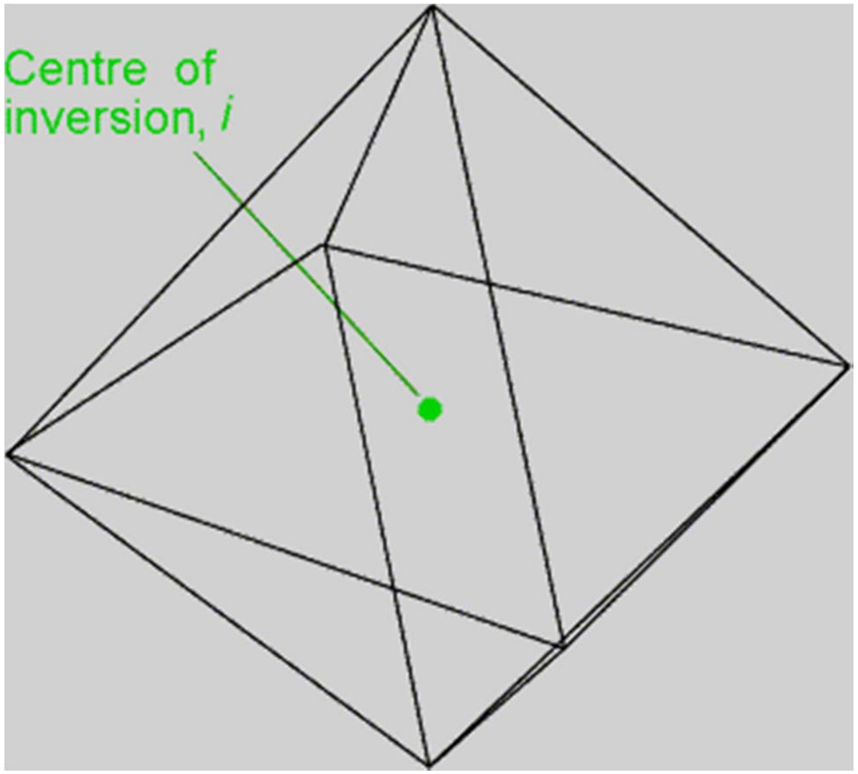
1) The identity (E)

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



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

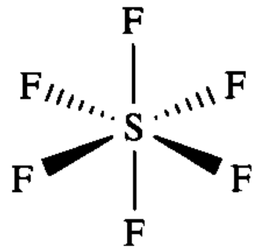
•An object has a center of inversion, ***i***, if it can be reflected through a center to produce an indistinguishable configuration.

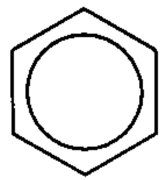


A regular octahedron has a centre of inversion (i).

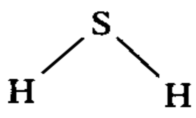
For example

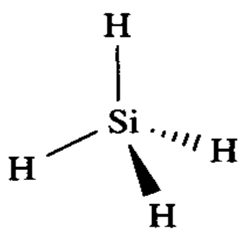
These have a center of inversion i.



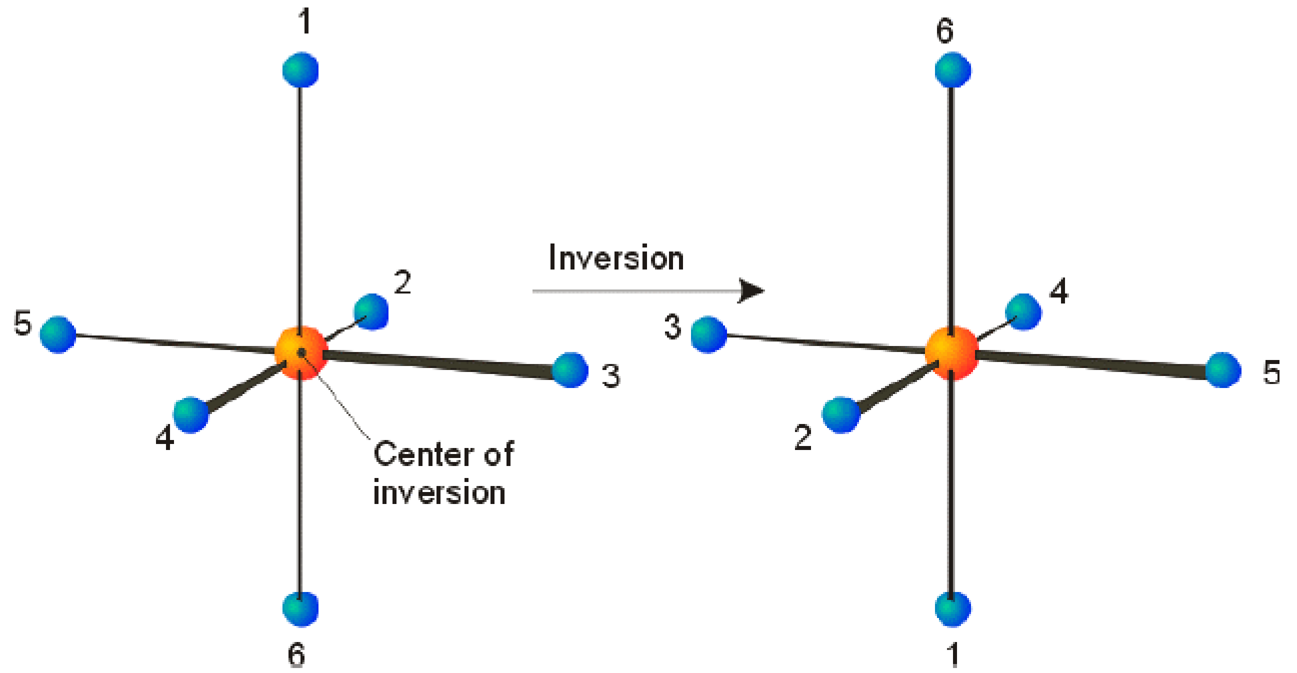


These do not have a center of inversion.





- Inverts all atoms through the centre of the object



- Its matrix representation

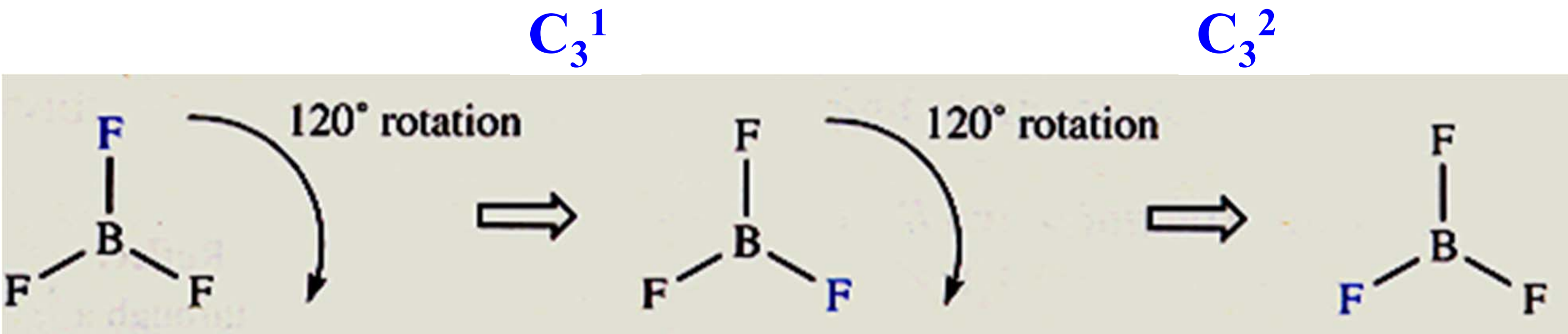
$$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

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

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

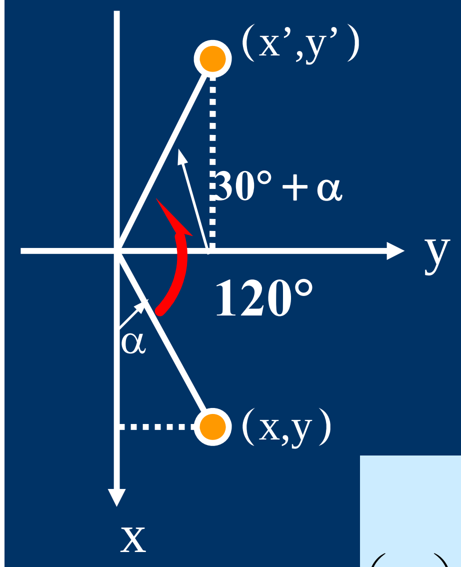
Rotation about an n-fold axis (rotation through 360°/n) is denoted by the symbol C_n.

- Example: Rotation of trigonal planer BF_3.
  - One three-fold (C_3) rotation axes. ($\alpha=2\pi/3$)



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

The matrix representations:



$C_3^{\,1}$

x'=-rsin(30° + α)= -rsin30°cosα - rcos30°sinα

= (-1/2)x + (-√3/2)y

y'=rcos(30° + α)= rcos30°cosα - rsin30°sinα

= (√3/2)x + (-1/2)y

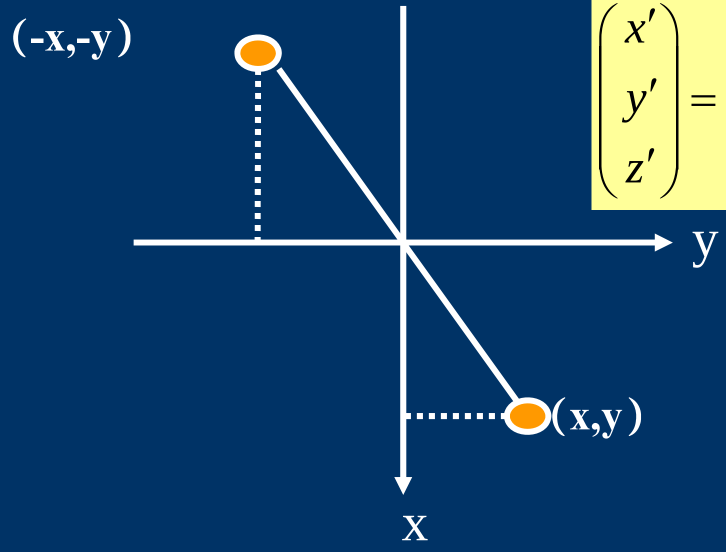
$$\begin{pmatrix} x_1 \\ y_1 \\ z_1 \end{pmatrix} = C_3^1 \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} \cos\frac{2\pi}{3} & -\sin\frac{2\pi}{3} & 0 \\ \sin\frac{2\pi}{3} & \cos\frac{2\pi}{3} & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -\frac{x}{2} - \frac{\sqrt{3}}{2} y \\ \frac{\sqrt{3}}{2} x - \frac{y}{2} \\ z \end{pmatrix}$$

$$\begin{pmatrix} x_2 \\ y_2 \\ z_2 \end{pmatrix} = C_3^2 \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} \cos\frac{4\pi}{3} & -\sin\frac{4\pi}{3} & 0 \\ \sin\frac{4\pi}{3} & \cos\frac{4\pi}{3} & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -\frac{x}{2} + \frac{\sqrt{3}}{2} y \\ -\frac{\sqrt{3}}{2} x - \frac{y}{2} \\ z \end{pmatrix}$$

The matrix representations:

Conditions:

- The centre of mass of the molecule is located at the origin of the Cartesian Coordinate System
- Principle axis is aligned with the z-axis



C_2

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = C_2 \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} \cos\pi & -\sin\pi & 0 \\ \sin\pi & \cos\pi & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -x \\ -y \\ z \end{pmatrix}$$

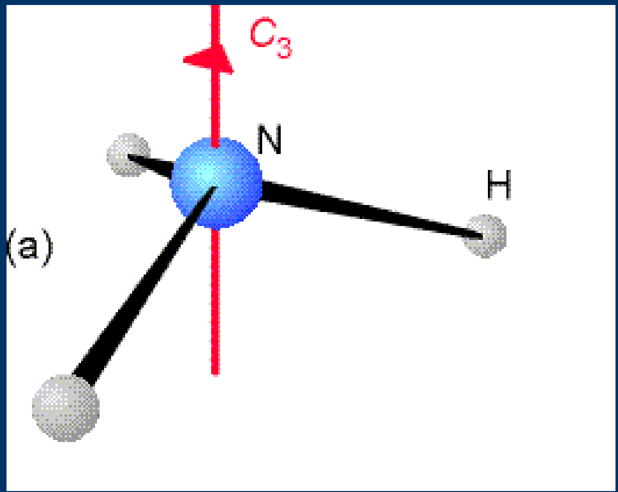
C_n

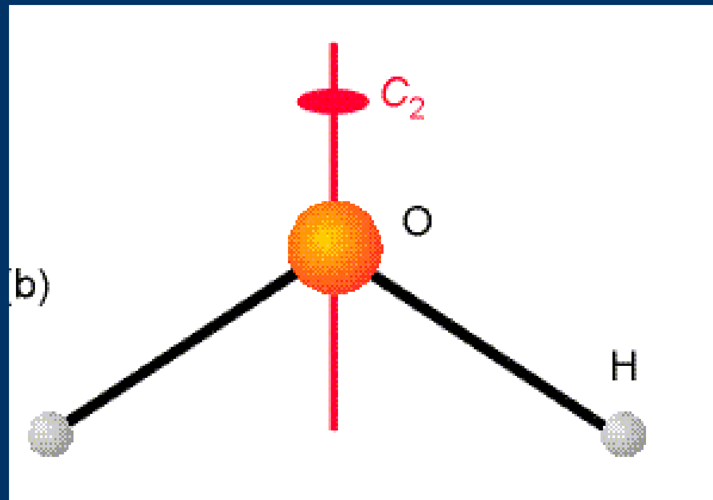
$$C_n^{\ k} = \begin{pmatrix} \cos\alpha & -\sin\alpha & 0 \\ \sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

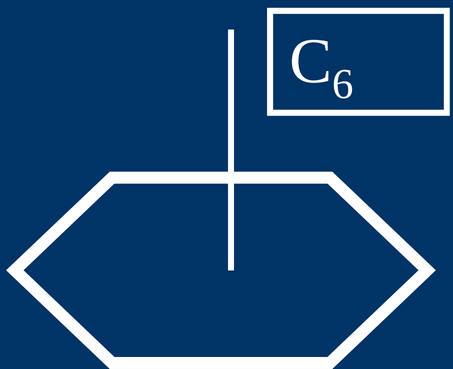
$$\alpha = \frac{2k\pi}{n}$$

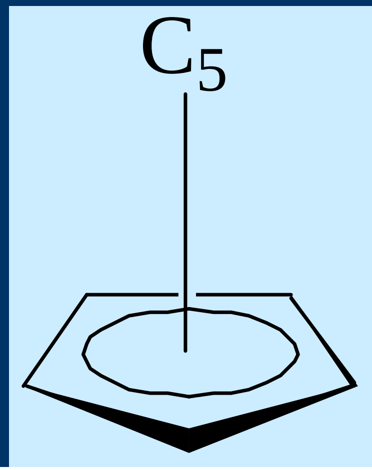
For example

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



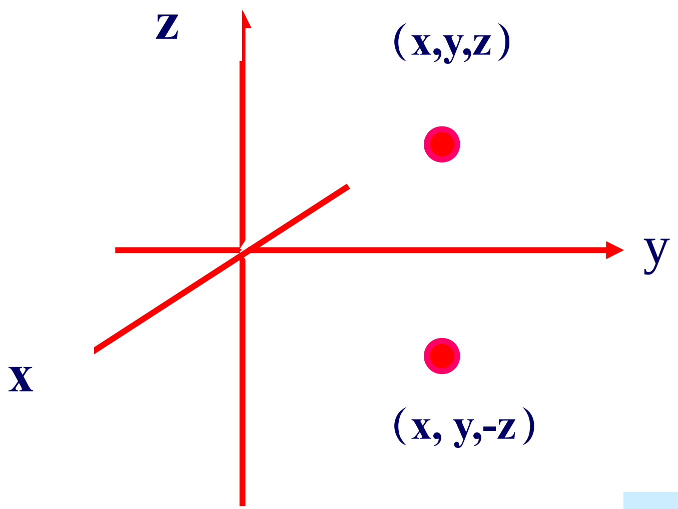






4) Reflection and the Mirror plane (σ)

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



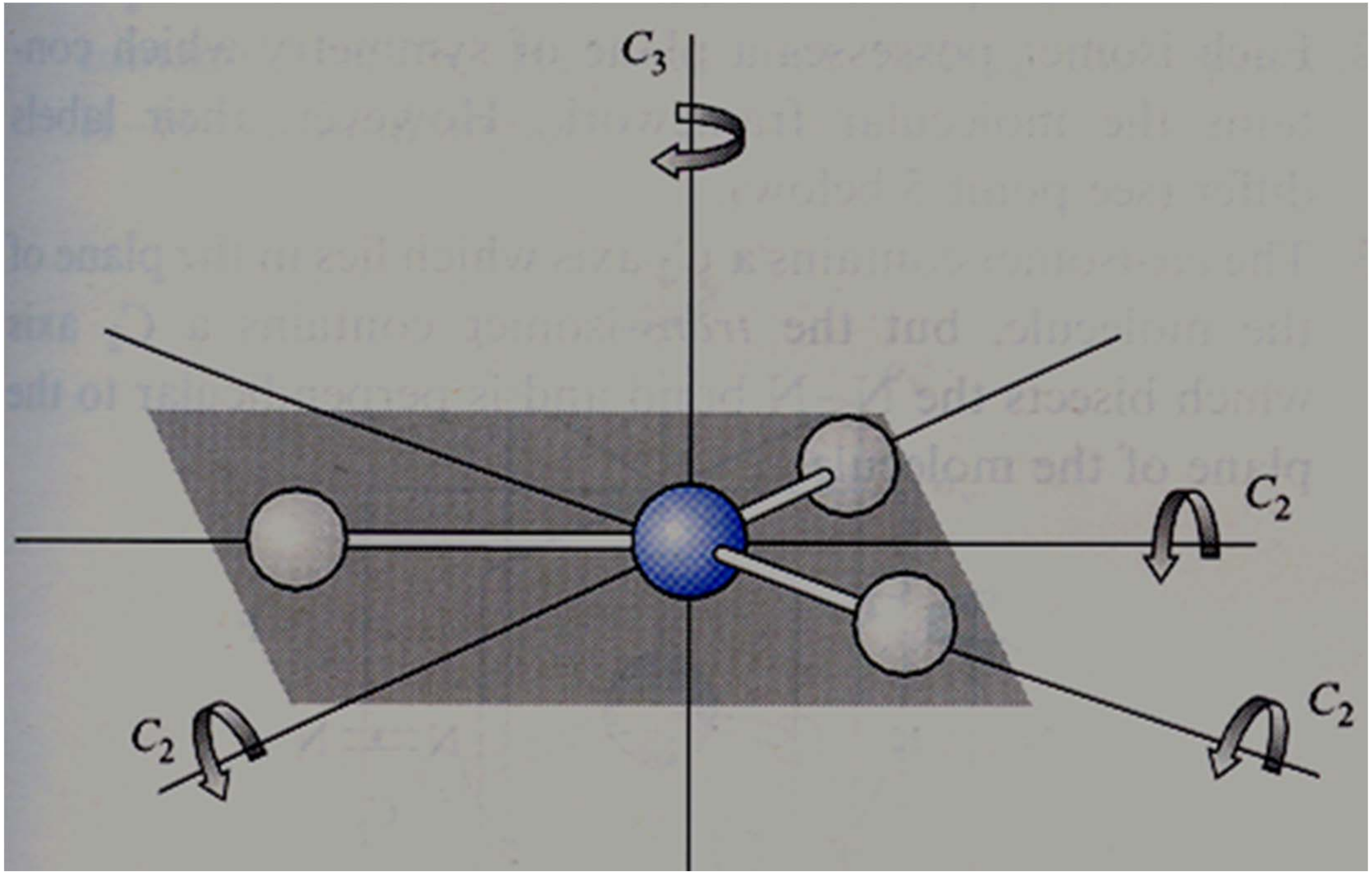
$$\sigma_{xy} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

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

- **There are three types of mirror planes:**
  - If the plane is **perpendicular** to the vertical principle axis then it labeled $\boldsymbol{\sigma_h}$.
  - If the plane **contains** the principle axis then it is labeled σ_v.
  - If a σ plane **contains** the principle axis and **bisects** the angle between two adjacent 2-fold axes then it is labeled σ_d.

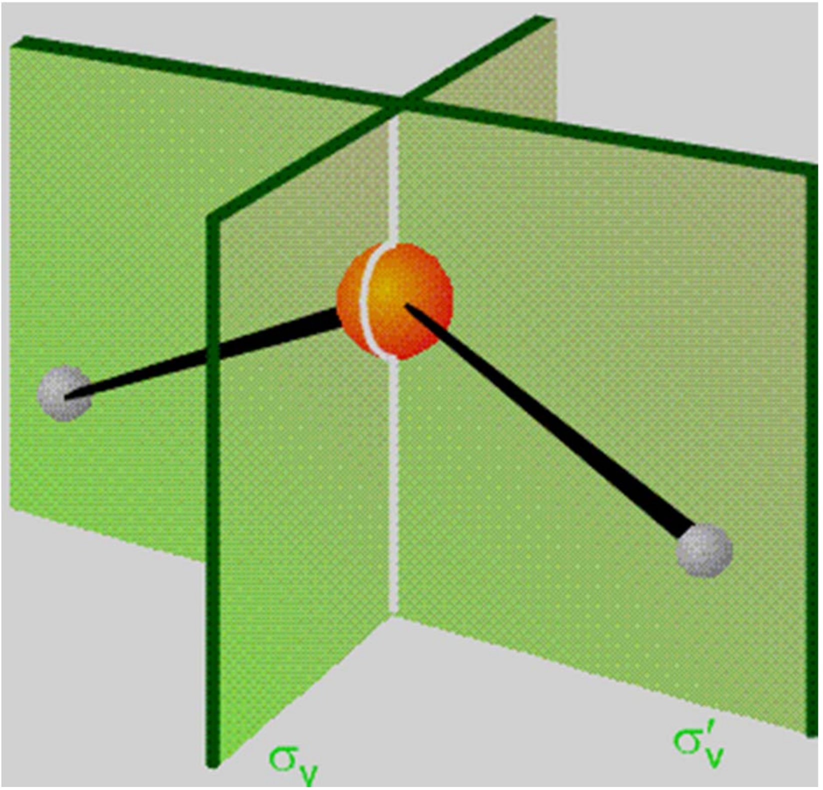
If the plane is **perpendicular** to the vertical principle axis then it labeled σ_h.

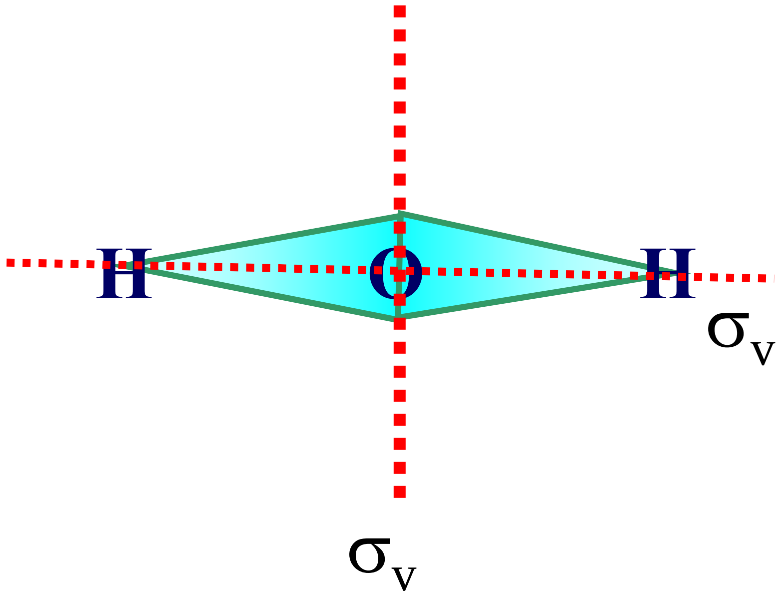
- Example: BF_3 also has a σ_h plane of symmetry.



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

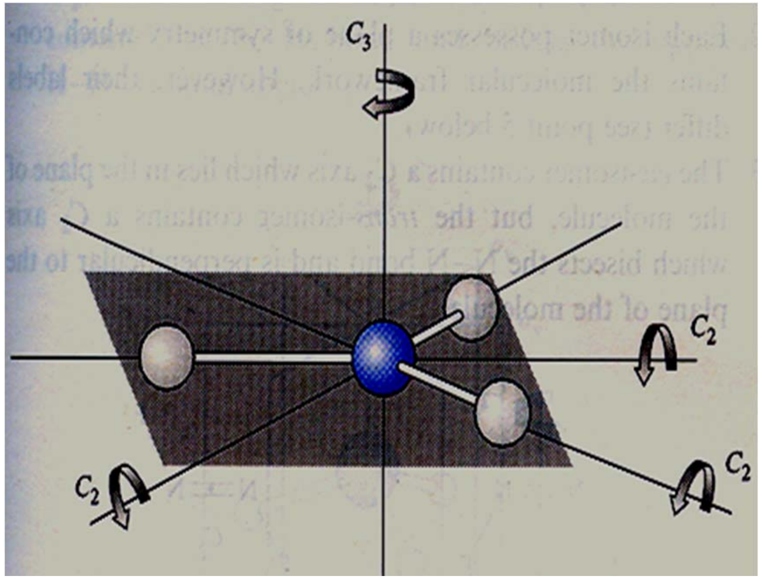
- Example: Water
  - Has a C_2 principle axis.
  - Has two planes that contain the principle axis, σ_v and σ_v'.

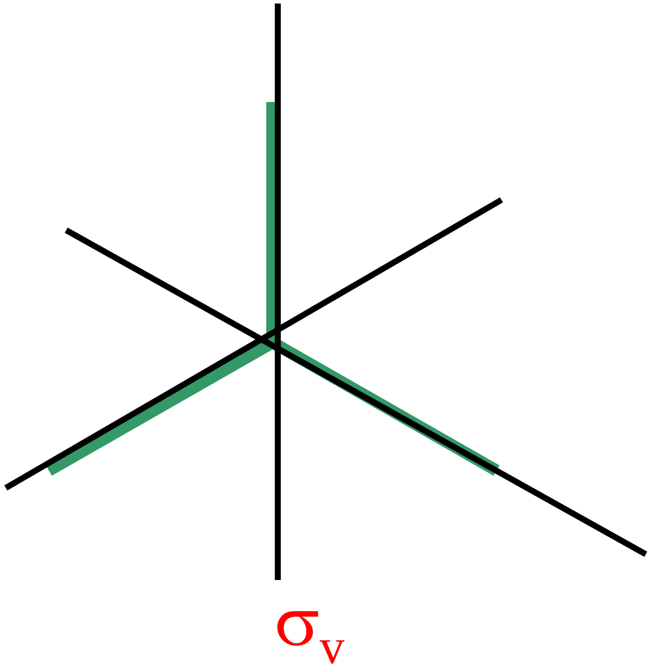




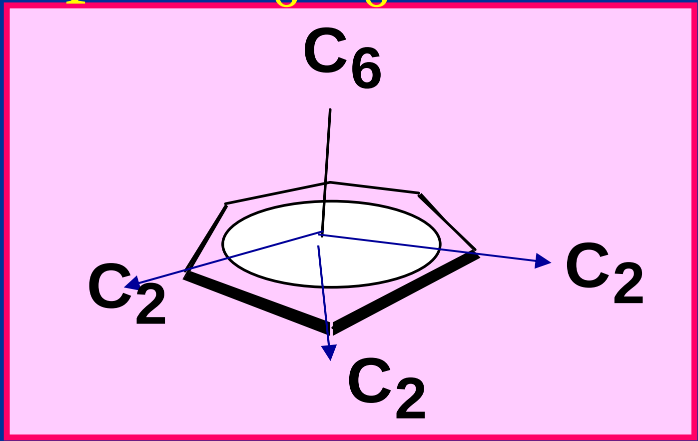
If a σ plane **contains** the principle axis and **bisects** the angle between two adjacent 2-fold axes then it is labeled σ_d.(*Dihedral* mirror planes)

- Example: BF_3
  - Has a C_3 principle axis
  - Has three-C_2 axes.
  - Has three σ_d planes (?).

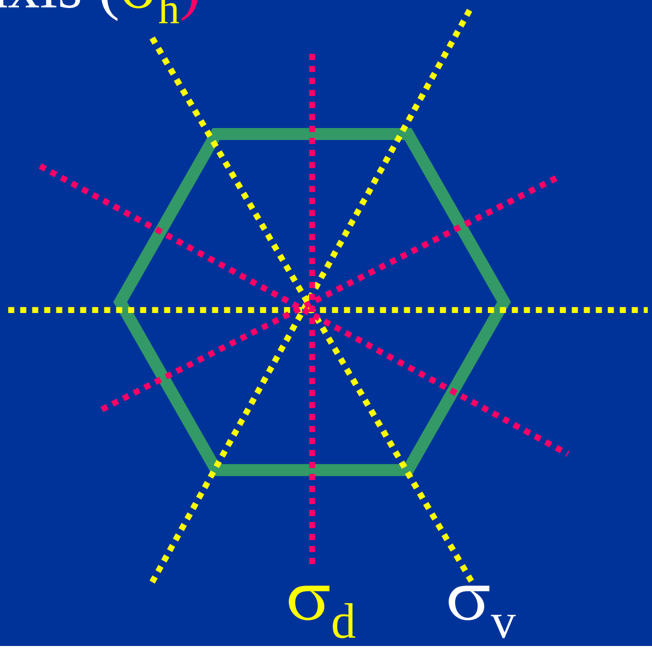


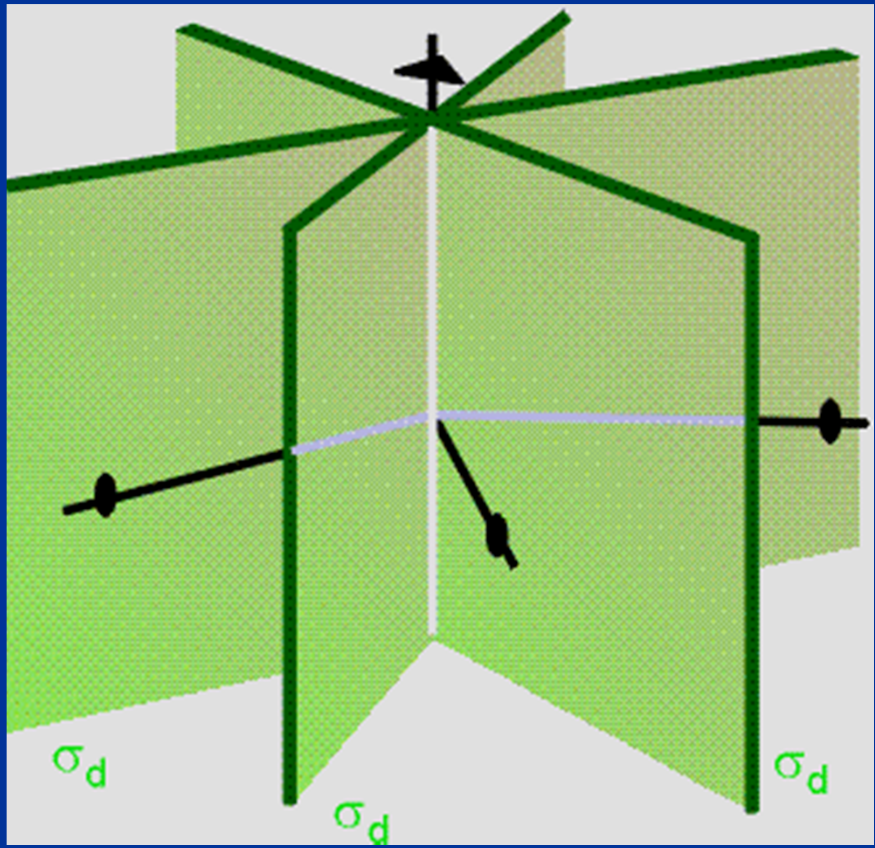


Example: C_6H_6



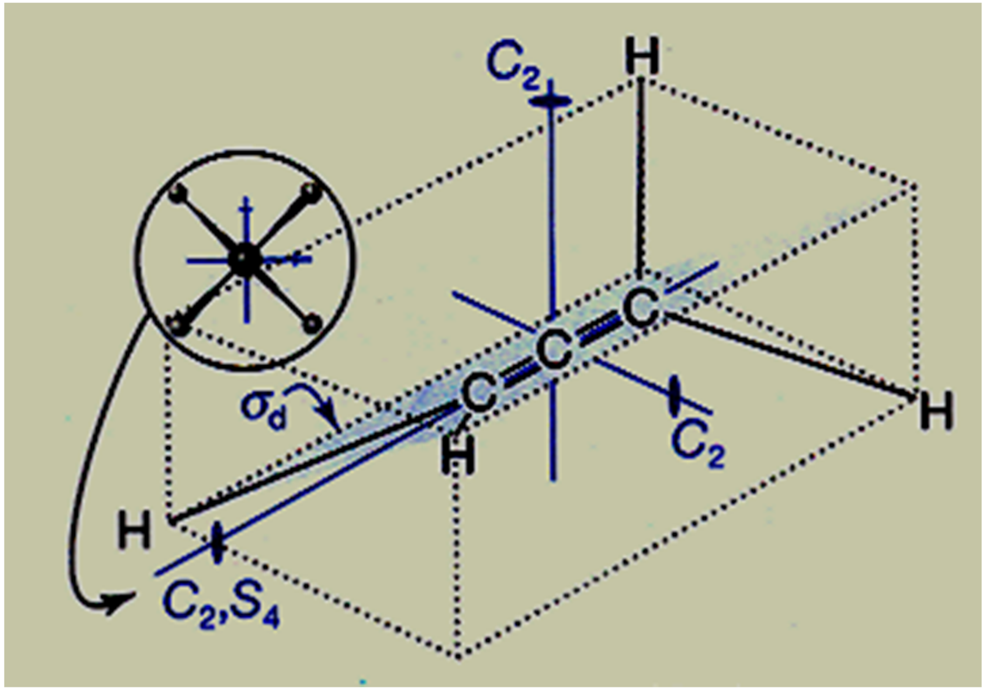
Benzene has one mirror plane perpendicular to the principle C_6 axis (σ_h)

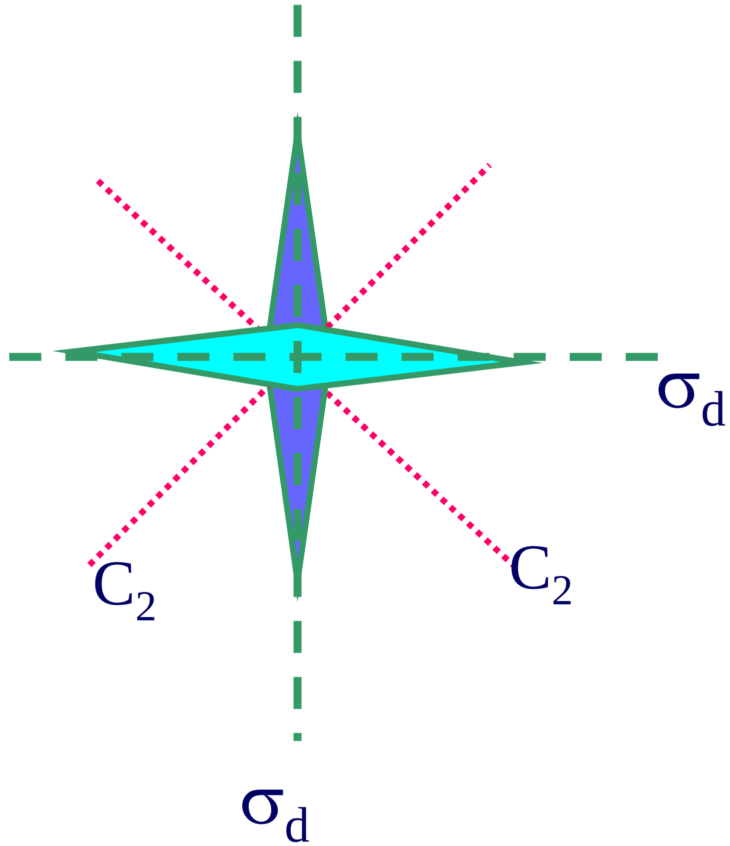




Dihedral mirror planes (σ_d) bisect the C_2 axis perpendicular to the principle axis.

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

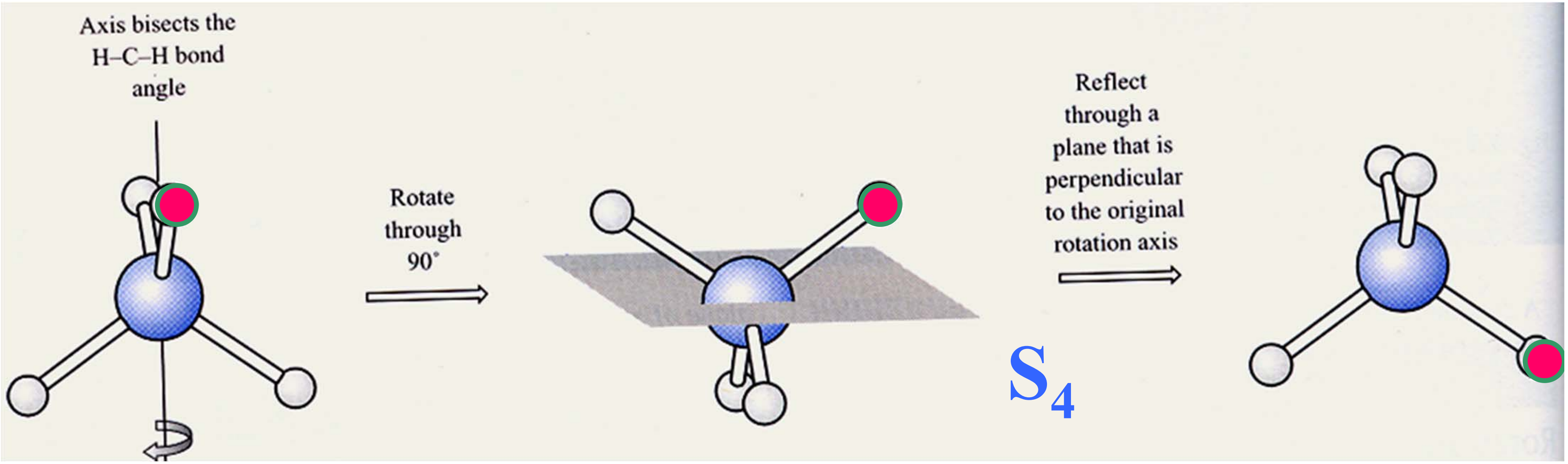




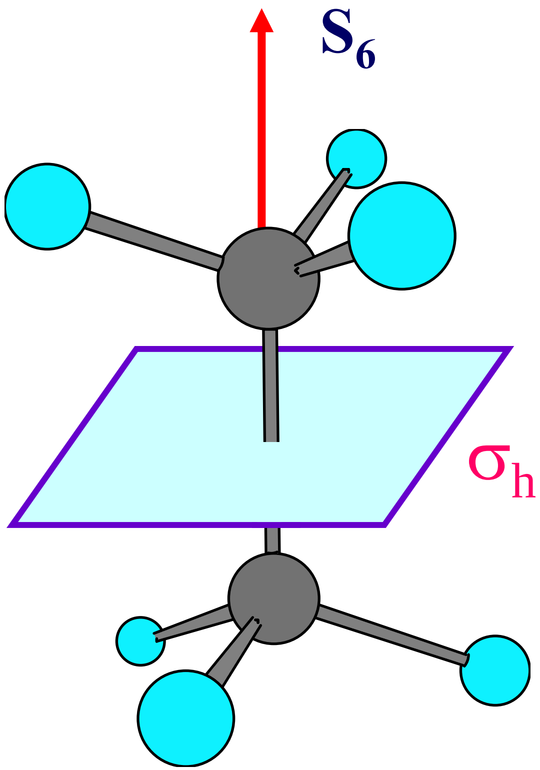
5) The improper rotation axis

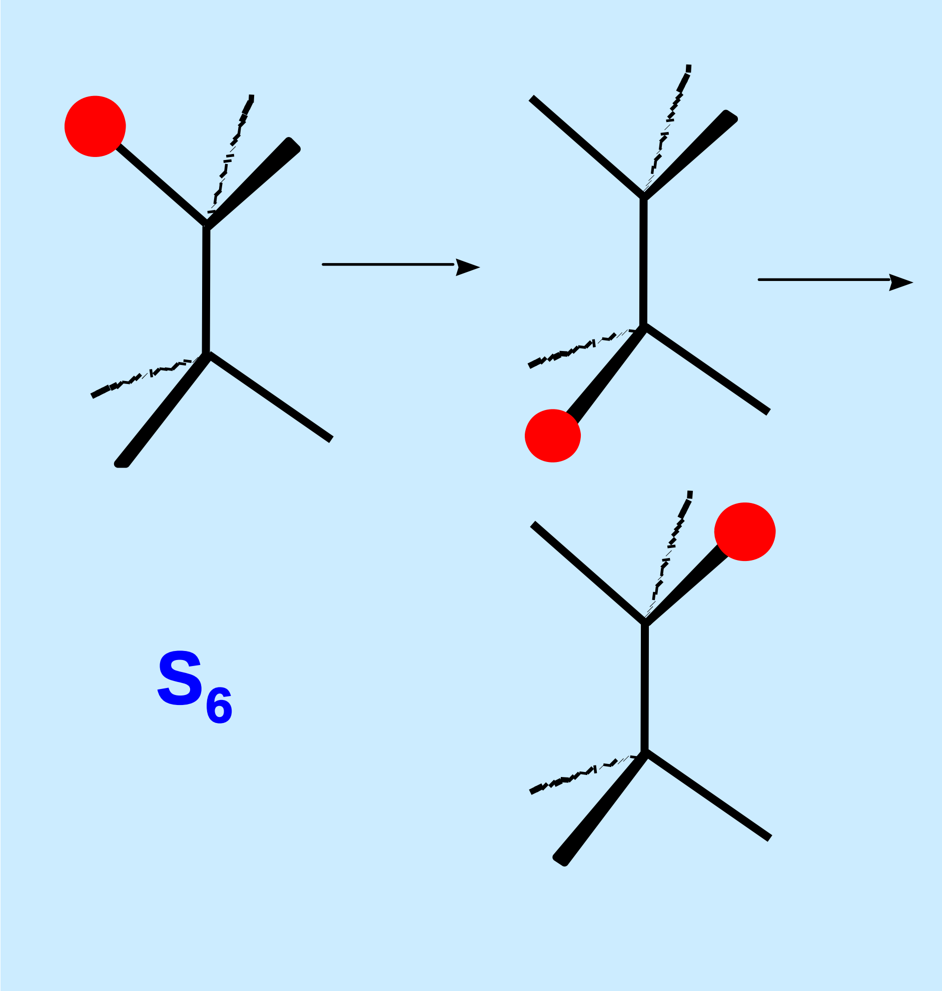
a. *n*-fold rotation + reflection, Rotary-reflection axis (S_n)

Rotate 360° /n followed by reflection in mirror plane perpendicular to axis of rotation



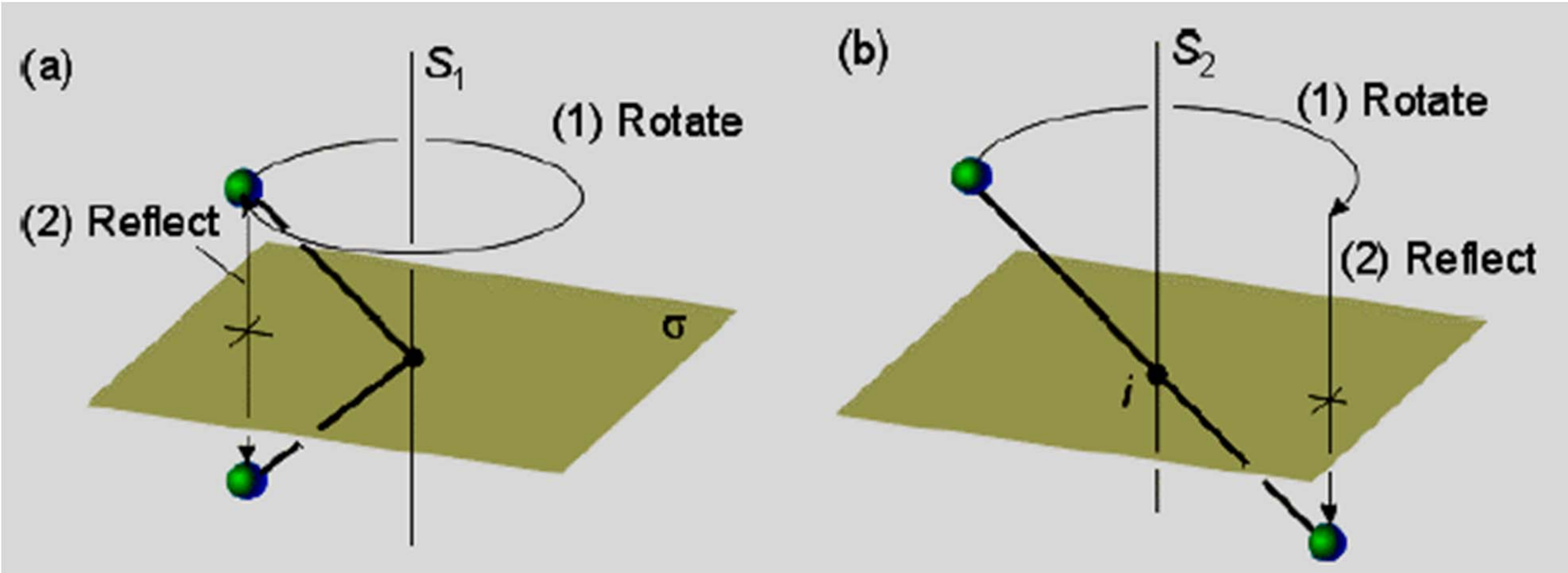
Example: $H_3C\text{-}CH_3$





The staggered form of ethane has an S_6 axis composed of a 60 rotation followed by a reflection.

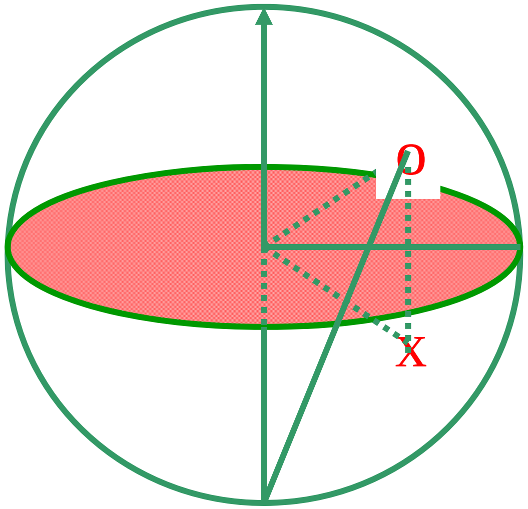
Special Cases: S_1 and S_2

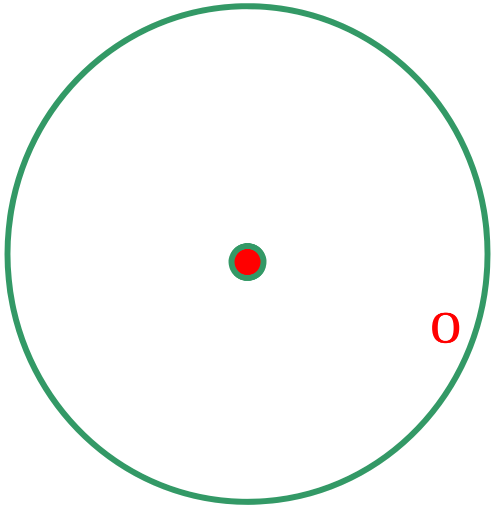


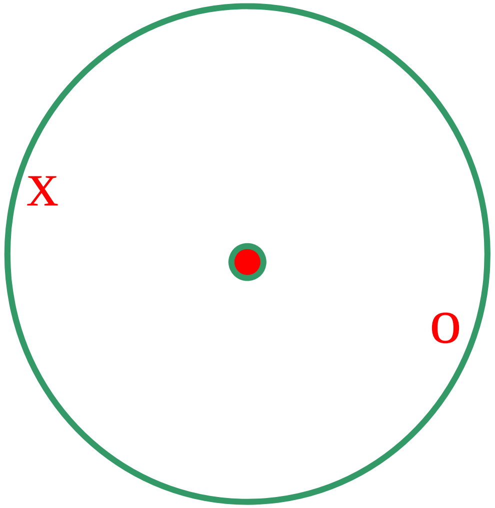
$$S_1 = \sigma_h C_1 = \sigma_h$$

$$S_2 = \sigma_h C_2 = i$$

Stereographic Projections





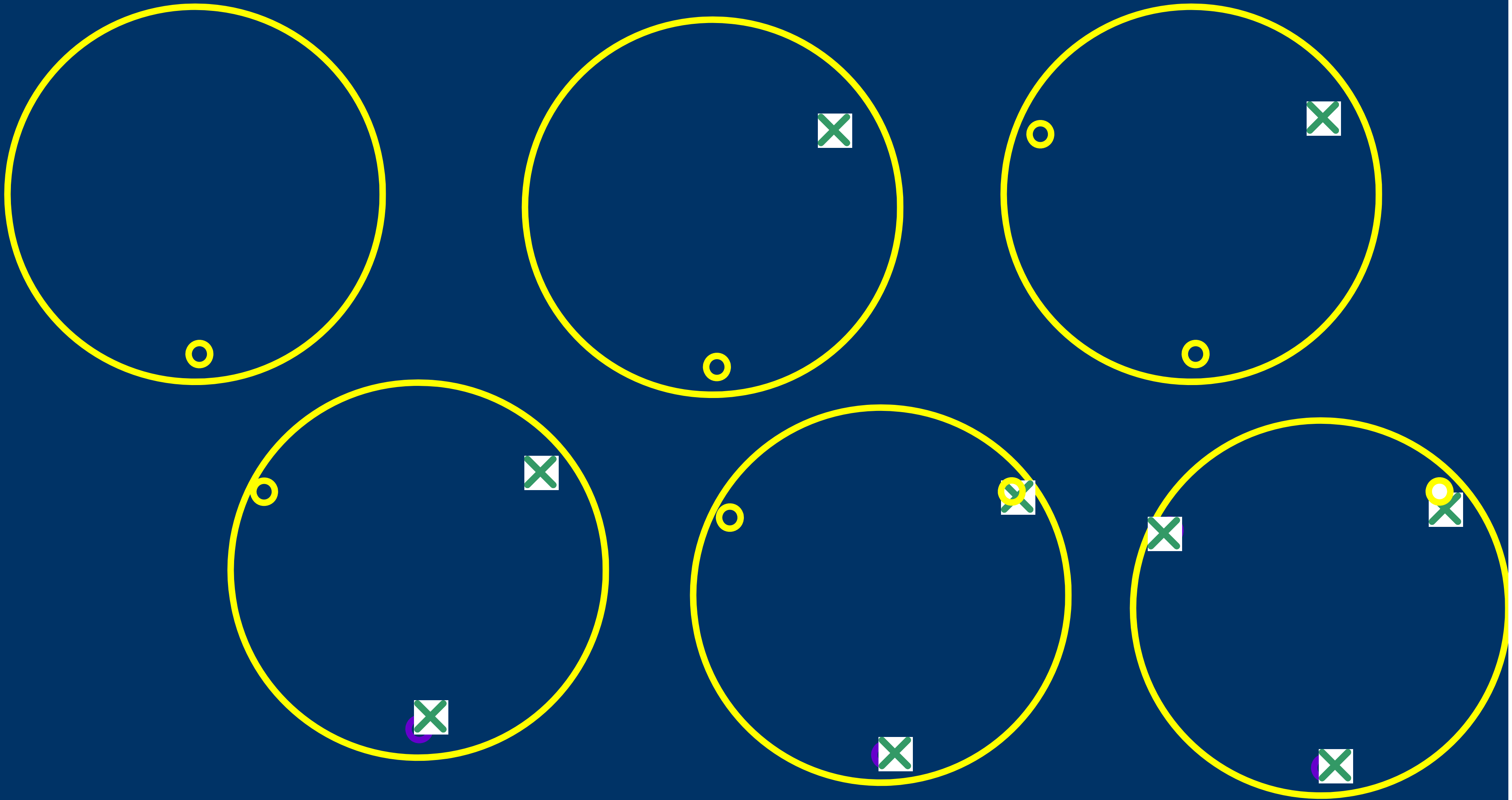


We will use stereographic projections to plot the perpendicular to a general face and its symmetry equivalents, to display crystal morphology

- **o for upper hemisphere; x for lower**

S_3

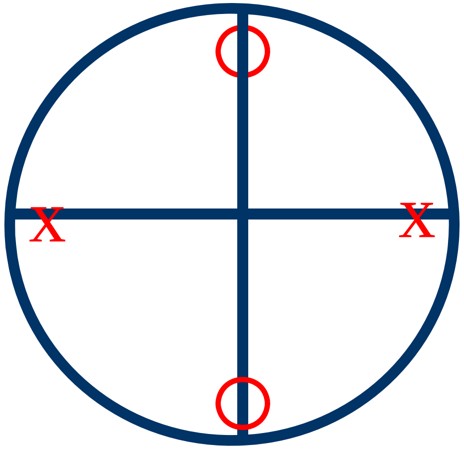
$$S_3^{\ 1} = \sigma C_3^{\ 1}; S_3^{\ 2} = C_3^{\ 2}; S_3^{\ 3} = \sigma; S_3^{\ 4} = C_3^{\ 1}; S_3^{\ 5} = \sigma C_3^{\ 2}; S_3^{\ 6} = E$$



$$\boldsymbol{S}_3 = \boldsymbol{\sigma_h C}_3 = \boldsymbol{C}_3 + \boldsymbol{\sigma_h}$$

$$S_4 = \sigma_h C_4$$

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



$$S_5 = \sigma_h C_5 = C_5 + \sigma_h$$

$$S_5{}^1 = \sigma C_5{}^1; S_5{}^2 = C_5{}^2; S_5{}^3 = \sigma C_5{}^3; S_5{}^4 = C_5{}^4; S_5{}^5 = \sigma;$$

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

$$S_6 = \sigma_h C_6$$

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

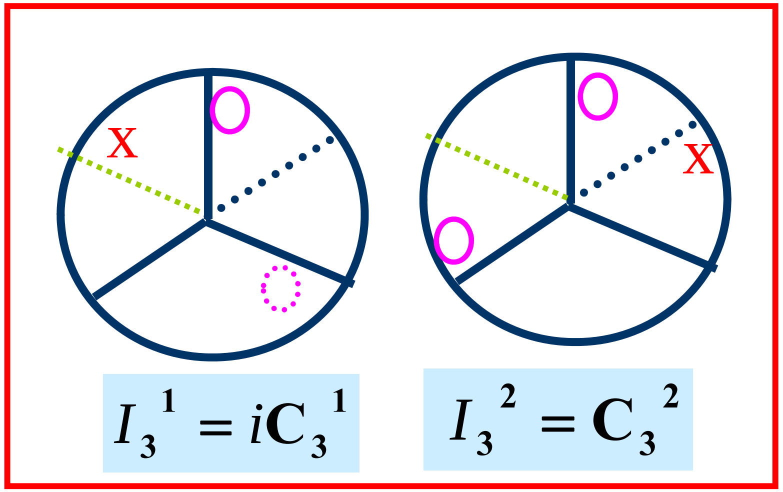
Rotation of Cn followed by inversion through the center of the axis

$$I_n = i\mathbf{C_n}$$

$$I_1 = i\mathbf{C_1} = i,$$

$$I_2 = i\mathbf{C_2} = \sigma_h$$

$$I_3 = C_3 + i$$



$$I_3^{\ 1} = i\mathbf{C_3}^{1} \quad I_3^{\ 2} = \mathbf{C_3}^{2} \quad I_3^{\ 3} = i \quad I_3^{\ 4} = \mathbf{C_3}^{1} \quad I_3^{\ 5} = i\mathbf{C_3}^{2} \quad I_3^{\ 6} = \mathbf{E}$$

Summary

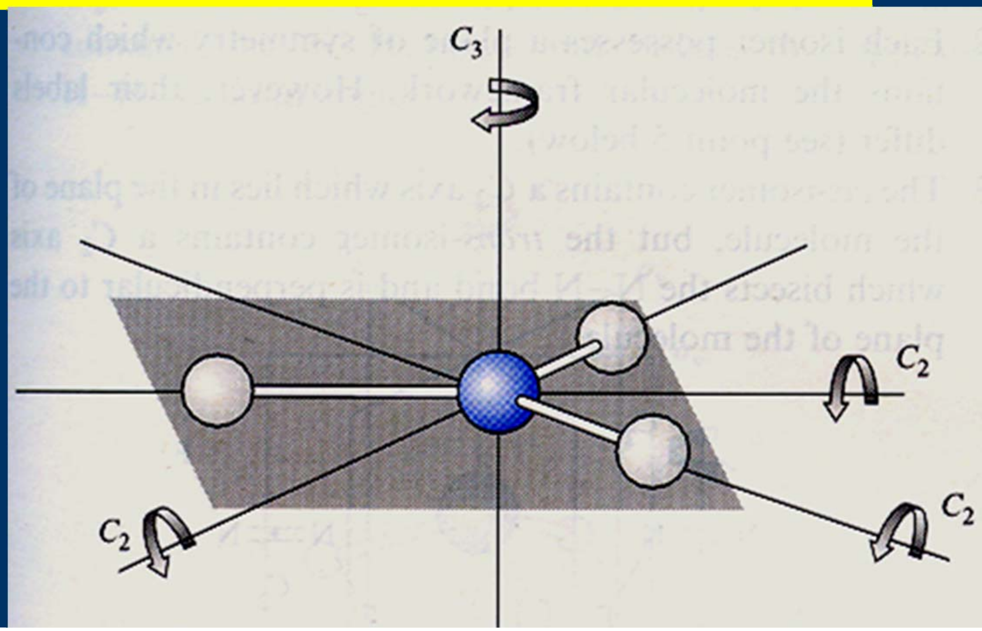
Element	Name	Operation
C_n	**n-fold rotation**	**Rotate by 360° /n**
σ	**Mirror plane**	**Reflection through a plane**
i	**Center of inversion**	**Inversion through the center**
S_n	**Improper rotation axis**	**Rotation as Cn followed by reflection in perpendicular mirror plane**
E	**identity**	**Do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

2. Combination rules of symmetry elements

A. Combination of two axes of symmetry

The combination of two C_2 axes intersecting at 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 nC_2 axes in the plane perpendicular to the C_2 axis.

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



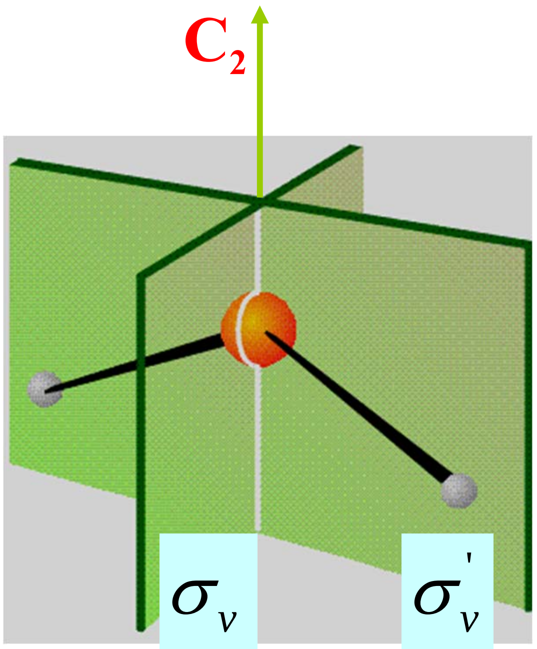
B. Combination of two planes of symmetry.

If two mirrors planes intersect at an angle of 2π/2n, there will be a C_n axis of order n on the line of intersection. Similarly, the combination of an axis C_n with a mirror plane parallel to and passing through the axis will produce n mirror planes intersecting at angles of 2π/2n.

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

$$C_2 + \sigma_v \Rightarrow \mathbf{2}\sigma_v$$
$$C_3 + \sigma_v \Rightarrow \mathbf{3}\sigma_v$$

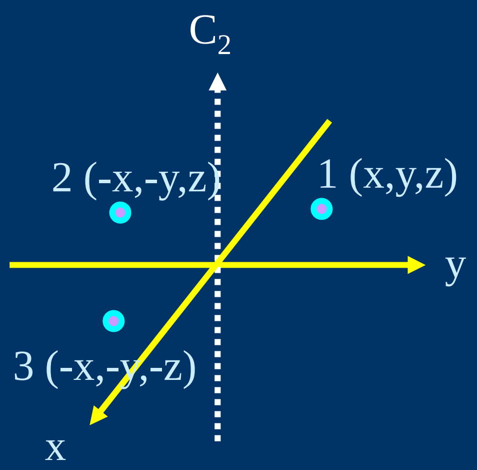
Ex. H_2O, NH_3



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 centre of symmetry at the point intersection.

Each of the three operations σ_{xy}, C_{2n} and i is the product of the other two operations



$$C_2^1 = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

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

$$C_2^1 \sigma_{xy} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

$$\boldsymbol{\sigma_h C_{2m}^m = \sigma_h C_2 = i}$$

§ 2 Groups and group multiplications

1. Definition: A mathematical group, G = {*G*,·}, consists of a set of elements *G* = {E, A,B,C,D,....}

(a) **Closure**. The product of any two elements A and B in the group is another element in the group.

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

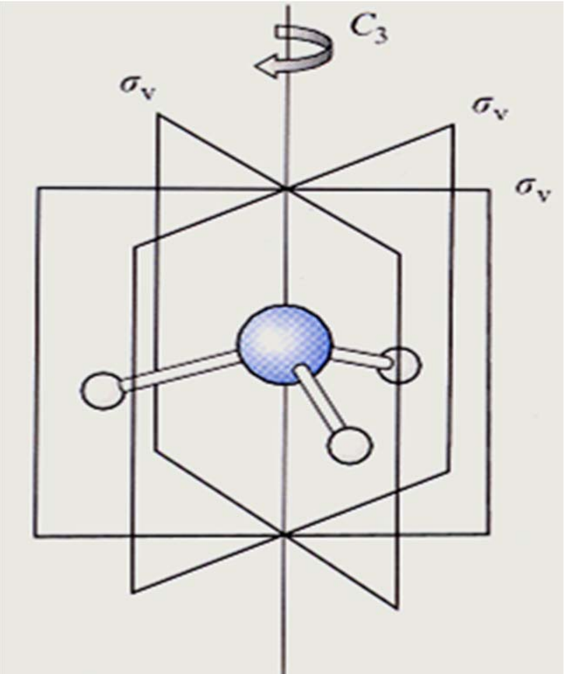
(c) **Associative rule**. If A, B, C are any three elements in the group then (A·B)·C = A·(B·C).

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

Example: NH_3

symmetry elements:

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



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

Closure.

$$E$$

Identity operation.

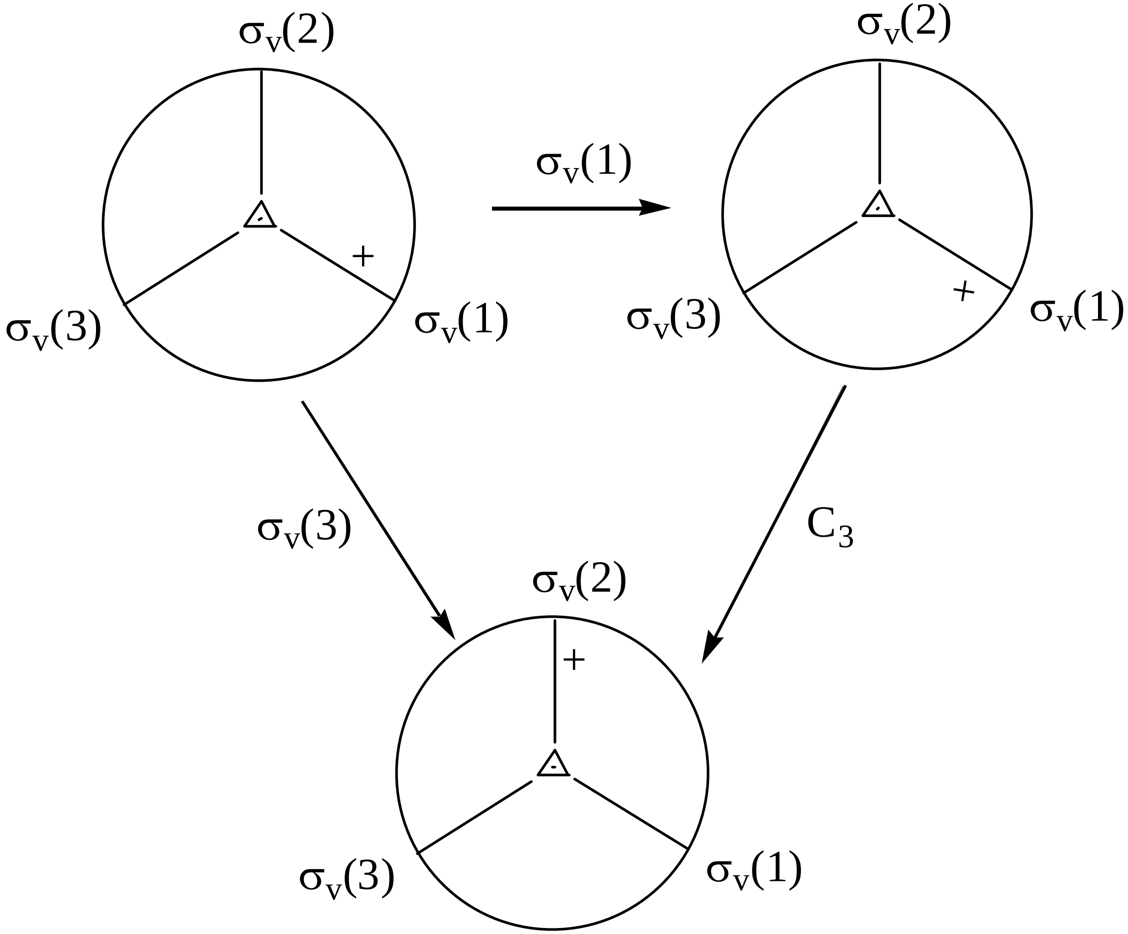
$$(C_3^1 \cdot C_3^2) \cdot C_3^1 = C_3^1 (C_3^2 \cdot C_3^1)$$

Associative rule.

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

Therefore, these symmetry elements constitute a group, C_{3V}

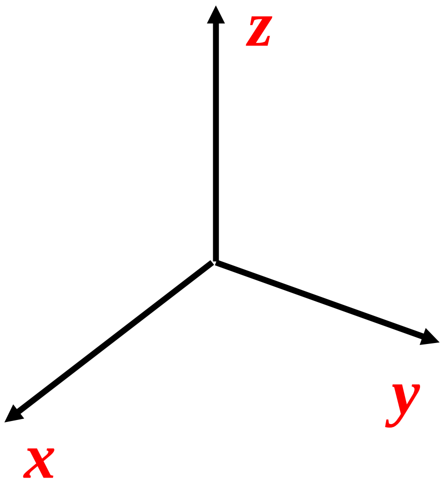
Example: $G = \{E, C_3, C_3^2, \sigma_v(1), \sigma_v(2), \sigma_v(3)\}$ NH_3: C_{3v}

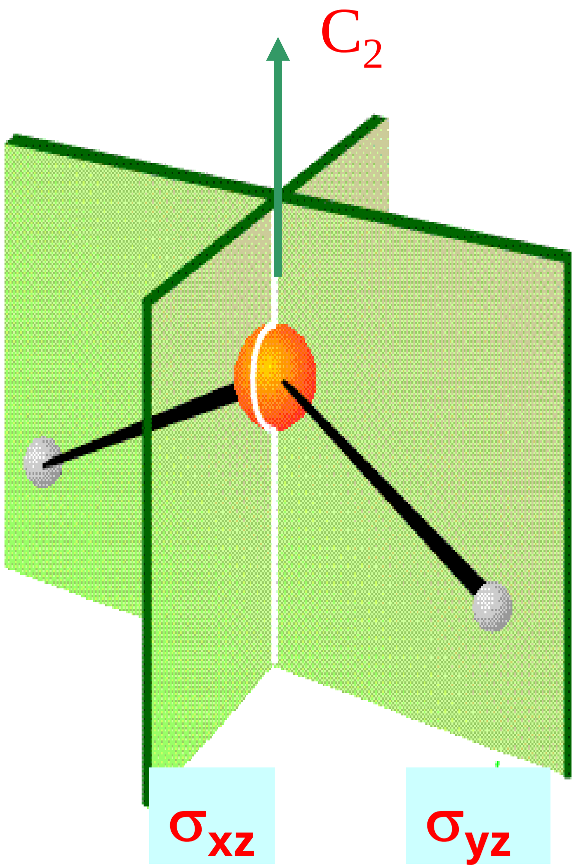


$$C_3\sigma_v(1) = \sigma_v(3) \qquad \sigma_v(1)C_3 = \sigma_v(3) \ \cdots$$

2. Group Multiplication

Example: H_2O





C_{2v}

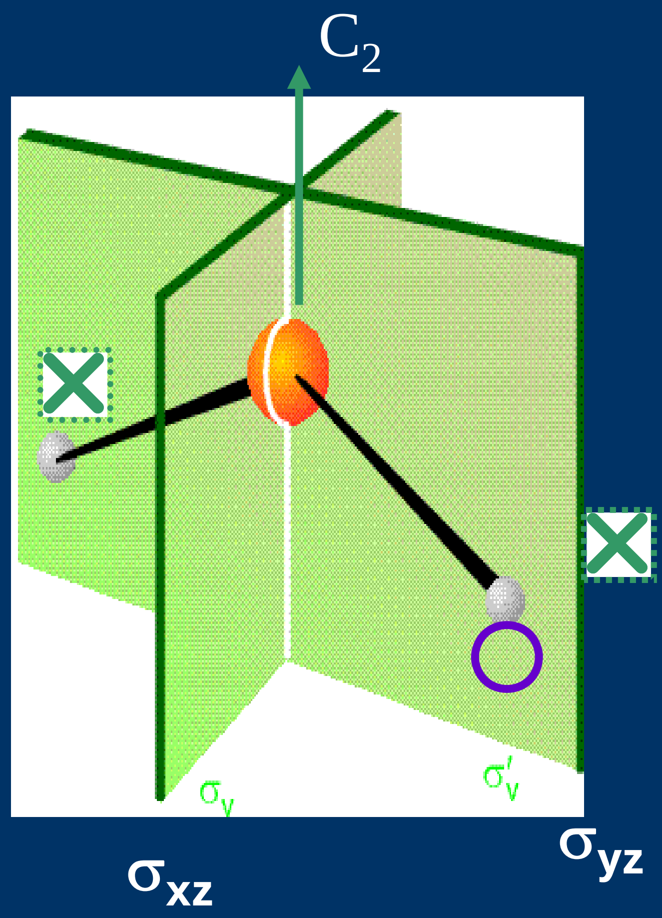
Its total symmetry elements: E, C_2^1, σ_{xz} σ_{yz}

2. Group Multiplication

Example: H_2O

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



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

(1). In each row and each column, each operation appears once and only once.

(2) We can identify smaller groups within the larger one. For example, {E, C_2} is a group.

(3) The group order is the total number of the group

Example: NH_3

C_{3v}

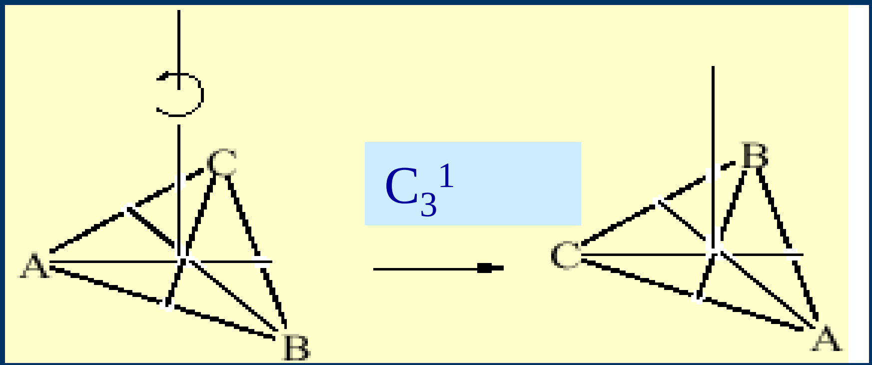
Its total symmetry elements: E, C_3^1, C_3^2, σ_v, σ_v', σ_v''

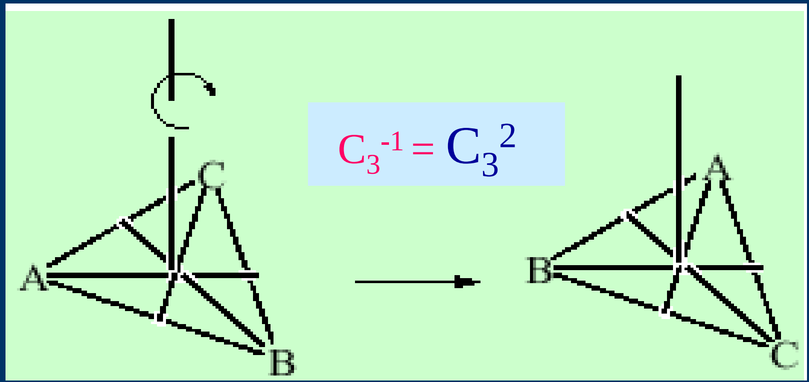
Multiplication table of C_{3v}

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

C_{3v}	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			
σ_v	σ_v					
σ_v’	σ_v’					
σ_v”	σ_v”					





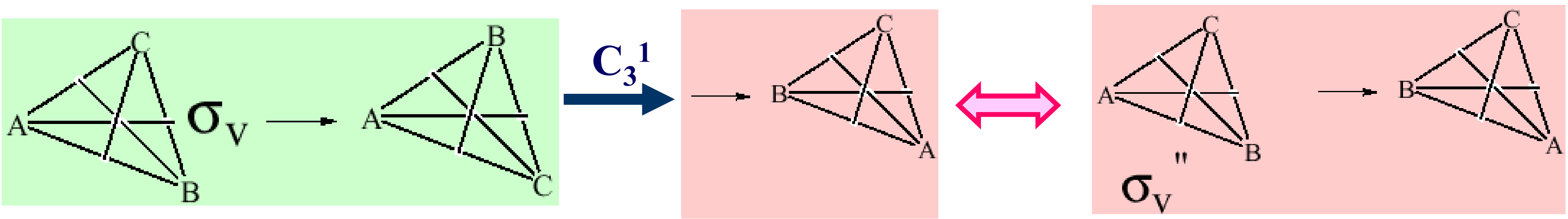
$$C_3^1 \cdot C_3^1 = C_3^2$$

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

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

Group Multiplication

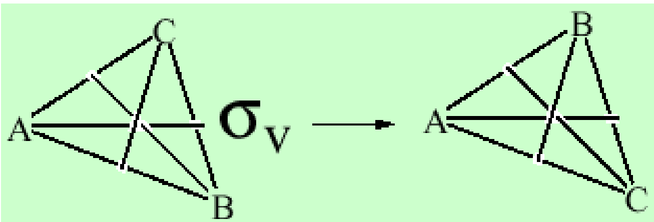
C_{3v}	E	C_3^1	C_3^2	σ_v	σ_v'	σ_v''
E	E	C_3^1	C_3^2	σ_v	σ_v'	σ_v''
C_3^1	C_3^1	C_3^2	E	σ_v''	σ_v	σ_v'
C_3^2	C_3^2	E	C_3^1	σ_v'	σ_v''	σ_v
σ_v	σ_v	σ_v'	σ_v''			
σ_v'	σ_v'	σ_v''	σ_v			
σ_v''	σ_v''	σ_v	σ_v'			

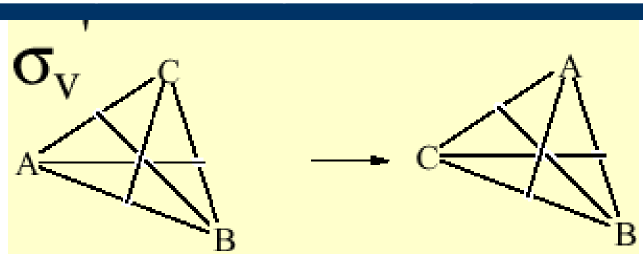


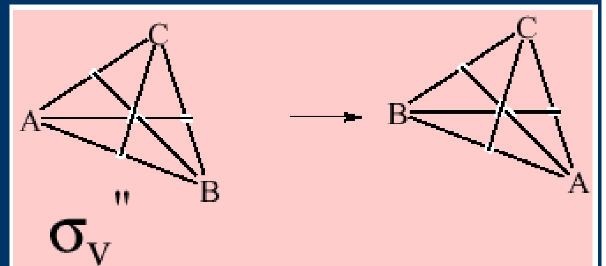
$$C_3^1 \sigma_v = \sigma_v''$$

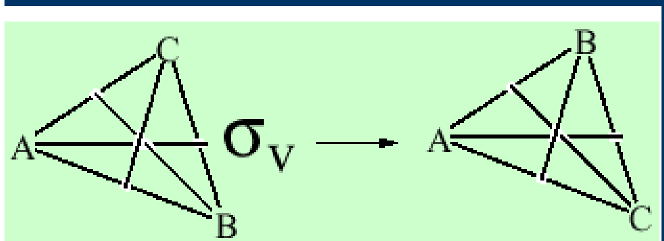
Group Multiplication

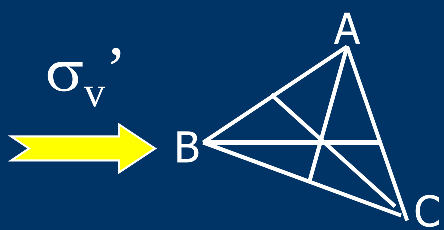
C_{3v}	E	C_3^1	C_3^2	σ_v	σ_v'	σ_v''
E	E	C_3^1	C_3^2	σ_v	σ_v'	σ_v''
C_3^1	C_3^1	C_3^2	E	σ_v''	σ_v	σ_v'
C_3^2	C_3^2	E	C_3^1	σ_v'	σ_v''	σ_v
σ_v	σ_v	σ_v'	σ_v''	E	C_3^1	C_3^2
σ_v'	σ_v'	σ_v''	σ_v	C_3^2	E	C_3^1
σ_v''	σ_v''	σ_v	σ_v'	C_3^1	C_3^2	E











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

Multiplication table of C_{3v}

C_{3v}	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_3^1	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

§ 3 Point groups, the symmetry classification of molecules

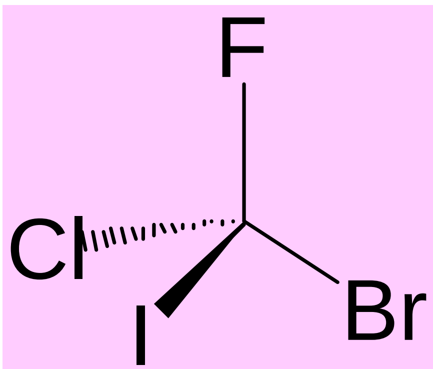
Point group:

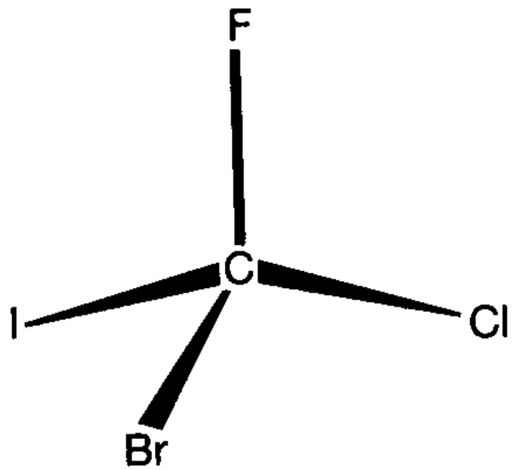
All symmetry elements corresponding to operations have at least one common point unchanged.

1. The groups C_1, C_i, and C_s

The group C_1

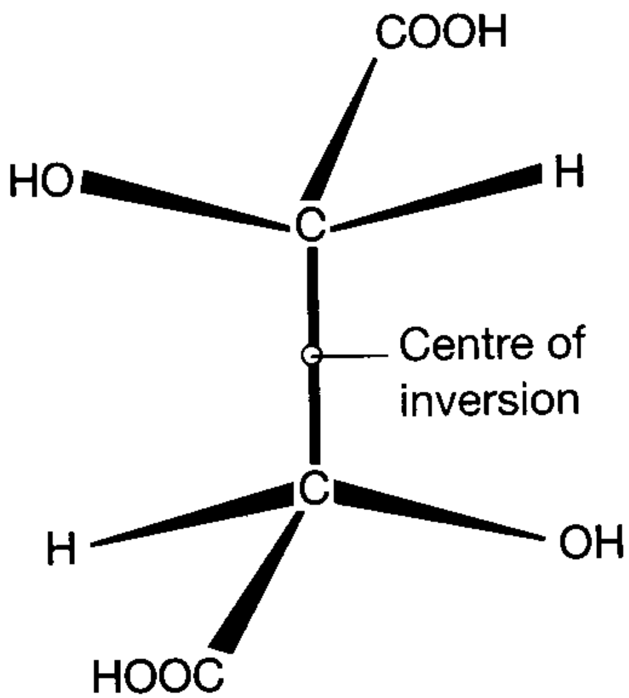
- A molecule belongs to the group C_1 if it has no element of symmetry other than the identity.
  - Example: **CBrClF**

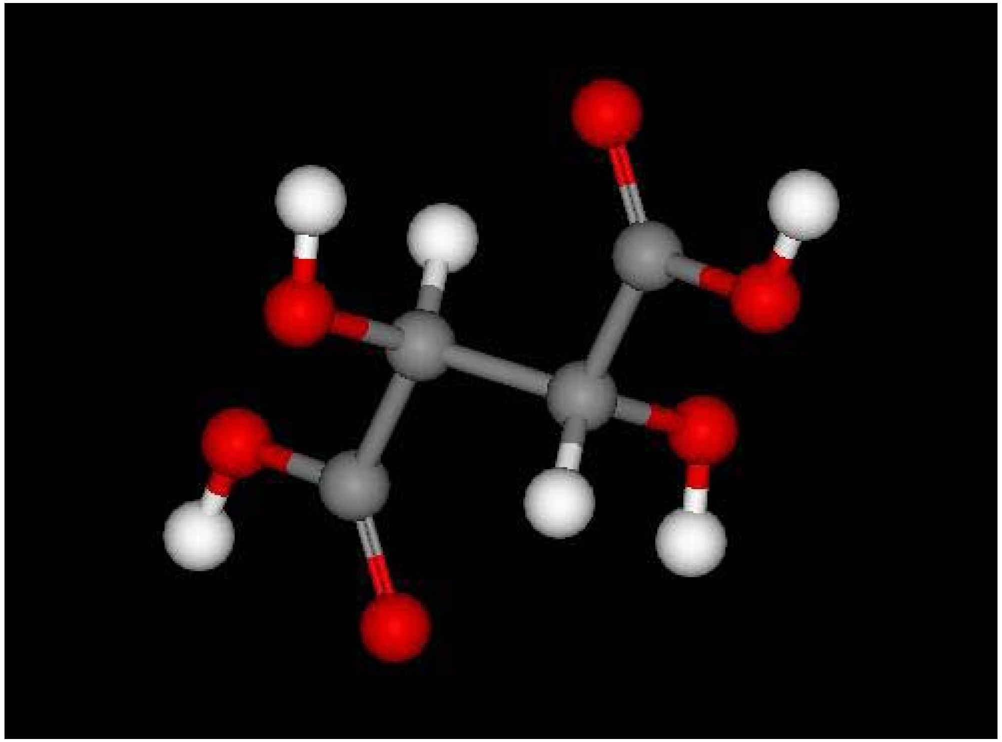




The group C_i

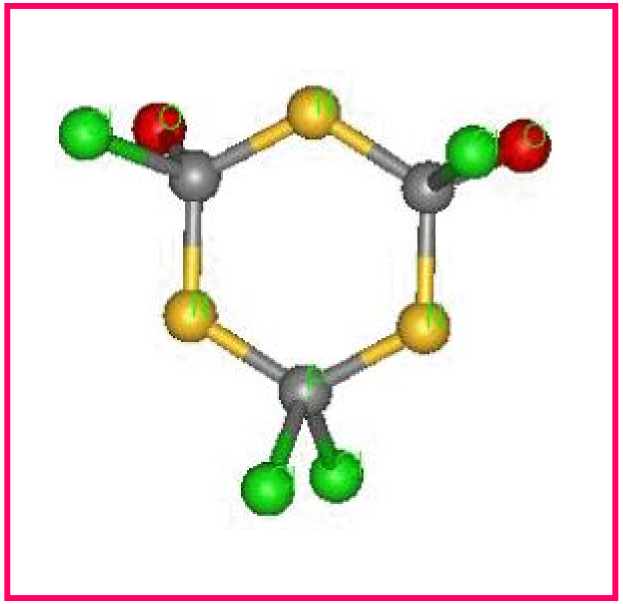
- It belongs to C_i if it has the identity and inversion alone.
  - Example: meso-tartaric acid, HClBrC-CHClBr



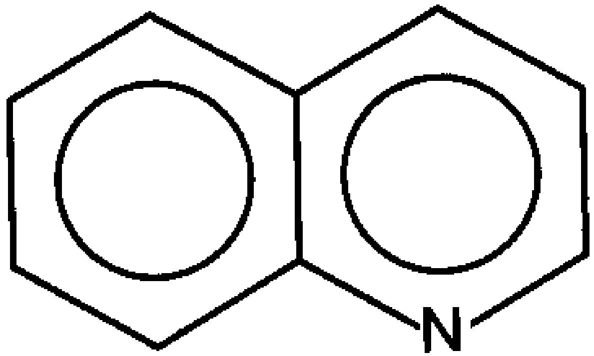


The group C_s

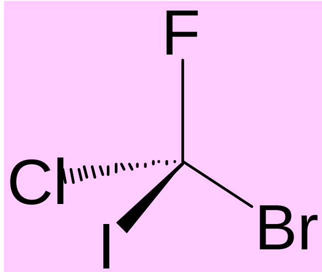
- It belongs to C_s if it has the identity and a mirror plane alone.

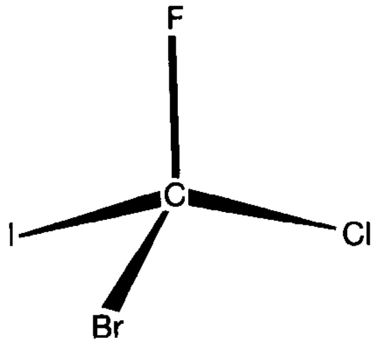


$N_3S_3Cl_4O_2$

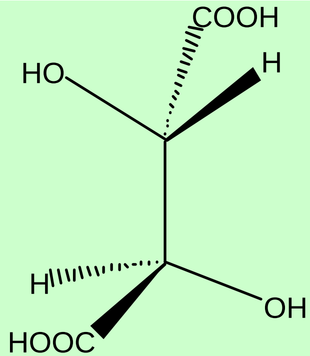


A molecule belongs to $\mathbf{C_1}$ if it has only the identity **E**.





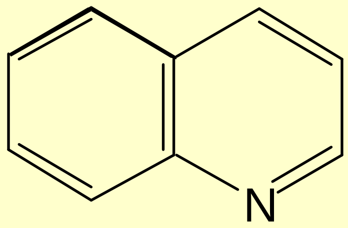
A molecule belongs to C_i if it has only the identity E and i.



Meso-tartaric acid

HClBrC-CHClBr

A molecule belongs to C_s if it has only the identity E and a mirror plane.



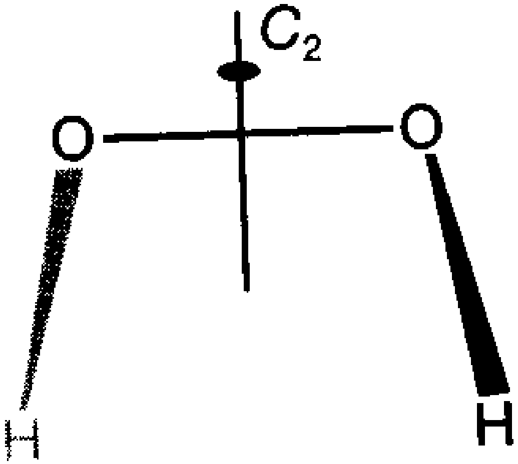
Quinoline

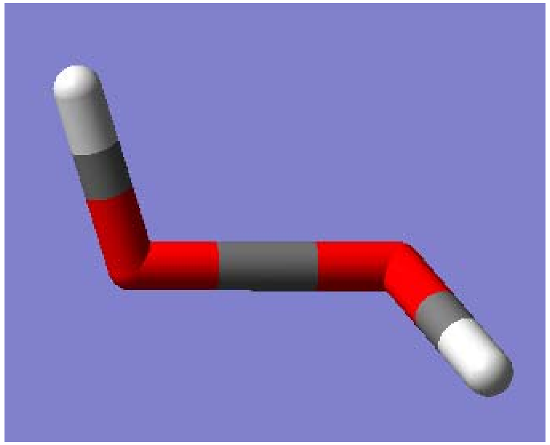
$H_2C=CClBr$

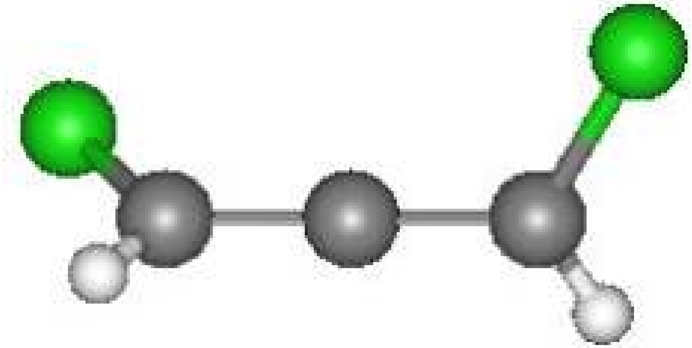
2. The groups C_n, C_{nv}, C_{nh} and S_n

The group $\mathbf{C_n}$

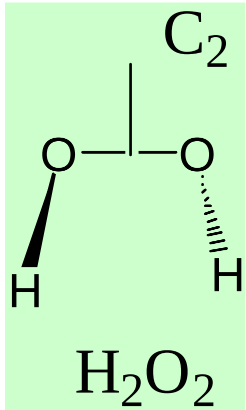
- A molecule belongs to the group C_n if it possess an **only** n-fold axes.
- Example: H_2O_2

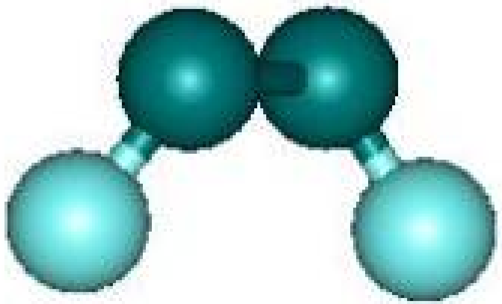




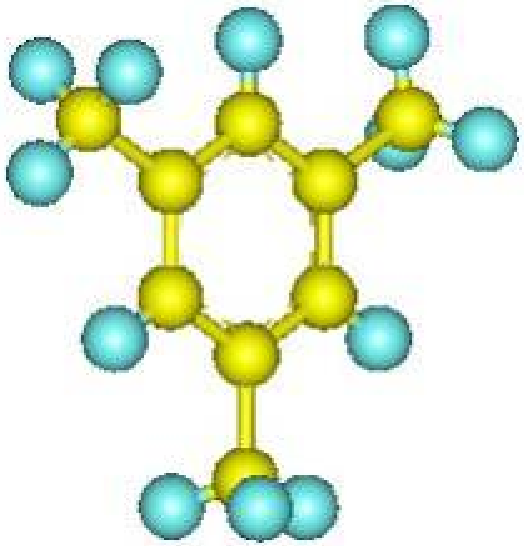


$C_3H_2Cl_2$



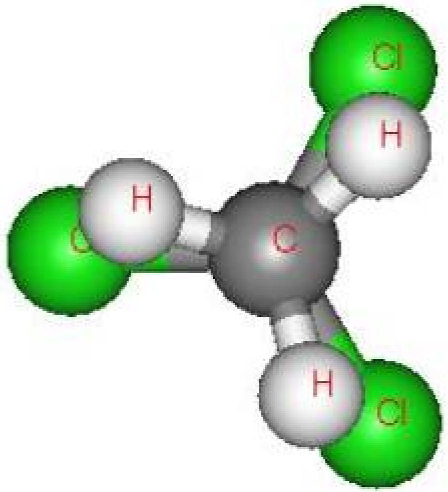


C_2



$C_6H_3(CH_3)_2$

C_3

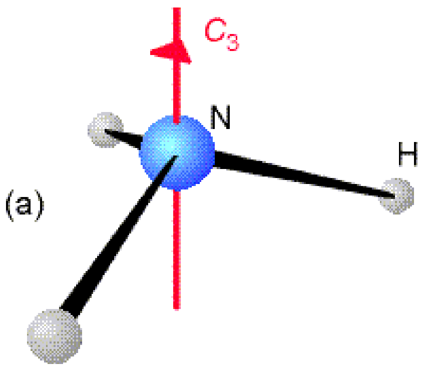


$C_2H_3Cl_3$

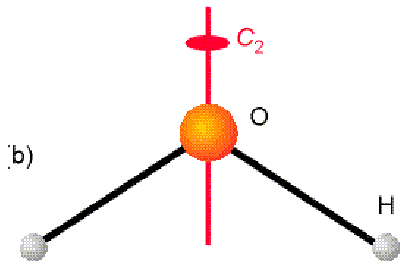
The group C_{nv}

- If in addition to a C_n axis it also has n vertical mirror planes σ_v, then it it belongs to the C_{nv} group.

C_n , $n\sigma_v$



C_{3v}

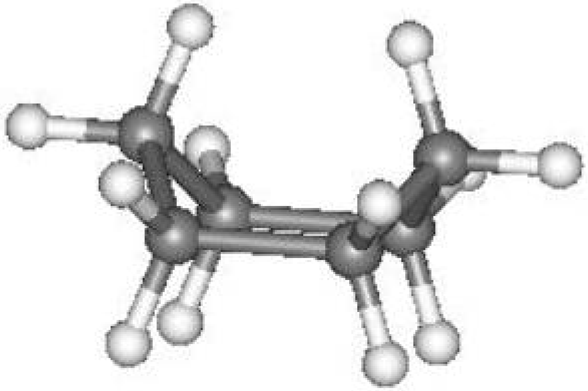


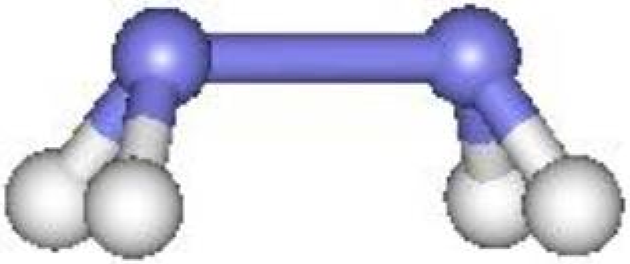
C_{2v}

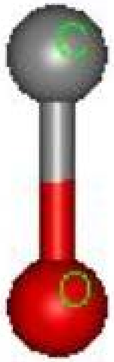
C=O

$C_{\infty v}$

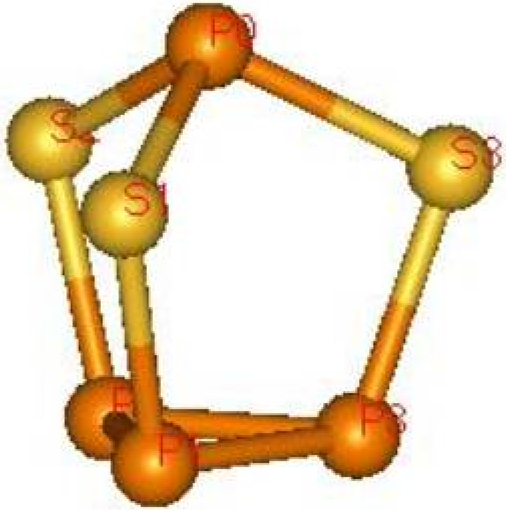
C_{2v} $C_{\infty v}$

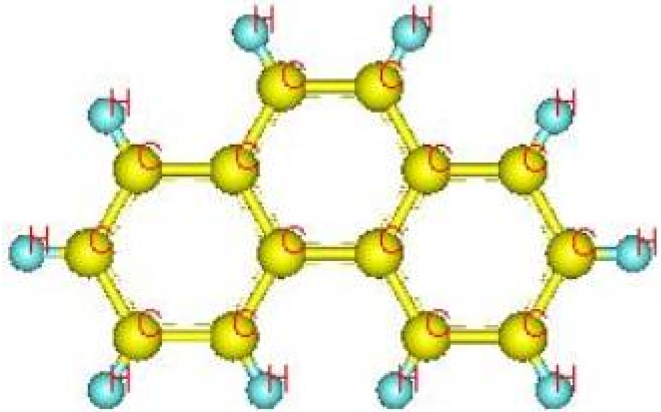






C_6H_{12} N_2H_4 CO



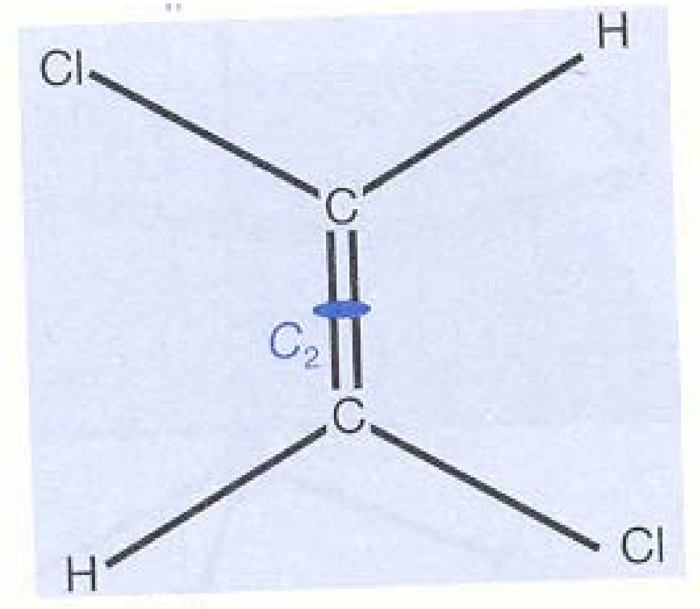


P_4S_3 C_{3v}

$C_{14}H_{10}$

The group C_{nh}

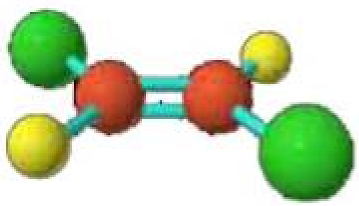
- **Objects having a C_n axis and a horizontal mirror plane belong to C_{nh}.**



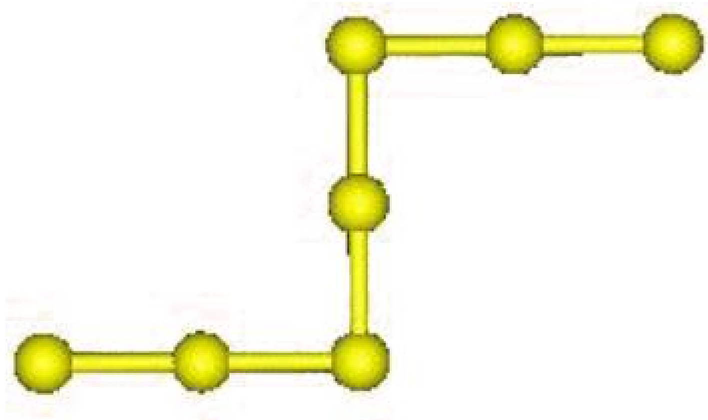
C_n , σ_h

trans-CHCl=CHCl

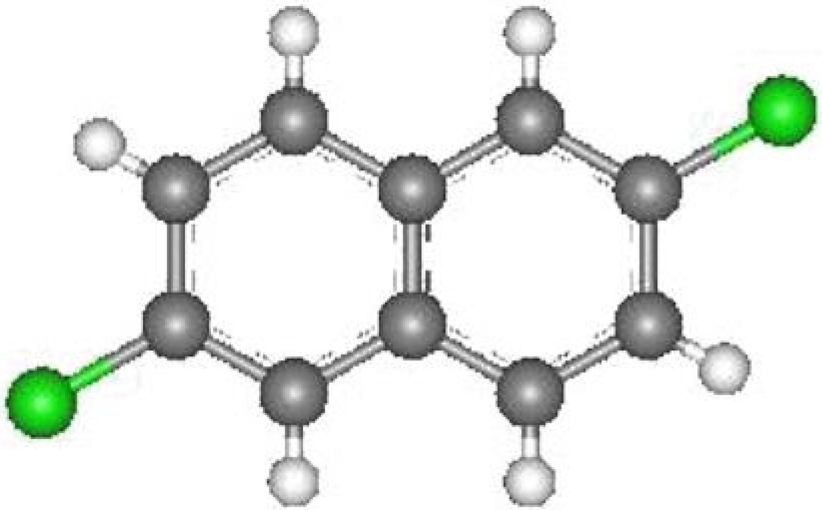
C_{2h}



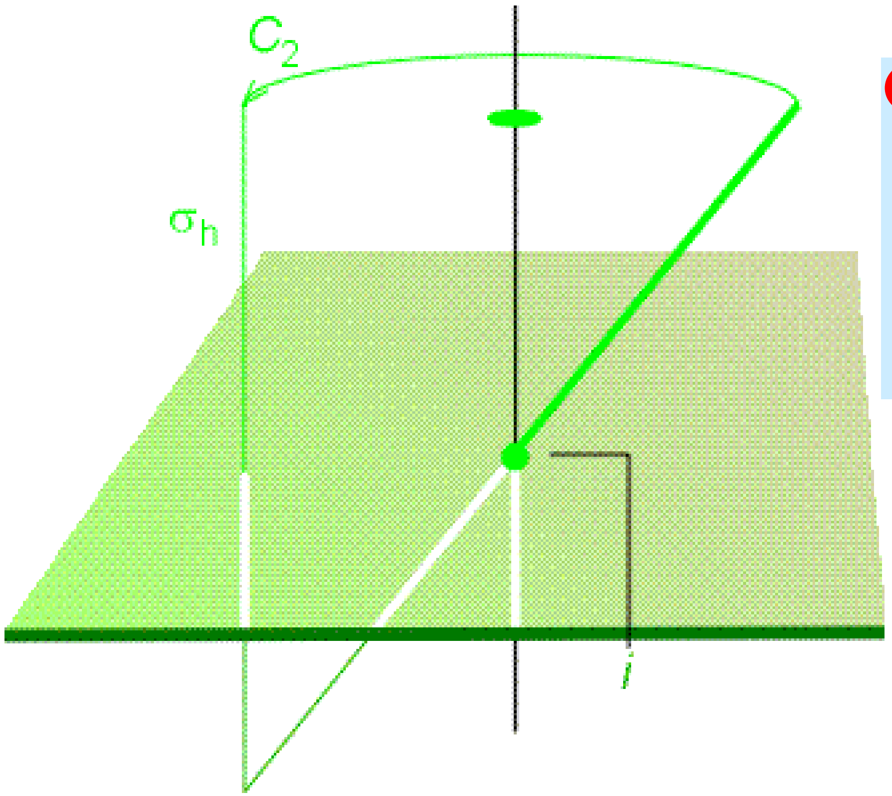
$C_2H_2Cl_2$

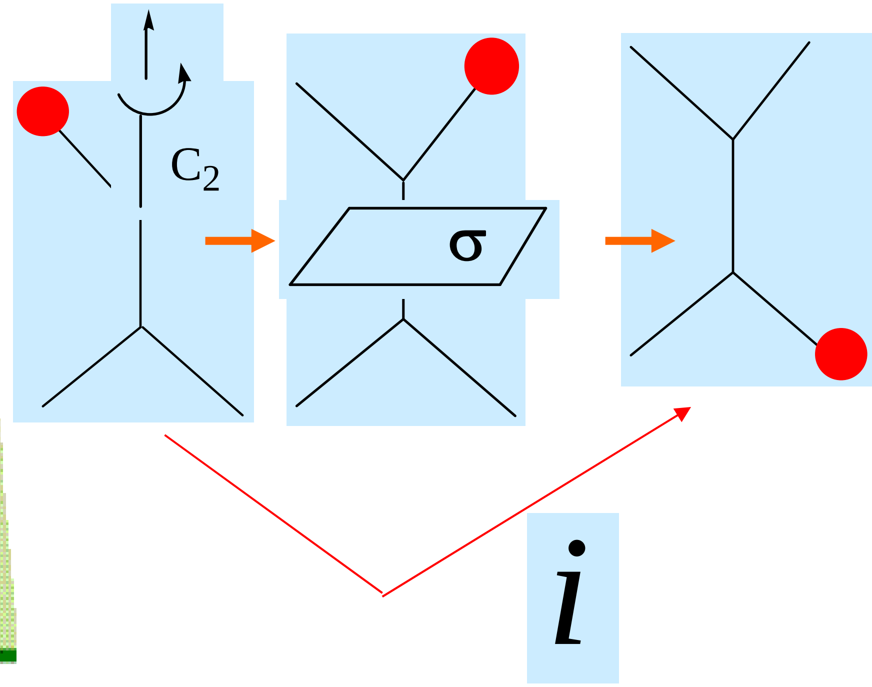


I_7^-

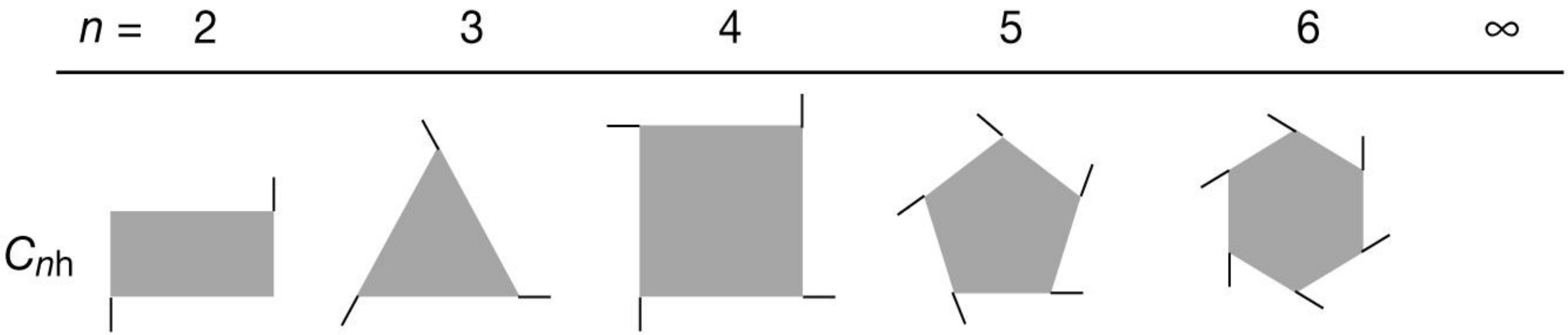


$C_{10}H_6Cl_2$

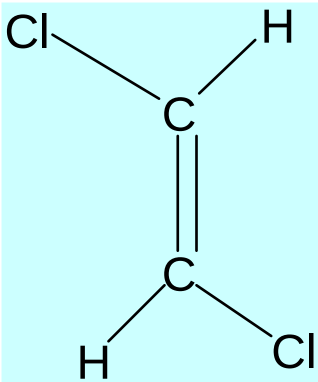




The presence of a twofold axis and a horizontal mirror plane jointly imply the presence of a centre of inversion in the molecule.



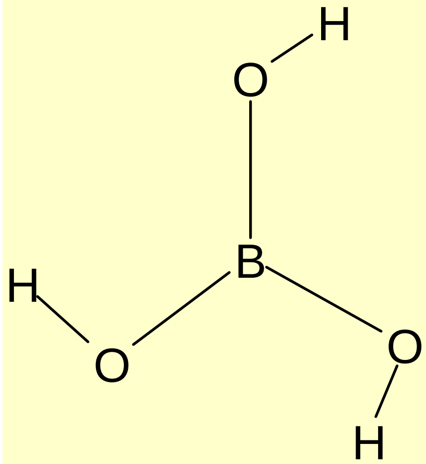
C_{2h} C_{3h} C_{4h} C_{5h} C_{6h}



Trans CHCl=CHCl

C_{2h}

C_{3h}



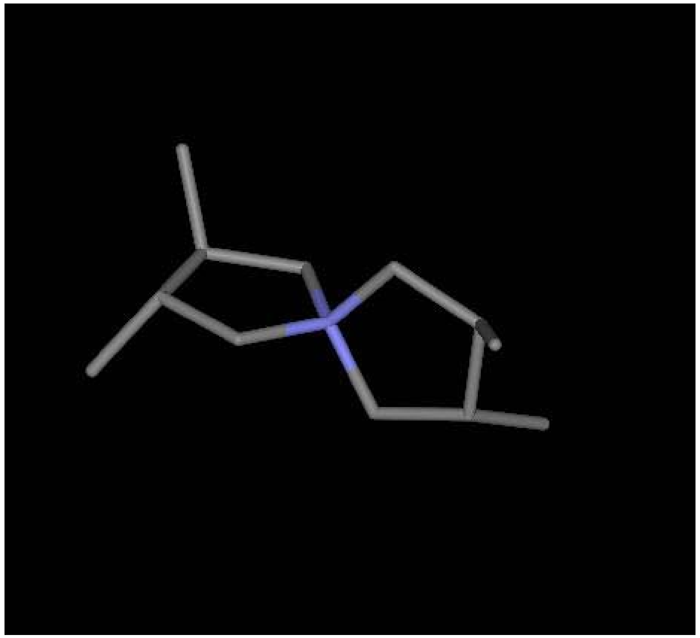
$B(OH)_3$

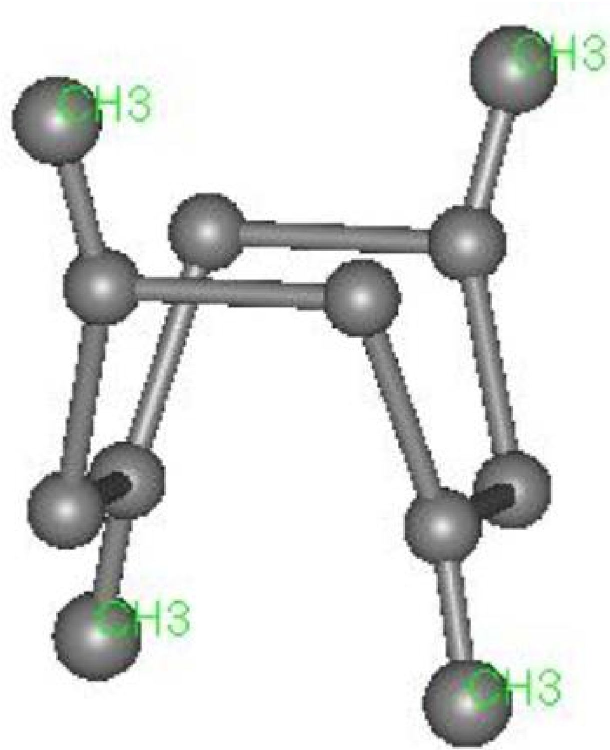
The group $\mathbf{S_n}$

- Objects having a S_n improper rotation axis belong to S_n.

Group $S_2 = C_i$

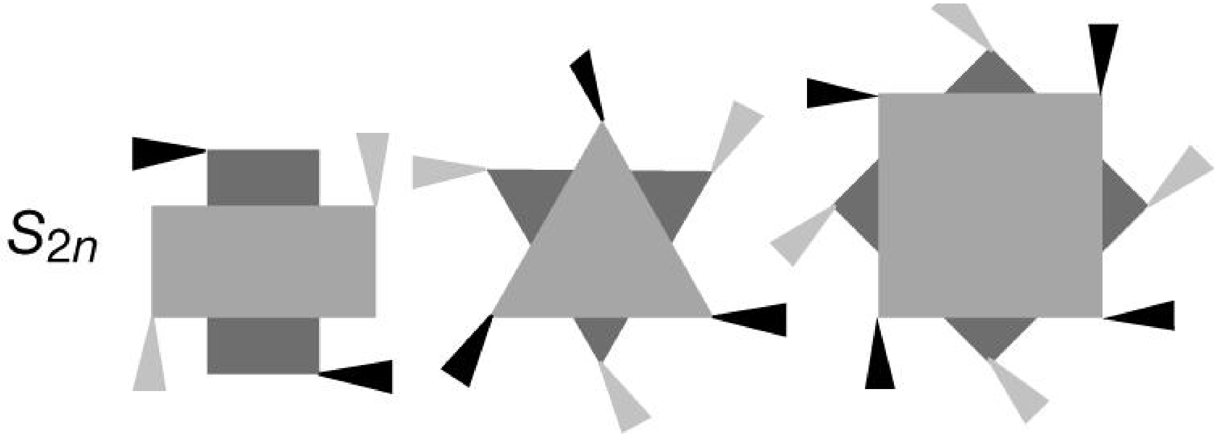
Group $S_1 = C_s$



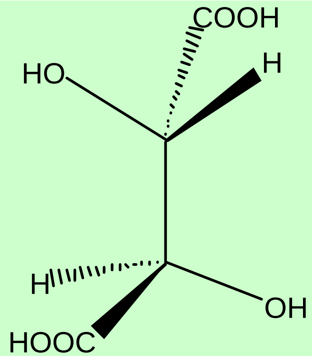


$\mathbf{S_4}$

S_2 same as C_i



S_4 S_6 S_8



Meso-tartaric acid

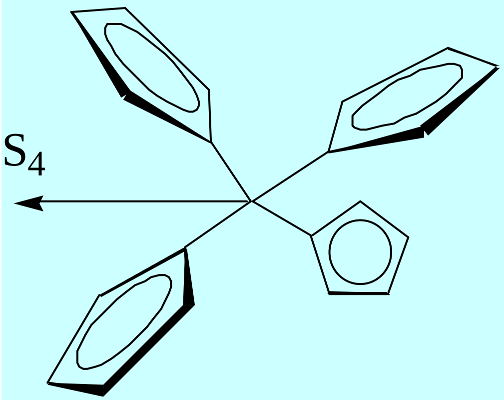
$S_4 : \; S_4, C_2, S_4^3$

$S_4^2 = C_2$

$C_3, C_3^2, i, S_6^5, S_6$

$S_2; C_4; S_8^3, C_2$

S_8^5, C_4^3, S_8^7

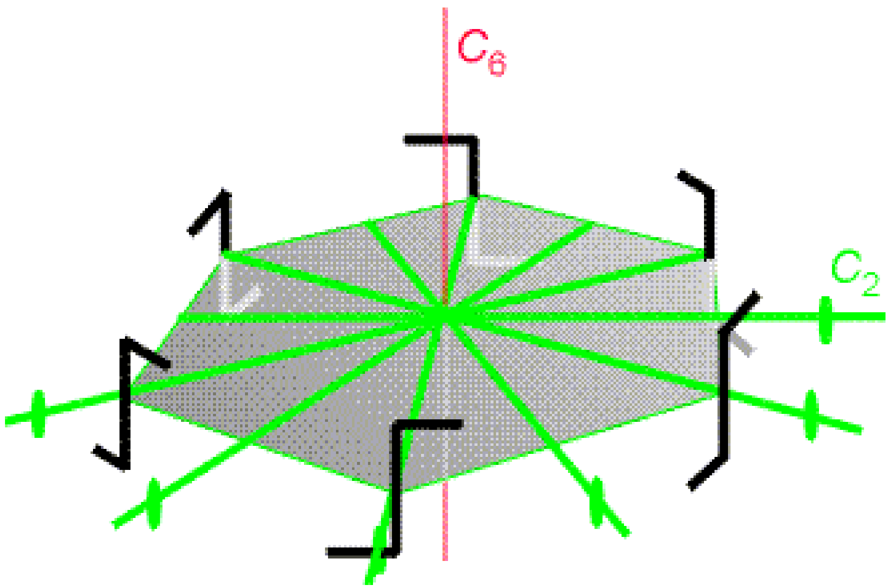


Single-axis group

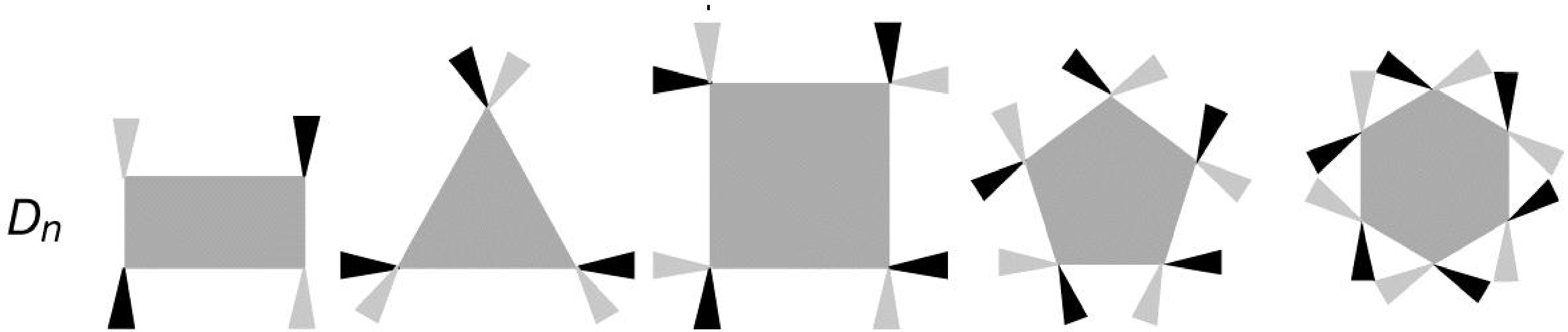
3. The group D_n, D_{nh}, D_{nd}

The group D_n

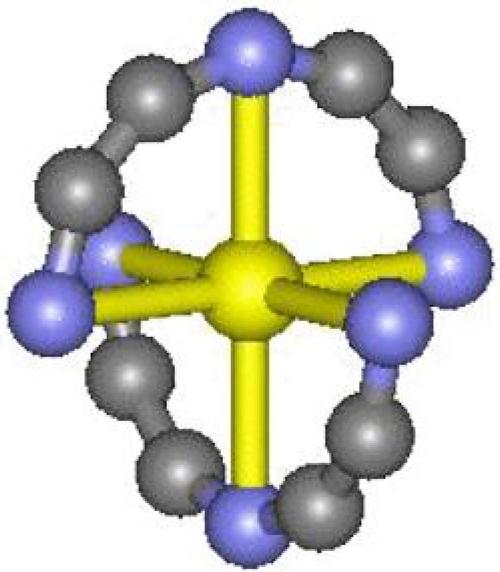
A molecule that has an *n*-fold principle axis and *n* twofold axes perpendicular to C_n belongs to D_n.



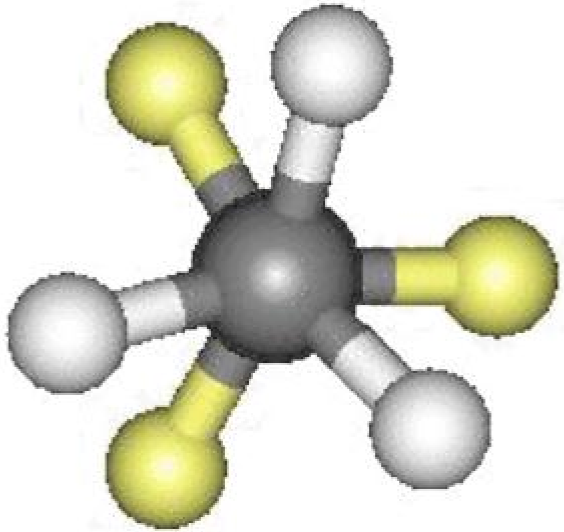
$$\mathbf{C}_n\ ,\ \mathbf{nC}_2 \perp$$



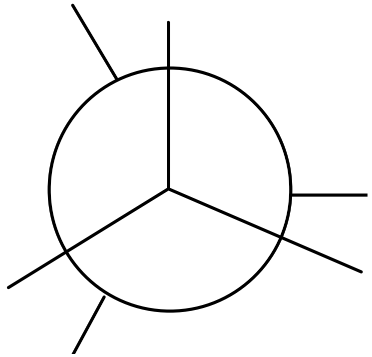
D_2 D_3 D_4 D_5 D_6



$Co(dien)_2$



$C_2H_3Cl_3$ (mediate state)

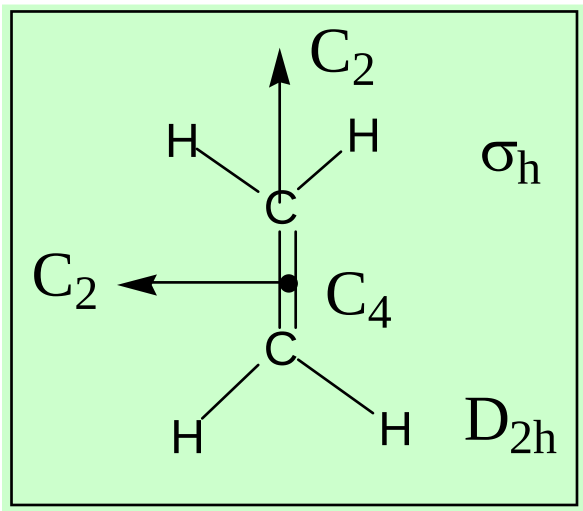


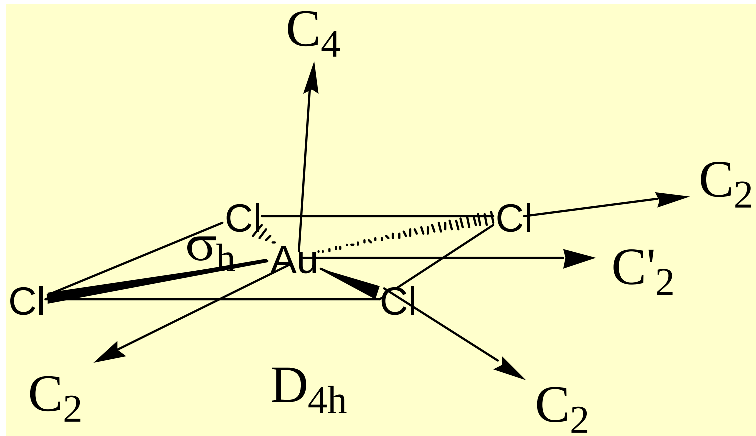
C_2H_6

The groups D_{nh}

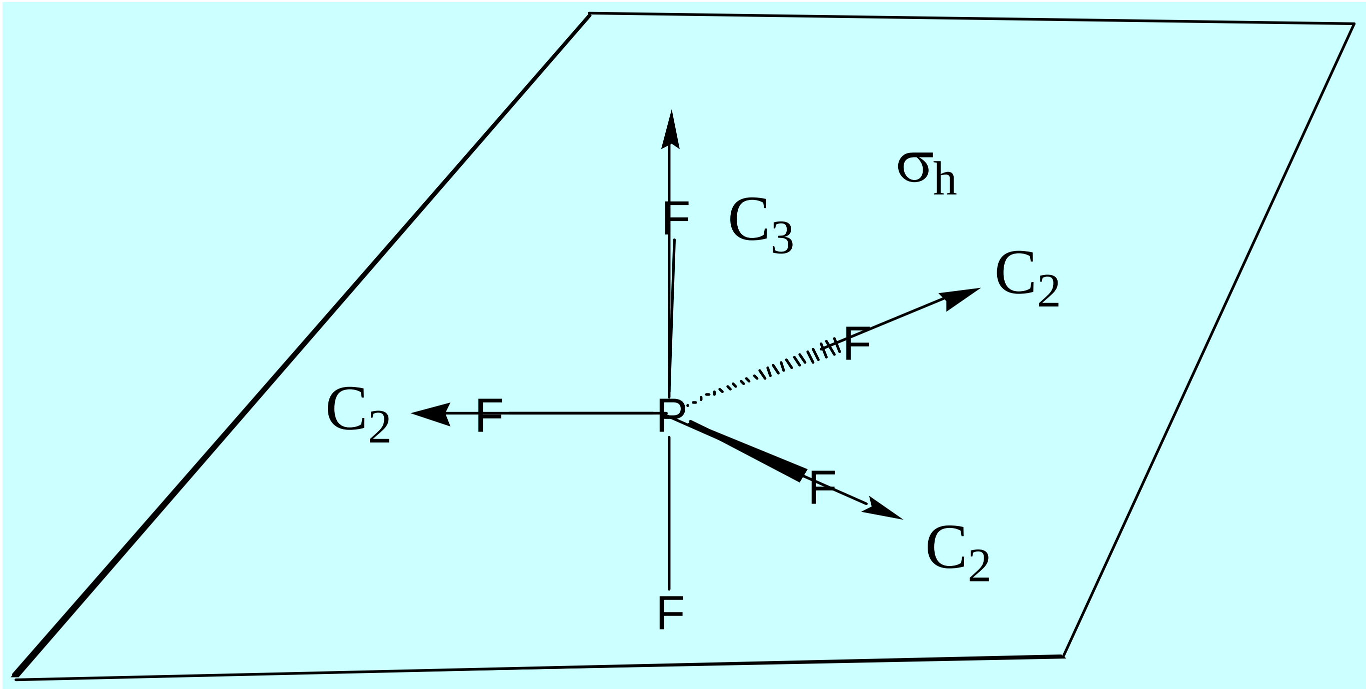
A molecule with a Mirror plane perpendicular to a C_n axis, and with n two fold axes in the plane, belongs to the group D_{nh}.

D_n , σ_h





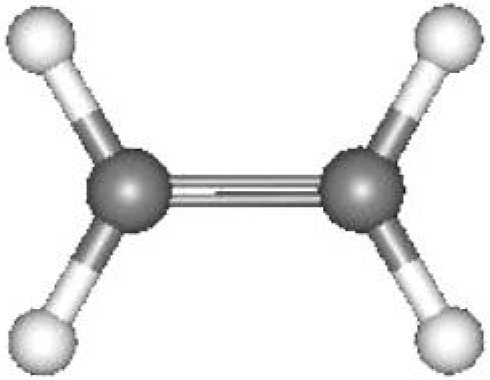
D_{nh}



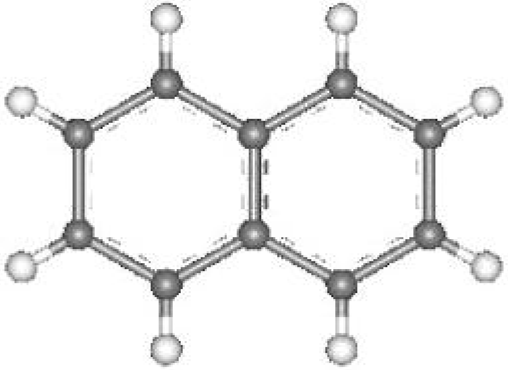
D_{3h}

D_{2h}

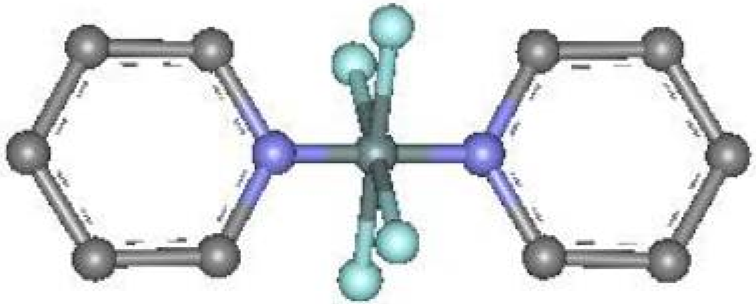
D_{nh}



C_2H_4

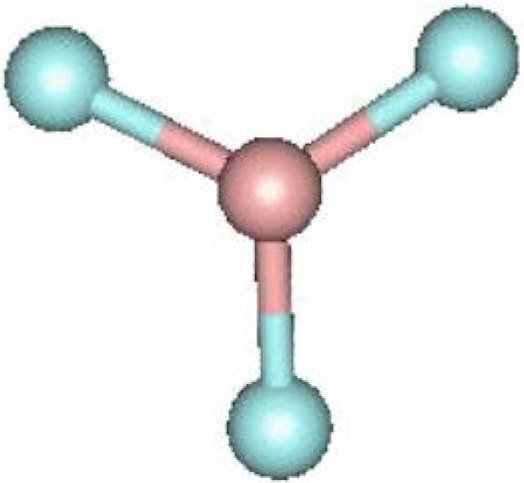


$C_{10}H_{10}$

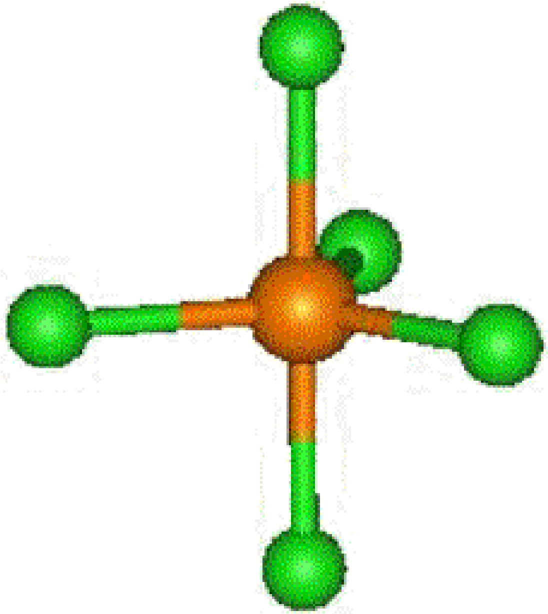


$SiF_4(C_5H_5N)_2$

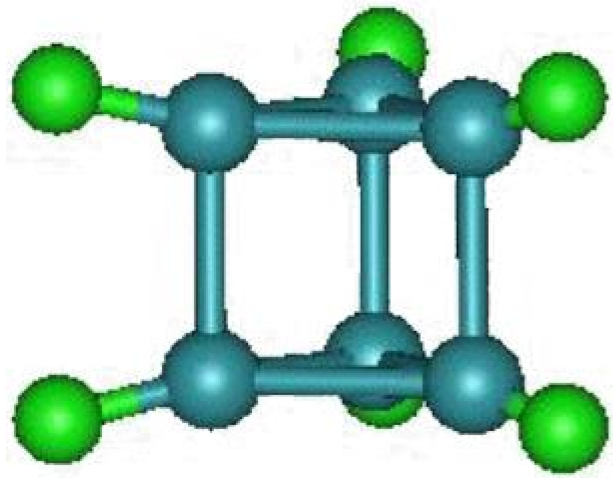
D_{3h}



BF_3

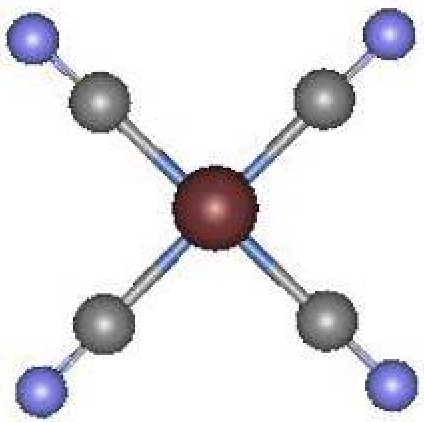


PCl_5

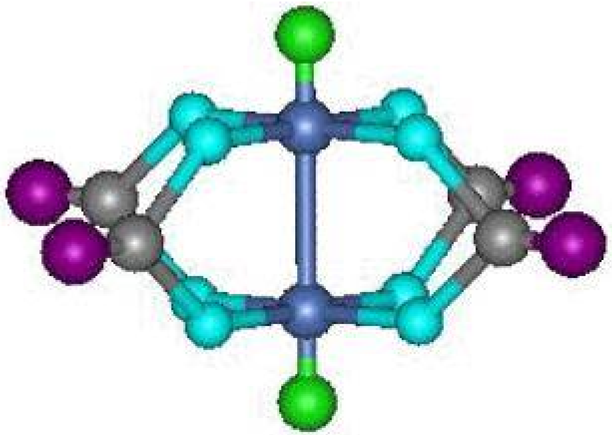


Tc_6Cl_6

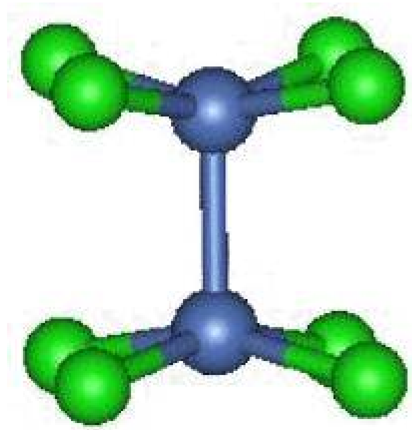
D_{4h} **D_{nh}**



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

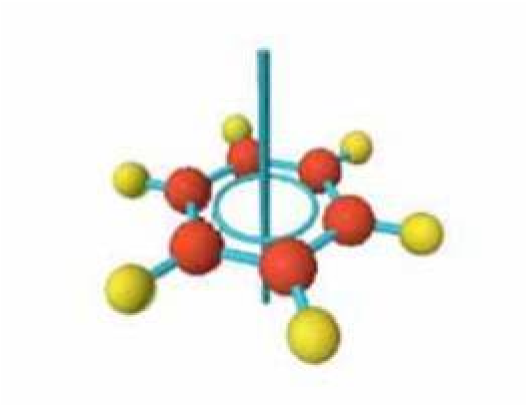


$[M_2(COOR)_4X_2]$

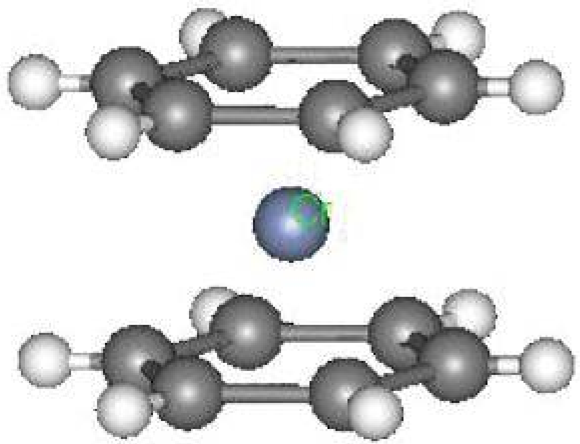


Re_2Cl_8

D_{6h}



C_6H_6



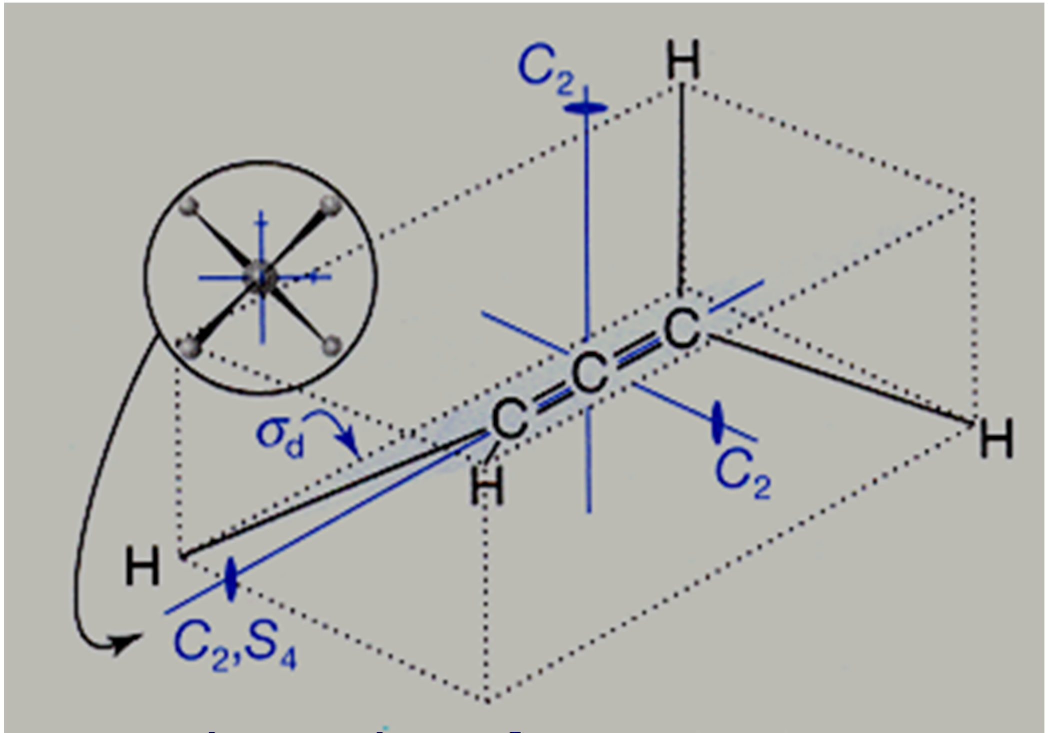
$Cr(C_6H_5)_2$

$D_{\infty h}$

O=C=O

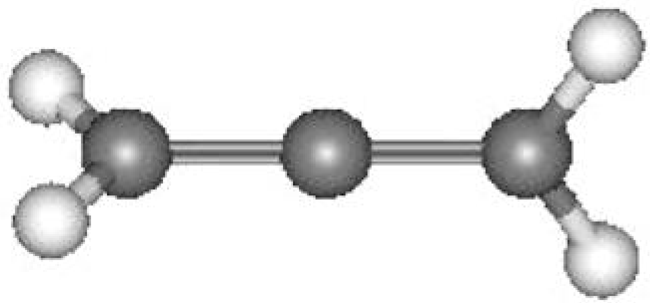
The group D_{nd}

- A molecule that has an *n*-fold principle axis and *n* twofold axes perpendicular to C_n belongs to D_{nd} if it posses *n* dihedral mirror planes.



The order of group=4n

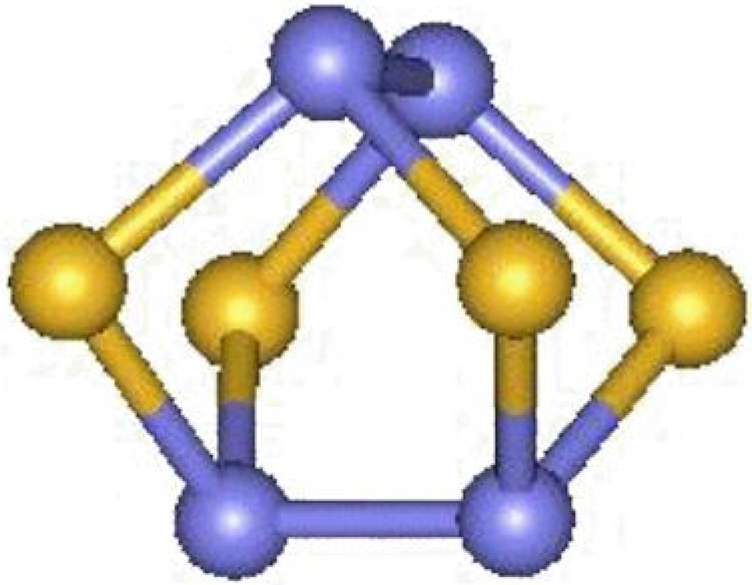
D_n , $n\sigma_d$



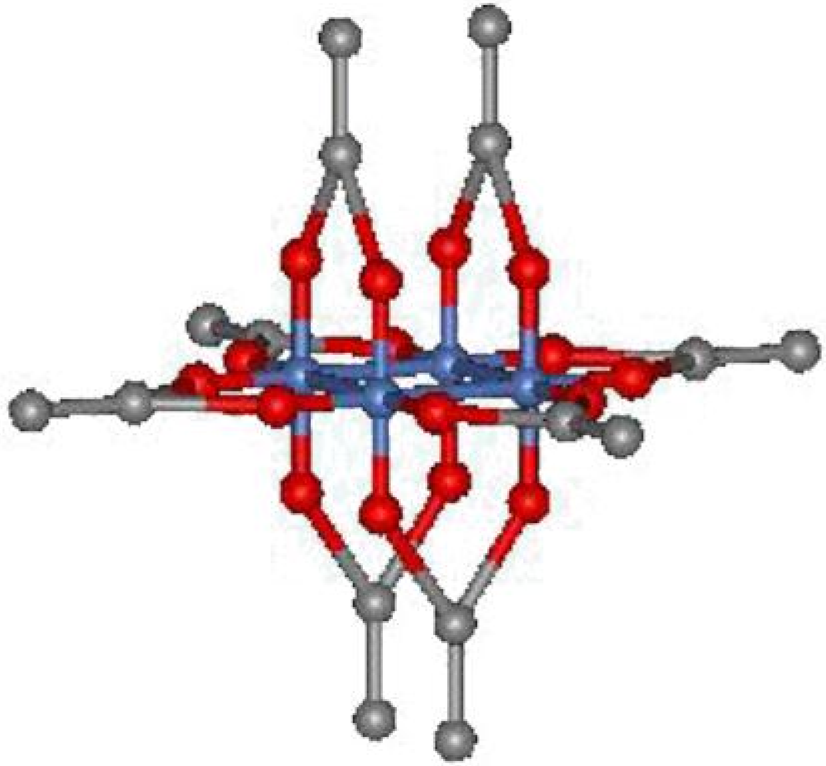
D_{2d}

D_{2d}

D_{nd}

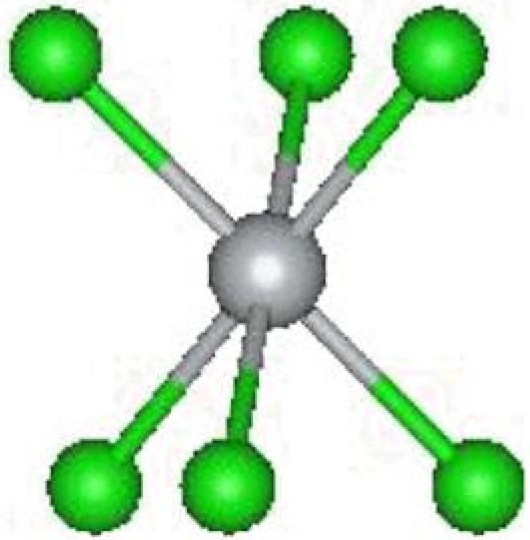


N_4S_4

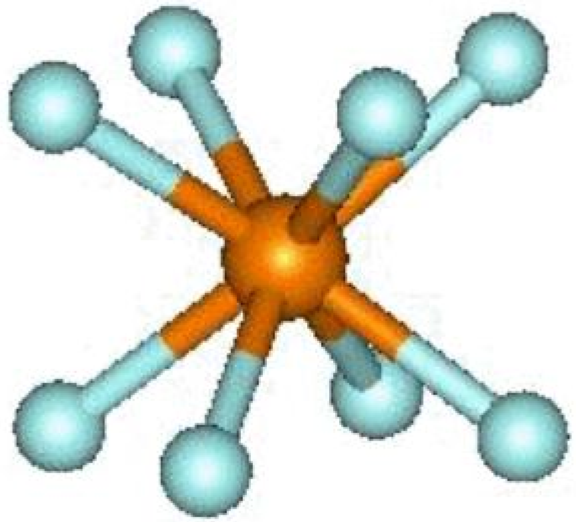


$Pt_4(COOR)_8$

D_{3d}

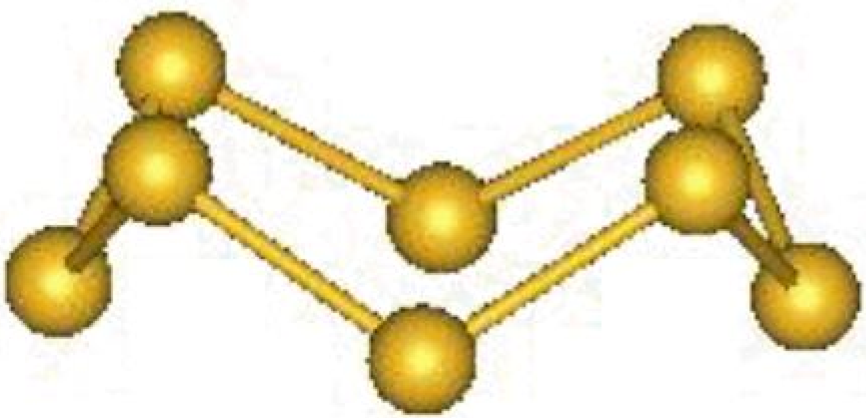


$TiCl_6^{2-}$

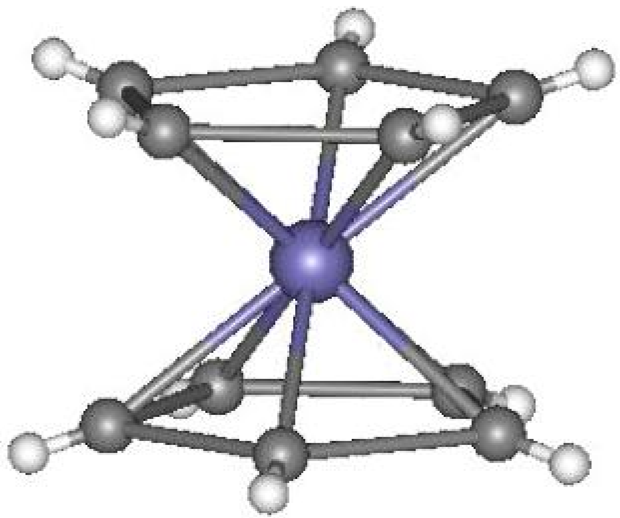


TaF_8^{3-}

D_{4d}



S_8



D_{5d}

4. High order point groups

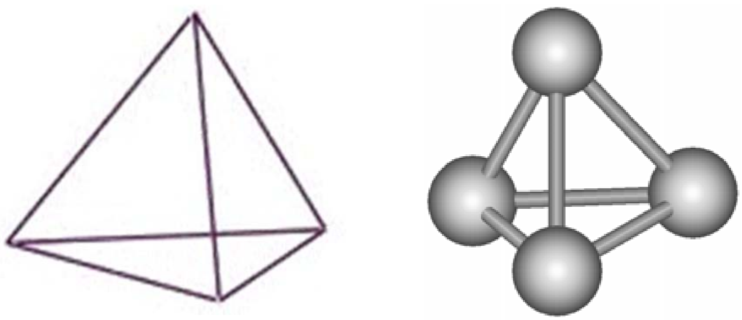
- Molecules having three or more high symmetry elements may belong to one of the following:

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: $+3\sigma_h$)

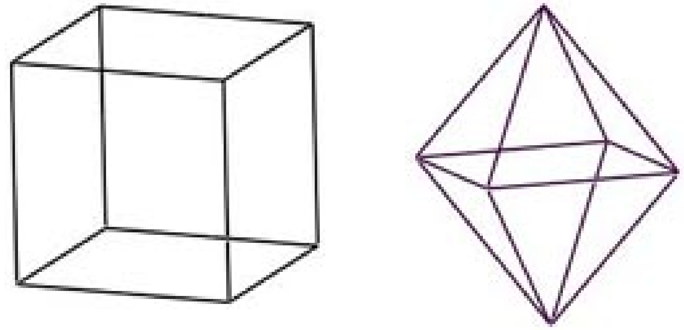
I: $6\ C_5$, $10C_3$ (I_h: $+i$)

T_d – Species with tetrahedral symmetry

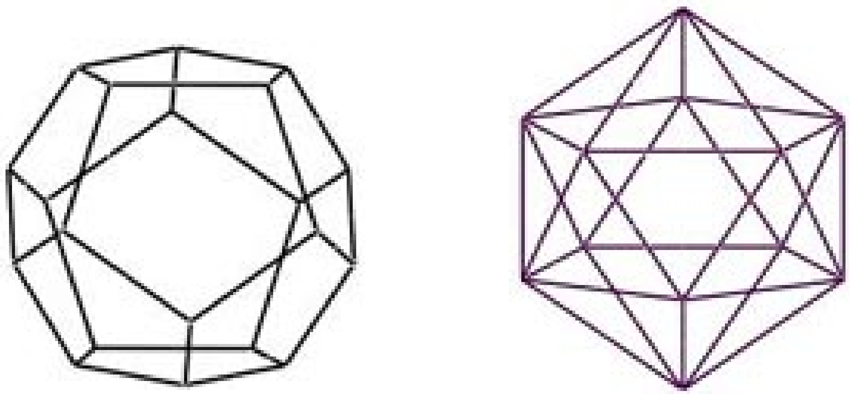


tetrahedral symmetry group

O_h – Species with octahedral symmetry (many metal complexes)



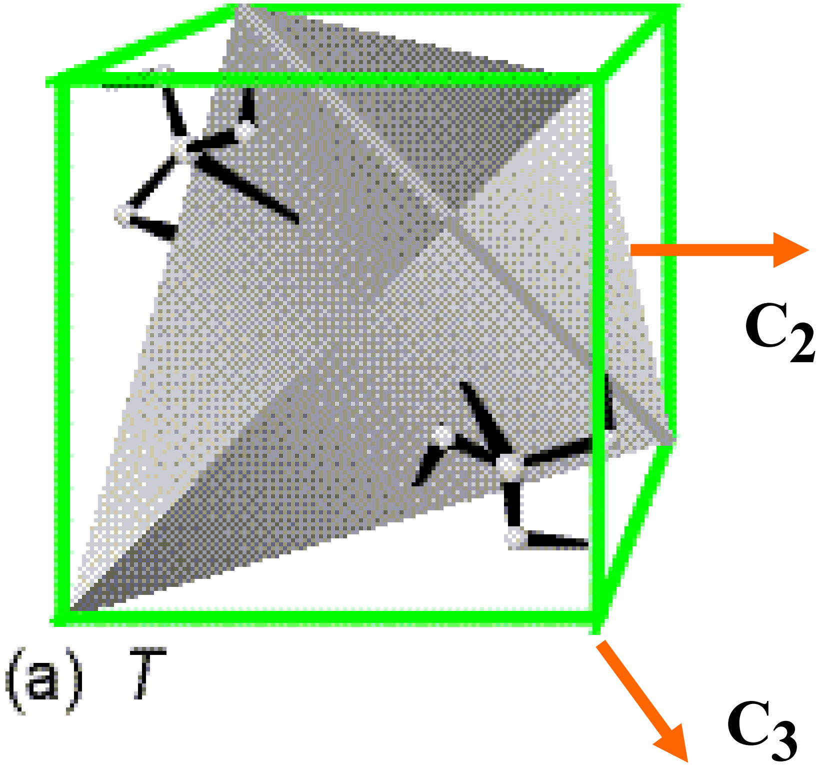
octahedral symmetry group



Icosahedral symmetry group

I_h – Icosahedral symmetry (Buckminsterfullerene, C_{60})

Cubic groups



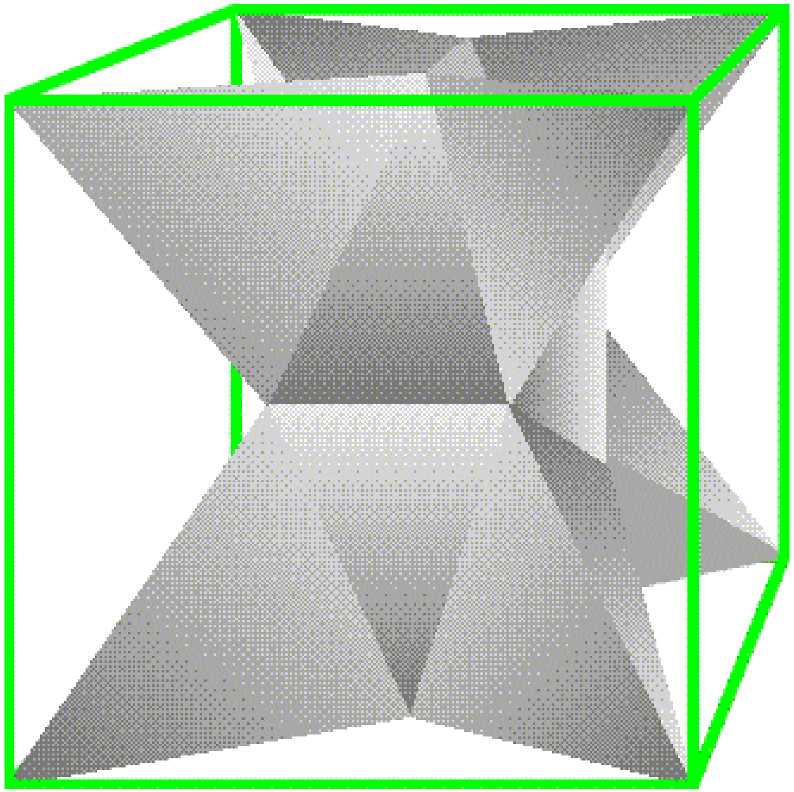
$4C_3$, $3C_2$

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

Shapes corresponding to the point groups (a) T.
The presence of the windmill-like structures reduces the symmetry of the object from Td.

Cubic groups

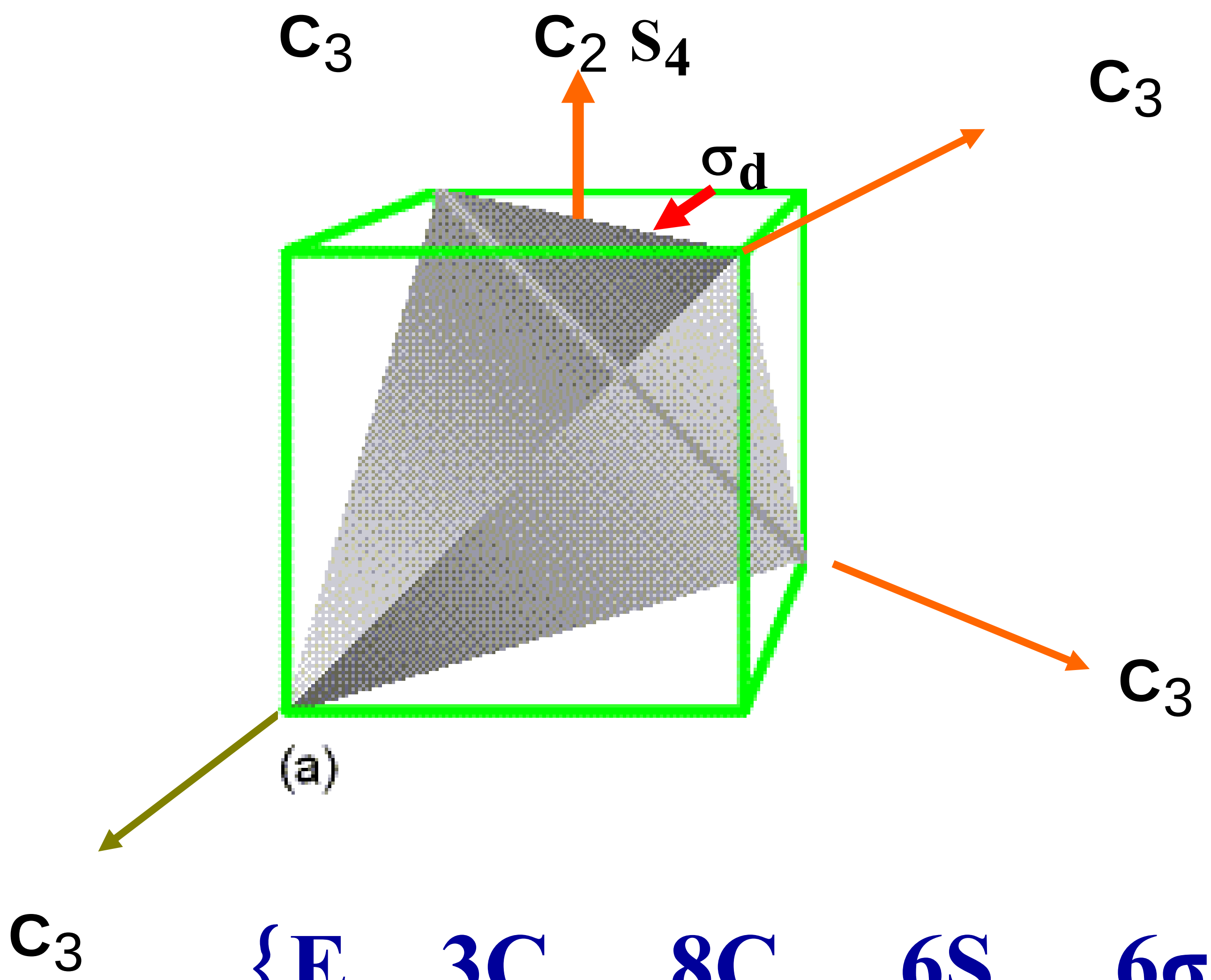
T_h

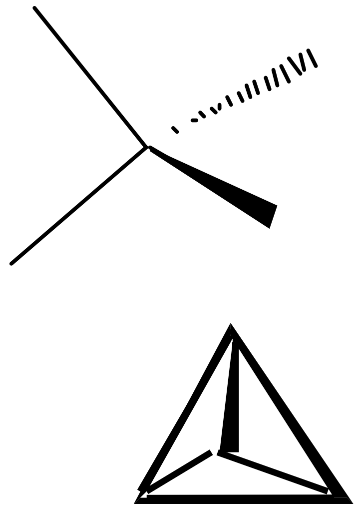


$\{E,\ 4C_3,\ 4C_3^2,\ 3C_2,\ I,\ 4S_6,\ 4S_6^5,\ 3\sigma_h\}$

Cubic groups

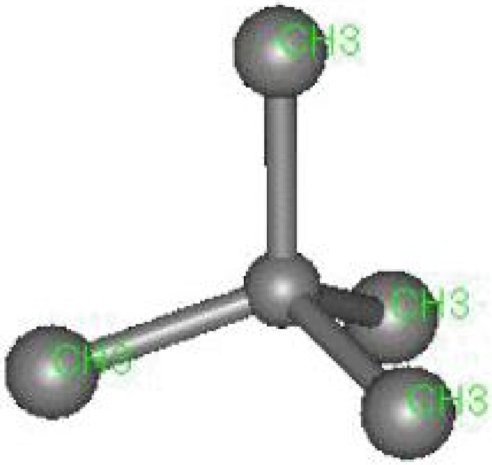
T_d





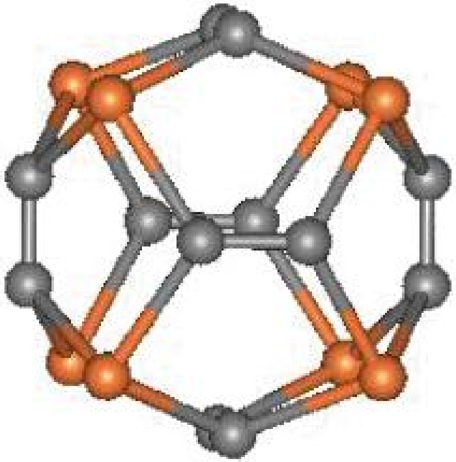
$$\{E,\ 3C_2,\ 8C_3,\ 6S_4,\ 6\sigma_d\}$$

T



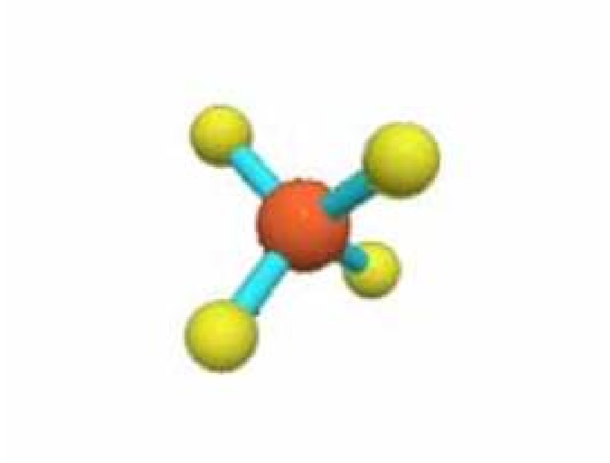
$C(CH_3)_4$

T_h



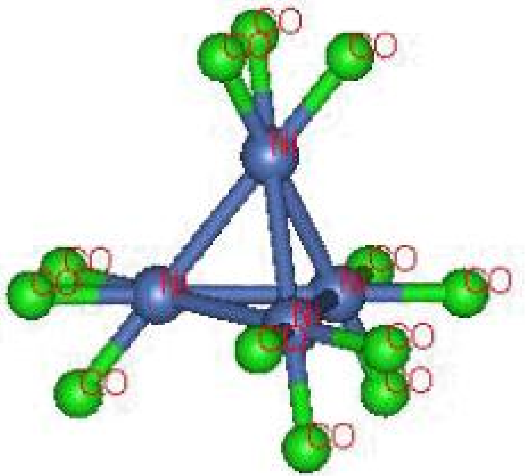
$Ti_8C_{12}^{\ +}$

T_d

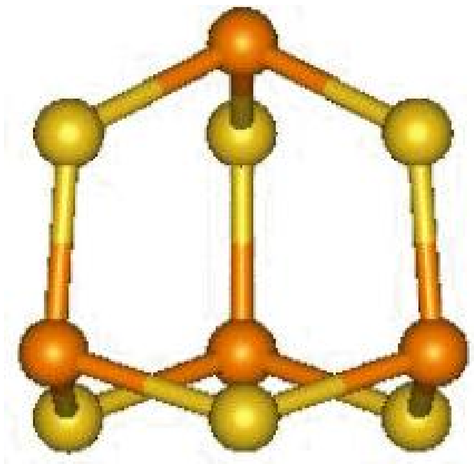


CH_4

T_d



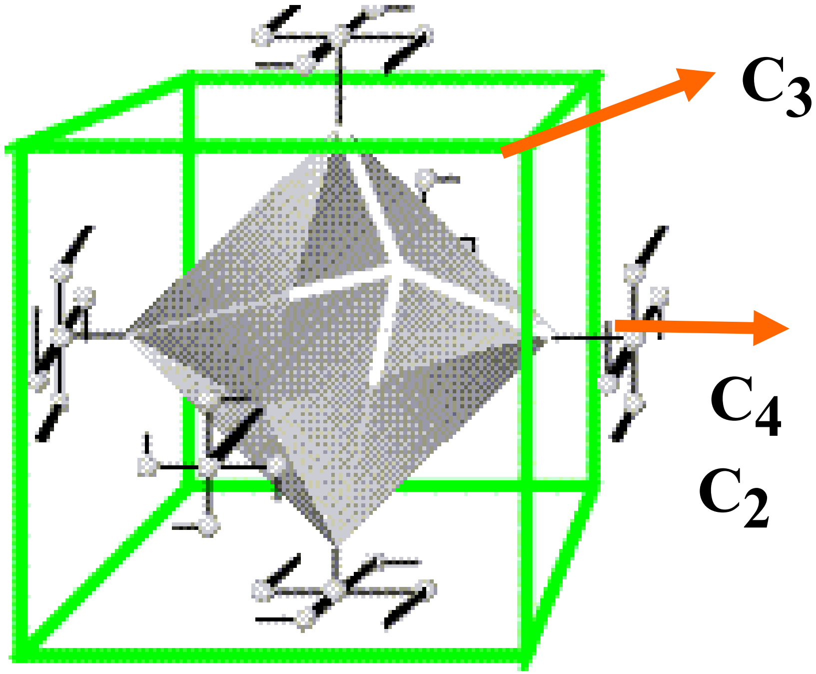
$Co_4(CO)_{12}$



P_4O_6

Cubic groups

O

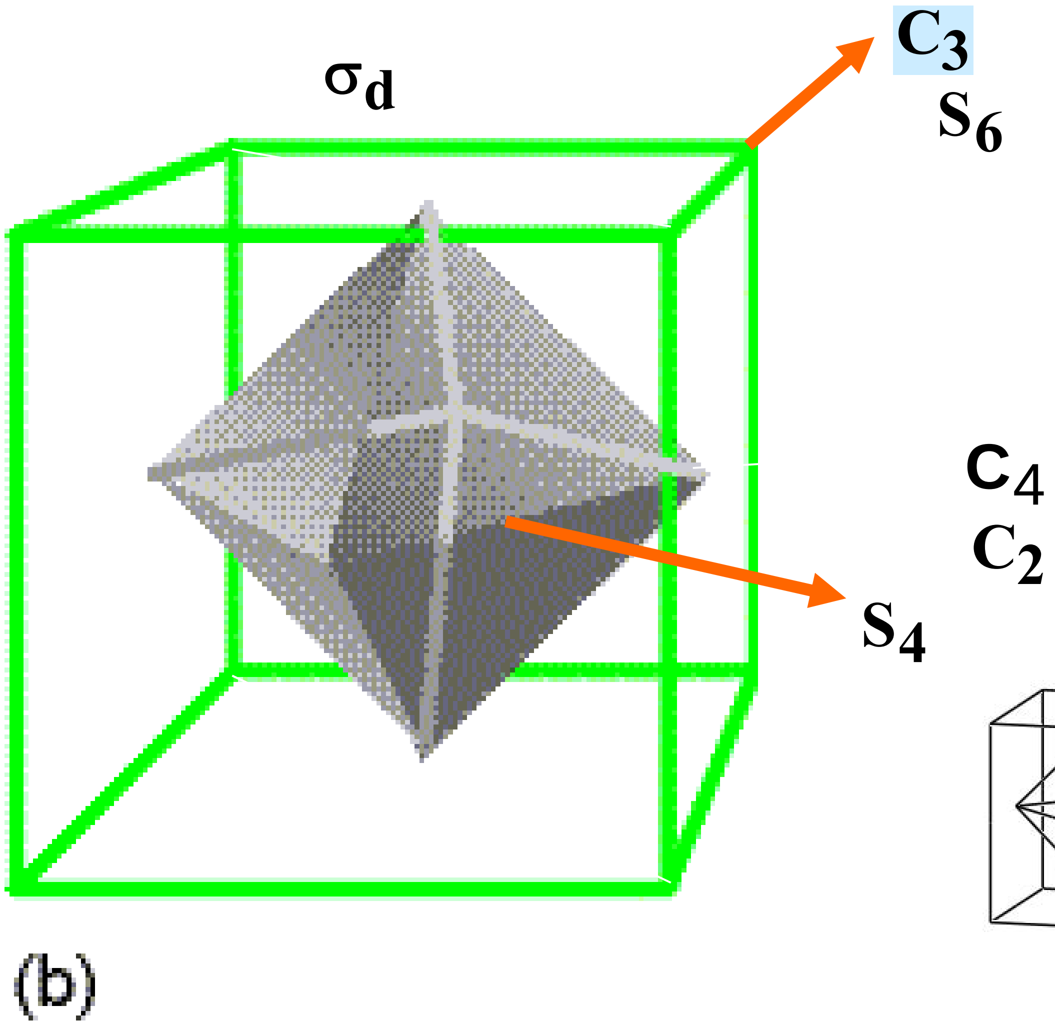


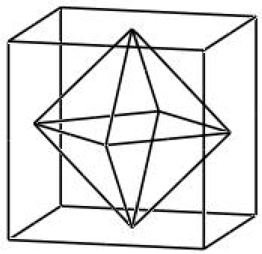
(b) O

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

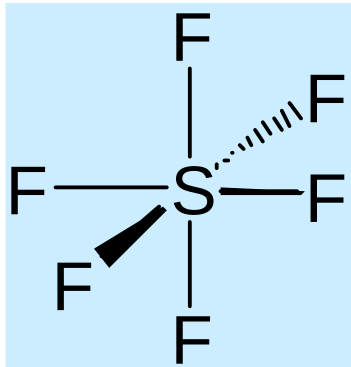
Shapes corresponding to the point groups (b) O. The presence of the windmill-like structures reduces the symmetry of the object from O_h.

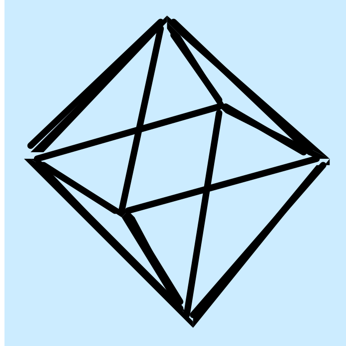
Cubic groups



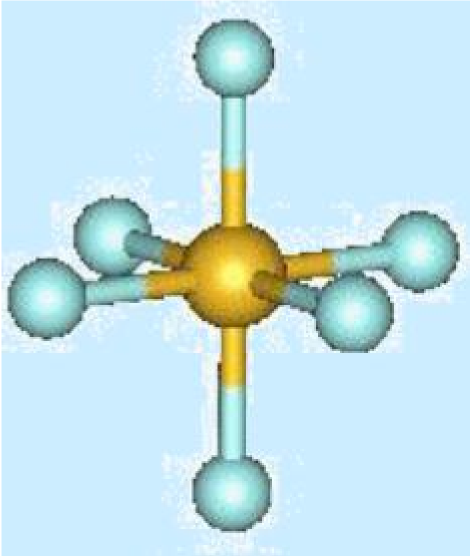


O_h

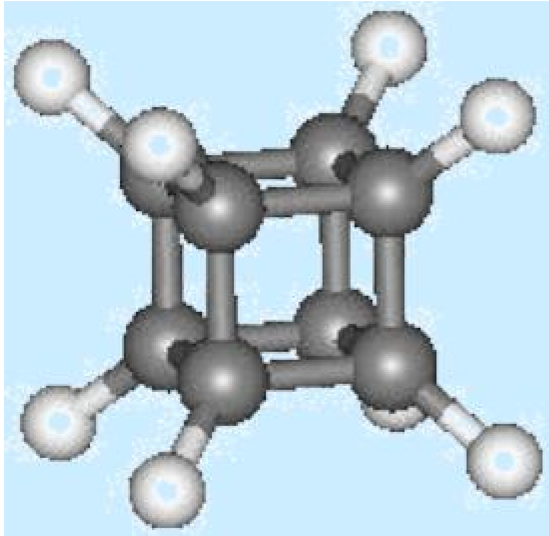




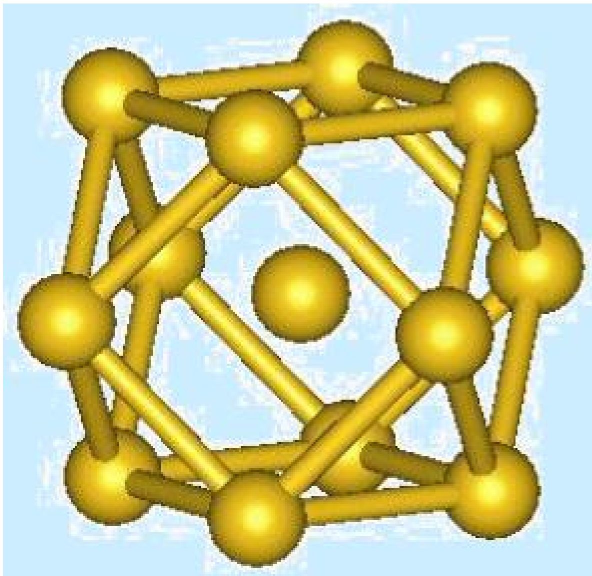
Cubic groups



SF_6



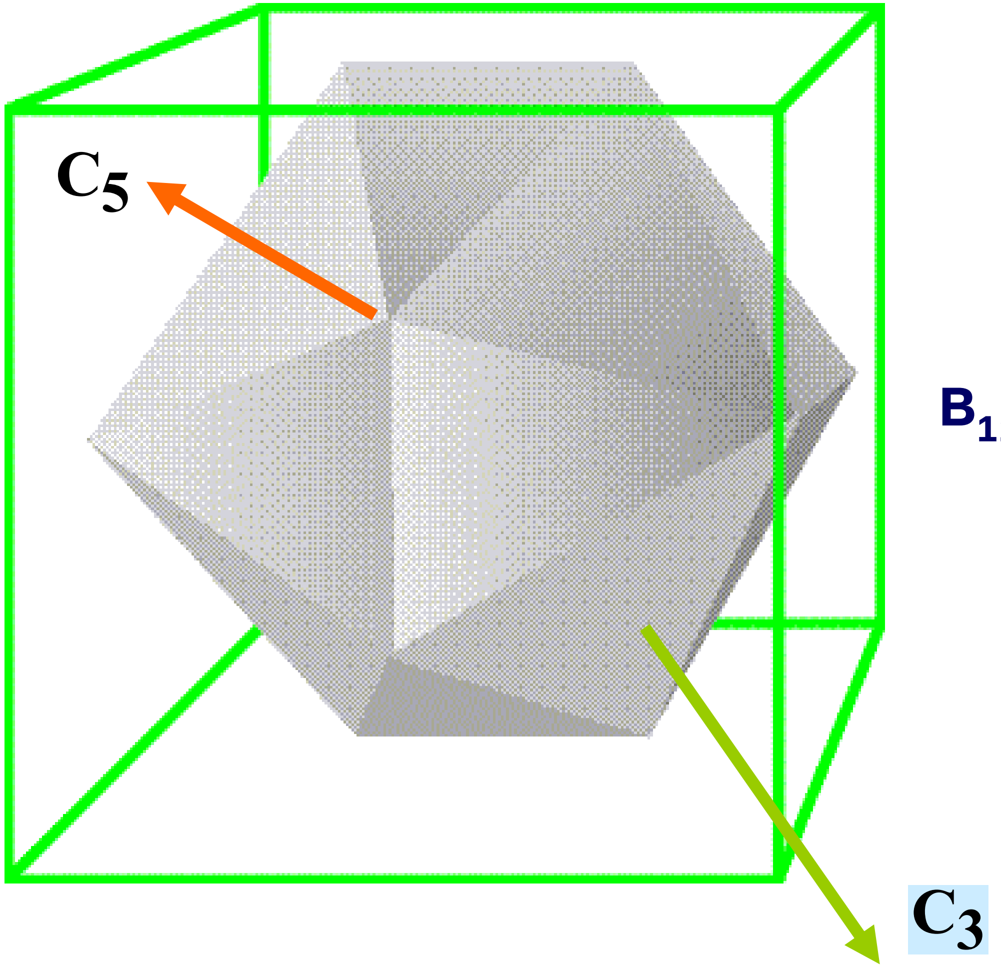
C_8H_8 OsF_8



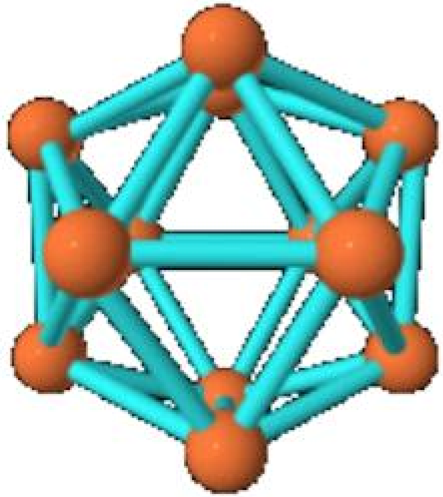
Rh_{13}

O_h

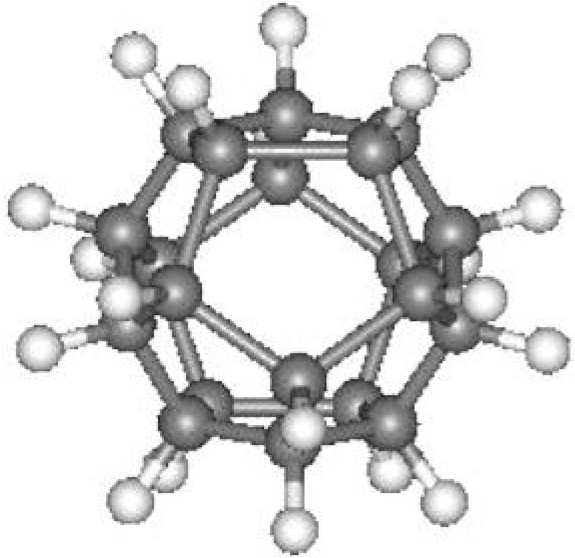
I group



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



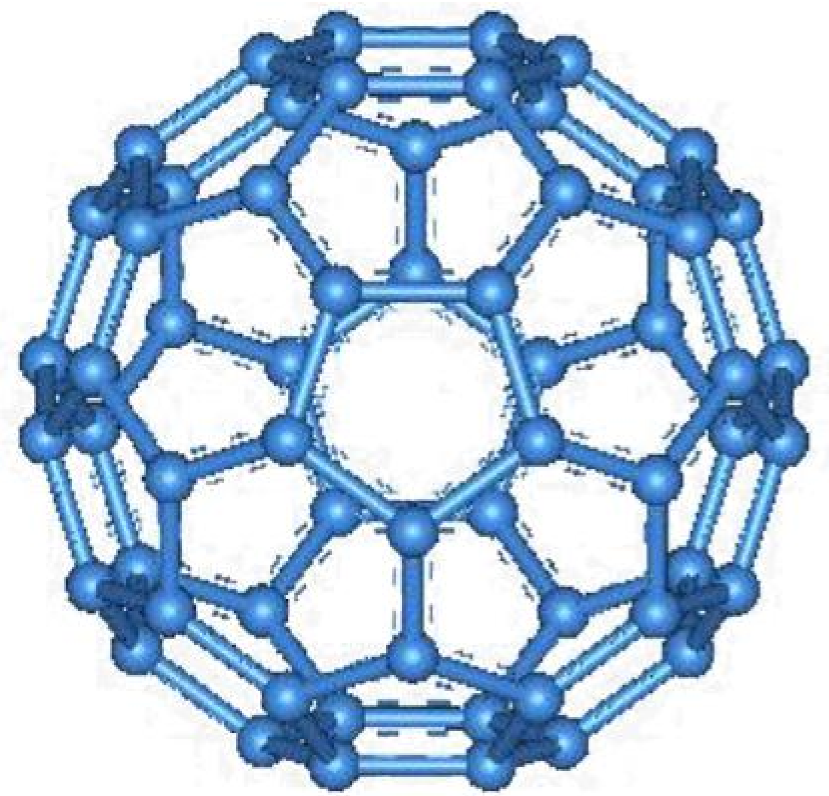
$B_{12}H_{12}$ (with hydrogen omitted)

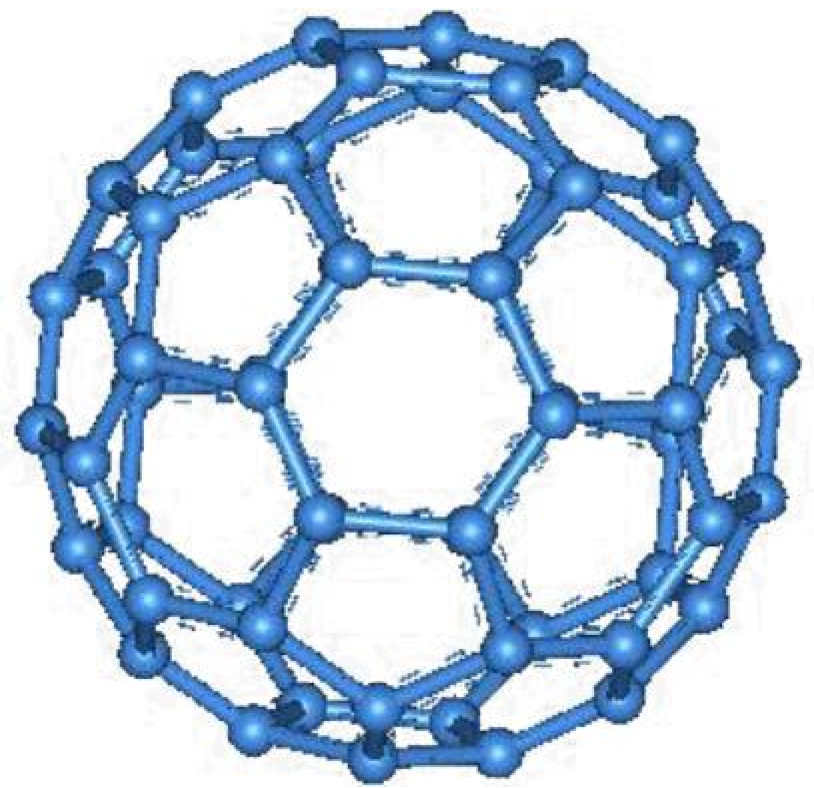


$C_{20}H_{20}$

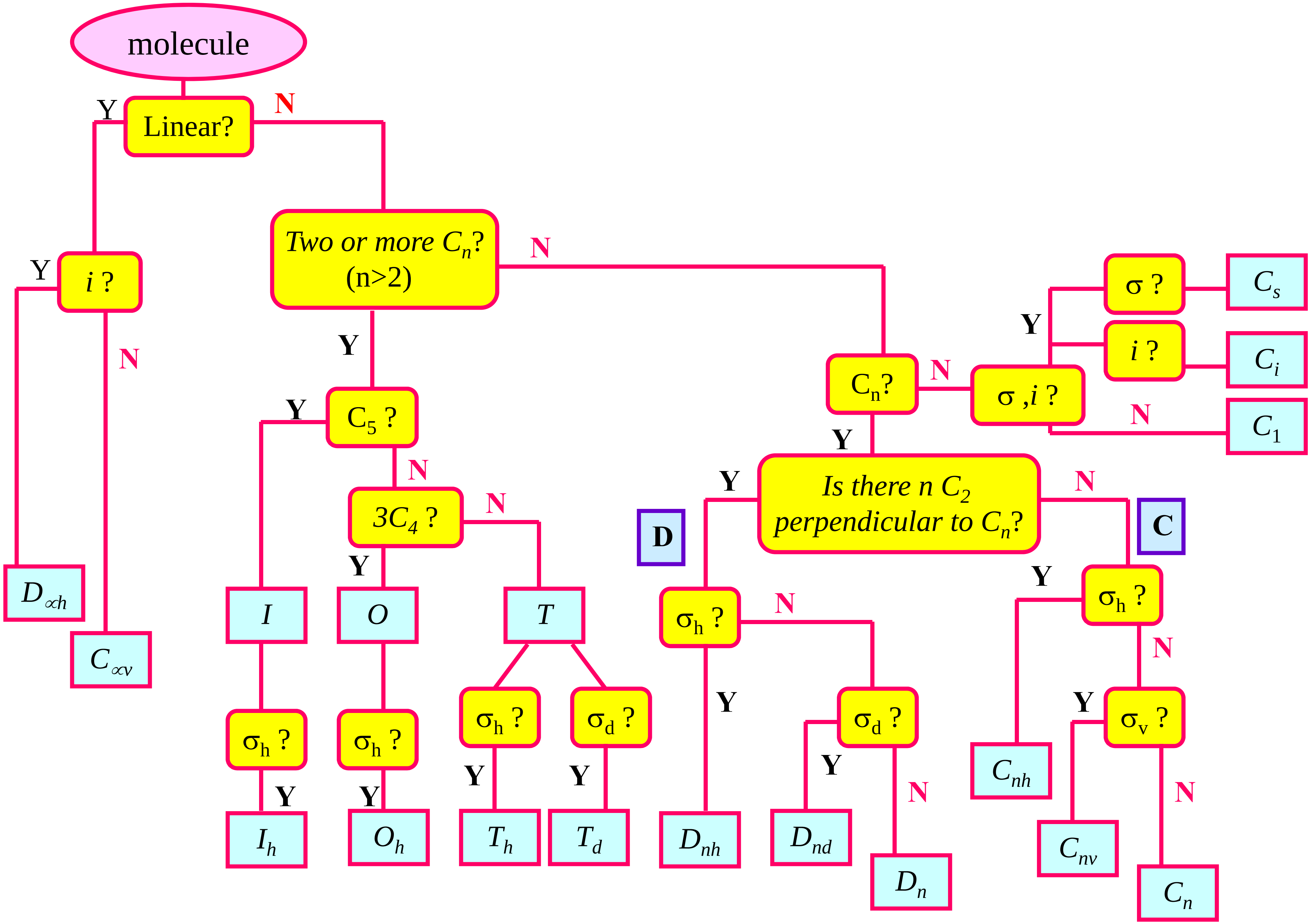
I_h

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



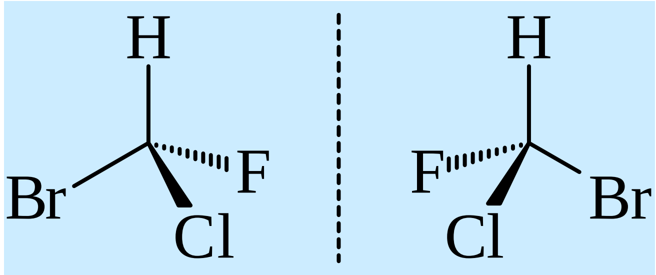


C60, the bird-view from the 5-fold axis and 6-fold axis



molecule
Linear?
Y
N
i ?
$D_{\infty h}$
$C_{\infty v}$
Two or more C_n?
(n>2)
C_5 ?
$3C_4$?
I
O
T
σ_h ?
σ_d ?
I_h
O_h
T_h
T_d
C_n?
σ ,i ?
σ ?
C_s
C_i
C_1
Is there n C_2
perpendicular to C_n?
D
C
D_{nh}
D_{nd}
D_n
σ_v ?
C_{nh}
C_{nv}
C_n

§ 4 Application of symmetry



1. Chirality

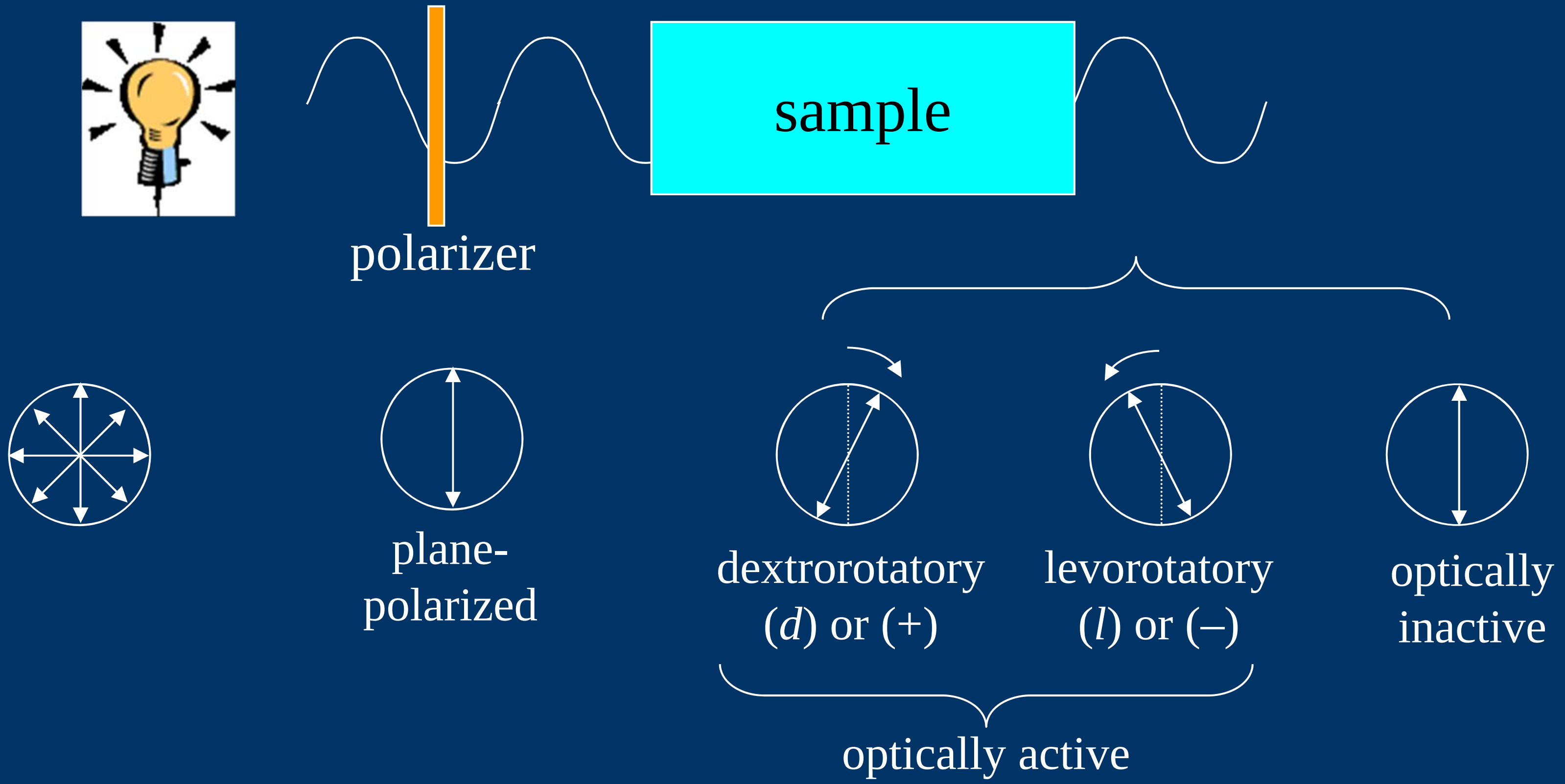
A chiral molecule is a molecule that can not be superimposed on its mirror image

These molecules are:

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

$$\mathbf{S_n\ (i=S_2;\ \sigma)}$$

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**

- 50/50 mixture of two enantiomers

Optically pure: 100% of one enantiomer

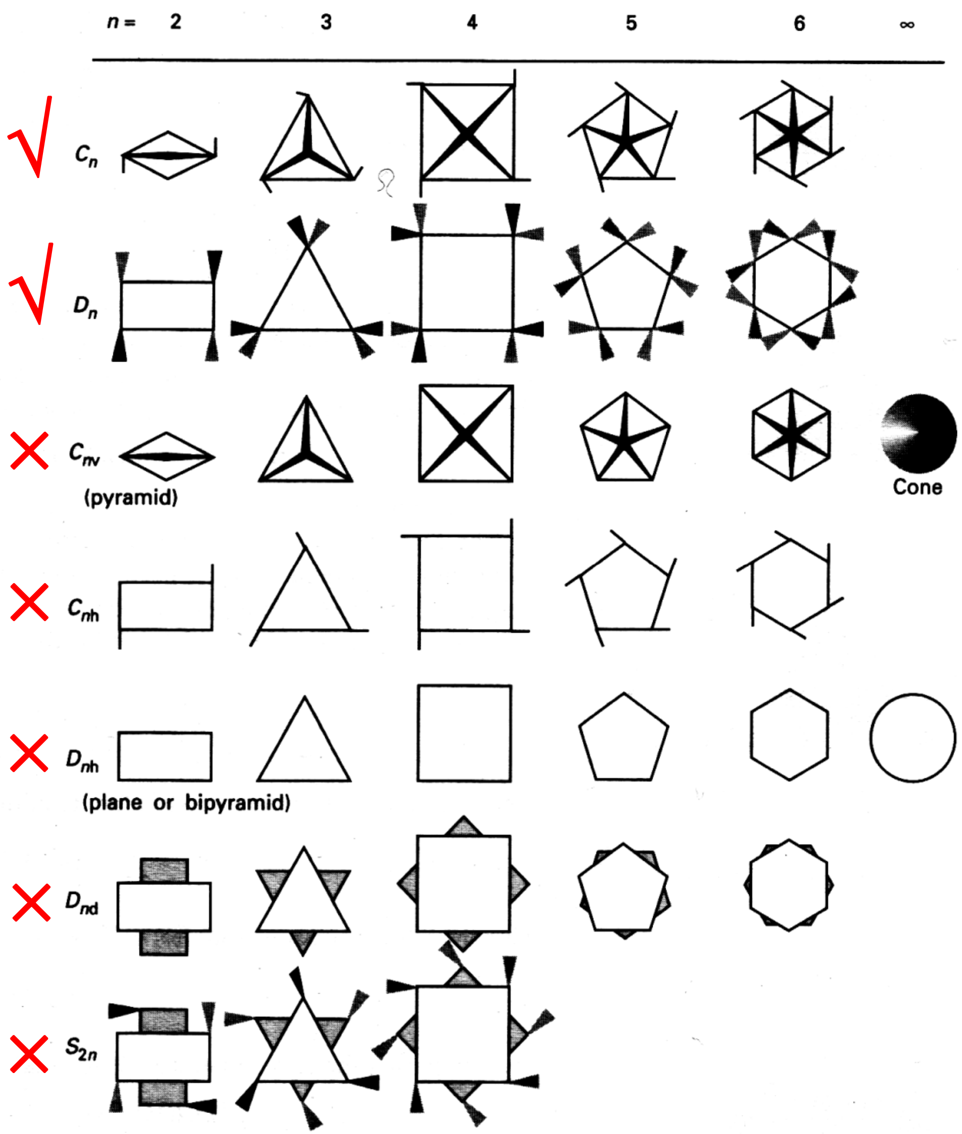
Optical purity (enantiomeric excess)

= 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)

2. Polarity, Dipole Moments and molecular symmetry

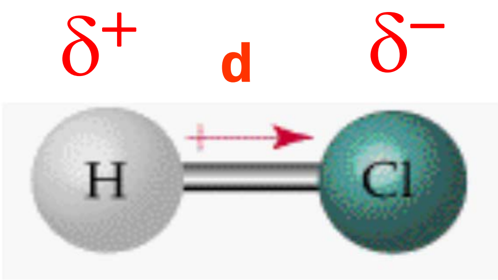
A **polar molecules** is one with a permanent electric dipole moment.

Dipole Moments

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

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

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

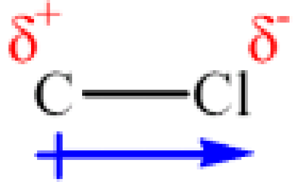


Bond Dipole Moments

$H_3C\text{-}CH_3$ $H_3C\text{-}NH_2$ $H_3C\text{-}OH$ $H_3C\text{-}Cl$

nonpolar → Increasing polarity

- Individual covalent bonds are polar if the atoms being connected are of different electronegativities.
- *Example:* CH_3Cl
  - The C—H bonds are *nonpolar* since C and H have about the same electronegativity.
  - Since Cl is more electronegative than C, the C—Cl bond is *polarized* so that the Cl atom is slightly electron-rich (partial negative charge, δ^-) and the C atom is slightly electron-poor (partial positive charge, δ^+). This bond is a **polar covalent bond** (or just **polar bond**).



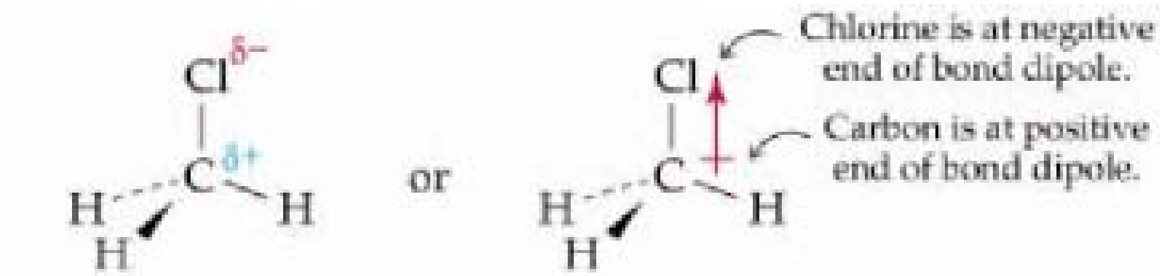
Molecular Dipole Moments

Depend on bond polarity and bond angles

- Vector sum of the bond dipole moments

    Symmetric molecules may have zero net dipole --- CO_2: O=C=O

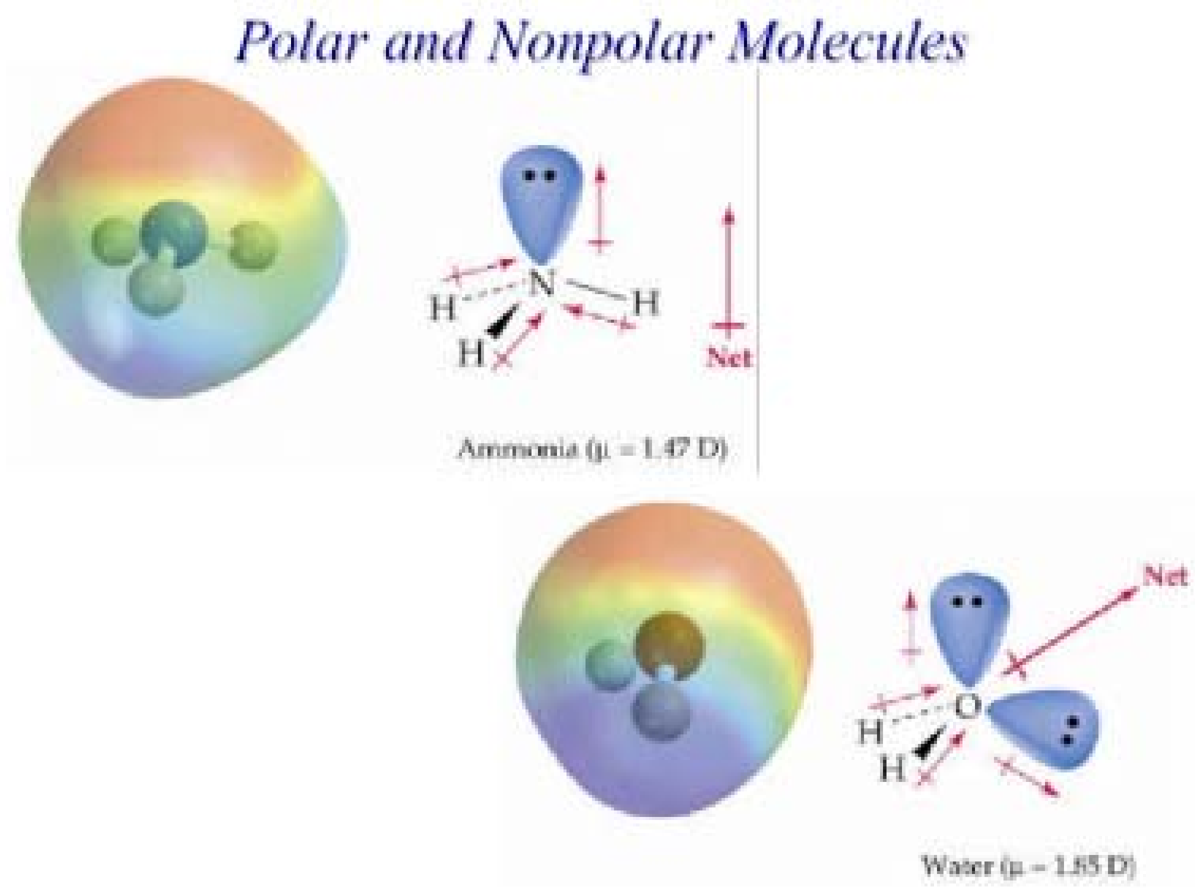
- Lone pairs of electrons contribute to the dipole moment



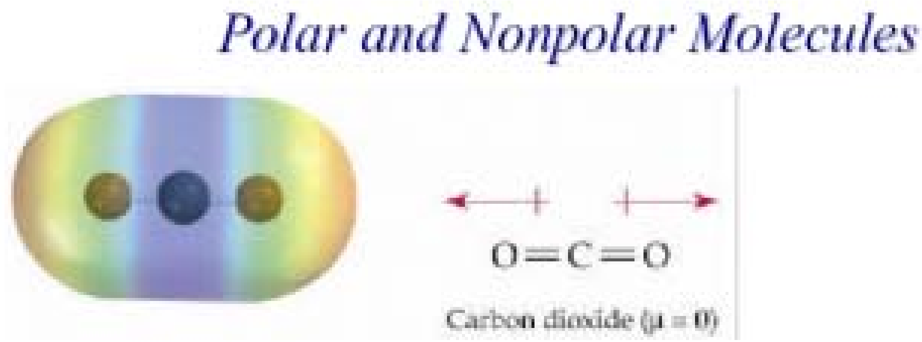
Chloromethane, CH_3Cl

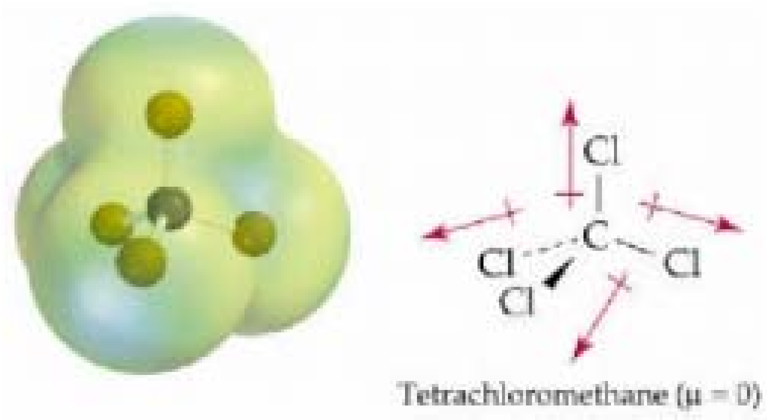
Since CH_3Cl has a *tetrahedral* shape, with one polar bond and three nonpolar bonds, there is an overall molecular dipole in the molecule, pointing towards the Cl atom.

Molecular Dipole Moments



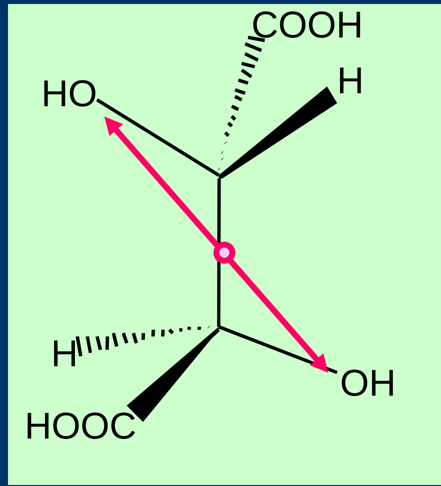
Molecular Dipole Moments





Permanent Dipole Moments

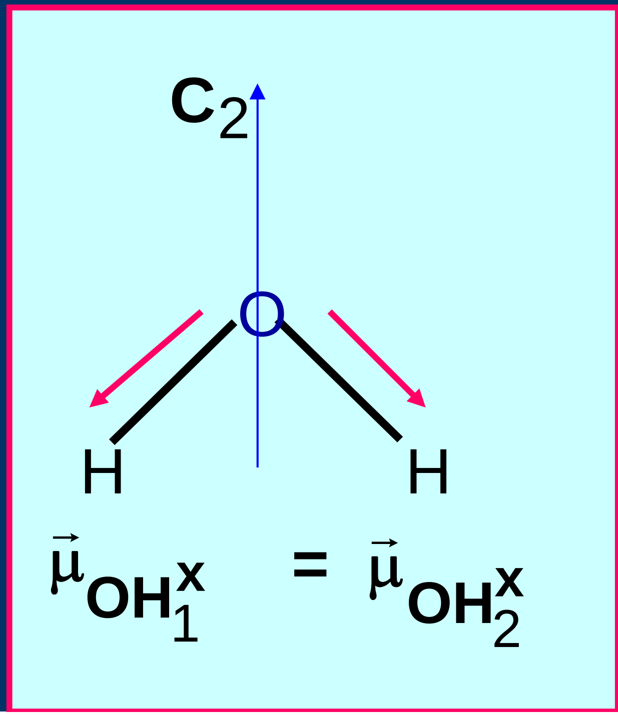
(a) A permanent dipole moment can not exist if *inversion center* is present. Only molecules belonging to the groups C_n, C_{nv} and C_s may have an electric dipole moment



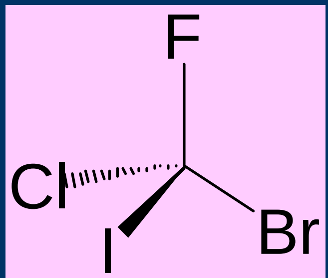
Meso-tartaric acid

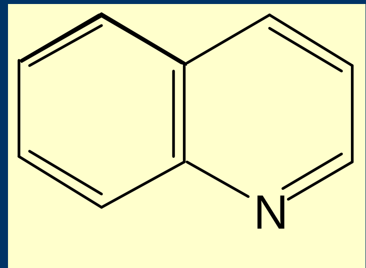
$\mu = 0$
inversion

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

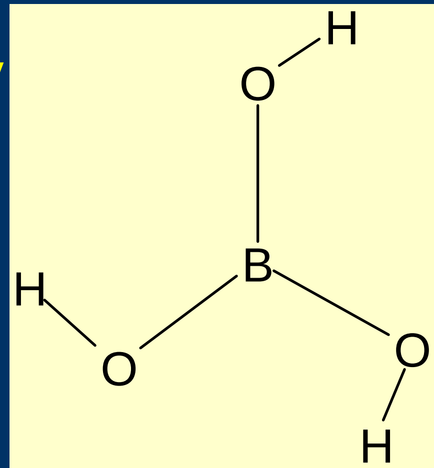


Molecular Dipole Moments and molecular symmetry



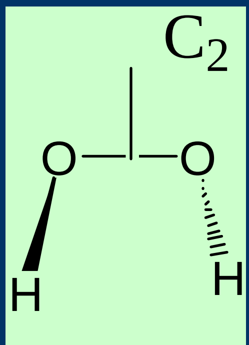


Quinoline

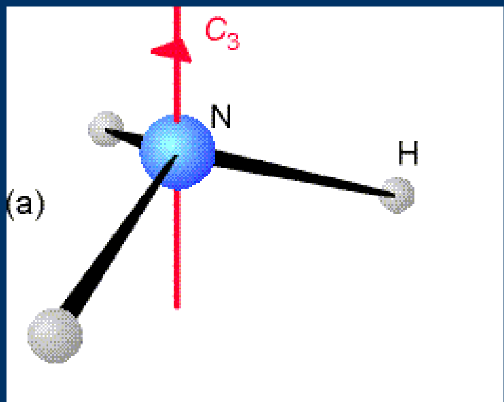


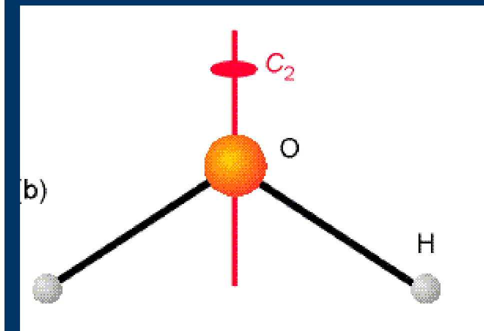
$B(OH)_3$

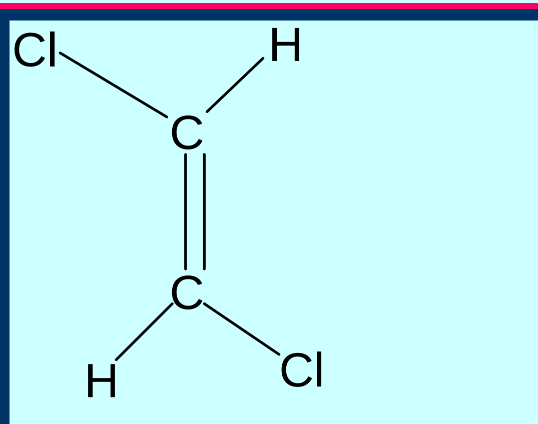
$\mu \neq 0$	$\mu \neq 0$ **in plane**	$\mu = 0$ **σ_h symmetry**



H_2O_2







Trans CHCl=CHCl

$\mu \neq 0$ **along C_2**	$\mu \neq 0$ **along C_3**	$\mu \neq 0$ **along C_2**	$\mu = 0$ **inversion**