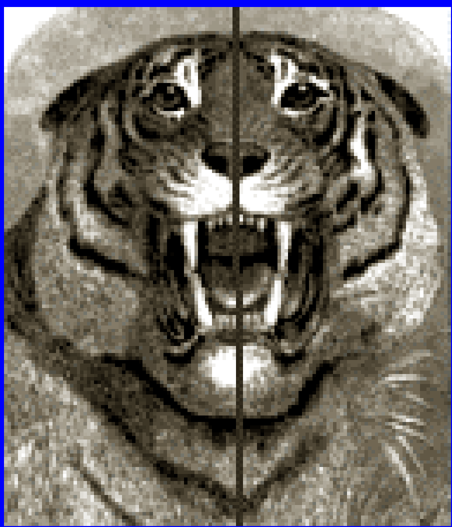
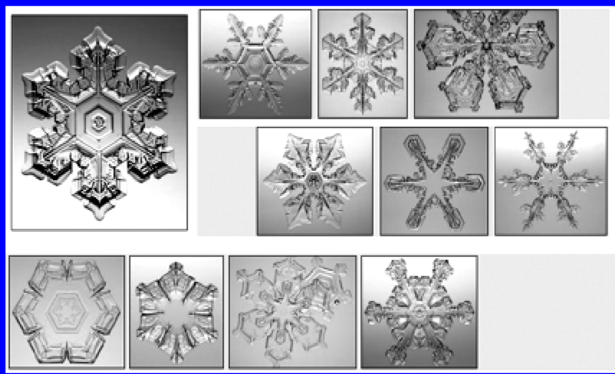
Chapter 3

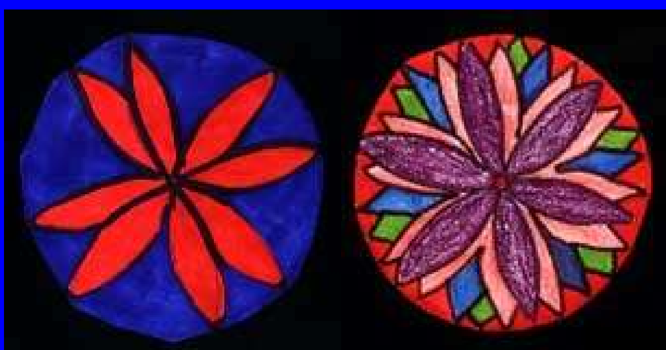
Molecular symmetry and symmetry point group

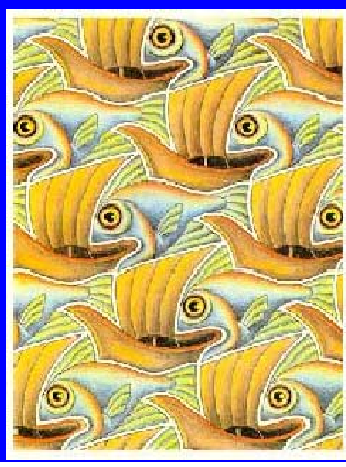




§ 1 Symmetry elements and symmetry operations

- 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.





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.

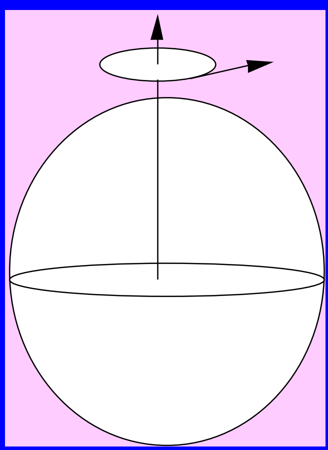
➢ To direct chemical syntheses; the compatibility in symmetry is a factor to be considered in the formation and reconstruction of chemical bonds.

1. Symmetry elements and symmetry operations

symmetry operation

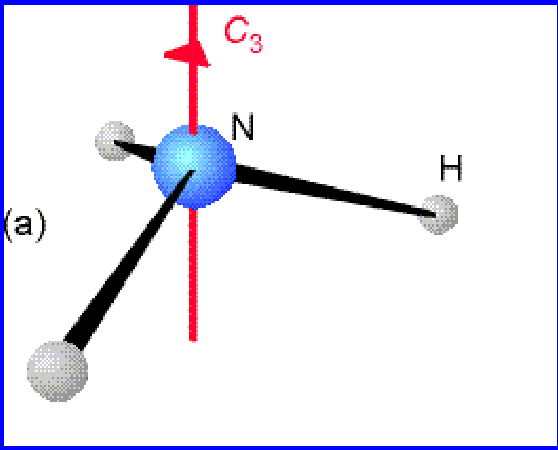
- **A action that leaves an object the same after it has been carried out is called symmetry operation.**

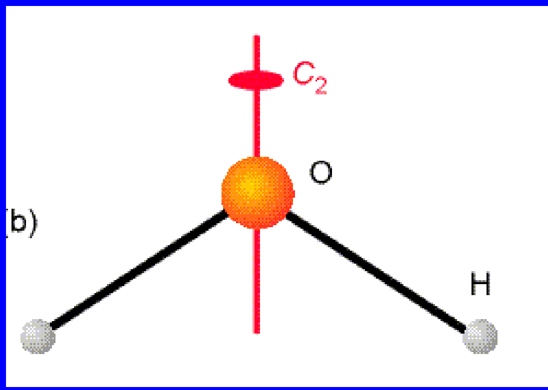
Example:



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

Example:





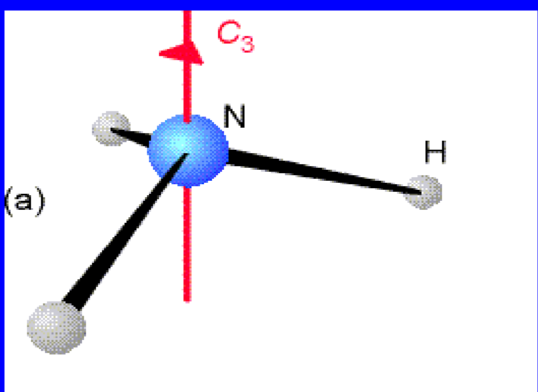
(a) An NH_3 molecule has a threefold (C_3) axis

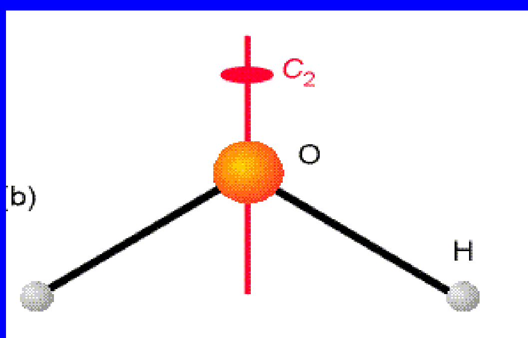
(b) an H_2O molecule has a twofold (C_2) axis.

symmetry elements

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

Example:

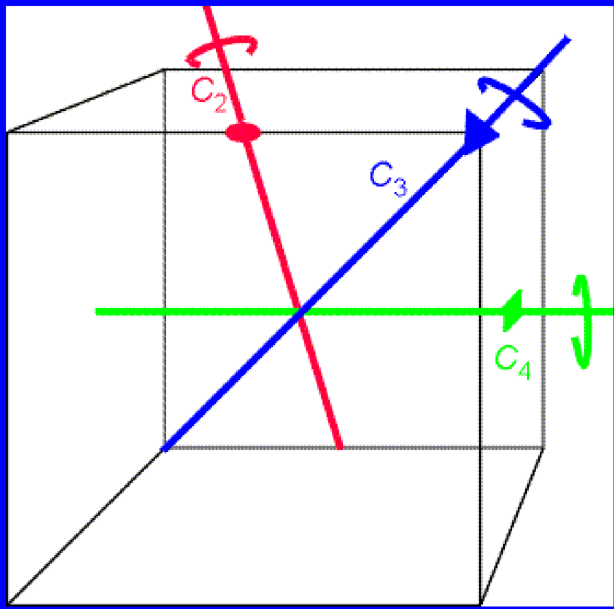




(a) An NH_3 molecule has a threefold (C_3) axis

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

Symmetry elements



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

Symmetry Operation

Symmetry operations are:

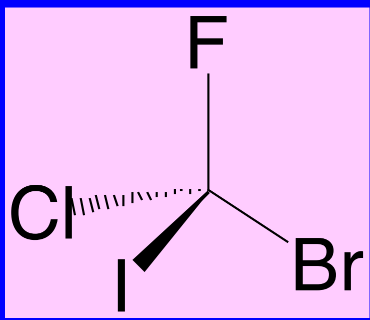
Rotation **Reflection** **Inversion**

The corresponding symmetry elements are:

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

1) The identity (E)

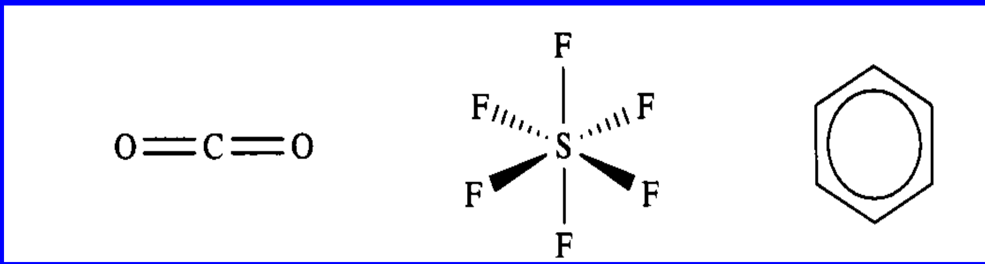
- **Operation by the identity operator leaves the molecule unchanged.**
- **All objects can be operated upon by the identity operation.**



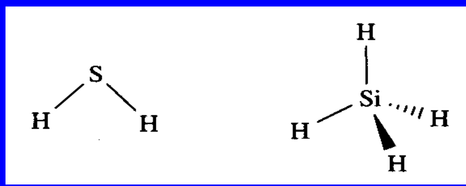
2) Inversion and the inversion center (*i*)

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

For example

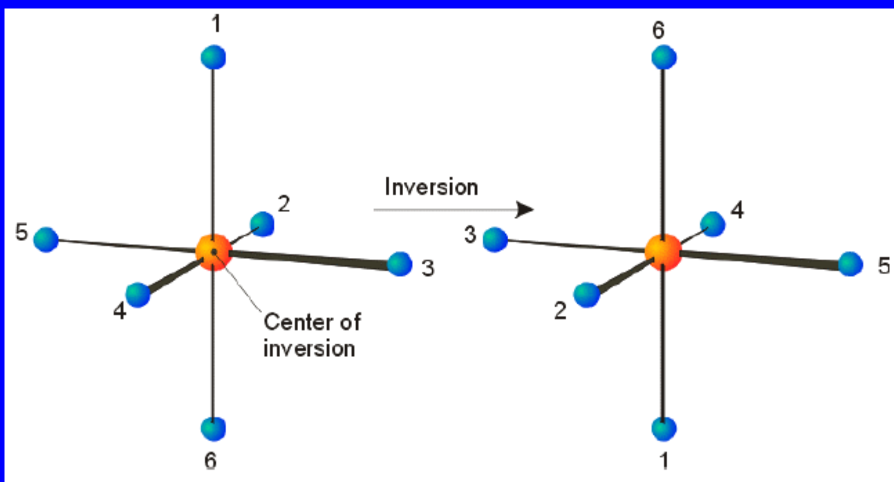


These have a center of inversion i.



These do not have a center of inversion.

- Inverts all atoms through the centre of the object



- Its matrix representation

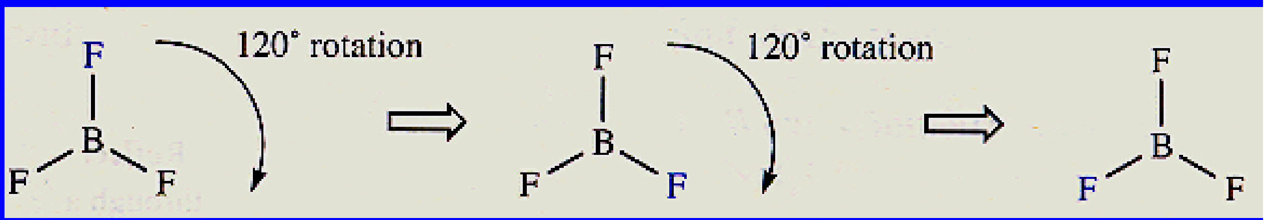
$$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

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

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

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

- Example: Rotation of trigonal planer BF_3

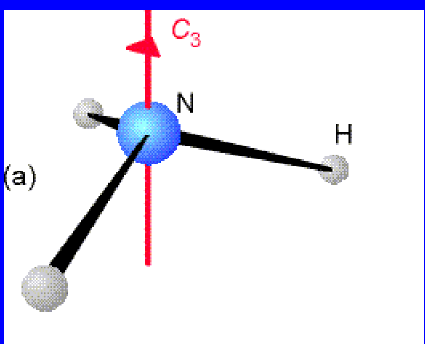


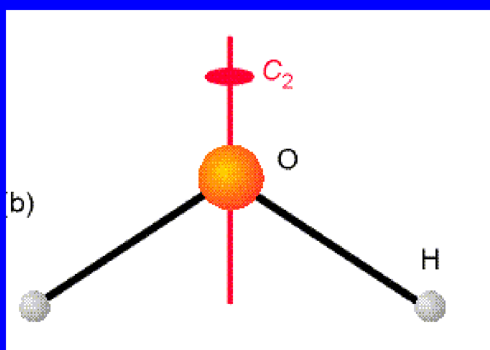
C_3^1 C_3^2

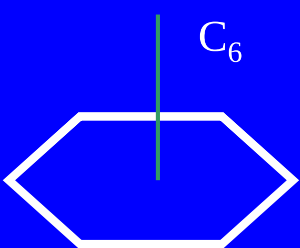
–**One three-fold (C_3) rotation axes.** **($\alpha=2\pi/3$)**

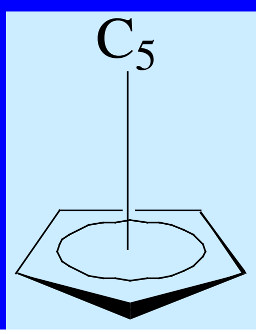
The principle rotation axis is the axis of the highest fold.

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

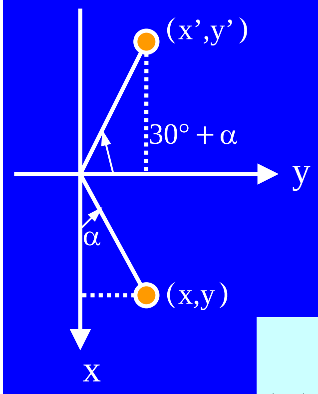








The matrix representations:



x'=-sin(30° + α)= -sin30°cosα - cos30°sinα

= (-1/2)x + (-√3/2)y

y'=cos(30° + α)= cos30°cosα - sin30°sinα

= (√3/2)x + (-1/2)y

C_3^{1}

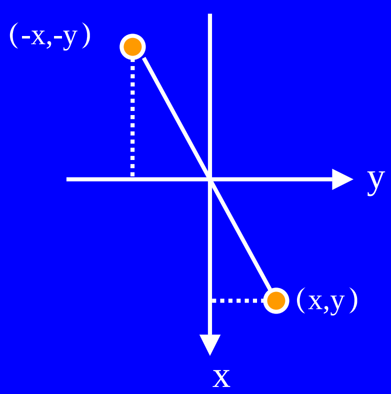
$$\begin{pmatrix} x_1 \\ y_1 \\ z_1 \end{pmatrix} = C_3^1 \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} \cos\frac{2\pi}{3} & -\sin\frac{2\pi}{3} & 0 \\ \sin\frac{2\pi}{3} & \cos\frac{2\pi}{3} & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -\frac{1}{2}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

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

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

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

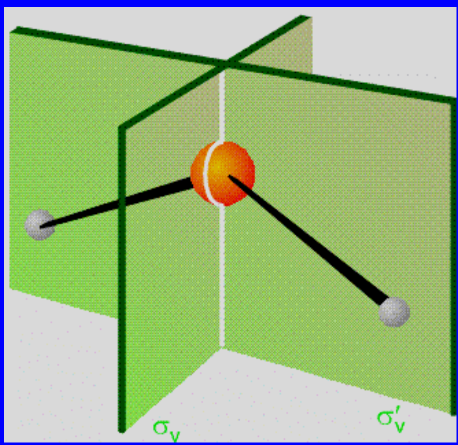
C_n

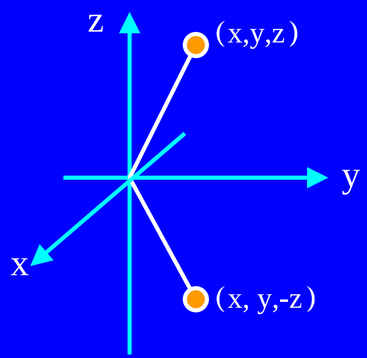
$$C_n^{\,k} = \begin{pmatrix} \cos\alpha & -\sin\alpha & 0 \\ \sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

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

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 s.





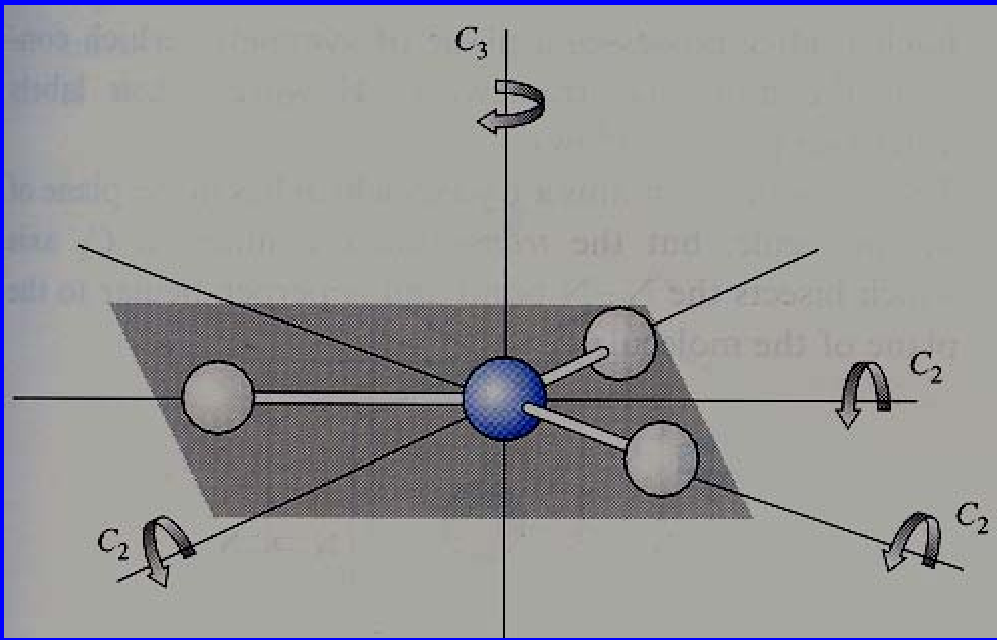
$$\sigma_{xy} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \qquad \sigma_{xy} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x \\ y \\ -z \end{pmatrix}$$

➢There are three types of mirror planes:

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

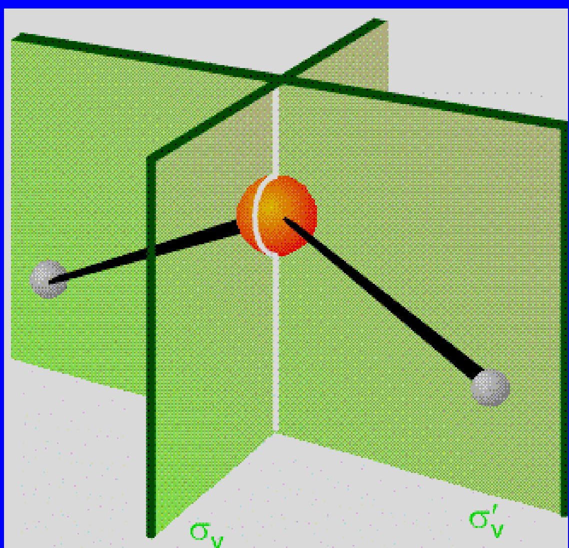
If the plane is **perpendicular** to the vertical principle axis then it labeled σ_h.

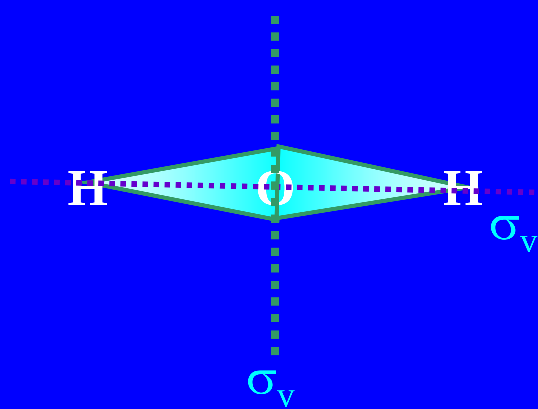
- Example: BF_3 also has a σ_h plane of symmetry.



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

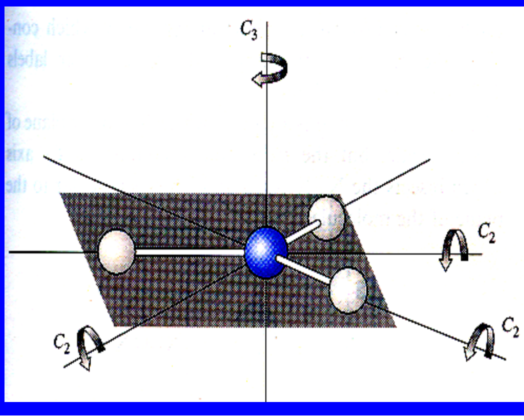
- Example: Water
  - Has a C_2 principle axis.
  - Has two planes that contain the principle axis, σ_v and σ_v'.

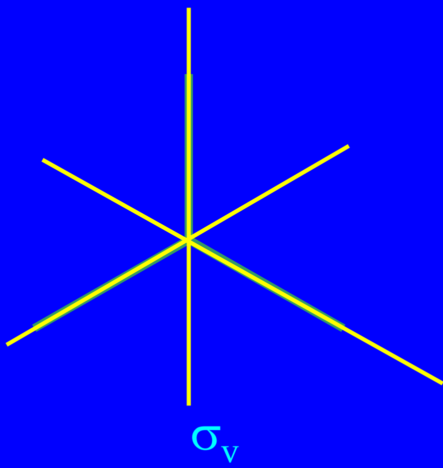




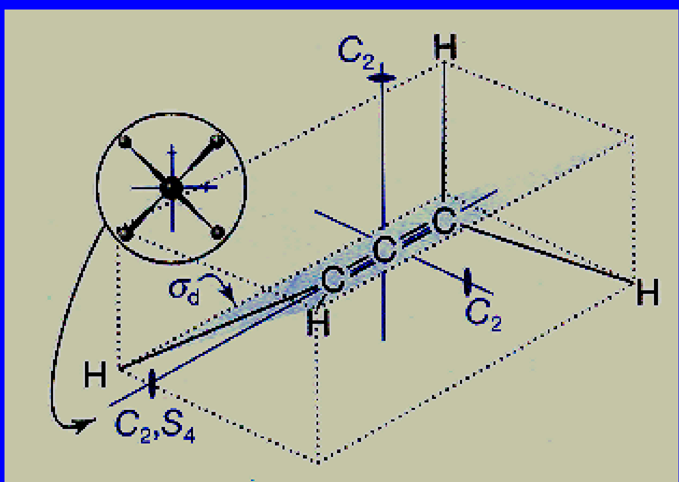
If a σ plane **contains** the principle axis and **bisects** the angle between two adjacent 2-fold axes then it is labeled σ_d (*Dihedral* mirror planes)

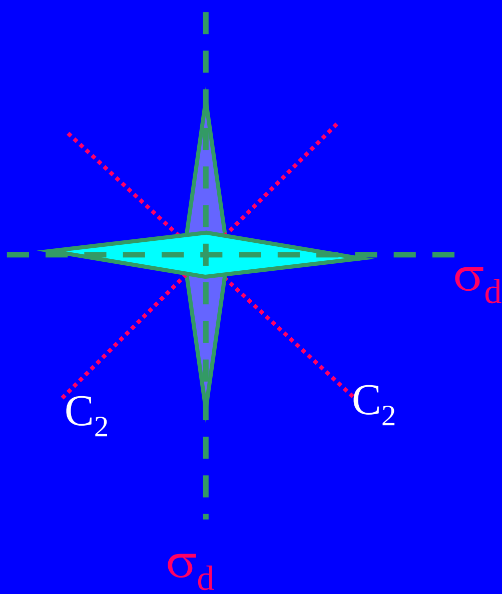
- Example: BF_3
  - Has a C_3 principle axis
  - Has three-C_2 axes.
  - Has three σ_d planes (?).





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

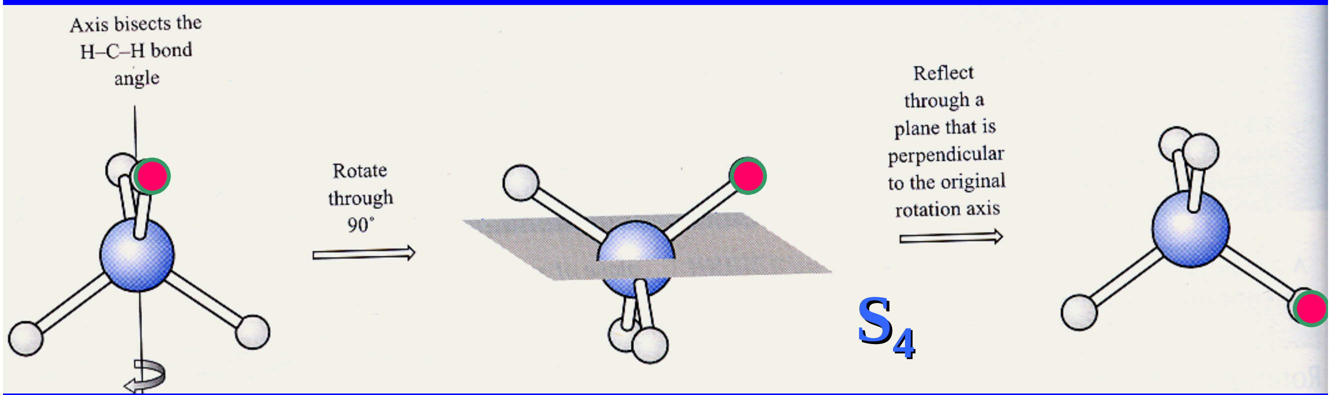




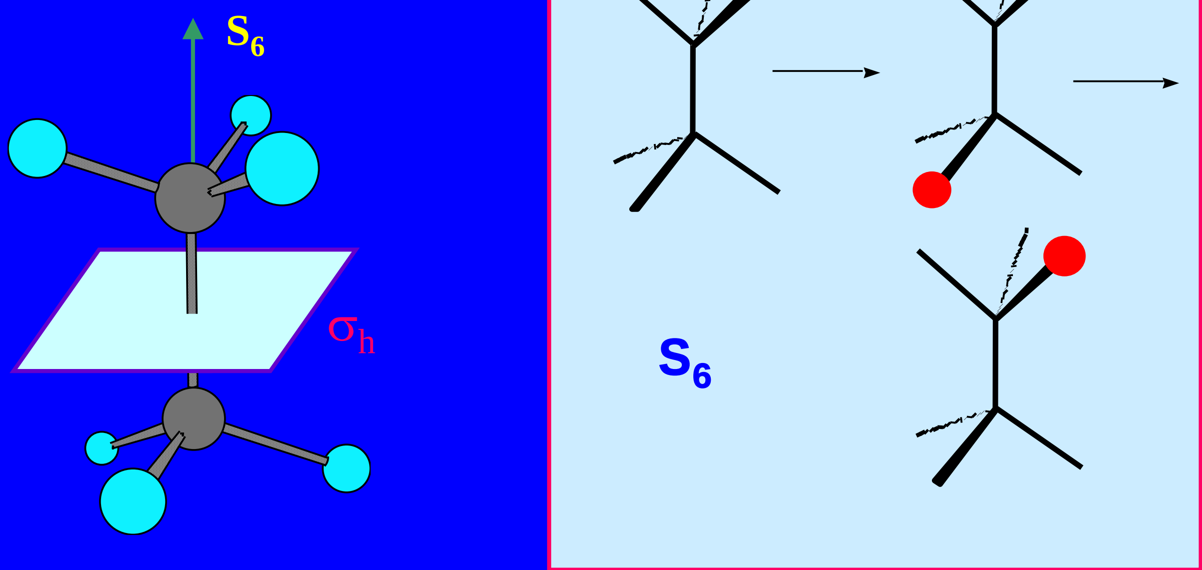
5) The improper rotation axis

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

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

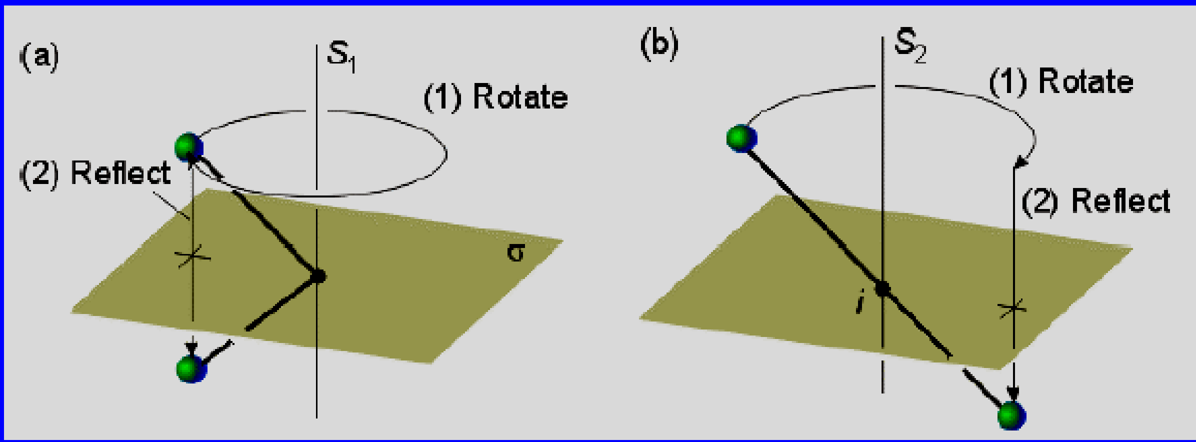


Example: $H_3C\text{-}CH_3$



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

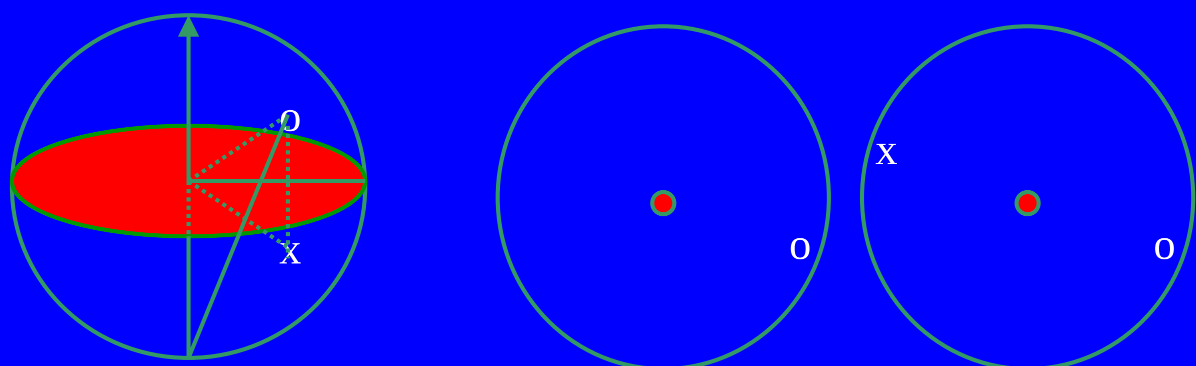
Special Cases: S_1 and S_2



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

$$S_2 = \sigma_h C_2 = i$$

Stereographic Projections

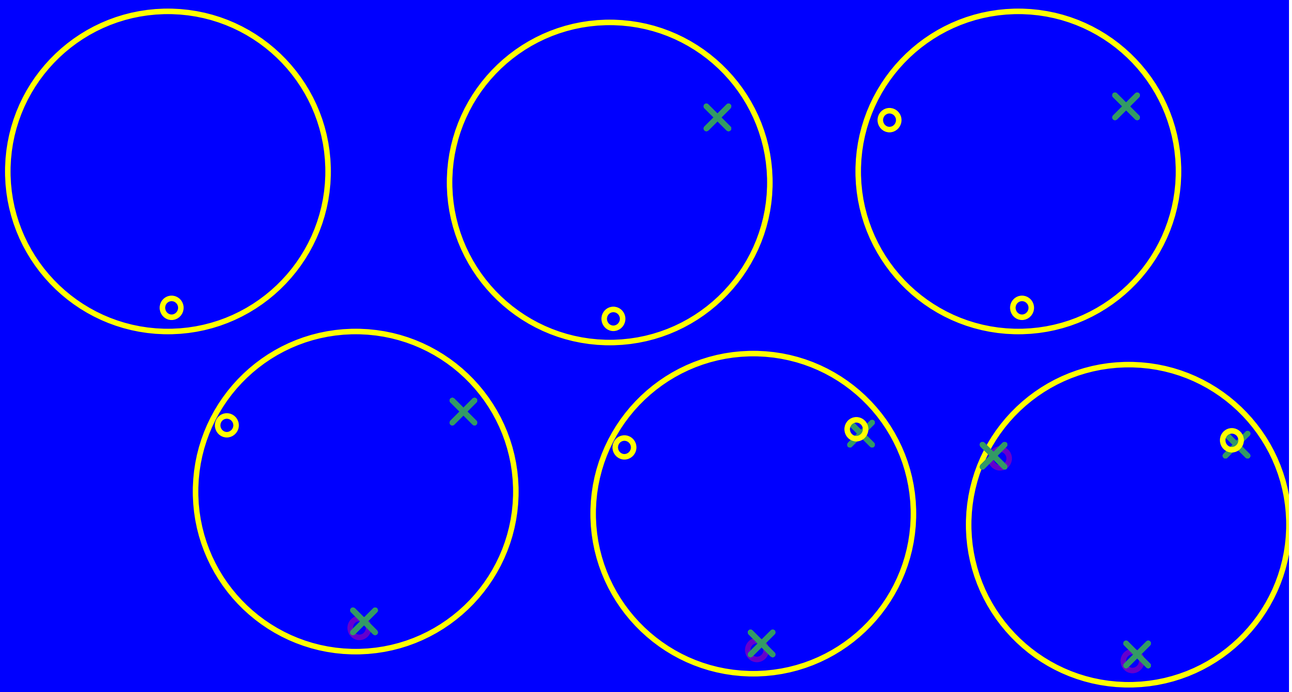


We will use stereographic projections to plot the perpendicular to a general face and its symmetry equivalents, to display crystal morphology

- o for upper hemisphere; x for lower

S$_3$

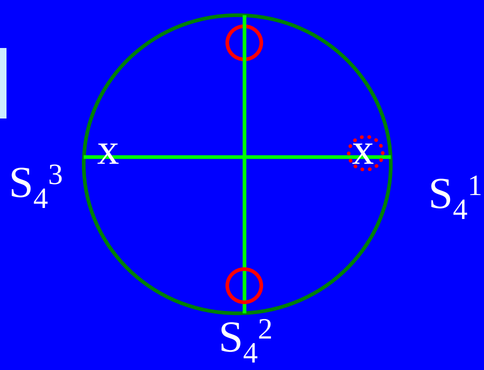
$$S_3^{\ 1} = \sigma C_3^{\ 1}; S_3^{\ 2} = C_3^{\ 2}; S_3^{\ 3} = \sigma; S_3^{\ 4} = C_3^{\ 1}; S_3^{\ 5} = \sigma C_3^{\ 2}; S_3^{\ 6} = E$$



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

$$S_4 = \sigma_h C_4$$

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



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

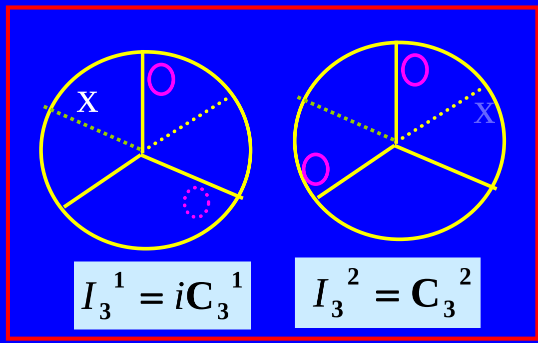
$$S_5^{\ 1} = \sigma C_5^{\ 1}; S_5^{\ 2} = C_5^{\ 2}; S_5^{\ 3} = \sigma C_5^{\ 3}; S_5^{\ 4} = C_5^{\ 4}; S_5^{\ 5} = \sigma;$$
$$S_5^{\ 6} = C_5^{\ 1}; S_5^{\ 7} = \sigma C_5^{\ 2}; S_5^{\ 8} = C_5^{\ 3}; S_5^{\ 9} = \sigma C_5^{\ 4}; S_5^{\ 10} = E$$

$$S_6 = \sigma_h C_6$$

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

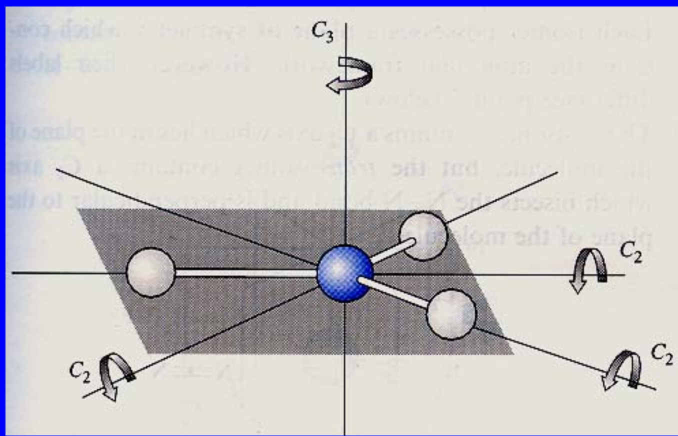
Element	Name	Operation
C_n	**n-fold rotation**	**Rotate by 360°/n**
σ	**Mirror plane**	**Reflection through a plane**
i	**Center of inversion**	**Inversion through the center**
S_n	**Improper rotation axis**	**Rotation as Cn followed by reflection in perpendicular mirror plane**
E	**identity**	**Do nothing**

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.

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



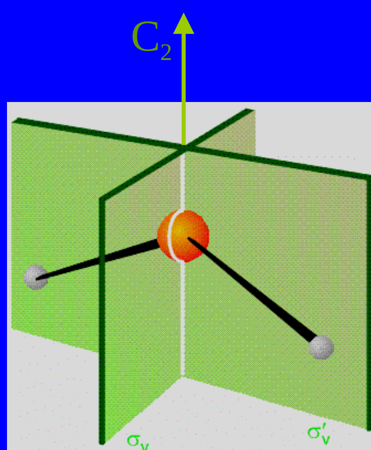
B. Combination of two planes of symmetry.

If two mirrors planes intersect at an angle of $2\pi/2n$, 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 $2\pi/2n$.

$$C_n + \sigma_v \rightarrow n\,\sigma_v$$

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

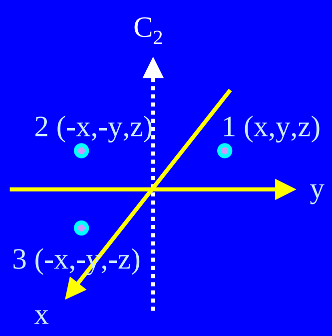
Ex. H_2O, NH_3



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



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

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

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

§ 2 Groups and group multiplications

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

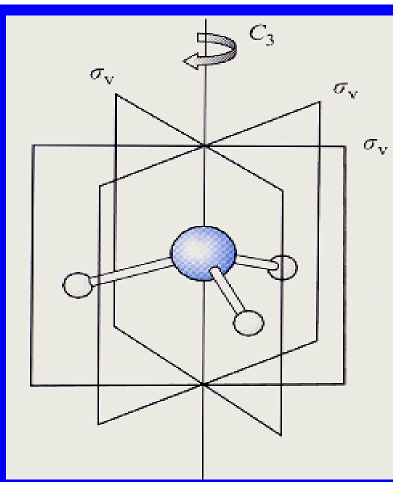
(a) Closure. The product of any two elements A and B in the group is another element in the group.

(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:

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

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

E $\quad$ Identity operation.

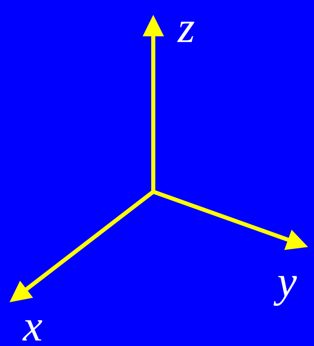
$(C_3^1 \cdot C_3^2) \cdot C_3^1 = C_3^1 (C_3^2 \cdot C_3^1)$ $\quad$ Associative rule.

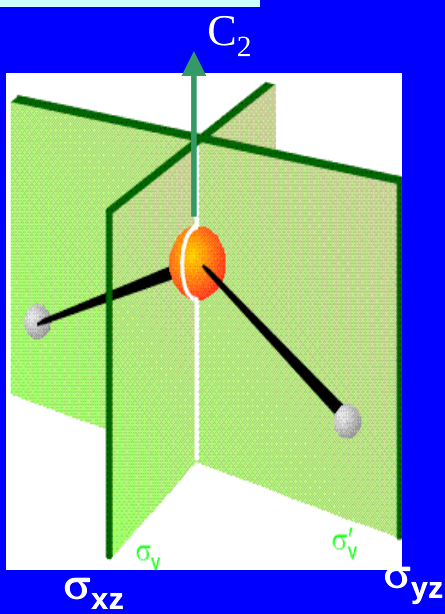
$C_3^1 \cdot C_3^2 = E$ $\quad$ Inversion.

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

2. Group Multiplication

Example: H_2O





C_{2v}

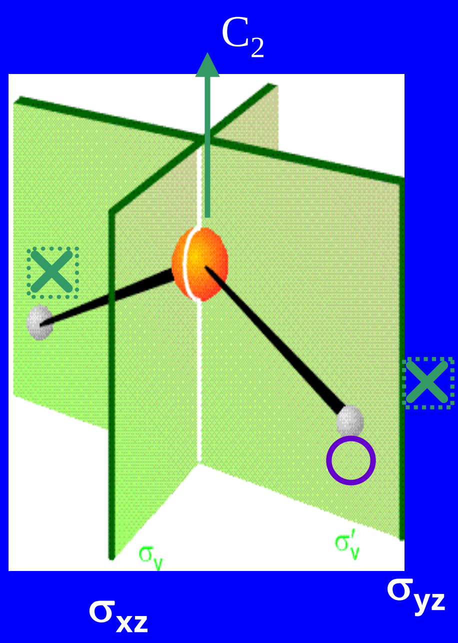
Its total symmetry elements: E, C_2^1, σ_{xz} σ_{yz}

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}

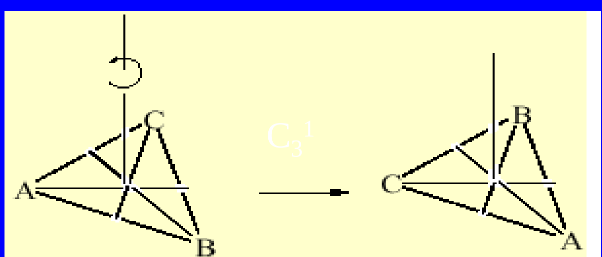
Its total symmetry elements: E, C_3^1, C_3^2, **σ_v, σ_v', σ_v''**

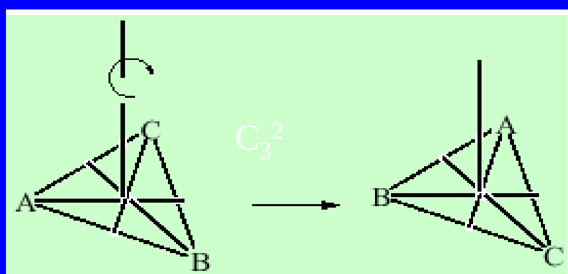
Multiplication table of C_{3v}

C3v	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''					





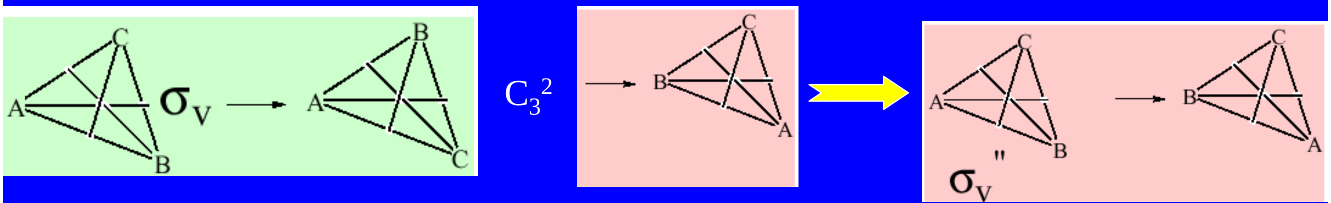
$$C_3^1 \cdot C_3^1 = C_3^2$$

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

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

Group Multiplication

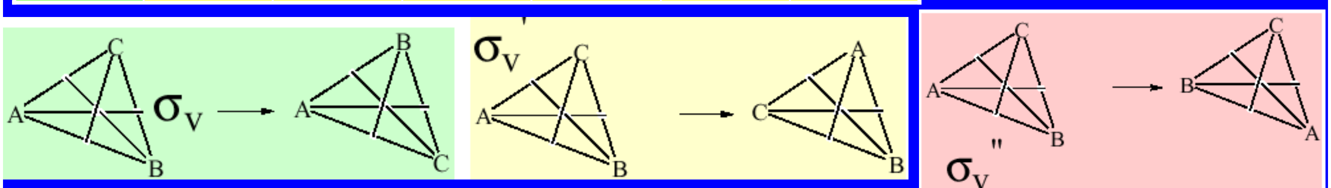
C3v	E	C_3^1	C_3^2	σ_v	σ_v'	σ_v''
E	E	C_3^1	C_3^2	σ_v	σ_v'	σ_v''
C_3^1	C_3^1	C_3^2	E	σ_v''	σ_v	σ_v'
C_3^2	C_3^2	E	C_3^2	σ_v'	σ_v''	σ_v
σ_v	σ_v	σ_v'	σ_v''			
σ_v'	σ_v'	σ_v''	σ_v			
σ_v''	σ_v''	σ_v	σ_v'			

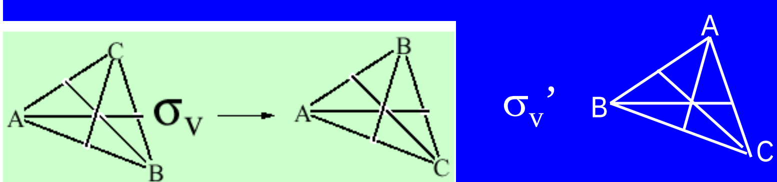


$$C_3^2\sigma_v = \sigma_v''$$

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

§ 3 Point Groups, the symmetry classification of molecules

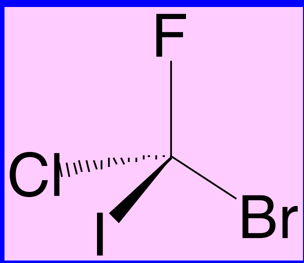
Point group:

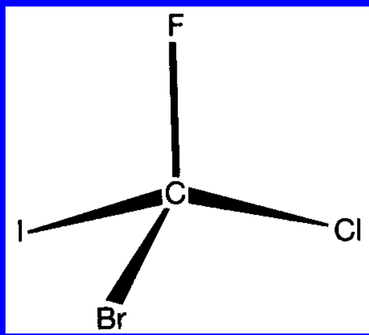
All symmetry elements corresponding to operations have at least one common point unchanged.

1. The groups C_1, C_i, and C_s

The group C_1

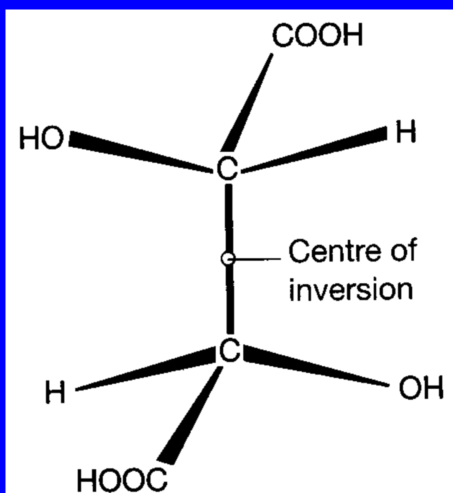
- A molecule belongs to the group C_1 if it has no element of symmetry other than the identity.
  - Example: CBrClF





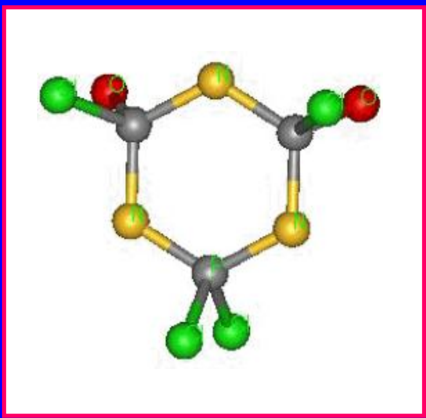
The group C_i

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

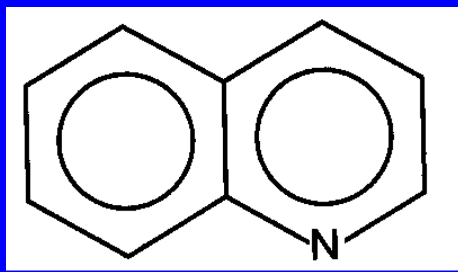


The group C_s

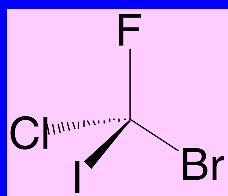
- It belongs to C_s if it has the identity and a mirror plane alone.

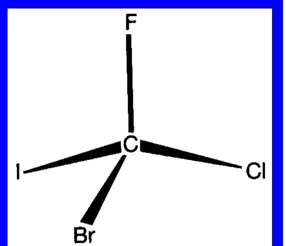


$N_3S_3PCl_4O_2$

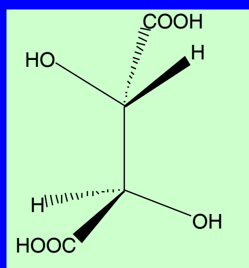


A molecule belongs to C_1 if it has only the identity E.





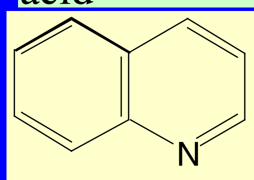
A molecule belongs to C_i if it has only the identity E and i.



Meso-tartaric acid

HClBrC-CHClBr

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



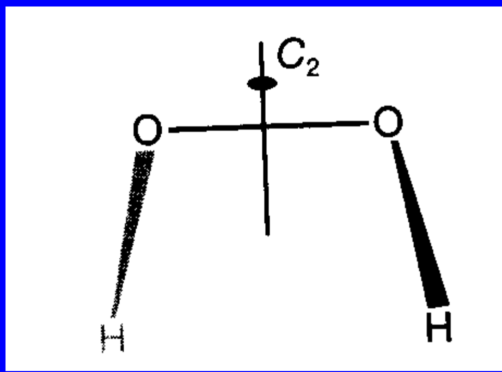
Quinoline

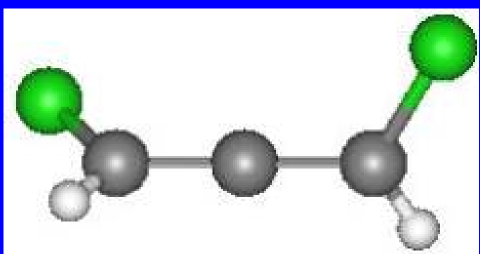
$H_2C{=}CClBr$

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

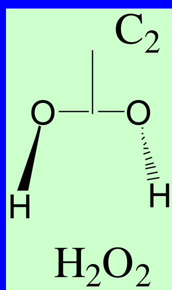
The group C_n

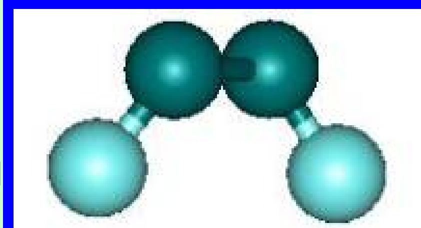
- A molecule belongs to the group C_n if it possess an <u>only</u> n-fold axes.
- Example: H_2O_2



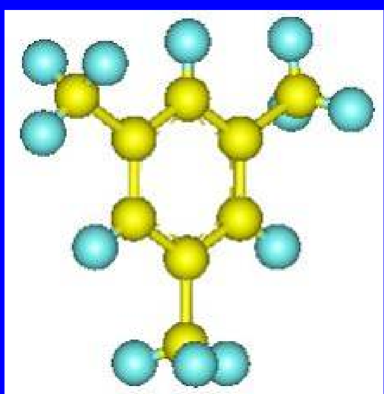


$C_2H_2Cl_2$



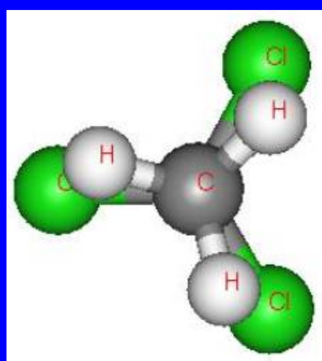


C_2



$C_6H_3(CH_3)_2$

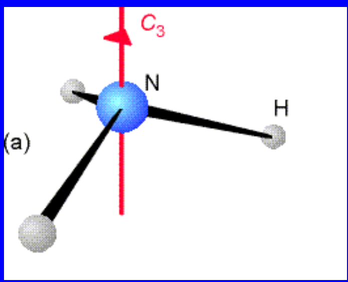
C_3

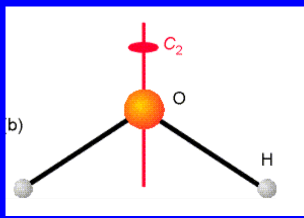


$C_2H_3Cl_3$

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.

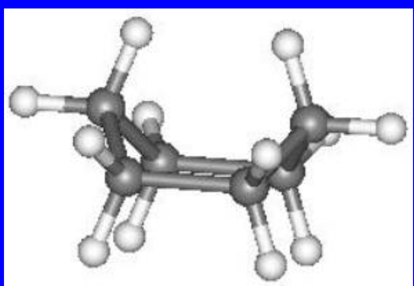


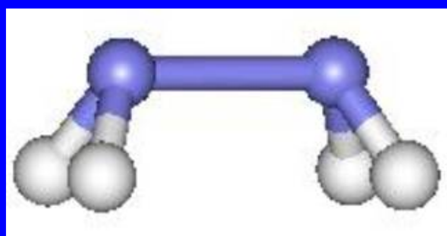


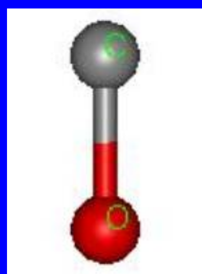
C=O

C_{3v} C_{2v} $C_{\infty v}$

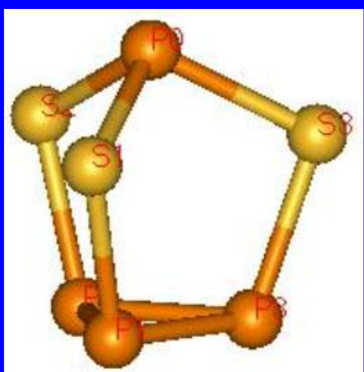
C_{2v} $C_{\infty v}$





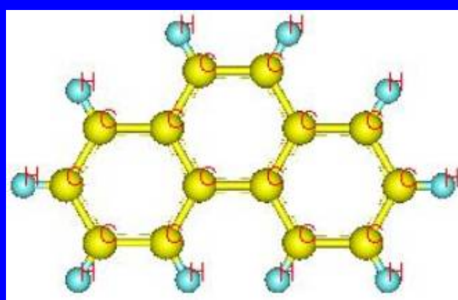


C_6H_{12}



N_2H_4

CO

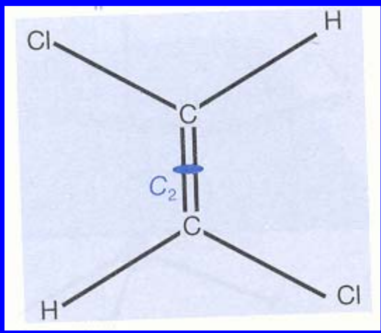


P_4S_3 C_{3v}

$C_{10}H_{14}$

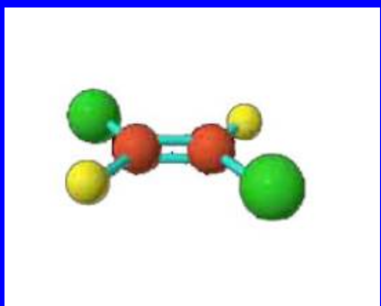
The group C_{nh}

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

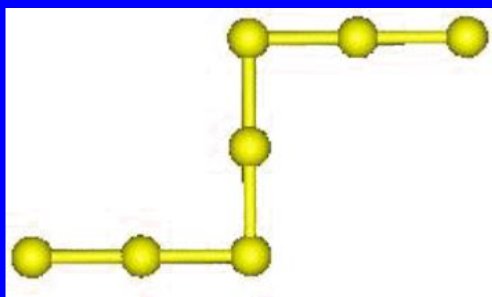


trans-CHCl=CHCl

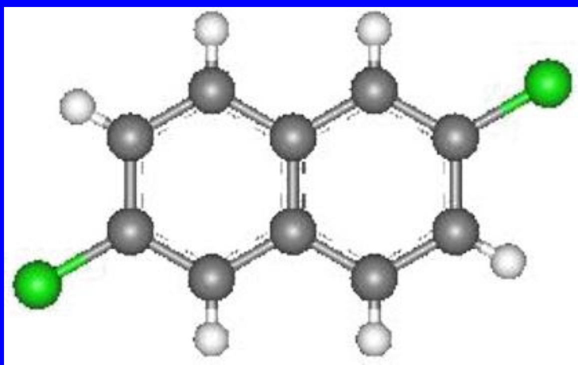
C_{2h}



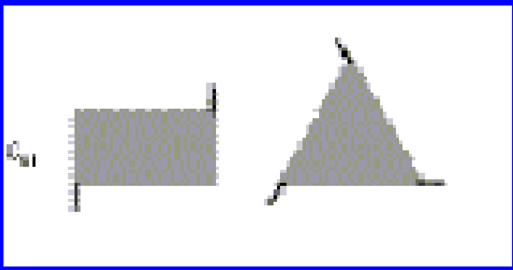
$C_2H_2Cl_2$



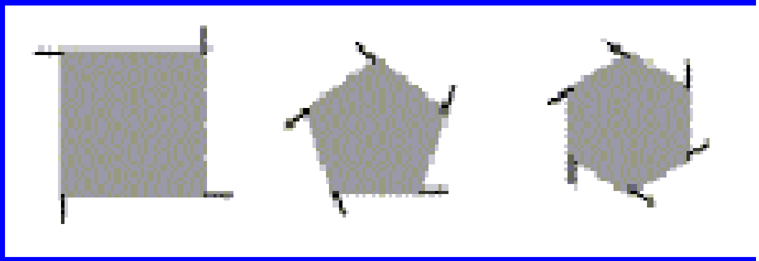
I_7^-



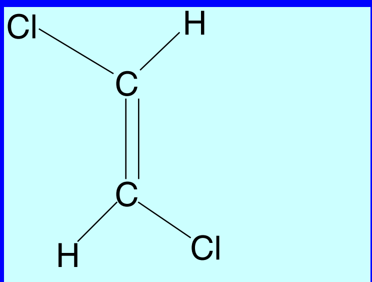
$C_{10}H_6Cl_2$



C_{2h} C_{3h}



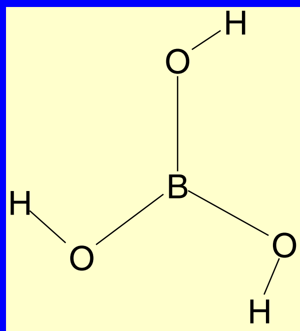
C_{4h} C_{5h} C_{6h}



Trans CHCl=CHCl

C_{2h}

C_{3h}



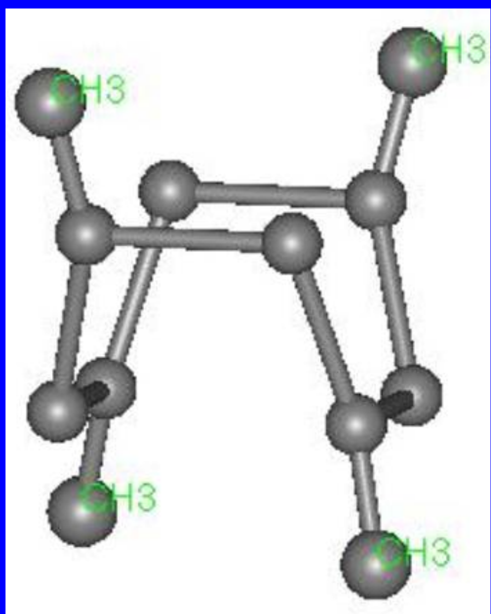
$B(OH)_3$

The group S_n

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

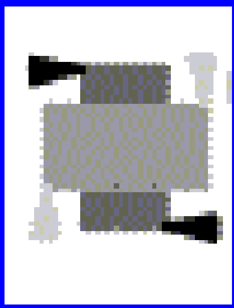
Group $S_2 = C_i$

Group $S_1 = C_s$

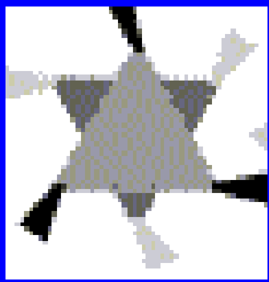


S_4

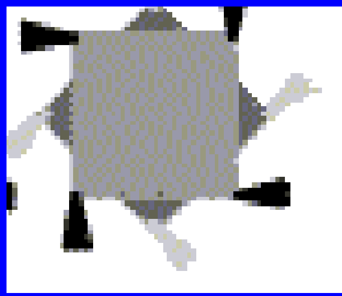
$S_2 = C_i$



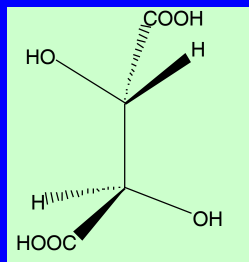
S_4



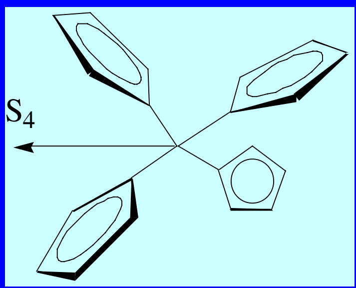
S_6



S_8



Meso-tartaric acid

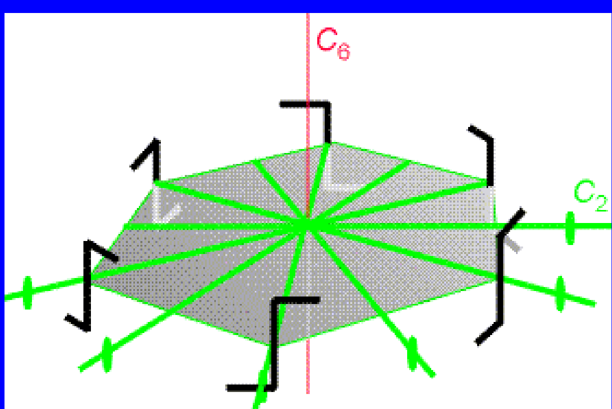


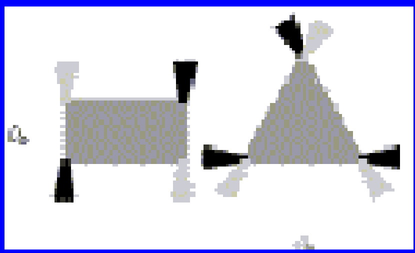
Single-axis group

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

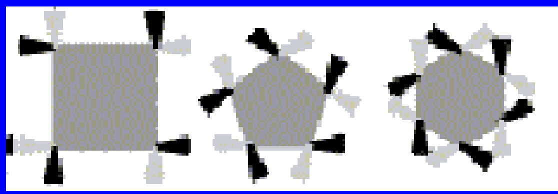
The group D_n

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

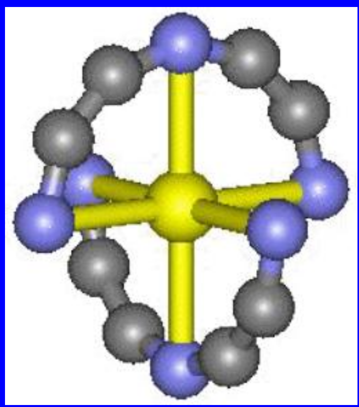




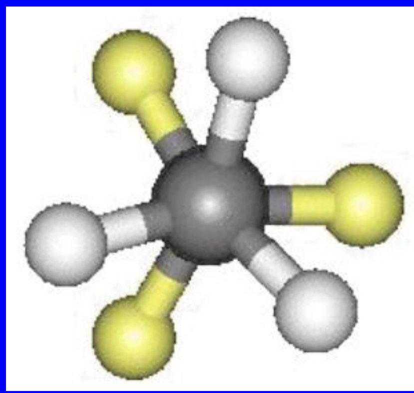
D_2 D_3



D_4 D_5 D_6



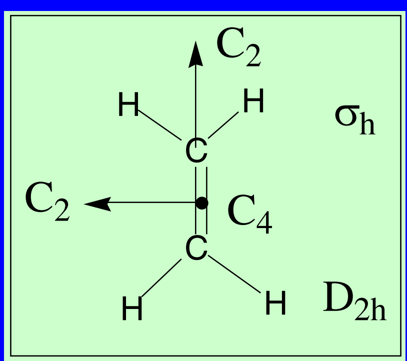
Co(dien)$_2$

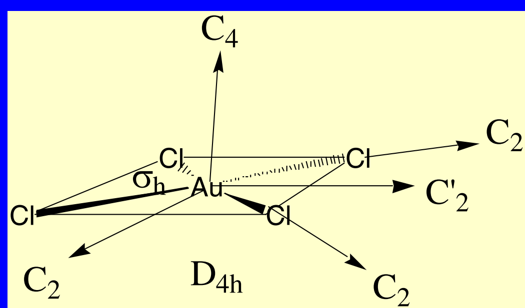


C_2H_6 (mediate state)

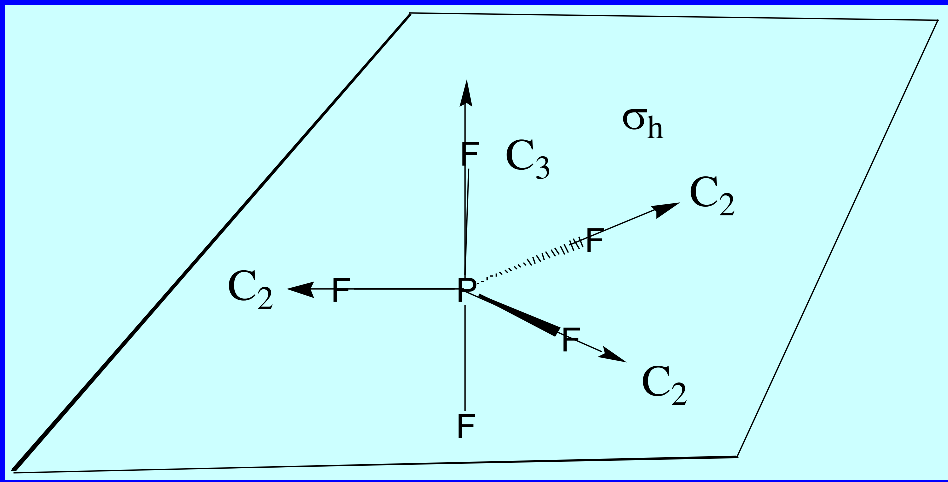
The groups D_{nh}

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}.



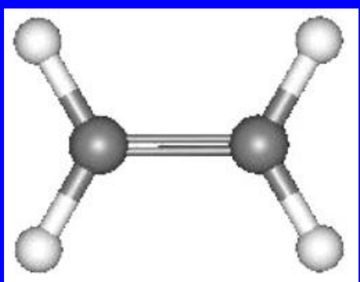


D_{nh}

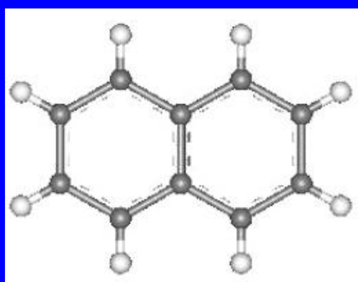


D_{3h}

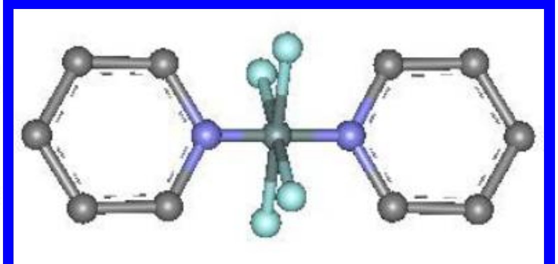
D_{2h}



C_2H_4

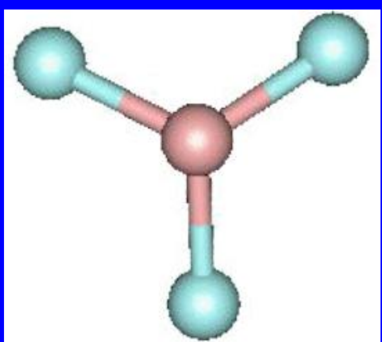


$C_{10}H_{10}$

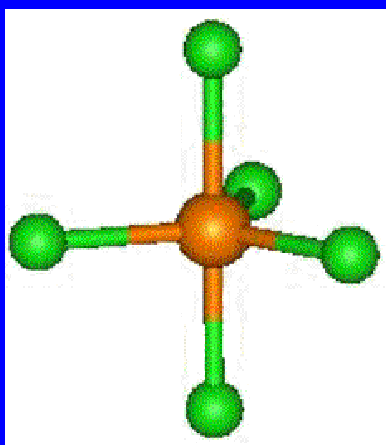


$SiF_4(C_5H_5N)_2$

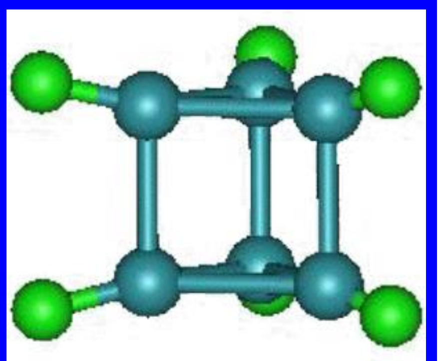
D_{3h}



BF_3

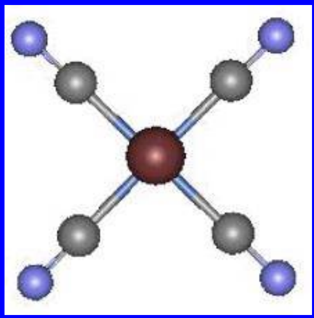


PCl_5

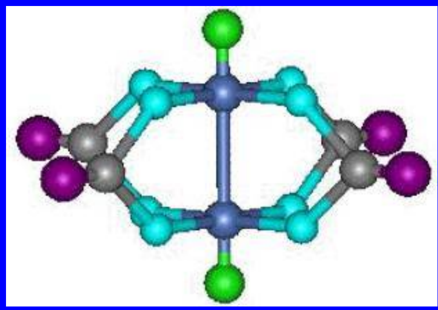


Tc_6Cl_6

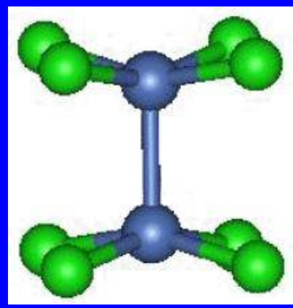
D_{4h}



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

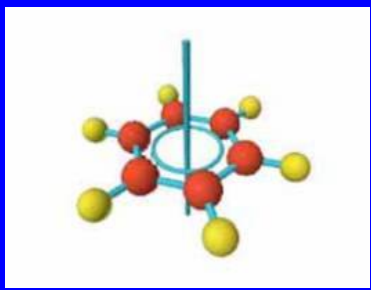


$[M_2(COOR)_4X_2]$

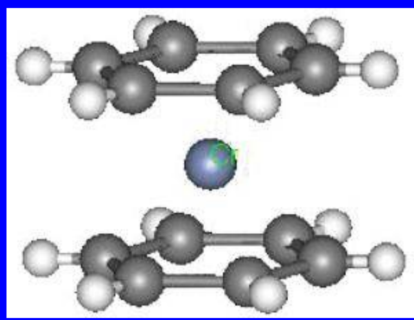


Re_2Cl_8

D_{6h}



C_6H_6

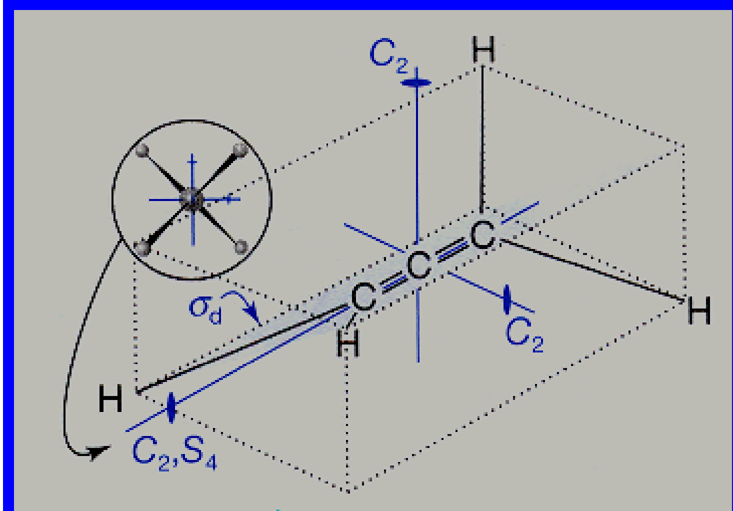


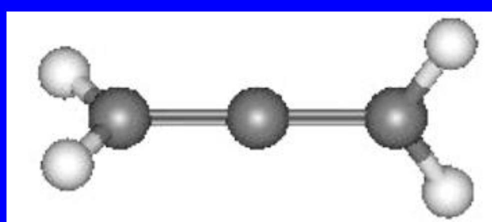
$Cr_2(C_6H_5)_2$

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.



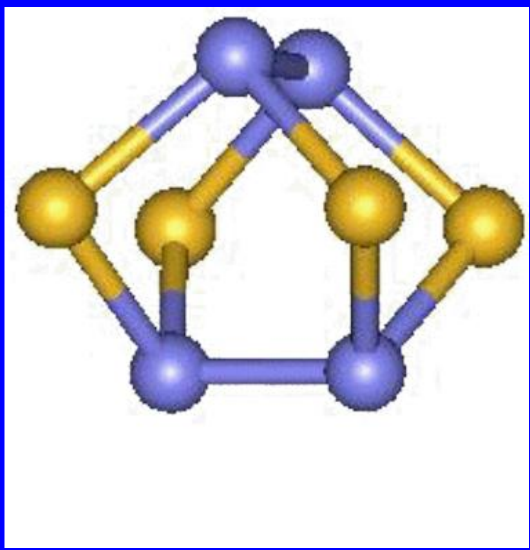


The order of group=4n

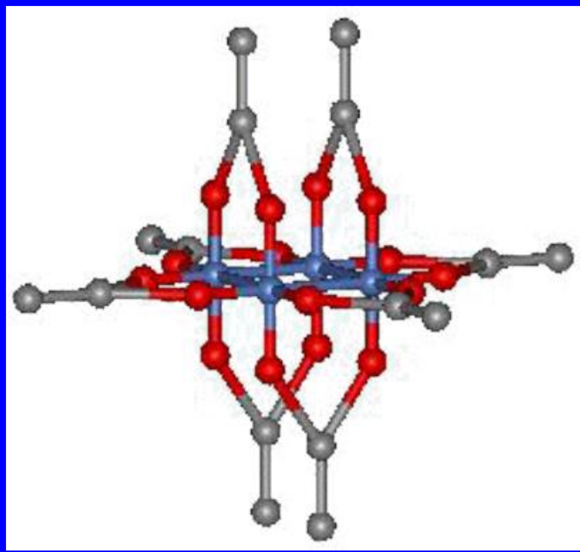
D_{2d}

D_{nd}

D_{2d}

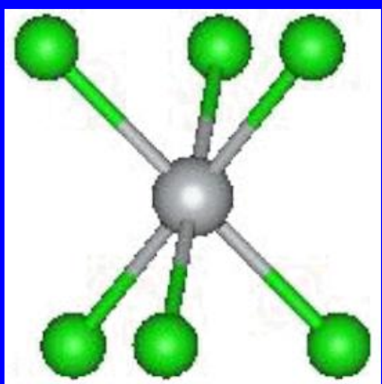


N_4S_4

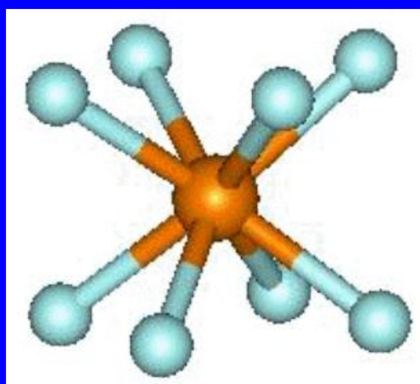


$Pt_4(COOR)_8$

D_{3d}

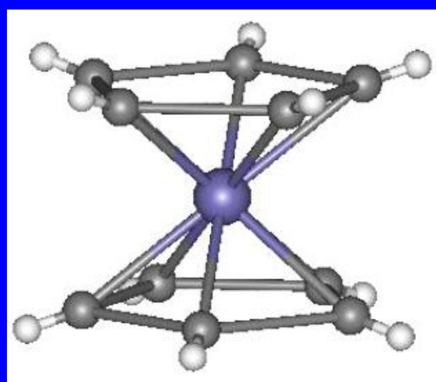


$TiCl_6^{2-}$

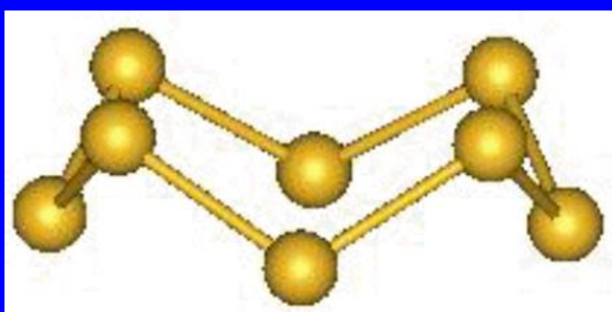


TaF_8^{3-}

D_{5d}



D_{4d}



S_8

4. High order point groups

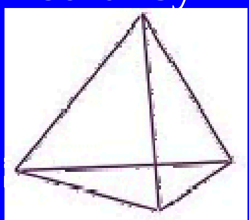
- Molecules having three or more high symmetry elements may belong to one of the following:

T: 4 C_3, 3 C_2 (T_h: +3σ_h) (T_d: +3S_4)

O: 4 C_3, 3 C_4 (O_h: +3σ_h)

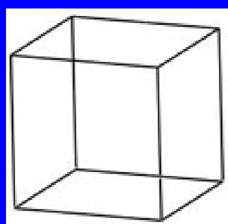
I: 6 C_5, 10C_3 (I_h: +i)

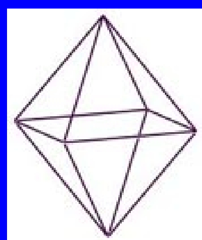
T_d – Species with tetrahedral symmetry



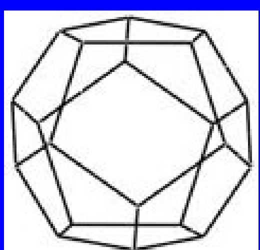
tetrahedral symmetry group

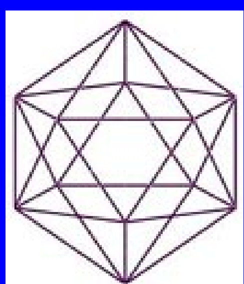
O_h – Species with octahedral symmetry (many metal complexes)





octahedral symmetry group

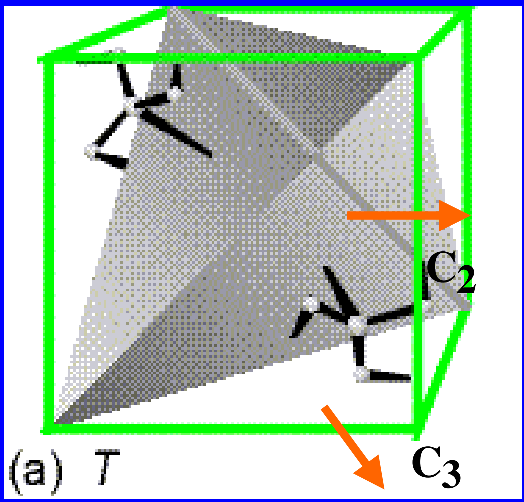




Icosahedral symmetry group

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

Cubic groups

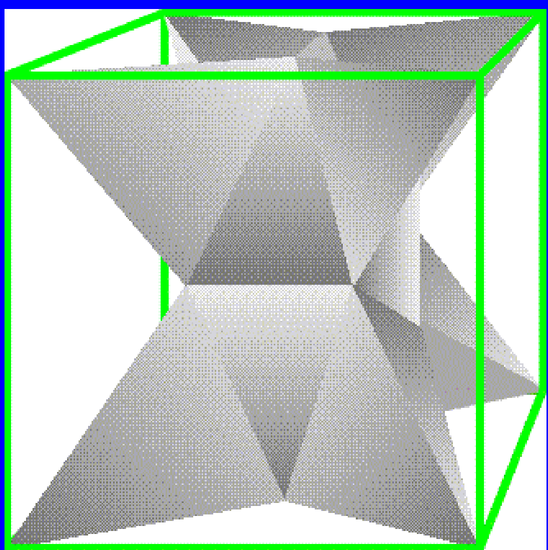


T: $4\ C_3$, $3\ C_2$ (T_h: $+3\sigma_h$) (T_d: $+3S_4$)

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

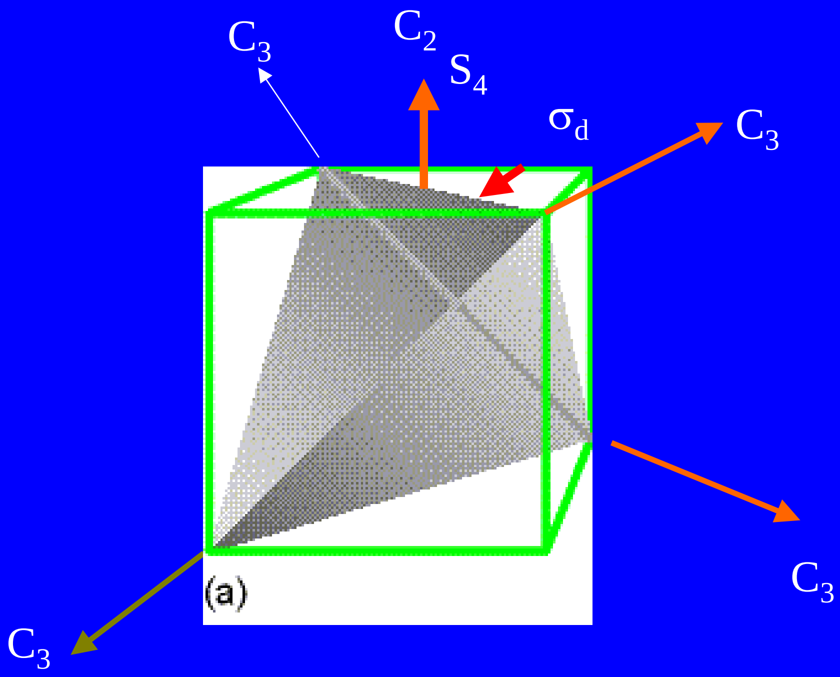
T_h

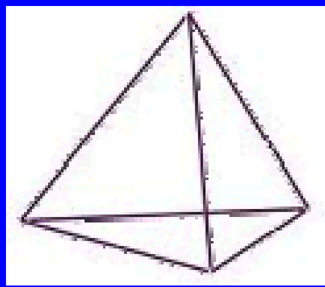


$\{E,\ 4C_3,\ 4C_3^2,\ 3C_2,\ I,\ 4S_6,\ 4S_6^5,\ 3\sigma_h\}$

Cubic groups

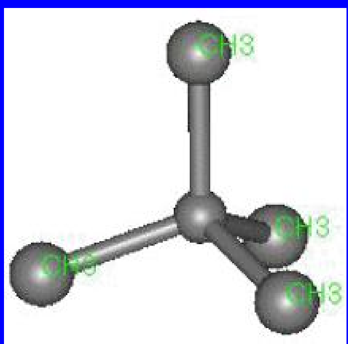
T_d



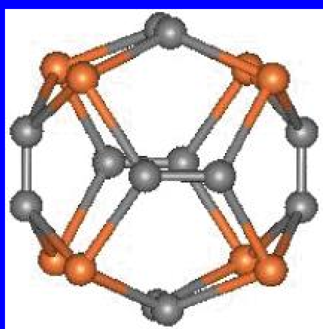


$\{E,\ 3C_2,\ 8C_3,\ 6S_4,\ 6\sigma_d\}$

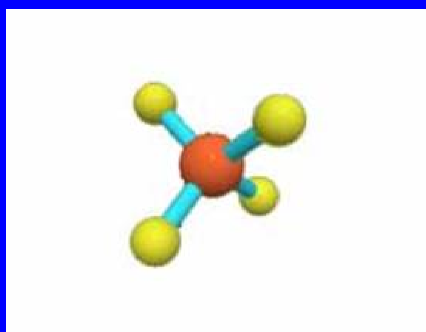
T	T_h	T_d



$C(CH_3)_4$

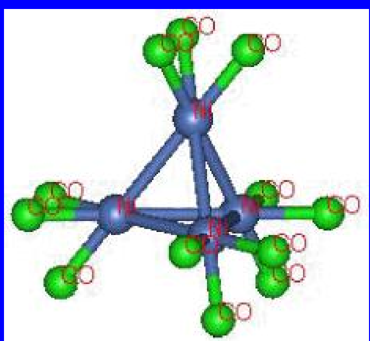


$Ti_8C_{12}^{+}$

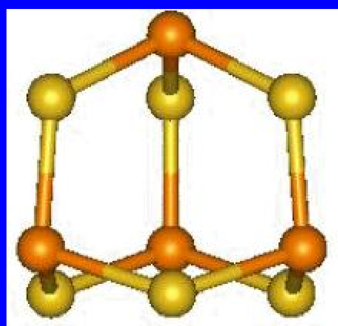


CH_4

T_d



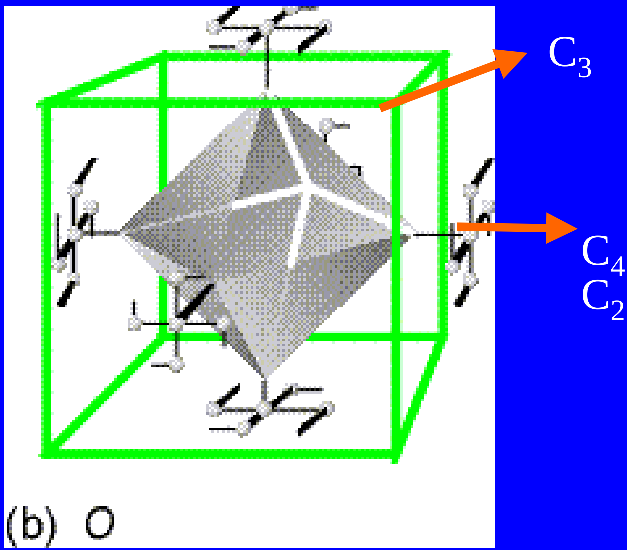
$Co_4(CO)_{12}$



P_4O_6

Cubic groups

O

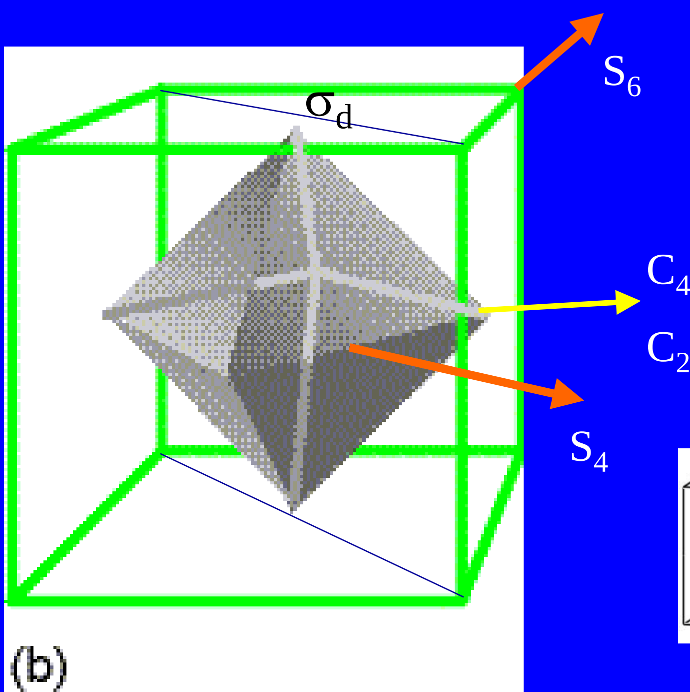


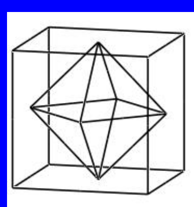
$$O: \quad 4\ C_3, 3\ C_4 \quad (O_h: \ +3\sigma_h)$$

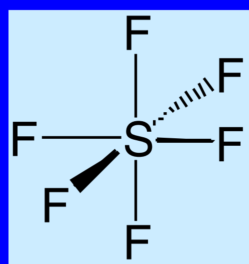
Shapes corresponding to the point groups (b) O. The presence of the windmill-like structures reduces thesymmetry of the object from O_h.

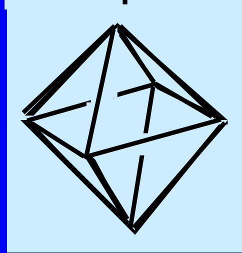
Cubic groups

O_h

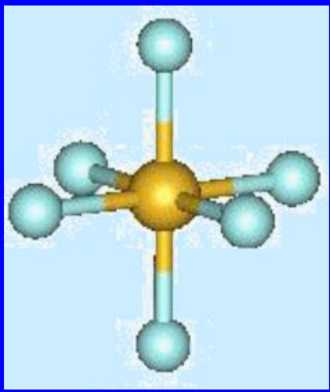




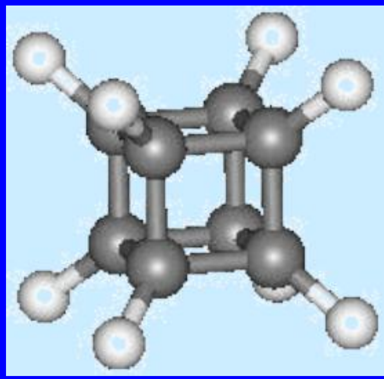




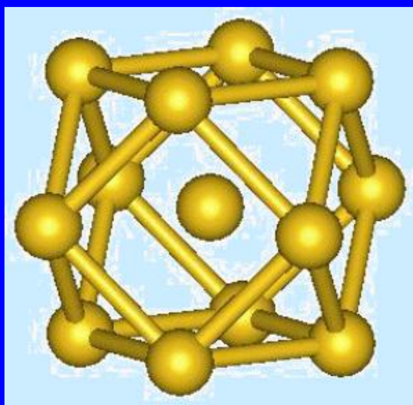
Cubic groups



SF_6



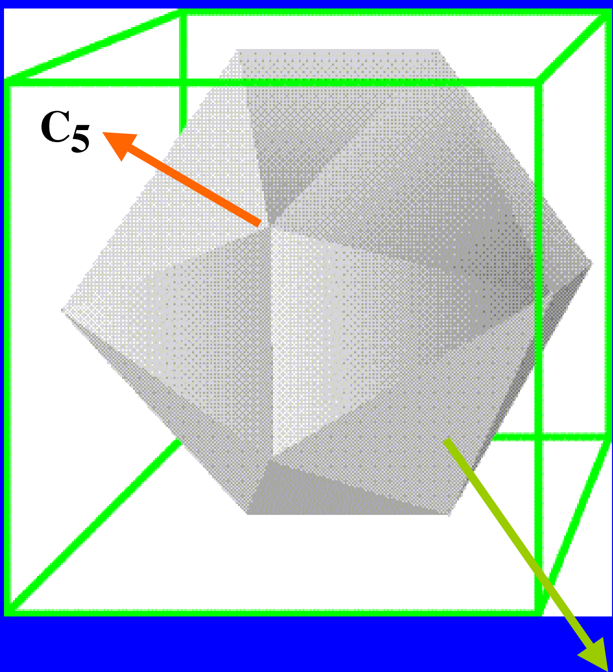
C_8H_8 OsF_8



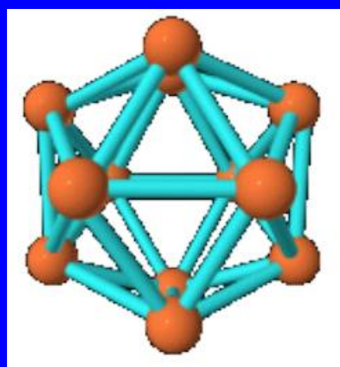
Rh_{13}

O_h

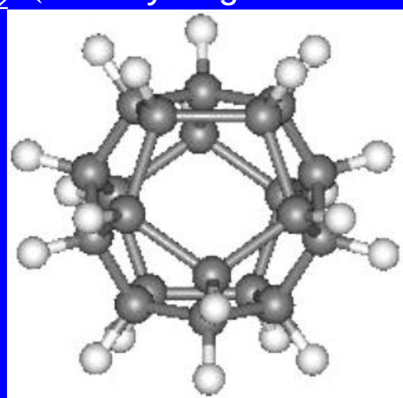
I group



C_3



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

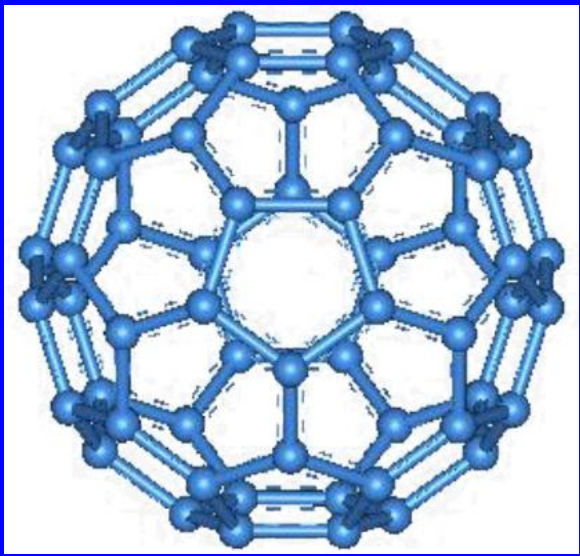
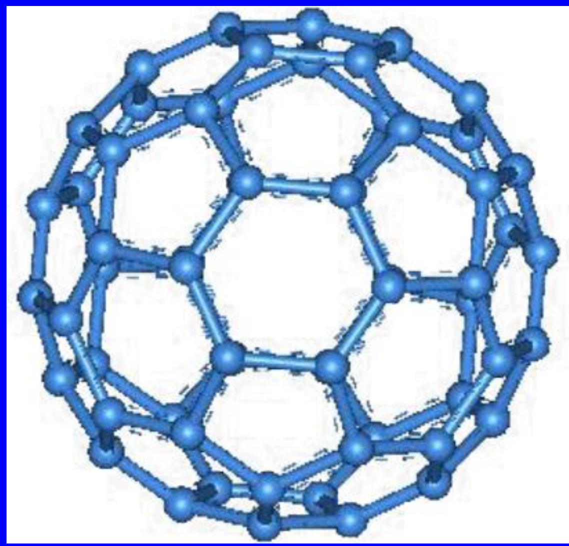


$C_{20}H_{20}$

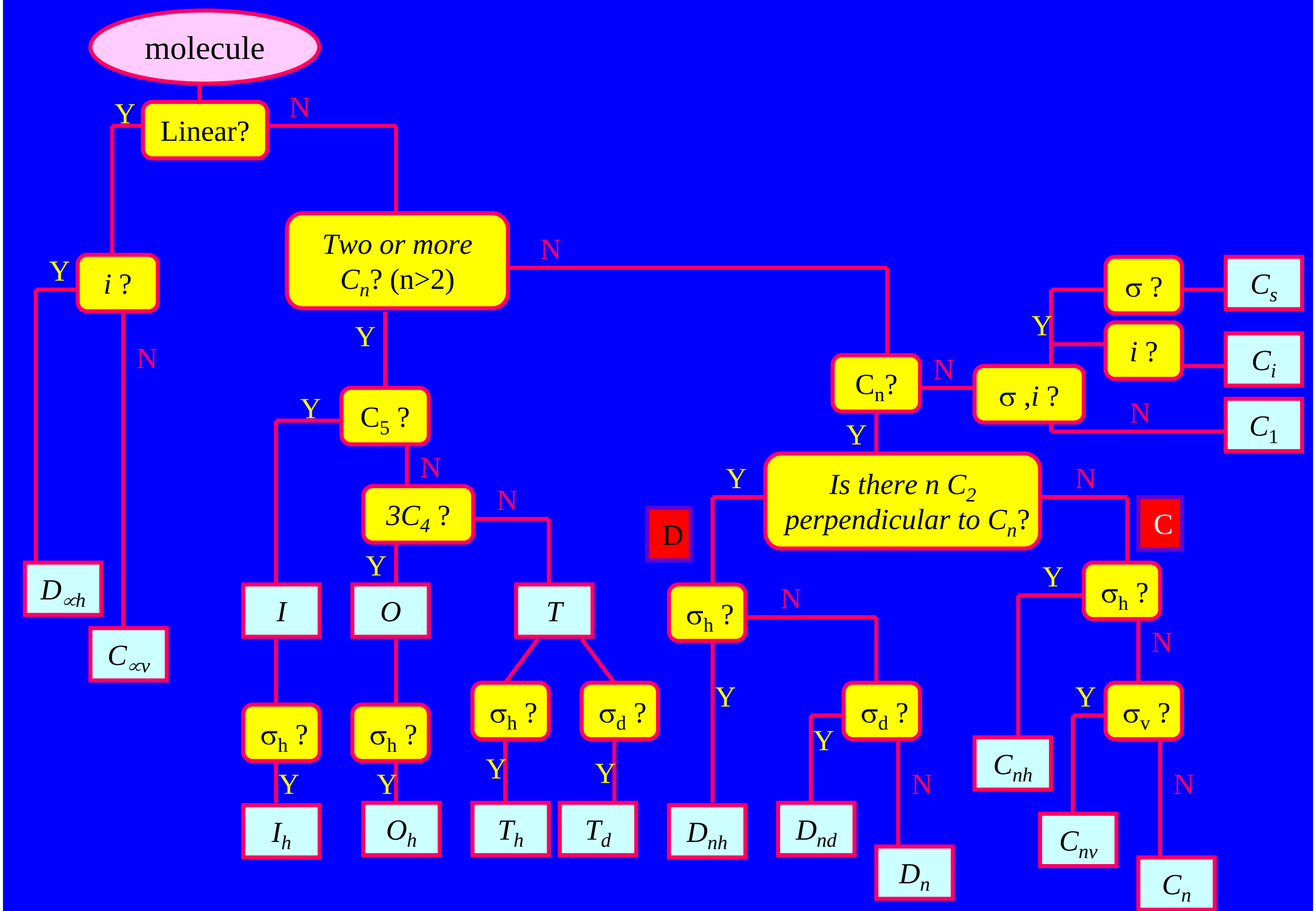
I: $6\ C_5$, $10C_3$ (I_h: +i)

I_h

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

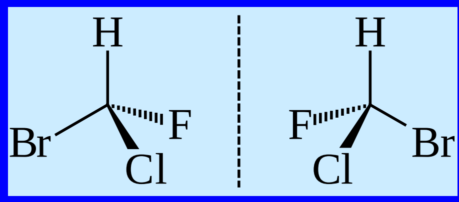



C60, the bird-view from the 5-fold axis and 6-fold axis



§ 4 Application of symmetry

1. Chirality

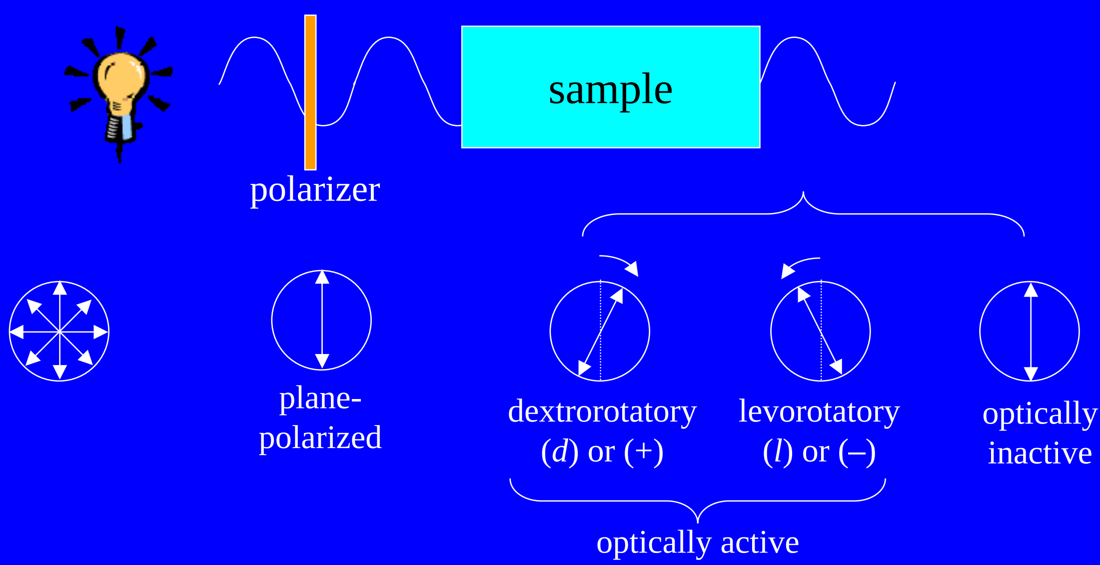


A chiral molecule is a molecule that can not be superimposed on its mirror image

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 ratation,** S_n
- Ability to rotate the plane of polarized light (**Optical activity**)

Optical activity is the ability of a chiral molecule to rotate the plane of plane-polairsed 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

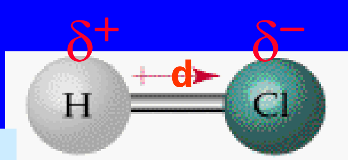
2. Polarity, Dipole Moments and molecular symmetry

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

Dipole Moments

- are due to differences in electronegativity
- depend on the amount of charge and distance of separation
- in debyes (D), μ= 4.8 × δ (electron charge) × d (angstroms)

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

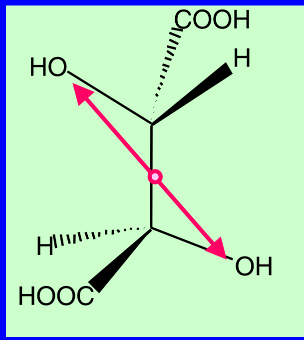


$$\mu = (1.60 \times 10^{-19})(100 \times 10^{-12}\, m)\left(\frac{1D}{3.34 \times 10^{-30}\, C \cdot m}\right) = 4.80 D$$

Permanent Dipole Moments

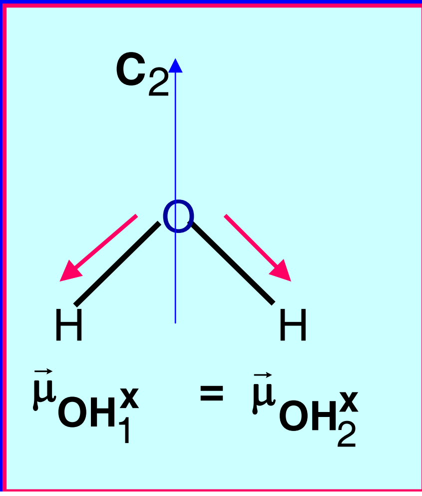
(a) A permanent dipole moment can not exist if *inversion center* is present.

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



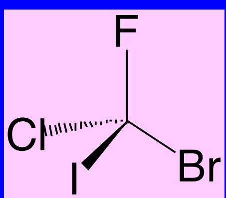
Meso-tartaric acid

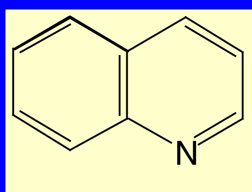
$\mu = 0$
inversion



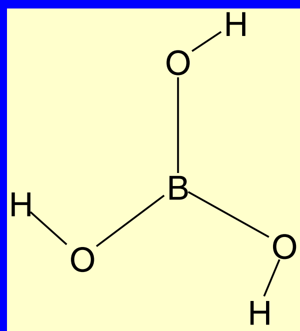
(b) Dipole moment cannot be perpendicular to any mirror plane or C_n.

Molecular Dipole Moments and molecular symmetry



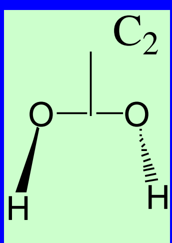


Quinoline

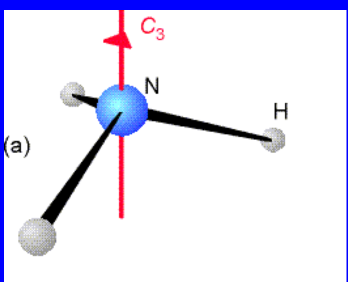


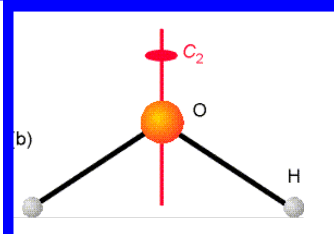
$B(OH)_3$

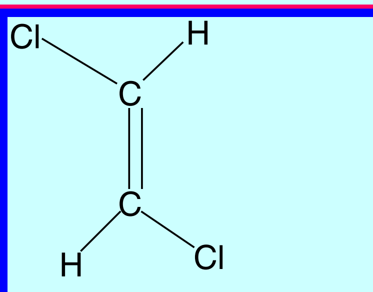
$\mu \neq 0$	$\mu = 0$ **inversion**	$\mu \neq 0$ **in plane**	$\mu = 0$ σ_h **symmetry**



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**