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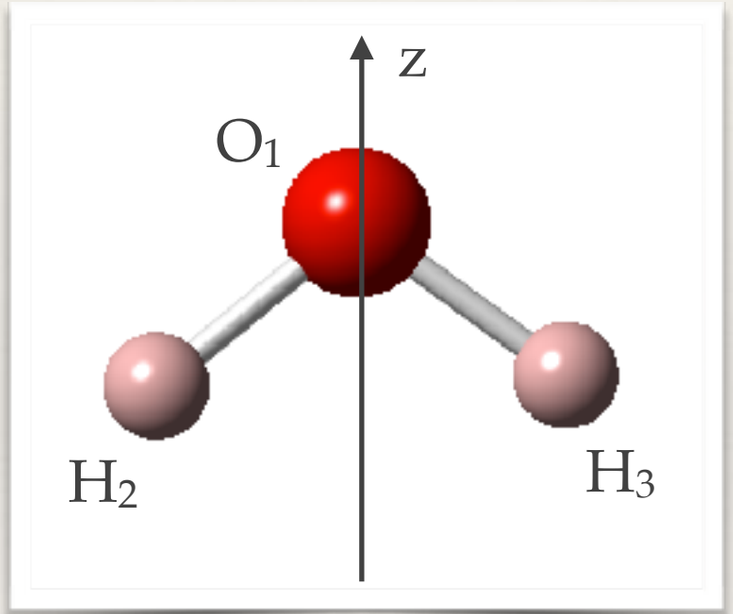
Molecular symmetry

Pere Alemany
Universitat de Barcelona

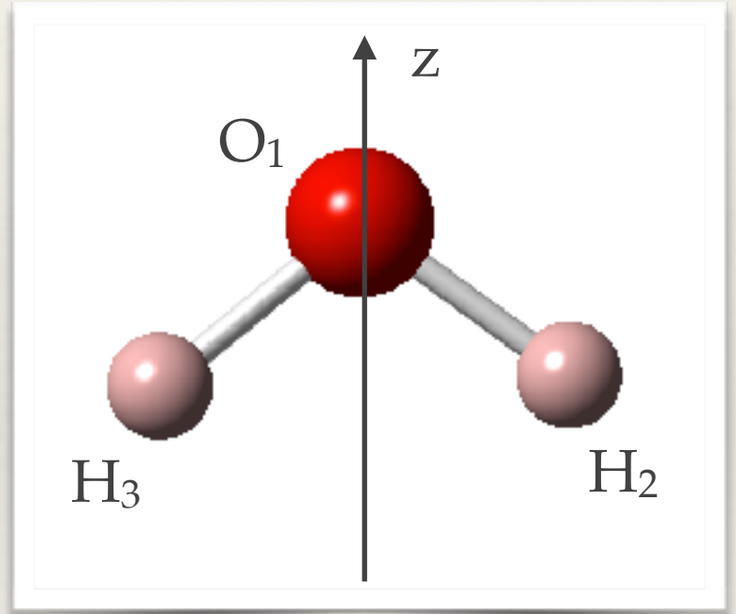
Molecular symmetry

A molecular structure is a **labelled set of points in space** indicating the positions of nuclei. Since atoms of the same type are indistinguishable, the symmetry of the molecule will be given by the **set of geometrical transformations** that lead to an **indistinguishable arrangement of the atoms in space**.



O1	0.000	0.000	0.000
H2	-0.750	0.000	-0.580
H3	0.750	0.000	-0.580

180º rotation
around z axis

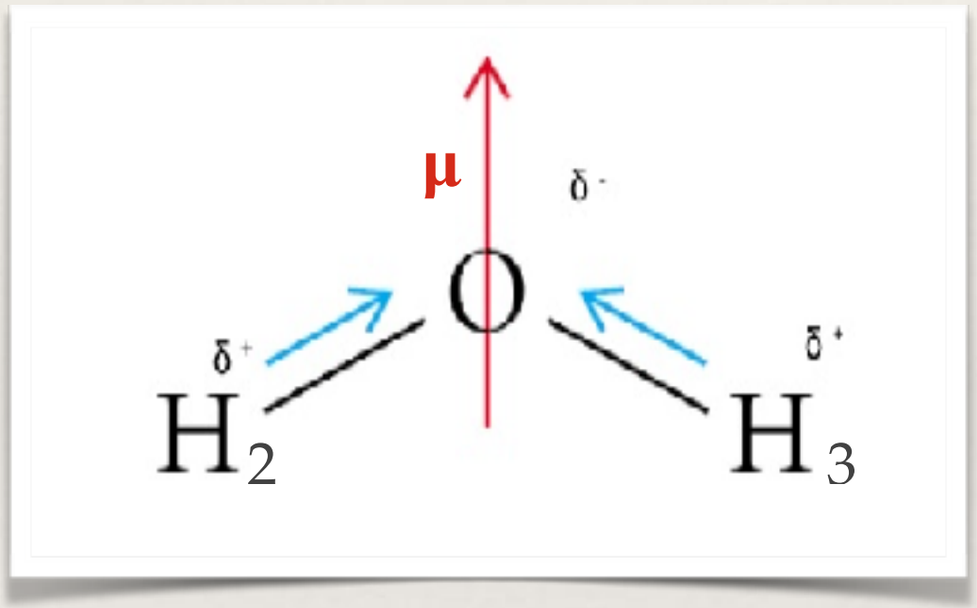


O1	0.000	0.000	0.000
H2	0.750	0.000	-0.580
H3	-0.750	0.000	-0.580

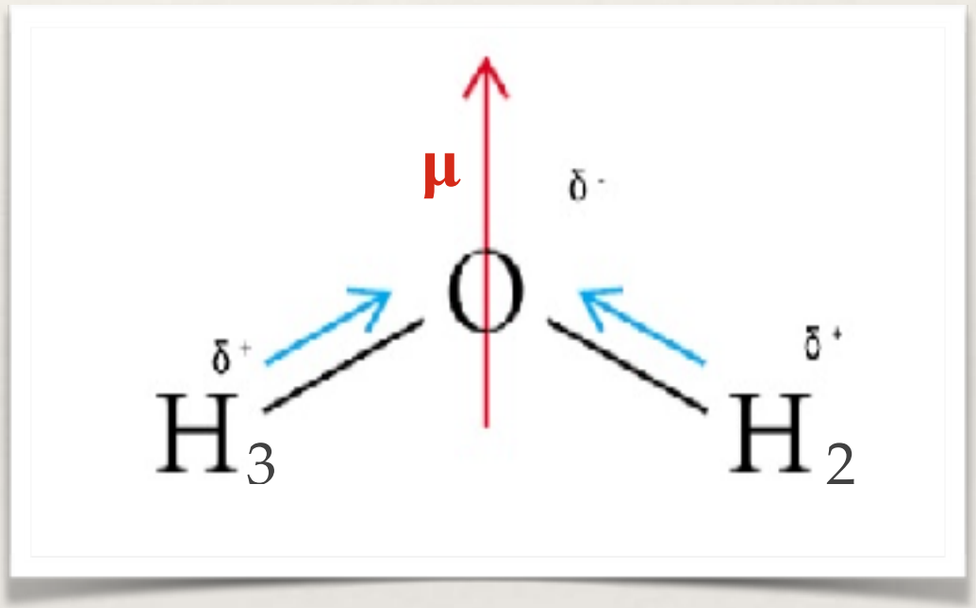
An alternative view is to consider the set of **all label permutations** for equivalent atoms in the structure.

Molecular symmetry & physical properties

Since the physical properties of a molecule (energy, dipole moment, …) depend only on the relative location of atoms in space, these properties are invariant with respect to symmetry transformations

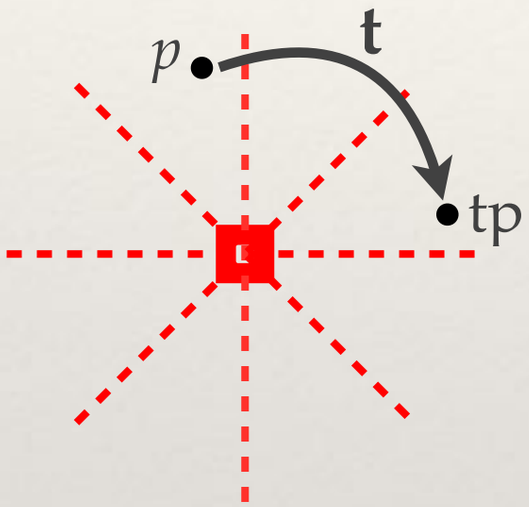


180° rotation around z axis



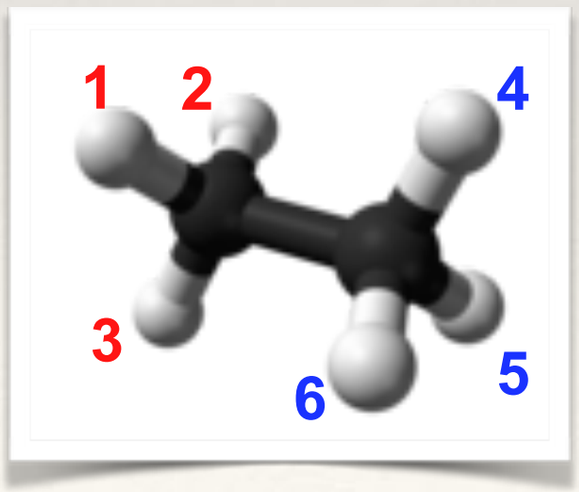
Symmetry operations for finite objects

Symmetry operations are distance preserving mappings (isometries) of the whole Euclidean space into itself, t: $R^3 \rightarrow R^3$, and **affect all points in space**, not only points where nuclei are located.

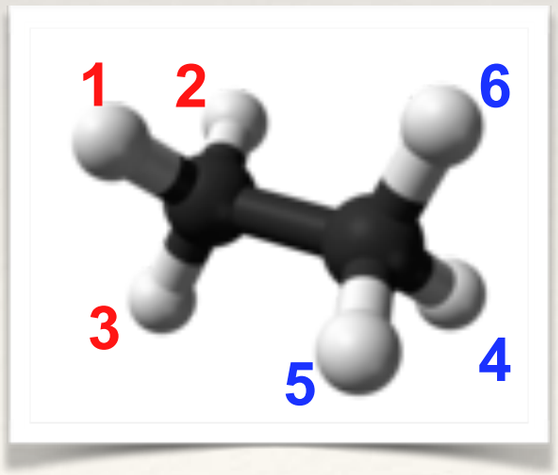


Some points may be mapped into themselves (**invariant points)**. For a finite object, all symmetry transformations leave at least one point invariant (the **symmetry center**) and we speak of **point symmetry operations**.

Warning: internal rotations around bond are not proper symmetry operations. Not all valid permutations of labels of identical atoms are symmetry operations.

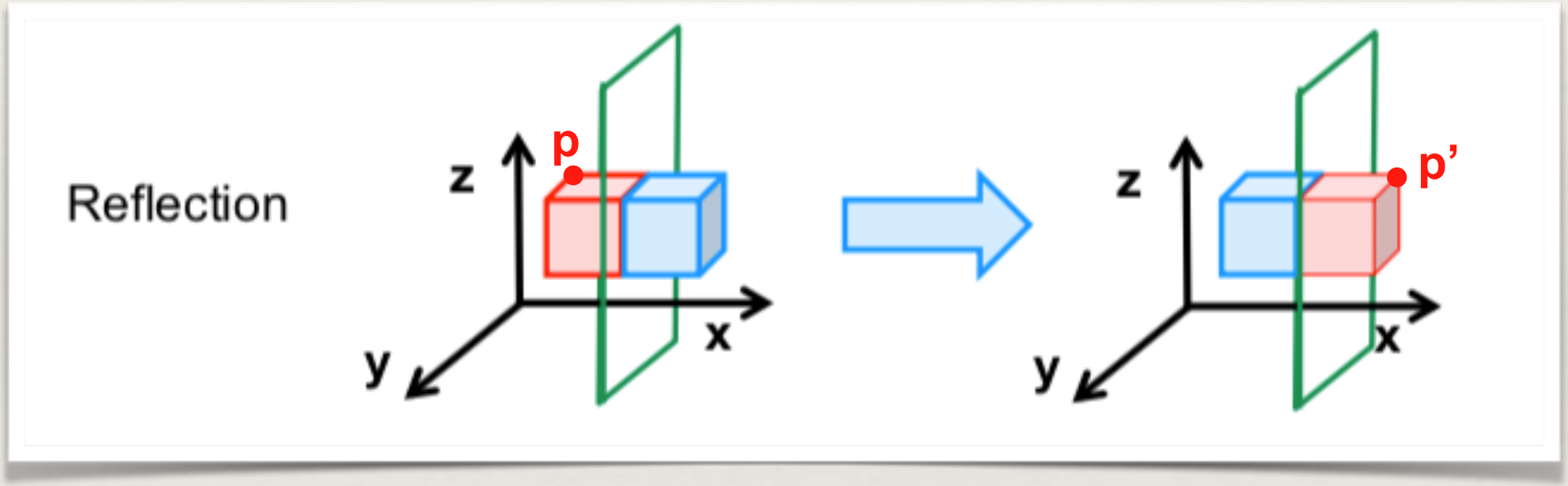


120º rotation
C-C bond



Reflection symmetry

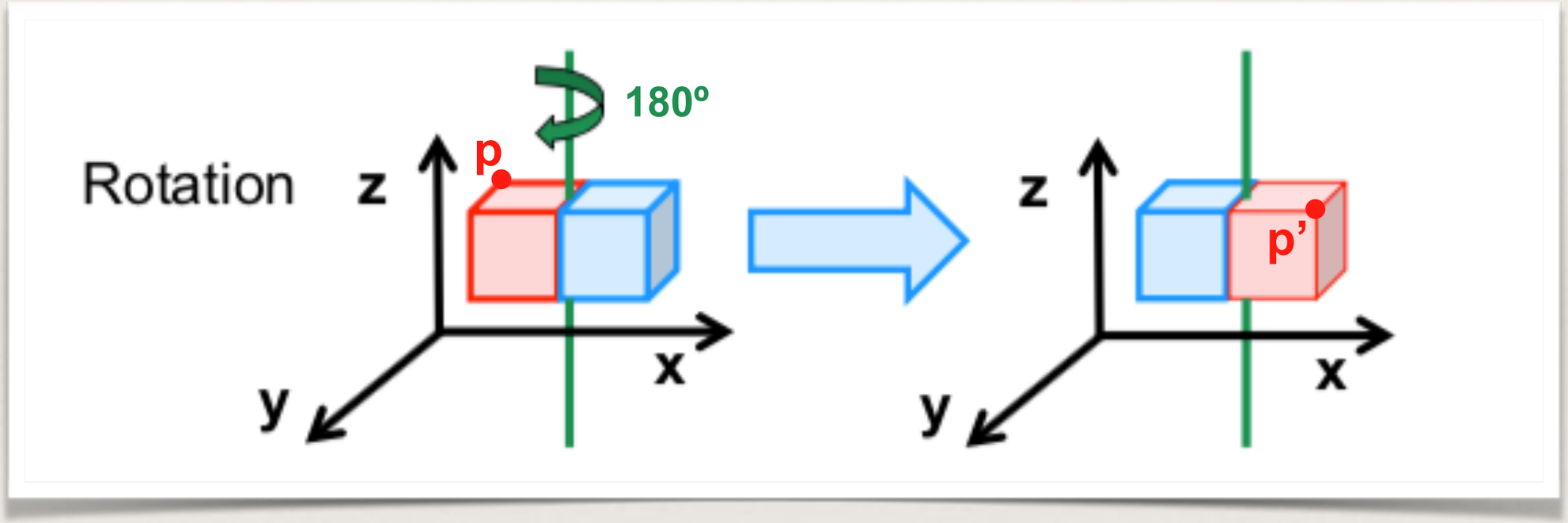
A reflection maps a point in space to a point on the opposite side of a plane (line in 2D) called the **mirror plane**. Reflection symmetry is also known as mirror symmetry.



All points on the mirror plane are mapped into themselves (invariant points) by a reflection operation. In chemistry reflections are indicated using the symbol **σ**, in crystallography the symbol **m**.

Rotation symmetry

Rotation means the circular movement of an object around a line (point in 2D) called the **rotation axis** and is characterized by the angle of the movement, indicated as the fraction of a whole turn: C_n with n = 2 corresponds to a 360°/2 = 180° rotation.



All points on the rotation axis are mapped into themselves (invariant points) by a rotation operation. In chemistry reflections are indicated using the symbol $\mathbf{C_n}$, in crystallography just by the number **n**.

Identity operation

Any object has a trivial symmetry, the **identity** operation, which just maps each point in space into itself:

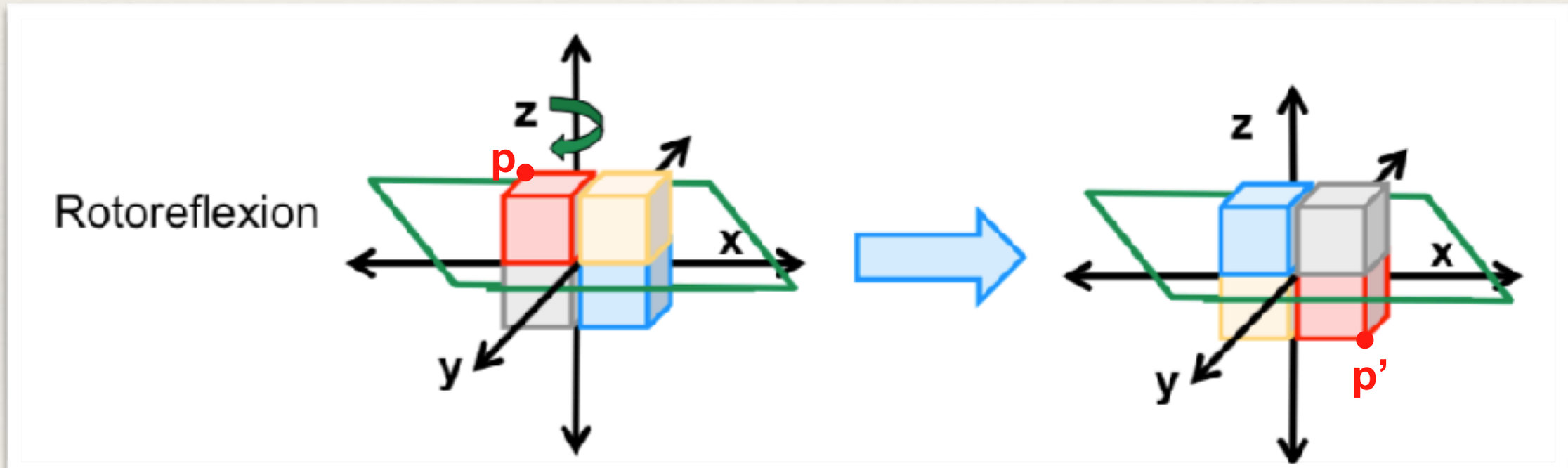
$$E: p \rightarrow p \quad \forall\ p \text{ in } R^3$$

Inclusion of this operation is fundamental in the mathematical theory of symmetry (group theory) where it plays the role of 0 in addition or 1 in multiplication of integer numbers.

The identity is equal to a C_1 rotation, where a whole turn around the axis leaves all points in space invariant.

Improper rotation symmetry

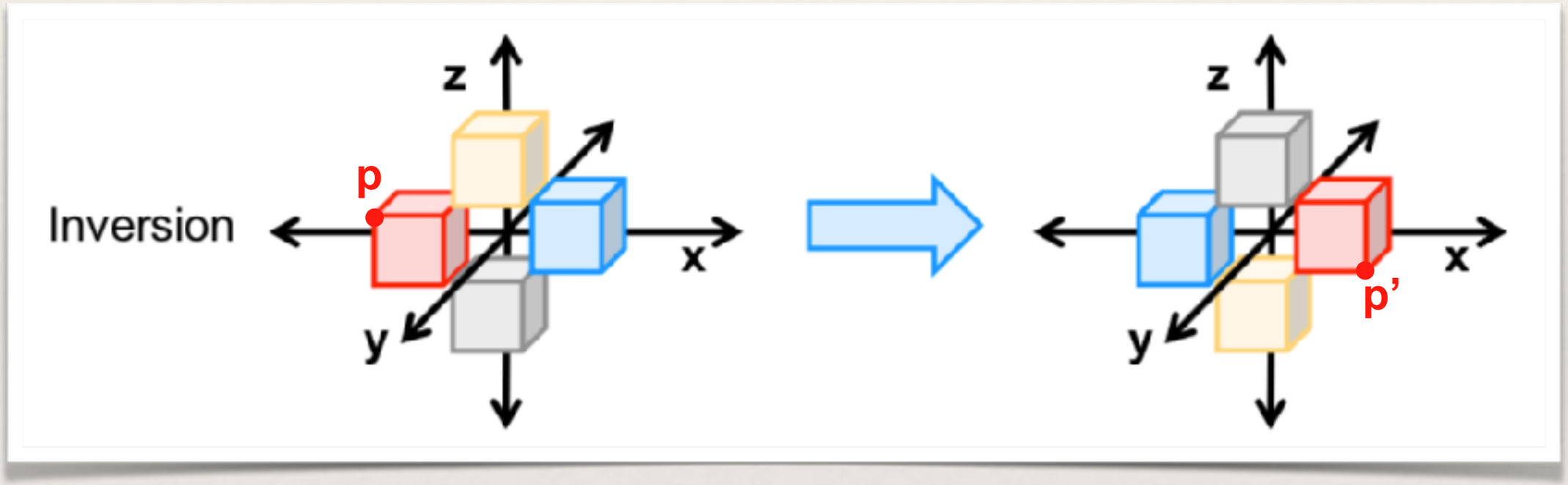
An improper rotation consists in the combination of a rotation followed by a reflection on a plane perpendicular to the rotation axis. Neither the rotation nor the reflection need to be symmetry operations of the object by themselves.



Only the point where the axis and the plane cross remains invariant in a rotoreflection. In chemistry rotoreflections are indicated using the symbol $\mathbf{S_n}$, in crystallography by n with a tilde, $\tilde{\mathbf{n}}$.

Inversion symmetry

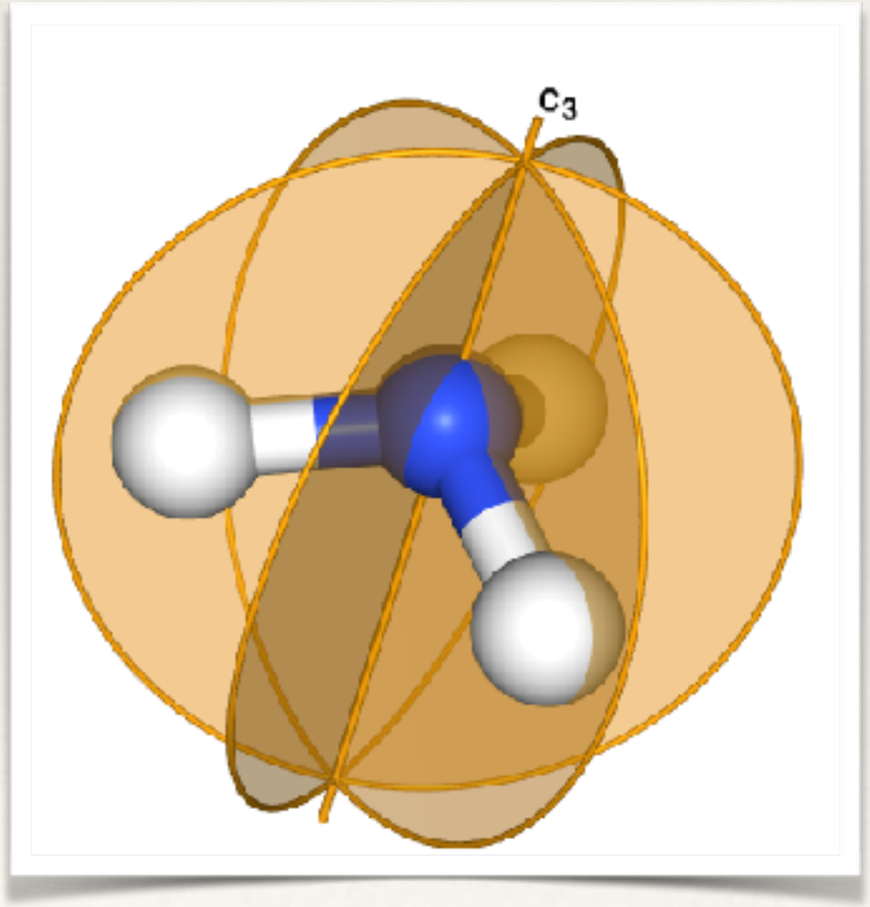
An improper rotation S_2 with a 180º rotation followed by a reflection is also called an inversion. The point where the rotation axis and the plane cross is called inversion center.



The symbol **i** is used to denote the inversion operation. The only invariant point in an inversion is the inversion center itself.

Symmetry elements and symmetry operations

Symmetry operations are defined using certain geometric objects (planes, lines or points) which are called symmetry elements. The same symbol is often used for the symmetry element and the operation, do not confuse them.



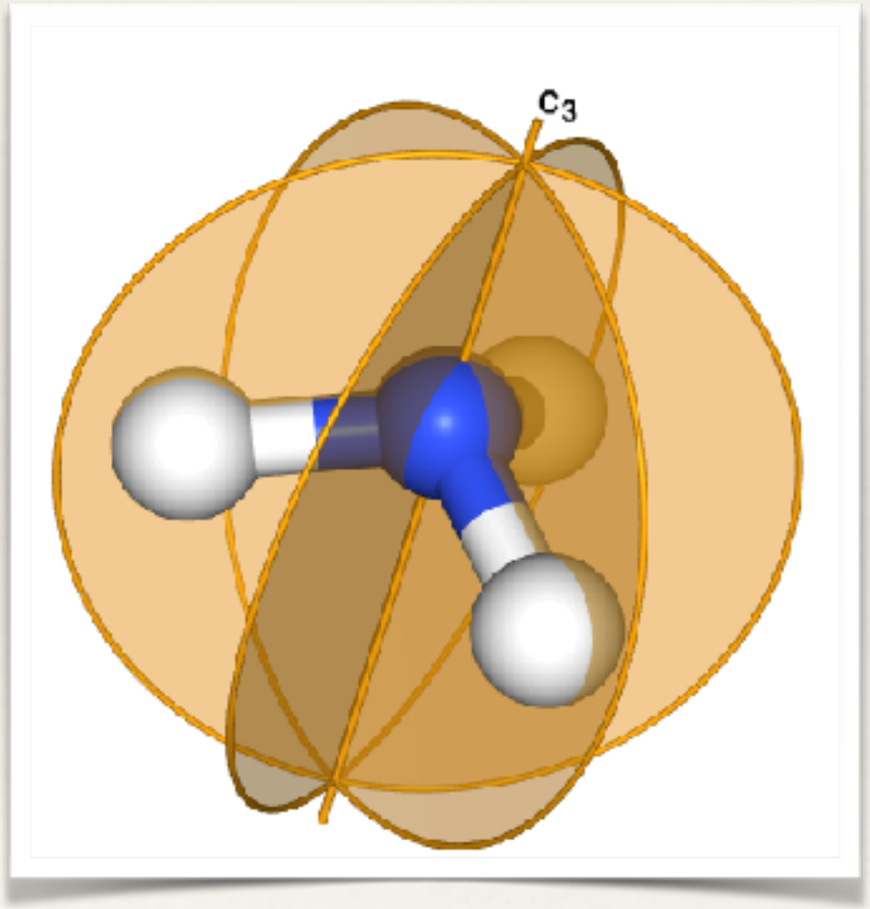
A single axis may support more than one rotation, for example, a C_3 axis implies the existence of a C_3 (turn by 120º) and a C_3^2 (240º turn, or two consecutive 120º turns) operations.

A given object may have several independent symmetry elements. For instance, one C_3 axis and three σ_v planes for the ammonia molecule.

All points on the intersection of all symmetry elements remain invariant under all symmetry transformations. For a finite object, all symmetry elements must share, at least, one common point.

Molecular symmetry groups

The **set of all symmetry operations** of an object has the algebraic structure of a **group**. Symmetry groups can be classified according to the different symmetry elements in an object.



$$C_{3v} = \{E, C_3, C_3^2, \boldsymbol{\sigma}_1, \boldsymbol{\sigma}_2, \boldsymbol{\sigma}_3\}$$

symmetry group

symmetry operations

The number of symmetry operations h is called the **order** of the group: $h(C_{3v}) = 6$.

We say that the NH_3 molecule in its equilibrium geometry has C_{3v} symmetry or that it belongs to the C_{3v} group.

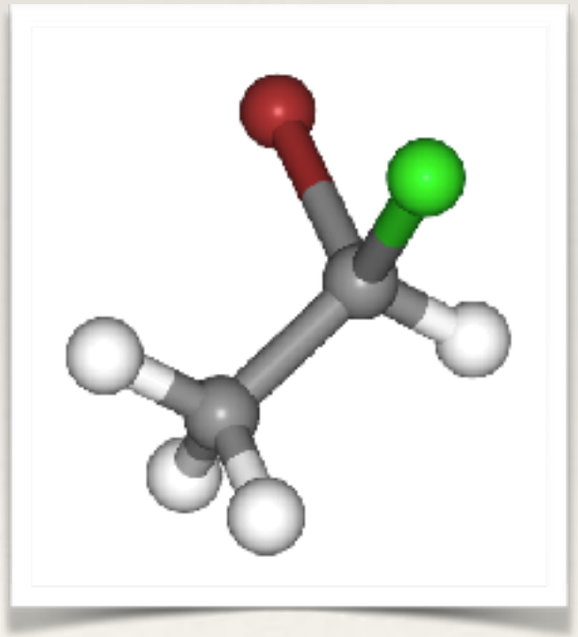
You can find a large collection of interactive examples of molecules at the Symmetry Resources at Otterbein University page (symotter.org)

Low symmetry molecules

Asymmetric molecules do not have any symmetry operation besides the identity operation. They belong to the trivial $C_1 = \{E\}$ group of order 1.

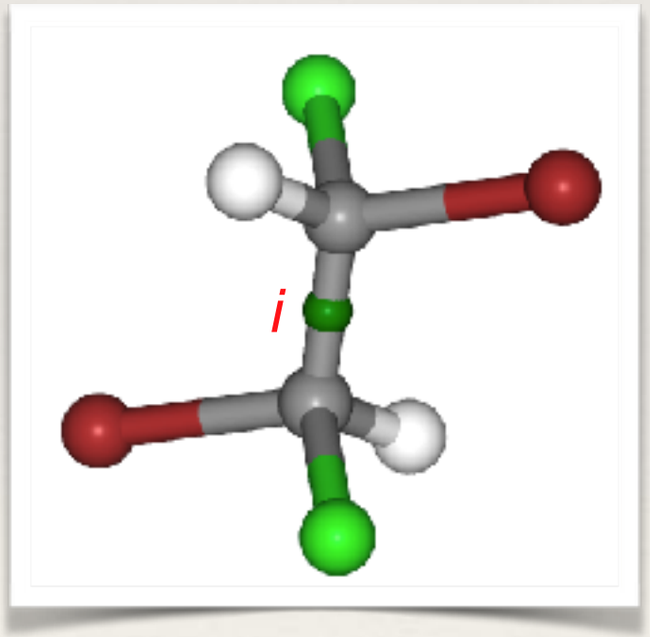
There are three possible symmetry groups with one symmetry operation besides the identity: $C_2 = \{E,C_2\}$, $C_s = \{E,\boldsymbol{\sigma}\}$ and $C_i = \{E,i\}$. All three groups have order 2.

All planar molecules have, at least, C_s symmetry.



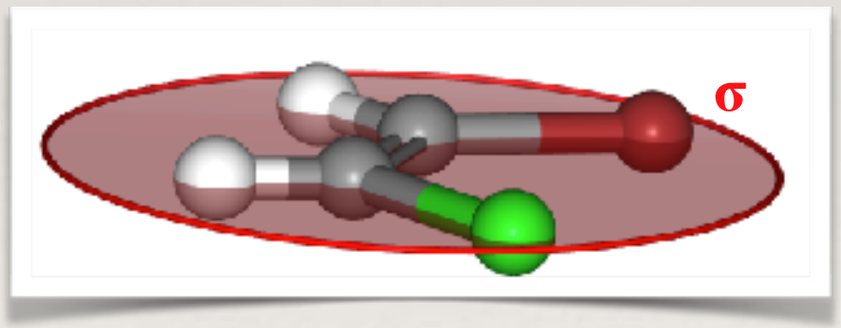
CH_3-CHFCl

C_1 symmetry



CHFCl-CHFCl

C_i symmetry

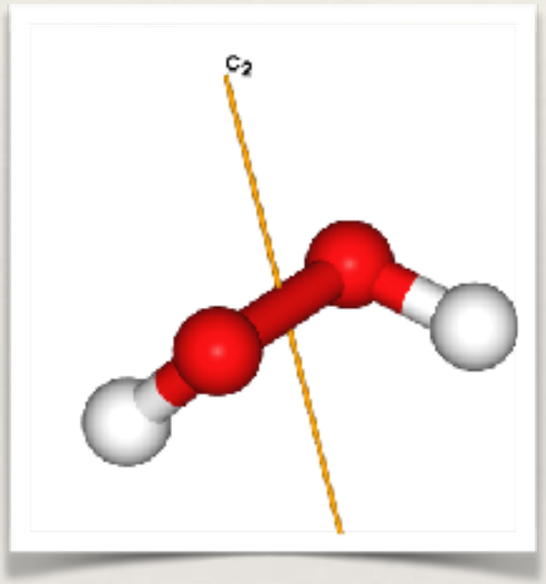


CHF=CHCl

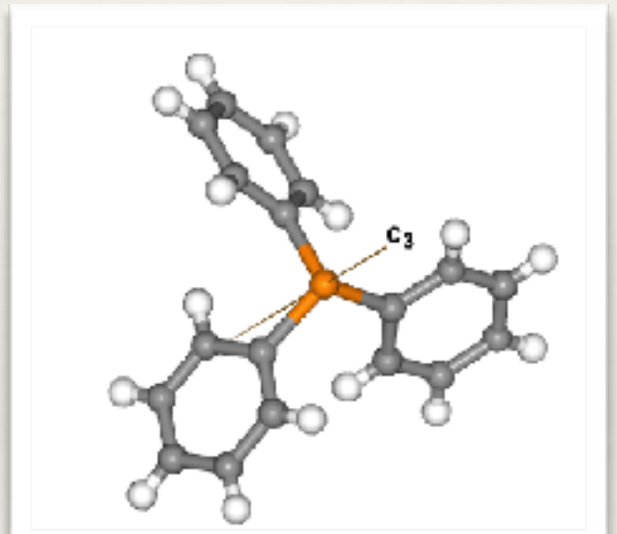
C_s symmetry

Molecules with cyclic symmetry

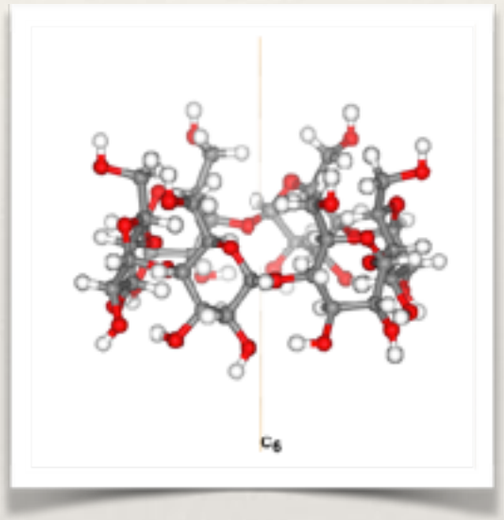
Molecules with a C_n rotation axis belong to the $C_n = \{C_n, C_n^2, \ldots, C_n^n = E\}$ groups of order n.

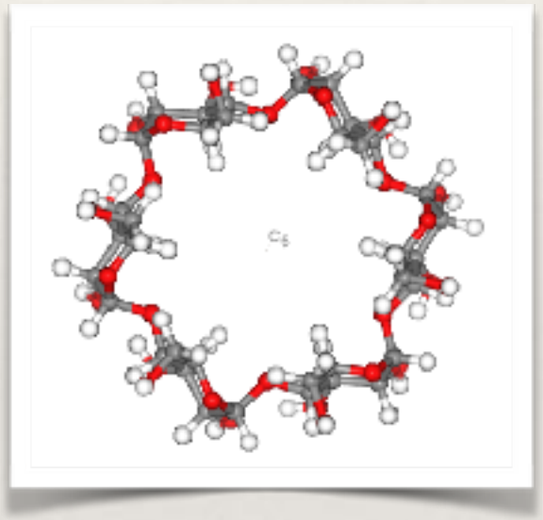


H_2O_2
C_2 symmetry



triphenylphosphine
C_3 symmetry

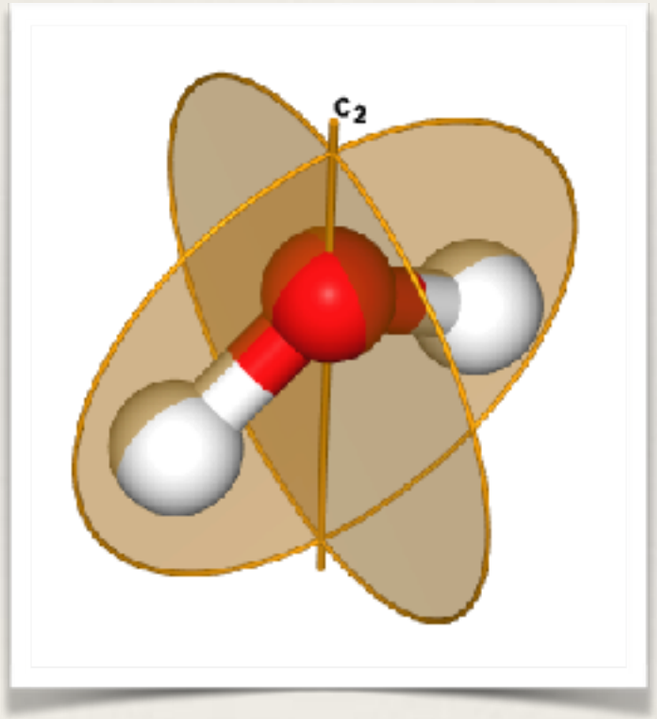




cyclodextrine
C_6 symmetry

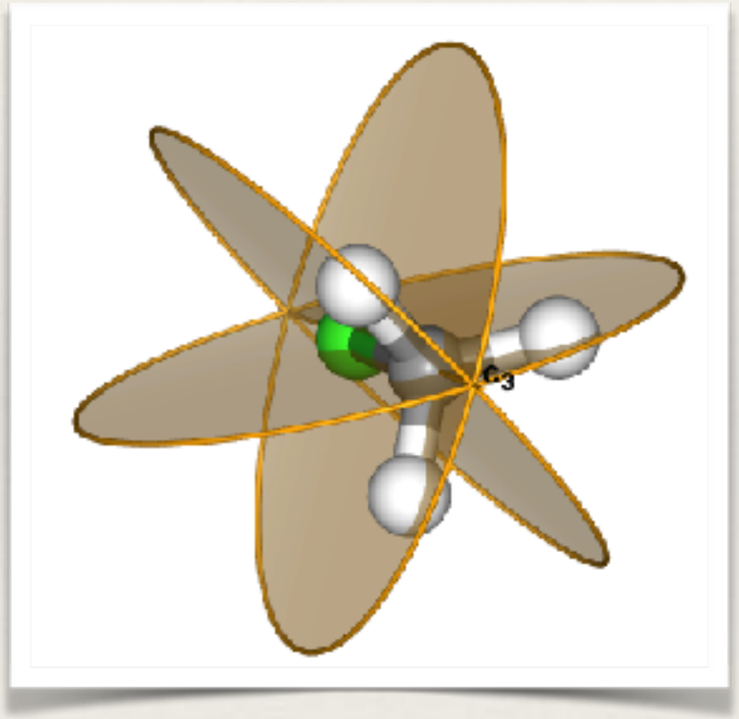
Molecules with pyramidal symmetry

A C_n rotation axis may be combined with n $\boldsymbol{\sigma}_v$ mirror planes whose intersection coincides with the rotation axis to give molecules with C_{nv} symmetry. For even values of n > 2, half of the planes are labelled as $\boldsymbol{\sigma}_d$ (diagonal).



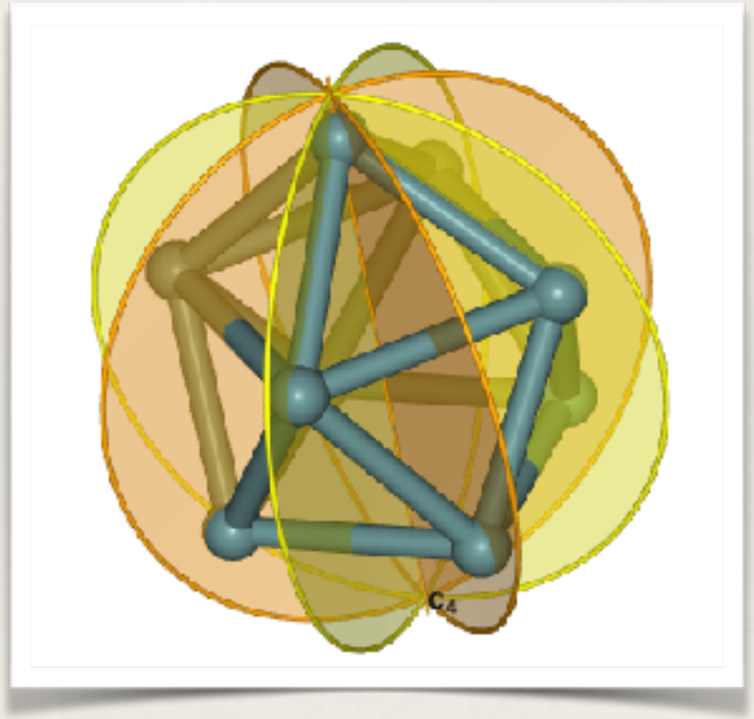
H_2O

C_{2v} symmetry



CH_3Cl

C_{3v} symmetry

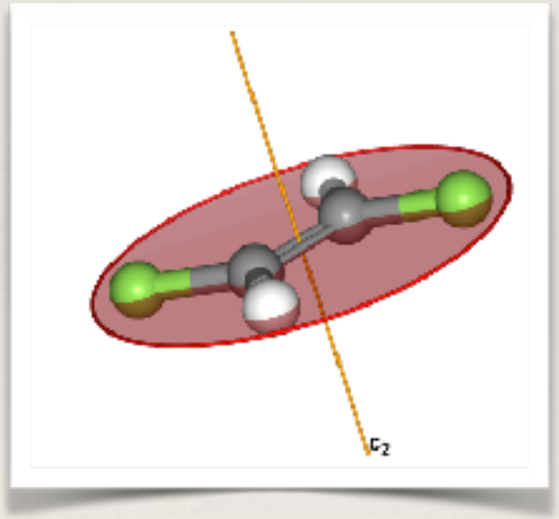


$[Ge_9]^{4-}$

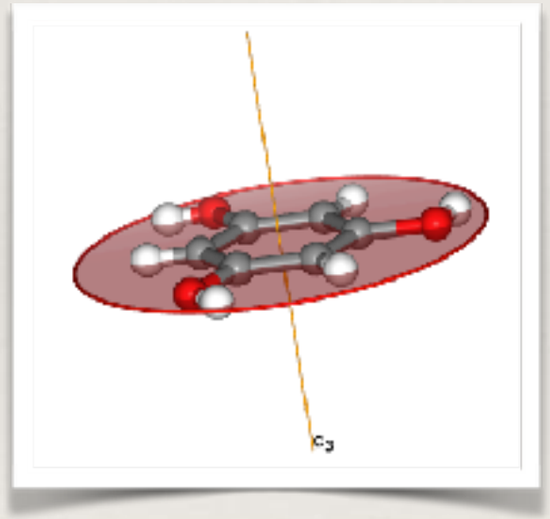
C_{4v} symmetry

Rotation axis perpendicular to a mirror plane

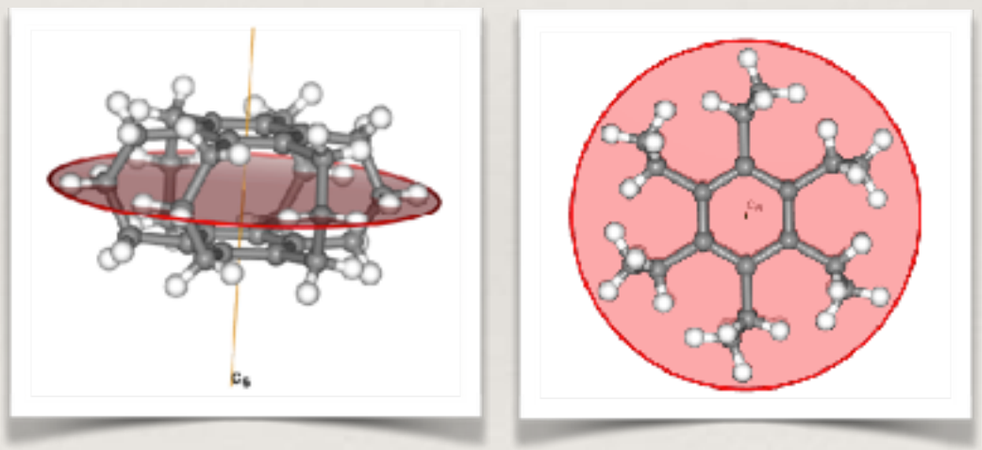
A C_n rotation axis may be combined with a single $\boldsymbol{\sigma}_h$ mirror plane perpendicular to it, giving molecules with C_{nh} symmetry. The simultaneous presence of C_n and $\boldsymbol{\sigma}_h$ imply the presence of an improper rotation axis S_n. Molecules with even n have an implicit $S_2 = i$ inversion symmetry operation.



trans $C_2H_2F_2$
C_{2h} symmetry



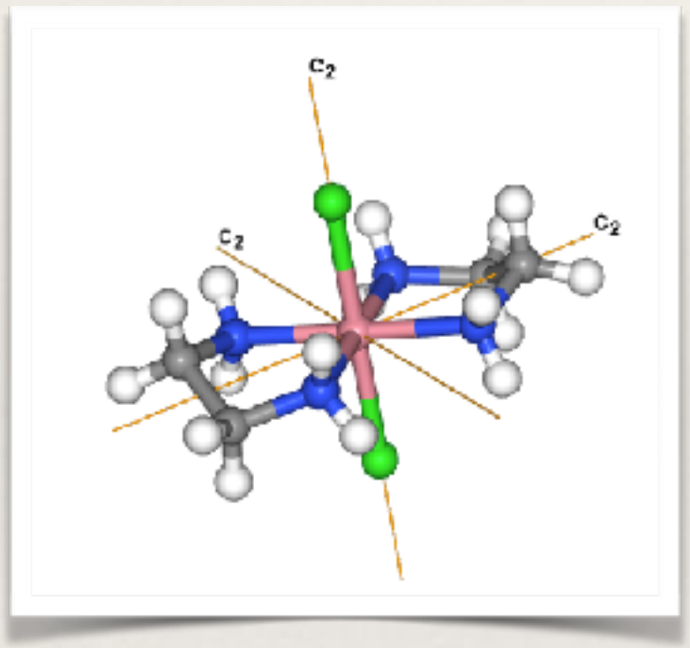
benzene-1,3,5-triol
C_{3h} symmetry



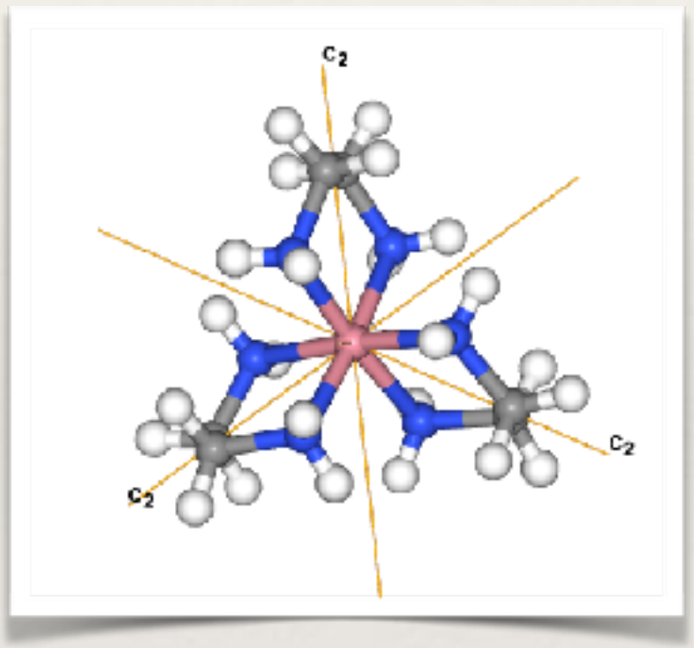
cyclophane
C_{6h} symmetry

Molecules with dihedral symmetries

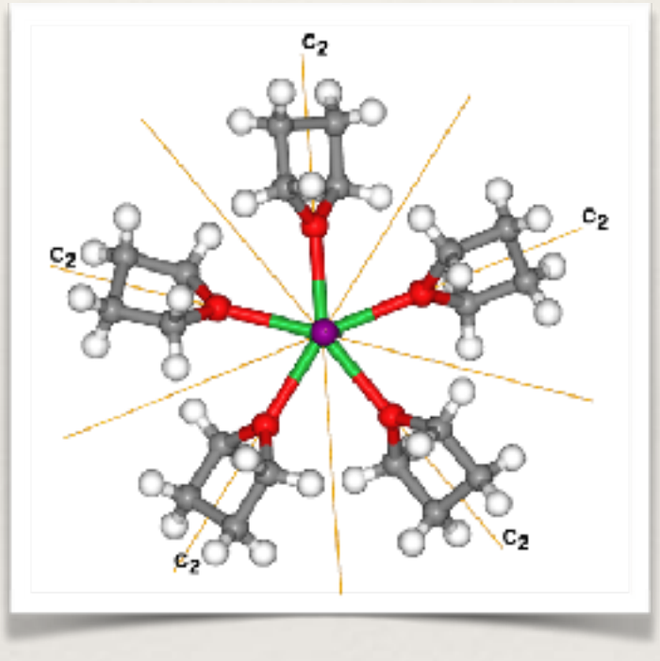
A C_n rotation axis may be combined with n perpendicular C_2 axes, but no mirror planes, to give molecules with D_n symmetry.



(δ,δ)-*trans*-$[Co(en)_2Cl_2]^+$
D_2 symmetry



$[Co(en)_3]$
D_3 symmetry

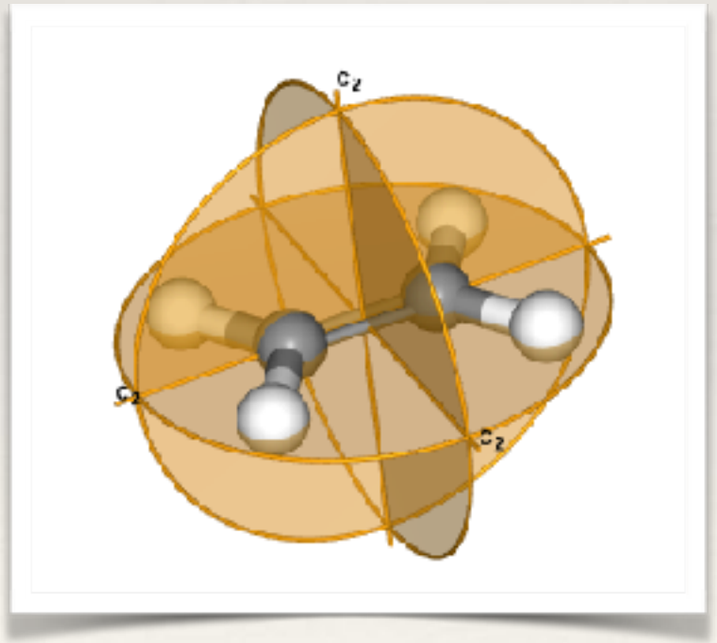


$[YbI_2(THF)_5]$
D_5 symmetry

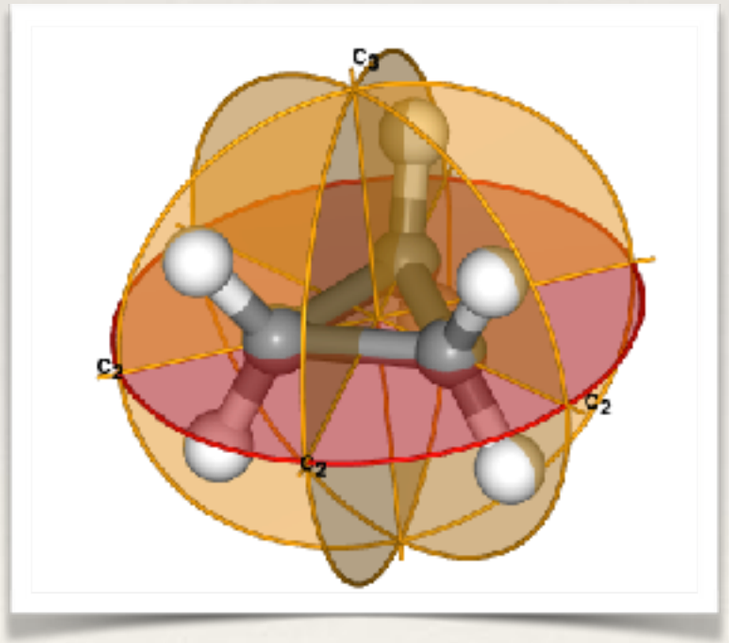
Molecules with prismatic symmetry

A C_n rotation axis may be combined with n perpendicular C_2 axes and a perpendicular $\boldsymbol{\sigma}_h$ mirror plane to give D_{nh} symmetry.

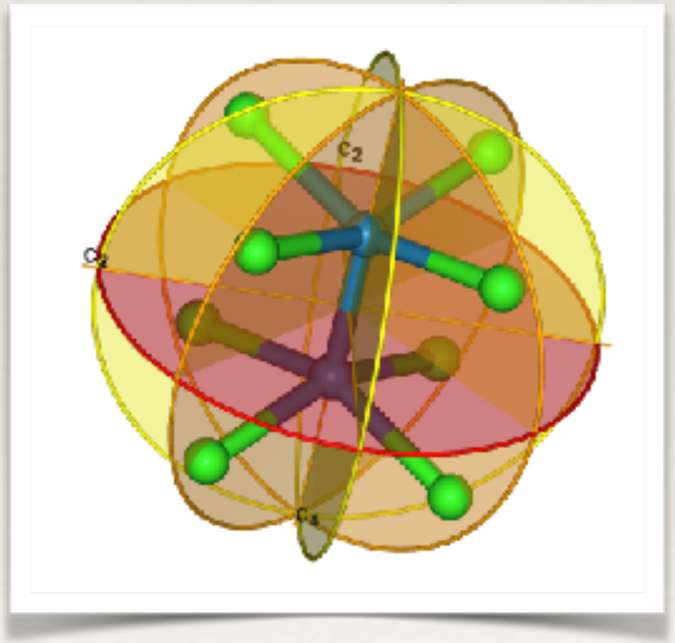
A C_n axis perpendicular to a $\boldsymbol{\sigma}_h$ plane implies the presence of S_n symmetry operations. The presence of C_2 axes lying on the mirror plane implies the presence of additional $\boldsymbol{\sigma}_v$ and $\boldsymbol{\sigma}_d$ vertical mirror planes.



C_2H_2
D_{2h} symmetry



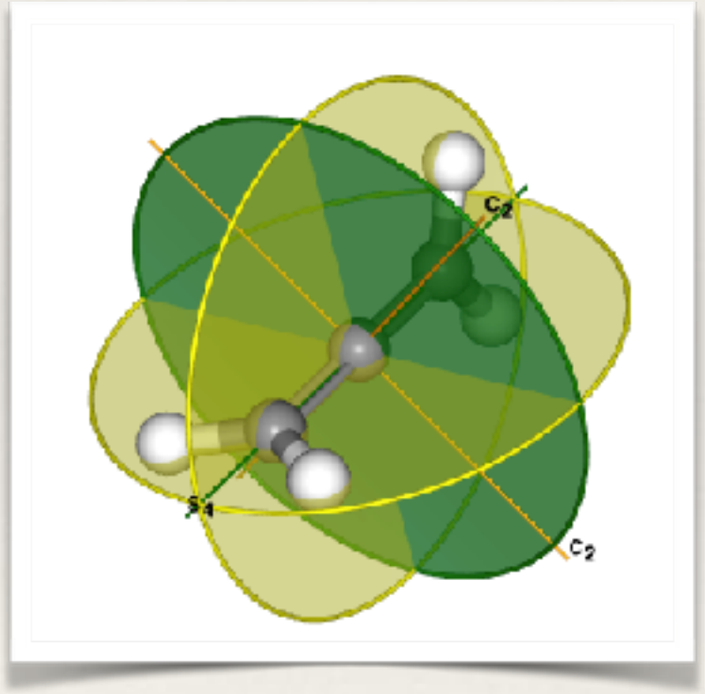
C_3H_3
D_{3h} symmetry



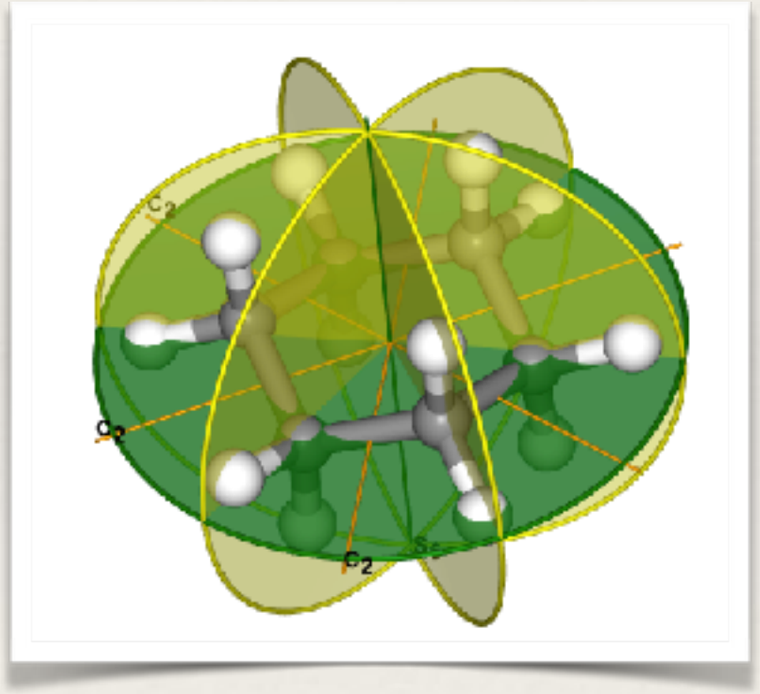
$[Re_2Cl_8]^{2-}$
D_{4h} symmetry

Molecules with anti prismatic symmetry

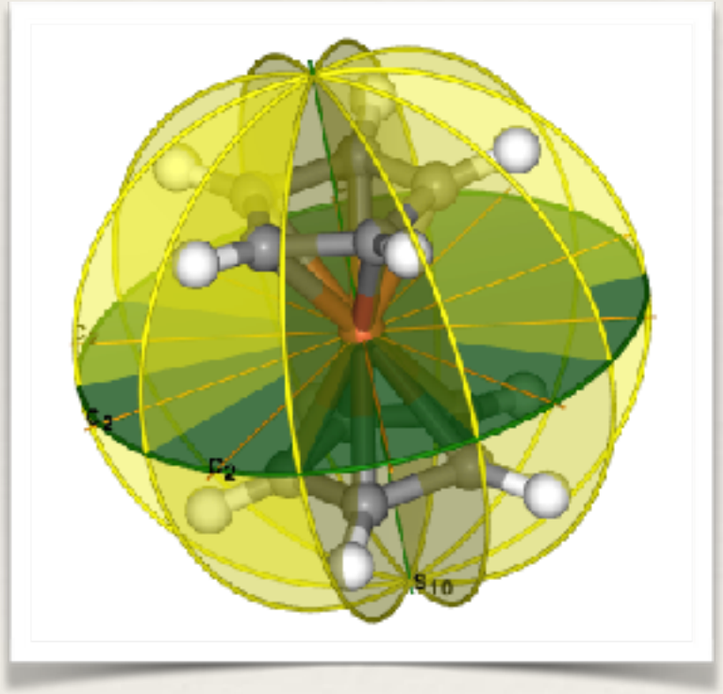
A S_{2n} rotation axis may be combined with n perpendicular C_2 axes to give molecules with D_{nd} symmetry. The presence of perpendicular C_2 axes implies the presence of additional $\boldsymbol{\sigma}_d$ mirror planes.



allene (C_3H_4)
D_{2d} symmetry



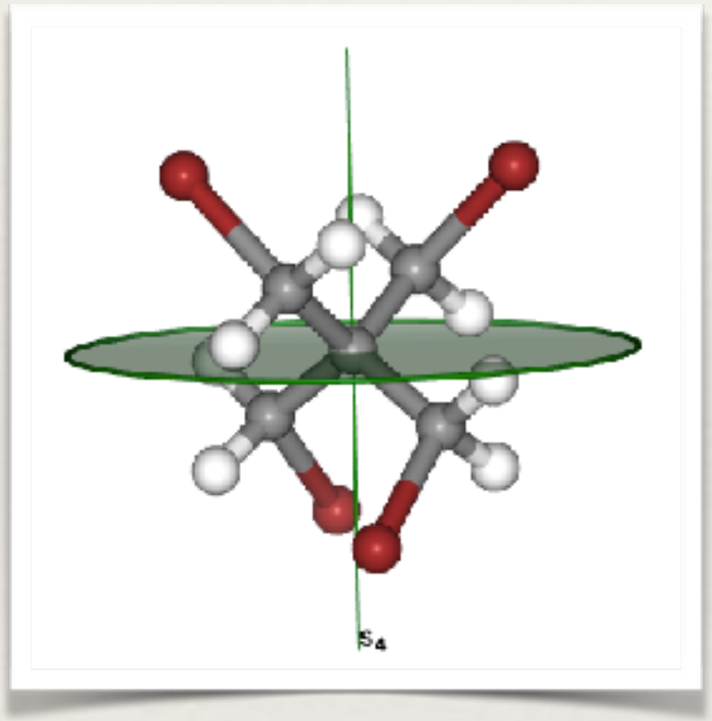
cyclohexane chair conf.
D_{3d} symmetry



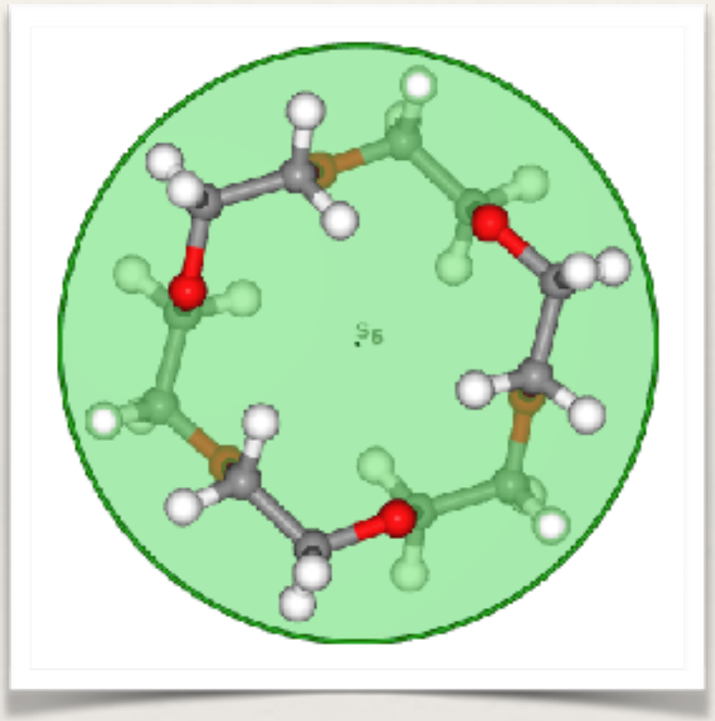
Ferrocene (staggered)
D_{5d} symmetry

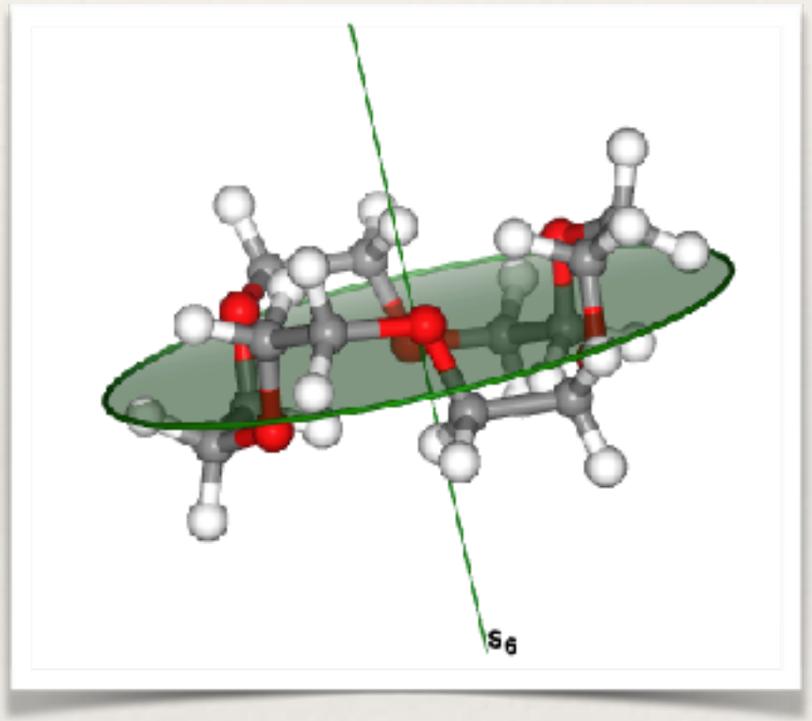
Molecules with just improper rotation symmetry

Molecules with only improper symmetry rotations belong to the S_n groups where n is an even number greater than 2 (remember that $S_1 = C_s$ and $S_2 = C_i$).



tetrabromoneopentane
S_4 symmetry

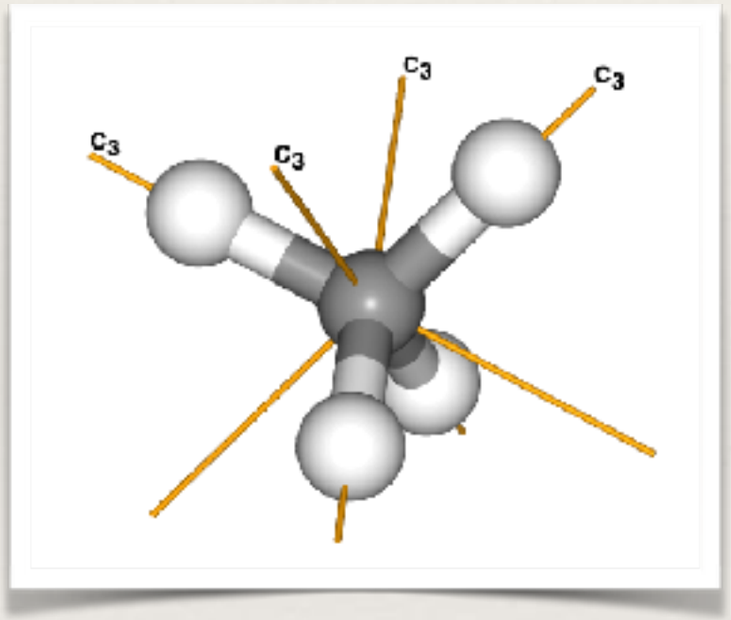


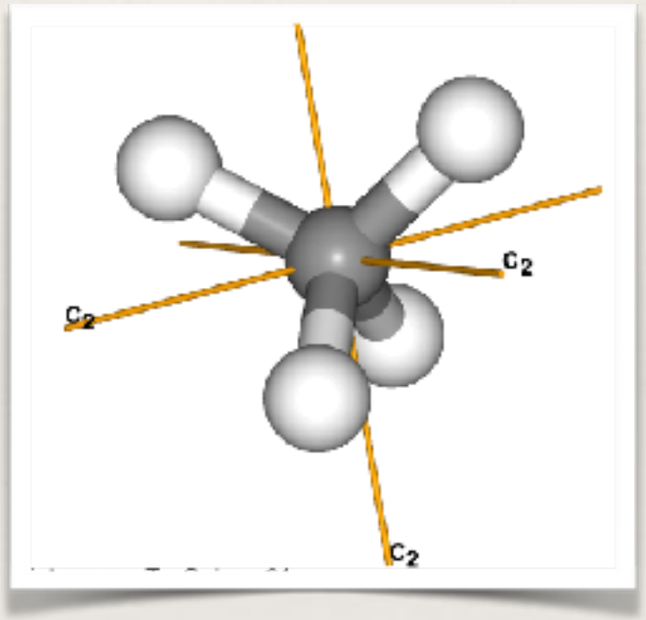


18-crown-6 eter
S_6 symmetry

High symmetry molecules

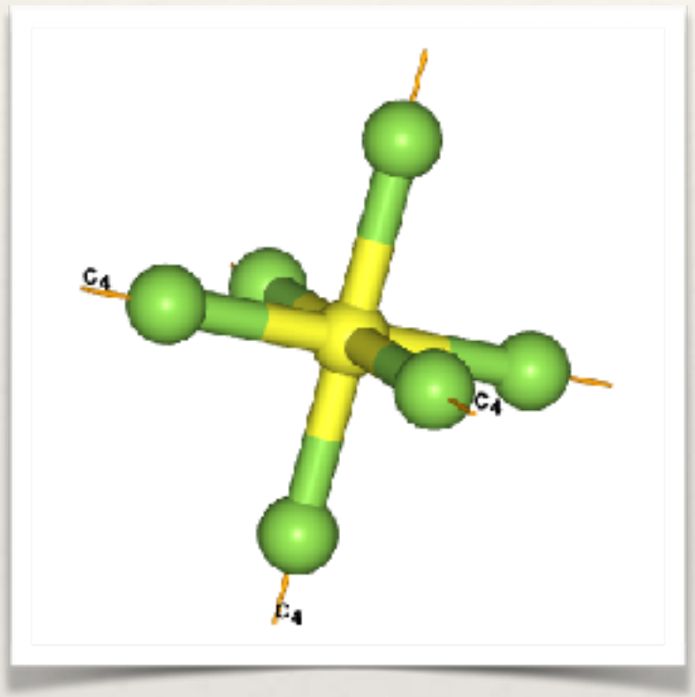
Highly symmetric molecules belong either to tetrahedral, octahedral or icosahedral groups. The main features of these groups is the presence of several independent rotational axes with n >2

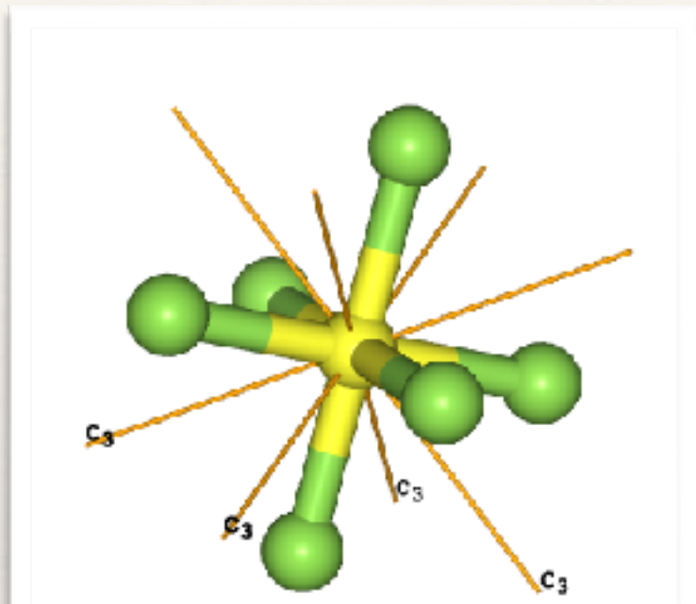


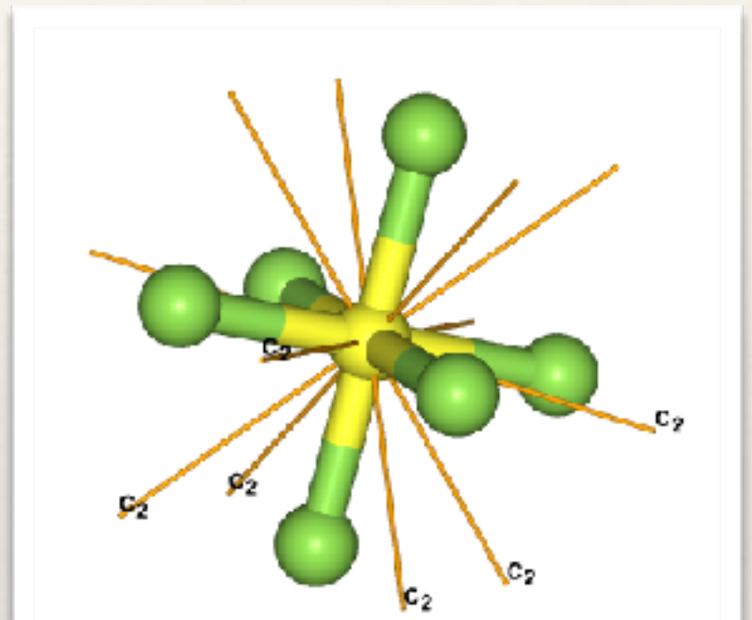


Molecules with tetrahedral symmetry have 4 C_3 axes and 3 C_2 axes. They belong to groups **T** (only rotations), $\mathbf{T_h}$, or $\mathbf{T_d}$. The tetrahedron has the full $\mathbf{T_d}$ symmetry with 24 symmetry operations.

High symmetry molecules

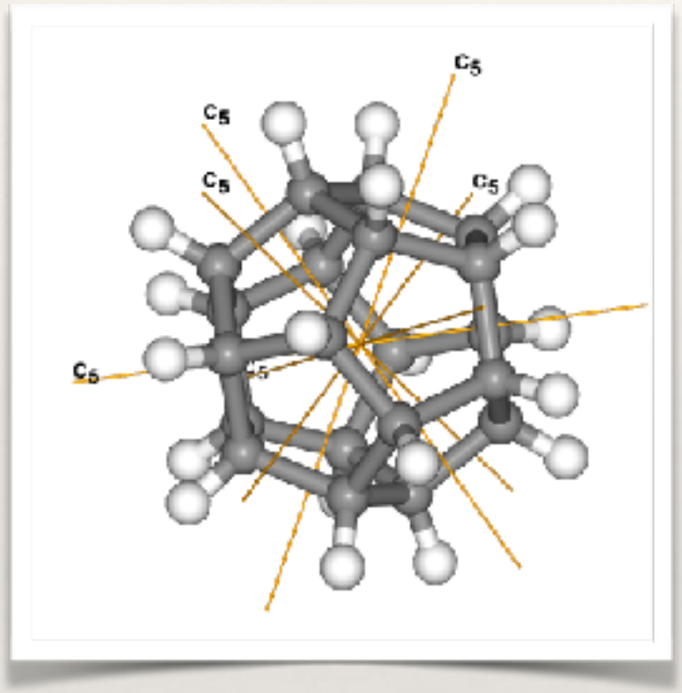


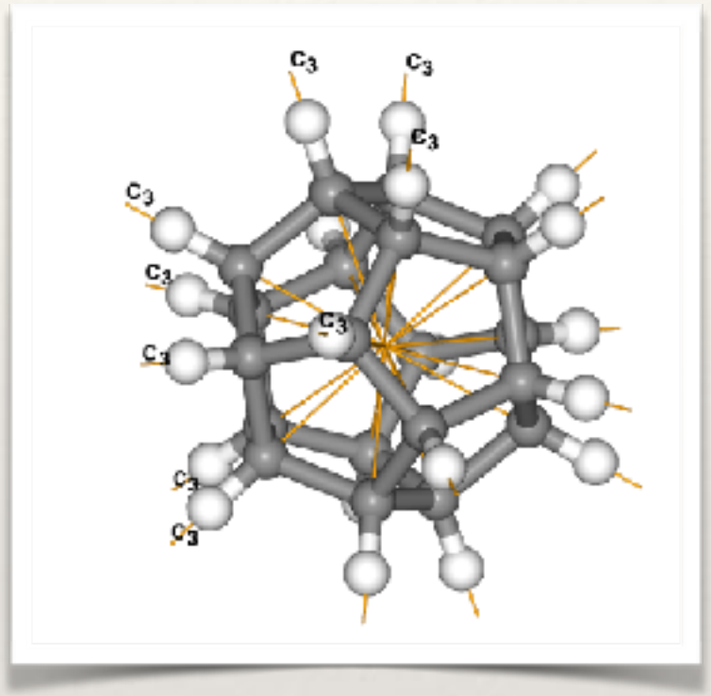


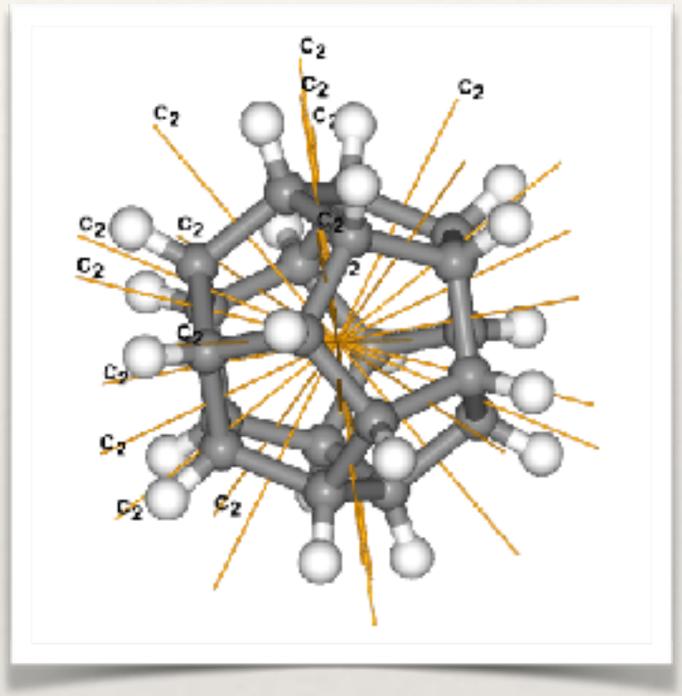


Molecules with octahedral symmetry have 3 C_4 axes, 4 C_3 axes and 6 C_2 axes. They belong to groups **O** (only rotations) or **O_h**. The octahedron and the cube have the full **O_h** symmetry with 48 symmetry operations.

High symmetry molecules





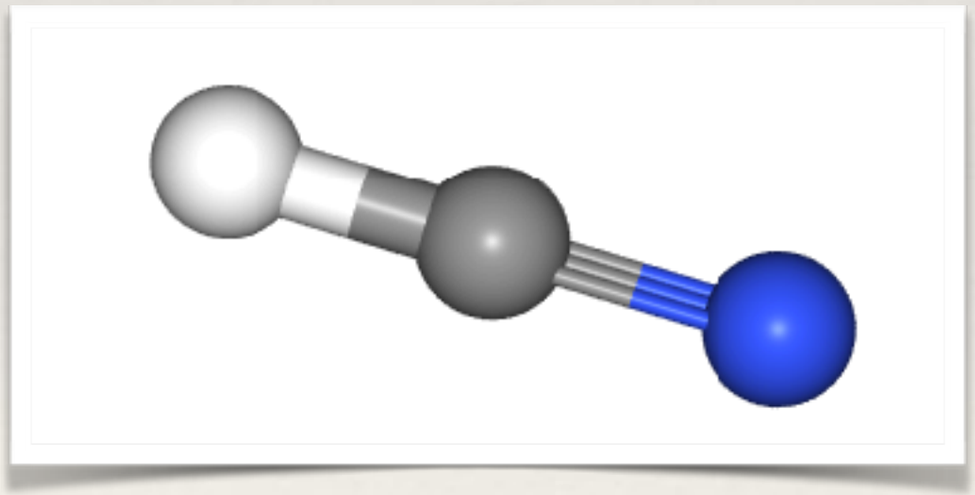


Molecules with icosahedral symmetry have 6 C_5 axes, 10 C_3 axes and 15 C_2 axes. They belong to groups **I** (only rotations) or **I_h**. The dodecahedron and the icosahedron have the full **I_h** symmetry with 60 symmetry operations.

Symmetry of linear molecules

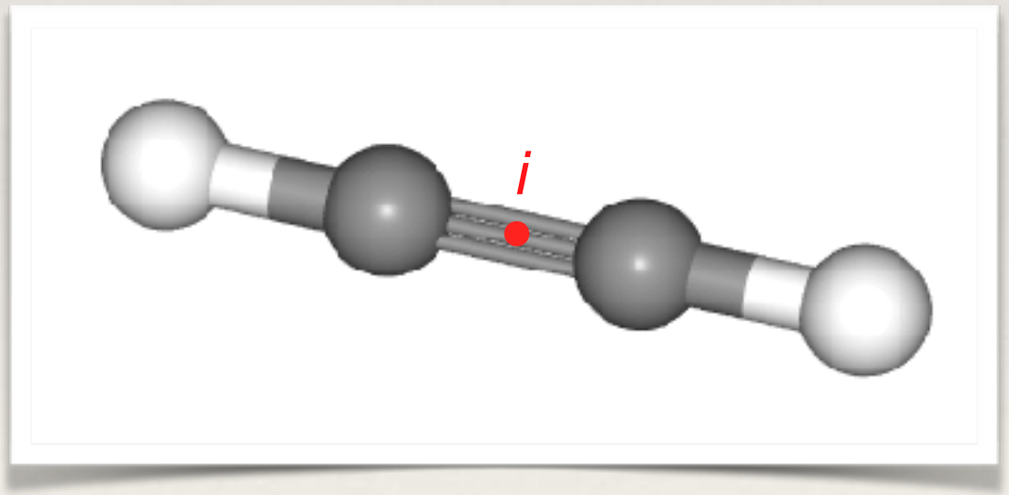
The line containing all atoms is a C_∞ rotation axis, meaning that any rotation around it is a symmetry operation. The C_∞ axis is located at the intersection of infinite $\boldsymbol{\sigma}_v$ mirror planes.

There are two possibilities, depending on whether there is an inversion center (or a perpendicular $\boldsymbol{\sigma}_h$ mirror plane) or not:



HCN

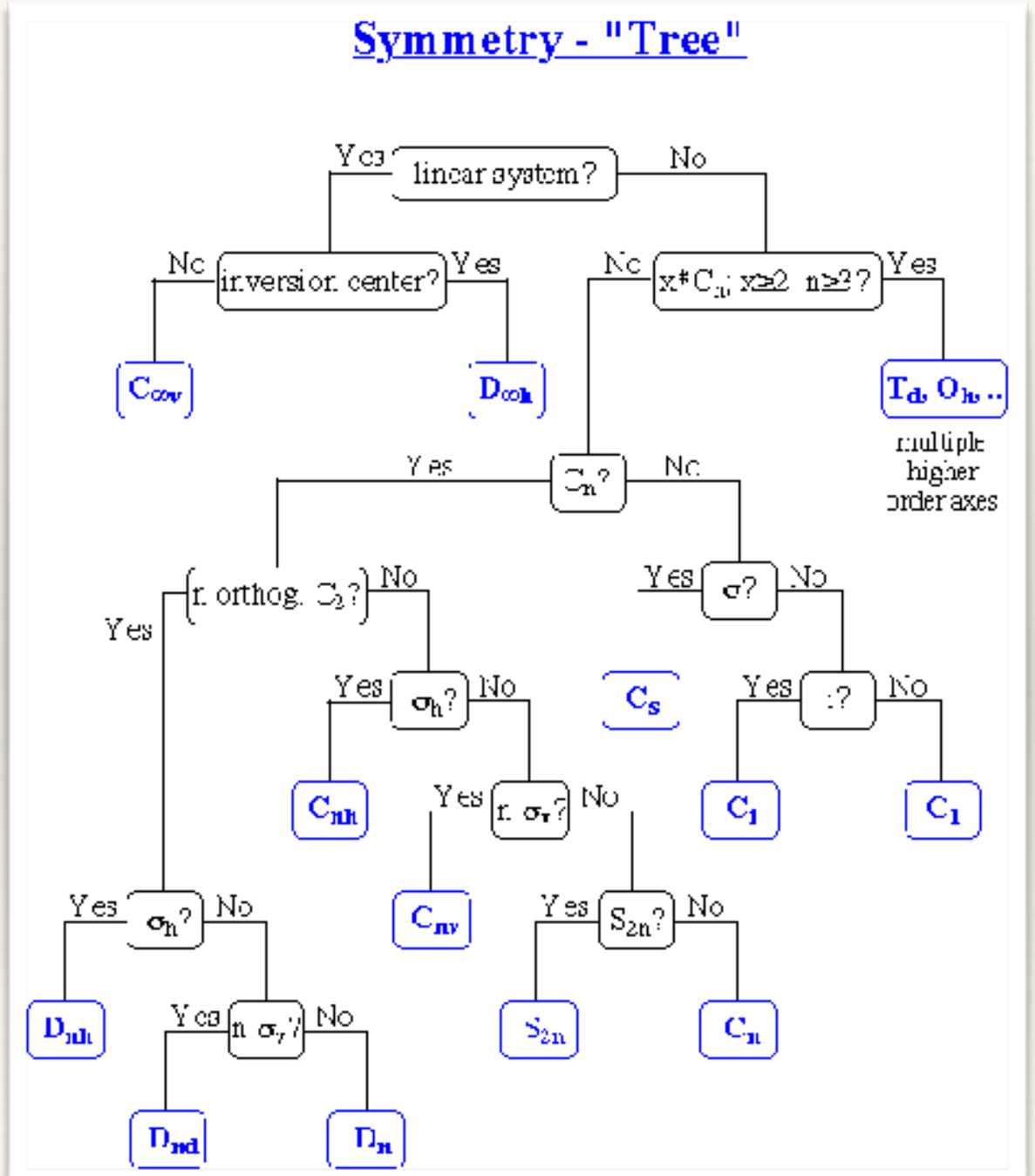
$C_{\infty v}$ symmetry



C_2H_2

$D_{\infty h}$ symmetry

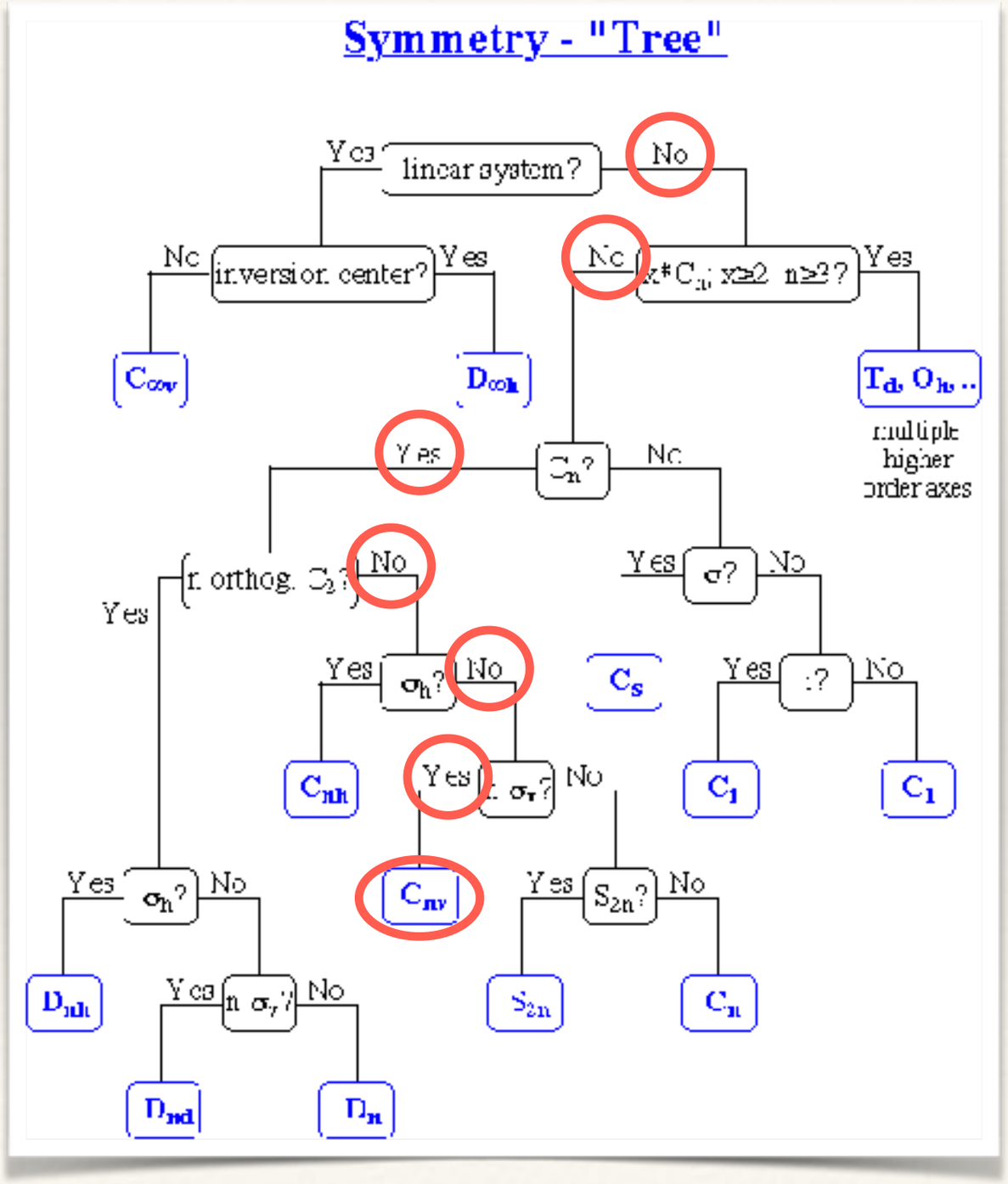
How to find a molecule's symmetry group

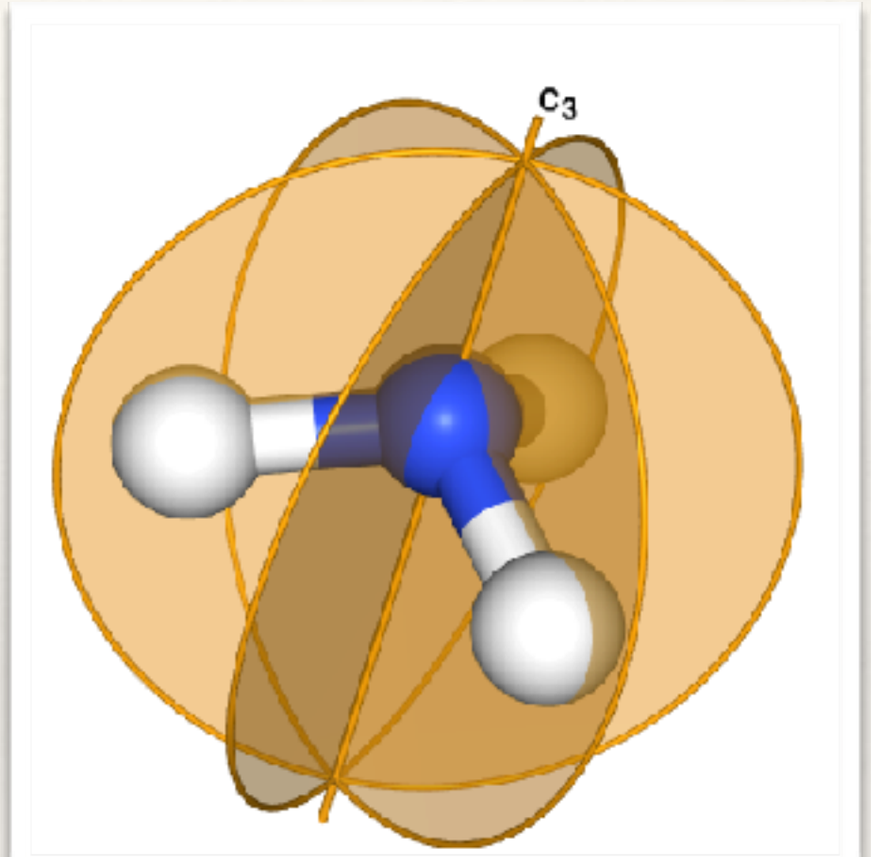


It is only necessary to identify some key symmetry elements to find the symmetry group of a molecule.

You just need to follow a flow diagram similar to the one at the left of the slide.

How to find a molecule's symmetry group

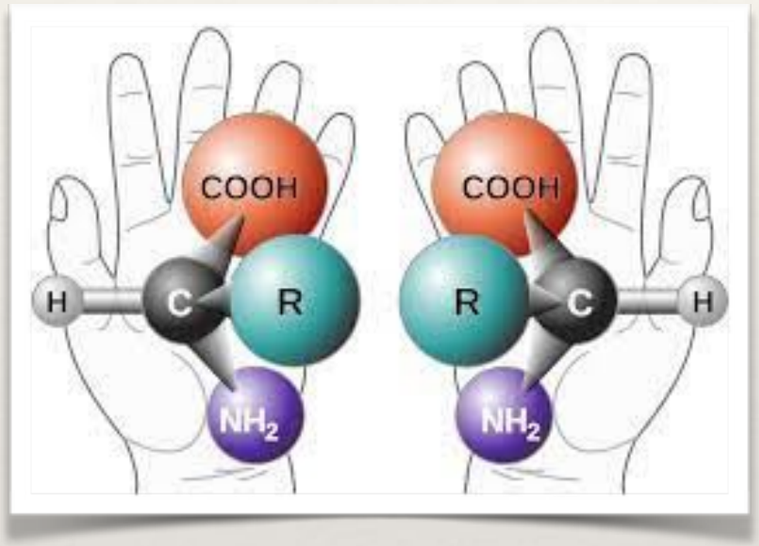


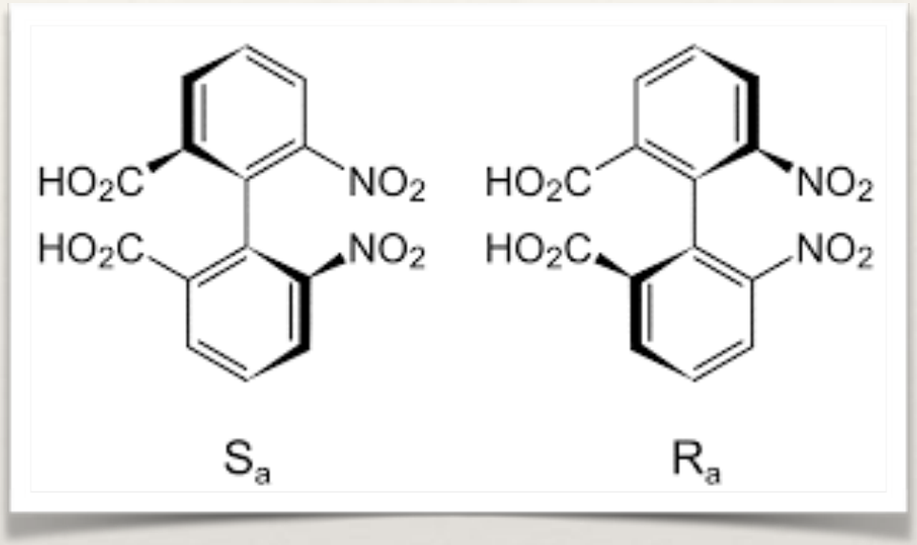


$C_{3v} = \{E, C_3, C_3^2, \boldsymbol{\sigma}_1, \boldsymbol{\sigma}_2, \boldsymbol{\sigma}_3\}$

Chirality

A molecule is said to be chiral if it can exist in two distinct forms that are one the mirror image of the other.

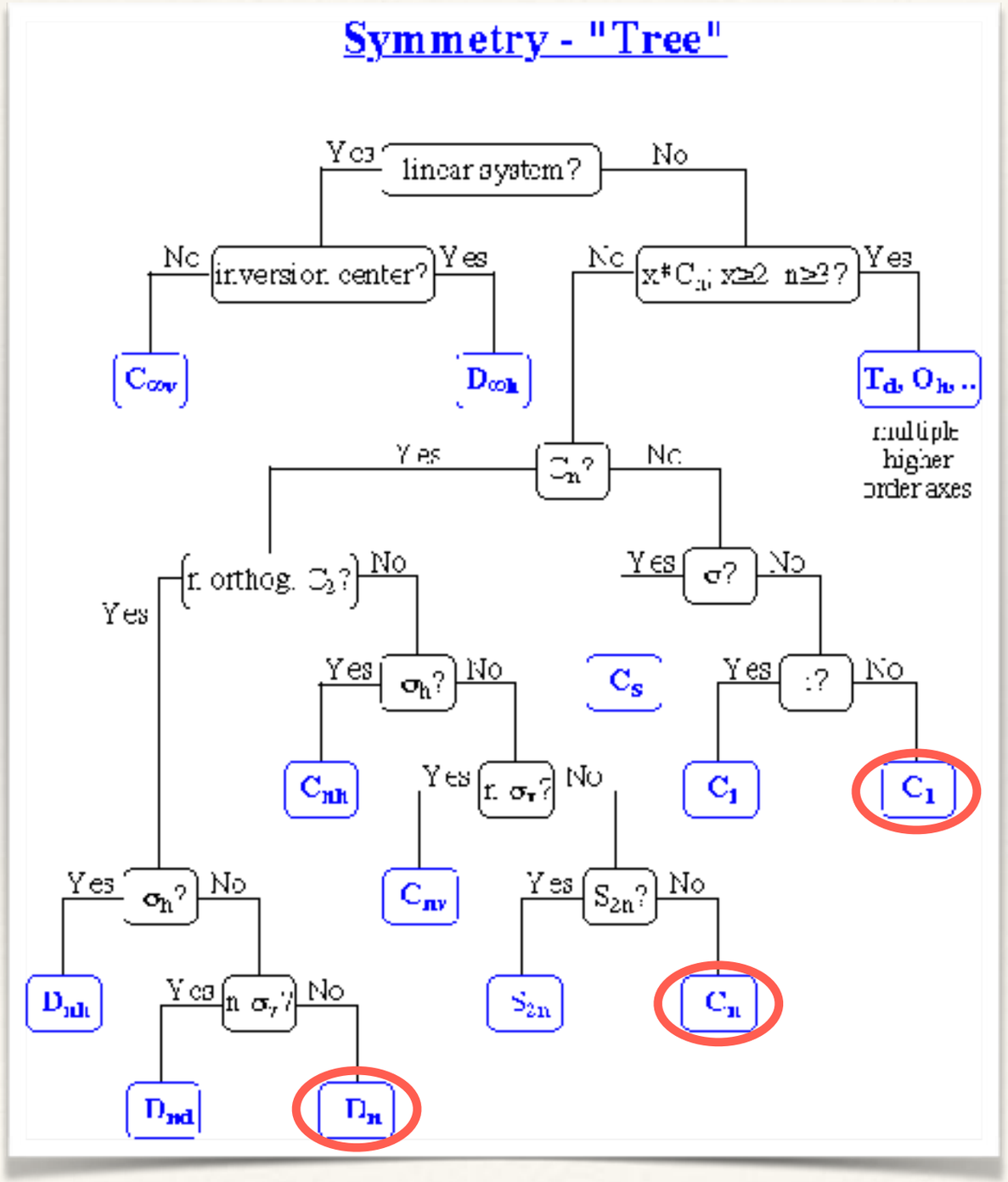




A chiral structure can contain no improper axis of rotation (S_n with even n), which includes planes of symmetry, $\boldsymbol{\sigma} = S_1$, and inversion center, $i = S_2$.

Note that only C_1 molecules are really asymmetric and that it is wrong to associate chirality with the lack of symmetry, chiral molecules are not necessarily asymmetric.

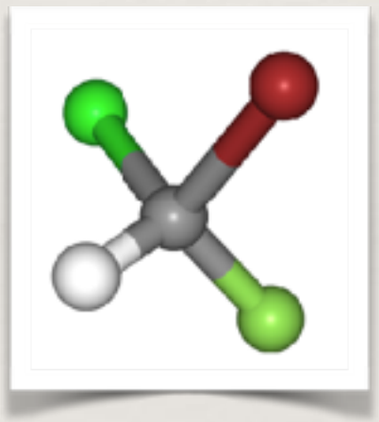
Chiral symmetry groups



Chiral molecules must belong to one of the following groups:

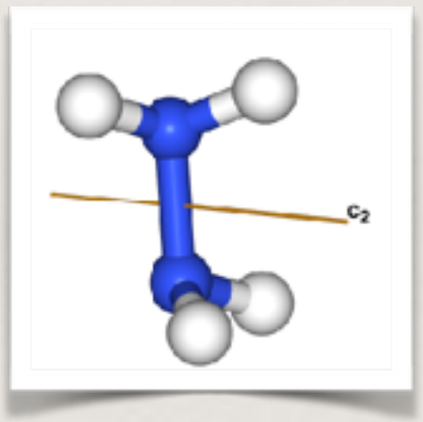
C_1, C_n, D_n, T, O, or I,

which are called the **chiral groups**.



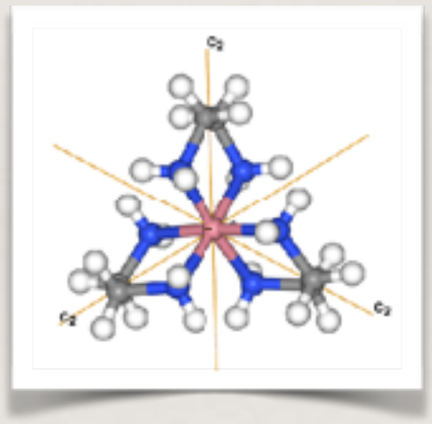
CHClBrI

C_1 symmetry



Hydrazine

C_2 symmetry



$[Co(en)_3]$

D_3 symmetry