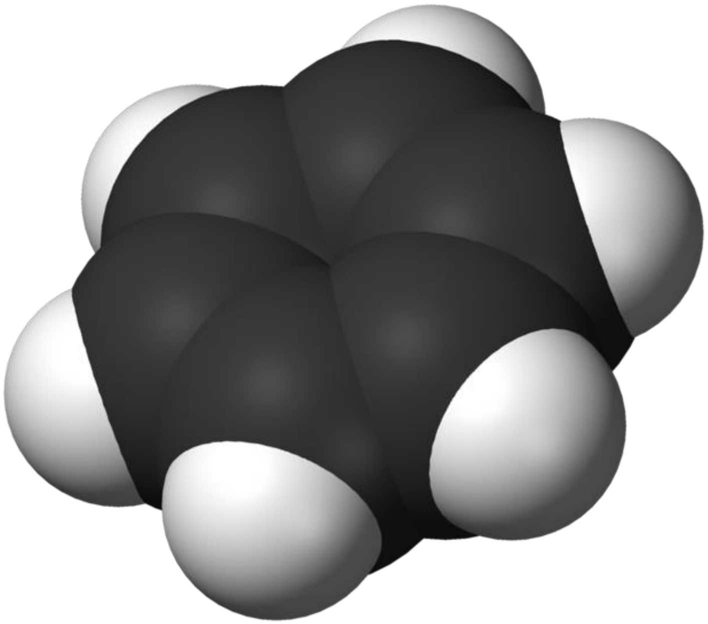
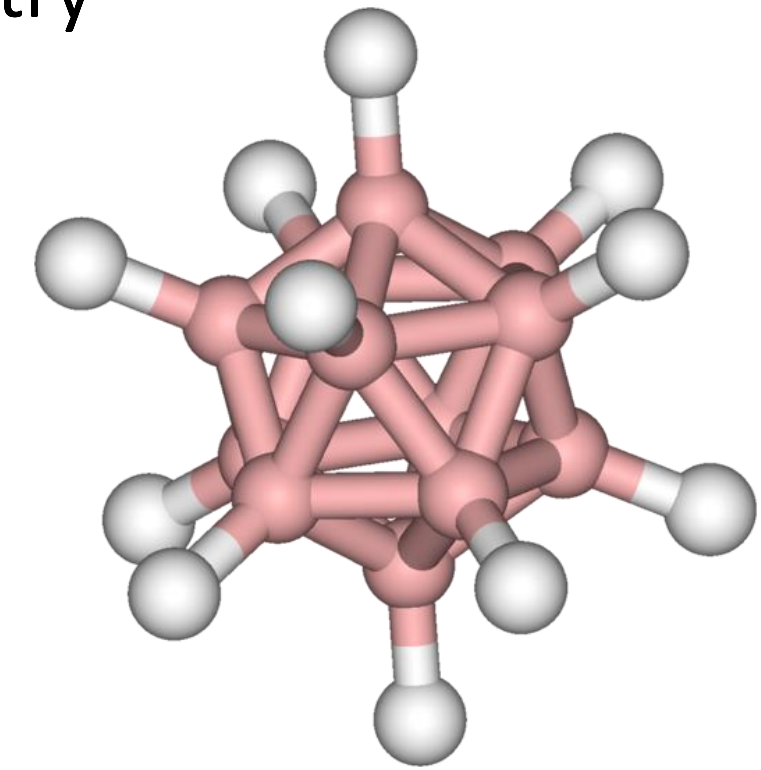
Lecture 7 Sept. 10, 2020

- ***Symmetry in Nature and in Molecules***
- ***Symmetry Operations***
- ***Symmetry Elements***
- ***Point Groups and Assignments***

Symmetry



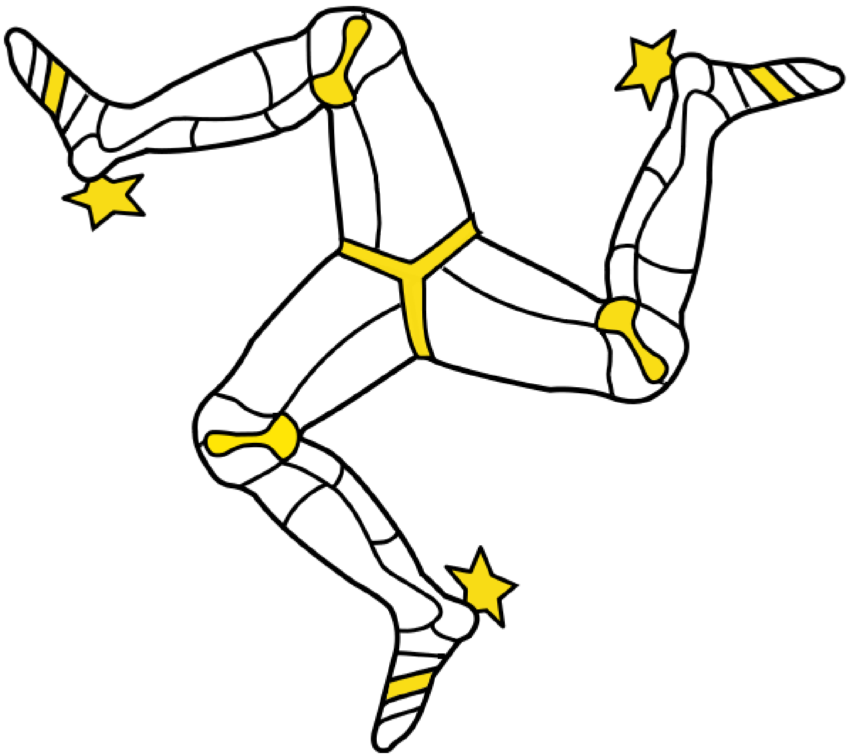


Intuitively, we know symmetry when we see it.

But how do we put in quantitative terms that allows us to compare, assign, classify?

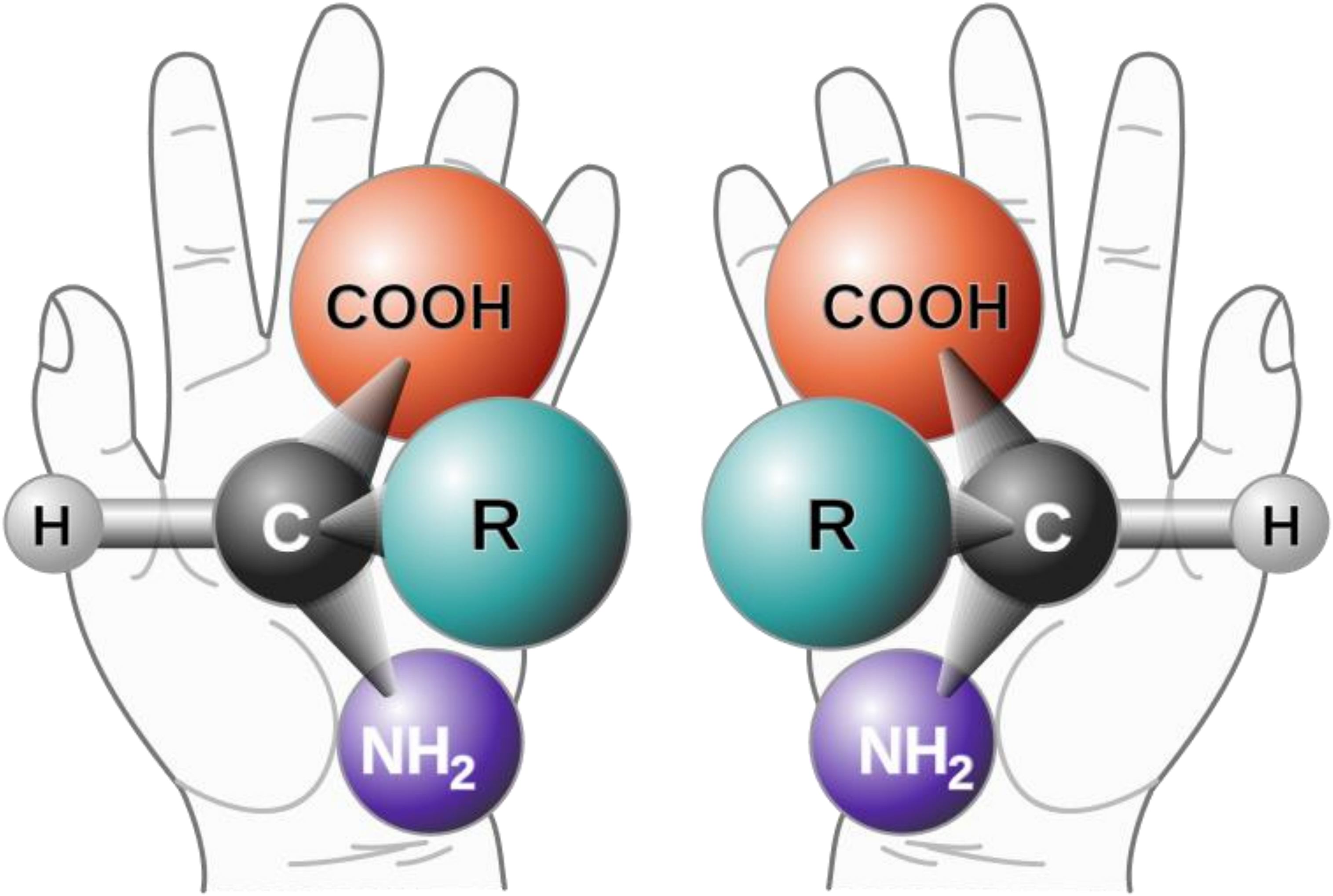
Symmetry: mirror planes

Symmetry



C_3 Rotation Axis

Chirality: Non-superimposable mirror images (aka optical isomers or enantiomers)



Specifically, a chiral compound can contain no improper axis of rotation (S_n), which includes planes of symmetry and inversion center. Asymmetric molecules are always chiral.

Symmetry in Nature and in Molecules

The symmetry of a molecule is determined by the existence of **symmetry operations** performed with respect to **symmetry elements**. A ***symmetry element*** is a line, a plane or a point within or through an object, about which a rotation or reflection leaves the object in an orientation indistinguishable from the original. A ***plane*** of symmetry is designated by the symbol **σ** (or sometimes s), and the reflection operation is the coincidence of atoms on one side of the plane with corresponding atoms on the other side, as though reflected in a mirror. A ***center or point of symmetry is labeled i,*** and the inversion operation demonstrates coincidence of each atom with an identical one on a line passing through and an equal distance from the inversion point. Finally, a ***rotational axis is designated C_n***, where the degrees of rotation that restore the object is 360/n (C_2= 180º rotation, C_3= 120º rotation, C_4= 90º rotation, C_5= 72º rotation). C_1 is called the identity operation **E** because it returns the original orientation.

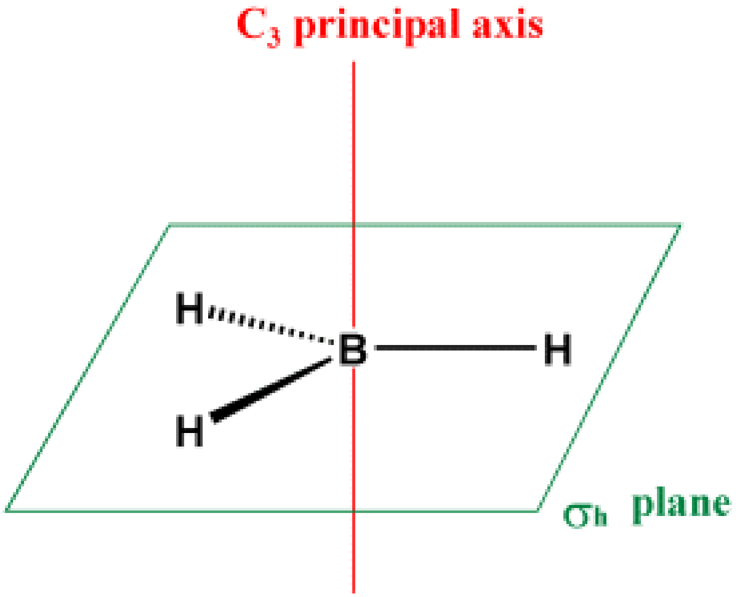
An object having no symmetry elements other than E is called **asymmetric**. Such an object is necessarily chiral. Since a plane or point of symmetry involves a reflection operation, the presence of such an element makes an object **achiral**. One or more rotational axes of symmetry may exist in both chiral, **dissymmetric**, and achiral objects.

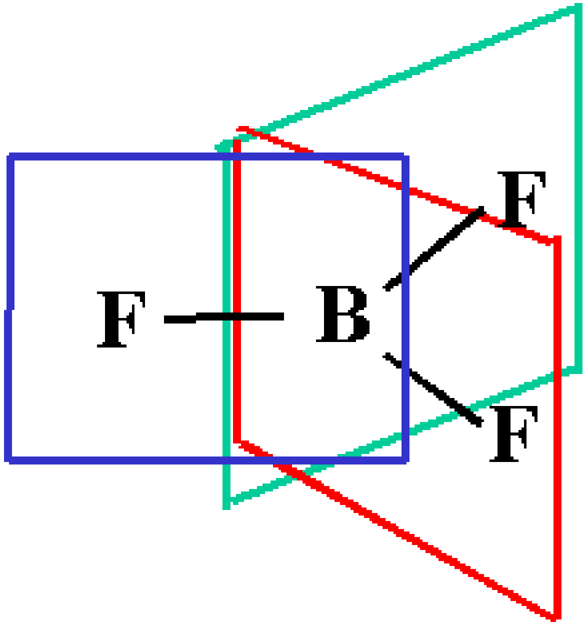
Symmetry Operations and Symmetry Elements

Definitions:

- A **symmetry operation** is an operation on a body such that, after the operation has been carried out, the result is indistinguishable from the original body (every point of the body is coincident with an equivalent point or the same point of the body in its original orientation).
- A **symmetry element** is a geometrical entity such as a line, a plane, or a point, with respect to which one or more symmetry operations may be carried out

Symmetry Operation	Symmetry Element	Notation
Identity	-	E
Reflection in a plane	Plane of symmetry	σ
Proper rotation	Rotation axis (line)	C_n
Rotation followed by reflection in the plane perpendicular to the rotation axis	Improper rotation axis (line)	S_n
Inversion	Center of inversion	I


C3 principal axis
H
B
H
H
σh plane


F
F
B
F

Let's look for these in molecules

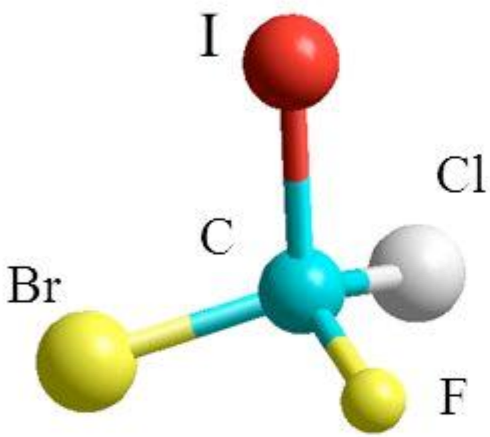
What is a **point group**?

A collection of symmetry elements for a specific symmetry, intersecting at a specific point for molecules, and displayed in a character table.

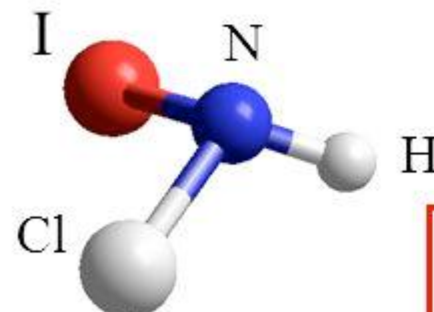
The C_1 point group:

Molecules that have no symmetry elements at all except the trivial one where they are rotated through 360º and remain unchanged, belong to the C_1 point group. In other words, they have an axis of 360º/360º = 1-fold, so have a C_1 axis. Examples are:

C_1



Bromo-chloro-fluoro-iodo-methane



C_1

chloro-iodo-amine

Two symmetry approaches or notations

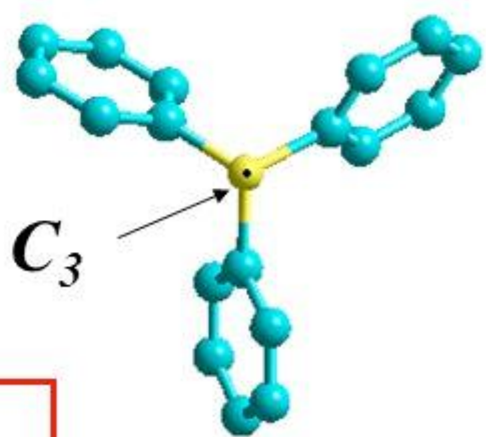
Schoenflies notation
(for molecules—interior lines, points, planes)

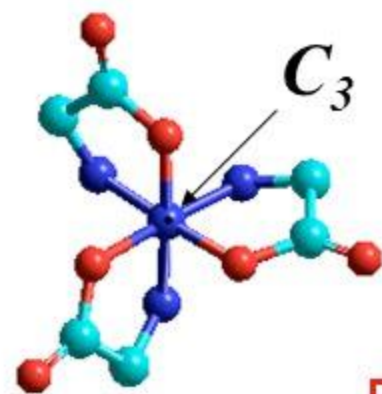
Herrman-Mauguin (crystallographic point groups
—translations, crystal classes)

The C_n point groups:

These have a C_n axis as their only symmetry element. They generally resemble propellers which have the front and back different. Important examples are (hydrogens omitted for clarity):

triphenyl phosphine viewed down C_3 axis



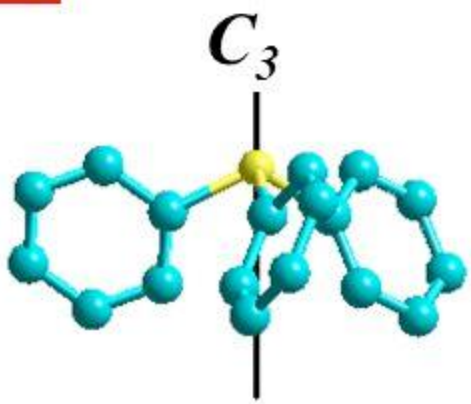


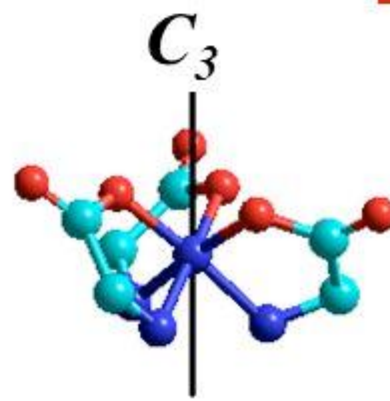
Cobalt(III) tris-glycinate viewed down C_3 axis

C_3

C_3

triphenyl phosphine viewed from the side





Cobalt(III) tris-glycinate viewed from the side

Notes

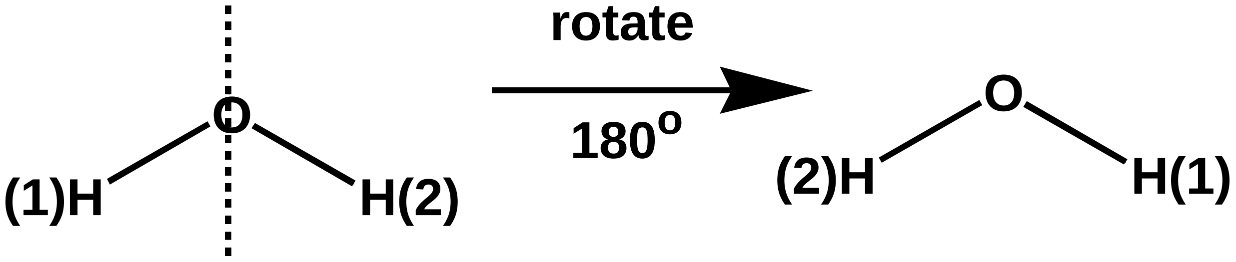
(i) symmetry operations more fundamental, but elements often easier to spot.

(ii) some symmetry elements give rise to more than one operation - especially rotation - as above.

ROTATIONS - AXES OF SYMMETRY

Some examples for different types of molecule: e.g.

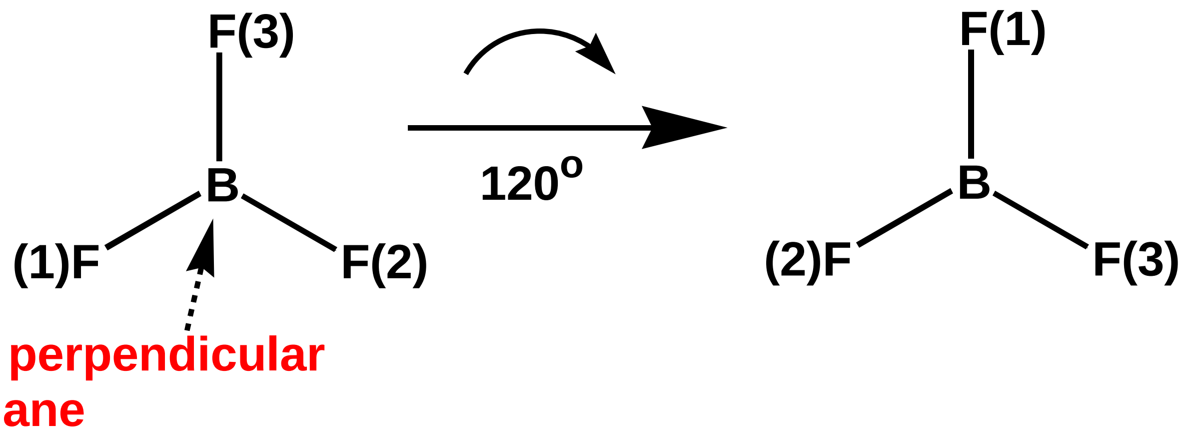
H_2O



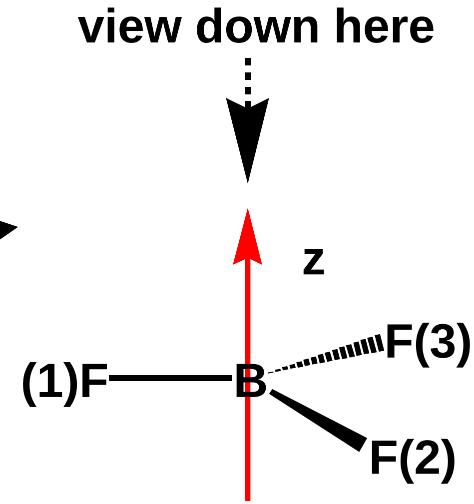
Line in molecular plane, bisecting HOH angle is a rotation axis, giving indistinguishable configuration on rotation by 180°.

BF_3

By VSEPR - trigonal, planar, all bonds equal, all angles 120°. Take as axis a line perpendicular to molecular plane, passing through B atom.



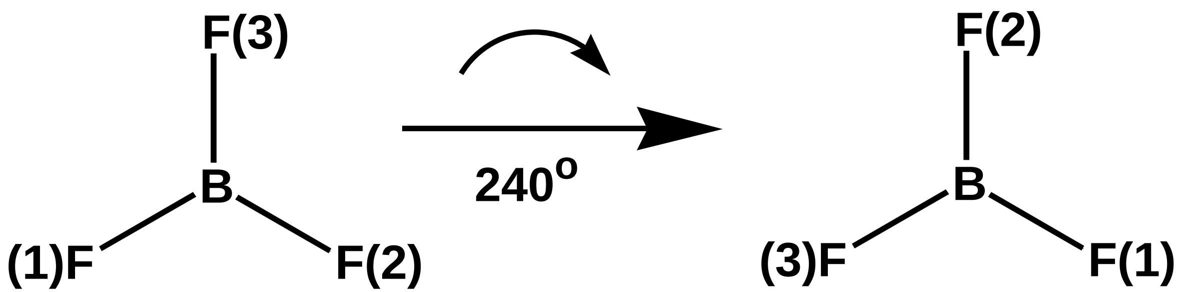
N.B. all rotations CLOCKWISE when viewed along -z direction.



Symbol for axes of symmetry

C_n where rotation about axis gives indistinguishable configuration every $(360/n)^o$ (i.e. an n-fold axis)

Thus H_2O has a C_2 (two-fold) axis, BF_3 a C_3 (three-fold) axis. One axis can give rise to >1 rotation, e.g. for BF_3, what if we rotate by 240^o?



Must differentiate between two operations.

Rotation by 120^o described as C_3^1,

rotation by 240^o as C_3^2.

In general C_n axis (minimum angle of rotation $(360/n)^o$) gives operations C_n^m, where both m and n are integers.

When m = n we have a special case, which introduces a new type of symmetry operation.....

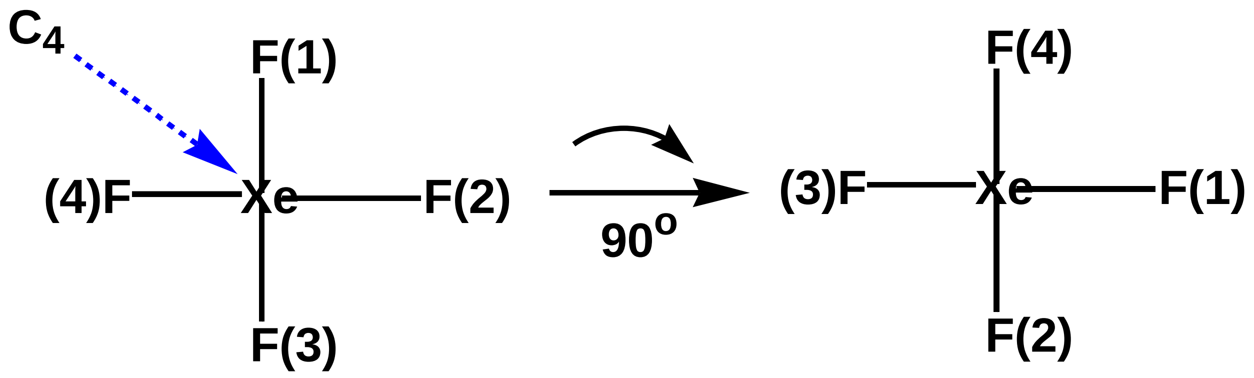
IDENTITY OPERATION

For H_2O, C_2^2 and for BF_3 C_3^3 both bring the molecule to an IDENTICAL arrangement to initial one.

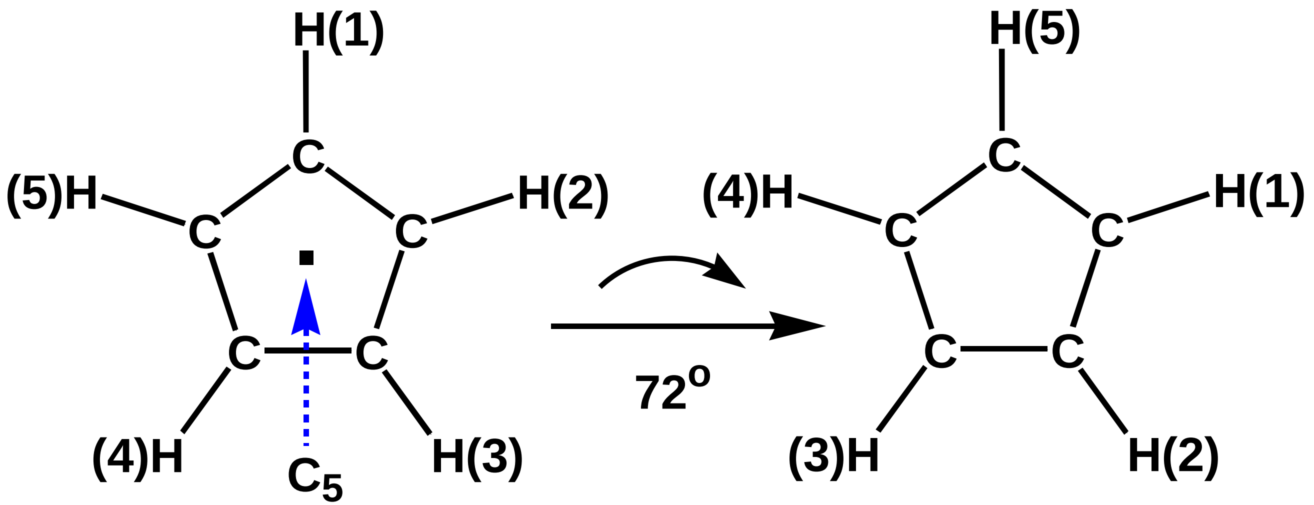
Rotation by 360^o is exactly equivalent to rotation by 0^o, i.e. the operation of doing NOTHING to the molecule.

MORE ROTATION AXES

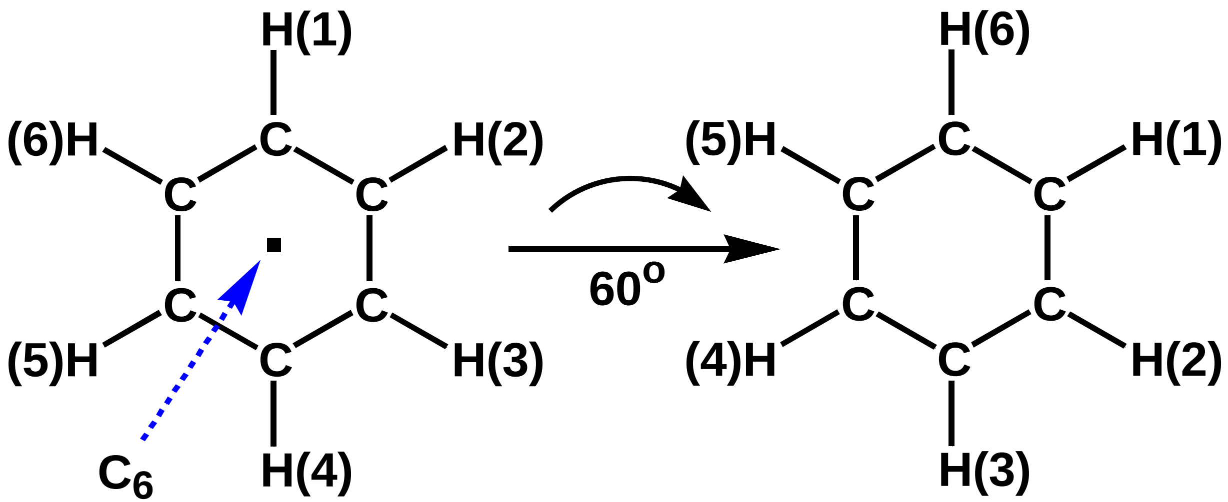
xenon tetrafluoride, XeF_4



cyclopentadienide ion, $C_5H_5^-$

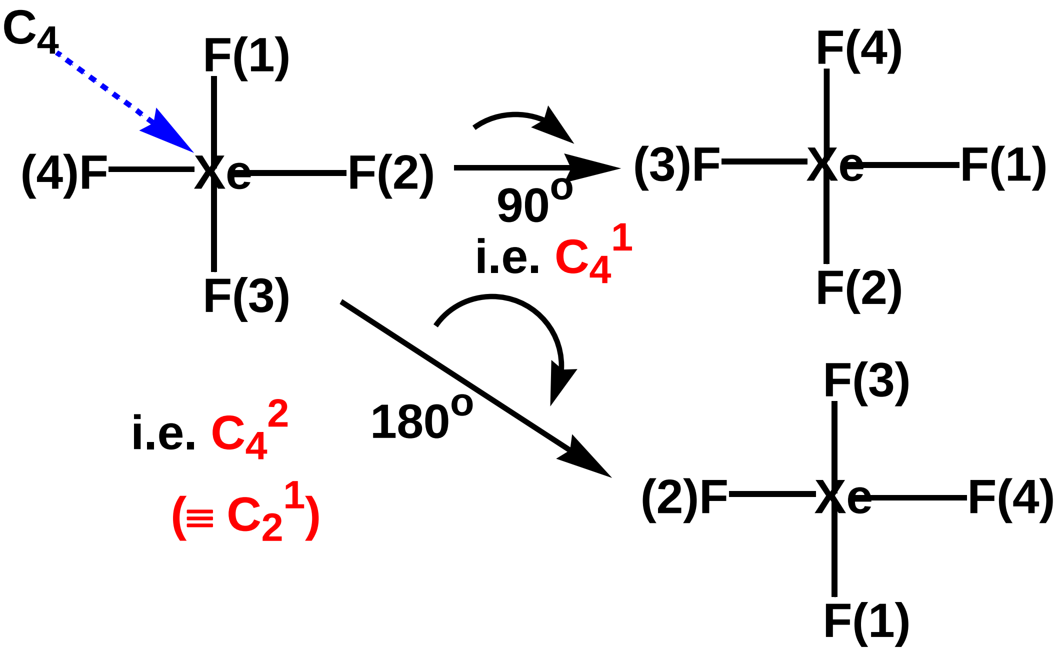


benzene, C_6H_6



Examples also known of C_7 and C_8 axes.

If a C_{2n} axis (i.e. even order) present, then C_n must also be present:



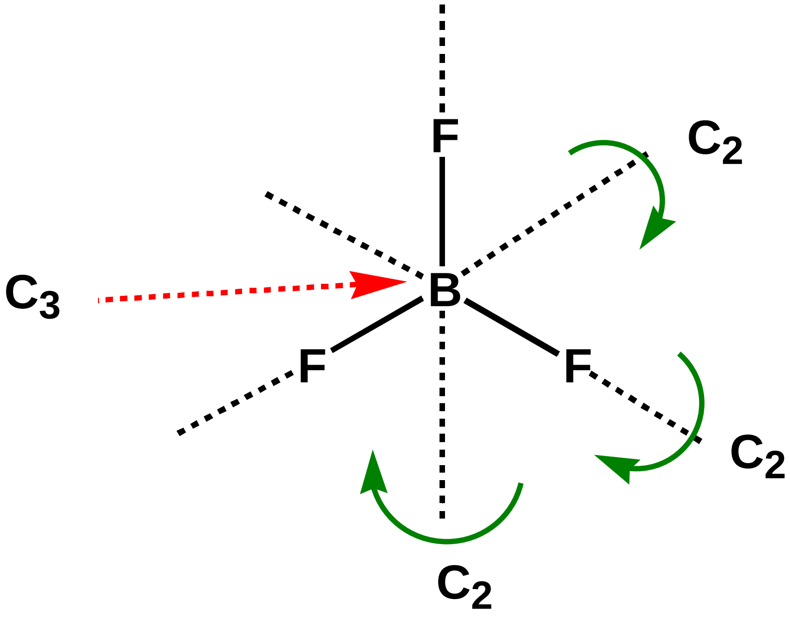
Therefore there must be a C_2 axis coincident with C_4, and the operations generated by C_4 can be written:

C_4^1, C_4^2 (C_2^1), C_4^3, C_4^4 (E)

Similarly, a C_6 axis is accompanied by C_3 and C_2, and the operations generated by C_6 are:

C_6^1, C_6^2 (C_3^1), C_6^3 (C_2^1), C_6^4 (C_3^2), C_6^5, C_6^6 (E)

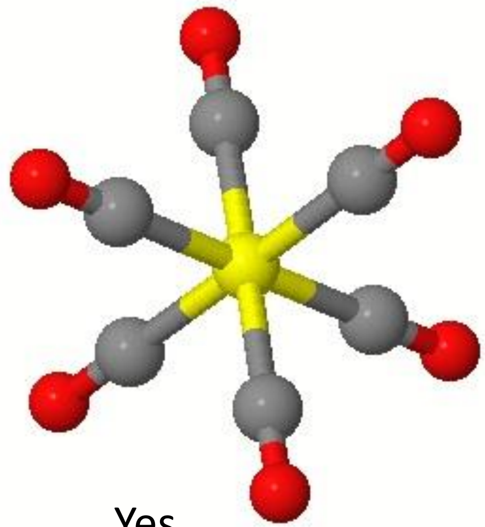
Molecules can possess several distinct axes, e.g. BF_3:



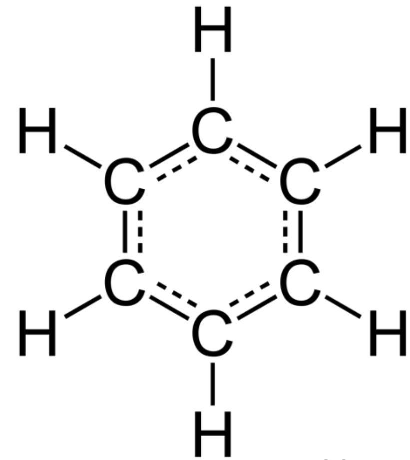
Three C_2 axes, one along each B-F bond, perpendicular to C_3

Mirror Planes within BF_3. Of two types,

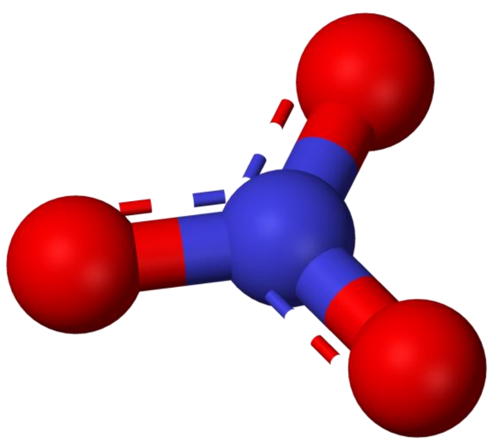
Center of Inversion in Molecules: x,y,z -> -x, -y, -z



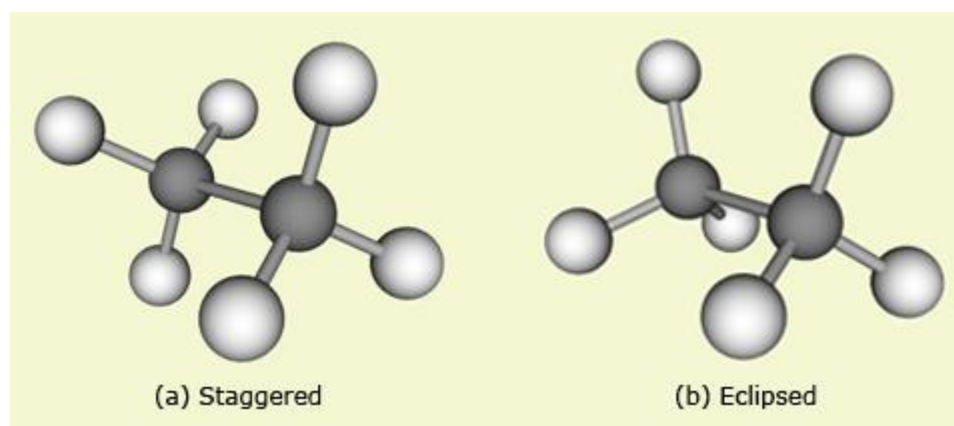
Yes



Yes



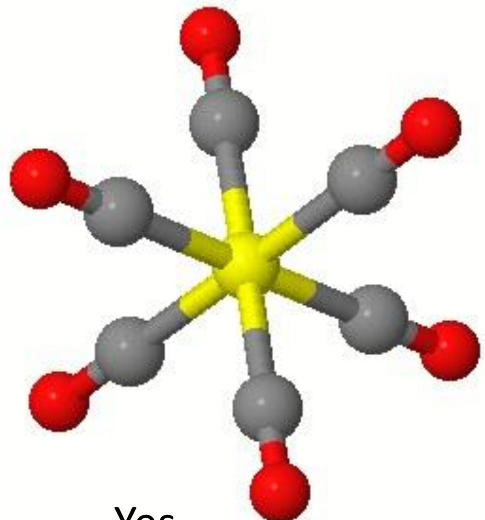
No



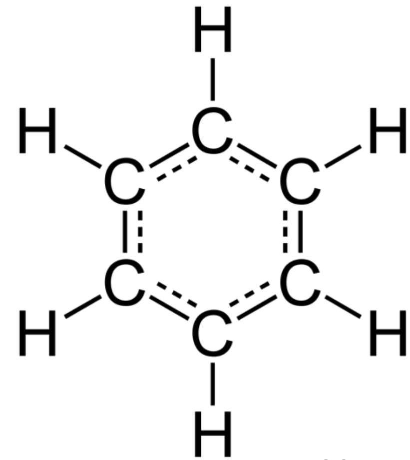
Yes

No

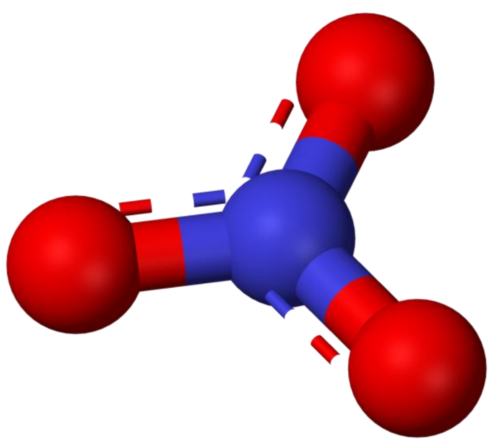
(Proper) Rotation in Chemistry



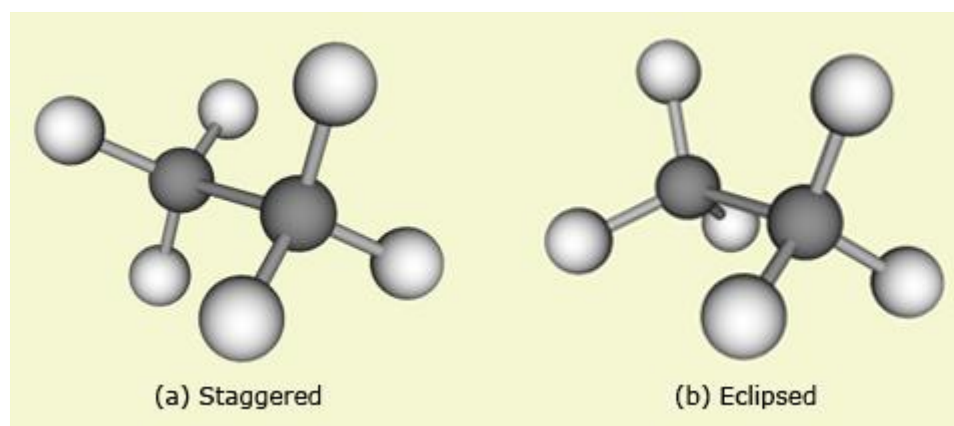
Yes



Yes



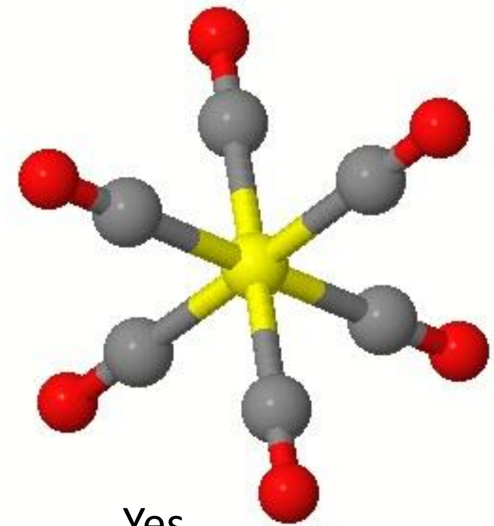
Yes



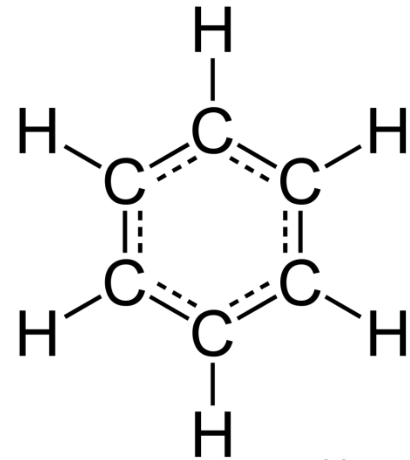
Yes

Yes

Reflection in a Plane in Chemistry



Yes



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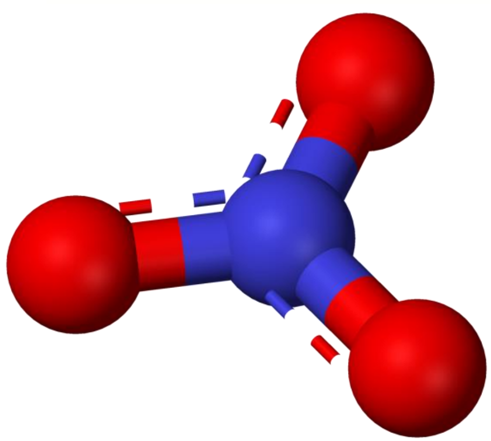

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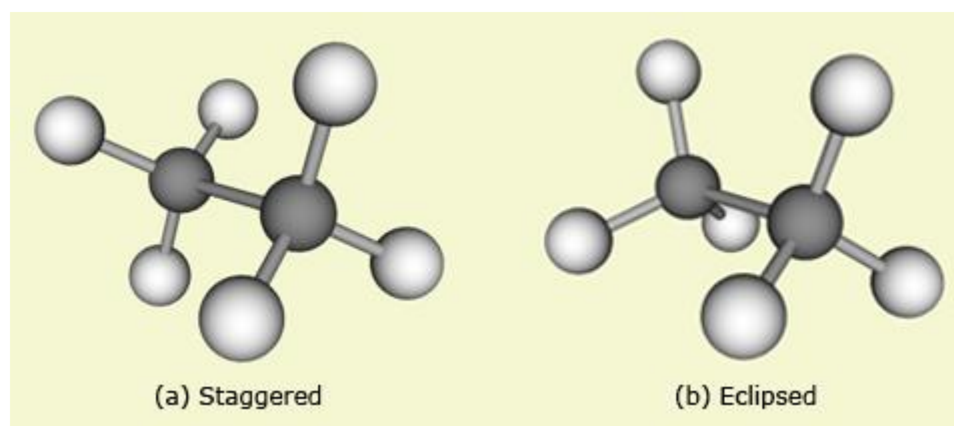
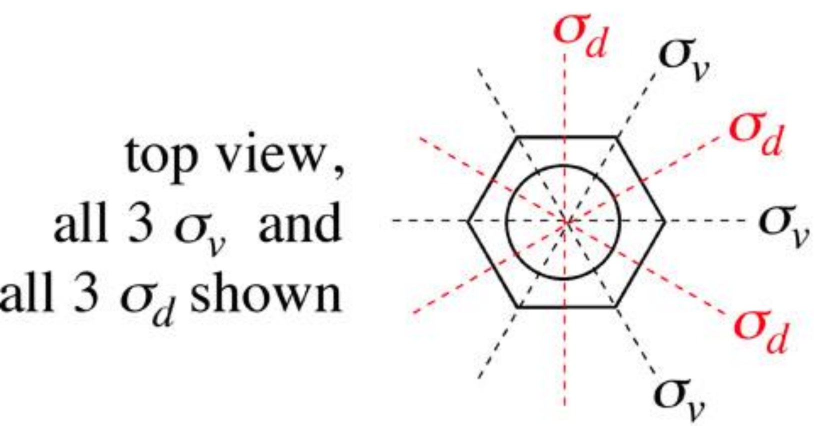
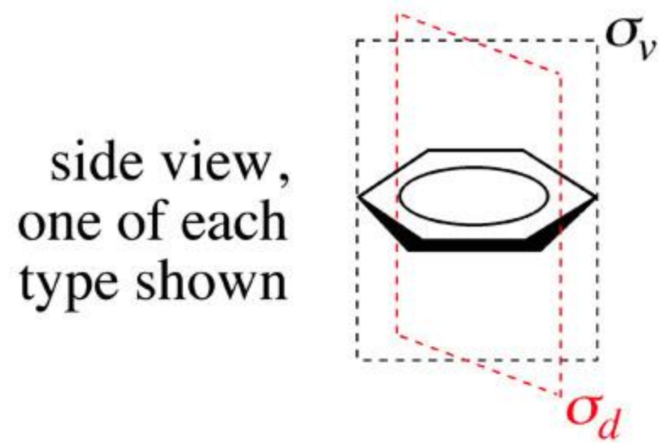


Yes Yes

Vertical and Dihedral (σ_v that bisects C_2 axes) Mirror Planes

Benzene, C_6H_6 : 3 σ_d mirror planes and 3 σ_v mirror planes



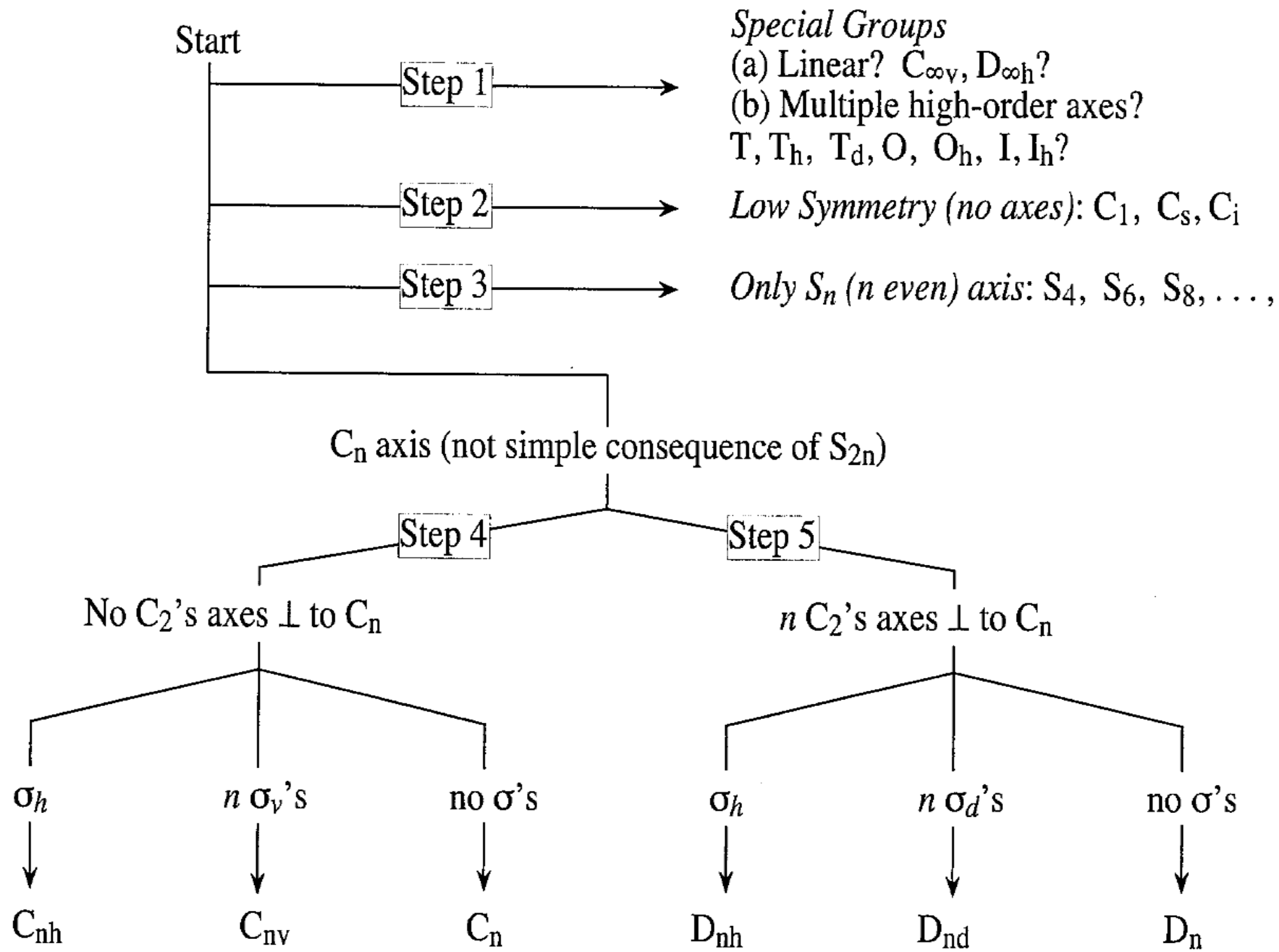


In a molecule that has **both** σ_v and σ_d mirror planes, the σ_v planes bisect as many atoms as possible and the σ_d planes bisect as many bonds as possible.

Symmetry Point Group Assignments

An object may be classified with respect to its symmetry elements or lack thereof. This is done by assigning a symmetry point group, reflecting the combination of symmetry elements present in the structure. For example, bromochlorofluoromethane has no symmetry element other than C_1 and is assigned to that point group. All C_1 group objects are chiral. Other low symmetry point groups are C_s (only a single plane of symmetry) and C_i (only a point of symmetry). Objects in either of these point groups are achiral.
Some objects are highly symmetric and incorporate many symmetry elements. Methane is an example of a high symmetry molecule, having 4 C_3 axes, 3 C_2 axes and 6 σ (planes); it belongs to the tetrahedral point group T_d. When combinations of rotational axes and planes are present, their relationship is designated by a v (vertical), h (horizontal) or d (diagonal). Thus, a plane containing the principle rotation axis is σ_v, a plane perpendicular to the principle rotation axis is σ_h, and a plane parallel to the principle rotation axis but bisecting the angle between two C_2 axes is σ_d. By this notation, the six planes of the methane tetrahedron are all σ_d.

A Simple Approach to Point Group Assignments



The process used to assign a molecule to a point group is straightforward with a few exceptions. Use this schematic to guide you.

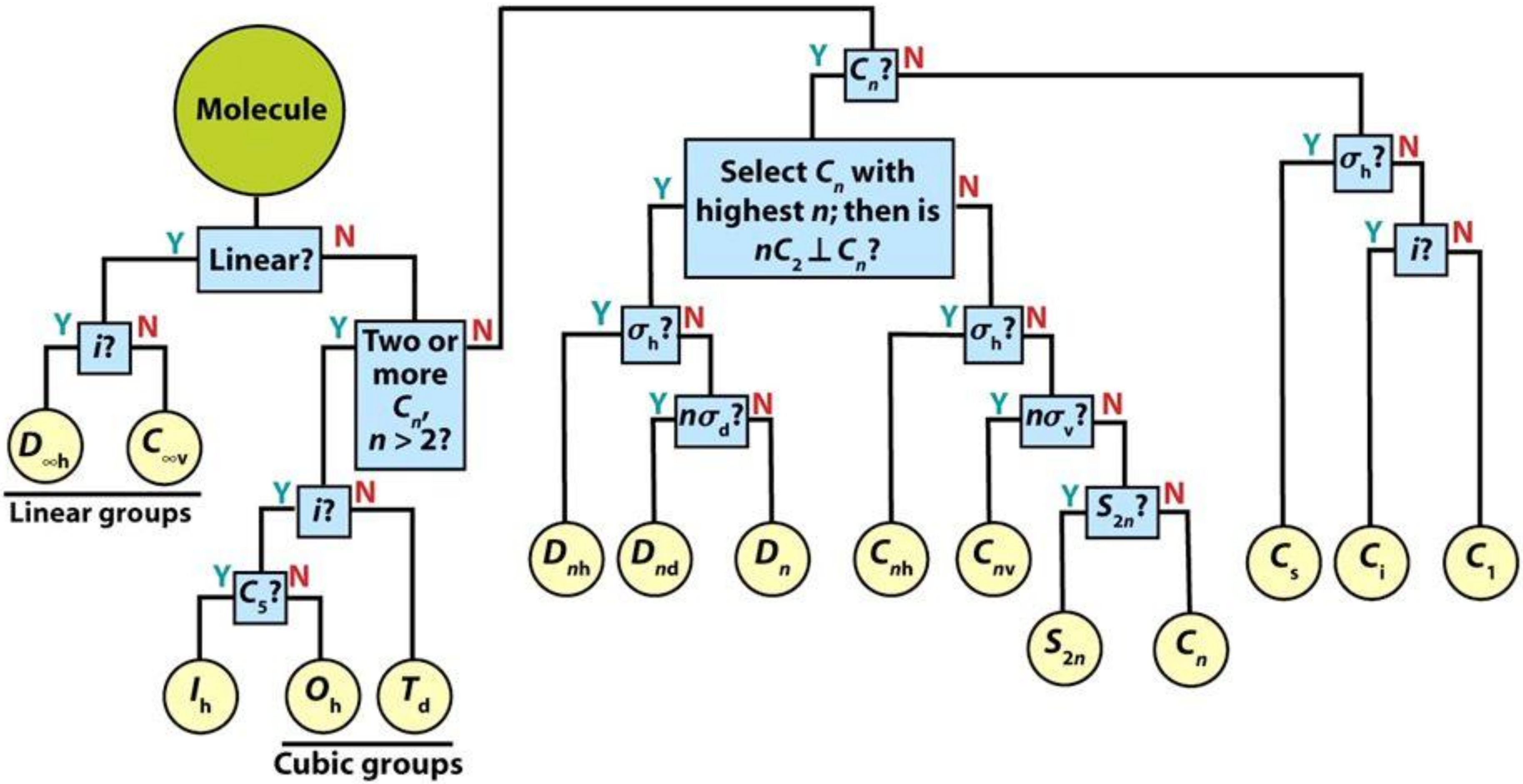


Figure 7-9

Shriver & Atkins Inorganic Chemistry, Fourth Edition

The D_{nh} point groups: