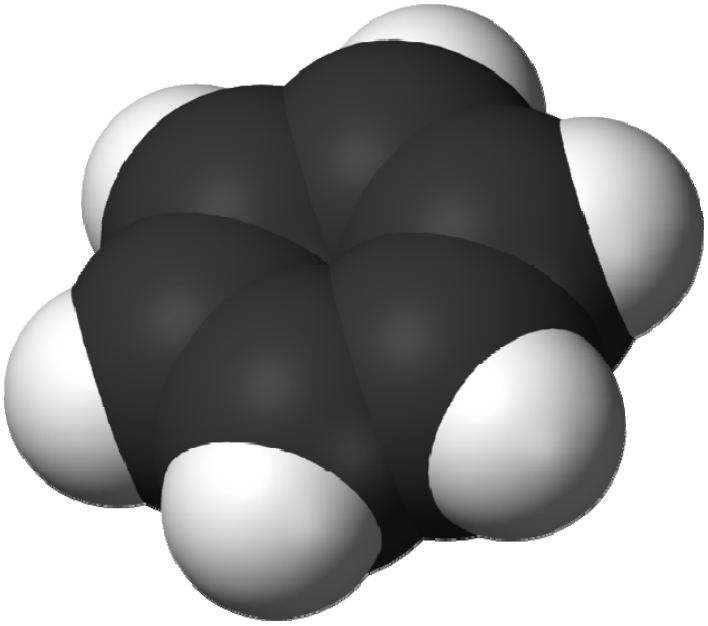
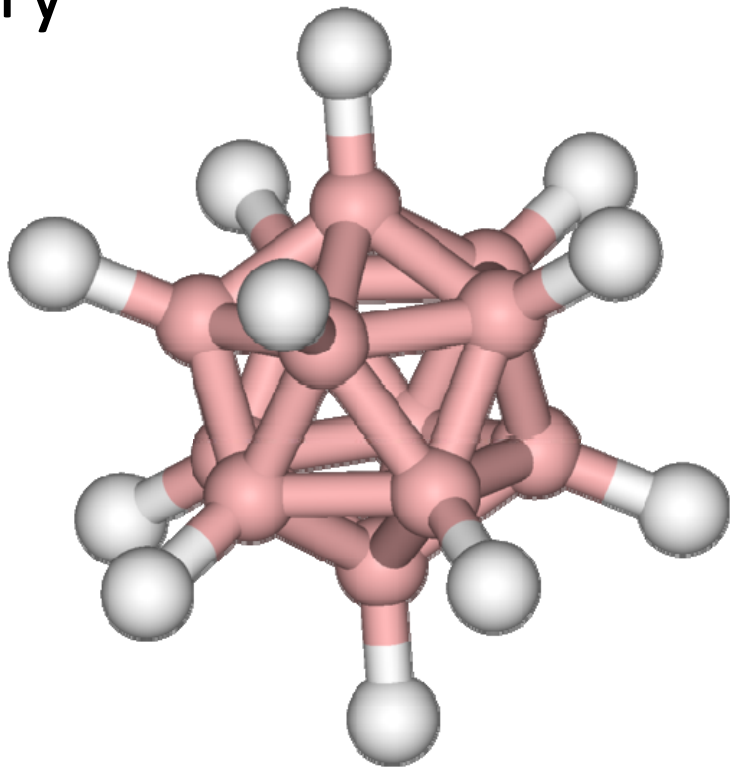
Lecture 11 February 8, 2019

- ***Using the shapes of Molecules to define:***
- ***Symmetry Operations***
- ***Symmetry Elements***
- ***Point Groups and Assignments***

Symmetry

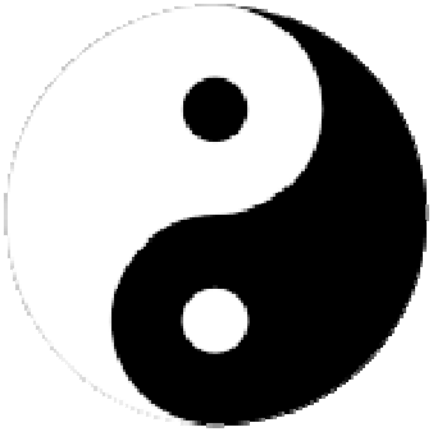




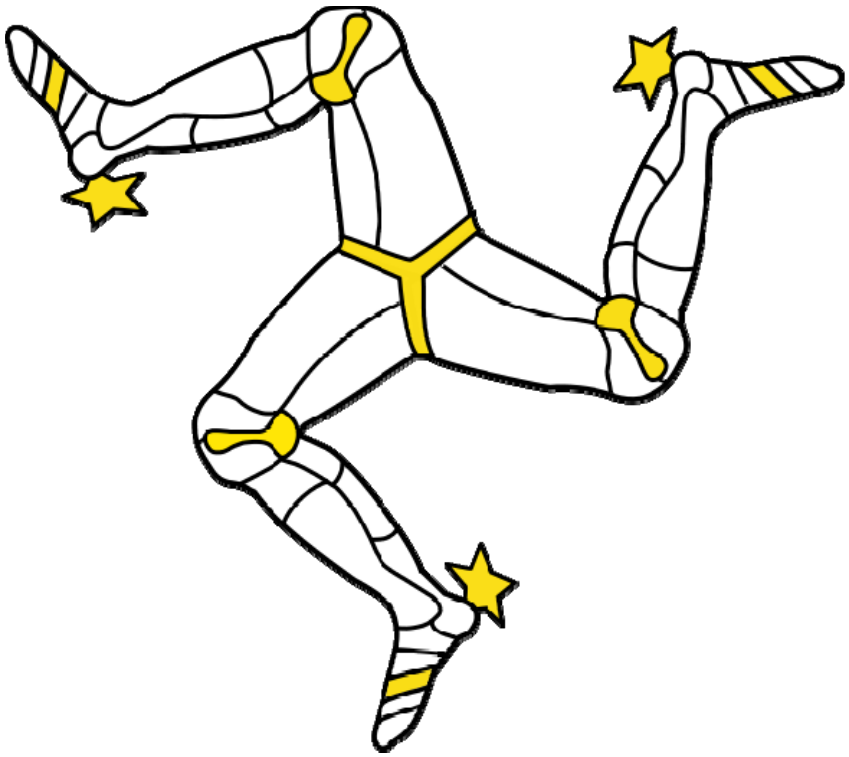
Intuitively, we know symmetry when we see it.

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

Symmetry: mirror planes

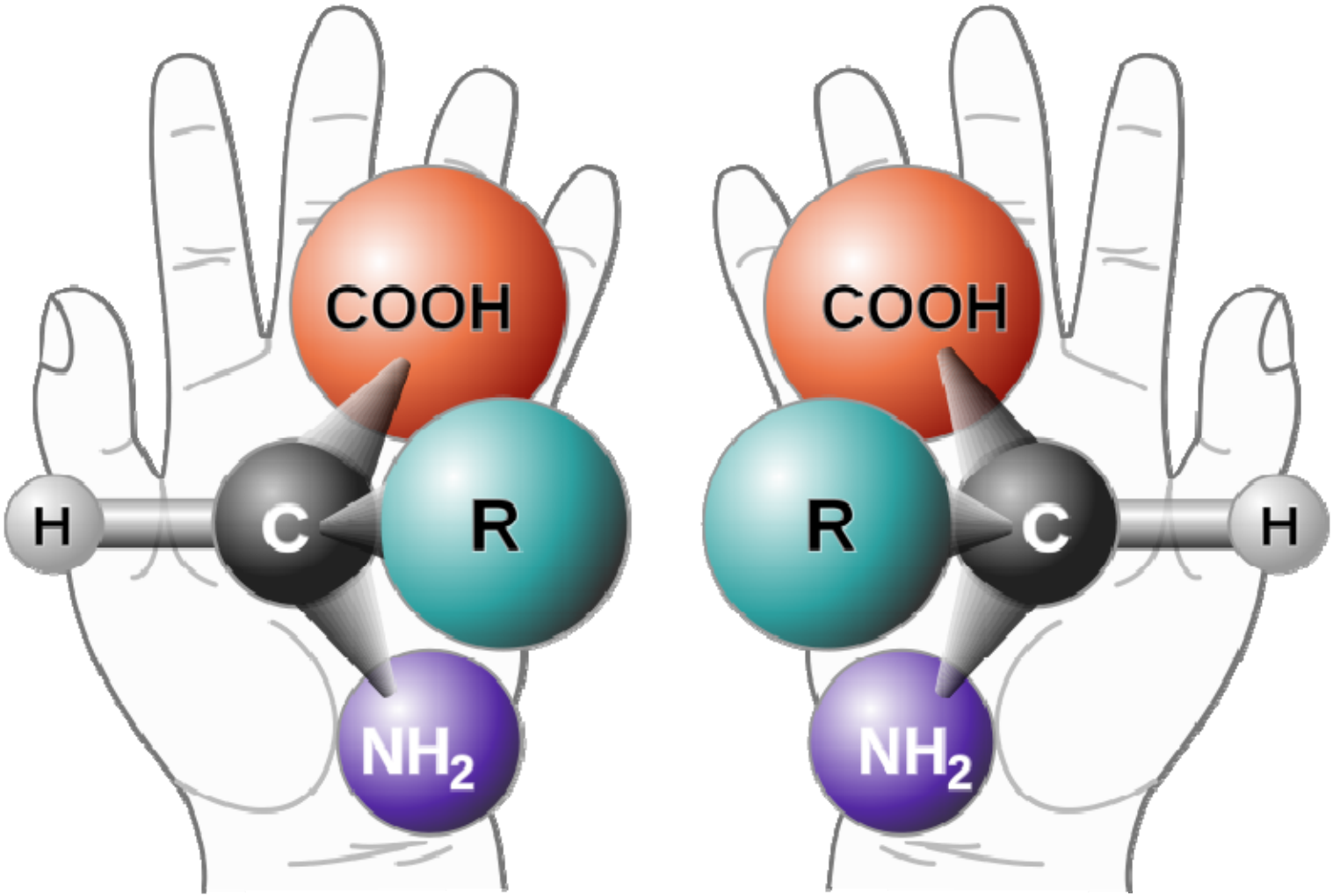


Symmetry



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 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

Let’s look for these in molecules

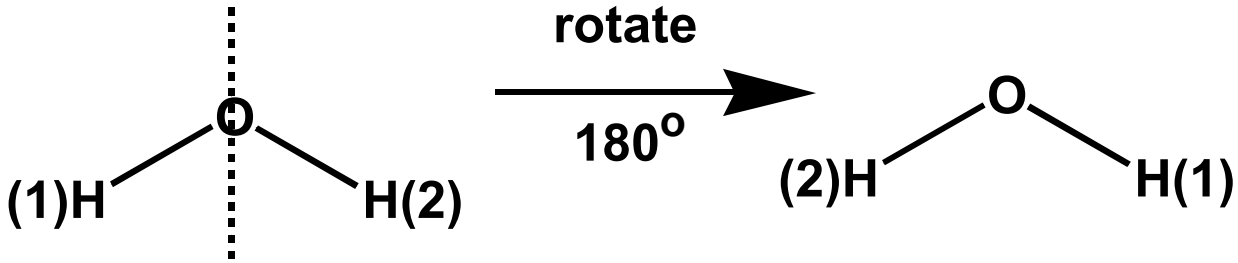
Notes
(i) symmetry operations more fundamental, but elements often easier to spot.

(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.

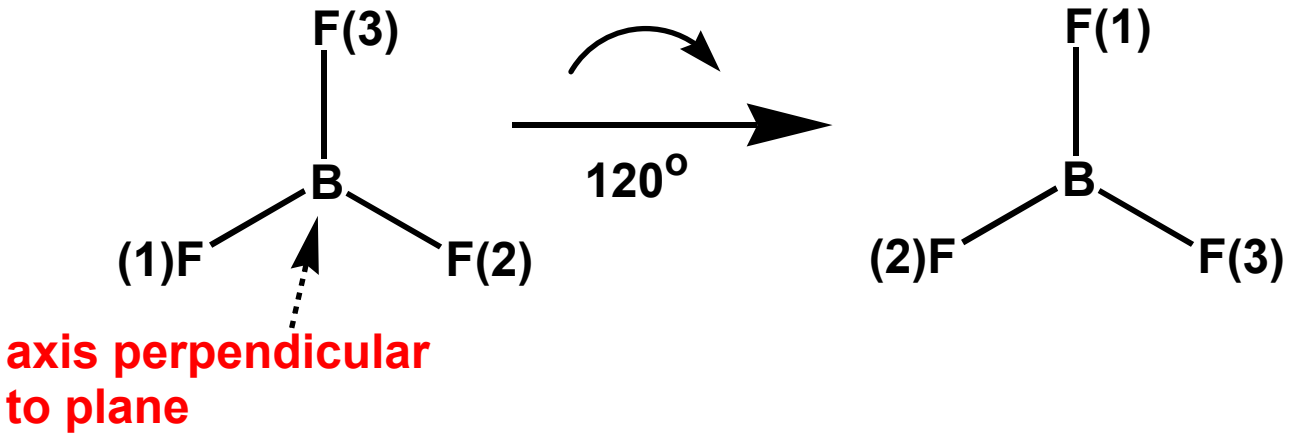
H_2O



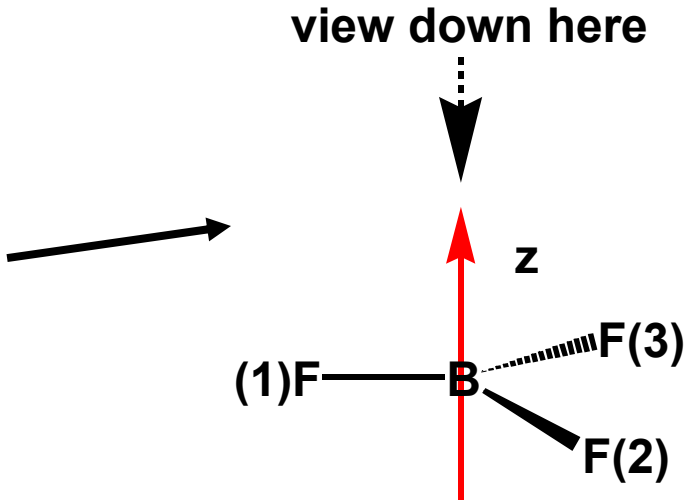
Line in molecular plane, bisecting HOH angle is a rotation axis, giving indistinguishable configuration on rotation by 180°.

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.

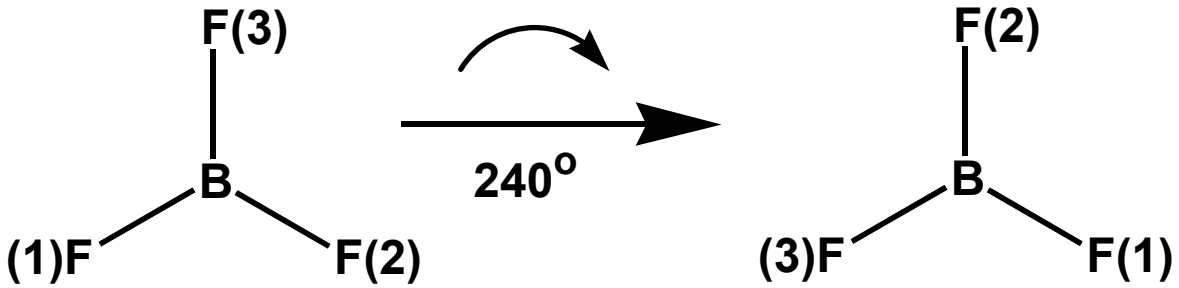


Symbol for axes of symmetry

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.....

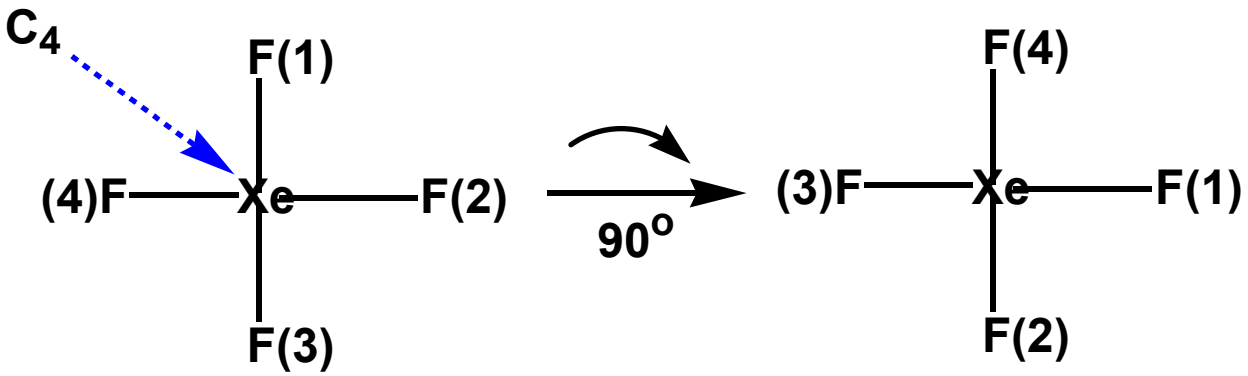
IDENTITY OPERATION

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

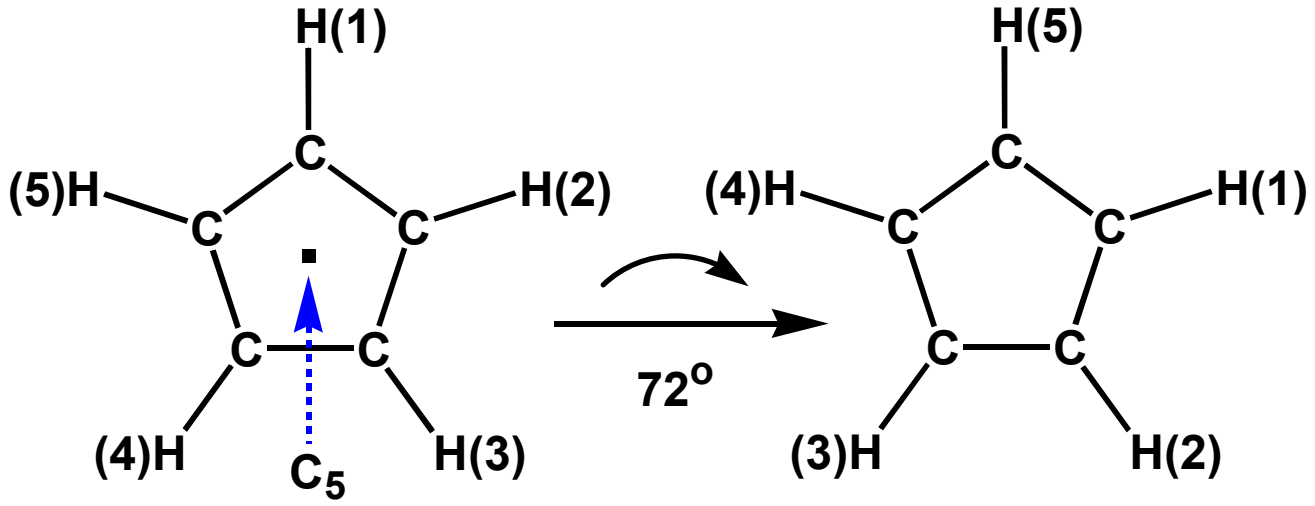
Rotation by 360^o is exactly equivalent to rotation by 0^o, i.e. the operation of doing NOTHING to the molecule.

MORE ROTATION AXES

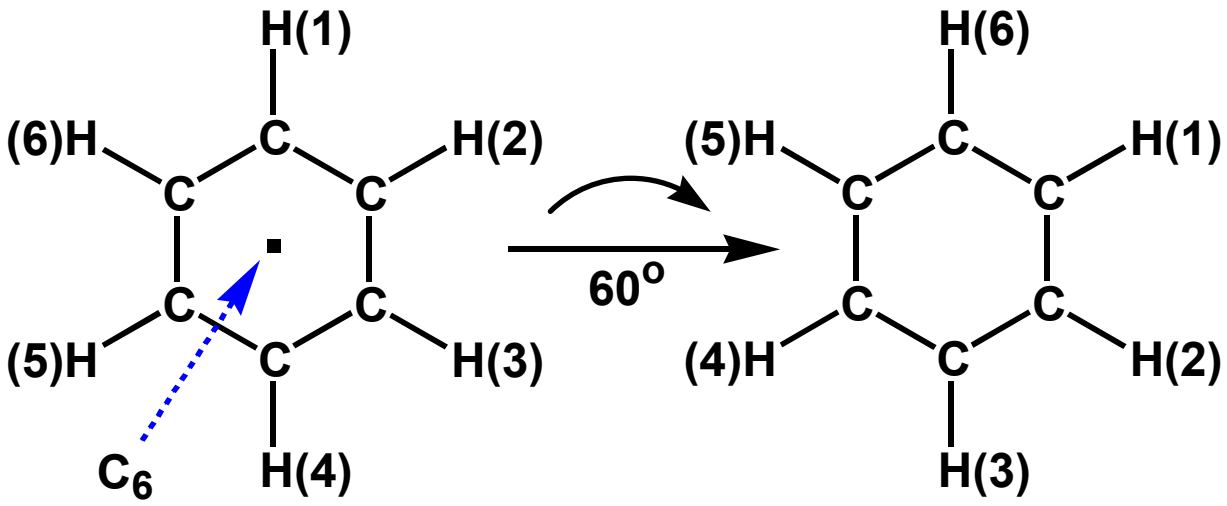
xenon tetrafluoride, XeF_4



cyclopentadienide ion, $C_5H_5^-$

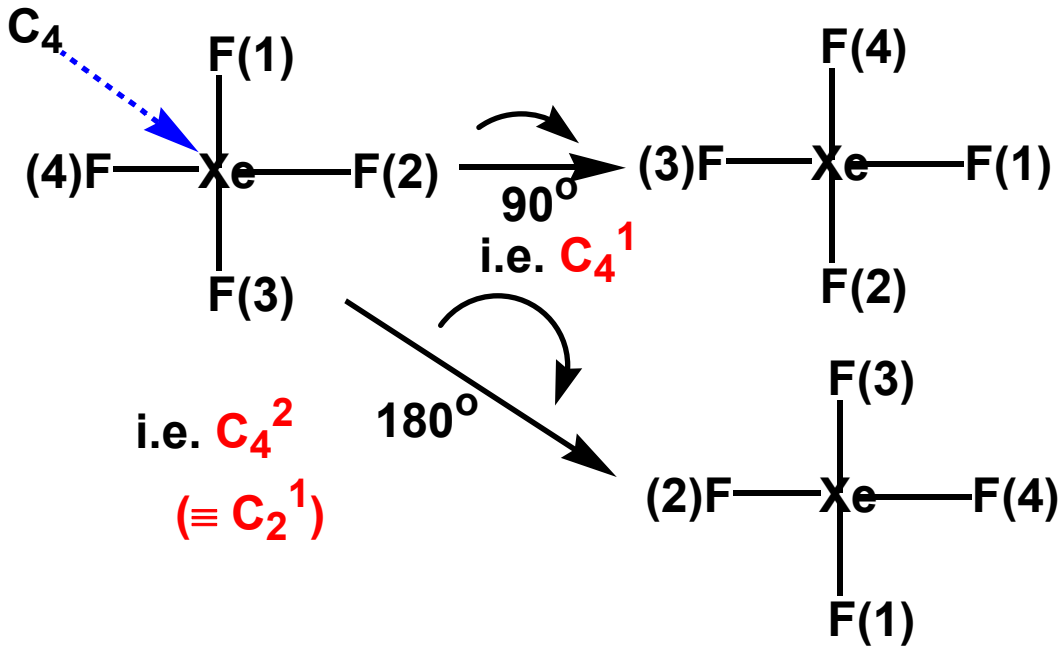


benzene, C_6H_6



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:



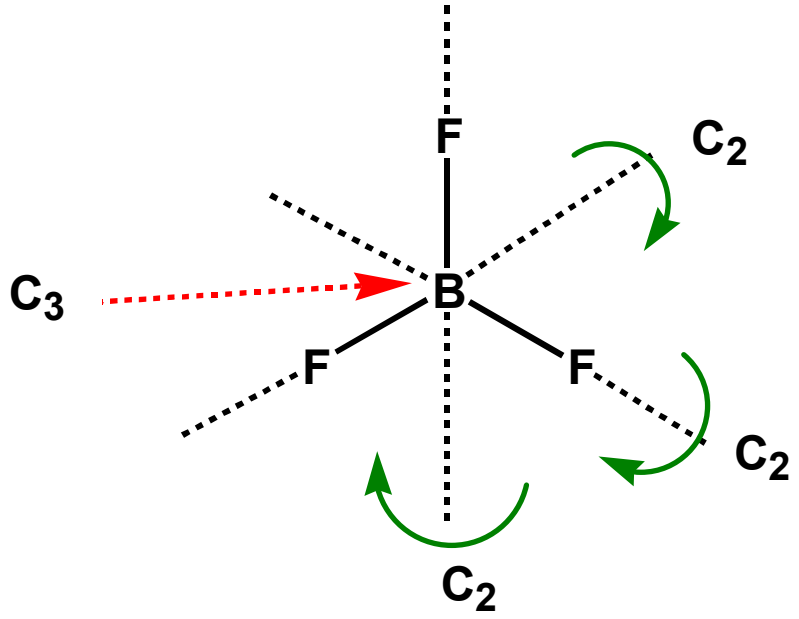
Therefore there must be a C_2 axis coincident with C_4, and the operations generated by C_4 can be written:

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

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

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

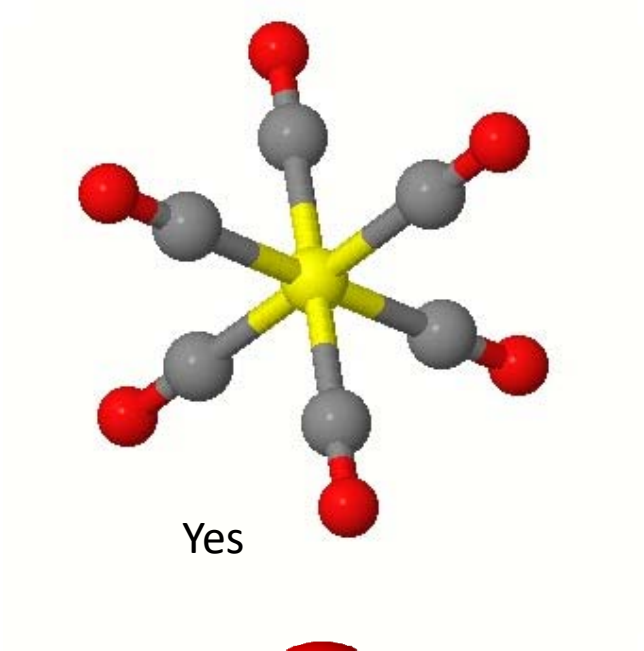
Molecules can possess several distinct axes, e.g. BF_3:



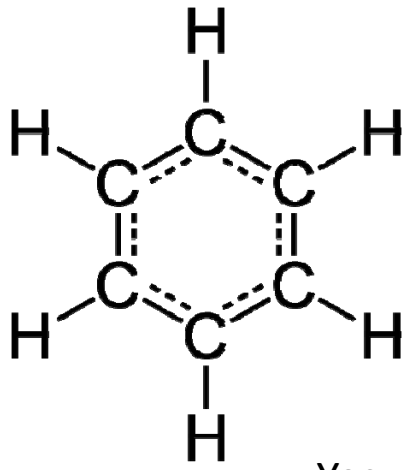
Three C_2 axes, one along each B-F bond, perpendicular to C_3

Mirror Planes within BF_3. Of two types,

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



Yes



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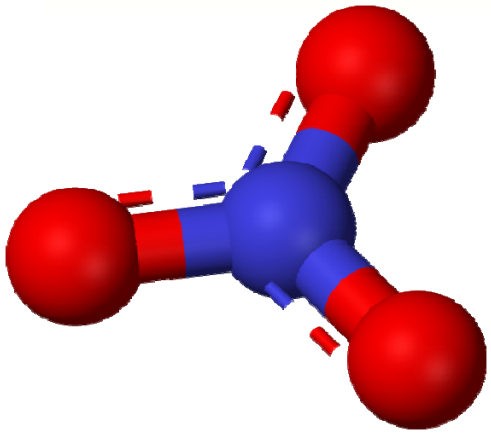

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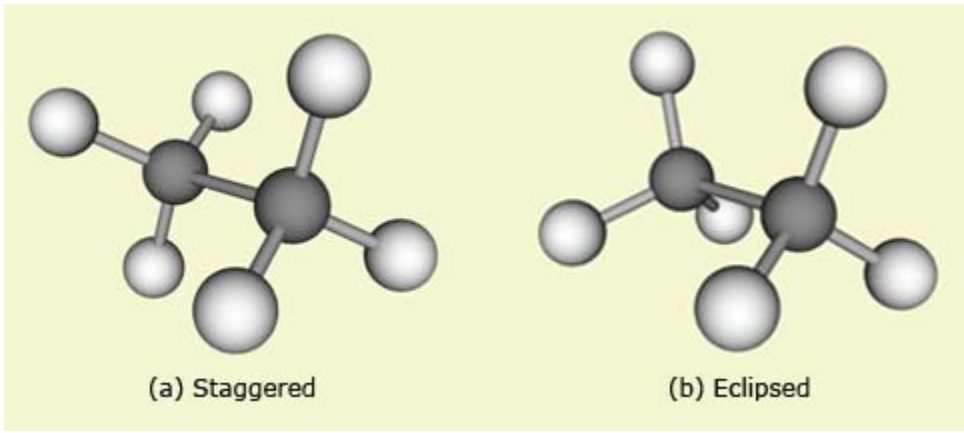
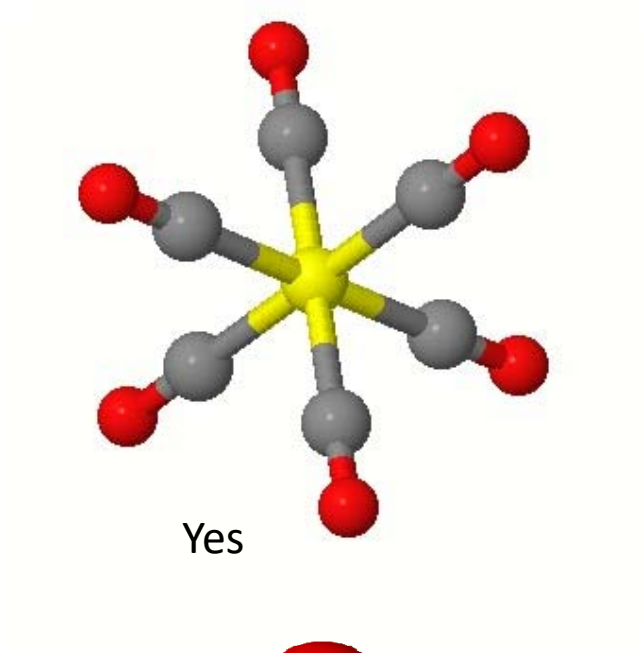


Yes

No

(Proper) Rotation in Chemistry



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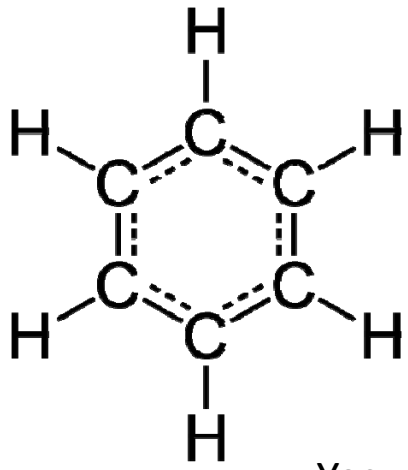

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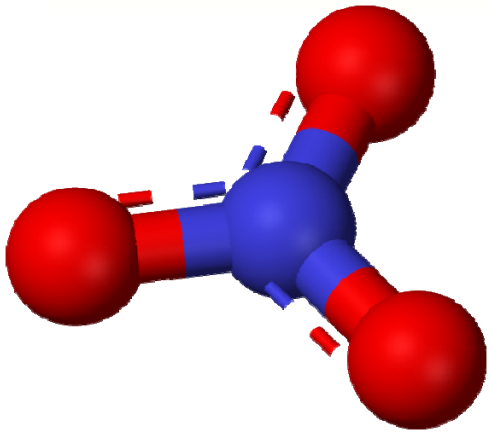

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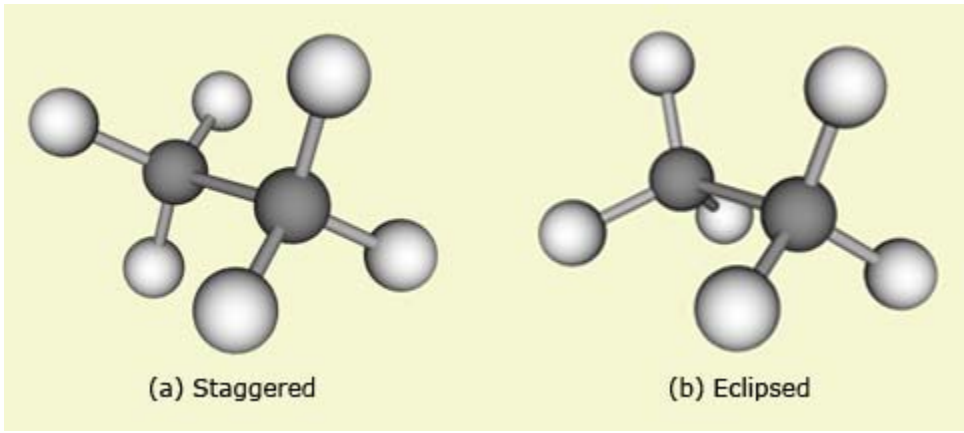
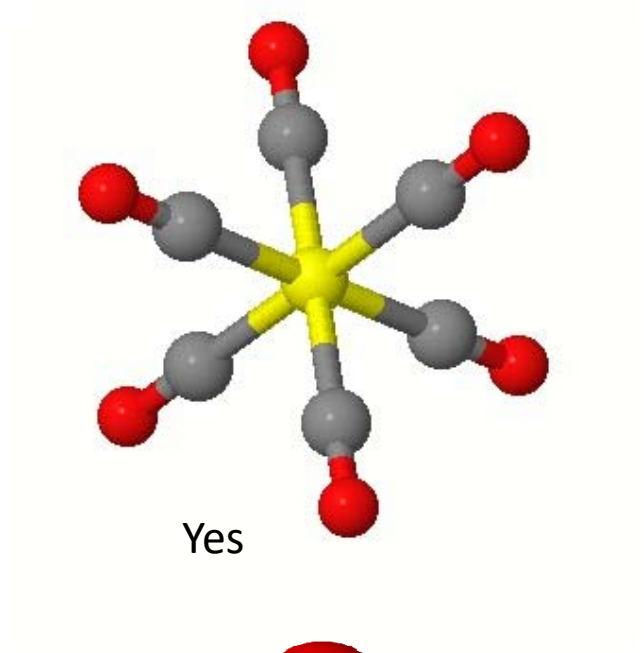


Yes

Yes

Reflection in a Plane in Chemistry



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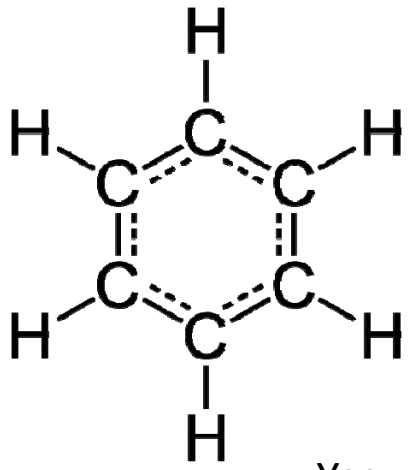

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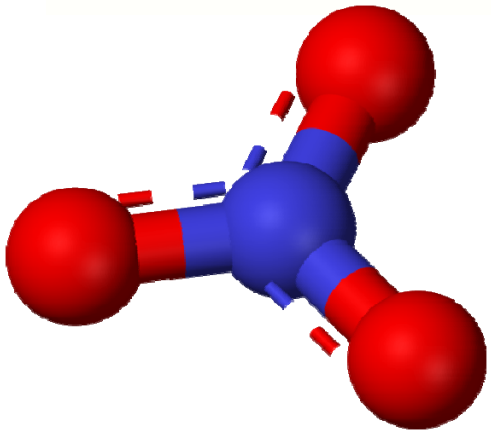

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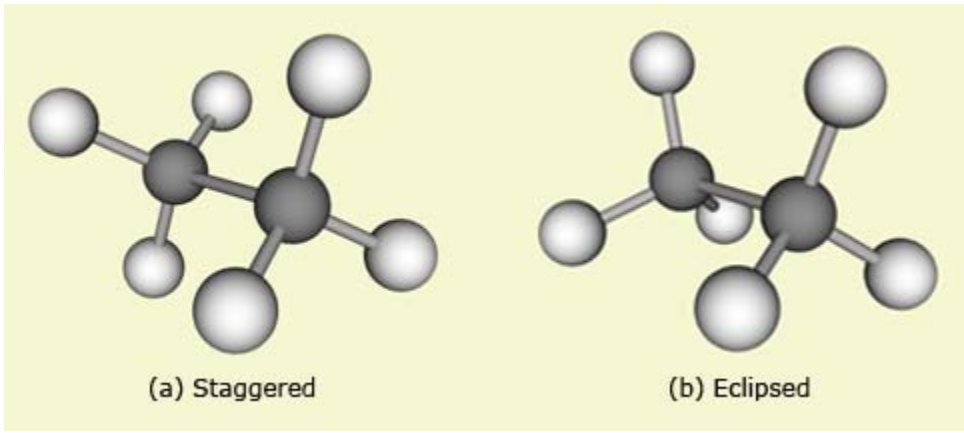

Yes

Yes

A Simple Approach to Point Group Assignments