STEREOCHEMISTRY
Part-III

(Symmetry elements & Symmetry operations)

B.Sc Hons (Chemistry)
Sem-I, Paper-CC I

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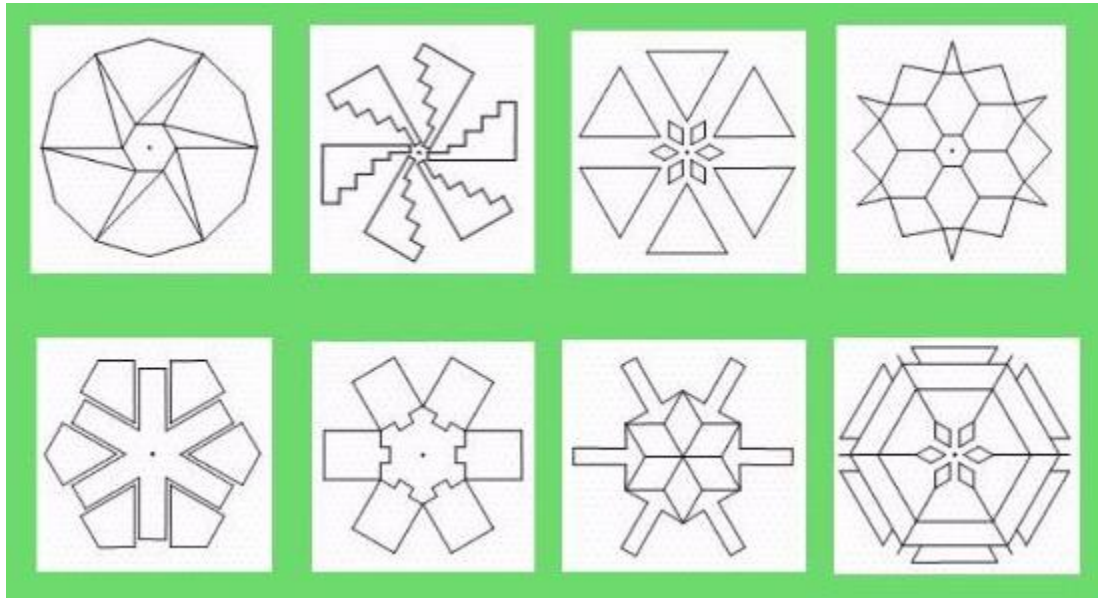
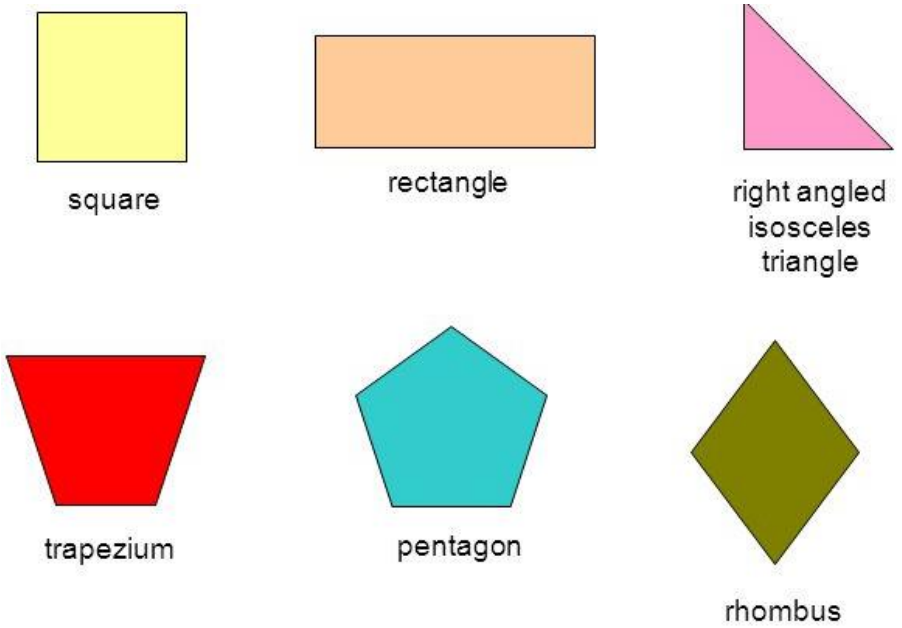
Symmetry in Nature & Human Culture

Symmetry: If a figure can be folded in half and both sides match, it has a line of symmetry.

This flower has 5 lines of symmetry.

Symmetry in Geometric structure

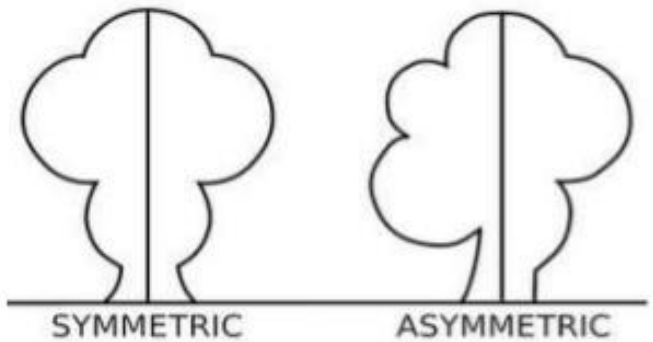




Symmetry in Monuments

What is symmetry ?

- Symmetry is when a shape looks identical to its original shape after being flipped or turned.



- Nature loves symmetry
- Most objects found in nature have symmetry
- Symmetry is associated with beauty

e.g. Flowers, diamonds, butterflies, snail shells,leaves, etc are all beautiful, highly symmetrical because of harmony and attractiveness of their forms and proportions.

THE TERM SYMMETRY IS ASSOCIATED WITH-

1. Beauty
2. Regularity
3. Periodicity
4. Harmonicity and
5. Systemization

SYMMETRY ELEMENTS AND OPERATIONS

Symmetry elements are geometrical entities such as a plane, an axis (of rotation), centers (of inversion), etc., through which a symmetry operation can be performed.

A molecule has a given symmetry element if the operation leaves the molecule looks as if nothing has changed (even though atoms and bonds may have been moved). A symmetry operation produces a superimposable configuration. (equivalent or identical configuration.)

IDENTITY, E

All molecules have Identity. This operation leaves the entire molecule unchanged. A highly asymmetric molecule such as a tetrahedral carbon with 4 different groups attached has only identity, and no other symmetry elements. It also signifies operation of doing nothing. It is there for mathematical reasons., such as in Group theory.

Note- some chemists do not consider this as an operation.

Symmetry Elements and Operations

A. Definitions

1. **Symmetry Element** = geometrical entity such as a line, a plane, or a point, with respect to which one or more symmetry operations can be carried out

2. **Symmetry Operation** = a movement of a body such that the appearance after the operation is indistinguishable from the original appearance (if you can tell the difference, it wasn't a symmetry operation)

B. The Symmetry Operations

1. E (Identity Operation) = no change in the object
   a. Needed for mathematical completeness
   b. Every molecule has at least this symmetry operation

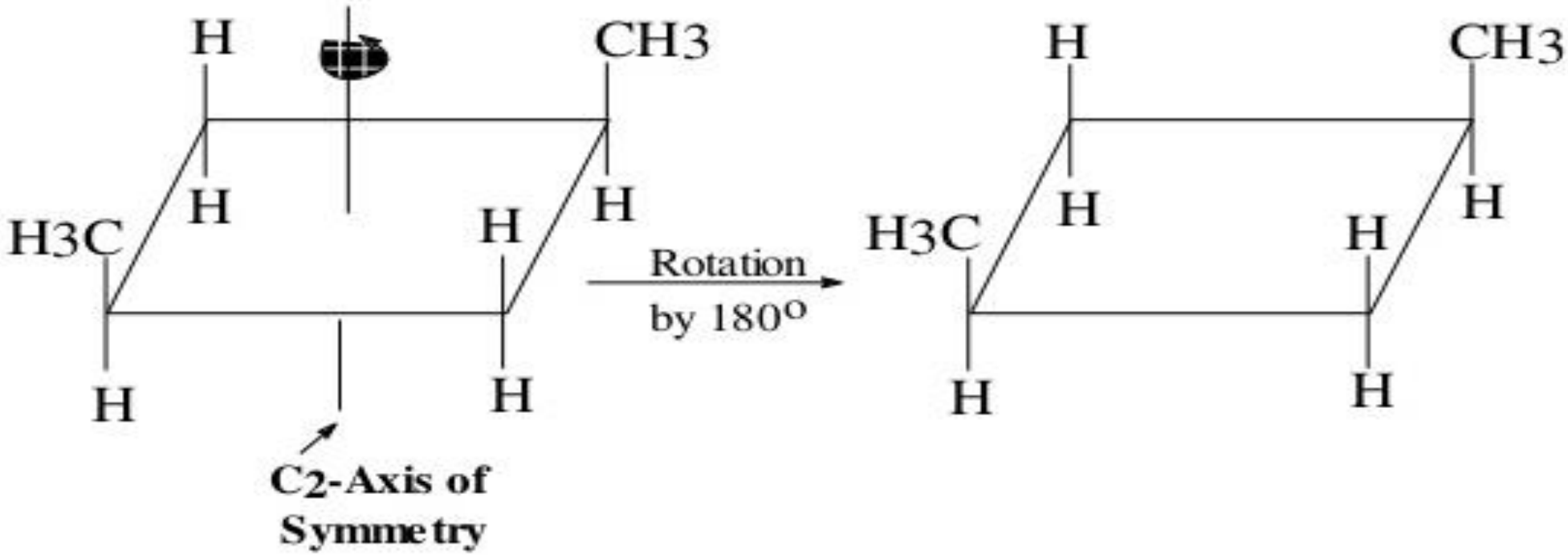
ELEMENTS OF SYMMETRY

Enatiomerism depends on whether a molecule in not superimposable on its mirror image. If it is superimposable, the molecule is optically inactive otherwise is optically active. The most convenient method of inspecting superimposability is to determine whether the molecule has any of the following four elements of symmetry:

Simple axis of symmetry (Cn)
Plane of symmetry ()
Alternating axis of symmetry(Sn)
Centre of symmetry (i)

Simple axis of symmetry (Cn)

- *An imaginary line passing through the molecule in such a way that when the molecule is rotated about it by an angle of 360°/n, an arrangement indistinguishable from the original is obtained*. **Such an axis is called n-fold axis of symmetry. For example, *cis*-1,3-dimethylcyclobutane has a two fold axis of symmetry (C_2) i.e. rotation by 180° gives indistinguishable appearance.**



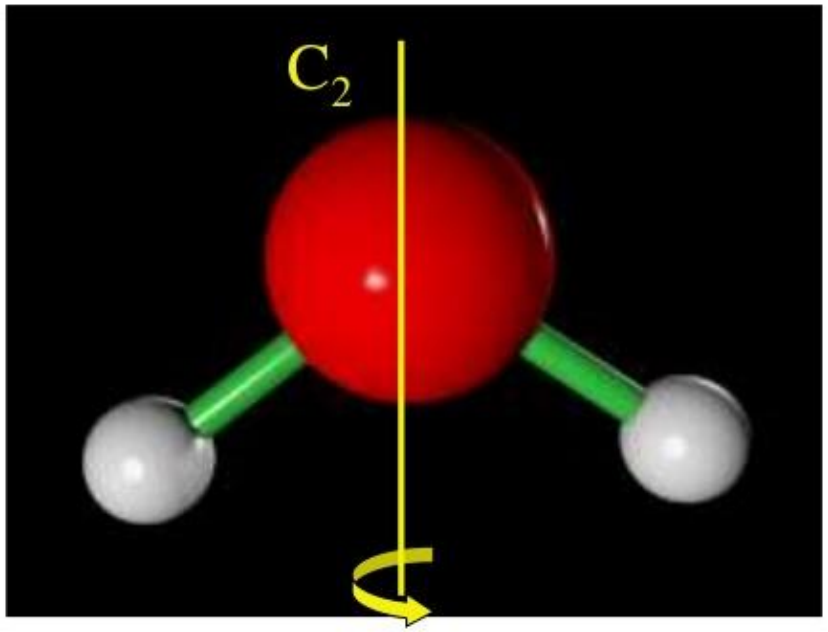
Principal and Subsidiary Axes :

- In molecules with more than one axis of symmetry, the axis with the highest fold symmetry (highest ***n*** in C_n) is called the **Principal Axis.** The other axes are called **Subsidiary Axes.**

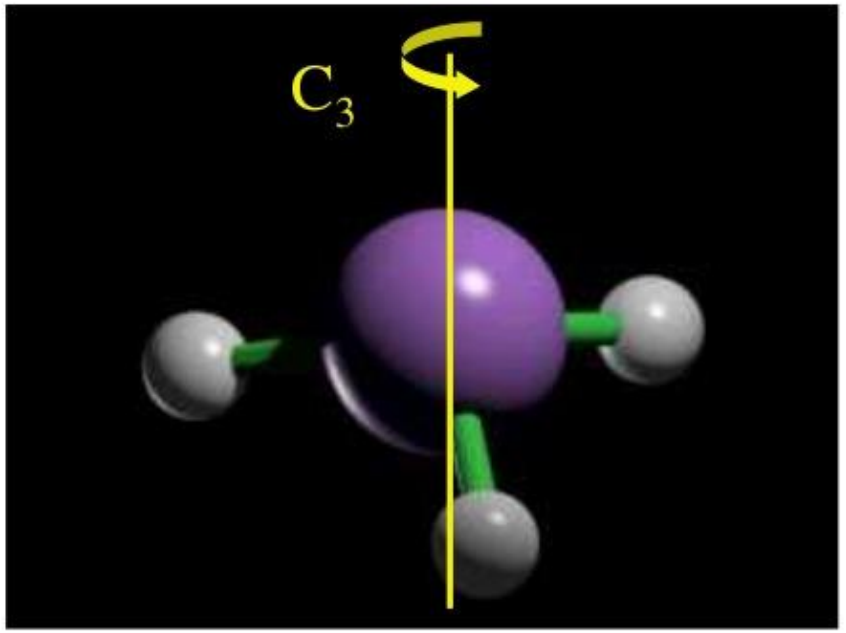
- In case there are more than one axes of same order, the axis passing through maximum number of atoms is the Principal Axis.

- The axis of symmetry can be C_∞ .

Operation 2: C_n, Proper Rotation:
Rotation about an axis by an angle of $2\pi/n = 360/n$

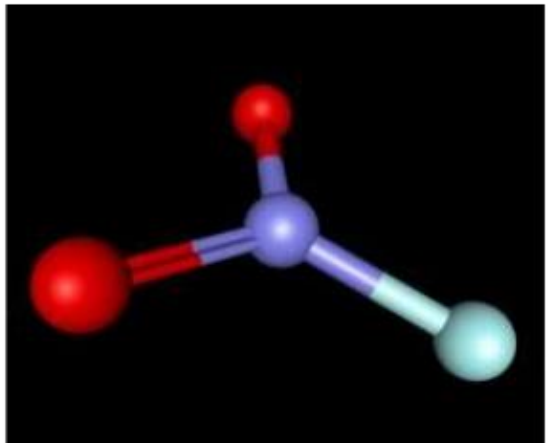


H_2O

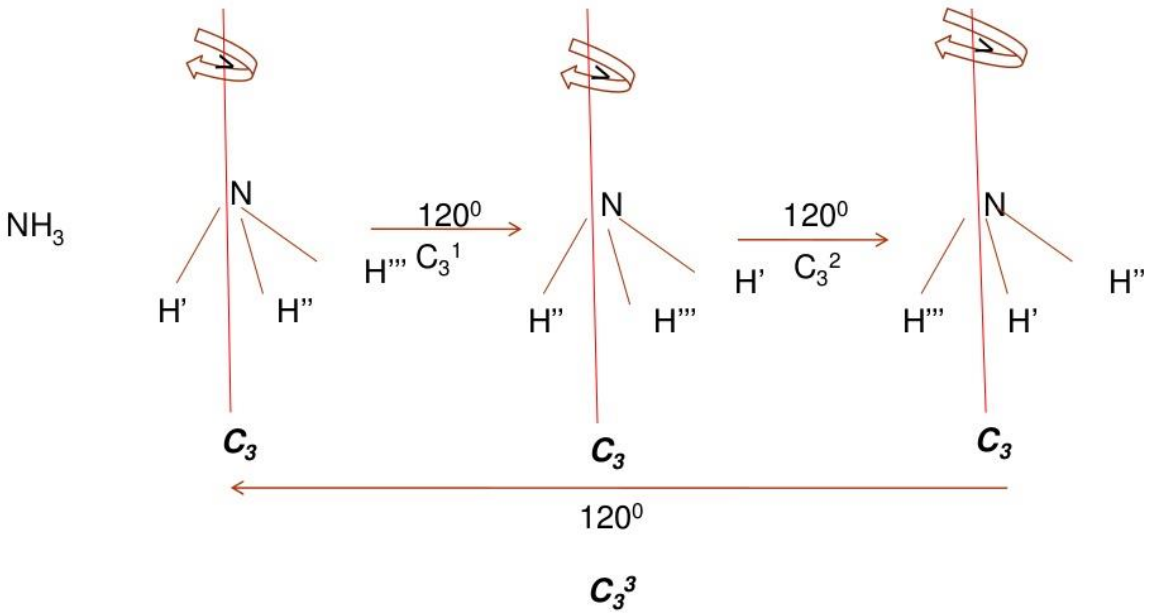


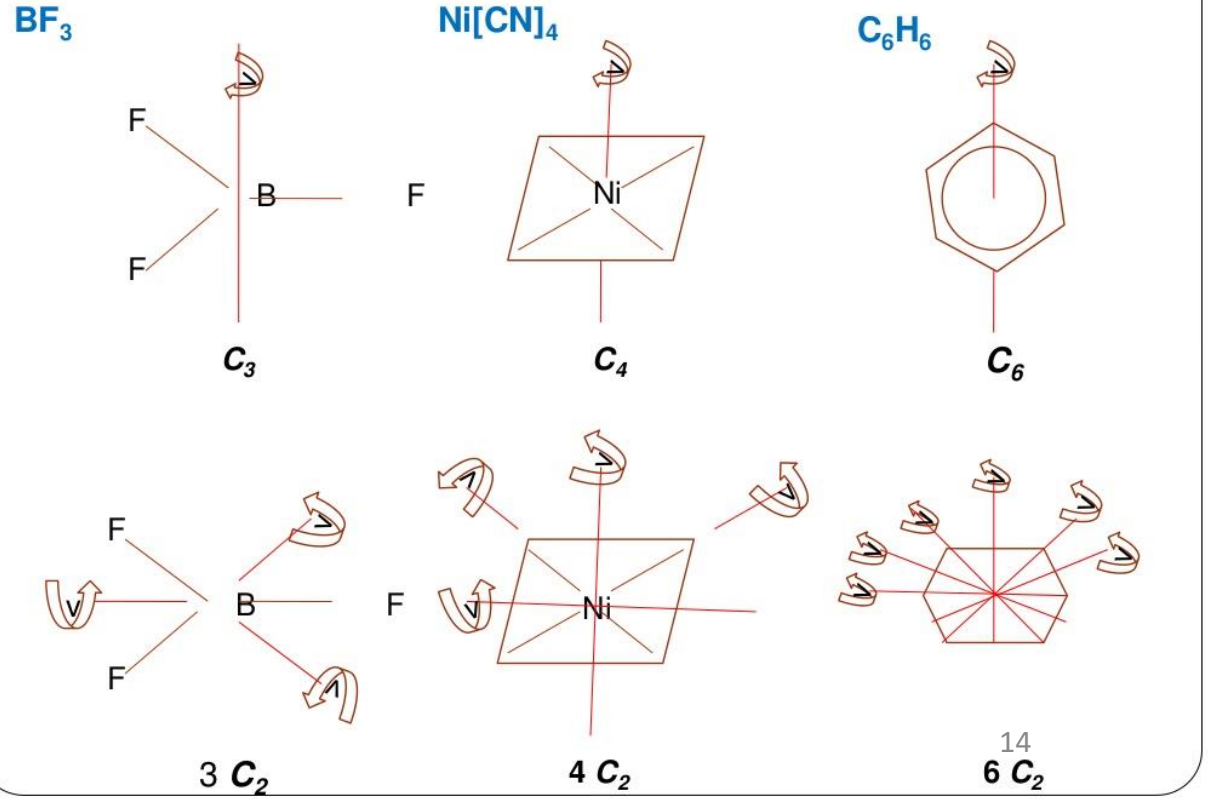
NH_3

How about:



NFO_2?


NH3
N
H'
H''
120⁰
H''' C3 1
N
H''
H'''
120⁰
H' C3 2
N
H'''
H'
H''
C3
C3
C3
120⁰
C3 3


BF3
F
B
F
C3
Ni[CN]4
F
Ni
C4
C6H6
C6
F
B
F
3 C2
F
Ni
4 C2
6 C2

Symbol of the proper rotation axis	Order of rotation axis	360^0 /n
1. C_2 (= C_6^3)	2	180
2. C_3 (= C_6^2)	3	120
3. C_4	4	90
4. C_5	5	72
5. C_6	6	60

Symmetry operations associated with axis of symmetry :-

In general a Cn axis can generated n operation

C_n , C_n^2, C_n^3, C_n^4..... C_n^n

$C_n^n = E$

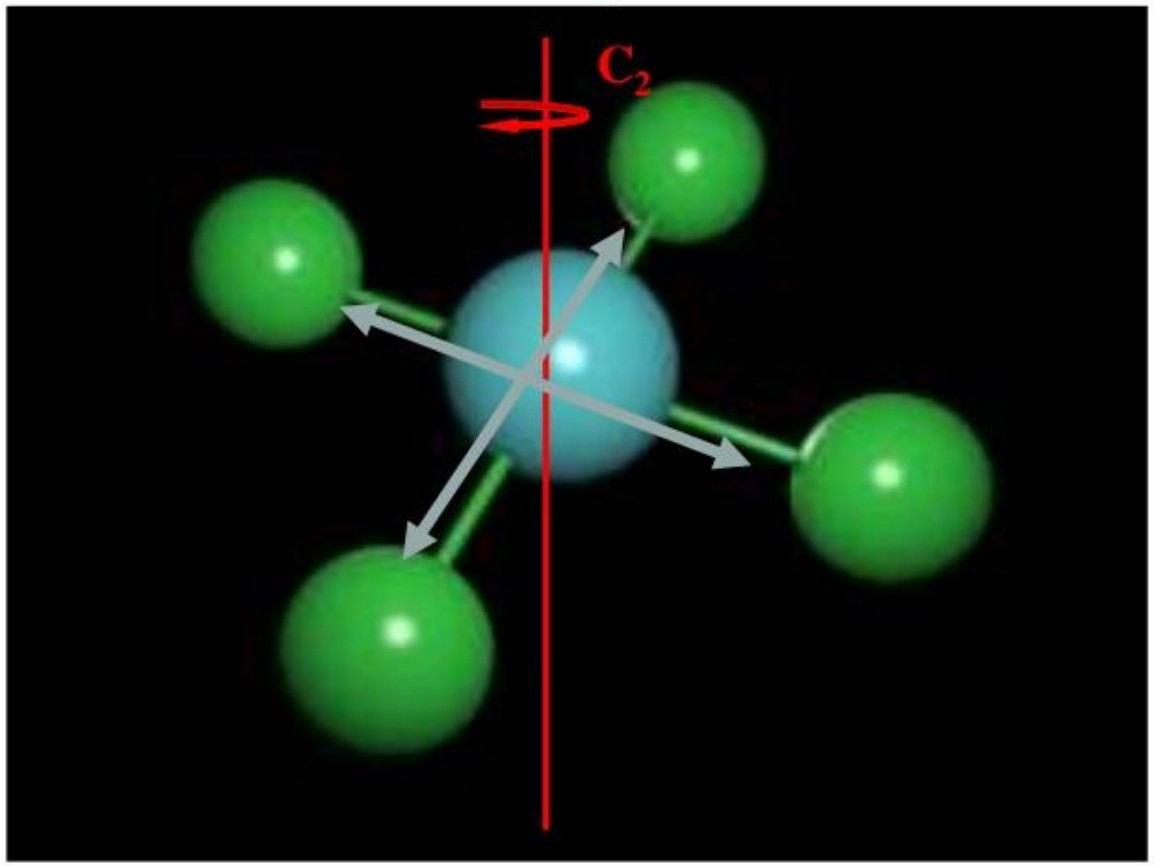
$C_n^{n+1} = C_n$

$C_n^{n+2} = C_n^2$ and so on

Proper Rotation:

C_n = *Rotation about an axis by an angle of* $2\pi/n$

$PtCl_4$



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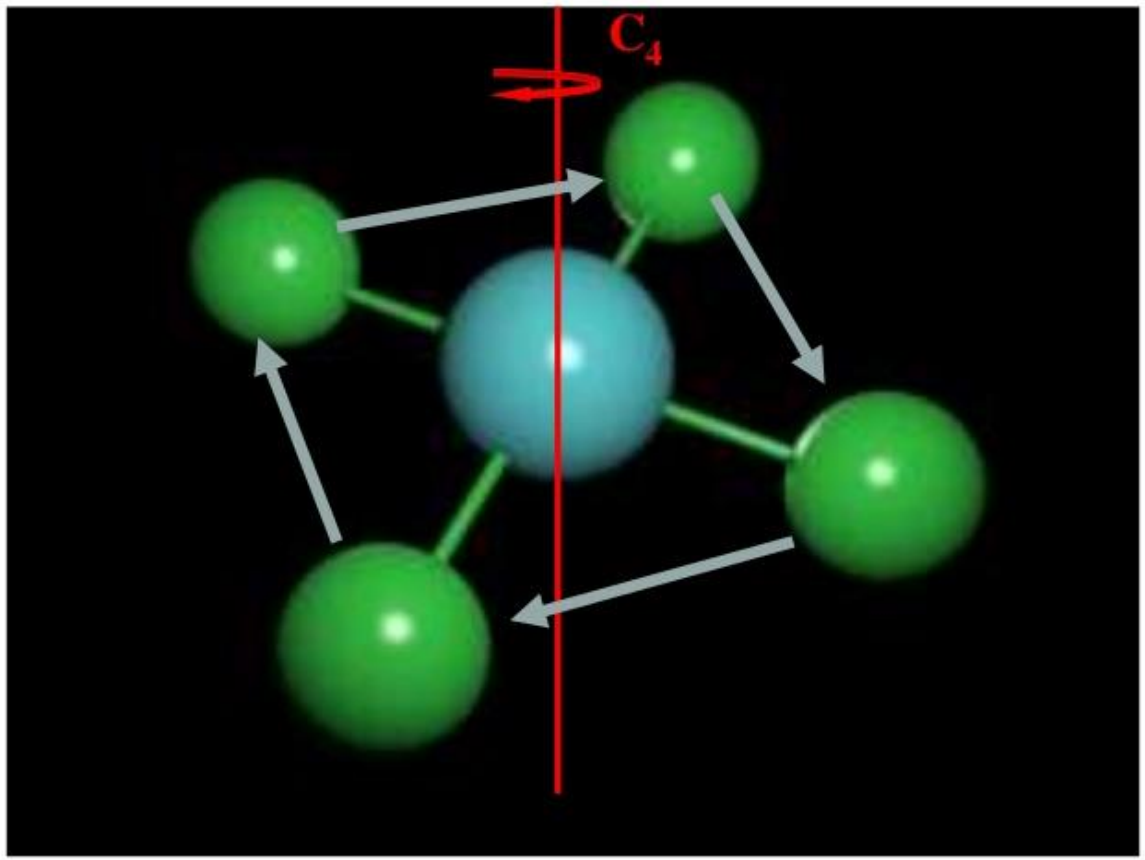
C_n = *Rotation about an axis by an angle of* $2\pi/n$

$PtCl_4$



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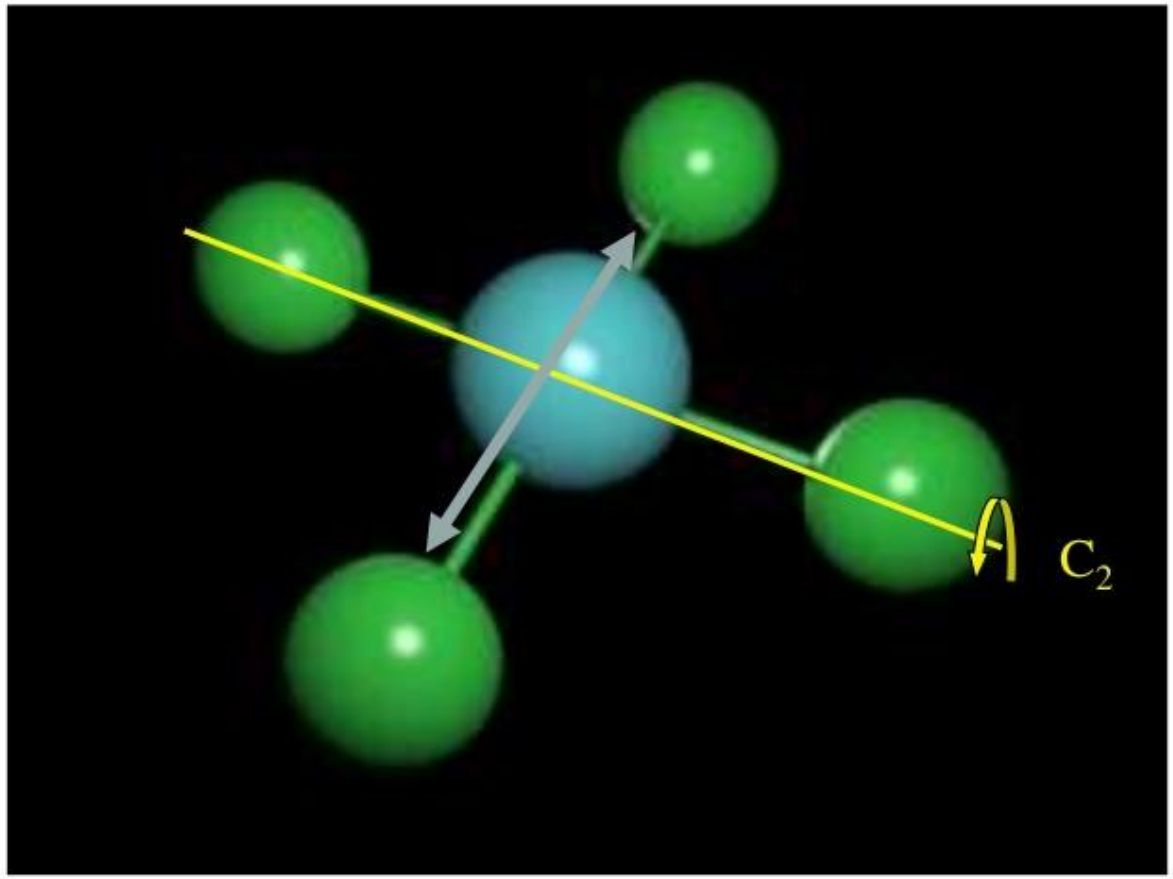

Proper Rotation:

C_n = Rotation about an axis by an angle of $2\pi/n$

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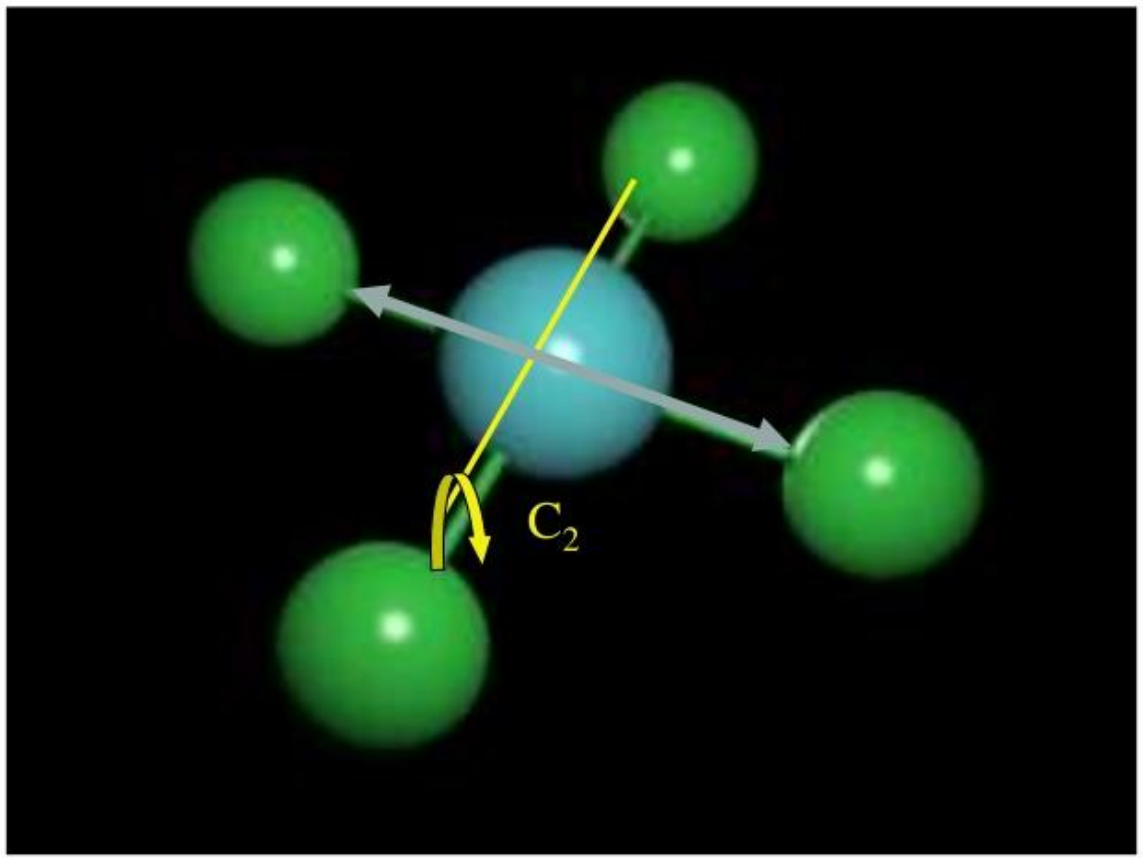
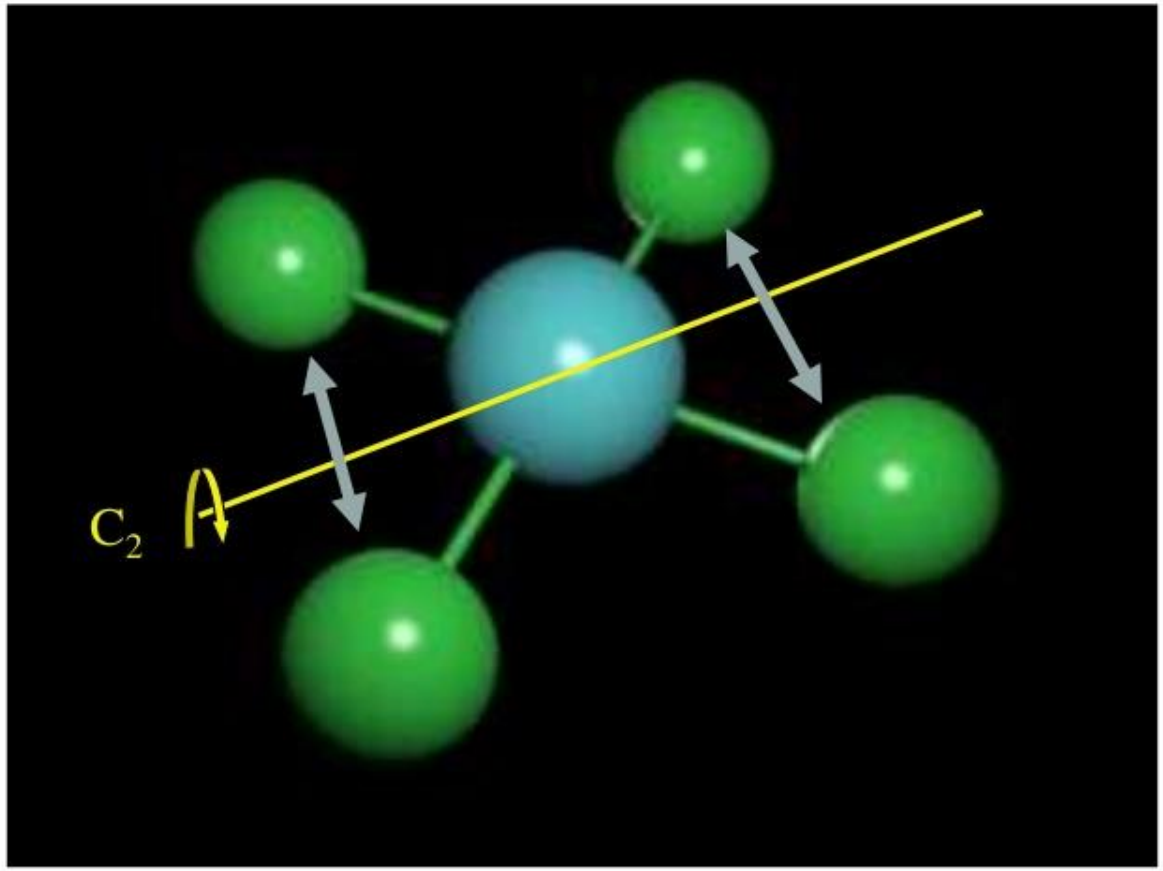


Proper Rotation:

C_n = Rotation about an axis by an angle of $2\pi/n$

$PtCl_4$



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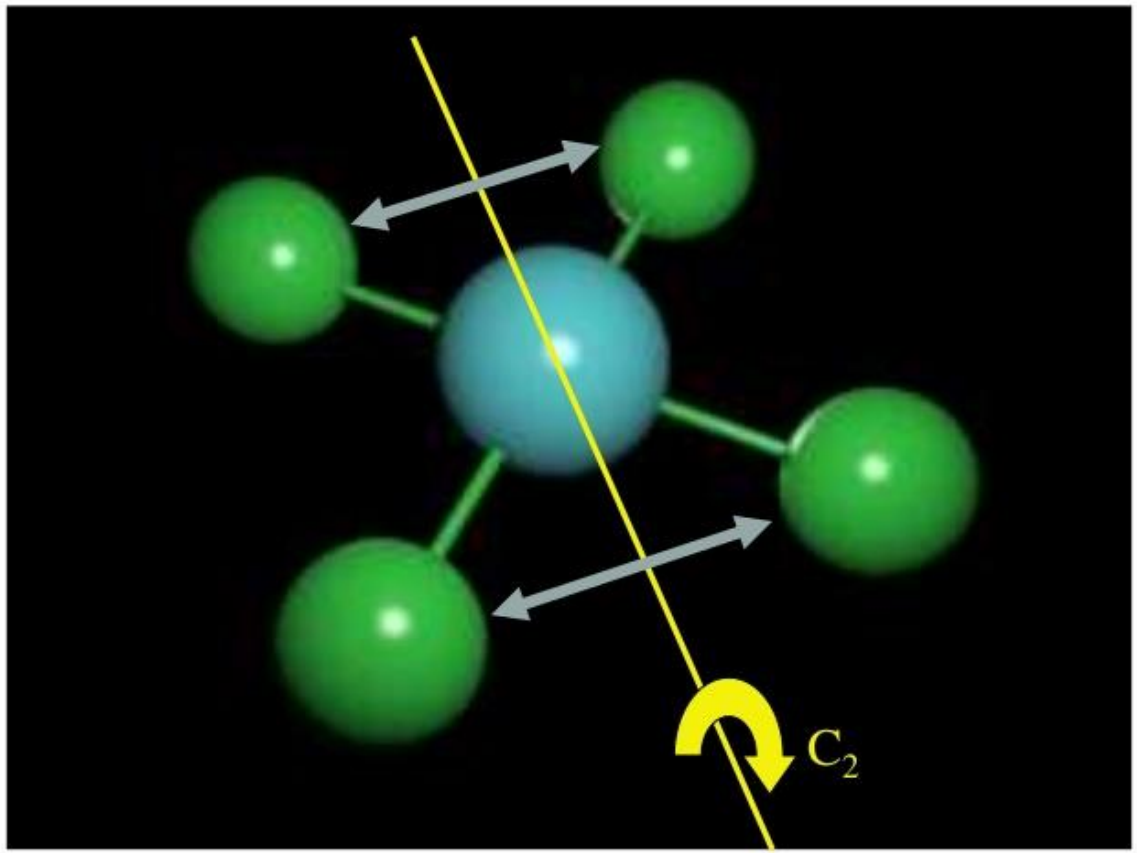
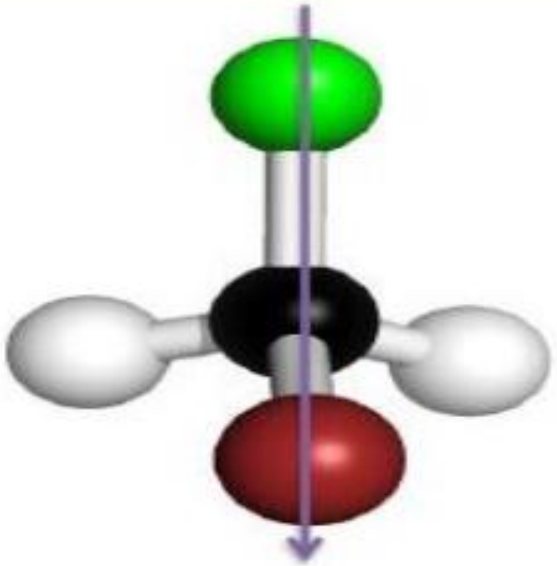
$PtCl_4$



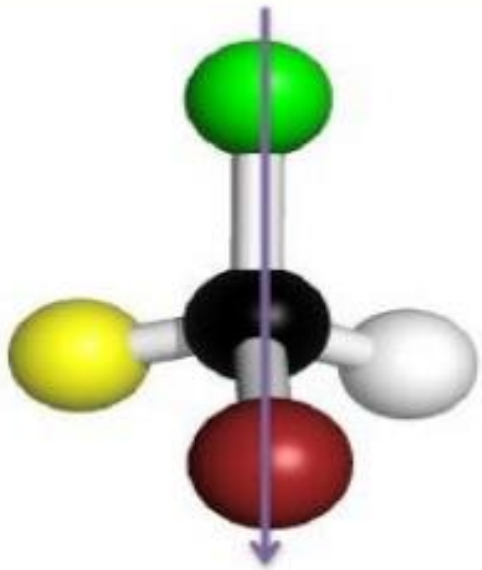
Plane of symmetry ()

❖ **plane of symmetry (internal mirror plane) is a mirror plane that cuts the molecule into two halves, so that one half of the molecule is a reflection of the other half.**

❖ The plane may pass through **atoms, between atoms, or both**



Has Plane of symmetry, achiral
This molecule has two identical halves



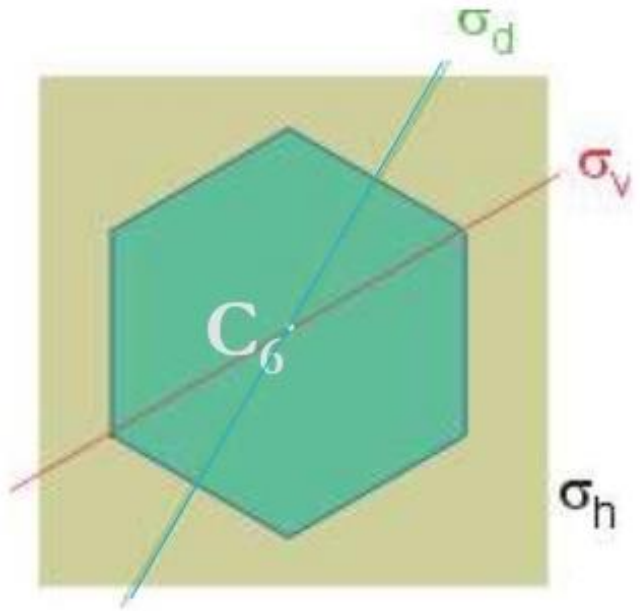
Has NO Plane of symmetry, chiral
This molecule has not two identical halves

- A mirror plane is an imaginary plane which divides a molecules into two equal halves such that one half is the exact mirror image of the other.
- It is denoted by 'σ'.
- Atoms on the surface of plane remain unshifted during reflection.

Classification of mirror planes:-

- Vertical plane(σ_v) :- The principal axis of symmetry lies in the this plane.
- Horizontal plane (σ_h):- The principal axis of symmetry is perpendicular to the plane.
- Dihedral plane (σ_d):- The plane passing through the principal axis but passing in between two subsidiary axis, is the dihedral plane.

MIRROR PLANES- DIHEDRAL PLANE

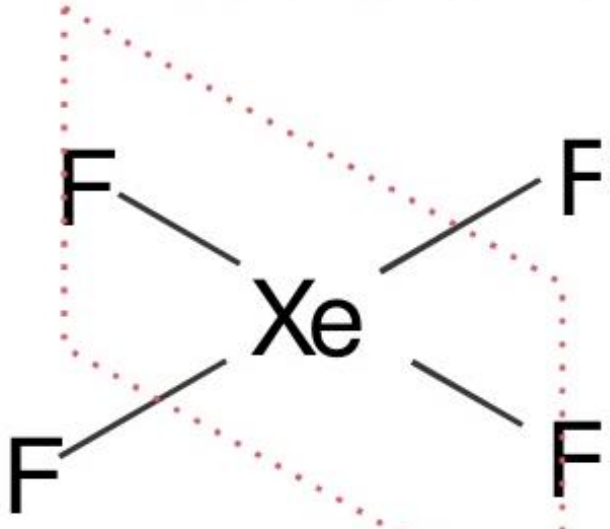


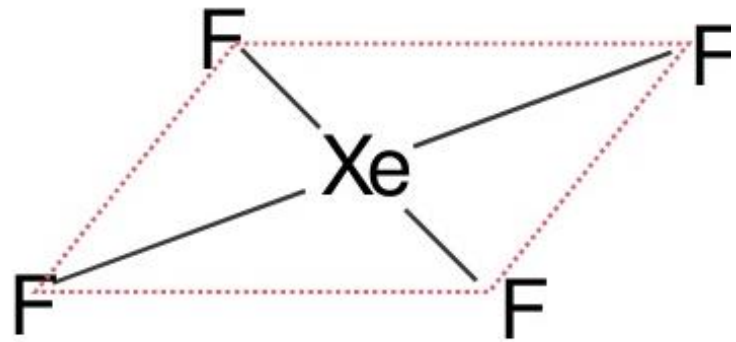
The vertical planes, σ_v, go through the carbon atoms, and include the C_6 axis.

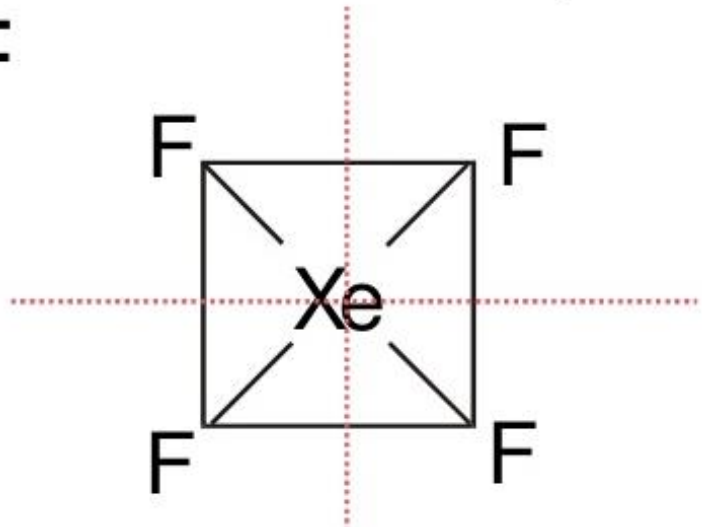
The planes that bisect the bonds are called *dihedral* planes, σ_d.

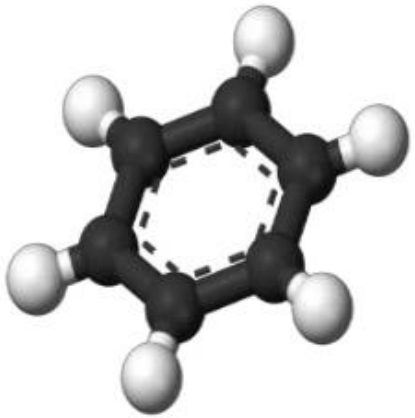
A dihedral plane passes between two mutually perpendicular C_2

XENON TETRAFLUORIDE MOLECULE CONTAINS ALL THREE TYPES OF PLANES-

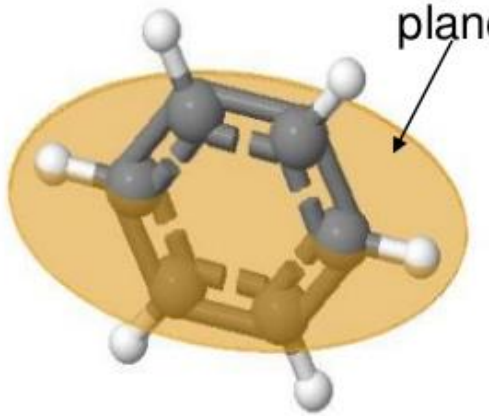


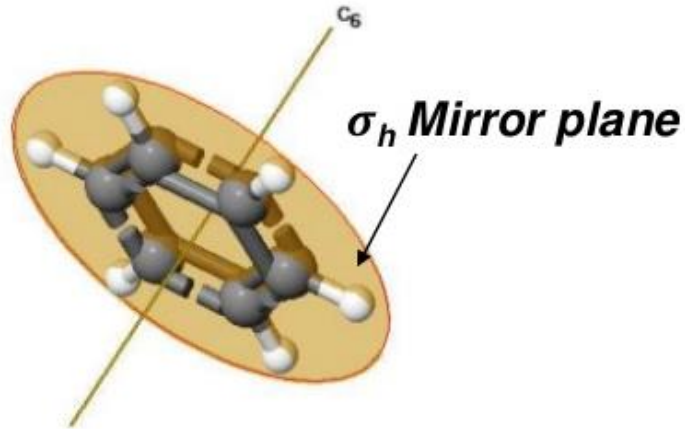


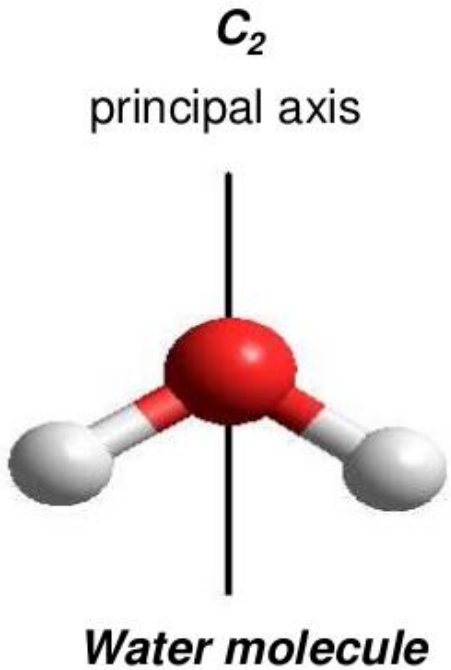




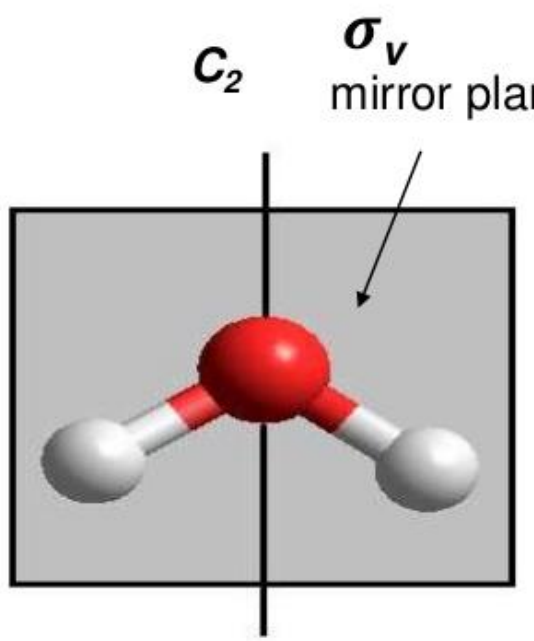
Benzene

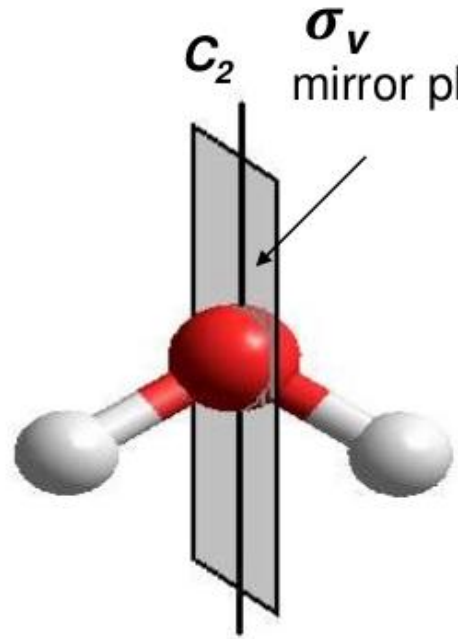




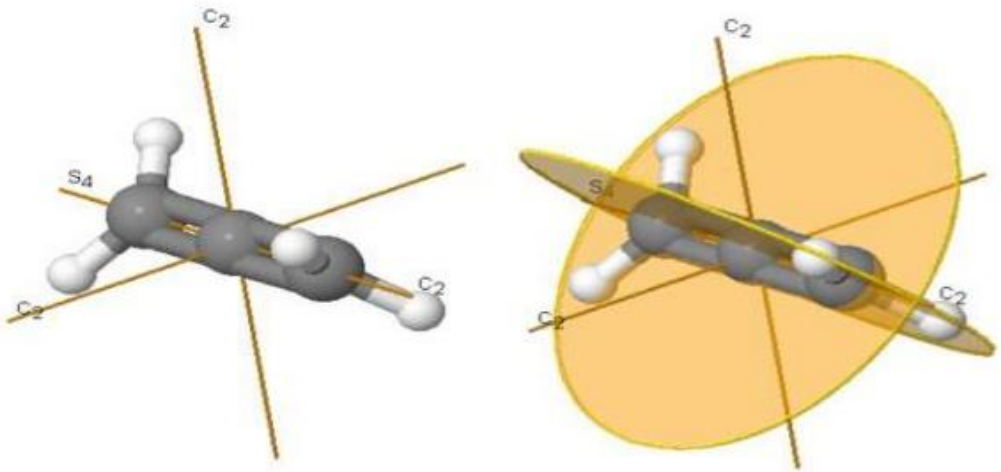


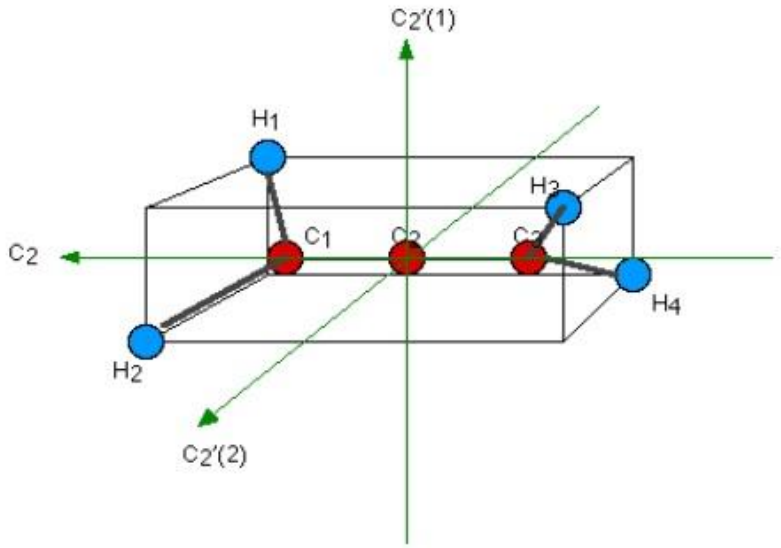
Water molecule





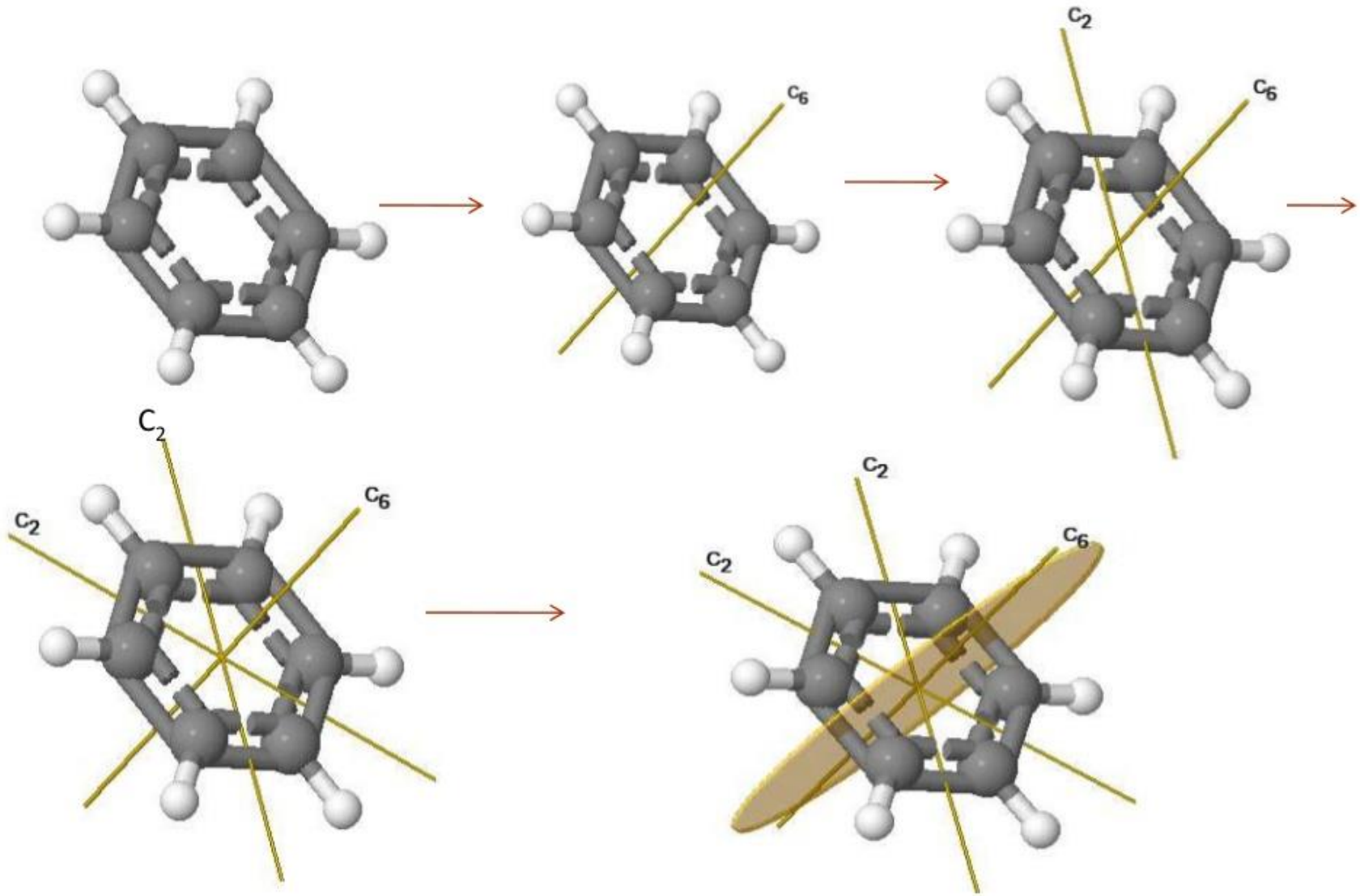
Allene molecule containing Dihedral plane

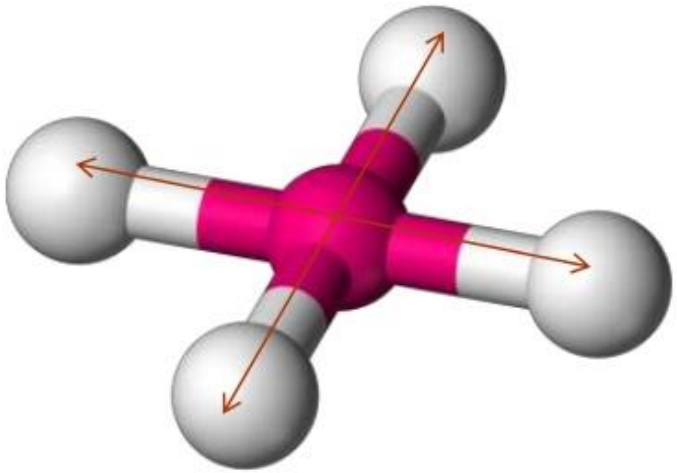




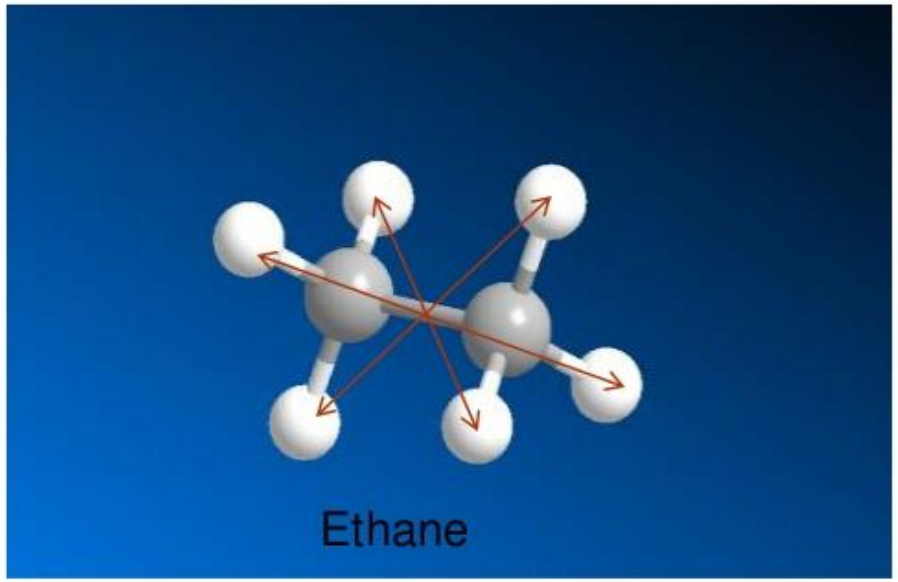
Allene - C2 - Before

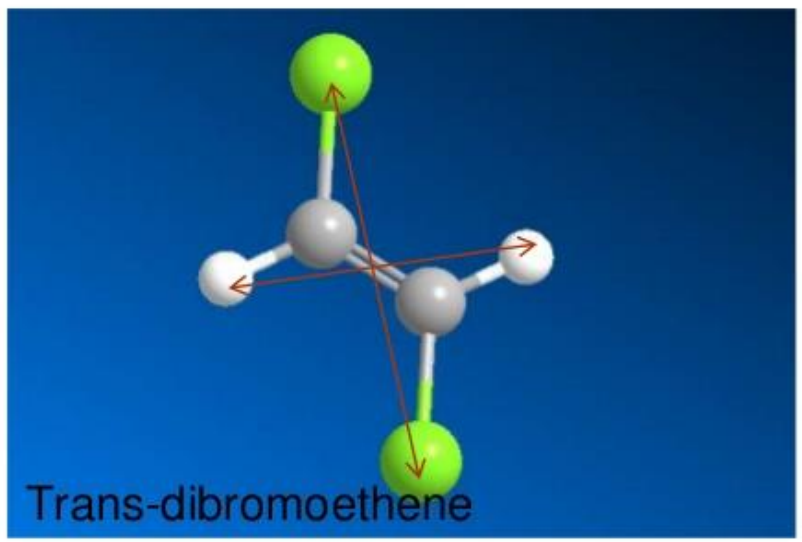
Benzene containing Dihedral plane

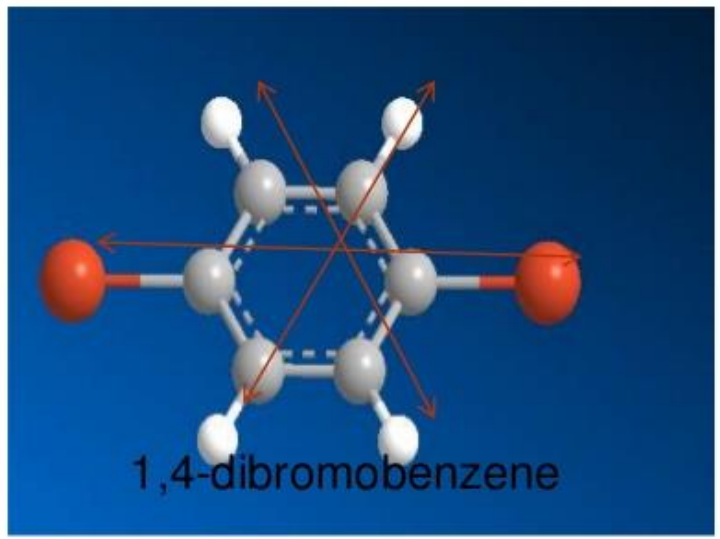




Square planar (AB_4)

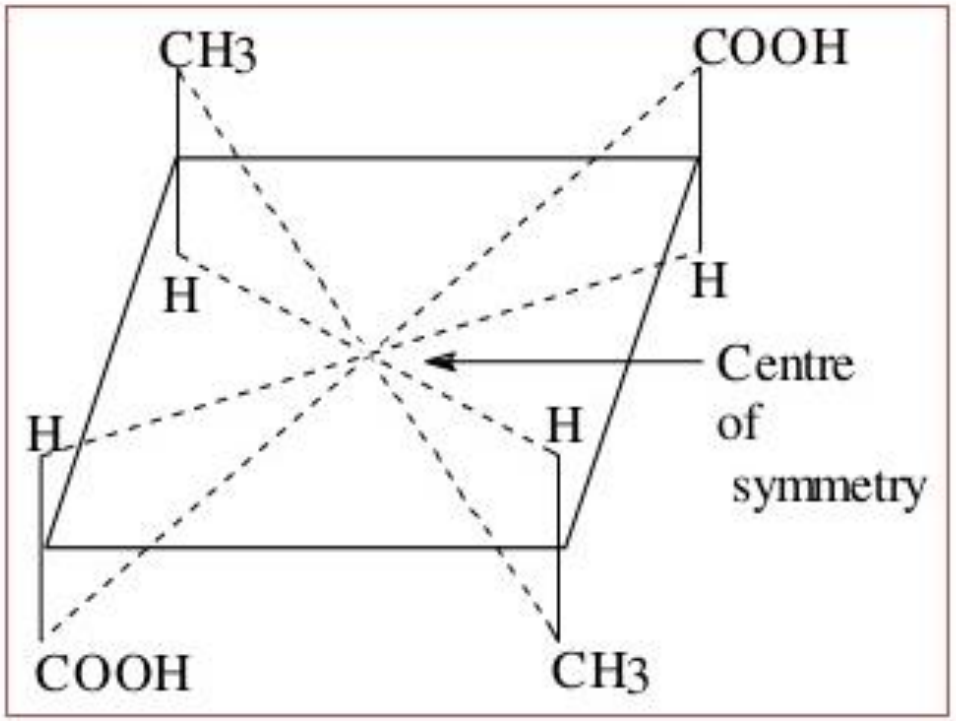






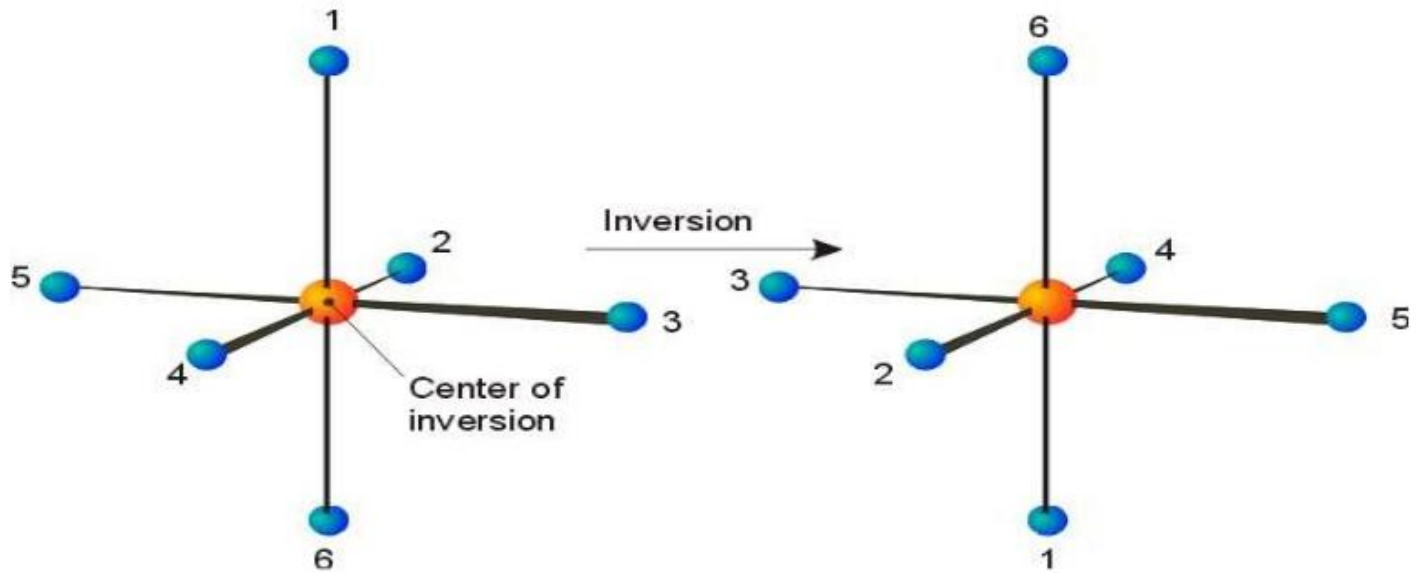
Centre of symmetry or Centre of inversion (i)

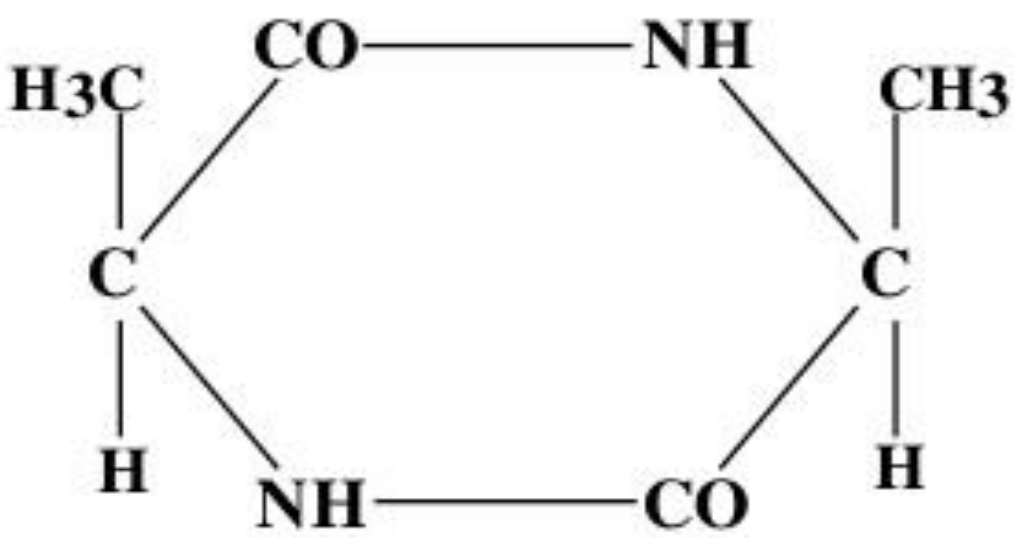
- ***A centre of symmetry (centre of inversion) is defined as a point within the molecule such that if an atom is joined to it by a straight line which if extrapolated to an equal distance beyond it in opposite direction meets an equivalent atom.*** **In other words *it is a point at which all the straight lines joining identical points in the molecule cross each other.***



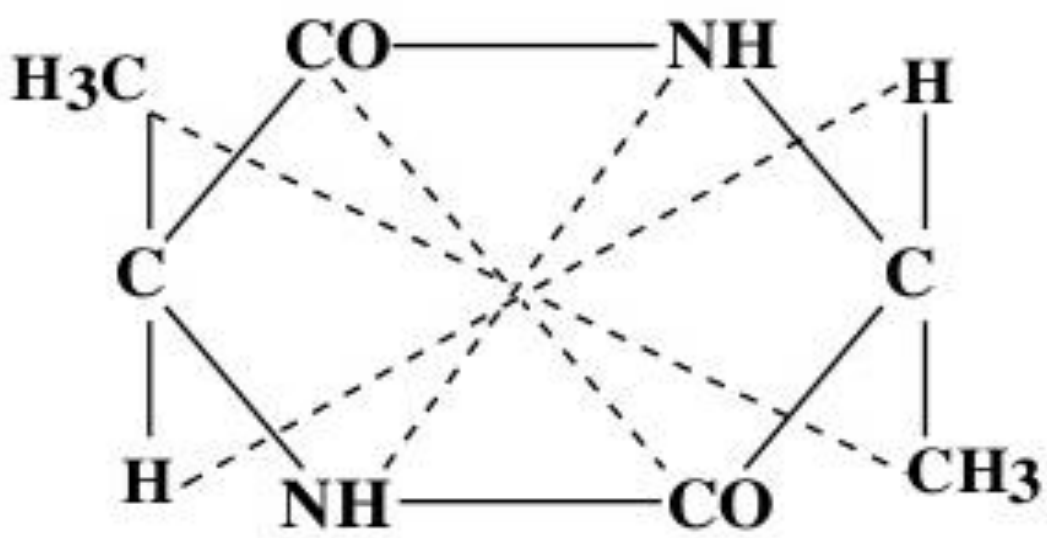
2,4-Dimethylcyclobutane - 1,3-dicarboxylic acid has C_i

- If a line drawn through a point in a molecule and extended in both directions encounters equivalent point in either, the point through which line is drawn is called an inversion centre.
- It denoted as ‘i’.



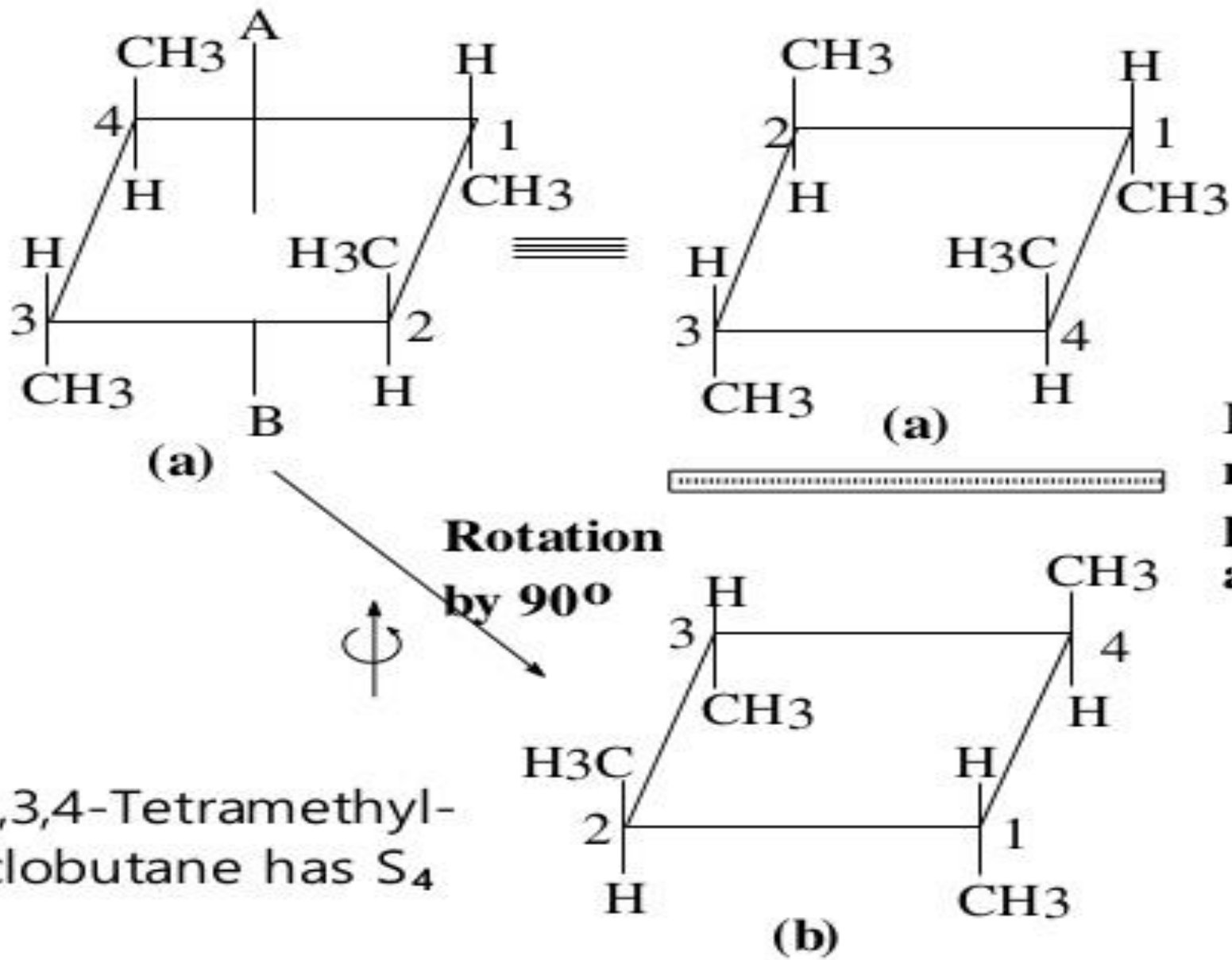


cis (chiral)



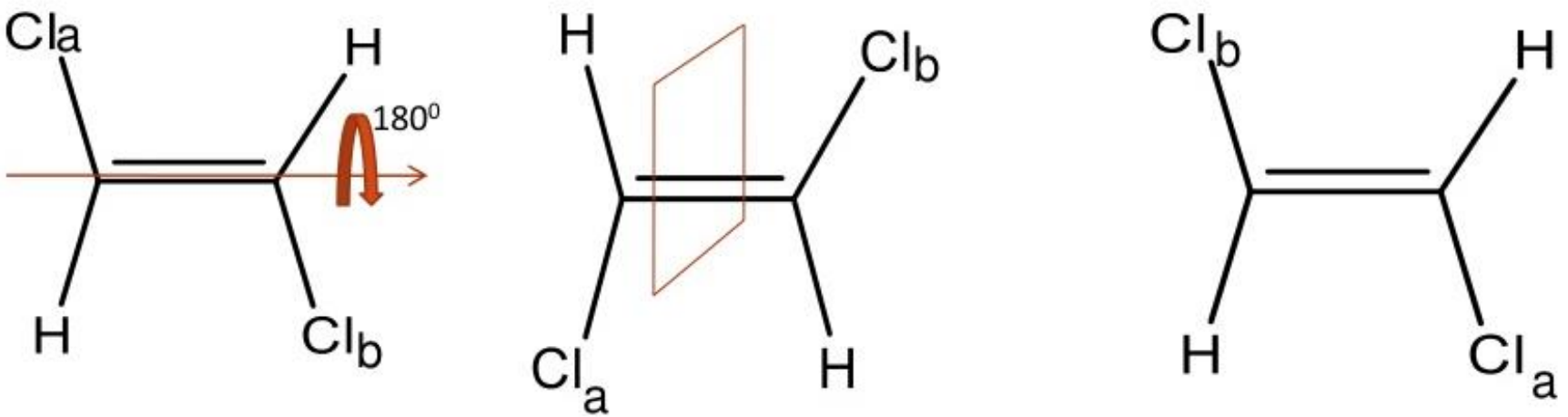
trans (achiral)

4. Alternating or improper axis of symmetry (S_n)



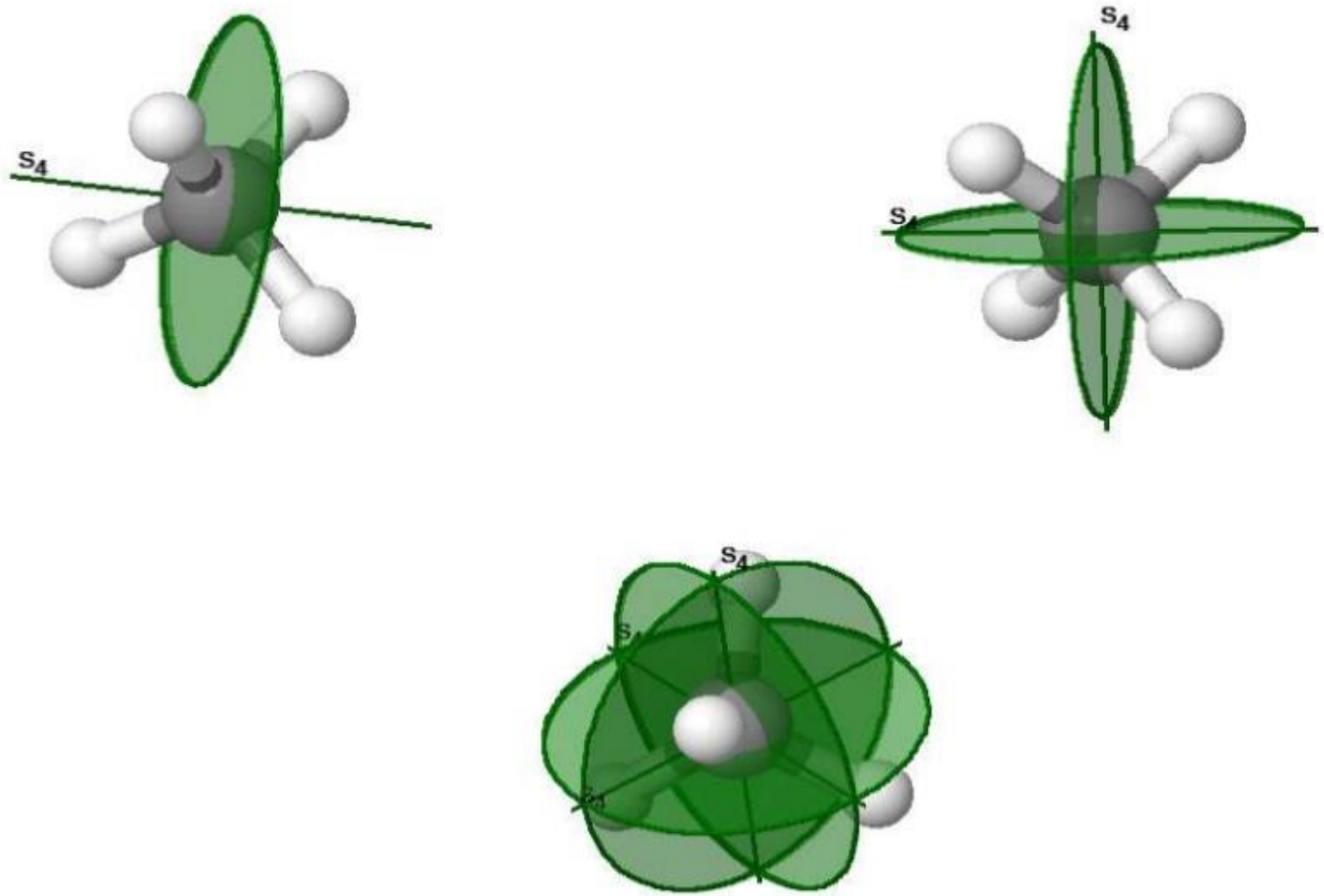
1,2,3,4-Tetramethyl-cyclobutane has S_4

- If a molecule is rotated about an axis through some angle and the resulting configuration is reflected in a plane perpendicular to this axis, if new configuration is indistinguishable from the original, then the axis is called an improper axis.
- It denoted as 'Sn'



- The symmetry element is denoted as S_2.

Methane molecule showing S4 symmetry element



Operations generated by Sn :-

- The no. Of operations generated by Sn depends on whether n is odd or even.
- If ‘n’ is even then generated operations are ‘n’.
- If ‘n’ is odd then generated operations are ‘2n’.

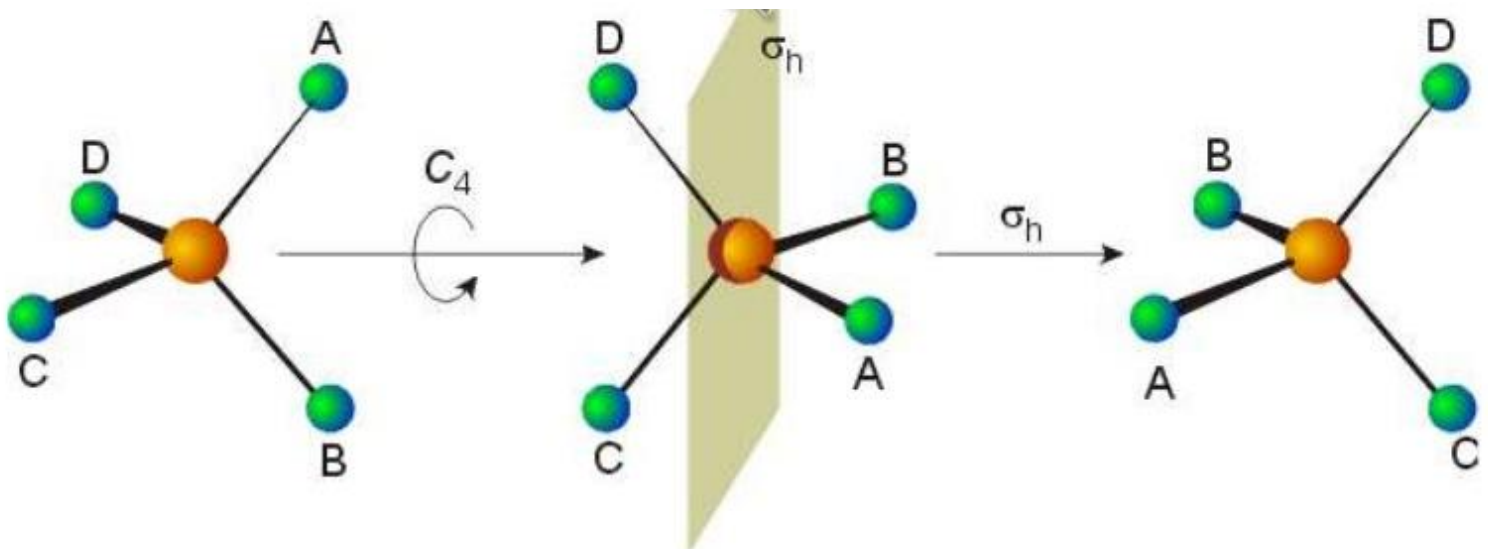
IMPROPER ROTATION

An improper rotation is rotation, followed by reflection in the plane perpendicular to the axis of rotation. Thus

$S_n = C_n * i = i * C_n$

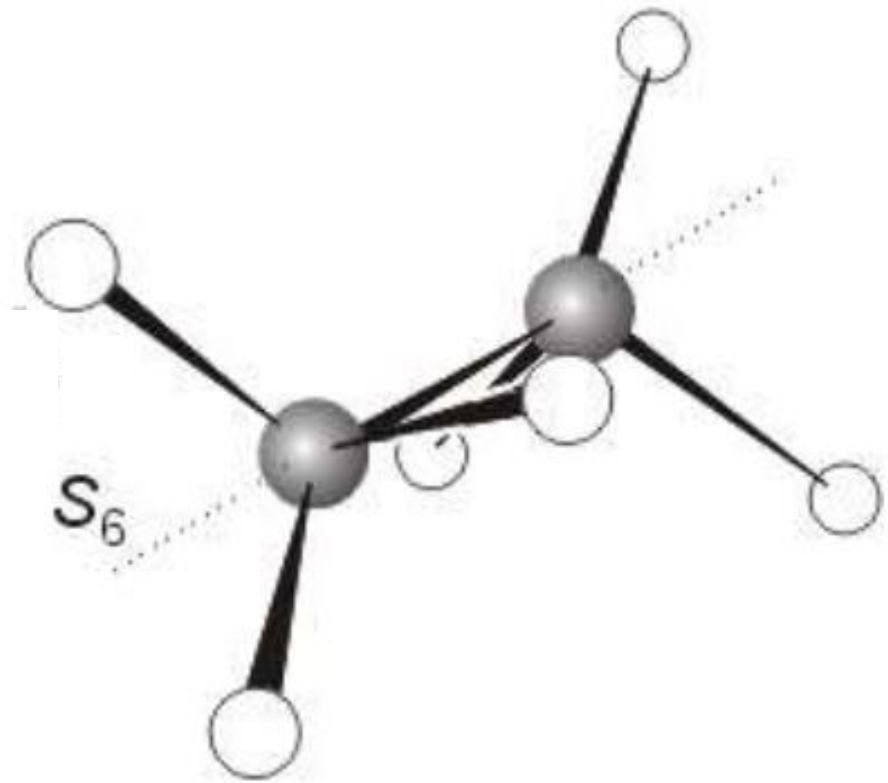
both independent symmetry operations commute. Essentially

$C_n \perp \sigma$



IMPROPER ROTATION

The staggered conformation of ethane has an S_6 axis that goes through both carbon atoms.



IDENTITY, E

All molecules have Identity. This operation leaves the entire molecule unchanged. A highly asymmetric molecule such as a tetrahedral carbon with 4 different groups attached has only identity, and no other symmetry elements. It also signifies operation of doing nothing. It is there for mathematical reasons., such as in Group theory.

Note- some chemists do not consider this as an operation.

LET US ROTATE BENZENE MOLECULE BY 60 DEGREE, PERPENDICULAR TO THE MOLECULAR PLANE

$C_6^1 = C_6^1$

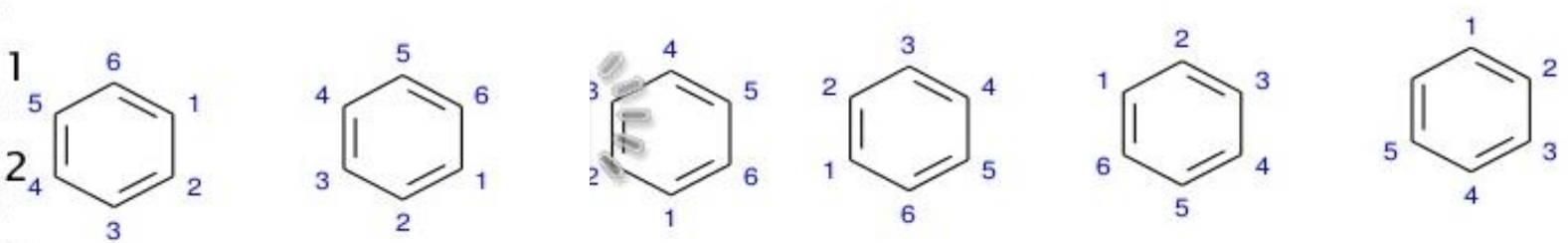
$C_6^2 = C_3^1$

$C_6^3 = C_2^1$

$C_6^4 = C_3^2$

$C_6^5 = C_6^5$

$C_6^6 = E$



Thus a C6 axis generates only two genuine C6 operations. Others can be seen as lower order operations. A C6 thus generates-

2 C_6 ,2 C_3 , 1C_2

Table 4.1 Important symmetry operations and symmetry elements

Symmetry element	Symmetry operation	Symbol
	Identity*	E
n-Fold symmetry axis	Rotation by $2\pi/n$	C_n
Mirror plane	Reflection	σ
Center of inversion	Inversion	i
n-Fold axis of improper rotation†	Rotation by $2\pi/n$ followed by reflection perpendicular to rotation axis	S_n

*The symmetry element can be thought of as the whole of space.
†Note the equivalences $S_1 = \sigma$ and $S_2 = i$.

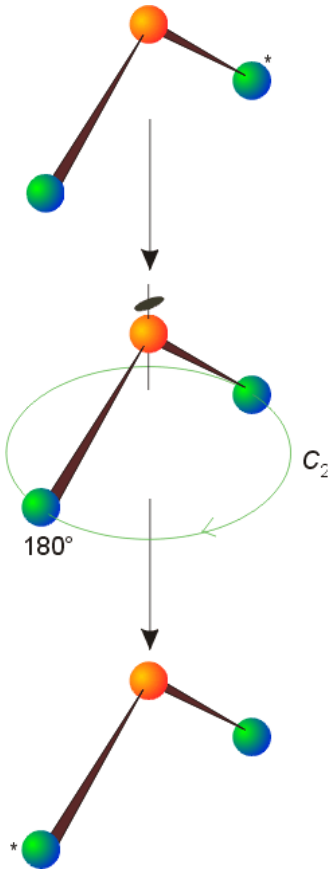
Symmetry Elements and Symmetry Operations

- Identity => E

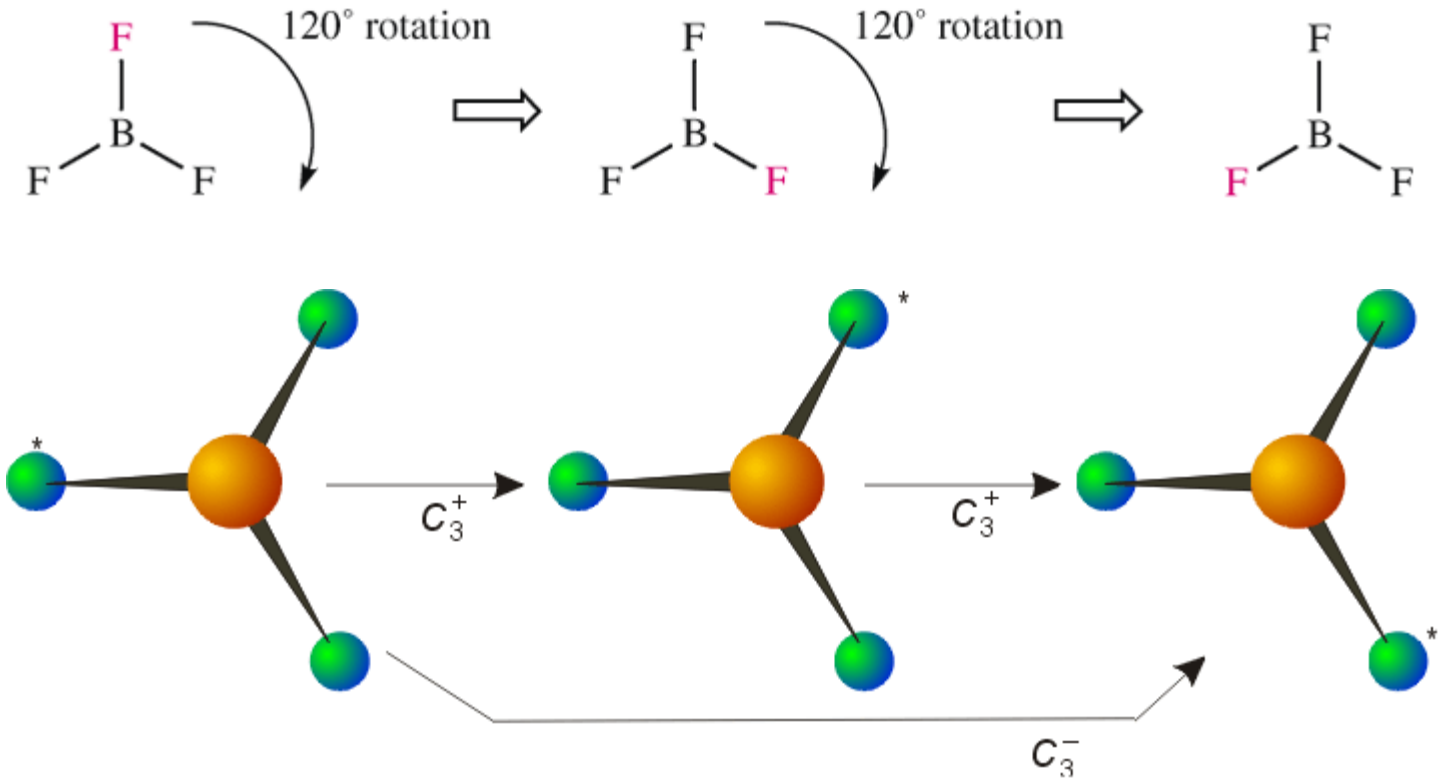
Symmetry Elements and Symmetry Operations

- Proper axis of rotation => C_n
  - where n = 2, 180° rotation
  - n = 3, 120° rotation
  - n = 4, 90° rotation
  - n = 6, 60° rotation
  - n = , (1/)° rotation
- principal axis of rotation, C_n

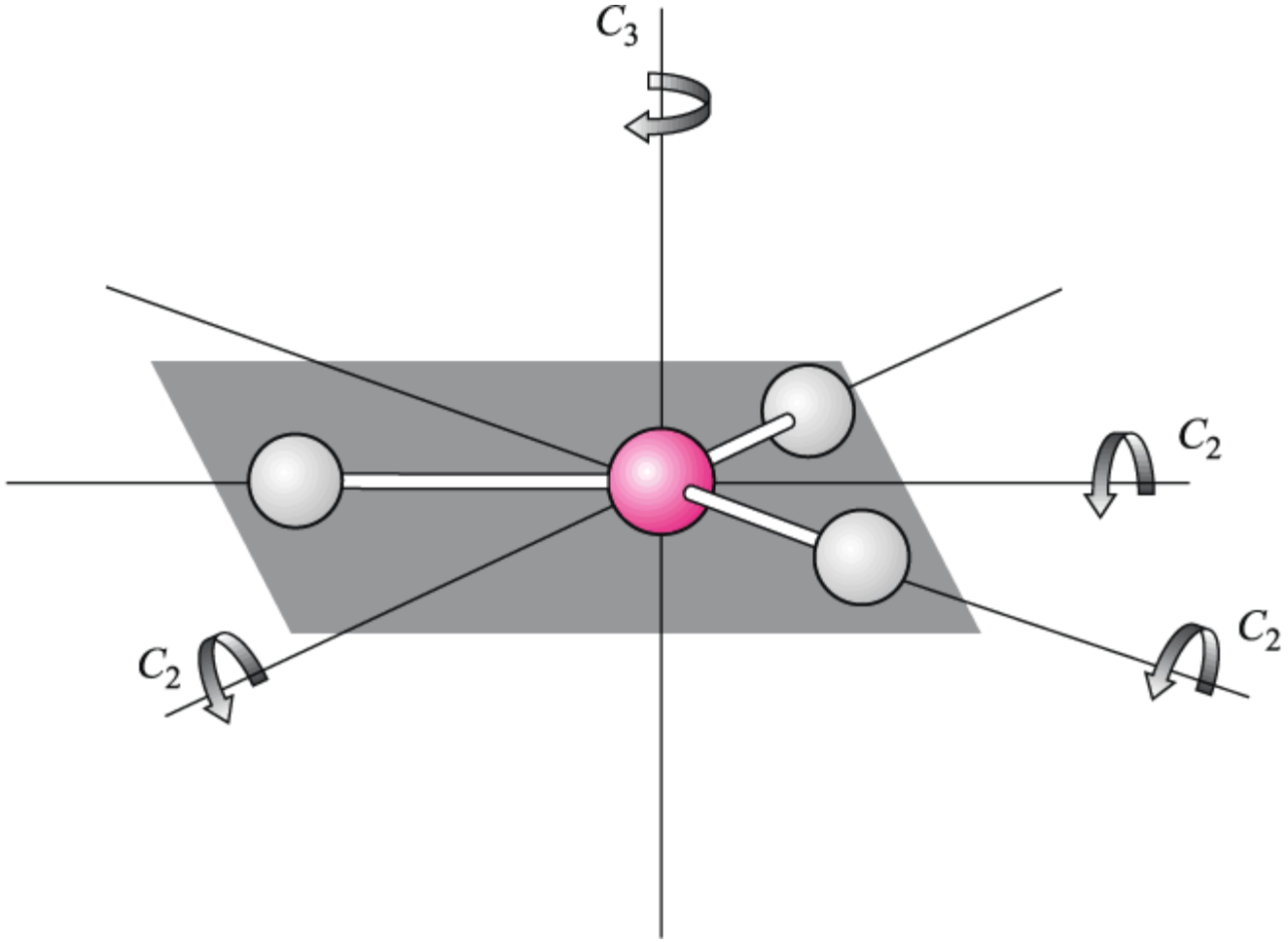
2-Fold Axis of Rotation



3-Fold Axis of Rotation



Rotations for a Trigonal Planar Molecule



Symmetry Elements and Symmetry Operations

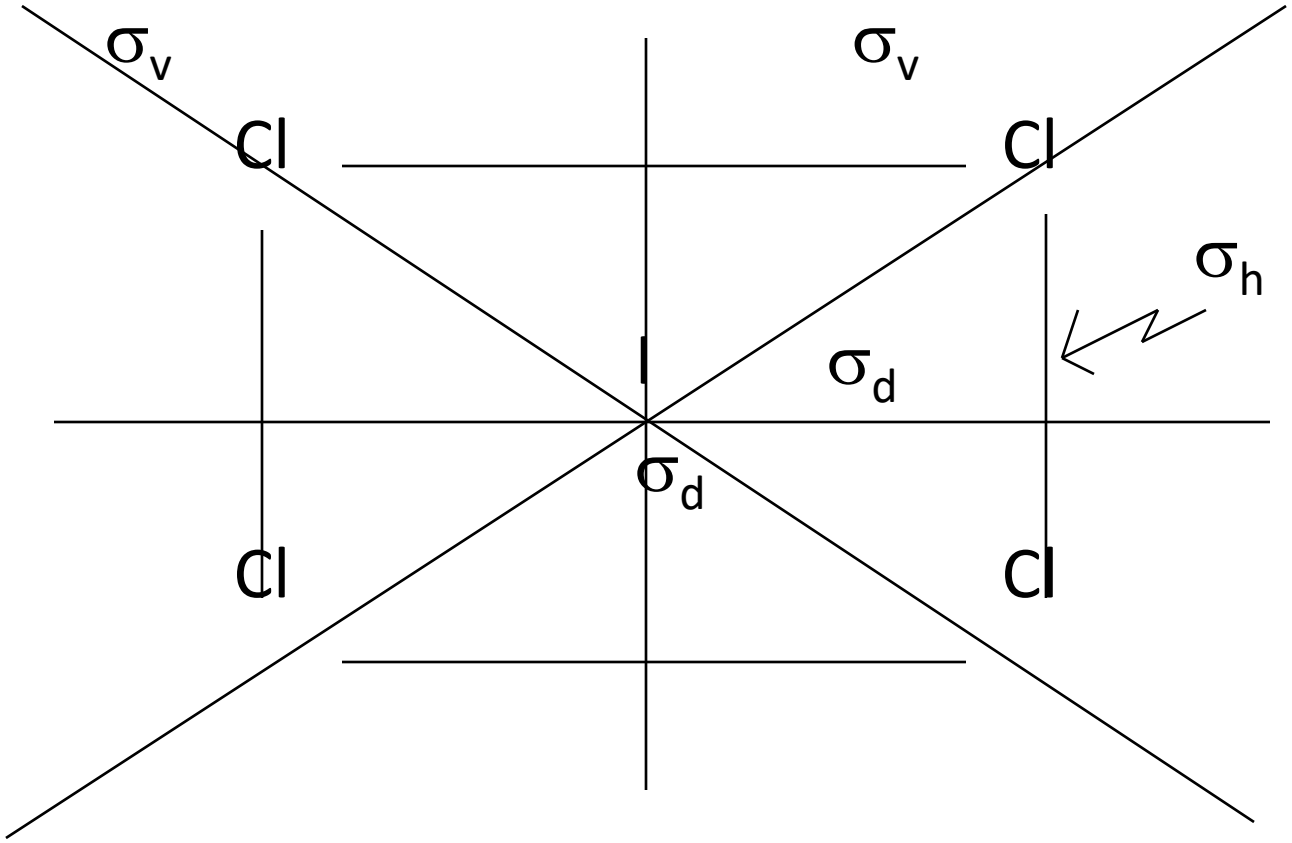
Mirror planes =>

σ_h => mirror plane perpendicular to a principal axis of rotation

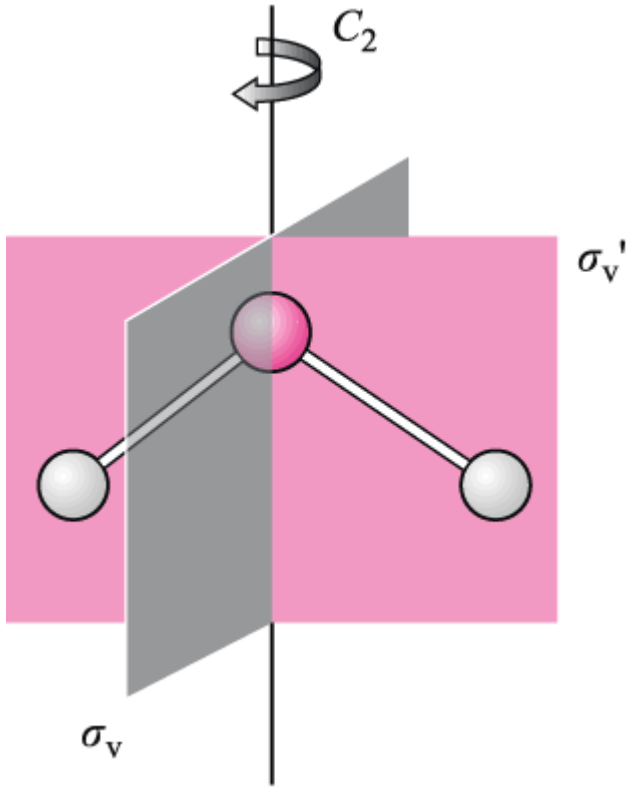
σ_v => mirror plane containing principal axis of rotation

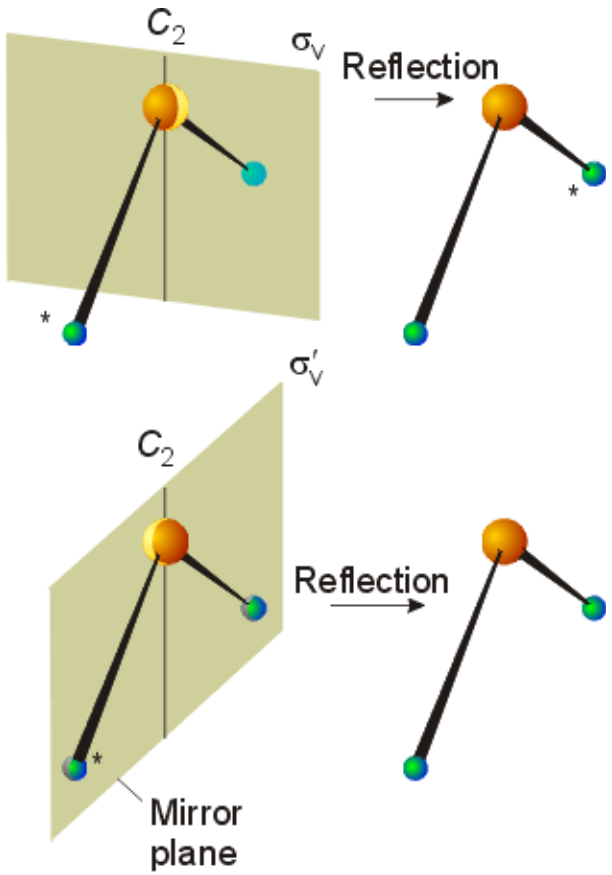
σ_d => mirror plane bisects dihedral angle made by the principal axis of rotation and two adjacent C2 axes perpendicular to principal rotation axis

Mirrors

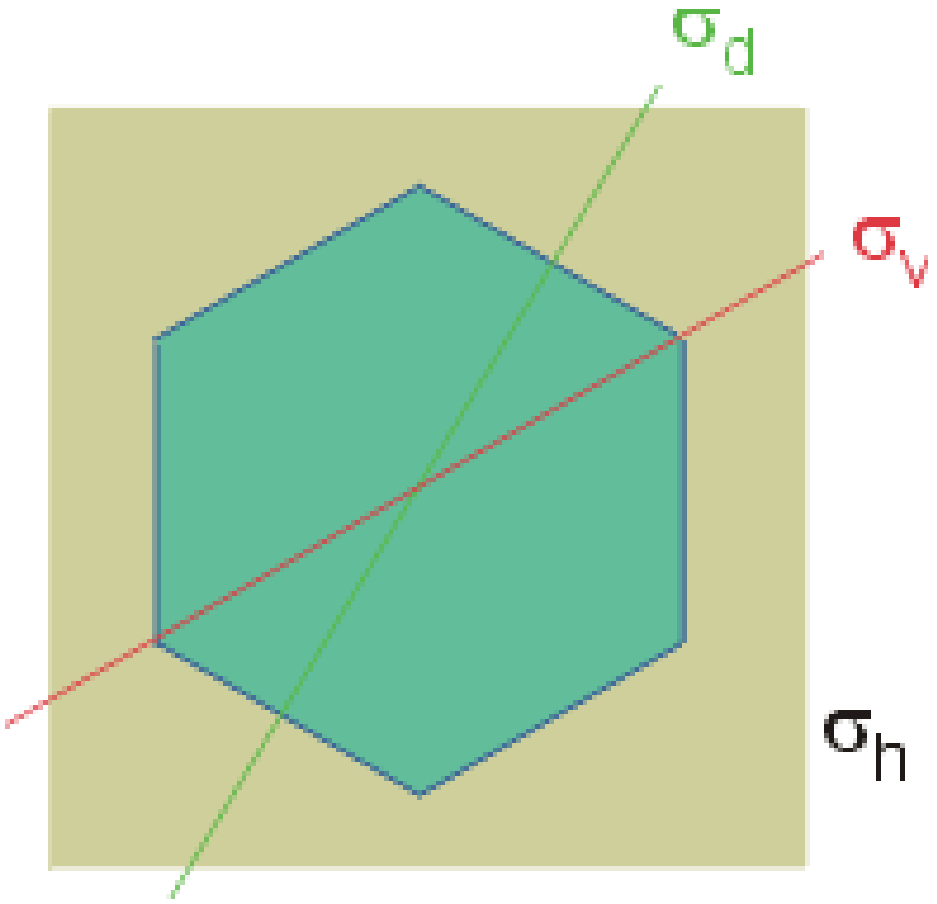


Rotations and Mirrors in a Bent Molecule





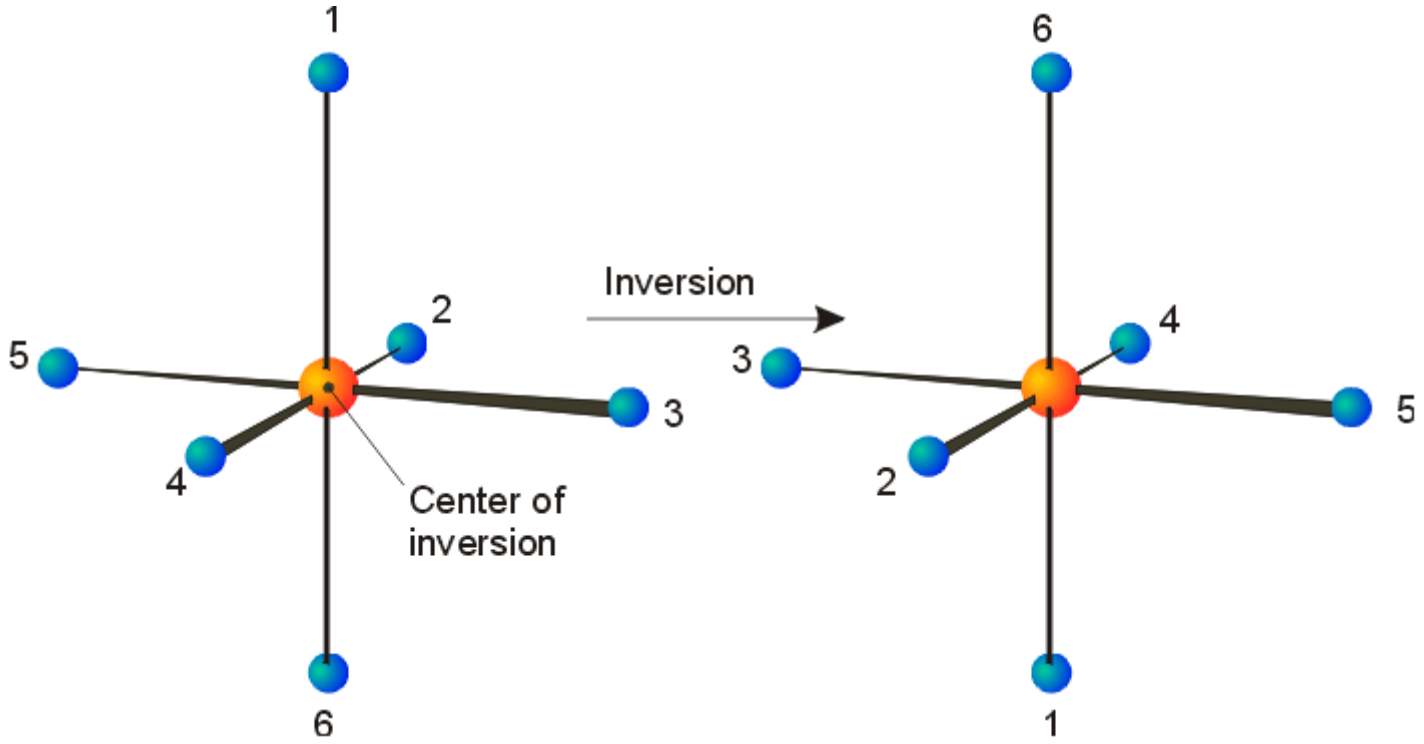
Benzene Ring



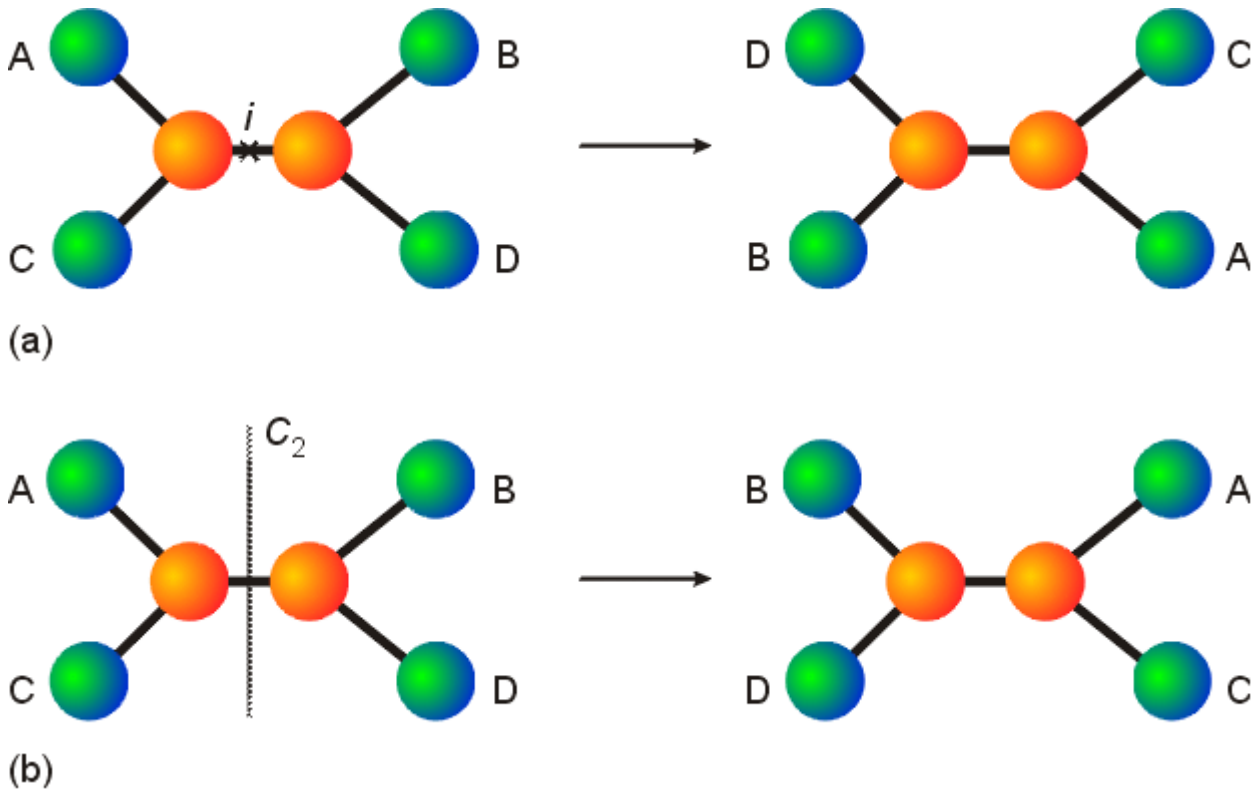
Symmetry Elements and Symmetry Operations

- Center of symmetry => i

Center of Inversion



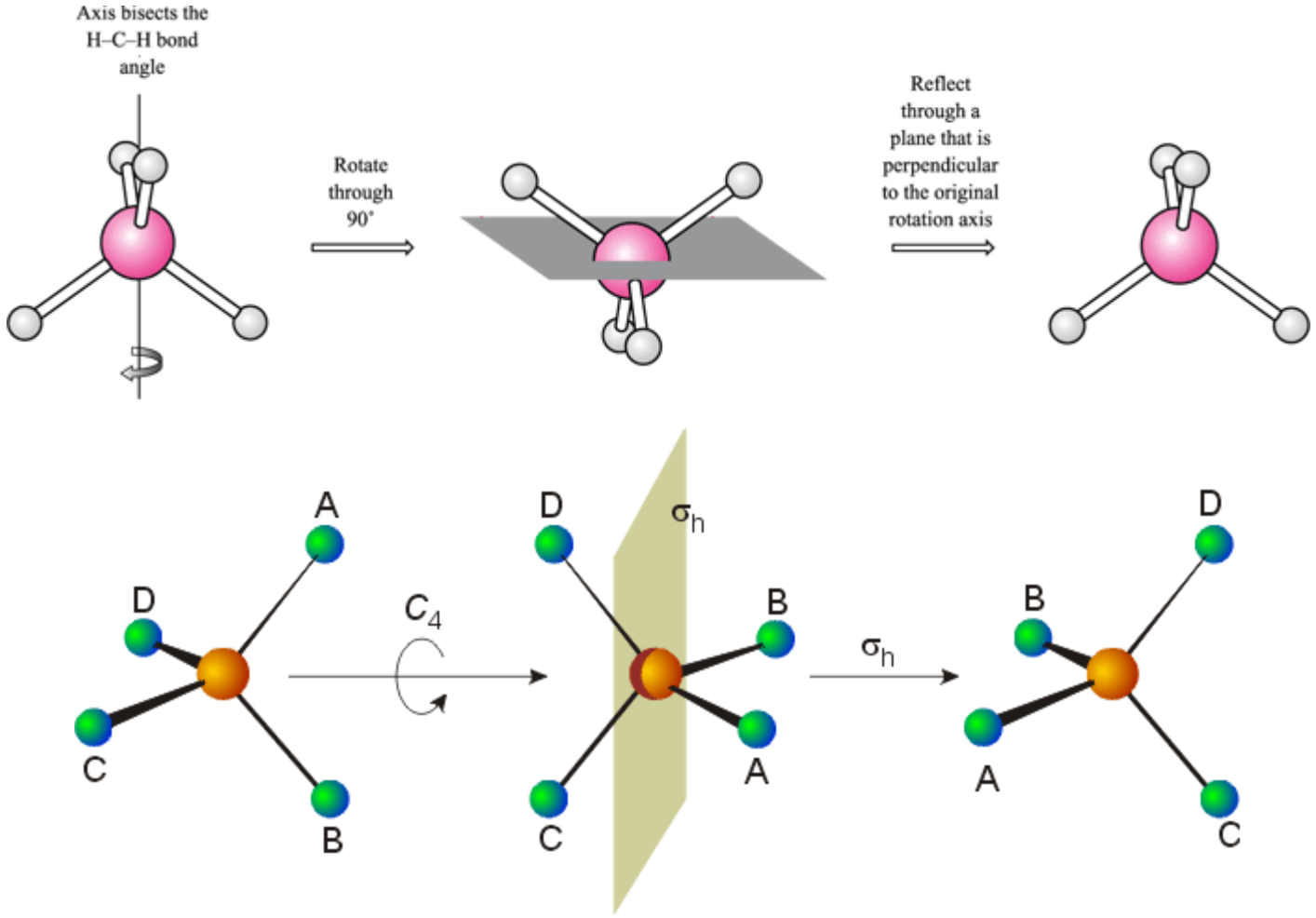
Inversion vs. C_2



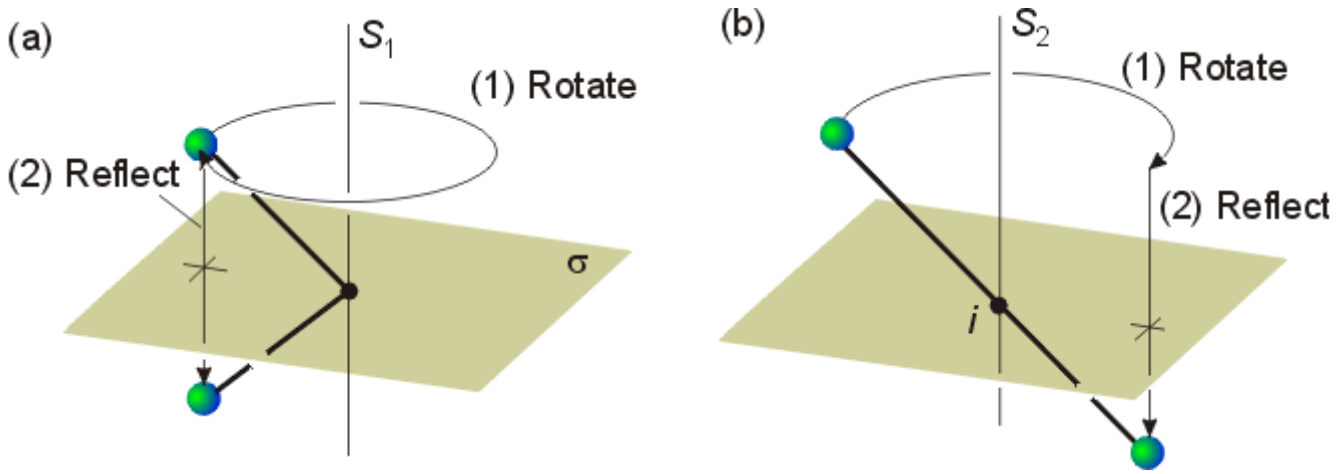
Symmetry Elements and Symmetry Operations

- Improper axis of rotation => S_n
  - rotation about n axis followed by inversion through center of symmetry

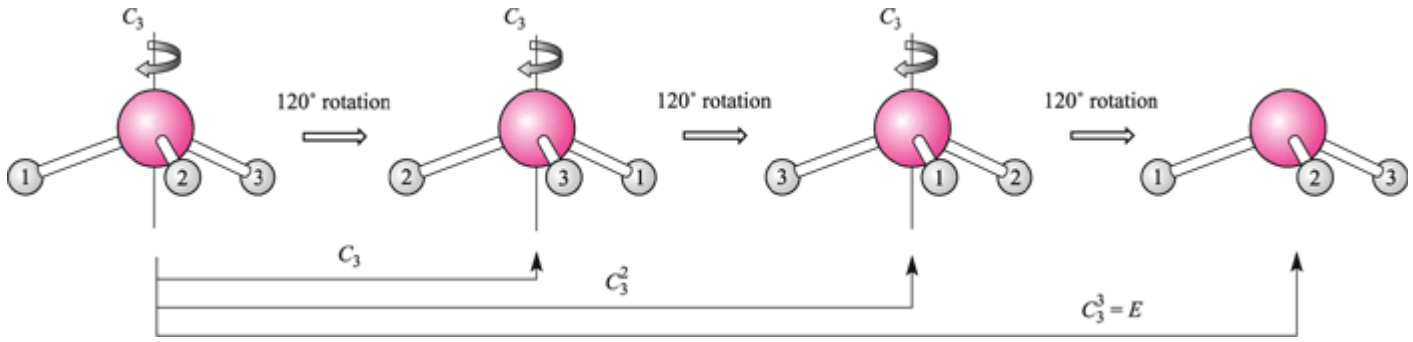
Improper Rotation in a Tetrahedral Molecule



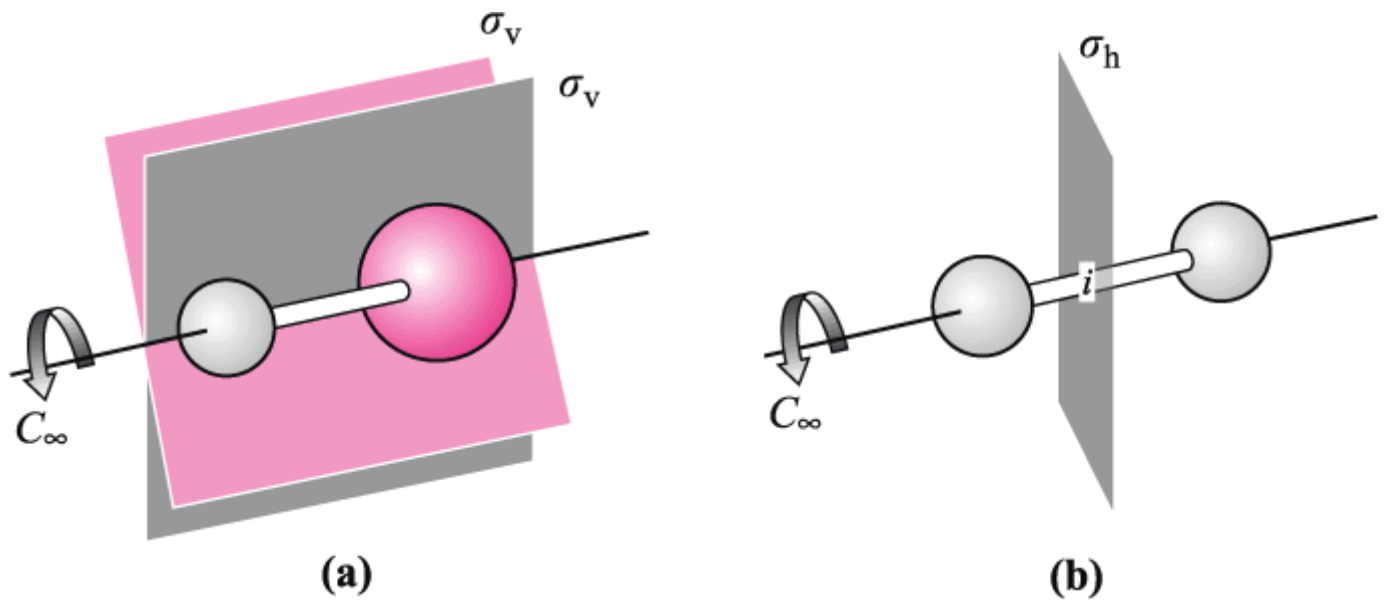
S_1 and S_2 Improper Rotations



Successive C_3 Rotations on Trigonal Pyramidal Molecule



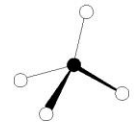
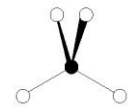
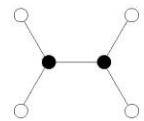
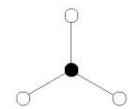
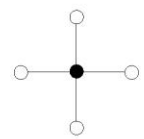
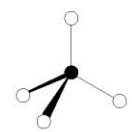
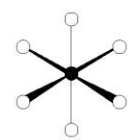
Linear Molecules



Selection of Point Group from Shape

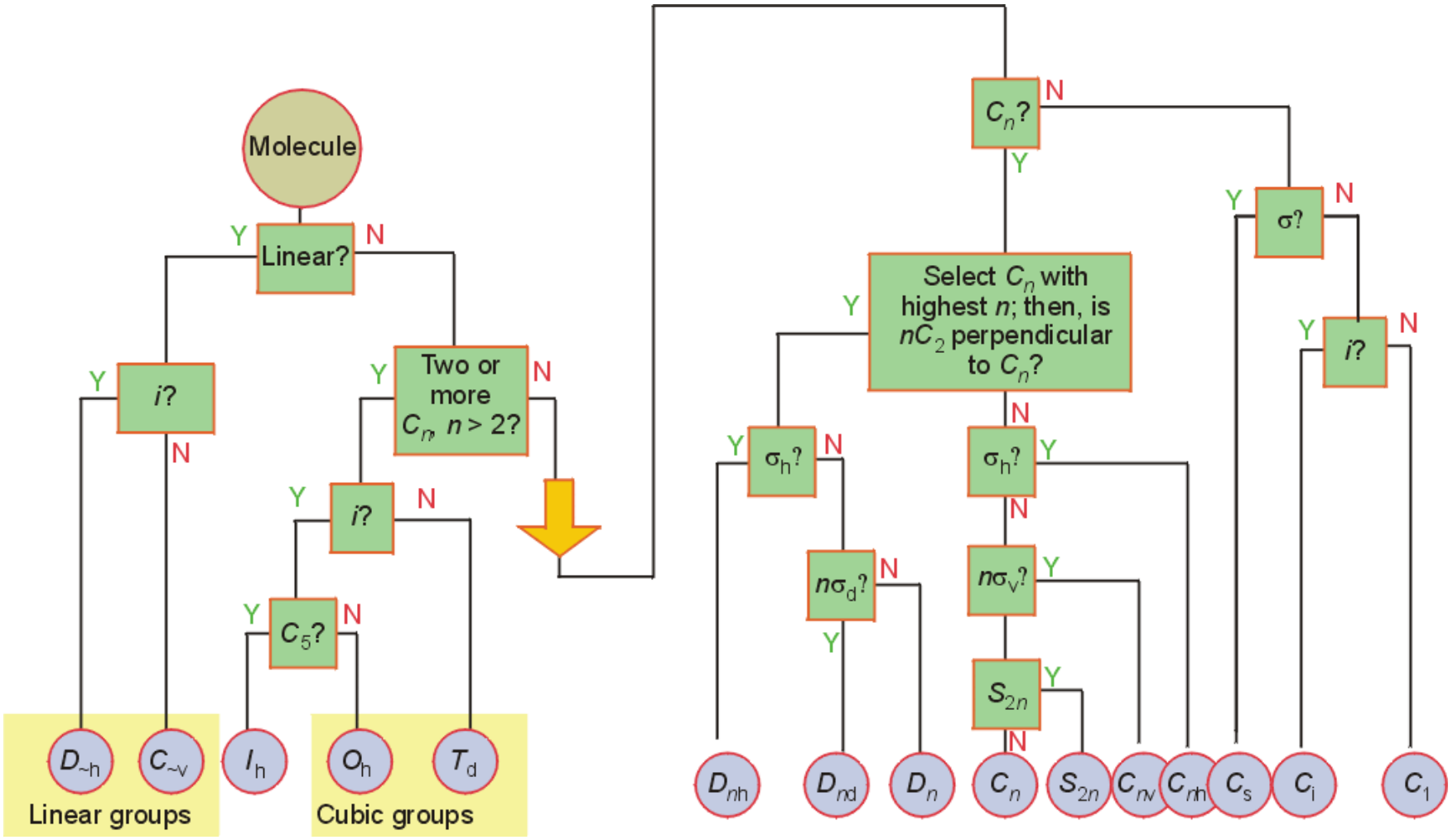
- first determine shape using Lewis Structure and VSEPR Theory
- next use models to determine which symmetry operations are present
- then use the flow chart Figure 3.9, Pg. 81 text to determine the point group

Table 4.2 The composition of some common groups*

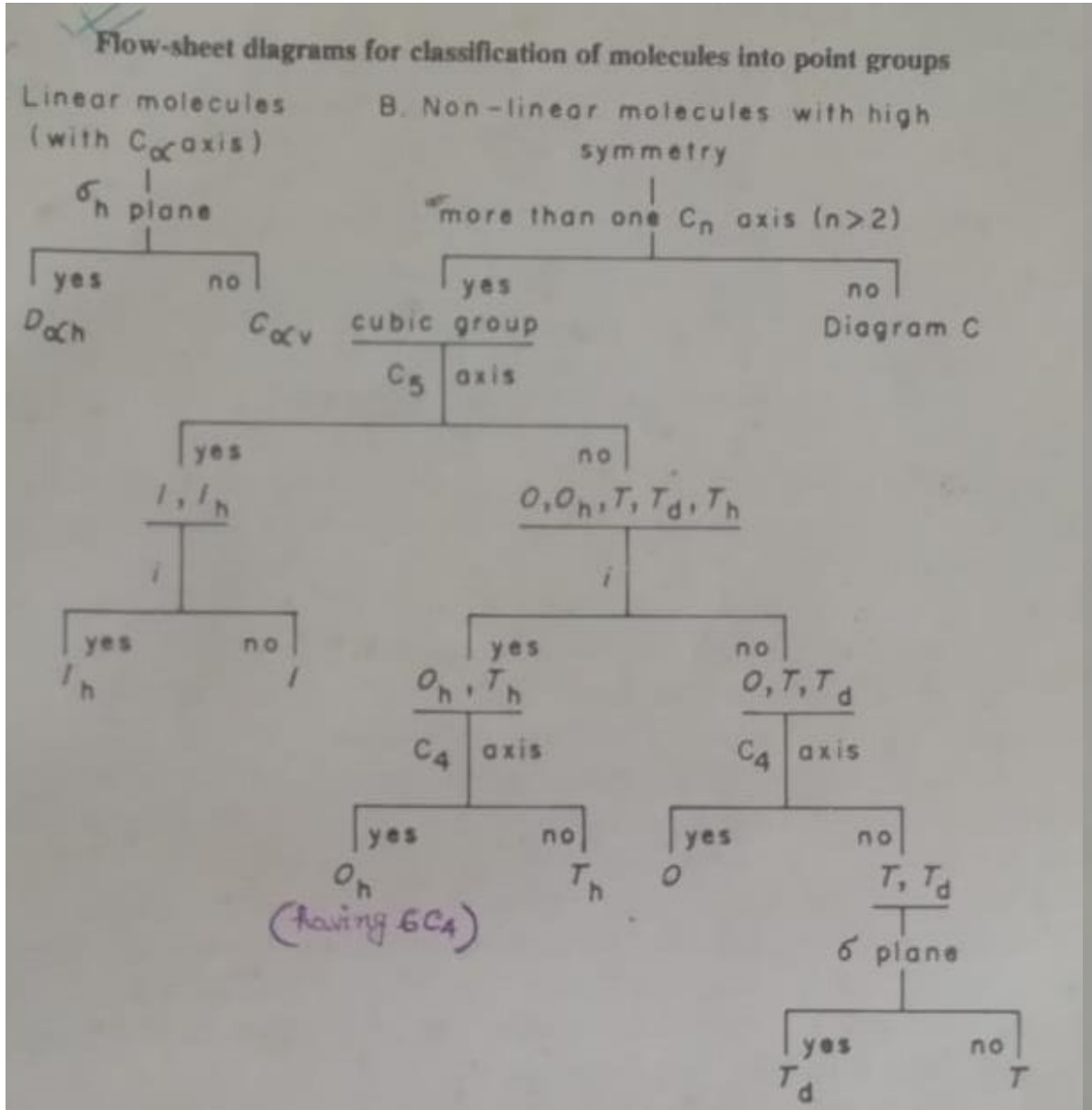
Point group	Symmetry elements	Shape	Examples
C_1	E		SiBrClFI
C_2	E, C_2		H_2O_2
C_s	E, σ		NHF_2
C_{2v}	$E, C_2, \sigma_v, \sigma_v$		H_2O, SO_2Cl_2
C_{3v}	$E, 2C_3, 3\sigma_v$		NH_3, PCl_3, $POCl_3$
$C_{\infty v}$	$E, C_2, 2C_\phi, \ldots \infty\sigma_v$		CO, HCl, OCS
D_{2h}	$E, C_2(x,y,z), \sigma(xy,yz,zx), i$		N_2O_4, B_2H_6
D_{3h}	$E, C_3, 3C_2, 3\sigma_v, \sigma_h, S_3$		BF_3, PCl_5
D_{4h}	$E, C_4, C_2, 2C_2', 2C_2'', i, S_4, \sigma_h, 2\sigma_v, 2\sigma_d$		XeF_4, *trans*-MA_4B_2
$D_{\infty h}$	$E, C_\infty, \ldots, \infty\sigma_v, i, S_\infty, \ldots, \infty C_2$		H_2, CO_2, C_2H_2
T_d	$E, 3C_2, 4C_3, 6\sigma_d, 4S_4$		CH_4, $SiCl_4$
O_h	$E, 6C_2, 4C_3, 3C_4, 4S_6, 3S_4, i, 3\sigma_h, 6\sigma_d$		SF_6

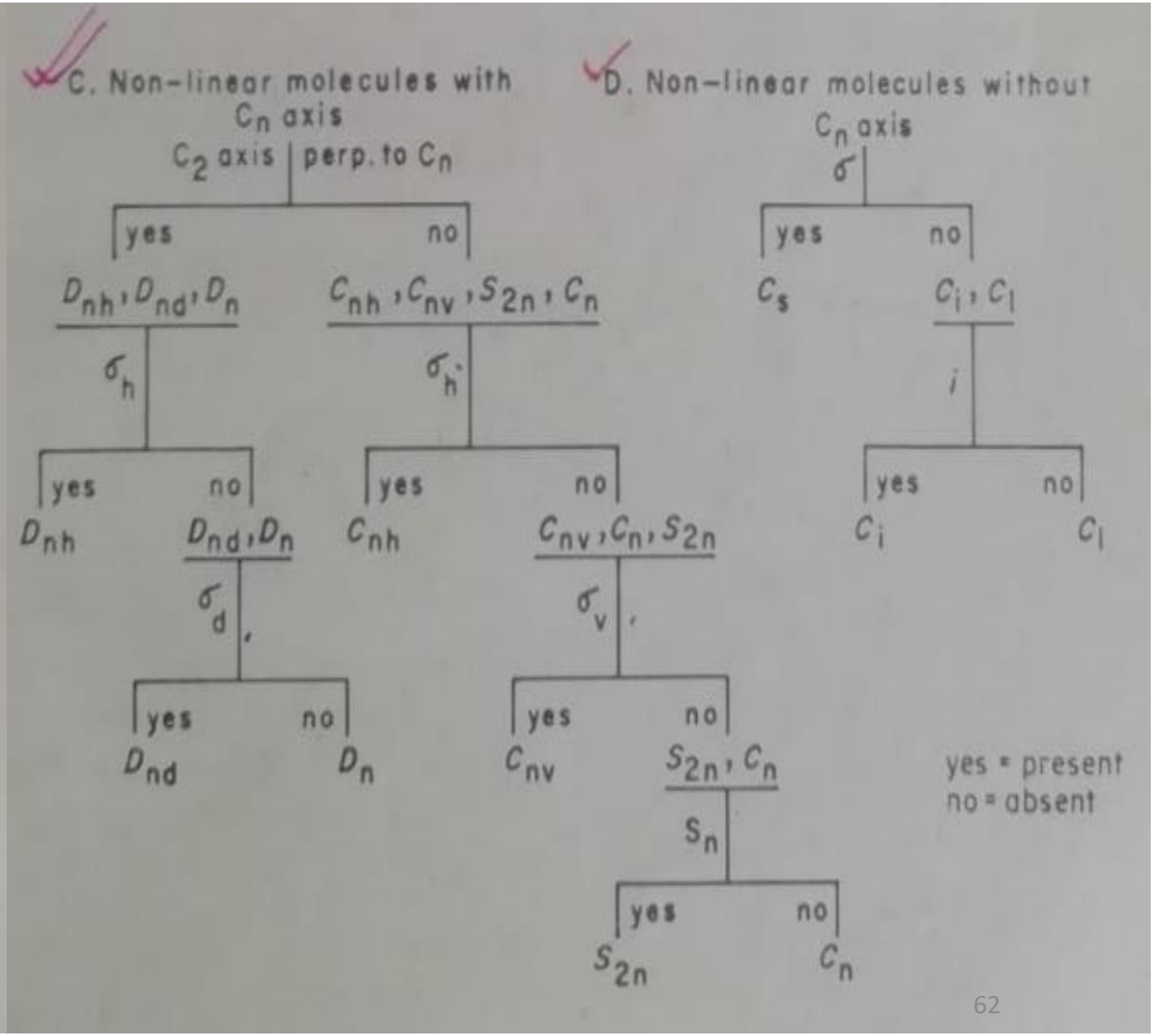
*Not all the elements of each group are listed, but enough are listed for unambiguous assignments to be made.

Decision Tree



Determination of symmetry point group

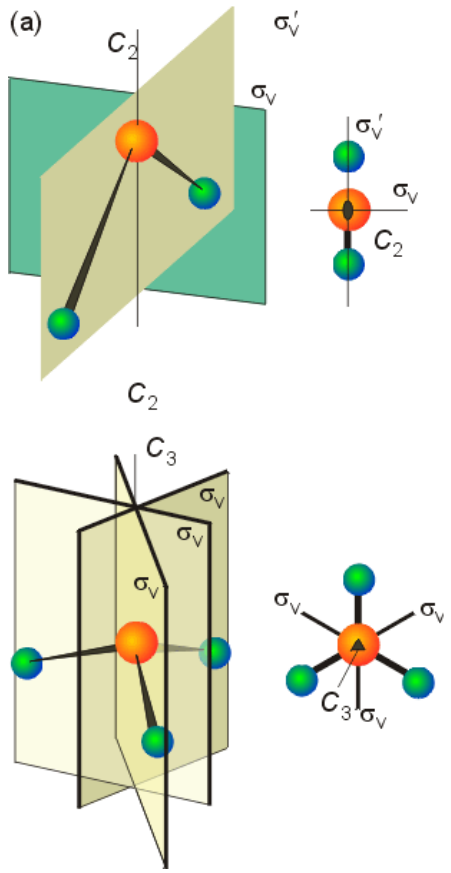


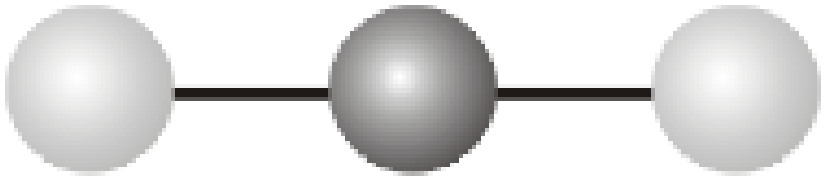


Selection of Point Group from Shape

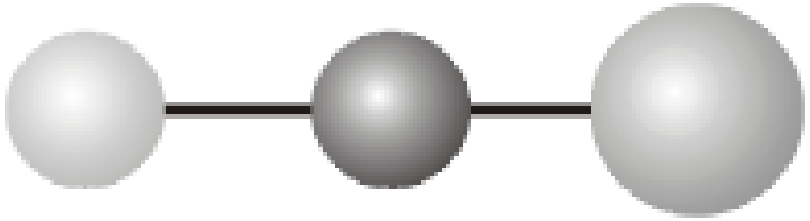
1. determine the highest axis of rotation
2. check for other non-coincident axis of rotation
3. check for mirror planes

H_2O and NH_3

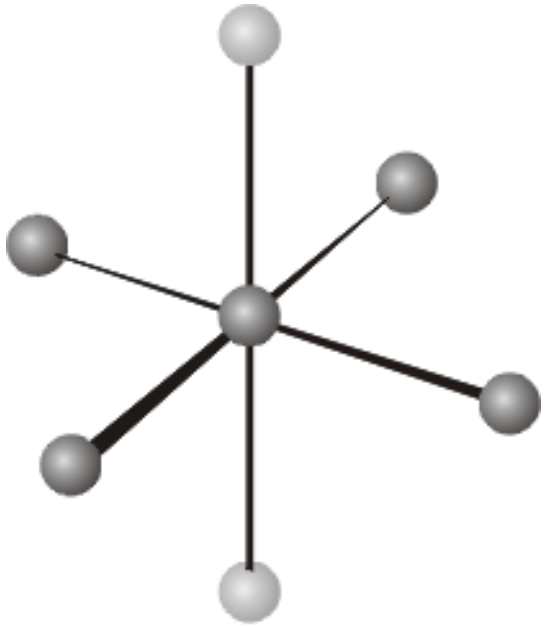

(a)
C_2
σ_v'
σ_v
σ_v'
σ_v
C_2
C_2
C_3
σ_v
σ_v
σ_v
σ_v
σ_v
C_3
σ_v



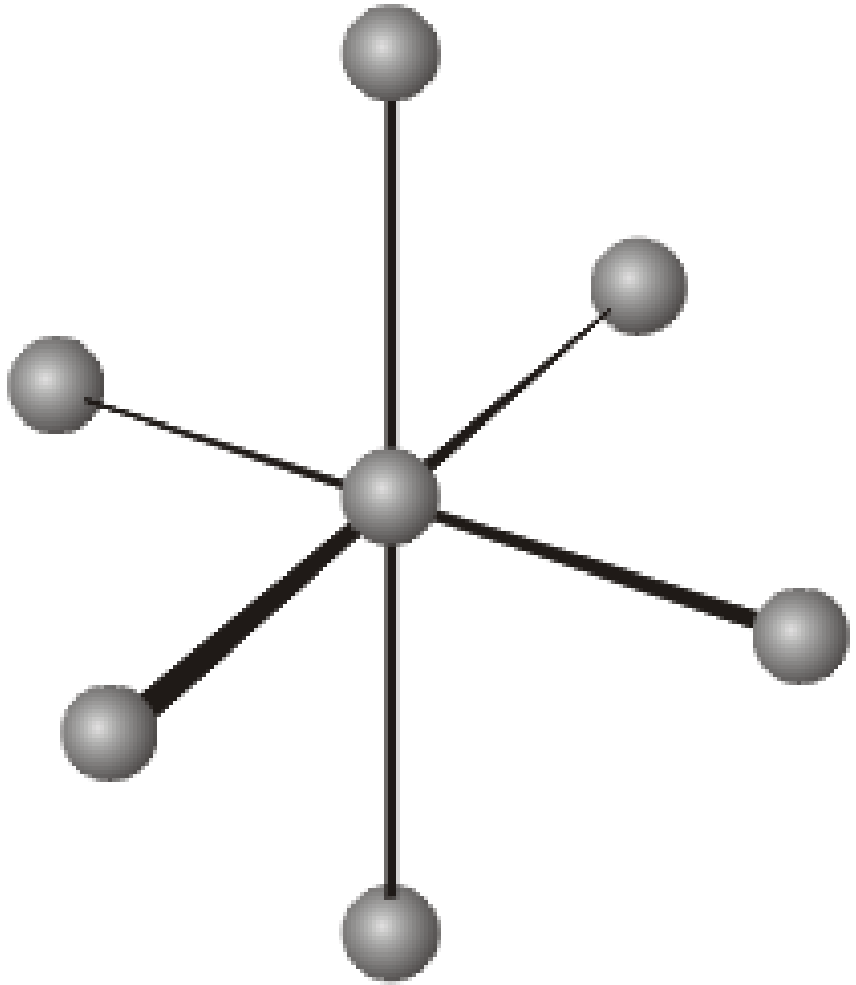
3 $D_{\infty h}$



4 $C_{\infty v}$



8 $[MX_4Y_2]$, D_{4h}

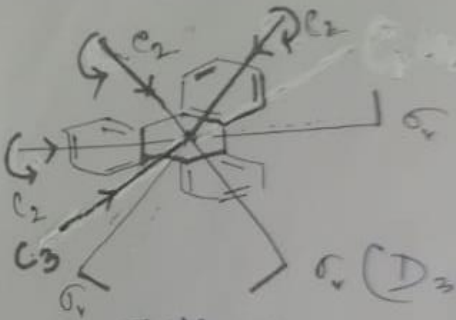


9 $[MX_6]$, O_h

$AC_3 + 3C_2 + 6\sigma_d + 3S_4 + i$

Comparable with methane as C_4, E, C_3, $8C_3$ are equivalent.

Adamantane



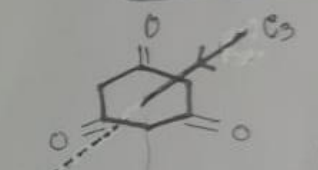
C_3 — Rest are σ_d

$+3C_2 + 3\sigma_d + \frac{2}{3} + E + h$

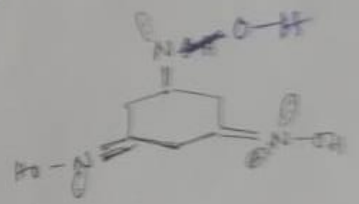
The three σ_d are along three C_2 axes

σ_v (D_{3h})

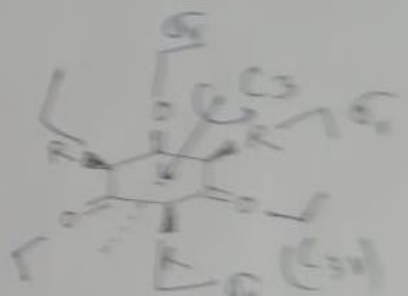
Triphenylene



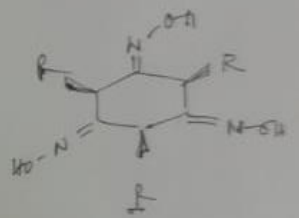
$C_3 + 3C_2 + 3\sigma_d + \sigma_h$



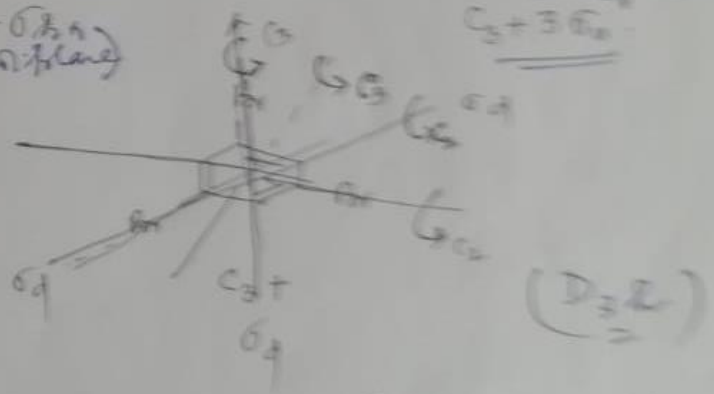
$C_3 + \sigma_h$ (molecular)



$C_3 + 3\sigma_d$

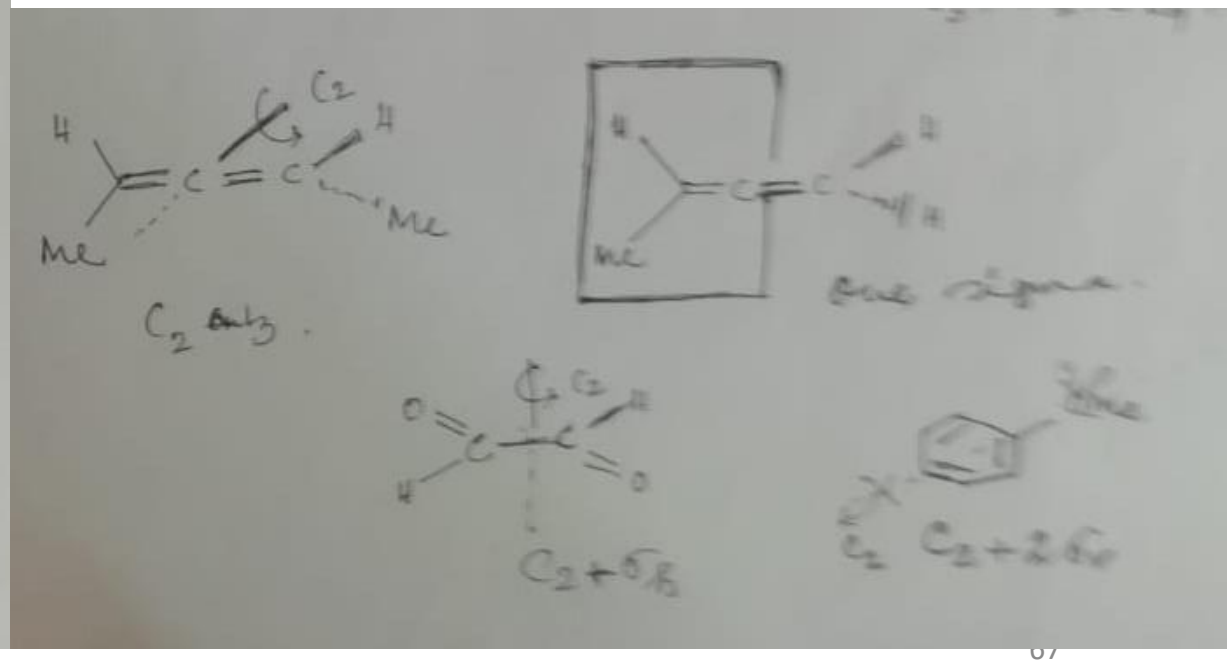


C_3 axis only.



(D_{3h})

$C_3 + 3C_2 + 3\sigma_d + \sigma_h$



C_2 only.

Me

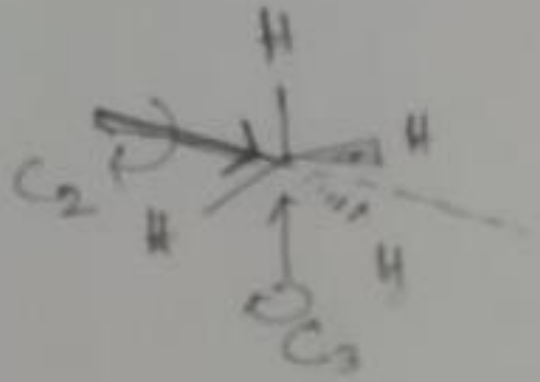
Me

Me

one sigma.

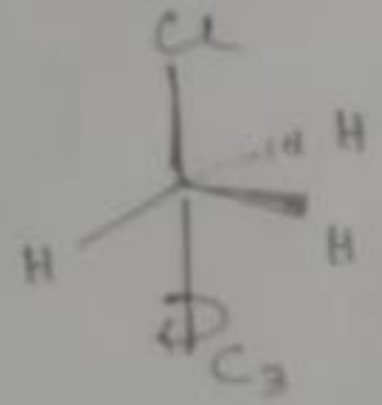
$C_2 + \sigma_h$

$C_2 + 2\sigma_d$



$4C_3, 3C_2, 6\sigma_d$ (each containing two C–H bonds)

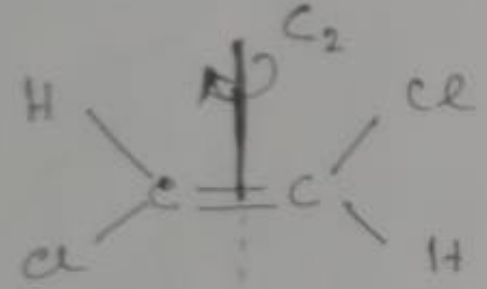
(T_d)



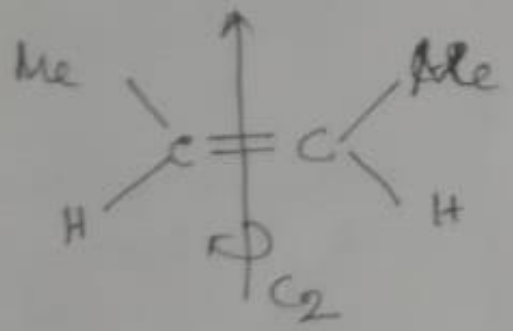
$1C_3$
$3\sigma_v$ (C_{3v})

no C_n
one σ
(Pt gr C_s)

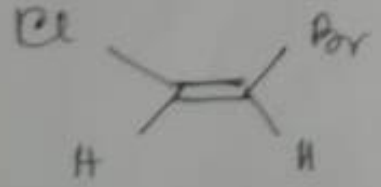
no symmetry element
(Pt gr = C_1)

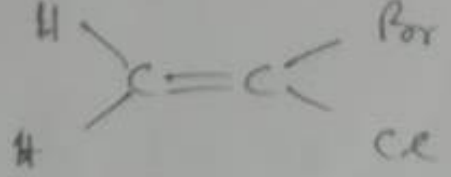


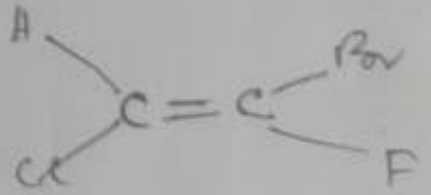
C_2, σ_h (C_{2h})



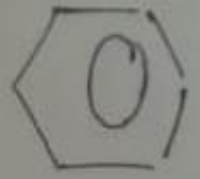
$C_2 + 2\sigma_v$ (C_{2v})



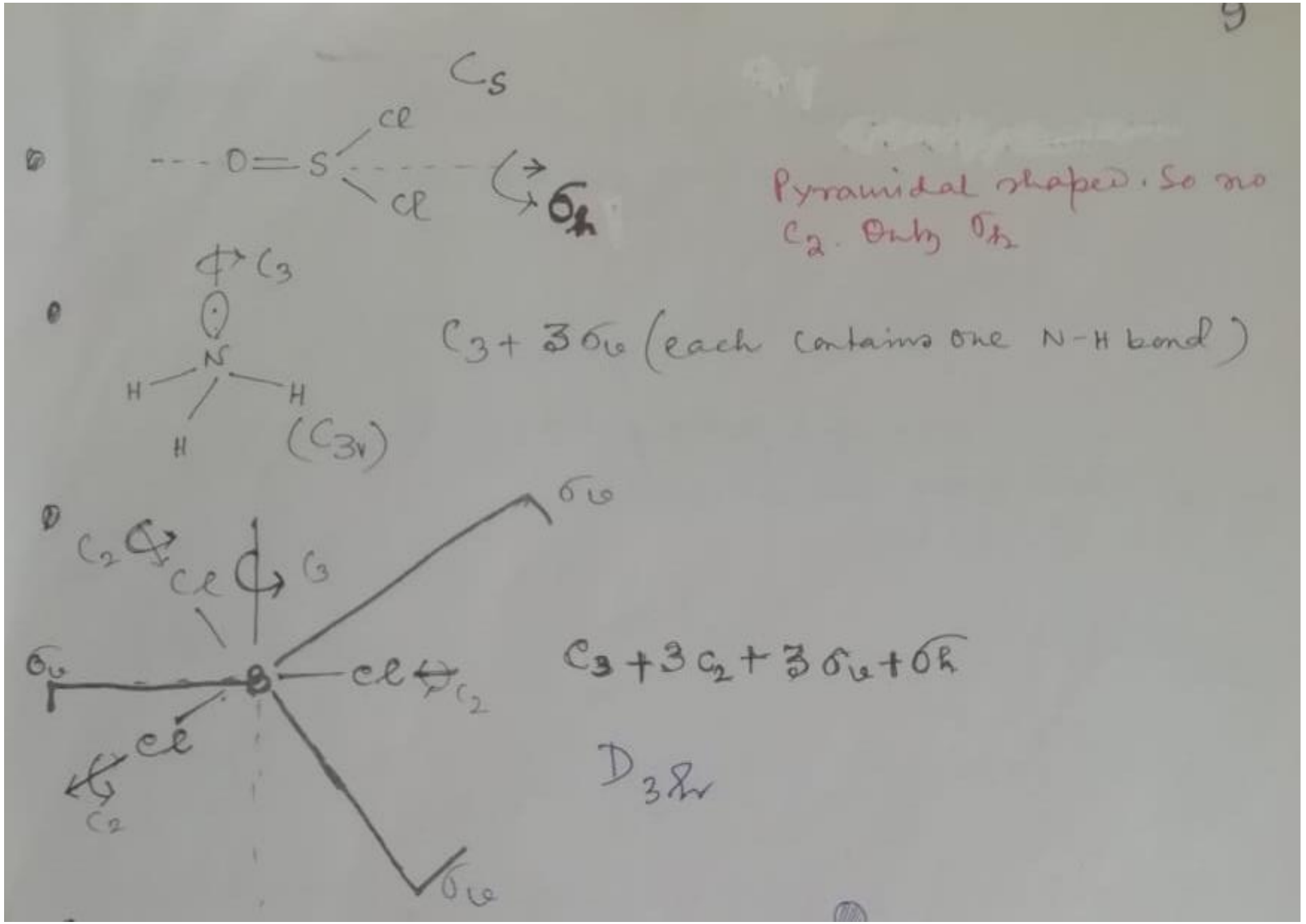


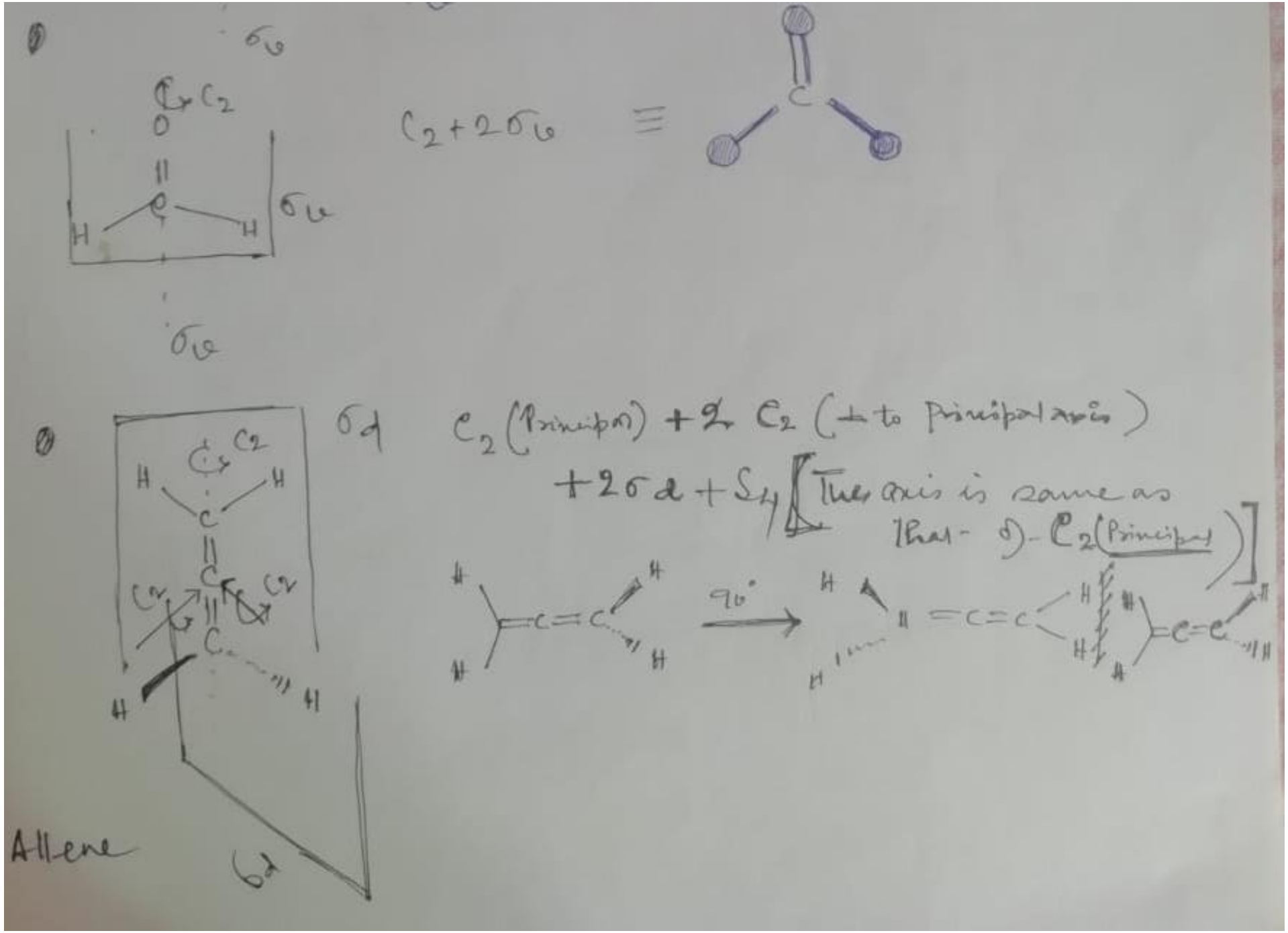


Only σ is present i.e the molecular plane.



$C_6 + 6C_2 + 6\sigma_v + \sigma_h$ (D_{6h})


C_s
O
S
Cl
Cl
σ_h
Pyramidal shaped. So no C_2. Only σ_h
C_3
N
H
H
H
(C_{3v})
$C_3 + 3\sigma_v$ (each contains one N-H bond)
C_2
Cl
C_3
σ_v
σ_v
Cl
C_2
Cl
C_2
σ_v
$C_3 + 3C_2 + 3\sigma_v + \sigma_h$
D_{3h}


C2
H
H
C2 + 2σv ≡
Allene