COMMONWEALTH OF AUSTRALIA

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Molecular Symmetry

Lecture 2

Interparticle Interactions

Molecular Symmetry

Lecture 3

Symmetry Elements

Point Groups

Lecture 4

Periodic Translation

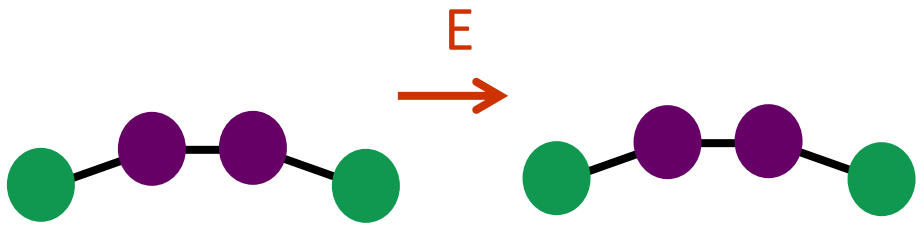
Unit Cells

Bravais Lattices

Crystal Symmetry Elements

The Identity Operator (E)

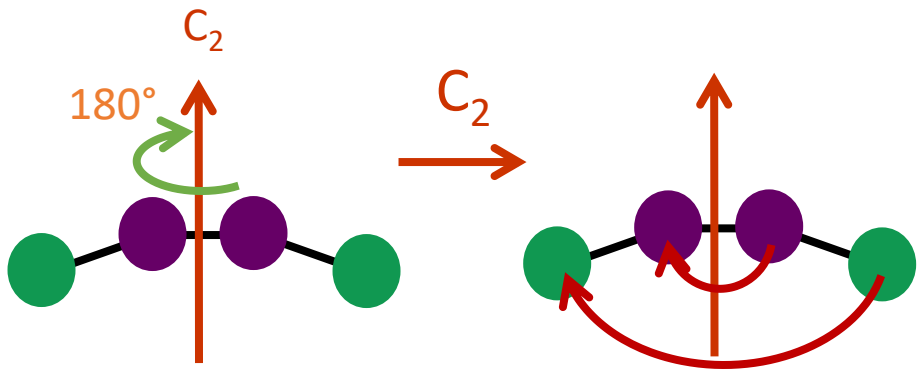
E is the identity operation where we ‘do nothing’



Every molecule has the E operation

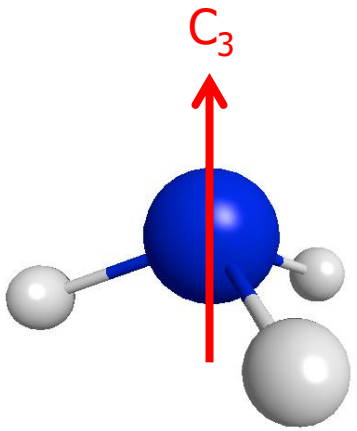
Rotation (C_n)

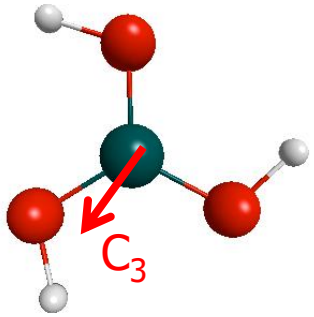
C_n is a rotation through $2\pi/n$ (or $360°/n$) about a fixed axis, i.e., the molecule has an n-fold rotation

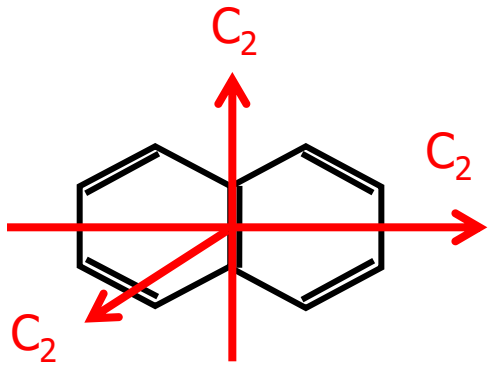


Rotation (C_n)

An axis about which an n-fold rotation by 360°/n gives an identical configuration.



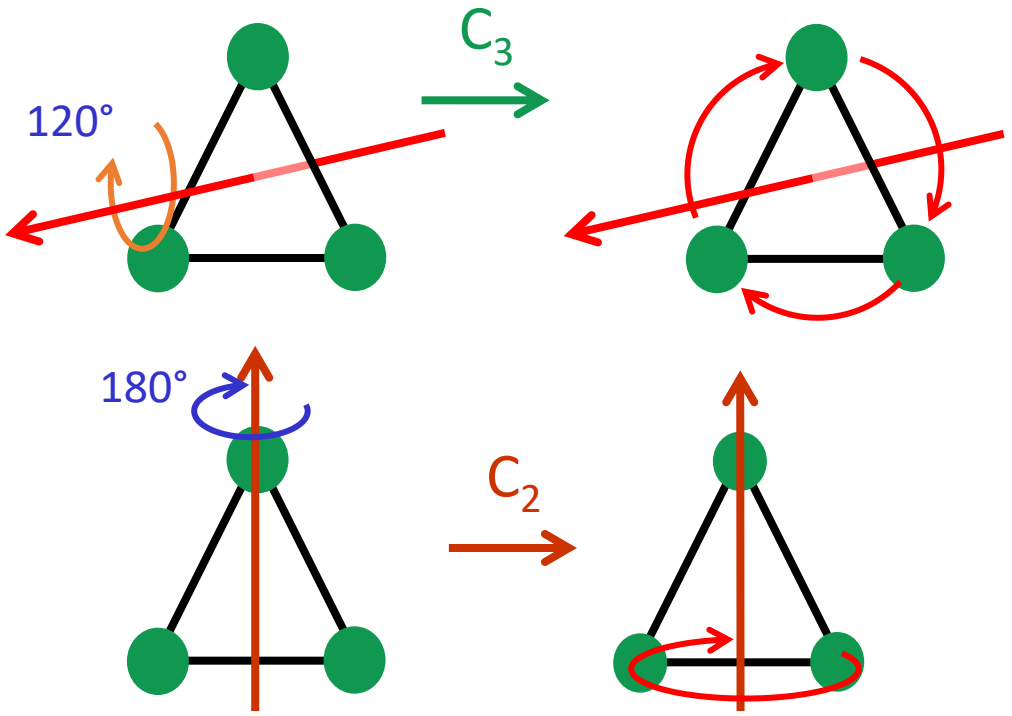




Rotation (C_n)

Some molecules have more than one axis of rotation.

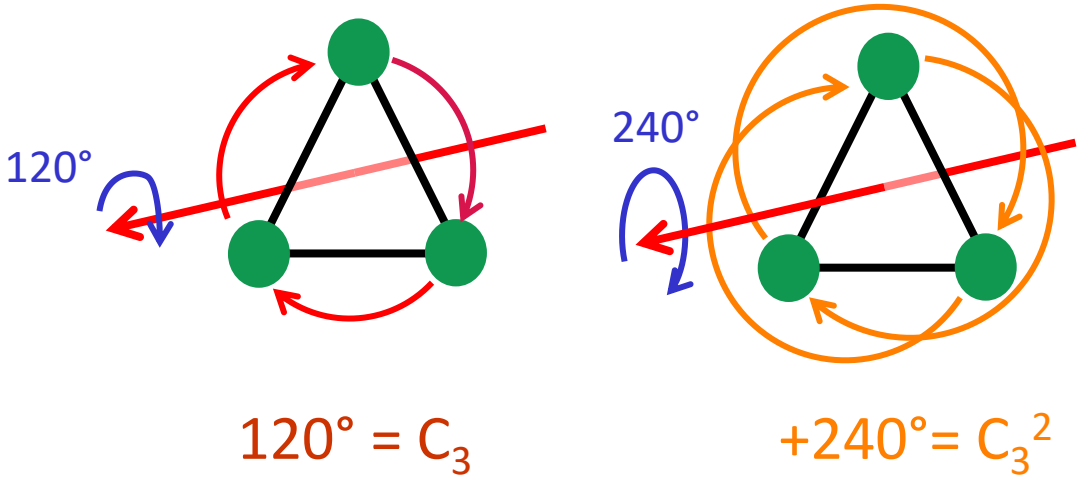
The **Principal Axis** is the axis with the highest n (here, C_3). By convention it is assigned as the z-axis.



Rotation (C_n)

Each C_n generates more than one operation.

There are (n-1) possible rotations about an n-fold (C_n) axis



120° = C_3

+240°= C_3^2

There are <u>two</u> C_3 rotations:

C_3 & C_3^2

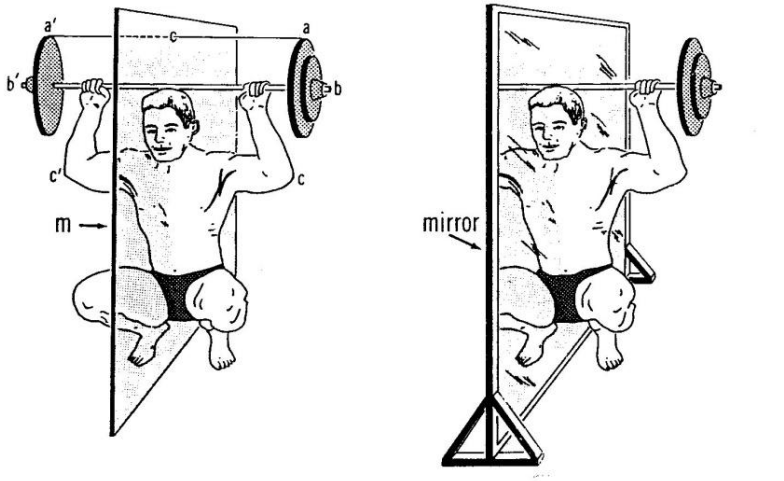
Also e.g.,

$C_4^2 \equiv C_2$

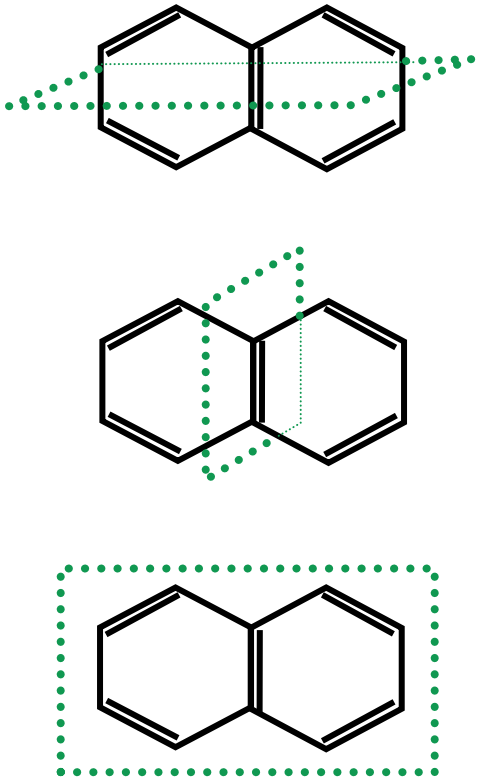
$C_n^n \equiv E$

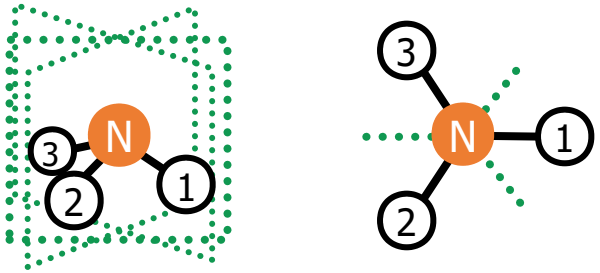
Reflection (Mirror) Planes

An imaginary plane where atoms on one side of the plane are an exact reflection of the other side.



Gray-shaded plane m is a plane of symmetry with respect to the external features of the weight lifter because he is composed of pairs of identical points, a' and a, b' and b, c' and c, and so on, which are at equal but opposite distances along perpendiculars ($a'a$, $b'b$, $c'c$) to plane m.

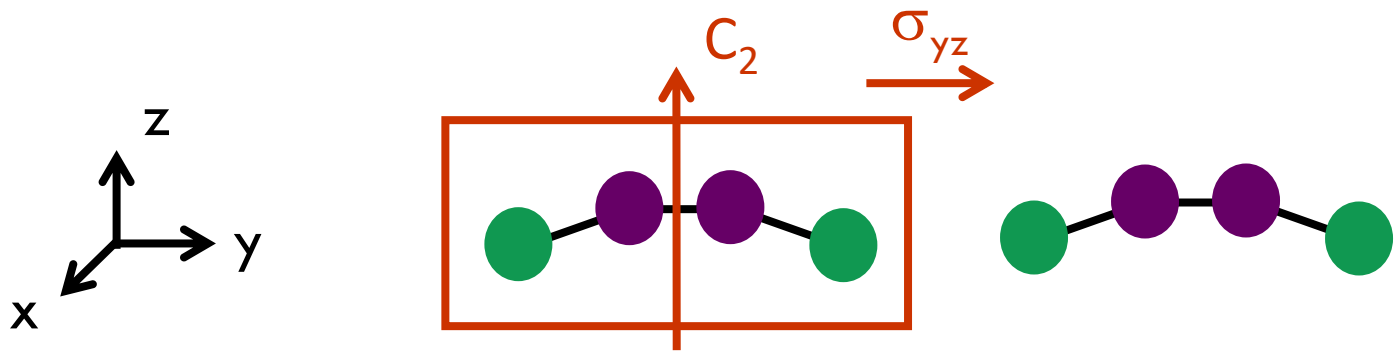




Reflection (σ)

σ corresponds to reflection of all the atoms through a mirror plane.

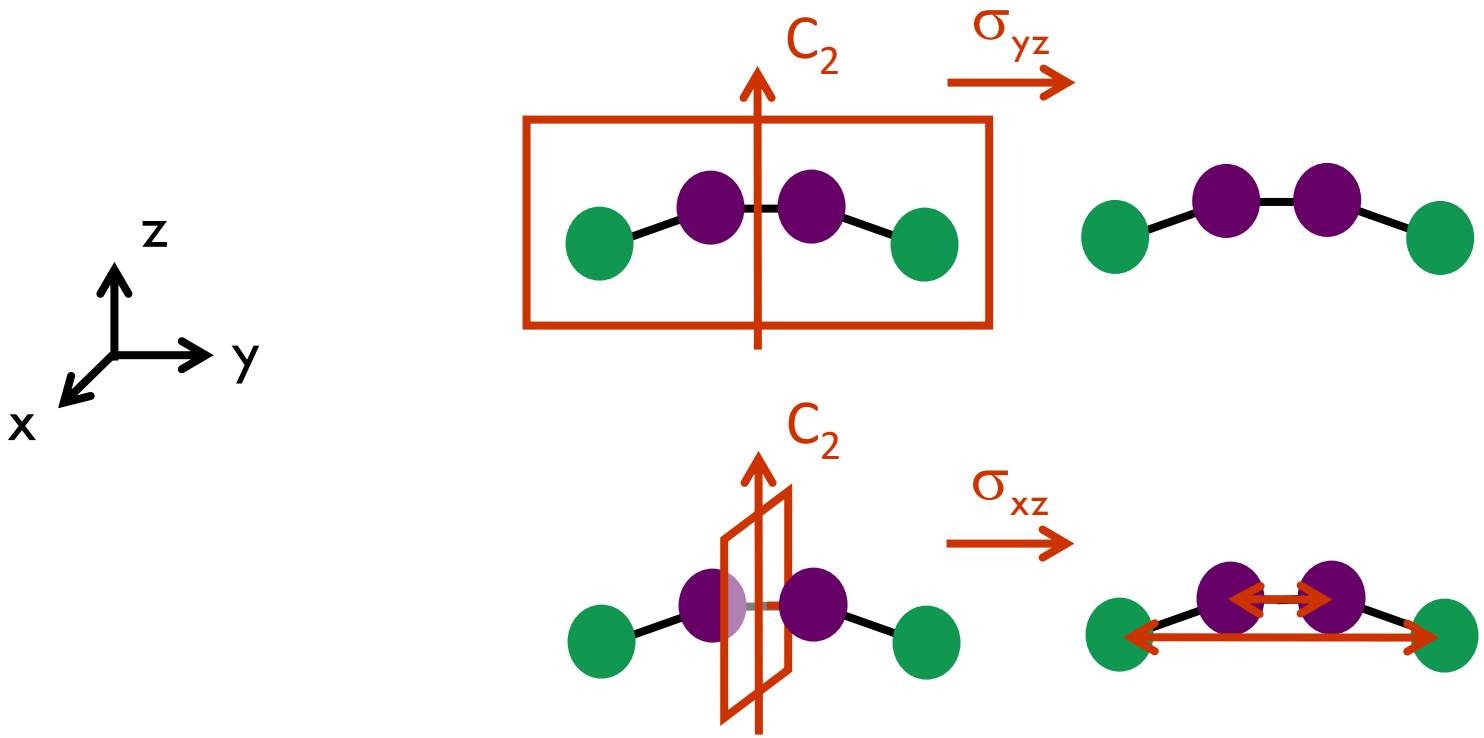
σ can be identified by the Cartesian coordinate plane in which it lies. E.g., σ_{yz} represents a mirror plane that coincides with the xy-Cartesian coordinate plane.



Recall that by convention the principal axis is assigned as the z-axis.

Reflection (σ)

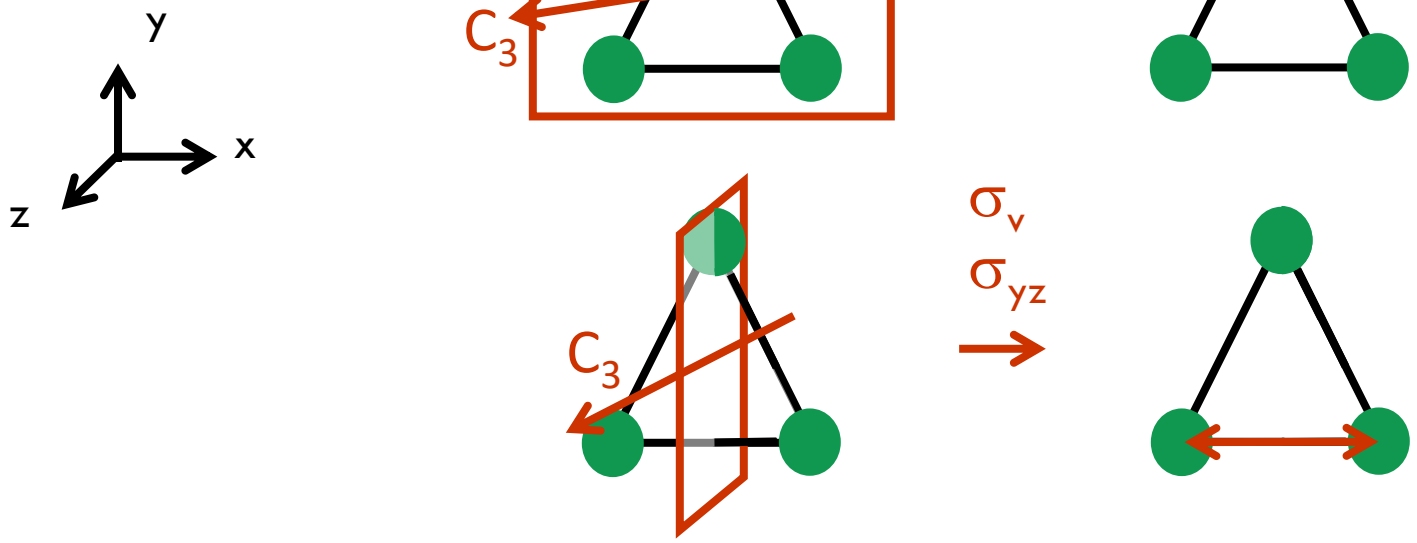
Some molecules have more than one mirror plane.



Reflection (σ)

Vertical mirror plane: σ_v (v for vertical) contains the principal axis.

Horizontal mirror plane: σ_h (h for vertical) is perpendicular to the principal axis.



Recall that by convention the principal axis is assigned as the z-axis.

Worksheet Model 1: Finding all reflection planes

1. Identify the reflection planes in the molecules below.

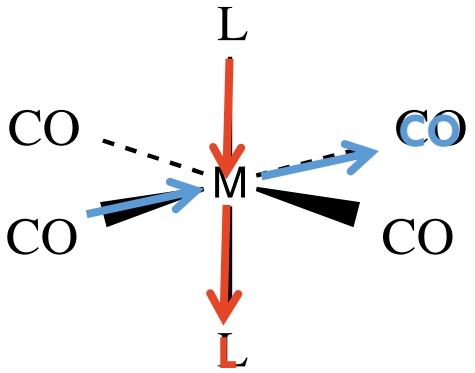
(a)	(b)	(c)
 $C_3H_3^+$	 $C_5H_5^-$	 C_6H_6

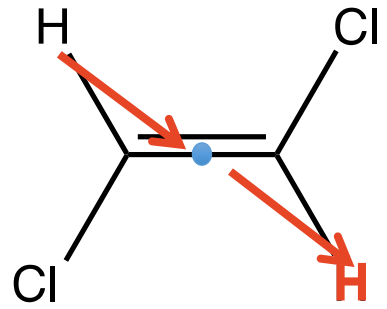
Inversion (i)

A point of inversion, or a Centre of Symmetry (i), is a point through which every atom can move in a straight line to an identical atom on the other side of the point at the same distance.

Inversion occurs through a point, called the inversion centre

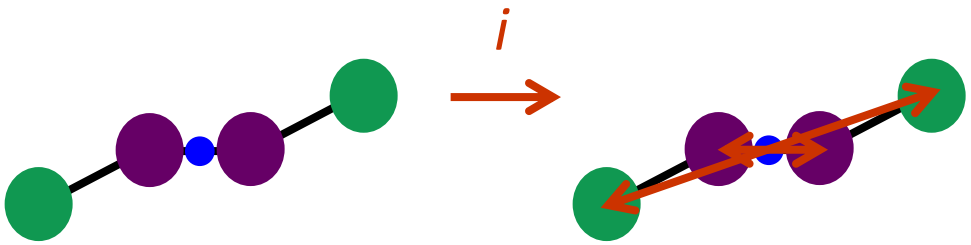
The inversion centre can be on an atom or on a bond.





Inversion (i)

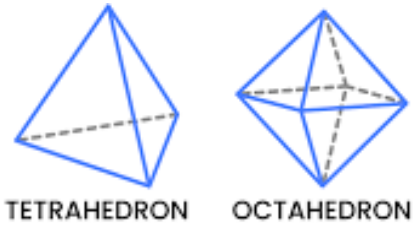
Inversion maps all atoms onto the point that lies equidistant from, but on the other side of, the inversion centre (or centre of symmetry).



Inversion goes through the centre of inversion

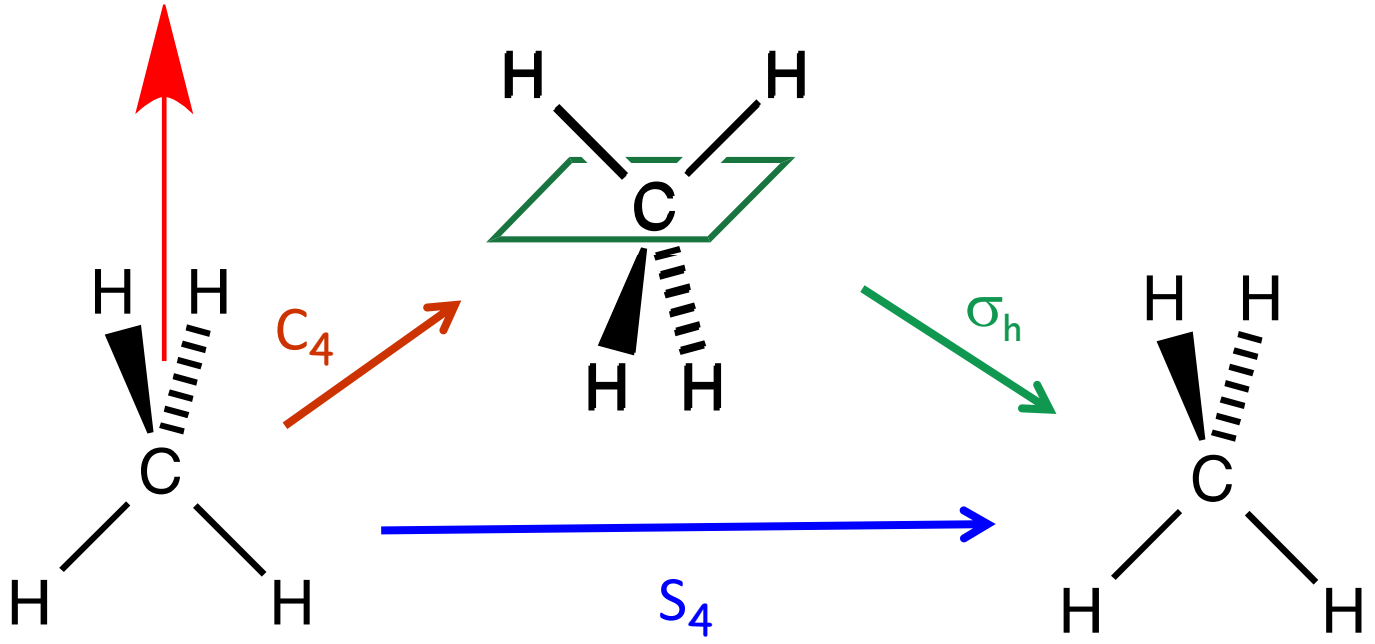
An inversion centre can **only** be at the centre-of-mass of a molecule

An octahedron has a centre of inversion, a tetrahedron does not!



Improper Rotation (S_n)

An improper rotation involves two steps. S_n consists of <u>rotation</u> through 360°/n (C_n) followed by <u>reflection</u> in a perpendicular mirror plane (σ_h), or vice versa. I.e., S_n is a commutative property; $S_n \equiv \sigma_h \times C_n \equiv C_n \times \sigma_h$



Improper Rotation (S_n)

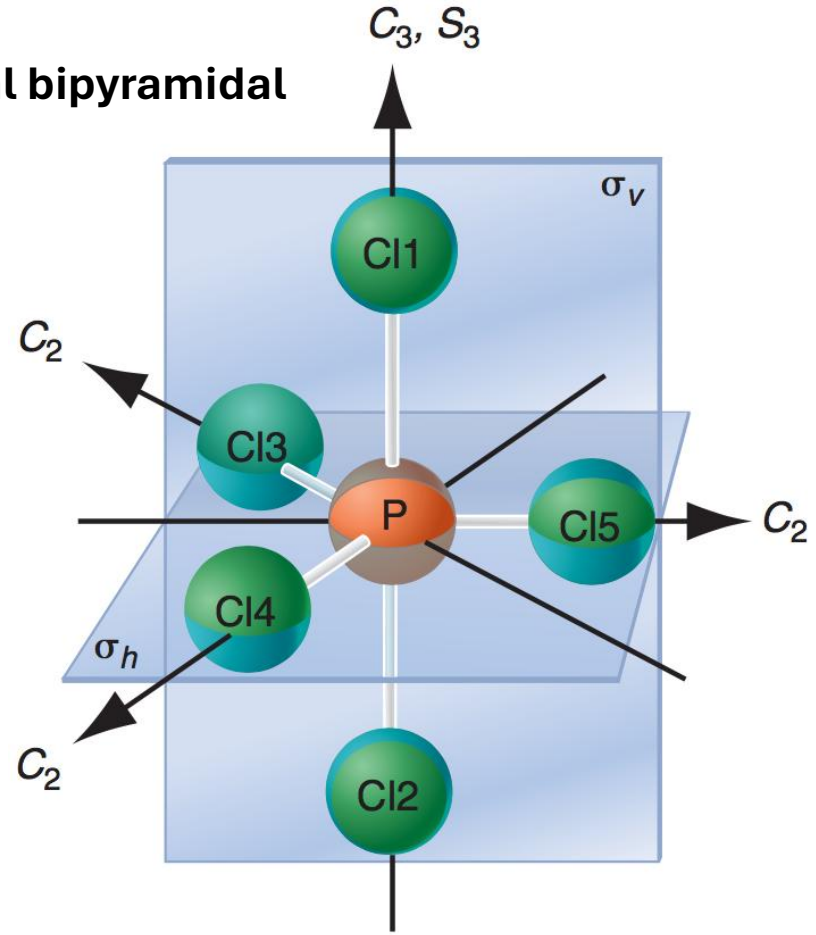
Use the space below to show that $S_1 \equiv \sigma$ and $S_2 \equiv i$

Therefore, all symmetry operations are either proper or improper rotation

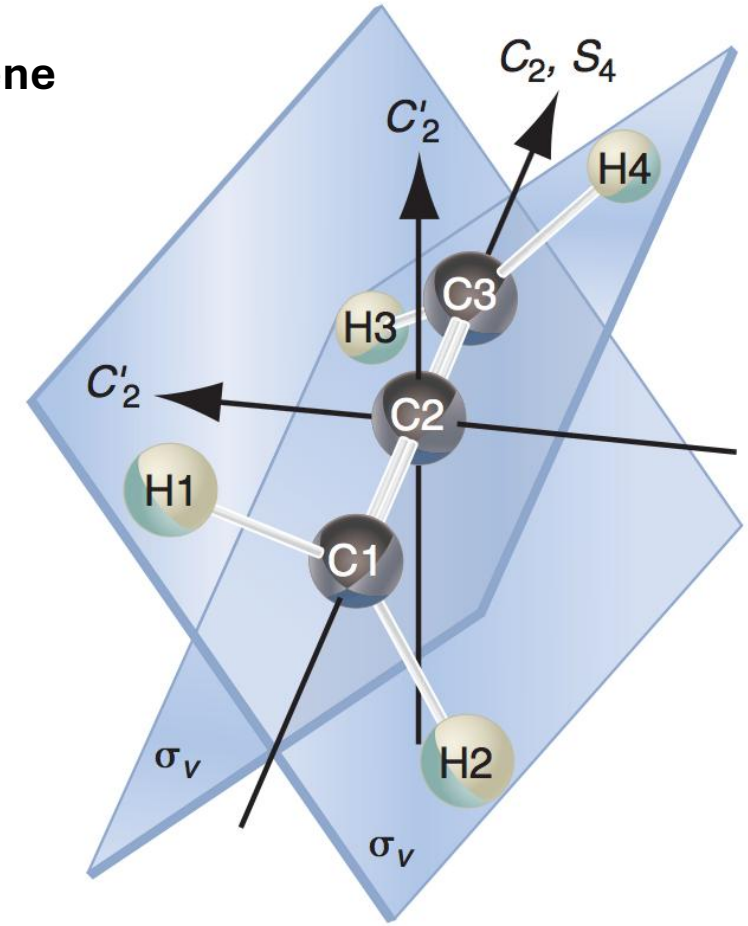
Improper Rotation (S_n)

If a molecule has C_n and σ_h then it will also have S_n.

PCl_5: trigonal bipyramidal

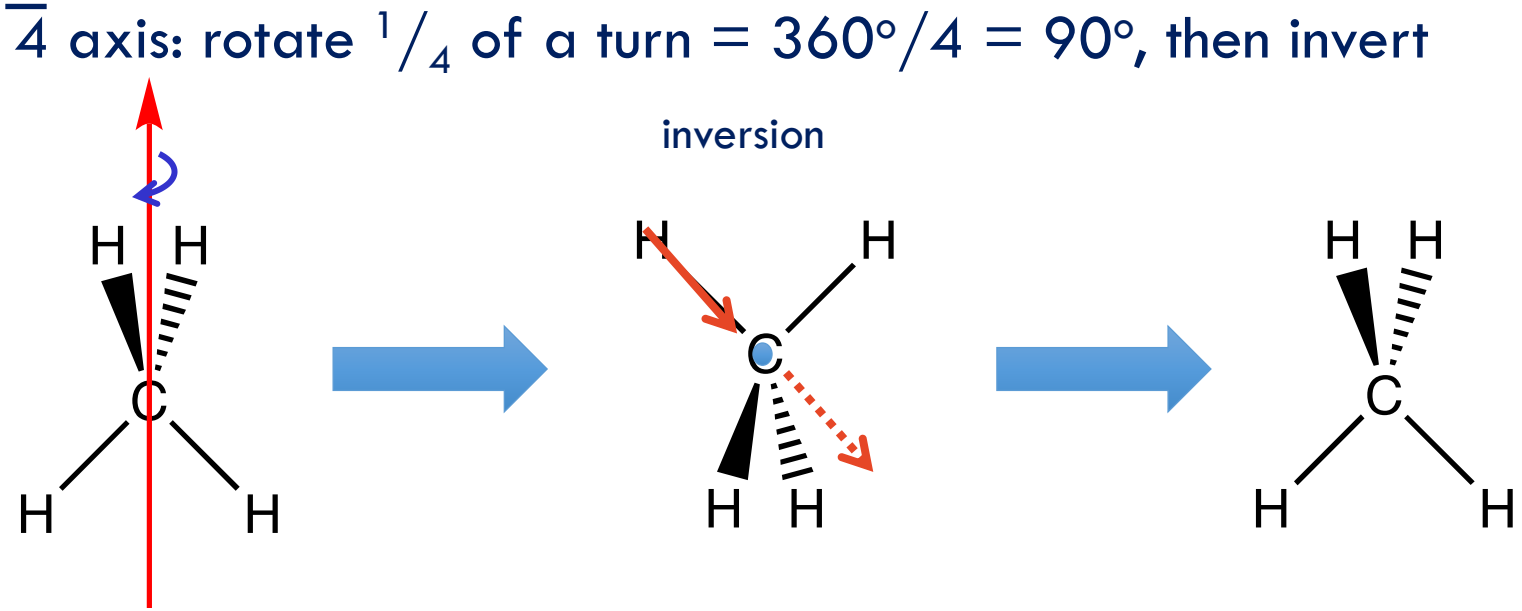


Allene



Inversion axes ($\bar{n}$)

An inversion axis involves two steps. An inversion axis ($\bar{n}$) is an axis which combines an n-fold rotation with inversion through a centre point.



Many of these are redundant (E, C_n, σ, i and S_n fully define the symmetry) and so are not commonly listed, but these can be important for crystal symmetry (see lectures 4 & 5)

Symmetry Operations

Proper Operations:

- The identity, E
- Pure rotations, C_n

Proper operations retain handedness.

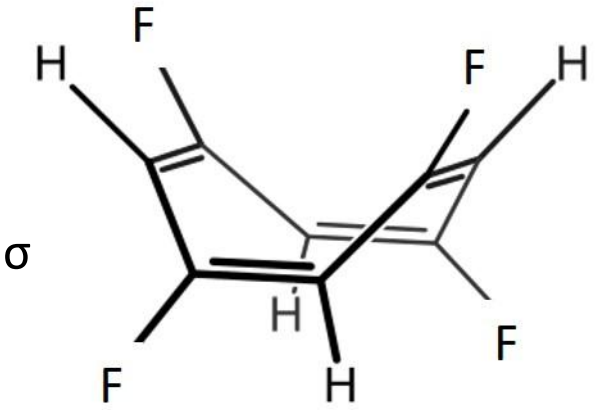
Improper Operations:

- Involve a reflection or inversion

Improper operations change handedness:

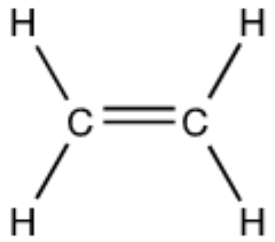
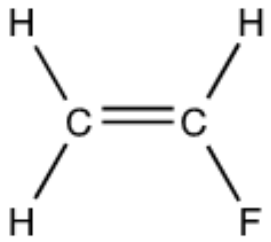
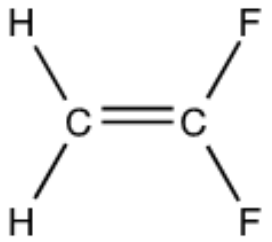
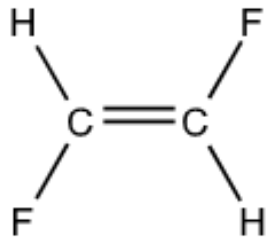
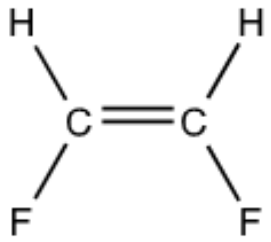
- A molecule with ***any*** improper symmetry elements ***cannot*** be chiral.
- A chiral molecule ***cannot*** have ***any*** improper symmetry elements.

You might have learned that a molecule is chiral if it doesn't have σ and *i*, but there are exceptions, such as 1,3,5,7- tetrafluorocyclooctatetraene, which lacks σ and *i* but is achiral because of its S_4 axis)



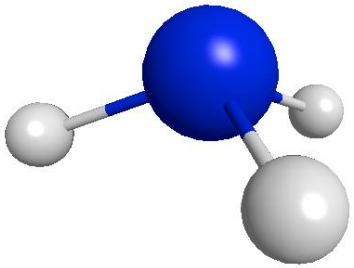
Worksheet Model 2: Finding all symmetry elements

1. Write down the set of symmetry operations possessed by the molecules below.

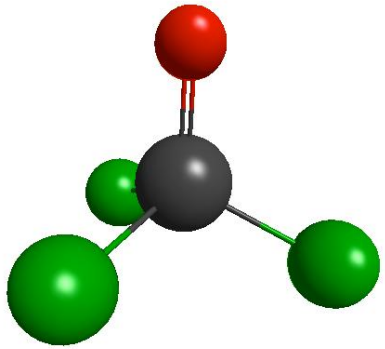
(a) 	(b) 	(c) 
(d) 	(e) 	

Classifying molecules according to their symmetry

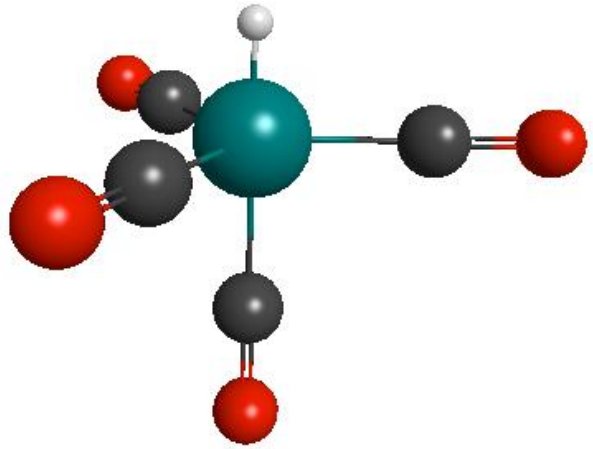
Molecules belong to same **point group** if they're symmetric in the same way:



NH_3



$POCl_3$



$HCo(CO)_4$

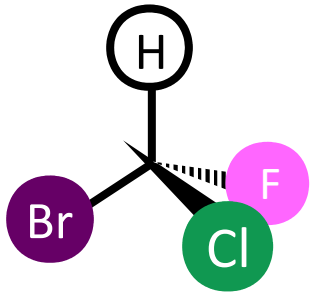
If we know a molecule's point group, we know all its symmetry operations, and much more …

Low Symmetry Point Groups

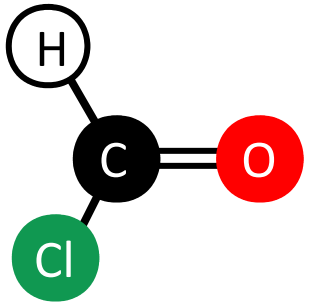
C_1 : No operations apart from E, e.g. CHFClBr, Biomolecules

C_s : Only a single mirror plane, e.g. HClC=O

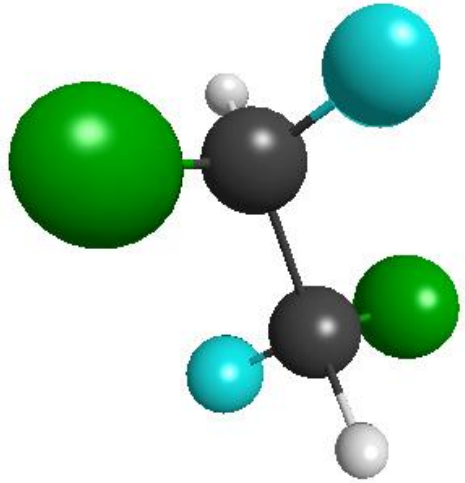
C_i : Only a centre of inversion, e.g. 1,2-dichloro,1,2-difluoroethane



CHFClBr (C_1)



HClC=O (C_s)



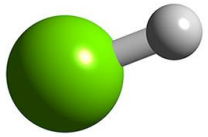
1,2-dichloro,1,2-difluoroethane (C_i)

Any planar molecule must possess at least C_s symmetry.

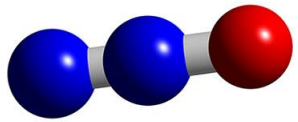
Linear Point Groups

$C_{\infty v}$: Linear molecules without a centre of symmetry (inversion)

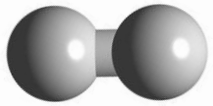
$D_{\infty h}$: Linear molecules with a centre of symmetry (centre of inversion)



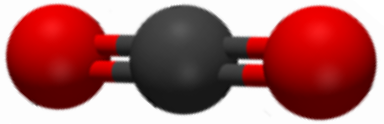
HCl ($C_{\infty v}$)



N_2O ($C_{\infty v}$)



H_2 ($D_{\infty h}$)



CO_2 ($D_{\infty h}$)

High Symmetry Point Groups

Multiple high order C_n axes

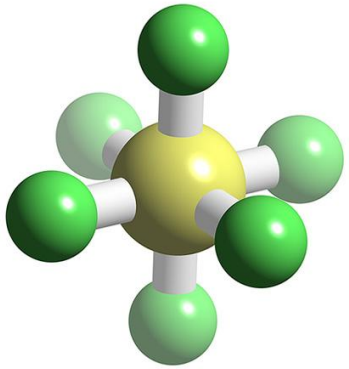
I_h : Icosahedron

O_h : Octahedron

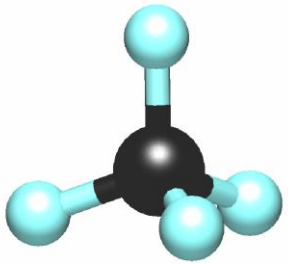
T_d : Tetrahedron



C_{60} (I_h)



SF_6 (O_h)



CH_4 (T_d)

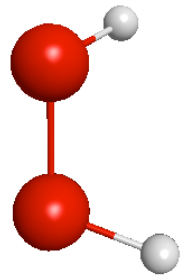
Cyclic Point Groups

One C_n axis of order $n \geq 2$:

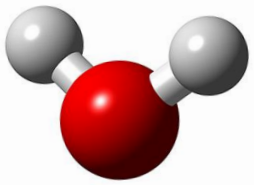
C_n: only C_n axis

C_{nv}: with n σ_v mirror planes each containing the principal axis

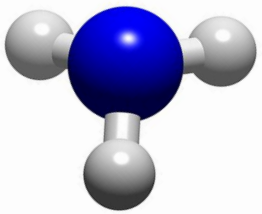
C_{nh}: with a σ_h mirror plane



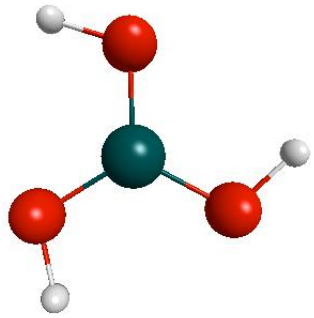
H_2O_2 (C_2)



H_2O (C_{2v})



NH_3 (C_{3v})

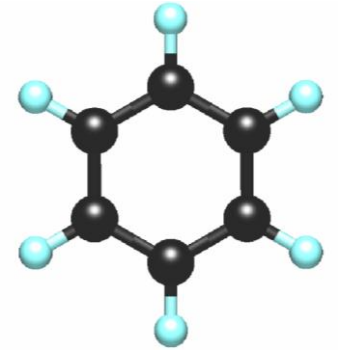


$B(OH)_3$ (C_{3h})

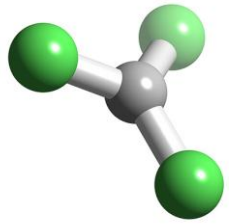
Dihedral Point Groups

D_{nh} : As for C_{nv} but with an additional mirror plane perpendicular to the principal C_n axis (and n additional C_2 axes perpendicular to C_n)

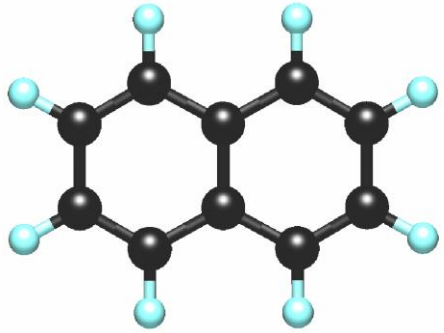
D_{nd} : As for C_{nv} but with n additional C_2 axes perpendicular to the principal C_n axis



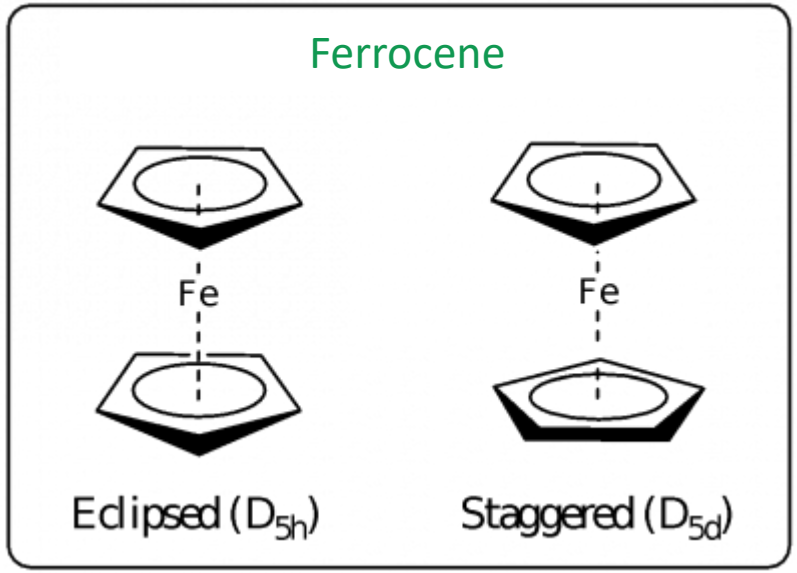
Benzene (D_{6h})



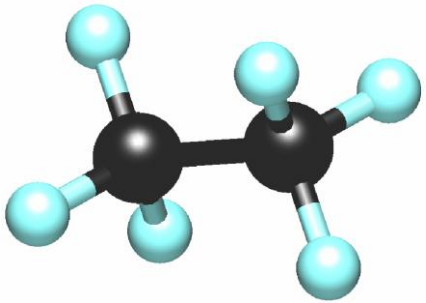
BF_3 (D_{3h})



Naphthalene (D_{2h})



Staggered Ethane (D_{3d})

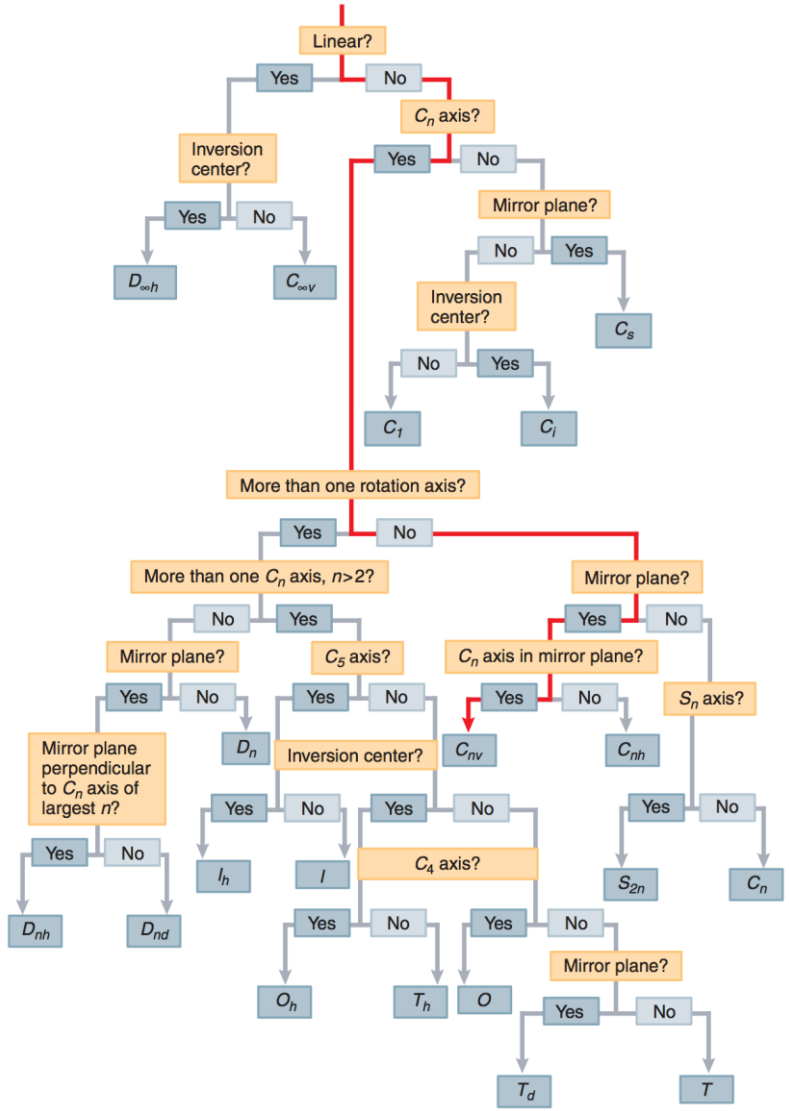


Determining Point Groups (the hard way)

Flow Charts:

- This one is in some textbooks and is quite complex to use…

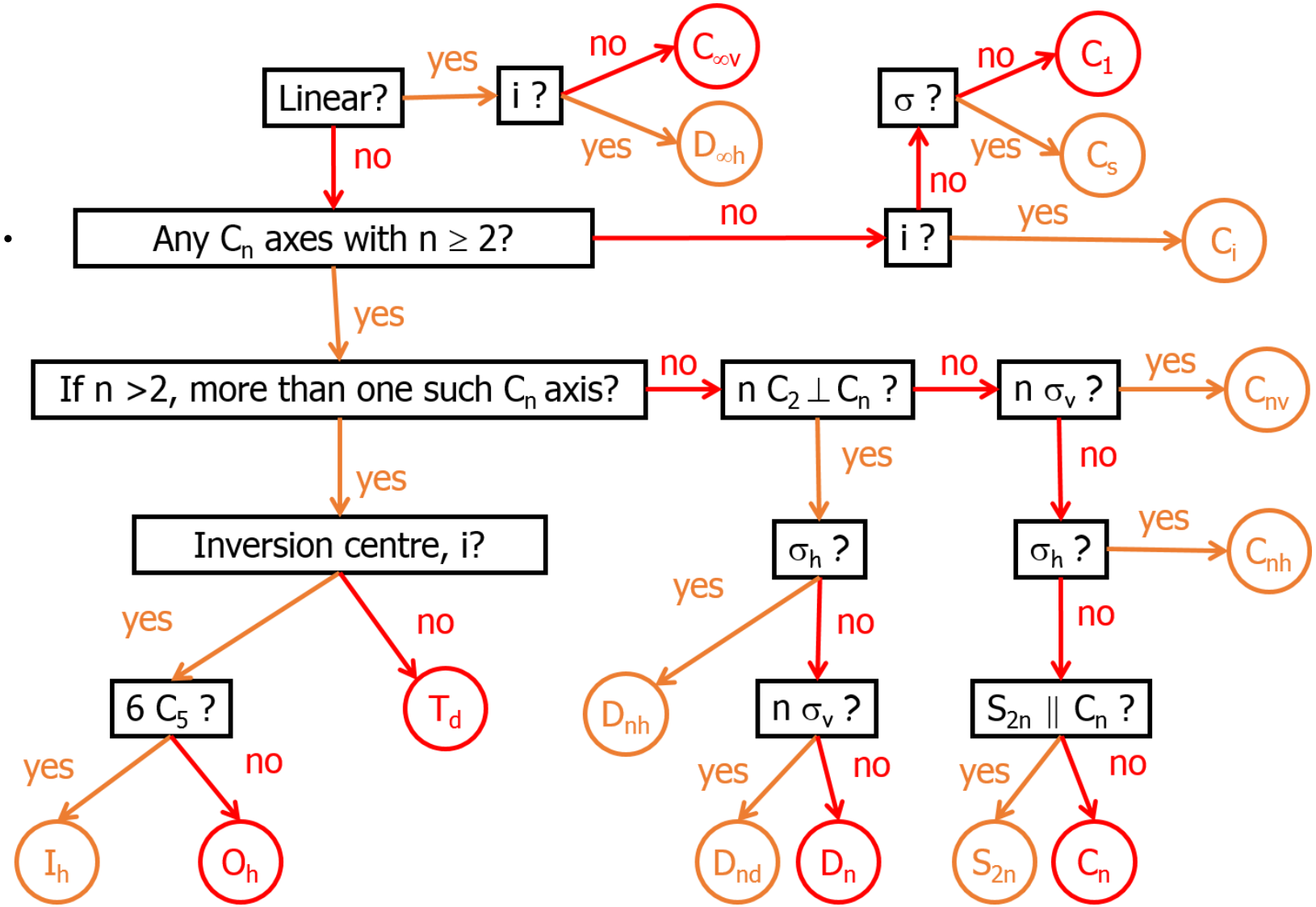
- Unless you go looking for them, you will never encounter molecules in the groups T, T_h, O, and I



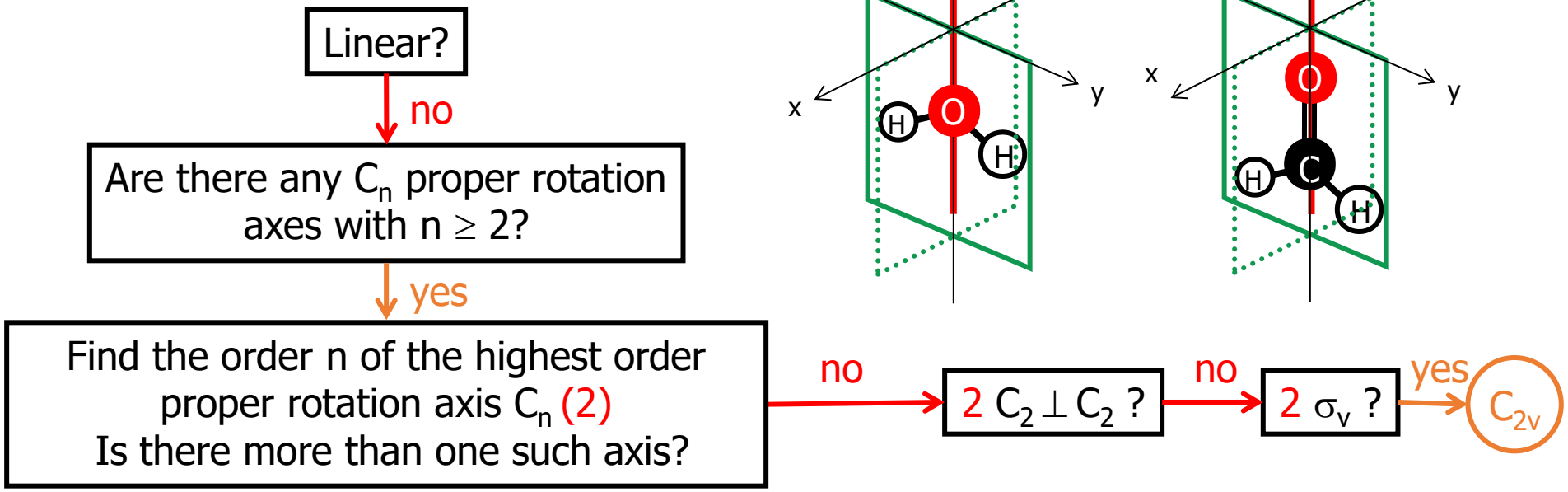
Determining Point Groups (an easier way)

Flow Charts:

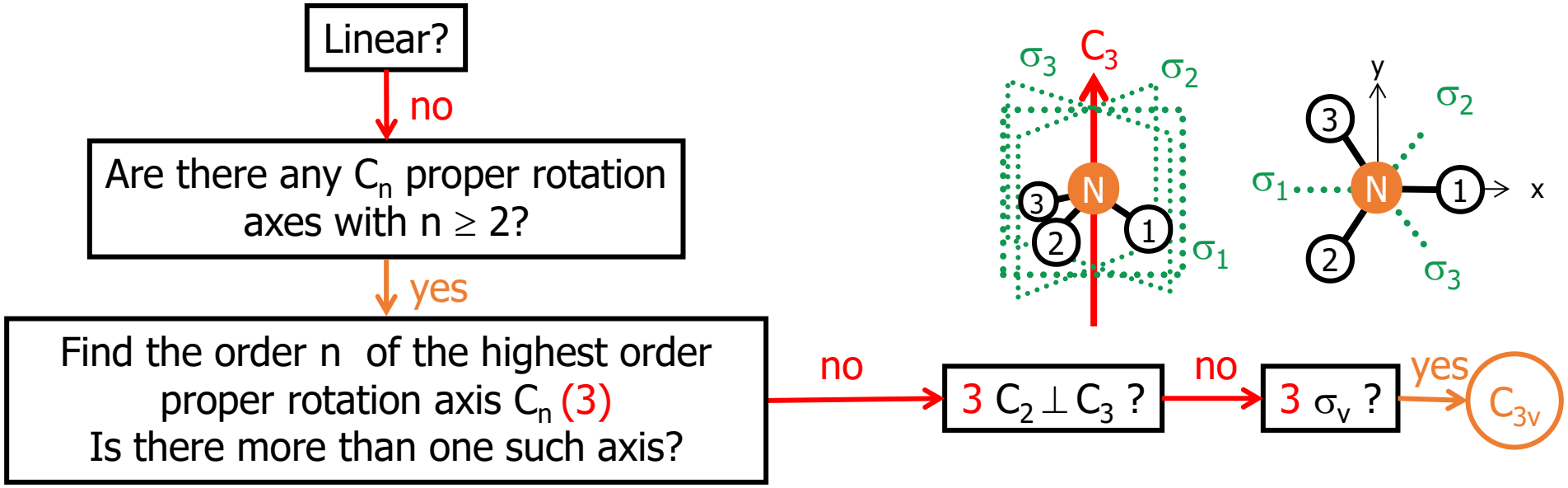
- This one is more practical to use…



Example 1: Formaldehyde/Water



Example 2: NH_3



Example 3: CH_4

Linear?

no

Are there any C_n proper rotation axes with $n \geq 2$?

yes

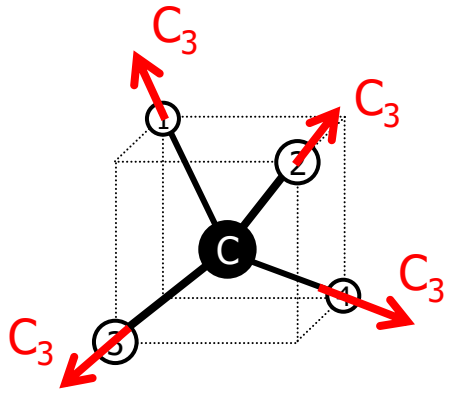
Find the order n of the highest order proper rotation axis C_n (3)
Is there more than one such axis?

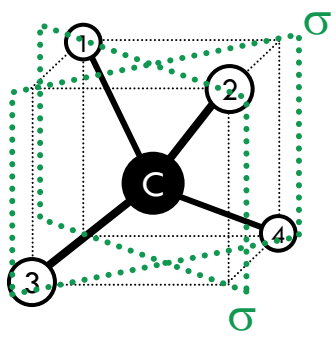
yes

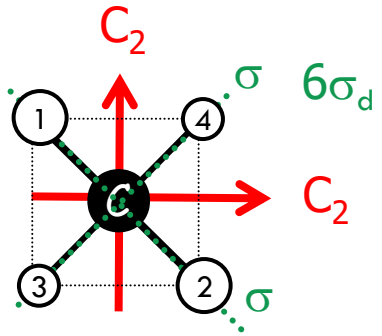
Value of n ?
5 ($6C_5$) 4 ($3C_4$) 3 ($4C_3$) 2 ($3C_2$)

i ? — no → σ ?

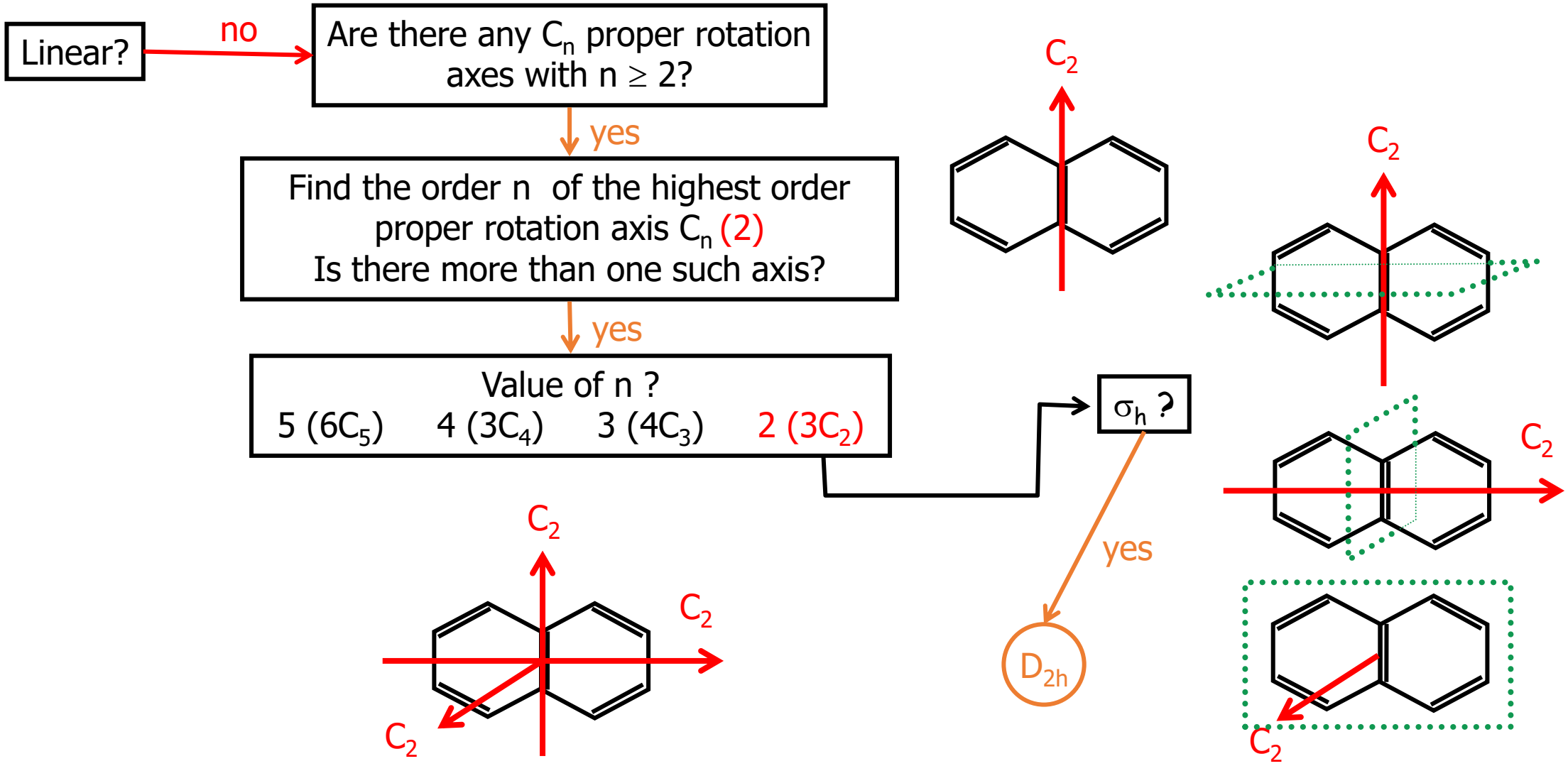
yes → T_d





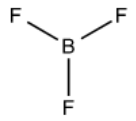
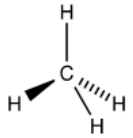
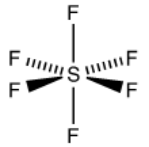
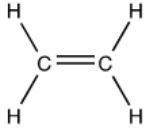
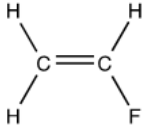
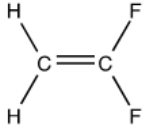
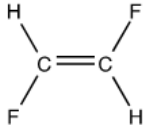
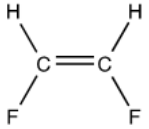
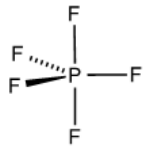
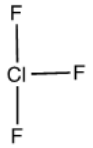


Example 4: Naphthalene



Worksheet Model 3: Determining point groups

1. Assign each of the molecules below to its point group.

(a) 	(b) 	(c) 
(d)  $C_3H_3^+$	(e)  $C_5H_5^-$	(f)  C_6H_6
(g) 	(h) 	(i) 
(j) 	(k) 	(l) 
(m) 	(n) 	(o) 

A quick (non-examinable) comment on terminology

As is common in science, particularly when different disciplines (e.g., chemistry/physics/maths) are involved, a number of different naming systems have evolved.

For point groups of molecules, chemists commonly use the Schönflies notation. For materials (see L4 & L5), we use International notation (also called Hermann–Mauguin).

Intl[*]	Geo [2]	Orbifold	Schönflies	Conway	Coxeter	Order
1	$\bar{1}$	1	C_1	C_1	$[\,]^+$	1
$\bar{1}$	$\bar{2}\,\bar{2}$	×1	$C_i = S_2$	CC_2	$[2^+,2^+]$	2
$\bar{2}$ = m	1	*1	$C_s = C_{1v} = C_{1h}$	$\pm C_1 = CD_2$	$[\,]$	2
2	$\bar{2}$	22	C_2	C_2	$[2]^+$	2
3	$\bar{3}$	33	C_3	C_3	$[3]^+$	3
4	$\bar{4}$	44	C_4	C_4	$[4]^+$	4
5	$\bar{5}$	55	C_5	C_5	$[5]^+$	5
6	$\bar{6}$	66	C_6	C_6	$[6]^+$	6
n	$\bar{n}$	nn	C_n	C_n	$[n]^+$	*n*
mm2	2	*22	C_{2v}	CD_4	[2]	4
3m	3	*33	C_{3v}	CD_6	[3]	6
4mm	4	*44	C_{4v}	CD_8	[4]	8
5m	5	*55	C_{5v}	CD_{10}	[5]	10
6mm	6	*66	C_{6v}	CD_{12}	[6]	12
nmm	n	*nn	C_{nv}	CD_{2n}	[n]	2*n*
nm						
2/m	$\bar{2}\,2$	2*	C_{2h}	$\pm C_2$	$[2,2^+]$	4
$\bar{6}$	$\bar{3}\,2$	3*	C_{3h}	CC_6	$[2,3^+]$	6
4/m	$\bar{4}\,2$	4*	C_{4h}	$\pm C_4$	$[2,4^+]$	8
$\bar{10}$	$\bar{5}\,2$	5*	C_{5h}	CC_{10}	$[2,5^+]$	10
6/m	$\bar{6}\,2$	6*	C_{6h}	$\pm C_6$	$[2,6^+]$	12
n/m	$\bar{n}\,2$	n*	C_{nh}	$\pm C_n$ / CC_{2n}	$[2,n^+]$	2*n*
$\bar{2n}$						
$\bar{4}$	$\bar{4}\,2$	2×	S_4	CC_4	$[2^+,4^+]$	4
$\bar{3}$	$\bar{6}\,2$	3×	S_6	$\pm C_3$	$[2^+,6^+]$	6
$\bar{8}$	$\bar{8}\,2$	4×	S_8	CC_8	$[2^+,8^+]$	8
$\bar{5}$	$\bar{10}\,2$	5×	S_{10}	$\pm C_5$	$[2^+,10^+]$	10
$\bar{12}$	$\bar{12}\,2$	6×	S_{12}	CC_{12}	$[2^+,12^+]$	12
$\bar{2n}$	$\bar{2n}\,2$	n×	S_{2n}	CC_{2n} / $\pm C_n$	$[2^+,2n^+]$	2*n*
$\bar{n}$						

Intl	Geo	Orbifold	Schönflies	Conway	Coxeter	Order
222	$\bar{2}\,\bar{2}$	222	D_2	D_4	$[2,2]^+$	4
32	$\bar{3}\,\bar{2}$	223	D_3	D_6	$[2,3]^+$	6
422	$\bar{4}\,\bar{2}$	224	D_4	D_8	$[2,4]^+$	8
52	$\bar{5}\,\bar{2}$	225	D_5	D_{10}	$[2,5]^+$	10
622	$\bar{6}\,\bar{2}$	226	D_6	D_{12}	$[2,6]^+$	12
n22	$\bar{n}\,\bar{2}$	22n	D_n	D_{2n}	$[2,n]^+$	2*n*
n2						
mmm	2 2	*222	D_{2h}	$\pm D_4$	[2,2]	8
$\bar{6}$m2	3 2	*223	D_{3h}	DD_{12}	[2,3]	12
4/mmm	4 2	*224	D_{4h}	$\pm D_8$	[2,4]	16
$\bar{10}$m2	5 2	*225	D_{5h}	DD_{20}	[2,5]	20
6/mmm	6 2	*226	D_{6h}	$\pm D_{12}$	[2,6]	24
n/mmm	n 2	*22n	D_{nh}	$\pm D_{2n}$ / DD_{4n}	[2,n]	4*n*
$\bar{2n}$m2						
$\bar{4}$2m	$4\,\bar{2}$	2*2	D_{2d}	$\pm D_4$	$[2^+,4]$	8
$\bar{3}$m	$6\,\bar{2}$	2*3	D_{3d}	$\pm D_6$	$[2^+,6]$	12
$\bar{8}$2m	$8\,\bar{2}$	2*4	D_{4d}	DD_{16}	$[2^+,8]$	16
$\bar{5}$m	$10\,\bar{2}$	2*5	D_{5d}	$\pm D_{10}$	$[2^+,10]$	20
$\bar{12}$2m	$12\,\bar{2}$	2*6	D_{6d}	DD_{24}	$[2^+,12]$	24
$\bar{2n}$2m	$n\,\bar{2}$	2*n	D_{nd}	DD_{4n} / $\pm D_{2n}$	$[2^+,2n]$	4*n*
$\bar{n}$m						
23	$\bar{3}\,\bar{3}$	332	T	T	$[3,3]^+$	12
m$\bar{3}$	$4\,\bar{3}$	3*2	T_h	±T	$[3^+,4]$	24
$\bar{4}$3m	3 3	*332	T_d	TO	[3,3]	24
432	$\bar{4}\,\bar{3}$	432	O	O	$[3,4]^+$	24
m$\bar{3}$m	4 3	*432	O_h	±O	[3,4]	48
532	$\bar{5}\,\bar{3}$	532	I	I	$[3,5]^+$	60
$\bar{5}\bar{3}$m	5 3	*532	I_h	±I	[3,5]	120

https://en.wikipedia.org/wiki/Point_group
See also /wiki/Hermann%E2%80%93Mauguin_notation

Learning Outcomes

After this lecture you should be able to

- Identify mirror planes, inversion centres, improper rotation axes and inversion axes.
- Appreciate that molecules can be categorised according to the combination of symmetry elements that they possess – the *point group* symmetry – and be able to recognise if two molecules have the same symmetry.
- Understand how to work out point group symmetries for molecules (and be able to do this after some practise).
- Appreciate that symmetry is a key determinant of many molecular properties, e.g., chirality, polarity (and e.g. greenhouse gas activity), chemical bonding, etc.!
- Complete the worksheet and Q1&2 (maybe also Q4) of Tute Sheet 1 (for week 2).

Further reading: Weller, Overton, Rourke & Armstrong, Inorganic Chemistry 6th Ed. OUP, 2014, Chapter 3.1–3.5.

A mathematical definition of Point Groups in case anyone has come across other types of mathematical group and was wondering what the connection was:

- The set of symmetry operations of a molecule {A, B, C, …} form a molecular **point group**, G, given an operation, ✧, if:
  - A symmetry operation produces an indistinguishable configuration, so any combination of symmetry operations is itself a symmetry operation,
    i.e., $A, B \in G$ implies $A \text{ ✧ } B \in G$ - **closure**
  - There exists a unique **identity** operation, E, such that for all $A \in G$:
    $A \text{ ✧ } E = E \text{ ✧ } A = A$
  - $(A \text{ ✧ } B) \text{ ✧ } C = A \text{ ✧ } (B \text{ ✧ } C)$ - **associativity**
  - every symmetry operation possesses a unique **inverse** operation in G,
    $A \in G \Rightarrow A^{-1} \in G$ where $A \text{ ✧ } A^{-1} = A^{-1} \text{ ✧ } A = E$

- If $A \text{ ✧ } B = B \text{ ✧ } A$, the group is further said to be commutative or abelian.
- A subgroup of G is a set of elements from G that themselves form a group.