2 The symmetry classification of molecules

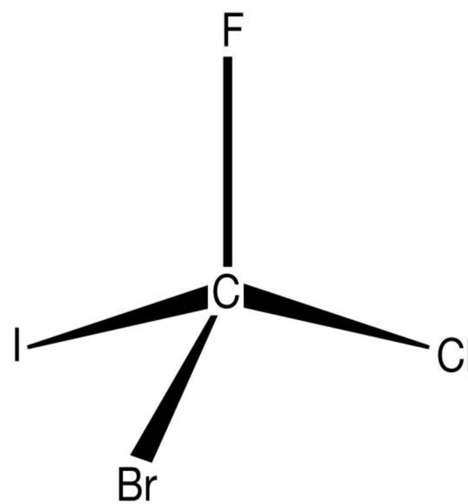
- To classify molecules according to their symmetries, we list their symmetry elements and collect together molecules with the same list of elements
- There are two systems of notation
- The **Schoenflies system** (in which a name looks like C_{4v}) is more common for the discussion of individual molecules,
- and the **Hermann-Mauguin system,** or **International system** (in which a name looks like *4mm*), is used almost exclusively in the discussion of crystal symmetry.

In the International system for point groups, a number *n* denotes the presence of an n-fold axis and m denotes a mirror plane. A diagonal line / indicates that the mirror plane is perpendicular to the symmetry axis. A bar over a number indicates that the element is combined with an inversion.

C_i	$\bar{1}$								
C_s	m								
C_i	1	C_2	2	C_3	3	C_4	4	C_6	6
		C_{2v}	2mm	C_{3v}	3m	C_{4v}	4mm	C_{6v}	6mm
		C_{2h}	2/m	C_{3h}	$\bar{6}$	C_{4h}	4/m	C_{6h}	6/m
		D_2	222	D_3	32	D_4	422	D_6	622
		D_{2h}	mmm	D_{3h}	$\bar{6}2m$	D_{4h}	4/mmm	D_{6h}	6/mmm
		D_{2d}	$\bar{4}2m$	D_{3d}	$\bar{3}m$	S_4	$\bar{4}/m$	S_6	$\bar{3}$
T	23	T_d	$\bar{4}3m$	T_h	m3				
0	432	O_h	m3m						

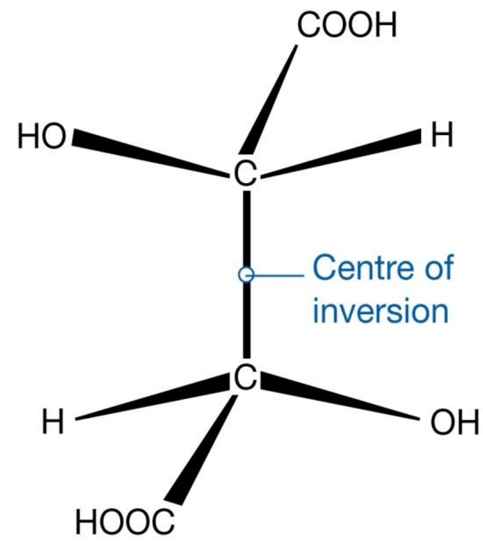
(a) The groups C_1, C_i, and C_s

- A molecule belongs to the group C_1 if it has no element other than the identity, as in (**1**).

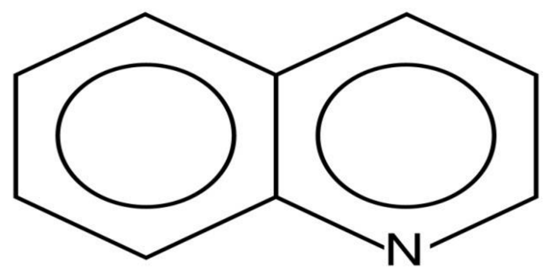


1 CBrClFI

It belongs to C_i if it has the identity and the inversion alone (3) and to C_s if it has the identity and a mirror plane alone (4).



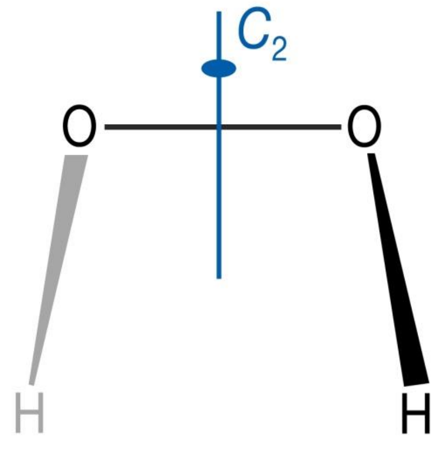
3 Meso-tartaric acid



4 Quinoline

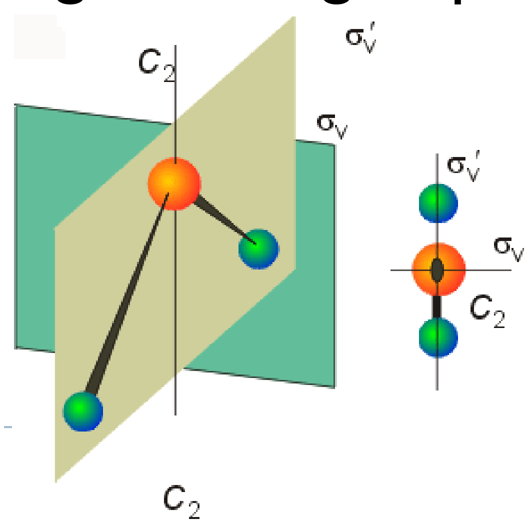
(b) The groups C_n, C_{nv}, and C_{nh}

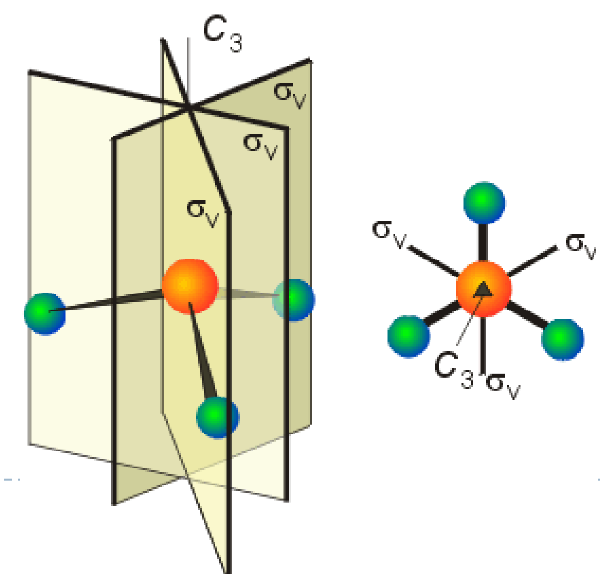
- A molecule belongs to the group C_n if it possesses an n-fold axis.
- An H_2O_2 molecule has the elements *E* and C_2 (**5**), so it belongs to the group C_2.



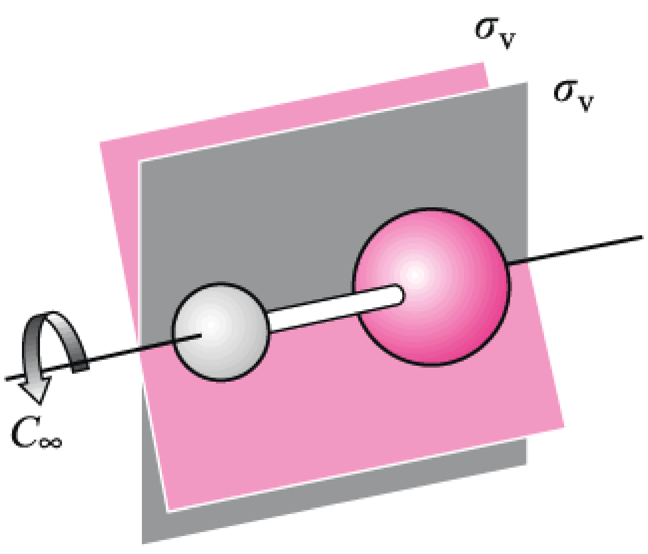
5 H_2O_2

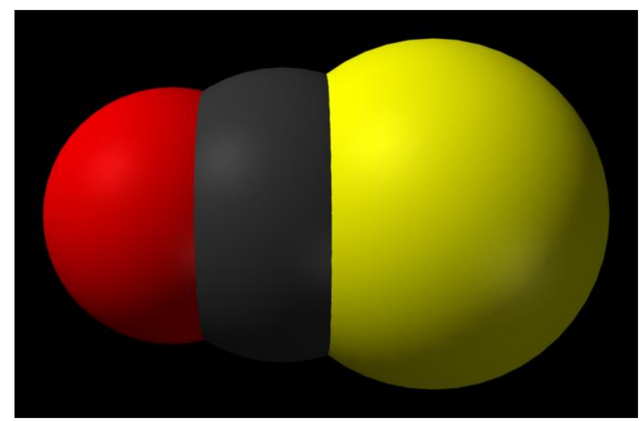
- If, in addition to the identity and a C_n, axis, a molecule has n vertical mirror planes σ_V, then it belongs to the group C_{nv}
- An H_2O molecule, for example, has the symmetry elements E, C_2, and $2\sigma_V$, so it belongs to the group C_{2v}
- An NH_3 molecule has the elements E, C_3, and $3\sigma_V$, so it belongs to the group C_{3v}



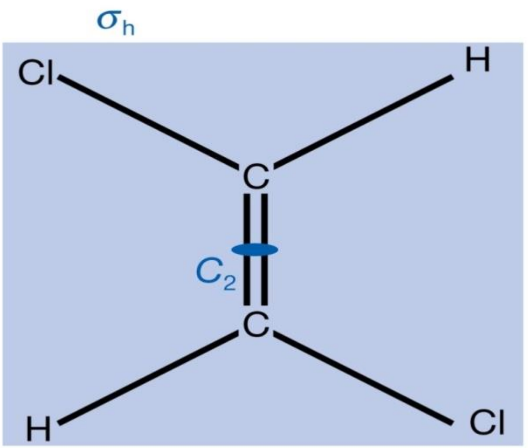


- A heteronuclear diatomic molecule such as HCl belongs to the group $C_{\infty v}$ because all rotations around the axis and reflections across the axis are symmetry operations.
- Other members of the group $C_{\infty v}$ include the linear OCS molecule and a cone.



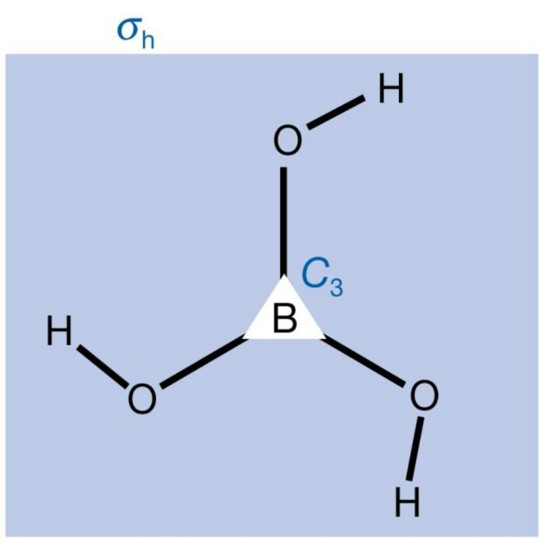


- Objects that, in addition to the identity and an n-fold principal axis, also have a horizontal mirror plane σ_h belong to the groups C_{nh}.
- An example is *trans*- CHC1=CHC1 (**6**), which has the elements E, C_2, and σ_h, so belongs to the group C_{2h};



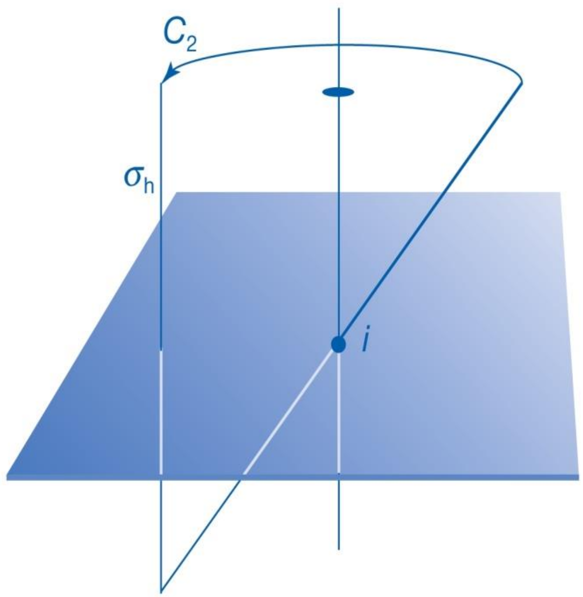
6 *trans*-CHCl═CHCl

- the molecule $B(OH)_3$ in the conformation shown in (**7**) belongs to the group C_{3h}.



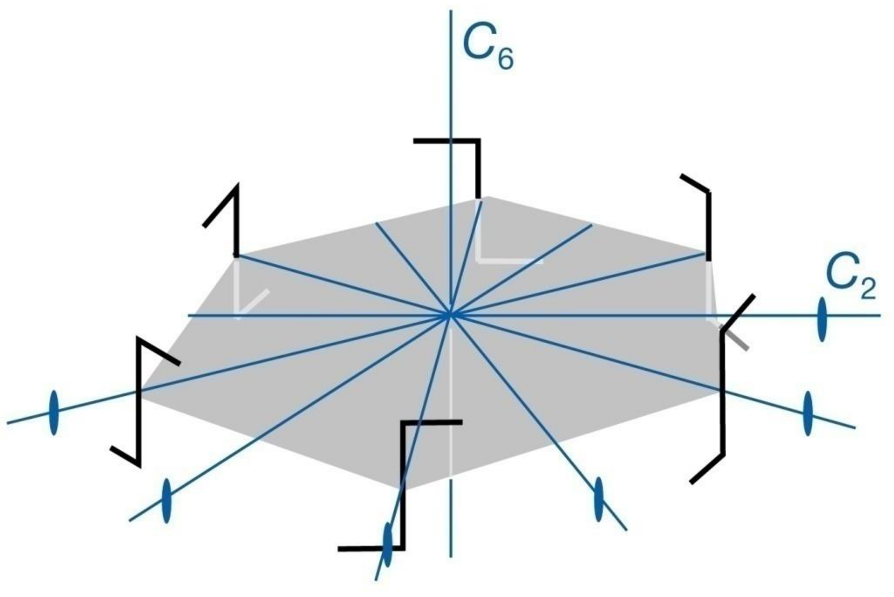
7 $B(OH)_3$

- The presence of certain symmetry elements may be implied by the presence of others: thus, in C_{2h} the operations C_2 and σ_h jointly imply the presence of a centre of inversion

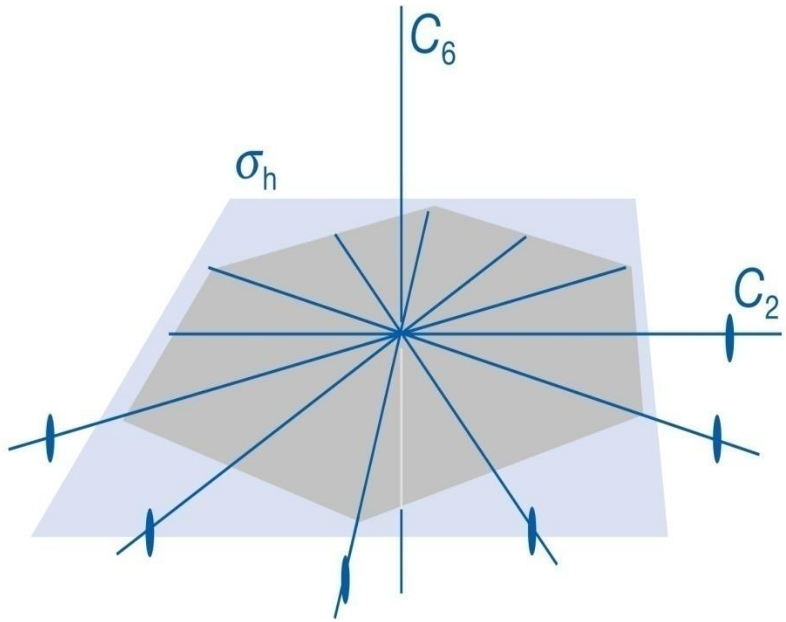


(c) The groups D_n, D_{nh}, and D_{nd}

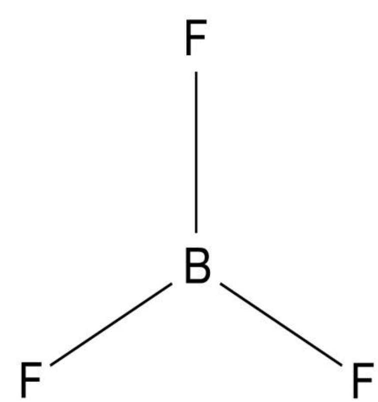
- A molecule that has an n-fold principal axis and n twofold axes perpendicular to C_n belongs to the group D_n



- A molecule belongs to D_{nh} if it also possesses a horizontal mirror plane

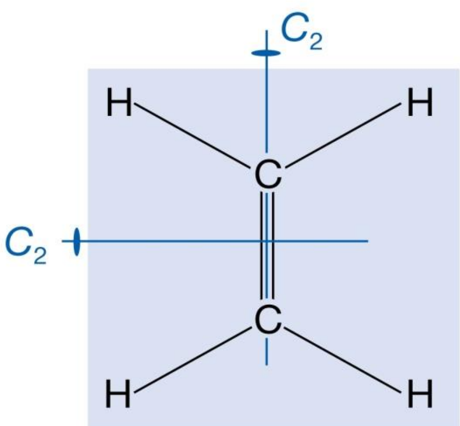


- The planar trigonal BF_3 molecule has the elements E, C_3, $3C_2$, and σ_h (with one C_2 axis along each B—F bond), so it belongs to D_{3h}

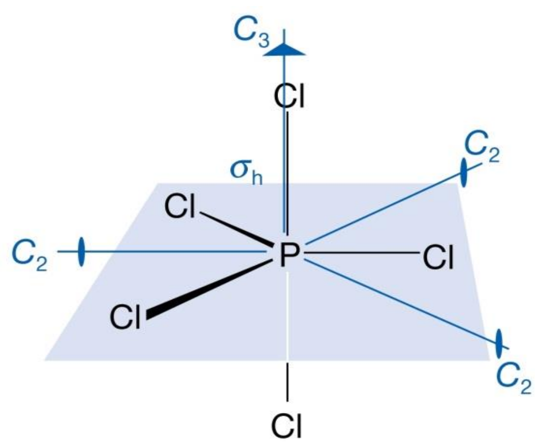


8 Boron trifluoride, BF_3

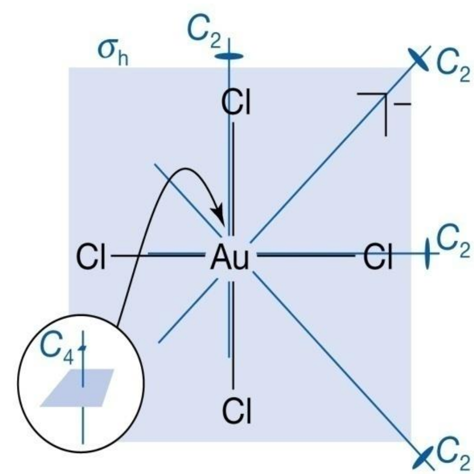
- All homonuclear diatomic molecules, such as N_2, belong to the group $D_{\infty h}$
- $D_{\infty h}$, is also the group of the linear OCO and HCCH molecules and of a uniform cylinder.



9 Ethene, $CH_2{=}CH_2$ (D_{2h})

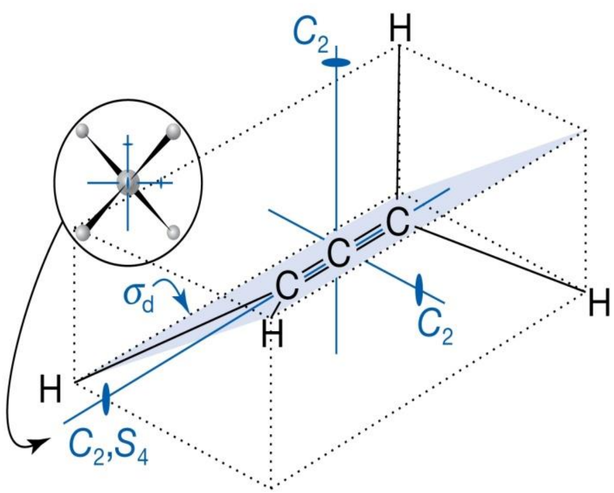


10 Phosphorus pentachloride, PCl_5 (D_{3h})

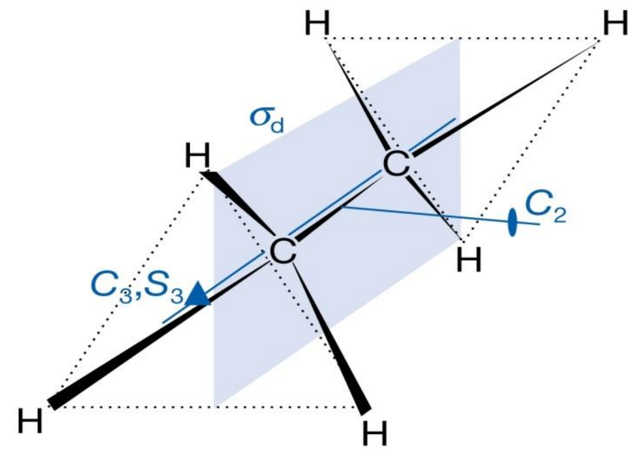


11 Tetrachloroaurate(III), $[AuCl_4]^-$ (D_{4h})

- A molecule belongs to the group D_{nd} if in addition to the elements of D_n it possesses n dihedral mirror planes σ_d.



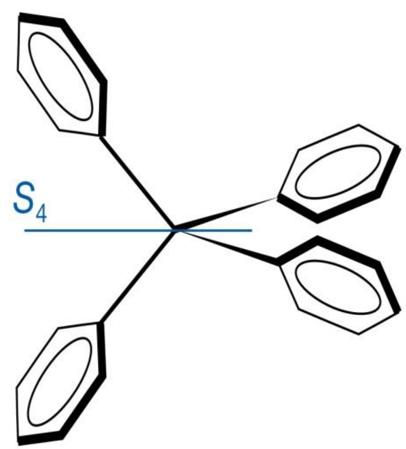
12 Allene, C_3H_2 (D_{2d})



13 Ethane, CH_3CH_3 (D_{3d})

(d) The groups S_n

- Molecules that have not been classified into one of the groups mentioned so far, but which possess one S_n axis, belong to the group S_n.

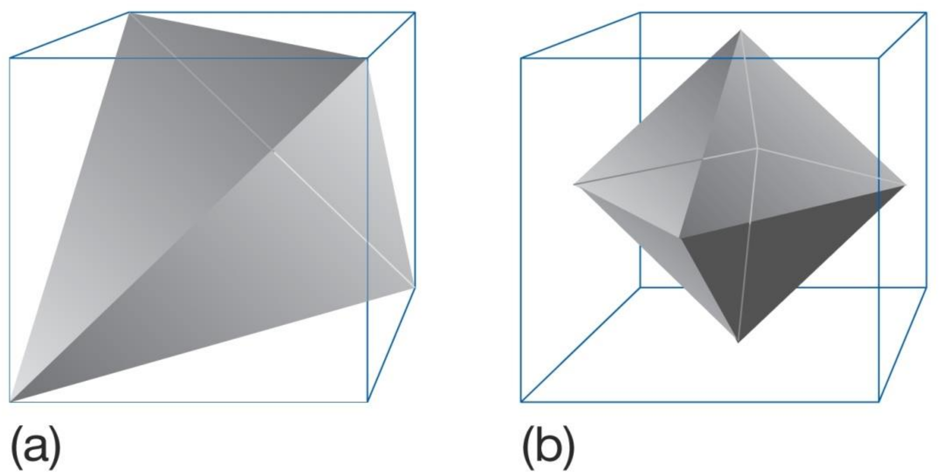


14 Tetraphenylmethane, $C(C_6H_5)_4$ (S_4)

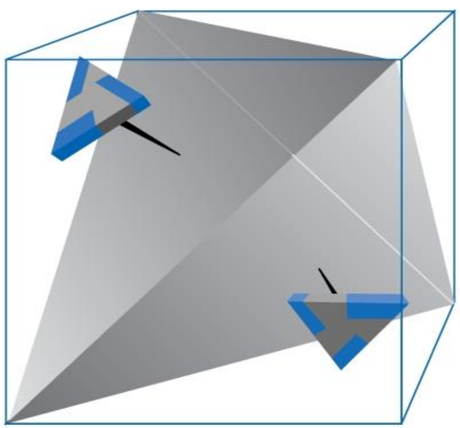
- Note that the group S_2 is the same as C_i, so such a molecule will already have been classified as C_i

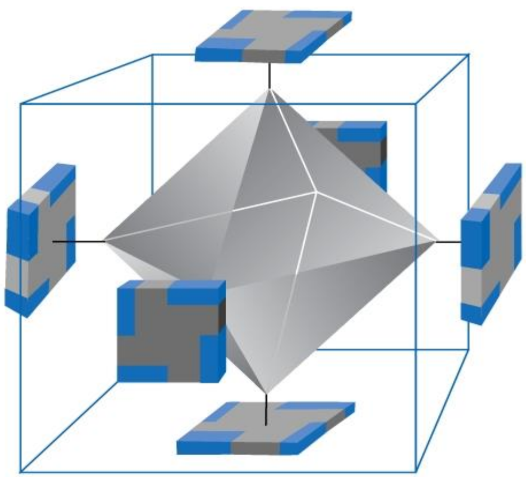
(e) The cubic groups

- A number of very important molecules (for example, CH_4 and SF_6) possess more than one principal axis.
- Most belong to the **cubic groups,** and in particular to the **tetrahedral groups** T, T_d, and T_h or to the **octahedral groups** O and O_h

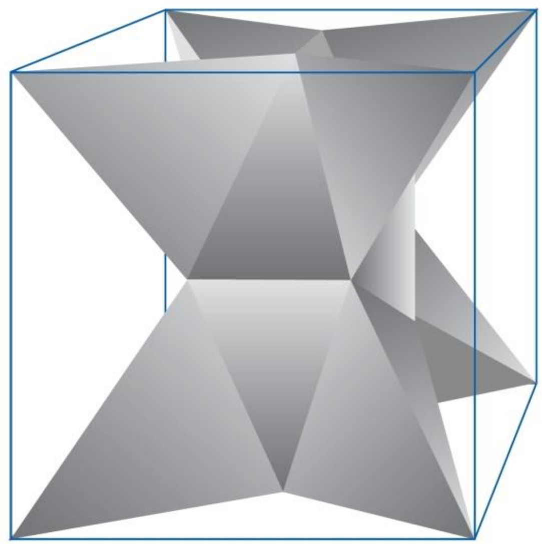


- The groups T_d and O_h are the groups of the regular tetrahedron and the regular octahedron, respectively
- If the object possesses the rotational symmetry of the tetrahedron or the octahedron, but none of their planes of reflection, then it belongs to the simpler groups *T* or *O*

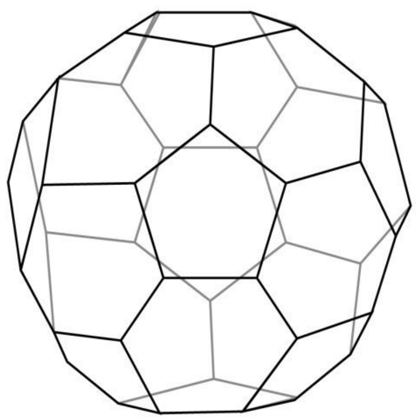

(a) *T*


(b) *O*

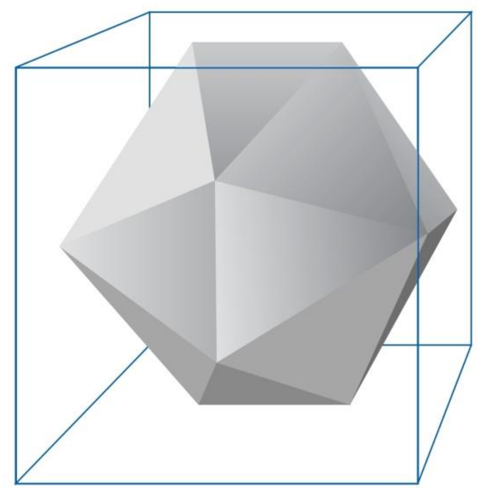
- The group T_h is based on T but also contains a centre of inversion



- A few icosahedral (20-faced) molecules belonging to the **icosahedral group,** I, are also known: they include some of the boranes and buckminster-fullerene, C_{60}

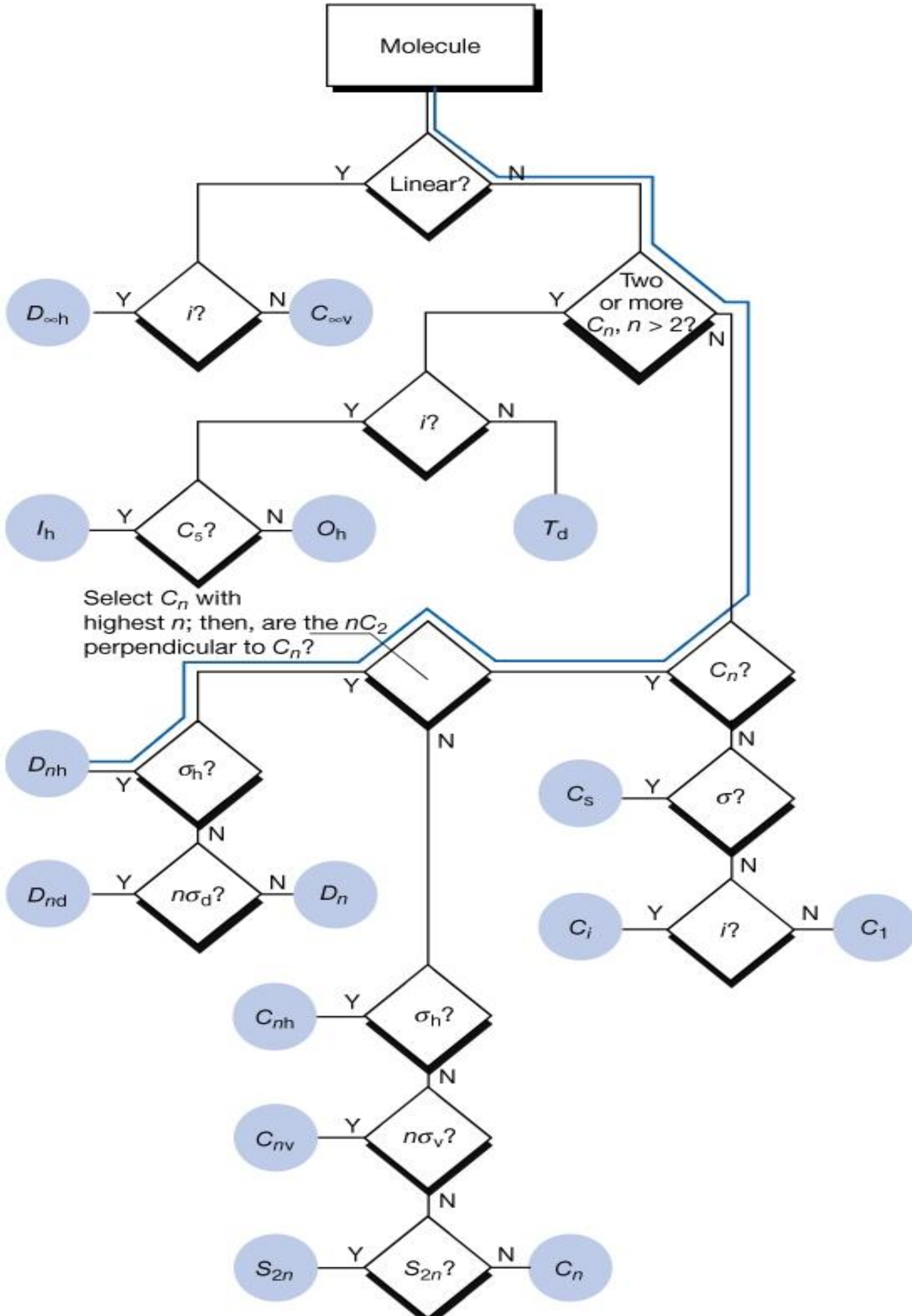


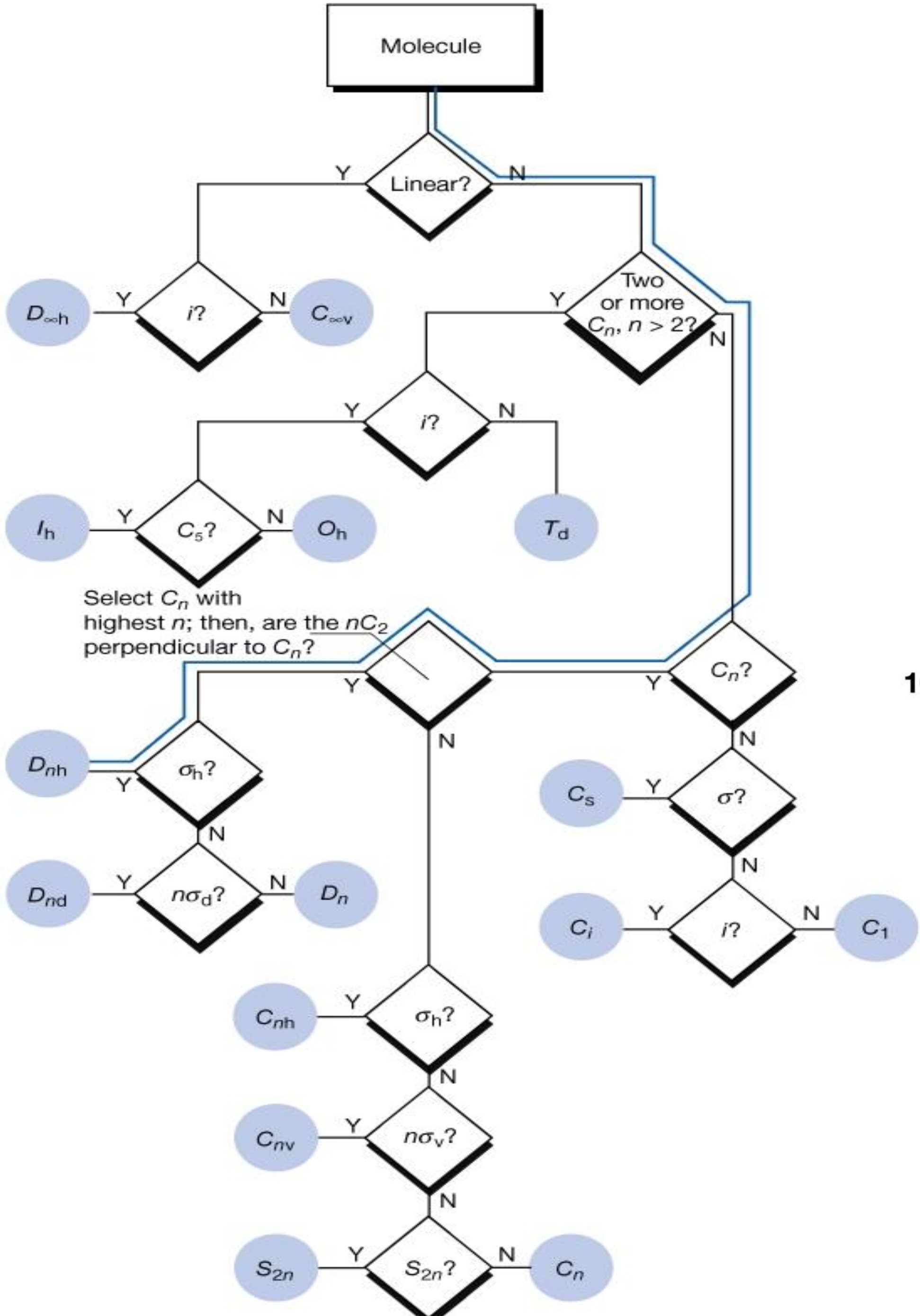
15 Buckminsterfullerene, C_{60} (*I*)

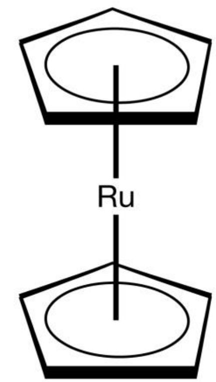


(f) The full rotation group

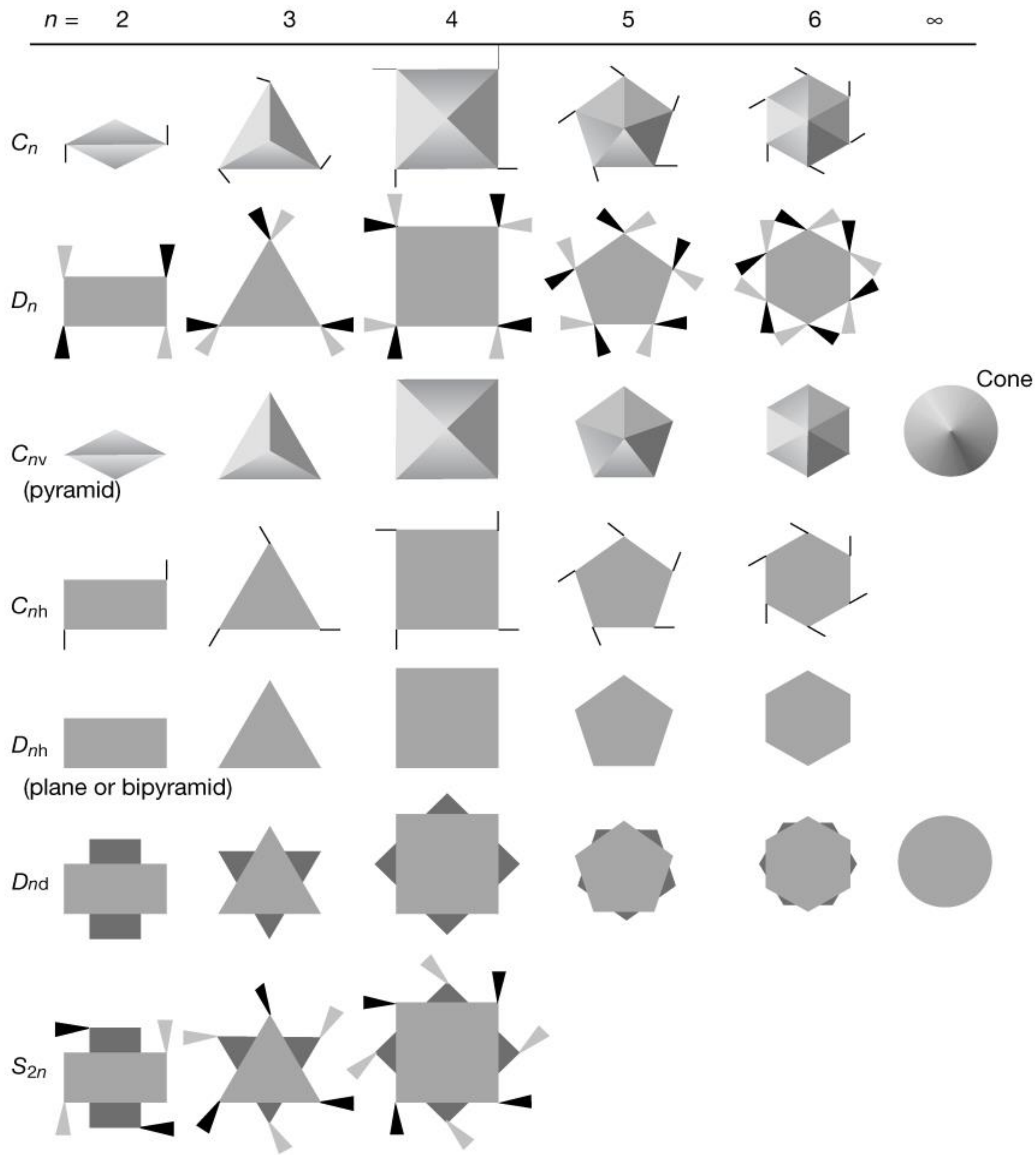
- The **full rotation group,** R_3 (the 3 refers to rotation in three dimensions), consists of an infinite number of rotation axes with all possible values of n.
- A sphere and an atom belong to R_3, but no molecule does.
- Exploring the consequences of R_3 is a very important way of applying symmetry arguments to atoms, and is an alternative approach to the theory of orbital angular momentum


Molecule
Linear?
Y
N
i?
Y
N
$D_{\infty h}$
$C_{\infty v}$
Two or more C_n, $n > 2$?
Y
N
i?
Y
N
C_5?
Y
N
I_h
O_h
T_d
Select C_n with highest n; then, are the nC_2 perpendicular to C_n?
Y
N
C_n?
Y
N
σ_h?
Y
N
D_{nh}
$n\sigma_d$?
Y
N
D_{nd}
D_n
σ?
Y
N
C_s
i?
Y
N
C_i
C_1
σ_h?
Y
N
C_{nh}
$n\sigma_v$?
Y
N
C_{nv}
S_{2n}?
Y
N
S_{2n}
C_n





16 Ruthenocene, $Ru(C_6H_5)_2$


n = 2 3 4 5 6 ∞
Cn
Dn
Cone
Cnv
(pyramid)
Cnh
Dnh
(plane or bipyramid)
Dnd
S2n

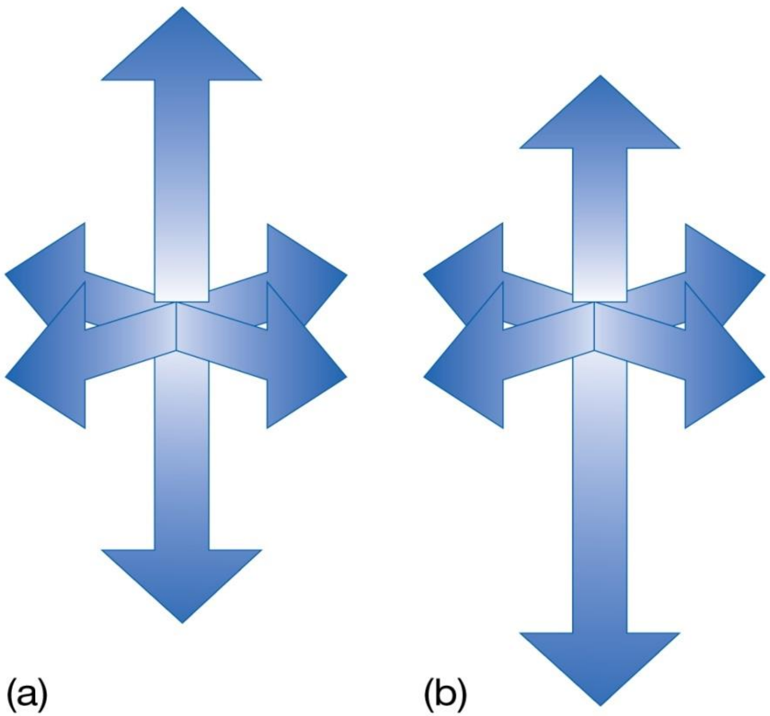
3 Some immediate consequences of symmetry

Some statements about the properties of a molecule can be made as soon as its point group has been identified

(a) Polarity

- If the molecule belongs to the group C_n with $n > 1$, it cannot possess a charge distribution with a dipole moment perpendicular to the symmetry axis because the symmetry of the molecule implies that any dipole that exists in one direction perpendicular to the axis is cancelled by an opposing dipole
- The perpendicular component of the dipole associated with one O—H bond in H_2O is cancelled by an equal but opposite component of the dipole of the second O—H bond, so any dipole that the molecule has must be parallel to the twofold symmetry axis.

However, as the group makes no reference to operations relating the two ends of the molecule, a charge distribution may exist that results in a dipole along the axis



(a) A molecule with a C_n axis cannot have a dipole perpendicular to the axis, but (b) it may have one parallel to the axis

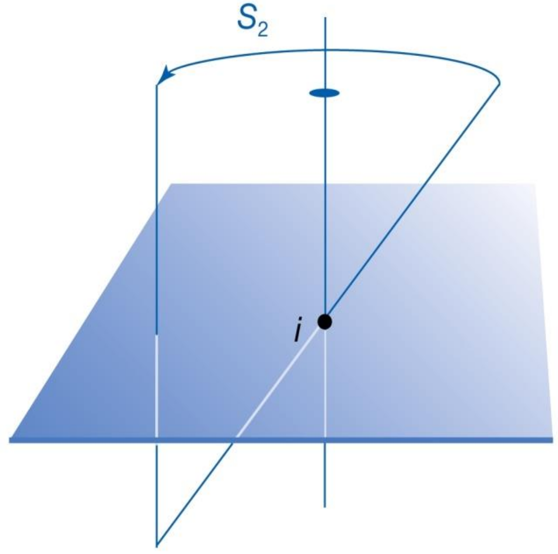
- The same remarks apply generally to the group C_{nv}, so molecules belonging to any of the C_{nv} groups may be polar.
- In all the other groups, such as C_{3h}, D, etc., there are symmetry operations that take one end of the molecule into the other.
- Therefore, as well as having no dipole perpendicular to the axis, such molecules can have none along the axis

- We can conclude that *only molecules belonging to the groups C_n, C_{nv}, and C_s may have a permanent electric dipole moment*
- For C_n and C_{nv}, that dipole moment must lie along the symmetry axis
- Thus ozone, O_3, which is angular and belongs to the group C_{2v}, may be polar (and is), but carbon dioxide, CO_2, which is linear and belongs to the group $D_{\infty h}$, is not

(b) Chirality

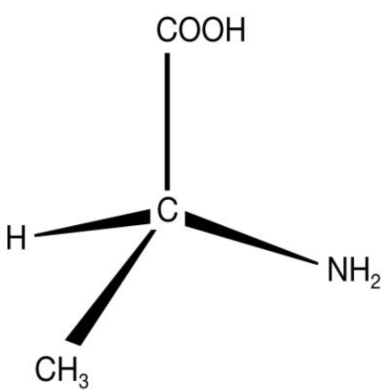
- A **chiral molecule** (from the Greek word for 'hand') is a molecule that cannot be superimposed on its mirror image.
- An **achiral molecule** is a molecule that can be superimposed on its mirror image
- Chiral molecules are **optically active** in the sense that they rotate the plane of polarized light
- A chiral molecule and its mirror-image partner constitute an **enantiomeric pair** of isomers and rotate the plane of polarization in equal but opposite directions

- *A molecule may be chiral, and therefore optically active, only if it does not possess an axis of improper rotation, S_n*
- *M*olecules belonging to the groups C_{nh} possess an S_n axis implicitly because they possess both C_n and σ_h, which are the two components of an improper rotation axis
- Any molecule containing a centre of inversion, *i*, also possesses an S_2 axis, because *i* is equivalent to C_2 in conjunction with σ_h, and that combination of elements is S_2

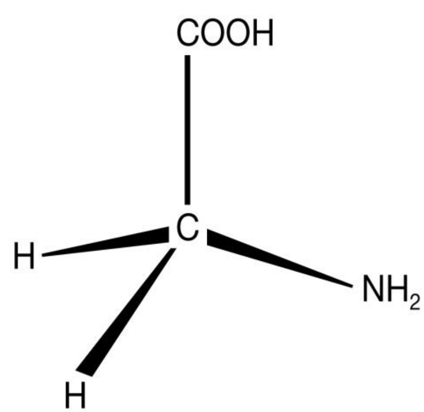


Some symmetry elements are implied by the other symmetry elements in a group. Any molecule containing an inversion also possesses at least an S_2 element because i and S_2 are equivalent

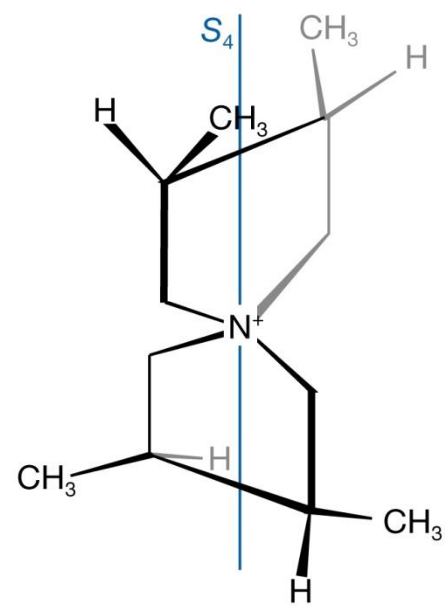
- All molecules with centers of inversion are achiral and hence optically inactive. Similarly, because $S_1 = \sigma$, it follows that any molecule with a mirror plane is achiral.
- However, a molecule may be achiral even though it does not have a centre of inversion



18 L-Alanine, $NH_2CH(CH_3)COOH$



19 Glycine, NH_2CH_2COOH



20 $N(CH_2CH(CH_3)CH(CH_3)CH_2)_2^+$