Non-rotational point groups

Schoenflies notation defines the following three improper symmetry operations in addition to the rotational and identity symmetry operations discussed earlier:

Space inversion	i	- equivalent to three mirror planes at right angles to each other
Mirror reflection	σ	- mirror reflection in a plane
Rotation reflection	S_n	- an n-fold rotation followed by reflection in the horizontal plane

In the Schoenflies system, non-rotational groups are based on underlying rotational groups so, for example, a cyclic group C_n of order n can be combined with a horizontal mirror plane to give point group C_{nh} or with a vertical mirror plane to give point group C_{nv} both of order $2n$. Cyclic sub groups C_n also occur in non-rotational groups S_{2n} where the defining operation is a 2n fold rotation-reflection about the z axis but the principle remains the same: the order of the non-rotational group is twice that of the rotational subgroup. Except for the S_n series, Schoenflies notation always expands from a symbol for the underlying rotational group, adding a subscript to the rotational group symbol and so non-rotational groups derived from cyclic and dihedral rotational groups appear as follows

Rotational group of order n	Non-rotational group of order $2n$
C_1	C_s, C_i
C_n	C_{nh}, C_{nv}, S_{2n}
D_n	D_{nh}, D_{nd}
T	T_d, T_i
O	O_i

The fact that Schoenflies group symbols are derived from their rotational subgroup symbols provides a easy way of assigning a molecule to the non-rotational group describing its symmetry. Every non-rotational point group contains a rotational sub-group of exactly half its order so, taking the simplest examples, point groups C_i and C_s of order 2 both contain rotational group C_1 of order 1. More generally, a specific cyclic rotational group only occurs as a sub-group within a non-rotational group in a very limited number of cases. The table below shows that, given a specific rotational cyclic group, there are only ever three non-rotational groups of twice its order

Rotational group	C_1	C_2	C_3	C_4	C_5	C_6	…….	C_∞
Centrosymmetric	C_i	C_{2h}	S_6	C_{4h}	S_{10}	C_{6h}		
Mirror symmetry (h)	C_s	S_4	C_{3h}	S_8	C_{5h}	S_{12}		
Mirror symmetry (v)		C_{2v}	C_{3v}	C_{4v}	C_{5v}	C_{6v}	…….	$C_{\infty v}$

This information is very useful in assigning molecules to point groups. Once a rotational subgroup is deduced there can never be more than three possible non-rotational higher order groups and the choice is usually obvious. Using the table above it is easy to deduce a non-rotational point group from the rotational group. If, for example, a molecule has visible 4-fold cyclic rotational symmetry about the main axis and no other rotational axis it could be a subgroup of point group C_{4h}, S_8 or C_{4v} but no other group. One of these has a centre of symmetry, one has 4 vertical mirrors while the other one has an 8-fold rotation-reflection axis. Notice that symbols in the first two rows alternate between the C_{nh} and S_n series because these two Schoenflies series alternate between centred and non-centred groups. This is the core problem with the Schoenflies approach: it was derived from the observation of visible crystal shapes (eg prisms and anti-prisms) rather than point group elements. It relates to the visible outer rotational shape not to the abstract group for that specific point group.

An n-fold cyclic group with n 2-fold rotational axes intersecting at the molecular centre suggests a dihedral rotational group D_n but this only occurs as a subgroup in two possible non-rotational groups as shown in the table below. Centred and non-centred examples in this case alternate between D_{nh} and D_{nd} groups because of the Schoenflies notation. Once again, a centre of symmetry is obvious and its presence or absence dictates the choice of non-rotational group.

	D_2	D_3	D_4	D_5	D_6	…….	D_∞
Centrosymmetric	D_{2h}	D_{3d}	D_{4h}	D_{5d}	D_{6h}	…….	$D_{\infty h}$
Mirror symmetry	D_{2d}	D_{3h}	D_{4d}	D_{5h}	D_{6d}	…….	

Spherical molecules have three rotational groups: those of the tetrahedron (*T*), the octahedron (*O*) and icosahedron (*I*). As in the previous examples, Schoenflies notation is based on the external shapes of polyhedra so the notation places great emphasis on the visible rotational subgroups of non-rotational point group objects. Tetrahedral or octahedral rotational subgroups only occur in the limited number of point groups below and the deduction is trivial

	T	O
Centrosymmetric	T_d	
Mirror symmetry	T_i	O_i

Every non-rotational point group contains a rotational subgroup of exactly half its order or conversely the non-rotational group is twice the order of its rotational subgroup. This is important because once a rotational group is known there are very few larger groups that can contain it.

In summary, all molecules can be assigned to a molecular point group even if that group is simply C_1. The steps involved in assigning a molecule are straightforward

- Assign the molecule to its highest order rotational group even if some non-rotational symmetry appears to be possible. If it has just rotational symmetry the job is finished.
- In the more likely situation that the rotational group is a subgroup of a larger group there is always a limited number of possible non-rotational groups. This larger group must be of twice the order of the rotational group and there are never more than the 2 or 3 supergroups shown in the tables above.

Laue classes of point groups

The basic ad-hoc nature of the Schoenflies approach was derived to describe the external forms of crystals and is not that helpful in molecular spectroscopic applications. Deriving the system from rotational subgroups combined with mirror reflections neglects major differences between the non-rotational groups themselves. When point groups are displayed in the Laue classes shown below the relationship between members of a class (rows of the table) is sufficient to overcome the deficiencies of the notation itself

Laue classes of point groups - Schoenflies

Partition	System	G		$\bar{G}$	Gi
[1,1,1]	Triclinic	C_1			C_i
	Monoclinic	C_2		C_s	C_{2h}
	Orthogonal	D_2	C_{2v}		D_{2h}
[2,1]	Trigonal	C_3			S_6
		D_3	C_{3v}		D_{3d}
	Tetragonal	C_4		S_4	C_{4h}
		D_4	C_{4v}	D_{2d}	D_{4h}
	Pentagonal	C_5			S_{10}
		D_5	C_{5v}		D_{5d}
	Hexagonal	C_6		C_{3h}	C_{6h}
		D_6	C_{6v}	D_{3h}	D_{6h}
	Heptagonal	C_7			S_{14}
		D_7	C_{7v}		D_{7d}
	Octagonal	C_8		S_8	C_{8h}
		D_8	C_{8v}	D_{4d}	D_{8h}
		....			
	Infinity	C_∞			$C_{\infty h}$
		D_∞	$C_{\infty v}$		$D_{\infty h}$
[3]	Tetrahedral	T			T_h
	Octahedral	O		T_d	O_h
	Icosahedral	I			I_h

Taking the C_3 group of order 3 again as an example, another group with this subgroup must be of order 6 because it is always index-2 to the larger group. The most obvious example is the 3-fold dihedral group D_3 with following multiplication table

3-fold dihedral operation table

D_3	E	c	c^2	u	u_1	u_2
E	E	c	c^2	u	u_1	u_2
c	c	c^2	E	u_2	u	u_1
c^2	c^2	E	c	u_1	u_2	u
u	u	u_1	u_2	E	c	c^2
u_1	u_1	u_2	u	c^2	E	c
u_2	u_2	u	u_1	c	c^2	E

It is easy to read the order of a point group from the Laue class table and it is obvious that the only non-rotational groups of order 6 are S_6, C_{3h} and C_{3v}. Point groups in cyclic and dihedral classes have orders n and 2n respectively, except for the centrosymmetric group of orders 2n and 4n. A multiplication table for the operations of the C_{3v} has the form shown below and if this is compared with the D_3 rotational group table shown above the similarities become obvious. Letter u representing a 2-fold horizontal rotation is replaced by letter m representing a mirror reflection but the form of the table is identical.

C_{3v} symmetry operation table						
	E	c	c^2	m	m_1	m_2
E	E	c	c^2	m	m_1	u_2
c	c	c^2	E	m_2	m	m_1
c^2	c^2	E	c	m_1	m_2	m
m	m	m_1	m_2	E	c	c^2
m_1	m_1	m_2	m	c^2	E	c
m_2	m_2	m	u_1	c	c^2	E

D_3 and C_{3v} are representations of the same abstract group and appear in the same Laue class of the Laue table above. Group C_{3v} contains three non-rotational operations m, m_1 and m_2 that may be obtained from rotational operations u, u_1 and u_2 through combination with central inversion i as follows $m = iu,\ m_1 = iu_1,\ m_2 = iu_2.$

Symmetry group C_{3h} of order 6 is a quite different structure and, in spite of the Schoenflies symbol, is actually an hexagonal molecule isomorphic to group C_6. Again, the three operations not in the subgroup are combined with space inversion to give a transformation that Schoenflies called rotation inversion.

C_{3h} symmetry operation table						
	E	ic	c^2	ic^3	c^4	ic^5
E	E	ic	c^2	ic^3	c^4	ic^5
ic	ic	c^2	ic^3	c^4	ic^5	E
c^2	c^2	ic^3	c^4	ic^5	E	ic
ic^3	ic^3	c^4	ic^5	E	ic	c^2
c^4	c^4	ic^5	E	ic	c^2	ic^3
ic^5	ic^5	E	ic	c^2	ic^3	c^4

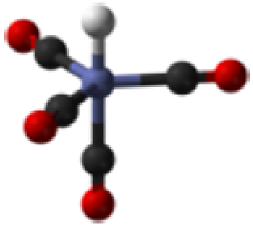
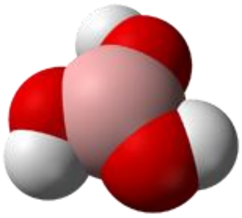
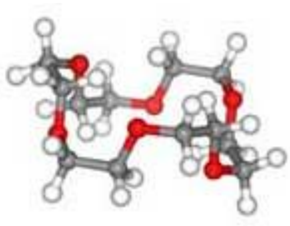
Finally, the centrosymmetric group is a simple direct product of the rotational group C_3 with space inversion. Obviously, the product of E and i is i and this means that space inversion is an operation in the resulting group. The table for this group is as follows

S_6 symmetry operation table						
	E	c	c^2	i	ic	ic^2
E	E	c	c^2	i	ic	ic^2
c	c	c^2	E	ic	ic^2	i
c^2	c^2	E	c	ic^2	i	ic
i	i	ic	ic^2	E	c	c^2
ic	ic	ic^2	i	c	c^2	E
ic^2	ic^2	i	ic	c^2	E	c

There is clearly a problem with the Schoenflies system in that the point group symbols are not clearly related to the operations in the group. Molecules with D_{nh} and D_{nd} symmetry for example alternate between the centrosymmetric forms and mirror image forms that give the molecules their characteristic behaviours

Some examples of point group deduction

A few examples demonstrate the use of subgroups in deductions starting with the following molecules that have 3-fold cyclic symmetry

Cobalt tetracarbonyl hydride Boric acid 18-crown-6

A cobalt tetracarbonyl hydride molecule has an obvious 3-fold axis so belongs to point group C_3. It has equally obvious mirror planes of symmetry so the C_3 group appears as a subgroup of larger non-rotational group of order 6. The possibilities for a non-rotational group with a C_3 are shown in the table above to be S_6, C_{3h} and C_{3v} but the first of these is centrosymmetric and cobalt tetracarbonyl hydride is not. This molecule has three vertical mirror symmetry planes and must therefore have C_{3v} symmetry. Boric acid has a 3-fold axis and a strikingly obvious horizontal mirror plane and thus belongs to point group C_{3h} also of order 6. Finally 18-crown-6 is a large (36 atom) molecule but, looking at its manipulatable image on the Otterbein site, a clear 3-fold axis is visible. If this is a subgroup of a non-rotational group the larger group must be S_6, C_{3h} or C_{3v}. No horizontal or vertical mirror is present, leaving the centrosymmetric S_6 point group as the only remaining possibility and some manipulation of the Otterbein image might convince a viewer that this is indeed the case.