Non-rotational point groups

Rotational point groups describe molecules with symmetry operations that can be physically performed in 3-dimensional space with the aid of a molecular model. Although there exists an infinite number of such groups, they are easily categorised into the cyclic groups n, dihedral groups n2 and the spherical groups 23, 432 and 532. Non-rotational groups, describing operations that cannot be performed in space, may be formed by combinations of the rotational group operations with space inversion i (parity inversion). The great advantage of using space inversion to describe non-rotational groups is that it commutes with all rotational operations so, if r is a rotational operation then it is always true that $ri = ir$ and the order in which operations are applied makes no difference to the outcome.

Rotational group operations are the products of repeated applications of a limited number of generators. Thus, the operations an n-fold cyclic group are just multiple applications of a single operation that is simply a rotation of 360/n degrees. Dihedral groups have two generators and spherical groups three. There are two ways in which non-rotational groups may be formed from rotational groups

1. A rotational group generator is combined with space inversion to produce a new group. Although this group describes a different physical entity to that of the rotational group it has the same abstract algebraic structure and belongs to the same class of the Laue table. This may be written as $G' = \{G - H + iH\}$

2. All the elements of a rotational group are combined with all the products of those elements with space inversion, producing a direct product group of twice the order of the rotational group. $Gi = G\ x\ i$

A conversion of the first kind can be illustrated by taking the 32 dihedral group and combining its 2-fold symmetry operation with space inversion. A multiplication table for the straightforward rotational group is reproduced below from the previous section

3-fold dihedral operation table

32	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

The 2-fold generator u in this group may be combined with space inversion $ui = iu$ to produce the new operations iu, iu_1 and iu_2 shown in the table below. One important point to gain from this is that results in the bottom right-hand corner of the table are the result of two operations each combined with space inversion. Since inversion commutes with all other operations the combination iu_1 followed by iu_2 multiplies out as follows

$$iu_2 iu_1 = \ iiu_2 u_1 = \ u_2 u_1 = c^2$$

3-fold dihedral operation table

$3\bar{2}$	E	c	c^2	iu	iu_1	iu_2
E	E	c	c^2	iu	iu_1	iu_2
c	c	c^2	E	iu_2	iu	iu_1
c^2	c^2	E	c	iu_1	iu_2	iu
iu	iu	iu_1	iu_2	E	c	c^2
iu_1	iu_1	iu_2	iu	c^2	E	c
iu_2	iu_2	iu	iu_1	c	c^2	E

Space inversion 'tags along' without altering the way in which rotational operations multiply out. This means that the two apparently distinct groups above are in fact two representations of the same abstract group – the 3-fold dihedral group. The distinct non-rotational group is distinguished from the rotational group by placing a bar over the 2-fold generator symbol $3\bar{2}$. Combinations of 2-fold rotation with inversion always produce mirror reflections and the rotational operations u, u_1 and u_2 combine with central inversion i as follows $m = iu,\ m_1 = iu_1,\ m_2 = iu_2.$ Letter u representing a 2-fold horizontal rotation is replaced by letter m representing a mirror reflection but the form of the table is similar

3-fold dihedral symmetry table

$3\bar{2}$	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

Point groups 32 and $3\bar{2}$ both contain cyclic group 3 as a subgroup but have a very close relationship in that they are isomorphic groups with same underlying structure. Two other groups have the same subgroups but are not isomorphic: $3i$ and $\bar{6}$. The first of these is just a direct product of the 3-fold rotational group with space inversion $3i = 3 \times i$ and has the multiplication below

3-fold cyclic centred operation table

$3i$	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^2	E	c
ic^2	ic^2	i	ic	c	c^2	E

Although this point group is of order 6 it is structurally different from the 3-fold dihedral tables. Like all non-rotational groups of the second kind described above, it includes space inversion as one of its operations.

The remaining group that has a 3-fold cyclic subgroup is $\bar{6}$ in which a six-fold rotation c is combined with space inversion i. This generates six group elements

$$\{ic, (ic)^2, (ic)^3, (ic)^4, (ic)^5, (ic)^6\}$$

But these simplify to give the set

$$\{ic, c^2, (ic)^3, c^4, (ic)^5, E\}$$

Notice again that space inversion does not alter the multiplication of the underlying 6-fold cyclic group so $\bar{6}$ shown below is an isomorph of the rotational group

6-fold symmetry operation table

$\bar{6}$	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

Deducing the non-rotational symmetry group of a molecule

Non-rotational groups must contain a rotational group of exactly half their order and this suggests a method of deducing the symmetry group to which the non-rotational group belongs. There is a very limited range of rotational groups: cyclic, dihedral and the spherical groups. Rotational transformations can be performed in space and are very visible and easily deduced, suggesting the following method of non-rotational group deduction

1. Find the rotational group to which the molecule belongs. This might be the final result but the observed group is more likely to be a subgroup.
2. Look for signs of non-rotational symmetry such as inversion, rotation inversion or mirror reflection. If there is any indication of improper transformations check possible non-rotation groups that are of twice the order of the rotational group. A table below shows the possibilities

Rotational group	Non-rotational group
n	$\overline{2n},\ n\bar{2},\ ni$
$n2$	$\overline{2n}2, n2i$
23	$\bar{4}32, 23i$
432	$432i$

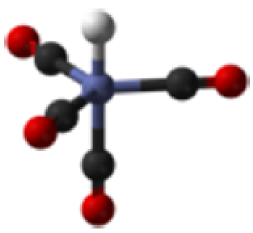
A cyclic group n only occurs as a subgroup in three possible non-rotational groups while a dihedral group 2n only occurs in two possible supergroups. More importantly, it is very easy to decide between the possibilities by first checking for a centre of symmetry then looking for mirror planes (combinations of 2-fold rotations with inversion). An examination of the Laue class table below helps to explain this relationship. Rotational cyclic group 3 used above can only appear as a subgroup in non-rotational group of order 6 so a brief scan of the Laue table below reveals the possibilities. Groups $3\bar{2}$ and 3i are obvious because the rotational group appears in the symbol but the remaining $\bar{6}$ is less obvious.

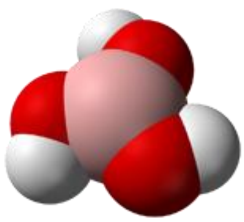
Point groups in 3-dimensional space

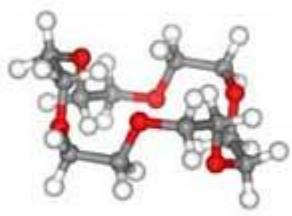
Partition	System	G	$\bar{G}$		Gi
	Triclinic	1			i
Asymmetric	Monoclinic	2		$\bar{2}$	$2i$
	Orthogonal	22	$2\bar{2}$		$22i$
	Trigonal	3			3i
Symmetric		32	$3\bar{2}$		$32i$
	Tetragonal	4		$\bar{4}$	4i
		42	$4\bar{2}$	$\bar{4}2$	$42i$
	Pentagonal	5			52
		52	$5\bar{2}$		$52i$
	Hexagonal	6		$\bar{6}$	$6i$
		62	$6\bar{2}$	$\bar{6}2$	$62i$
	Heptagonal	7			$7i$
		72	$7\bar{2}$		$72i$
	Octagonal	8		$\bar{8}$	$8i$
		82	82	$\bar{8}2$	$82i$
		……………………			
	Infinite	∞			∞i
		$\infty 2$	$\infty\bar{2}$		$\infty 2i$
	Tetrahedral	23			$23i$
Spherical	Octahedral	432		$\bar{4}32$	$432i$
	Icosahedral	532			$532i$

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 3. It has equally obvious mirror planes of symmetry so the 3 group appears as a subgroup of larger non-rotational group of order 6. The possibilities for a non-rotational group with this subgroup are shown in the table above to be $\overline{2x3}, 3\overline{2}$ and $3i$ but the last of these is centrosymmetric and cobalt tetracarbonyl hydride is not. This molecule has three vertical mirror symmetry planes and must therefore have $3\overline{2}$ symmetry.

Boric acid has a 3-fold axis and therefore belongs to the cyclic group 3. It also has a strikingly obvious horizontal mirror plane but is not centrosymmetric and does not have the axial mirror planes visible in the previous example. The only remaining non-rotational group is the rotation-inversion group $\overline{2x3} = \overline{6}$ 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 $\overline{23}, 3\overline{2}$ or $3i$ No horizontal or vertical mirror is present, leaving the centrosymmetric $3i$ point group as the only remaining possibility and some manipulation of the Otterbein image might convince a viewer that this is indeed the case.