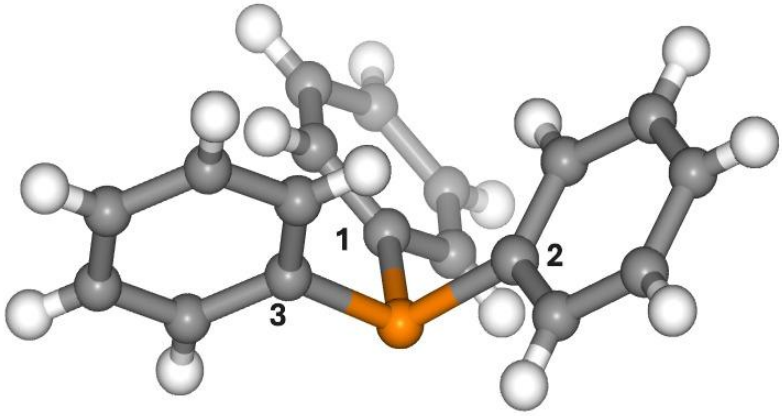
Rotational point groups

A molecule that appears unchanged following a rotation about an axis through itself is said to have rotational symmetry. Most small molecules have both rotational and non-rotational symmetry but the triphenyl phosphine molecule pictured below is an example of a molecule that has just 3-fold rotational symmetry about one axis with no other symmetry elements present.



Triphenyl phosphine

If the molecule such as triphenyl phosphine is rotated by 120 degrees in a clockwise rotation it falls into coincidence with itself and appears unchanged. Rotations of 240 and 360 degree also leave the molecule looking as though it has not moved. The image above was taken from the Otterbein site where it is possible to move the molecular model on the screen and mimic the symmetry elements. Transformations like this are called symmetry operations and are used to describe molecular shapes in mathematical form. The smallest rotation of 120 is called the generator given the symbol c so that so that higher order rotations can be shown as cc = c^2 and ccc = $c^3 = E$. This last symbol, E, is very important because it represents a return to the starting point or, equivalently, not moving the molecule at all. We have therefore a set of 3 symmetry operations $\{E, c, c^2\}$. It is useful to know the results of compositions of symmetry operations when one is followed by another. If, for example, symmetry operation c^2 is followed by symmetry operation c and then followed by symmetry operation c^2 we could write this as $c^2\, c\, c^2$ reading the operations from right to left. This composition of operations is equal to c^5 which in this 3-fold example is equal to c^2. A table of the various possible combinations is shown below

Cyclic 3-fold

C_3	E	c	c^2
E	E	c	c^2
c	c	c^2	E
c^2	c^2	E	c

Two operations may be combined by looking up the first one in the top row of operations and the second on in the first column of operations then reading the result form the intersection of the two operations. It is not difficult to imagine molecules with higher orders of this simple form of cyclic symmetry resulting from the repeated application of a single generator resulting in increasingly large sets of symmetry operations

3-fold $\{E, c, c^2\}$ $c = 120°$
4-fold $\{E, c, c^2, c^3\}$ $c = 90°$
5-fold $\{E, c, c^2, c^3, c^4\}$ $c = 72°$
…….
∞-fold $\{E, c, c^2, …., c^\infty\}$ c = infinitely small

Mathematically, molecular symmetry operations are a set of elements that can be combined with a composition operation called "followed by". A set of elements with a binary operation is a mathematical group if the elements of the set and their binary operation obey the three group requirements:

1. There is an identity element E which in combination with any other element X simply reproduces that element. The "do nothing" or full rotation symmetry operation provides this element

$$EX = XE = X$$

2. Every element must have an inverse element

$$XY = YX = E$$

3. Combinations of elements must be associative. This means that the different combinations of operations should produce the same result.

$$(XY)Z = X(YZ)$$

Combinations of sets of symmetry operations always obey the group conditions and are usually called point groups because they always move around central point. Point groups are said to be commutative if the order in which their elements are combined has no effect on the outcome: $XY = YX$. All cyclic point groups are commutative because the order in which two rotations are applied makes no difference to the outcome. Schoneflies labeled cyclic symmetry groups of order n with the symbol C_n and this practice is widely used in mathematics.

A cyclic 3-fold molecule like triphenyl phosphine has eleven sets of three equivalent atoms that are exchanged during transformation operations. In this example the molecule has 11 sets of 3 three equivalent atoms that move into equivalent positions during rotations and a central atom that stays in place during each of the operations. A molecule with simple rotational symmetry might have any number of atoms positioned on the axis of rotation but these atoms are only mapped onto themselves during cyclic symmetry operations.

Looking at just one of these equivalence sets, say the carbon atoms nearest to the phosphorus atom, and imagining them to be numbered 1, 2 and 3 as in the image above, applications of the 3-fold generator operation redistribute the three atoms as follows

$$\begin{pmatrix}1\\2\\3\end{pmatrix} \xrightarrow{c} \begin{pmatrix}3\\1\\2\end{pmatrix} \xrightarrow{c} \begin{pmatrix}2\\3\\1\end{pmatrix} \xrightarrow{c} \begin{pmatrix}1\\2\\3\end{pmatrix}$$

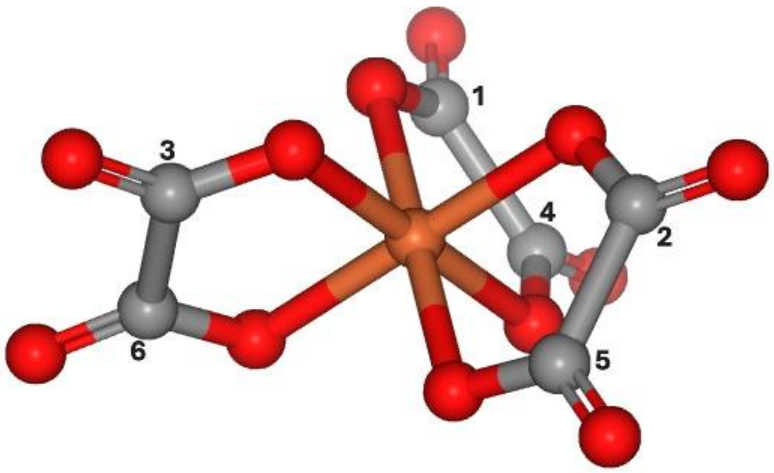
Initially the atoms are ordered by their positions but symmetry operations move numbered atoms to new positions until they return to their original setting. Two applications of the generator can be shown as a single operation

$$\begin{pmatrix}1\\2\\3\end{pmatrix} \xrightarrow{c^2} \begin{pmatrix}2\\3\\1\end{pmatrix}$$

Clearly, three applications of the operation return the molecule to its starting position $c^3 = E$ which is just the identity operation. There is nothing special about the three carbon atoms numbered in the diagram above and any three could have been chosen for the illustration. This molecule has six sets of 3 equivalent carbon atoms, five sets of 3 equivalent hydrogen atoms and single phosphorus atom positioned on the rotational axis.

Dihedral point groups

Cyclic rotational groups are an important basis for all other symmetry groups both rotational and non-rotational. This the illustrated by the trisoxalato iron III molecule ion shown below.



the trisoxalato iron III molecule ion $Fe(C_2O_4)_3$

This molecule has 3-fold symmetry about an imagined z axis and therefore belongs to the C_3 symmetry group. It also has 2-fold symmetry about the y axis and so belongs to a higher order dihedral symmetry group D_3 with six symmetry operations. In addition to the cyclic generator c already described there is now a generator u representing a 2-fold rotation about the y axis and these two operations can generate all six group operations of the group. Apart from the central iron atom this structure contains six equivalent carbon atoms and two separate sets of six equivalent oxygen atoms. D_3 group symmetry operations exchange all the atoms of one set of oxygen atoms with each other but not with the other set of oxygen atoms. Clearly, the number of equivalent atoms can never be greater than the order of the molecule.

In all dihedral groups except D_2 the order in which the two generator operations are applied produces a different symmetry transformation because the operations of dihedral groups are not commutative. Operation u is defined as a 2-fold rotation about the y axis so that rotation c followed by u produces the result $uc = u_1$ and c^2 followed by u produces $uc^2 = u_1$. This can be seen in the table below when the first operation is read from the top row of the table and the second operation is read from the left-hand side column. It is clear from the table that $uc = u_1$ but $cu = u_2$ so the order of application is critical.

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

Each of the six carbon atoms in the diagram above is numbered so that their movements during symmetry operations can be followed. Carbon atoms 1,2 and 3 are exchanged between themselves by the 3-fold cyclic rotation , forming a set of three equivalent atoms Those numbered 4,5 and 6 form a separate equivalent set as shown in the position vector diagram below

$$\begin{pmatrix}1\\2\\3\\4\\5\\6\end{pmatrix} \xrightarrow{c} \begin{pmatrix}3\\1\\2\\6\\4\\5\end{pmatrix} \xrightarrow{c} \begin{pmatrix}2\\3\\1\\5\\6\\4\end{pmatrix} \xrightarrow{c} \begin{pmatrix}1\\2\\3\\4\\5\\6\end{pmatrix}$$

An application of the u operation exchanges atoms of the two sets of three equivalent atoms, creating a set of six equivalent atoms that are exchanged as follows

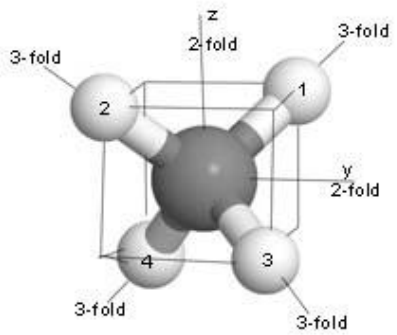
$$\begin{pmatrix}1\\2\\3\\4\\5\\6\end{pmatrix} \xrightarrow{u} \begin{pmatrix}4\\6\\5\\1\\3\\2\end{pmatrix} \xrightarrow{u} \begin{pmatrix}1\\2\\3\\4\\5\\6\end{pmatrix}$$

Combinations of the c and u generators applied to the molecule produce all six possible exchanges of the six atoms.

Spherical point groups

Spherical point groups include tetrahedral and octahedral rotational groups *T, O* of order 12 and 24 that are related in a similar way to the cyclic and dihedral groups in that one forms an index-2 subgroup of the other. These two are often called cubic groups because they are often shown inscribed in a cube. There is also an icosahedral rotational group *I* that has only limited application in molecular chemistry. It can be very difficult to find small molecules that have only rotational symmetry but it is possible to examine the rotational subgroup while simply ignoring the non-rotational elements of the larger group.

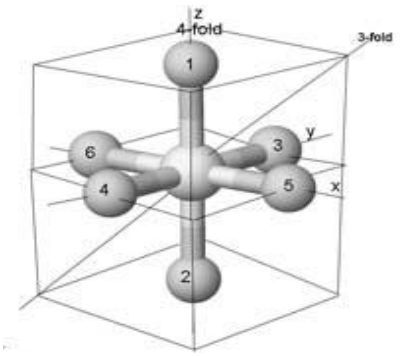
Methane belongs to the rotational tetrahedral group T of order 12 although it also belongs to a higher order non-rotational group T_d of order 24. All nonrotational groups have a rotational group of half the order of the larger group and it is always advantageous to deal first with the rational group because this limits the possible non-rotational groups and properties. A brief look at the diagram below shows that there are four 3-fold axes through the apices of the cube and three 2-fold axes about the mid-point of each pair of faces.



Methane inscribed in a cube

Consider for the moment just the rotational transformations of the molecule inscribed in a cube as shown above. Rotations of 180° degrees about each of the x, y and z axes bring the molecule into coincidence with itself and these operations, together with the identity operation, mean that it belongs to point group D_2 of order 4. These operations are $\{E, c, c_x, c_y\}$. Four distinct 3-fold symmetry axes running between opposite corners of the cube are equally obvious in the figure and these operations may be labeled $\{E, b, b^2\}$. As a result tetrahedral point group 23 is a combination of the 2-fold dihedral group and the 3-fold cyclic group, producing a group of order 12: the identity element, three 2-fold rotations about x, y and z axes and eight 3-fold rotations about axes between apices of the cube

Octahedral molecules also appear inscribed in cubes but might have atoms positioned at the midpoints of each face as in the following example



An octahedral molecule inscribed in an cube

An octahedral molecule has the 12 symmetry operations of a tetrahedral molecule described above together with twelve further operations not found in the tetrahedral case: six 4-fold rotations about the x, y and z axes plus six 2-fold rotations about lines bisecting the axes. Together these are the 24 symmetry operations of rotational group O. Generator c is now a clockwise rotation of 90° that also produces multiples of 180° and 270° as opposed to the tetrahedral case where it is a 180° rotation. Also present are the 3-fold rotations produced by generator b about the same four axes as in the tetrahedral group and these can be used in transforms to produce 4-fold rotations about the other two axes. These 3-fold rotations are exactly those of the tetrahedral group. In addition to the 3 and 4-fold axes there are three 2-fold axes bisecting opposite diagonals.

Rotational groups in Laue classes

Crystallographers define Laue classes by the centrosymmetric group on the right-hand side of the Laue class table because X-ray diffraction inserts a centre of symmetry into non-centred point groups. In molecular work the rotational group on the left-hand side is more useful because it has the same abstract structure as other members of the Laue class except the centrosymmetric group which is a direct product of the rotational group and the inversion operation. Rotational point groups contain all the necessary information required to construct the operations and representations of every non-rotational point group possible.