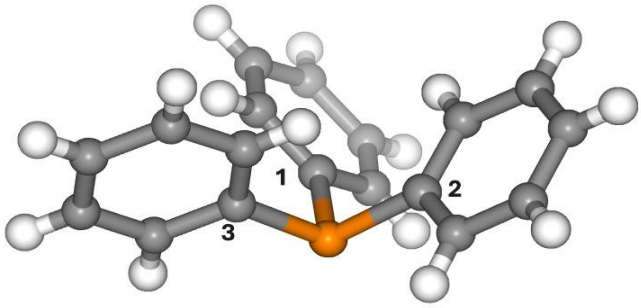
Representations of symmetry operations

Triphenyl phosphine has three hexagonal planar rings attached to a central phosphorus atom so that the molecule has 3-fold symmetry about a vertical axis passing through the phosphorous atom.



Triphenyl phosphine

The molecule has six sets of three equivalent carbon atoms and five sets of three equivalent hydrogen atoms. Looking again at just the carbon atoms nearest to the phosphorus atom, numbering them 1, 2 and 3 as in the image above, we noted that an application of the 3-fold generator operation c redistributed the three atoms as follows

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

This redistribution of the atoms from their original positions is faithfully mimicked by a permutation matrix as follows

$$\begin{pmatrix}3\\1\\2\end{pmatrix} = \begin{pmatrix}0&0&1\\1&0&0\\0&1&0\end{pmatrix}\begin{pmatrix}1\\2\\3\end{pmatrix}$$

In this way the following three permutation matrices are obtained

$$P(E) = \begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix} \qquad P(c) = \begin{pmatrix}0&0&1\\1&0&0\\0&1&0\end{pmatrix} \qquad P(c^2) = \begin{pmatrix}0&1&0\\0&0&1\\1&0&0\end{pmatrix}$$

Permutation matrices $P(x)$ mimic the behaviour of operations x and must multiply out in same way as the operations themselves. For example, $cc^2 = E$ and so $P(c)P(c^2) = P(E)$in the matrix multiplication

$$\begin{pmatrix}0&0&1\\1&0&0\\0&1&0\end{pmatrix}\begin{pmatrix}0&1&0\\0&0&1\\1&0&0\end{pmatrix} = \begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}$$

Only three atoms have so far been considered but the molecule has eleven sets of three equivalent atoms and a central atom and so $11 \times 3 + 1 = 34$ atoms and its symmetry operations would need to be described by a 34 x 34 square matrix. Fortunately, the atoms in each equivalence set are only exchanged with others of their equivalence set and the permutation matrix consists of eleven 3 x 3 submatrices identical to those above positioned on the leading diagonal together with a single 1 to represent the central atom.

Each of the 3×3 matrices can be reduced to irreps that are characteristic of the group being represented then the irreps deduced are added together. This is done by adding up the elements on the leading diagonals of each of the permutation matrices to deduce the character for each matrix. In the case of the three equivalent atoms above this gives $Ch(E) = 3$, $Ch(c) = 0$ and $Ch(c^2) = 0$. Group theory requires that the characters of the irreps add up to that of the larger representation and this allows the irreps to be deduced. Fortunately, this procedure is never required in practice because n equivalent atoms in an n -fold cyclic group always produces one of each irrep of the group. All that is required is the list below of the possible irreps for each order of rotation

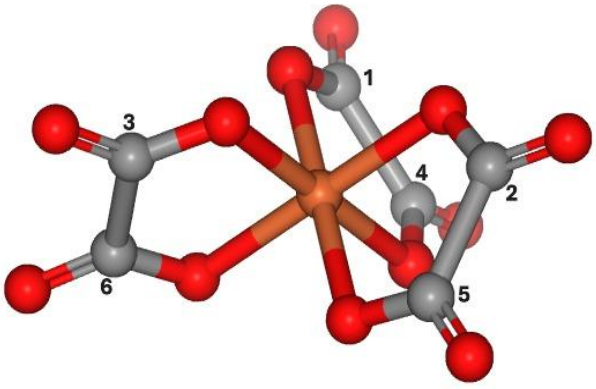
Cyclic group irreps

n	Irreps	n	Irreps
1	A	2	A, B
3	A, E_{+1}, E_{-1}	4	A, B, E_{+1}, E_{-1}
5	$A, E_{+1}, E_{-1}, E_{+2}, E_{-2}$	6	$A, B, E_{+1}, E_{-1}, E_{+2}, E_{-2}$
7	$A, E_{+1}, E_{-1}, E_{+2}, E_{-2}, E_{+3}, E_{-3}$	8	$A, B, E_{+1}, E_{-1}, E_{+2}, E_{-2}, E_{+3}, E_{-3}$
	.....		
∞	$A, E_{+1}, E_{-1}, E_{+2}, E_{-2}, .., E_{\infty}$		

All that needs to be done is to find the order of the rotation then assign its irreps according to the table above. Cyclic group irrep symbols are 1 dimensional so 3 x 3 matrices like the those above reduce to three 1 x 1 irreps i.e. three numbers. Matrices from one equivalence set reduce to irreps $A, E_{+1}, E_{-1}$and since the other 10 behave in the same way a total irrep count for the whole molecule will be $11(A, E_{+1}, E_{-1}) + A$. Group theory requires that the irreducible representations of each equivalence set contain the most symmetrical irrep once and only once so a single atom always has the most symmetrical irrep. The extension to other cyclic groups is simple and straightforward.

Dihedral symmetry groups

The trisoxalato iron III molecule ion shown below was used to illustrate symmetry operations in dihedral goups



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

This molecule belongs to symmetry group 3 but also has 2-fold symmetry about the y axis and so belongs to the higher order dihedral symmetry group D_3. Atoms 1,2 and 3 are exchanged by 3-fold symmetry operations in the same way as in the cyclic example above. A second set of atoms numbered 4,5 and 6 are also exchanged between themselves during these operations. When this molecule is considered to have C_3 symmetry the matrix representations of these two sets of atoms will

have irreps $2(A, E_{+1}, E_{-1})$. The matrix itself $P(c)$ is just two 3 x 3 matrices on the leading diagonal of a 6 x 6 matrix

$$\begin{pmatrix}3\\1\\2\\6\\4\\5\end{pmatrix} = \begin{pmatrix}0&0&1&0&0&0\\1&0&0&0&0&0\\0&1&0&0&0&0\\0&0&0&0&0&1\\0&0&0&1&0&0\\0&0&0&0&1&0\end{pmatrix}\begin{pmatrix}1\\2\\3\\4\\5\\6\end{pmatrix}$$

A 2-fold rotation u about the horizontal y axis exchanges the two sets of atoms, creating a new equivalence set of 6 atoms from the two sets of 3 equivalent atoms with matrix $P(u)$

$$\begin{pmatrix}4\\6\\5\\1\\3\\2\end{pmatrix} = \begin{pmatrix}0&0&0&1&0&0\\0&0&0&0&0&1\\0&0&0&0&1&0\\1&0&0&0&0&0\\0&0&1&0&0&0\\0&1&0&0&0&0\end{pmatrix}\begin{pmatrix}1\\2\\3\\4\\5\\6\end{pmatrix}$$

It is worth checking that the matrices multiply out in the same way as the operations

Operation $uc = u_1$ so we expect $P(u)P(c) = P(u_1)$

$$\begin{pmatrix}0&0&0&1&0&0\\0&0&0&0&0&1\\0&0&0&0&1&0\\1&0&0&0&0&0\\0&0&1&0&0&0\\0&1&0&0&0&0\end{pmatrix}\begin{pmatrix}0&0&1&0&0&0\\1&0&0&0&0&0\\0&1&0&0&0&0\\0&0&0&0&0&1\\0&0&0&1&0&0\\0&0&0&0&1&0\end{pmatrix} = \begin{pmatrix}0&0&0&0&0&1\\0&0&0&0&1&0\\0&0&0&1&0&0\\0&0&1&0&0&0\\0&1&0&0&0&0\\1&0&0&0&0&0\end{pmatrix}$$

A quick check of the image above shows that this is transformation u_1

$$\begin{pmatrix}6\\5\\4\\3\\2\\1\end{pmatrix} = \begin{pmatrix}0&0&0&0&0&1\\0&0&0&0&1&0\\0&0&0&1&0&0\\0&0&1&0&0&0\\0&1&0&0&0&0\\1&0&0&0&0&0\end{pmatrix}\begin{pmatrix}1\\2\\3\\4\\5\\6\end{pmatrix}$$

It is already clear that, when considered as a 3-fold cyclic group, the six equivalent atoms consist of two sets of 3 equivalent atoms with irreps $2(A + E_{+1} + E_{-1})$. An additional 2-fold rotational symmetry at right angles to the main axis merges conjugate pairs of E irreps to form a single two-dimensional representation. At the same time A and B irreps are split into two distinct one-dimensional irreps with subscripts 1 and 2. These changes produce the collection of the irreducible representations shown below. The cyclic irreps therefore become $A_1 + A_2 + 2E_1$ in a dihedral environment because the most symmetrical irrep A_1must occur once and only once so the second subscript has to be 2.

n	Dihedral irreps	n	Dihedral irreps
2	A_1, A_2, B_1, B_2	3	A_1, A_2, E_1
4	A_1, A_2, B_1, B_2, E_1	5	A_1, A_2, E_1, E_2
6	$A_1, A_2, B_1, B_2, E_1, E_2$	7	A_1, A_2, E_1, E_2, E_3
8	$A_1, A_2, B_1, B_2, E_1, E_2, E_3$		
	and so on until		
∞	$A_1, A_2, E_1, E_2, E_3, E_4, .., E_\infty$		

Representations for non-rotational group molecules

Non-rotational groups may be derived from rotational groups in two ways: either by combining rotational operations with mirror reflection or as a direct product of the rotational group with space inversion (i). These possibilities are shown in the table of Laue classes below with rotational group G on the left semi-direct product groups $\bar{G}$ in the middle and direct product groups Gi on the right. One row of the table contains the groups of one Laue class

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			$532i$

Point groups in a Laue class, other than the centrosymmetric group, are distinct manifestations of a single abstract group and, since irreps are characteristic of the abstract group rather than the individual point group, they *all have the same irreducible representations* and these are shown in the cyclic and dihedral irrep tables above. The centrosymmetric group is the direct product of any other member of

a Laue class with a 2-fold cyclic group representing space inversion. Its irreps are also direct products of the class irreps, producing two sets of irreps distinguished by g and u subscripts.

Take the ammonia molecule with point group symmetry $3\bar{2}$ as an example. This group belongs to the 3-fold dihedral Laue class and has the irreps for this group shown above. In point group $3\bar{2}$ the three equivalent hydrogen atoms have irreps A, E_{+1}, E_{-1} and the nitrogen atom contributes irrep A. Upgrading this to the dihedral class gives irreps $A_1 + E_1$ for the hydrogen atoms and A_1 for the nitrogen atom so the irrep total for the molecule is $2A_1 + E_1$

Staggered ethane belongs to point group $32i$ of order 12 and is the centrosymmetric group of the 3-fold dihedral Laue class. It has two sets of three hydrogen atoms attached to two carbon atoms that can be imagined to be placed in the z axis. When considered as a cyclic molecule the two sets of three equivalent hydrogen atoms contribute irreps $2(A, E_{+1}, E_{-1})$ and the carbon atoms contribute $2A$ because they are isolated atoms and both have the most symmetric irrep. Looking at this molecule as a dihedral point group, the two sets of hydrogen atoms merge to become a single set of six equivalent atoms with irreps $A_1 + A_2 + 2E_1$, following the reasoning in the example above. The two isolated carbon atoms become two equivalent atoms in the dihedral group because they can rotate to exchange position and their irreps in this group become $A_1 + A_2$. Finally, the dihedral irreps acquire g and u subscripts and a simple rule helps this process: if an atom is positioned at the centre of symmetry it contributes the most symmetrical irrep of the group otherwise there must be an equal number of g and u subscripts for each equivalence set. So, starting with irreps $A_1 + A_2 + 2E_1$ we have to add subscript g to the A_1 irrep to obtain the most symmetric irrep and, in order to then keep the numbers of subscripts equal we obtain $A_{1g} + A_{2u} + E_{1g} + E_{1u}$. Similarly, the carbon atom irreps become $A_{1g} + A_{2u}$ and the total for the molecule becomes

$$2A_{1g} + 2A_{2u} + E_{1g} + E_{1u}$$

This completes one example for each of the 3-fold dihedral Laue class groups. Irreps can always be deduced by inspection and the laborious us of the "Great Orthogonality Theorem" is completely unnecessary simply to find irreps.