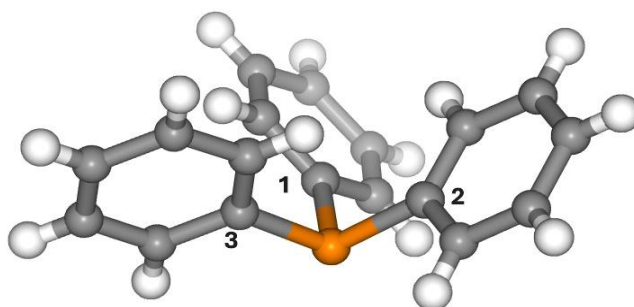# Representations of symmetry operations

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 $11 \times 3 + 1$ 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 positioned on the leading diagonal together with a single 1 to represent the central atom.

Point group representation matrices can be reduced to irreducible representations that are characteristic of the group being represented. One way of doing this is to sum 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 the procedure described above always shows that 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 ie 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 higher order 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
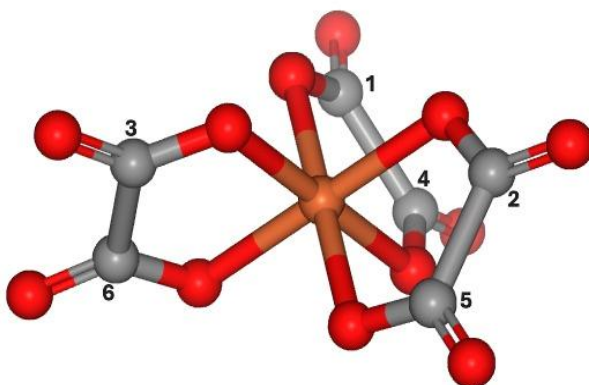
the trisoxalato iron III molecule ion $Fe(C_2O_4)_3$

This molecule belongs to the C_3 symmetry group 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 C_3 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_1 must 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

Laue classes of point groups

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

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**. 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 C_{3v} as an example. This group belongs to Laue class D_3 and has the irreps for this group shown above. In point group C_3 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 D_{3d} of order 12 and is the centrosymmetric group of the D_3 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 C_3 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 in a D_3 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 D_3 example above. The two isolated carbon atoms become two equivalent atoms in D_3 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 maintain 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 D_3 Laue class groups. Irreps can always be deduced by inspection and the laborious use of the "Great Orthogonality Theorem" is completely unnecessary simply to find irreps.