

3.2. POINT GROUPS AND CRYSTAL CLASSES

These four site-symmetry groups all have order 2. Accordingly, the multiplicity for each of the atoms discussed above is $8/2 = 4$. The atoms $H3^1 \dots H3^8$, however, are on a general position, their site symmetry is 1 and their multiplicity corresponds to the order 8 of the point group $4mm$. Their orbit belongs to the Wyckoff position $8d$. The Wyckoff position $1a$ on the fourfold rotation axis is not occupied.

3.2.4.3. Tables of the point groups

In Table 3.2.3.2 all crystallographic point groups are listed, *i.e.* all point groups with axes of orders 1, 2, 3, 4 and 6. As described in Section 3.2.1.2.3, the tables also contain the crystal forms which refer to the faces of crystals. As far as molecular symmetry is concerned, only the first four columns and the names of the polyhedra (point forms) in the fifth column given in italics are of interest.

The polyhedra listed in the fifth column result when the points of one orbit of the corresponding Wyckoff position are connected by lines. As for their names, see the remarks on 'point forms' in Sections 3.2.1.2.3 and 3.2.1.2.4.

In Table 3.2.3.2 each point group is headed by its short and, if it differs, full Hermann–Mauguin symbol and by its Schoenflies symbol. Each of the subsequent entries corresponds to one Wyckoff position, in order of increasing site symmetry. The last Wyckoff position of the list is always the one with the highest site symmetry and a multiplicity of 1. The sequence of the coordinate triplets follows the sequence as for the symmorphic space groups.

The columns of Table 3.2.3.2 contain the following data:

Column 1: The multiplicity, *i.e.* the number of equivalent points.

Column 2: The Wyckoff letter, which is an alphabetical label. For all point groups with a 'floating' origin, *i.e.*, where the origin is not fixed on a unique point of highest symmetry, the last entry is the Wyckoff letter *a*. For point groups with a fixed origin, the unique origin point has the highest site symmetry and has the letter *o* (for origin).

Column 3: The site symmetry, given as an 'oriented point-group symbol' (*cf.* Section 2.1.3.12).

Column 4: Coordinates x, y, z of equivalent points.

Column 5: The name of the polyhedron (point form) spanned by the set of symmetry-equivalent points with the coordinates from column 4 is given in italics. The names given in roman type refer to crystal forms described in Section 3.2.1.2.3 and have no importance for molecules. In some cases, a Wyckoff position has several entries in columns 5 and 6, with several polyhedron names. All but the first one correspond to orbits of the same Wyckoff position where some special values have been assigned to one or more of the variable coordinates, *e.g.* $z = 0$, with the consequence that the eigensymmetries of these orbits are higher than the symmetry of the generating point group (non-characteristic orbits, *cf.* Section 1.4.4.4).

Since there is no lattice, point groups of molecules, unlike point groups of crystals, have no 'natural' coordinate system. It is common for coordinates of atoms in molecules to refer to a Cartesian xyz coordinate system; with the exception of trigonal and hexagonal point groups, the coordinates given in Table 3.2.3.2 can be taken as Cartesian coordinates with arbitrary unit length. For point groups with a floating origin, the origin 0, 0, 0 has to be assigned to an arbitrarily chosen point of the Wyckoff position $1a$. The following conventions are used for the orientation of the coordinate axes:

Triclinic system: arbitrary orientation of the axes.

Monoclinic system: unique axis either y or z , as specified. The other two directions arbitrary but normal to the unique axis.

Orthorhombic system: Axes x, y and z along the symmetry directions.

Tetragonal system: z along the fourfold symmetry axis, x along the symmetry direction mentioned in the second position of the Hermann–Mauguin symbol. In the case of one-digit Hermann–Mauguin symbols the x direction is arbitrary within the plane normal to the unique axis. The axis y is normal to both x and z .

Trigonal and hexagonal systems: z along the unique symmetry axis, x along the symmetry direction mentioned second in the Hermann–Mauguin symbol. In the case of one-digit Hermann–Mauguin symbols the x direction is arbitrary within the plane normal to the unique axis. The axis y is also normal to z . *Note:* The coordinates given in Table 3.2.3.2 do not refer to a Cartesian, but to a symmetry-adapted coordinate system. For the hexagonal point groups and the trigonal point groups marked 'hexagonal axes' there is an angle of 120° between the x and y axes. These coordinates can be converted to a Cartesian system according to $x - \frac{1}{2}y, \frac{1}{2}\sqrt{3}y, z$. Coordinates that refer to 'rhombohedral axes' are not suited for separate molecules.

Cubic system: x, y and z along the symmetry directions described by the first position of the Hermann–Mauguin symbol.

For the trigonal and hexagonal systems, the following pairs of point-group types are distinguished in Table 3.2.3.2: 321 & 312 , $3m1$ & $31m$, $\bar{3}m1$ & $\bar{3}1m$ and $\bar{6}m2$ & $\bar{6}2m$. In fact, each of these pairs represents only one molecular point-group type, the difference being only the arbitrarily chosen direction of the x axis. The members of each pair can be interconverted by turning the coordinate system by 30° about the z axis (referred to hexagonal axes). The same applies to the tetragonal pair $\bar{4}2m$ & $\bar{4}m2$, the turning angle being then 45° .

The terms triclinic, monoclinic, orthorhombic, tetragonal, trigonal, hexagonal and cubic designate the crystal systems, *i.e.* the point groups of crystal lattices. As far as point groups of molecules are concerned, these terms only have the meaning of a classification by analogy with the crystal classes. For those who are accustomed to using Schoenflies symbols, it may seem odd to term the point groups $C_{3h} = S_3 = \bar{6}$ and $D_{3h} = \bar{6}2m$ hexagonal rather than trigonal, because the Schoenflies symbolism relies on roto-reflection operations rather than roto-inversion operations. In fact, some properties of C_{3h} and D_{3h} are rather more 'trigonal' than 'hexagonal'; for example, they have only one kind of degenerate irreducible representation (E), rather than two (E_1 and E_2) as do the other hexagonal point groups.

For the sake of treating molecular symmetries in the most uniform way, some recommendations for the preferred directions of the coordinate axes have been proposed (Joint Commission for Spectroscopy, 1955). These recommendations include:

- (1) If any specifications are being made that depend on the choice of the axes (*e.g.* certain irreducible representations), the choice should explicitly be stated.
- (2) For planar molecules with one three- or higher-fold axis (z axis): x axis through the greater number of atoms. For planar molecules with $mm2$ (C_{2v}) or mmm (D_{2h}) symmetry: x axis perpendicular to the plane of the molecule.

Molecular symmetry is not restricted to the crystallographic point groups. No detailed tables are given for noncrystallographic point groups, but the symbols for them can be found in Table 3.2.1.6. For the two icosahedral point groups see Section 3.2.1.4.2 and Table 3.2.3.3.

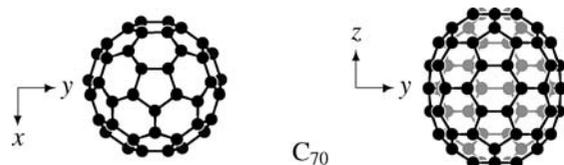
Certain physical properties depend on symmetry. In particular, a molecule can have a dipole moment only if it is polar, *i.e.* if it

has no rotoinversion axis ($\bar{2} = m$ excepted) and if it has at most one symmetry axis of order $N > 1$ and no reflection plane perpendicular to it. The polar point groups are N ($N = 1, 2, \dots$), m , Nm (N odd) and Nmm (N even). The corresponding crystallographic point groups are those marked with a + sign under the heading ‘First-rank tensor’ in Table 3.2.2.1.

Examples

For the example of metaldehyde mentioned in the preceding section, we find in Table 3.2.3.2, point group $4mm$, the Wyckoff positions $8d$, $4c$, $4b$ and $1a$. Looking at the image of the molecule, we choose a coordinate system with z along the fourfold axis and x and y perpendicular to the mirror planes marked m_{10} and m_{01} . Some value has to be assigned to the unit of the (Cartesian) coordinate system, say 1 \AA . The origin must be chosen at some arbitrary site on the Wyckoff position $1a$, say such that $z = 0$ for the $C1$ atoms. There is no atom on the Wyckoff position $1a$ ($0, 0, z$). The orbit consisting of the four oxygen atoms is on position $4b$ (x, x, z), $(-x, -x, z)$, $(-x, x, z)$, $(x, -x, z)$, with $x = 0.831$, $z = 0.586$; these atoms form a square and have the site symmetry $.m$, which in the image is on the mirror planes m_{11} and $m_{\bar{1}\bar{1}}$. Position $4c$ ($x, 0, z$), $(-x, 0, z)$, $(0, x, z)$, $(0, -x, z)$ has three occupied orbits: $C1$ with $x = 1.710$ and (the arbitrary) $z = 0$, $C2$ with $x = 3.194$, $z = 0.294$ and $H2$; each of these orbits again forms a square and their site symmetry is $.m$ on the mirror planes m_{01} and m_{10} . The orbit of the eight $H3$ atoms is on the general position $8d$; they form a truncated square. (The numerical values have been adapted from the coordinates of Barnett *et al.*, 2005).

The fullerene C_{70} is an example of a molecule with noncrystallographic symmetry, $\bar{10}2m$ (D_{5h}). This point-group type is not listed in Table 3.2.3.2, but it can be found in Table 3.2.1.6.



3.2.4.4. Polymeric molecules

Polymeric molecules actually consist of a finite number of atoms, but it is more practical to treat them as parts of infinitely extended molecules in the same way as crystals are treated as parts of ideal infinite crystals. If an infinitely long ideal molecule has translational symmetry in one direction, then its symmetry group is a rod group. If the molecule forms a layer with translational symmetry in two dimensions, its symmetry group is a layer group (not to be confused with a plane group, where space is restricted to two dimensions, *i.e.* to an infinitely thin plane).

Rod groups can have noncrystallographic symmetries, with axes of any order, such as the 10_3 screw axes in polymeric sulfur or the 29_9 axes in polyoxymethylene. Symbols for rod groups correspond to Hermann–Mauguin space-group symbols, but begin with a script style \mathcal{R} . The unique direction c is the direction with the translational symmetry; lattice vectors exist in this direction only and are integral multiples of c . This is also the direction of any rotation or screw axis with order $N > 2$. There is no natural length for the a and b vectors. If there are (twofold) rotation axes perpendicular to c or normals of mirror or glide planes perpendicular to c , these directions serve to determine the directions of a and b ; otherwise, their directions are arbitrary.

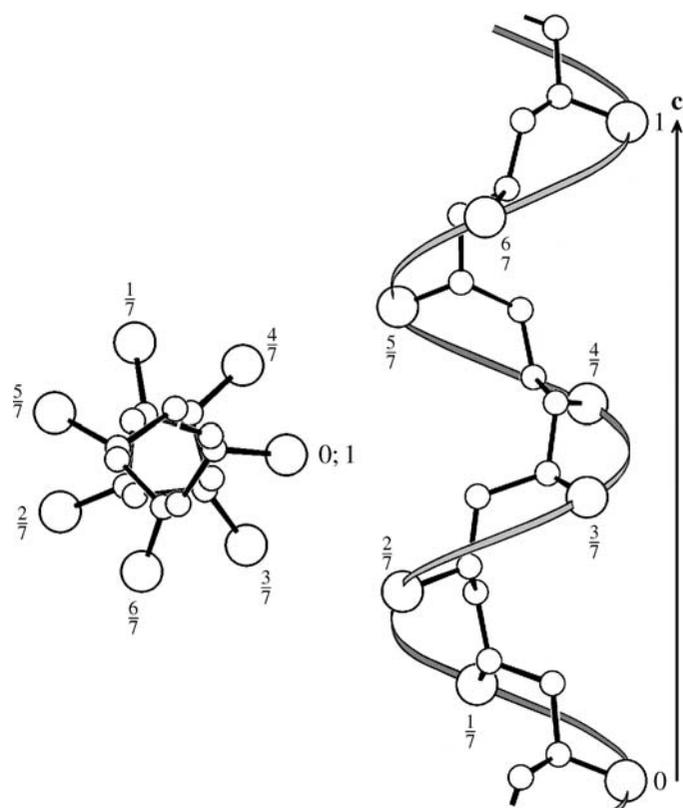


Figure 3.2.4.1

P-helix of isotactic poly-4-methyl-1-pentene (form I) with a $7/2$ helix which corresponds to a 7_4 helix in Hermann–Mauguin notation. Large circles represent isobutyl groups (adapted from Natta & Corradini, 1960).

Molecules of chain polymers tend to be entangled, in which case they have no overall symmetry; symmetry is then restricted to the local symmetry in the immediate surrounding of an atom. In crystalline polymers the chains are forced to align themselves and to adopt a symmetric conformation. This symmetry can be crystallographic, but often the symmetry of the single molecule within the crystal matrix is noncrystallographic.

Crystalline chain polymers often adopt helical molecular structures. In polymer science helices are designated according to the ‘helical point net system’ by N/r (N/r helix’) where N is the number of repeating units within one translation period and r is the corresponding number of helical coil turns along the molecular chain (Alexander, 1969; *Compendium of Polymer Terminology and Nomenclature* (2008); Spruiell & Clark, 1980).²⁵ Provided that all repeating units in the chain are symmetry-equivalent, the corresponding Hermann–Mauguin screw axis symbol N_q can be calculated from

$$Nn \pm 1 = rq,$$

where n ($= 0, 1, 2, \dots$) and q ($0 < q < N$) are integers to be chosen such that the equation is satisfied. The chemical handedness of the helix does not follow from the N/r symbol, but is specified by the letters M (minus; or L) and P (or R) for left and right, respectively.

Example

Isotactic poly-4-methyl-1-pentene (form I) consists of helical $7/2$ chains (7 monomers per two chain windings). The equation

²⁵ In the IUPAC Recommendations 2011, a different notation for polymeric helices is recommended, in that a $7/2$ helix be named 7_2 helix (Meille *et al.*, 2011). This is very unfortunate because it causes confusion with the Hermann–Mauguin symbols: the Hermann–Mauguin symbol of the $7/2$ helix is not 7_2 , but 7_4 or 7_3 .