# 3. ADVANCED TOPICS ON SPACE-GROUP SYMMETRY

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 ($N = 1, 2, \ldots$), 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 Å. 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 $m_{1\bar{1}}$. 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, $\overline{10}\,2\,m$ (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.

C_{70}
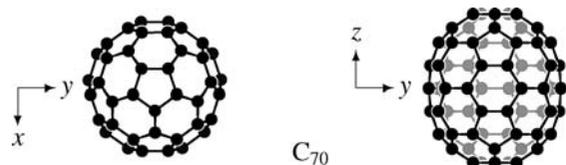
3.2.4.4. Polymeric molecules

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 $\wp$. The unique direction c is the direction with the translational symmetry; lattice vectors exist in this direction only and are integral multiples of $\mathbf{c}$. This is also the direction of any rotation or screw axis with order $N > 2$. There is no natural length for the $\mathbf{a}$ and $\mathbf{b}$ vectors. If there are (twofold) rotation axes perpendicular to $\mathbf{c}$ or normals of mirror or glide planes perpendicular to $\mathbf{c}$, these directions serve to determine the directions of $\mathbf{a}$ and $\mathbf{b}$; otherwise, their directions are arbitrary.
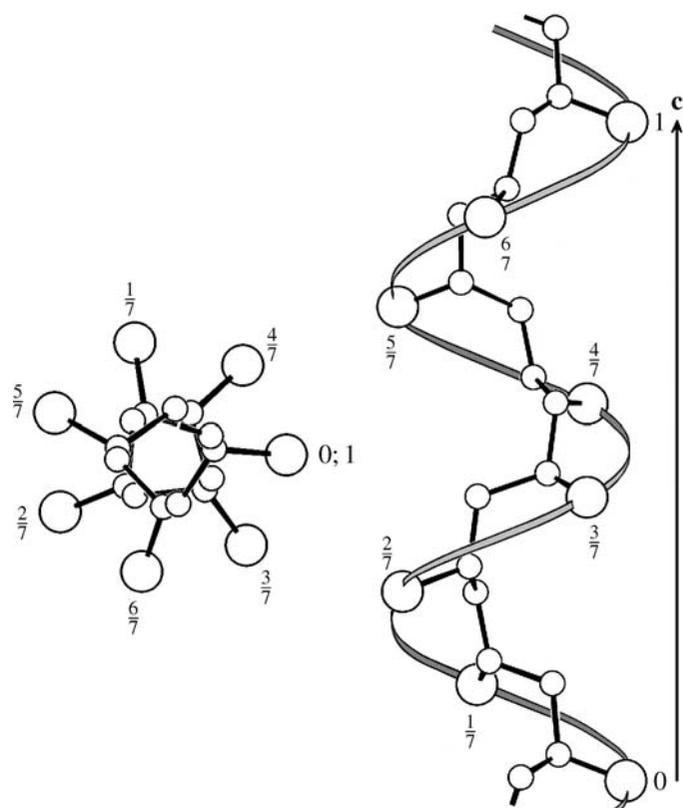
Figure 3.2.4.1
P-helix of isotactic poly-4-methyl-1-pentene (form I) with a 7/2 helix which corresponds to a 7_4 helix in Hermann–Mauguin notation. Large circles represent isobutyl groups (adapted from Natta & Corradini, 1960).

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 $(= 0, 1, 2, \ldots)$ 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

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[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.

above is fulfilled either as $7 \times 1 + 1 = 2 \times 4$ or $7 \times 1 - 1 = 2 \times 3$, *i.e.* $q = 4$ or $q = 3$, and the corresponding Hermann–Mauguin screw operation symbol is either 7_4 or 7_3, depending on chirality. The helix is shown in Fig. 3.2.4.1. The N/r symbol cannot be deduced uniquely from the Hermann–Mauguin symbol, because a 7/9 or any other 7/(2 modulo 7) P-helix and any 7/(5 modulo 7) M-helix also has $\mathscr{p}7_4$ symmetry.

Layer groups can have axes of orders of 1, 2, 3, 4 and 6 only. There exist 80 layer-group types. Layer-group symbols refer to a crystallographic coordinate system with **c** (of arbitrary length) perpendicular to the layer defined by the basis vectors **a** and **b**. Layer-group symbols are like space-group symbols, but begin with a lower-case p or c specifying the centring. Since plane-group symbols also begin by p or c and can therefore be confused with layer-group symbols, it is advisable to always mention what kind of group is meant.

Rod and layer groups with axis orders of 1, 2, 3, 4 and 6 are the subject of *International Tables for Crystallography* (2010), Volume E, *cf.* Section 1.7.3. Table 3.2.4.1 lists the rod-group types for any axis order.

3.2.4.5. Enantiomorphism and chirality

Definition: An object is *chiral* if it cannot be superposed by pure rotation and translation on its image formed by inversion through a point.

The symmetry group of a chiral object contains no symmetry operations of the second kind, *i.e.* no inversion, rotoinversion, reflection or glide reflection. As a consequence, a chiral object can occur in two different forms, which are related in the same way as are a right and a left hand. Further terms in this context are (Flack, 2003; Moss, 1996):

Absolute configuration	Spatial arrangement of atoms in a chiral molecule and its appropriate designation [*e.g.* by (*R*), (*S*) *etc.*]
Absolute (crystal) structure	Spatial arrangement of atoms in a chiral crystal and its description (lattice parameters, space group, atomic coordinates)
Enantiomorph	One out of a pair of objects of opposite chirality
Enantiomer	One molecule out of a pair of opposite chirality (special designation for enantio-morphic molecules)
Racemate	Equimolar mixture of a pair of enantiomers
Chirality sense (chirality)	Property which distinguishes enantiomorphs from one another; the two enantiomorphs of a pair have opposite chirality
Achiral	Refers to an object that is not chiral

Possible point groups for chiral molecules correspond to the crystal classes marked in Table 3.2.2.1 with a + sign under the heading 'Enantiomorphism'. In addition, the noncrystallographic point groups N, $N2$ (N odd, $N \geq 5$), $N22$ (N even, $N \geq 8$) and 235 are possible. Chiral crystal structures are compatible only with space groups that have no inversion centres, rotoinversion axes, reflection or glide-reflection planes. For a chiral molecular compound, these symmetry elements would generate the opposite enantiomer and the compound would be a racemate. Chiral

Table 3.2.4.1
Classes of rod groups

If $N = 2$, the conventional symbols differ (the symmetry direction with the N must by shifted to the last position of the symbol and $\bar{2}$ is to be replaced by m). n is an arbitrary positive integer.

Short symbol	Full symbol	N	q
$\mathscr{p}N$		$N = n$	
$\mathscr{p}N_q$		$N = n \geq 2$	$q = 1, \ldots, N-1$
$\mathscr{p}\bar{N}$		$N = n$	
$\mathscr{p}N/m$		$N = 2n$	
$\mathscr{p}N_q/m$		$N = 2n$	$q = \frac{1}{2}N$
$\mathscr{p}N2$		$N = 2n+1$	
$\mathscr{p}N22$		$N = 2n$	
$\mathscr{p}N_q2$		$N = 2n+1$	$q = 1, \ldots, N-1$
$\mathscr{p}N_q22$		$N = 2n$	$q = 1, \ldots, N-1$
$\mathscr{p}Nm$		$N = 2n+1$	
$\mathscr{p}Nmm$		$N = 2n$	
$\mathscr{p}Nc$		$N = 2n+1$	
$\mathscr{p}Ncc$		$N = 2n$	
$\mathscr{p}N_qmc$		$N = 2n$	$q = \frac{1}{2}N$
$\mathscr{p}\bar{N}m$	$\mathscr{p}\bar{N}2/m$	$N = 2n+1$	
$\mathscr{p}\bar{N}2m$		$N = 2n$	
$\mathscr{p}\bar{N}c$	$\mathscr{p}\bar{N}2/c$	$N = 2n+1$	
$\mathscr{p}\bar{N}2c$		$N = 2n$	
$\mathscr{p}N/mmm$	$\mathscr{p}N/m2/m2/m$	$N = 2n$	
$\mathscr{p}N/mcc$	$\mathscr{p}N/m2/c2/c$	$N = 2n$	
$\mathscr{p}N_q/mmc$	$\mathscr{p}N_q/m2/m2/c$	$N = 2n$	$q = \frac{1}{2}N$

crystals belong to one of the 11 crystal classes allowing enantiomorphism (Table 3.2.2.1); they can adopt one out of 65 space-group types. These are called the 65 *Sohncke space-group types* [after L. Sohncke who was the first to derive them; Flack (2003). Julian (2015) calls them 'proper space groups']. The Sohncke space-group types comprise the eleven pairs of enantiomorphic space-group types (*cf.* Section 1.3.4.1) and further 43 non-enantiomorphic space-group types. Whereas an enantiomorphic space group (*e.g.* $P3_1$ or $P4_122$) is chiral in itself, which means that its Euclidean normalizer is noncentrosymmetric, the space groups of the other 43 Sohncke space-group types (*e.g.* $P2_12_12_1$) are not chiral themselves; they have centrosymmetric Euclidean normalizers. Keep in mind that the symmetry of a molecule is specified by its point group; the symmetry of a crystal by its space group; and the symmetry of a space group by its Euclidean normalizer (*cf.* Section 3.5.1.2).[26] However, the arrangement of the atoms in any Sohncke space group is always chiral. In other words, an enantiomorphic space group is a sufficient but not a necessary condition for a chiral crystal structure. Chirality in a non-chiral space group results if the molecules or other building blocks of the crystal consist of only one kind of enantiomers or because the molecules or building blocks, without having to be chiral themselves, are arranged in a chiral manner in the crystal.

Examples

Trigonal selenium exhibits two enantiomorphic forms that consist of either right-handed or left-handed helical chain molecules (rod groups $\mathscr{p}3_12$ and $\mathscr{p}3_22$, respectively). The molecules as well as the space groups $P3_121$ and $P3_221$ are enantiomorphic and the helical molecules of right-handed

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[26] Many structural researchers are not aware of the difference between chiral (enantiomorphic) space groups and Sohncke space groups; frequently, even in textbooks, the term 'chiral space group' is used although an achiral Sohncke space group is meant.

references