

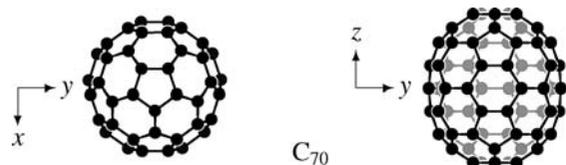
3. ADVANCED TOPICS ON SPACE-GROUP SYMMETRY

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 ($N = 1, 2, \dots$), 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

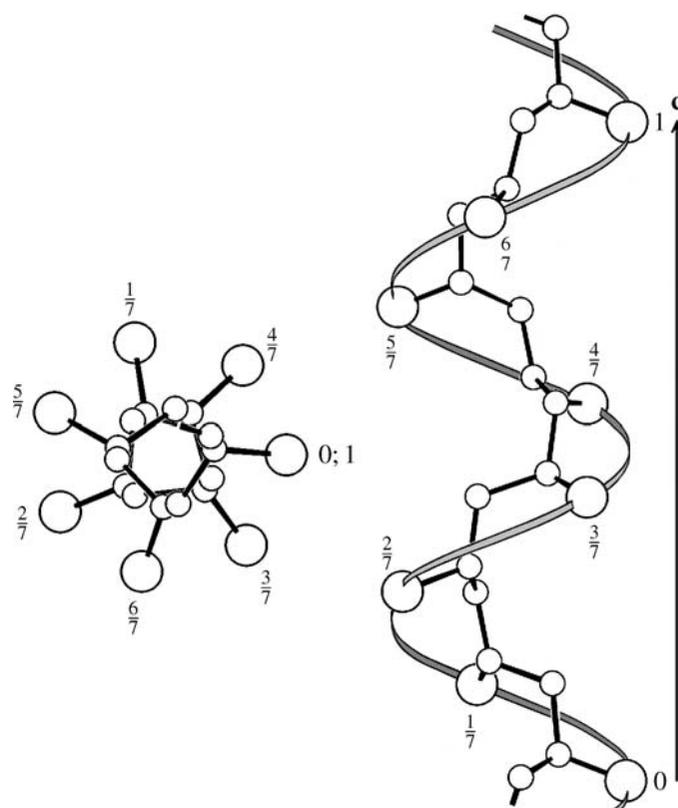
For the example of metaldehyde mentioned in the preceding section, we find in Table 3.2.3.2, point group $4mm$, the Wyckoff positions $8d$, $4c$, $4b$ and $1a$. Looking at the image of the molecule, we choose a coordinate system with z along the fourfold axis and x and y perpendicular to the mirror planes 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 .