

## 3. ADVANCED TOPICS ON SPACE-GROUP SYMMETRY

## 3.2.4. Molecular symmetry

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## 3.2.4.1. Introduction

In this section, by ‘molecule’ we mean a separate set of closely bonded atoms; this definition includes molecular ions. The term ‘molecule’ as used here also includes molecular aggregates held together by hydrogen bonds or other important molecular interactions. We consider only the symmetry of isolated molecules, *i.e.* we act as if the molecule had no surroundings or a completely isotropic surrounding (even if it is a molecular ion that in reality has nearby counter ions), and we do not consider any vibrational distortions. Of course, in crystals the surroundings are not isotropic; their anisotropy is reflected in the site symmetry of the molecule. The site symmetry of the molecule in the crystal may not be higher than the molecular symmetry, and, in most cases, it is lower, *i.e.* it is a subgroup of the point group of the isolated molecule. From experience we know that the actual deviation of the molecular symmetry in crystals as compared to the symmetry in an isotropic surrounding is usually unimportant; generally, only conformation angles are affected significantly.

According to the statistical data for organic molecules (molecules having C–C or C–H bonds), the point group 1 is the most frequent (70.9%), followed by  $\bar{1}$  (8.1%), 2 (7.5%),  $m$  (6.5%),  $2/m$  (2.1%) and  $mm2$  (1.7%); all others are <1% (Pidcock *et al.*, 2003). In crystals, the site symmetry of organic molecules is 1 with a frequency of 80.7%, followed by  $\bar{1}$  (~11%). Centrosymmetric molecules ( $\bar{1}$  and higher centrosymmetric point groups) almost always crystallize in centrosymmetric space groups (99%) and lie on centrosymmetric sites ( $\bar{1}$  and higher) with a frequency of 97% (Pidcock *et al.*, 2003; Müller, 1978).

Since all real molecules are objects of three-dimensional space, we consider only three-dimensional symmetry groups. This choice also applies to so-called ‘zero-’, ‘one-’ and ‘two-dimensional’ molecules; these misleading terms are sometimes used for, respectively, finite molecules, polymeric chain molecules and polymeric layer molecules. For chemists who use these terms, the ‘dimensionality’ mostly refers to the linkage by covalent bonds; for physicists, ‘dimensionality’ may refer to some other anisotropic property, *e.g.* conductivity.

## 3.2.4.2. Definitions

The set of all isometries that map a molecule onto itself is its *molecular symmetry*. Its symmetry operations form a group which is the *point group*  $\mathcal{P}_M$  of the molecule.

The group  $\mathcal{P}_M$  is finite if the molecule consists of a finite number of atoms and is mapped onto itself by a finite number of isometries. However, the group is infinite for linear molecules like HCl and CO<sub>2</sub>, because of the infinite order of the molecular axis. For the symmetry of polymeric molecules see below (Section 3.2.4.4).

All symmetry operations of a finite molecule leave its centre of mass unchanged. If this point is chosen as the origin, all symmetry operations can be represented by  $3 \times 3$  matrices  $\mathbf{W}_i$ , referred to some predefined coordinate system.

According to their equivalence, point groups are classified into *point-group types*. Two point groups  $\mathcal{P}_{M1}$  and  $\mathcal{P}_{M2}$  belong to the same *point-group type* if, after selection of appropriate coordinate systems, the matrix groups of  $\mathcal{P}_{M1}$  and  $\mathcal{P}_{M2}$  coincide. Why point groups and point-group types have to be distinguished is shown in the following example of metaldehyde; however, for

most molecules the distinction is usually of only minor importance.

In Section 1.1.7 a general definition is given for an *orbit* under the action of a group. Applied to molecules, we formulate this definition in the following way:

The set of points symmetry-equivalent to a point  $X$  of a molecule is the *orbit of  $X$  under  $\mathcal{P}_M$* .

A point  $X$  in a molecule has a definite *site symmetry*  $\mathcal{S}_X$  (site-symmetry group). It consists of all those symmetry operations of the point group  $\mathcal{P}_M$  which leave the point fixed. The site-symmetry group  $\mathcal{S}_X$  is always a subgroup of the point group of the molecule:  $\mathcal{S}_X \leq \mathcal{P}_M$ .

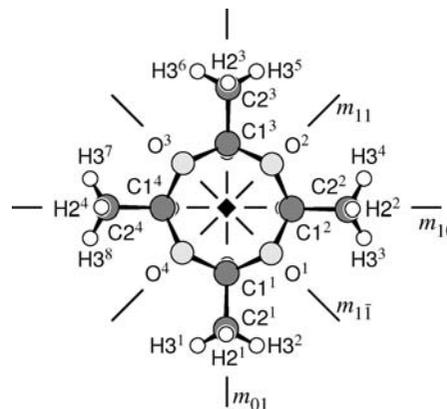
A point  $X$  is on a *general position* if its site symmetry  $\mathcal{S}_X$  consists of nothing more than the identity,  $\mathcal{S}_X = \mathcal{I}$ . Otherwise, if  $\mathcal{S}_X > \mathcal{I}$ , the point is on a *special position*.

The *multiplicity* of a point  $X$  in a molecule is equal to the number of points which are symmetry-equivalent to this point, *i.e.* the number of points in its orbit. If the point is on a general position, its multiplicity is equal to the group order  $|\mathcal{P}_M|$ . If  $|\mathcal{S}_X|$  is the order of the site symmetry of a point on a special position, the multiplicity of  $X$  is  $|\mathcal{P}_M|/|\mathcal{S}_X|$ .

Two points  $X$  and  $Y$  of a molecule belong to the same *Wyckoff position* if the site-symmetry groups  $\mathcal{S}_X$  and  $\mathcal{S}_Y$  are conjugate subgroups of  $\mathcal{P}_M$ , *i.e.* if  $\mathcal{S}_X$  and  $\mathcal{S}_Y$  are symmetry-equivalent under a symmetry operation of  $\mathcal{P}_M$ ; expressed mathematically, this is  $\mathcal{S}_Y = g\mathcal{S}_Xg^{-1}$  with  $g \in \mathcal{P}_M$ . The special case  $\mathcal{S}_X = \mathcal{S}_Y$  is included.

## Example

A molecule of metaldehyde [tetrameric acetaldehyde, 2,4,6,8-tetramethyl-1,3,5,7-tetraoxacyclooctane, (H<sub>3</sub>CCHO)<sub>4</sub>] has the point group  $\mathcal{P}_M = 4mm$  ( $C_{4v}$ ) of order  $|\mathcal{P}_M| = 8$ , consisting of the symmetry operations 1, 4<sup>+</sup>, 2, 4<sup>−</sup>,  $m_{10}$ ,  $m_{01}$ ,  $m_{11}$  and  $m_{\bar{1}\bar{1}}$ .



The atoms C1<sup>1</sup>...C1<sup>4</sup>, the four H atoms bonded to them (not labelled in the figure and largely hidden), C2<sup>1</sup>...C2<sup>4</sup> and H2<sup>1</sup>...H2<sup>4</sup> make up four sets of symmetry-equivalent atoms and thus form four orbits. All these atoms are placed on the mirror planes  $m_{10}$  and  $m_{01}$ ; their site-symmetry groups are  $\{1, m_{10}\}$  or  $\{1, m_{01}\}$ .  $\{1, m_{10}\}$  and  $\{1, m_{01}\}$  are conjugate subgroups of  $4mm$  because they are equivalent by a fourfold rotation, *i.e.*  $\{1, m_{01}\} = 4^+\{1, m_{10}\}4^-$ . All of these atoms belong to *one* Wyckoff position, labelled 4c in Table 3.2.3.2. The symmetry-equivalent atoms O<sup>1</sup>...O<sup>4</sup> make up another orbit which belongs to a different Wyckoff position, labelled 4b, with the conjugate site symmetries  $\{1, m_{11}\}$  and  $\{1, m_{\bar{1}\bar{1}}\}$ . Although the site symmetries of both 4b and 4c consist of the identity and one reflection, they are not conjugate because there is no symmetry operation of  $4mm$  that relates them. The subgroups  $\{1, m_{10}\}$  and  $\{1, m_{11}\}$  are different point groups of the same point-group type.

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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  $120^\circ$  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  $30^\circ$  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  $45^\circ$ .

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.

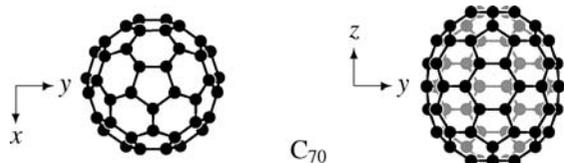
Certain physical properties depend on symmetry. In particular, a molecule can have a dipole moment only if it is polar, *i.e.* if it

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  $1 \text{ \AA}$ . 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).

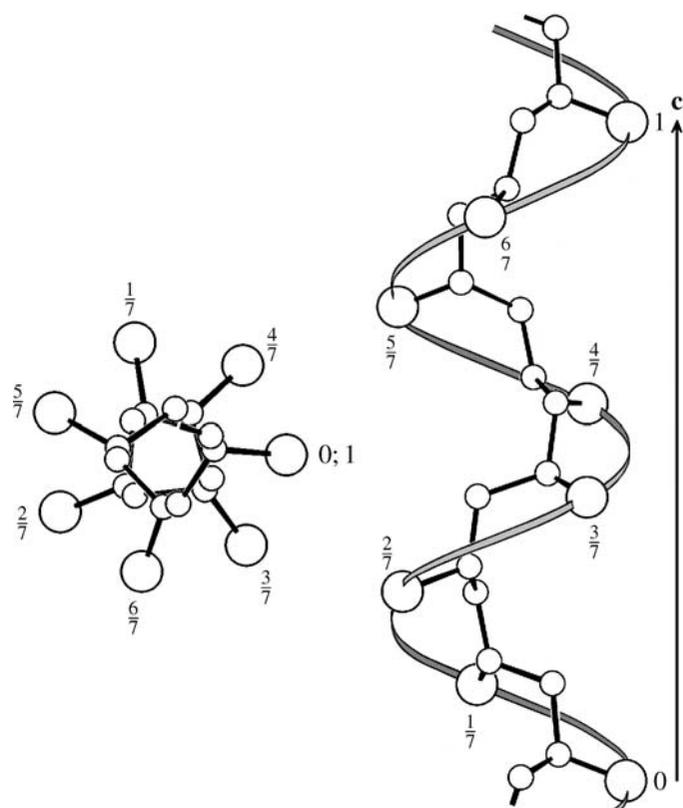
The fullerene  $C_{70}$  is an example of a molecule with noncrystallographic symmetry,  $\bar{10}2m$  ( $D_{5h}$ ). This point-group type is not listed in Table 3.2.3.2, but it can be found in Table 3.2.1.6.



#### 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).<sup>25</sup> 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

<sup>25</sup> 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  $7_3$ .

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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  $7/(2 \text{ modulo } 7)$   $P$ -helix and any  $7/(5 \text{ modulo } 7)$   $M$ -helix also has  $7_4$  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 [ <i>e.g.</i> by ( <i>R</i> ), ( <i>S</i> ) <i>etc.</i> ]
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 enantiomorphous 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 be 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	$N$	$q$
$\bar{1}N$		$N = n$	
$\bar{1}N_q$		$N = n \geq 2$	$q = 1, \dots, N - 1$
$\bar{1}\bar{N}$		$N = n$	
$\bar{1}N/m$		$N = 2n$	
$\bar{1}N_q/m$		$N = 2n$	$q = \frac{1}{2}N$
$\bar{1}N2$		$N = 2n + 1$	
$\bar{1}N22$		$N = 2n$	
$\bar{1}N_q2$		$N = 2n + 1$	$q = 1, \dots, N - 1$
$\bar{1}N_q22$		$N = 2n$	$q = 1, \dots, N - 1$
$\bar{1}Nm$		$N = 2n + 1$	
$\bar{1}Nmm$		$N = 2n$	
$\bar{1}Nc$		$N = 2n + 1$	
$\bar{1}Ncc$		$N = 2n$	
$\bar{1}N_qmc$		$N = 2n$	$q = \frac{1}{2}N$
$\bar{1}\bar{N}m$	$\bar{1}\bar{N}2/m$	$N = 2n + 1$	
$\bar{1}\bar{N}2m$		$N = 2n$	
$\bar{1}\bar{N}c$	$\bar{1}\bar{N}2/c$	$N = 2n + 1$	
$\bar{1}\bar{N}2c$		$N = 2n$	
$\bar{1}N/mmm$	$\bar{1}N/m2/m2/m$	$N = 2n$	
$\bar{1}N/mcc$	$\bar{1}N/m2/c2/c$	$N = 2n$	
$\bar{1}N_q/mmc$	$\bar{1}N_q/m2/m2/c$	$N = 2n$	$q = \frac{1}{2}N$

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 enantiomorphous space-group types (*cf.* Section 1.3.4.1) and further 43 non-enantiomorphous space-group types. Whereas an enantiomorphous 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).<sup>26</sup> However, the arrangement of the atoms in any Sohncke space group is always chiral. In other words, an enantiomorphous 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 enantiomorphous forms that consist of either right-handed or left-handed helical chain molecules (rod groups  $\bar{1}3_12$  and  $\bar{1}3_22$ , respectively). The molecules as well as the space groups  $P3_121$  and  $P3_221$  are enantiomorphous and the helical molecules of right-handed

<sup>26</sup> Many structural researchers are not aware of the difference between chiral (enantiomorphous) 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.

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selenium are incompatible with the space group of left-handed selenium.

The case of selenium can be contrasted to that of NaP (details for NaP are given at the end of Section 3.5.3.2 in the *Example for case I*). Crystalline NaP contains one kind of enantiomeric, helical  $(P^-)_\infty$  ions that are either  $4_1$  or  $4_3$  helices (rod groups  $\mu 4_1 22$  and  $\mu 4_3 22$ , respectively). In this case the space group  $P2_1 2_1 2_1$  is a non-enantiomorphic (achiral) Sohncke space group. It is therefore compatible with either of the two different NaP enantiomorphs.

The building blocks of  $\text{NaClO}_3$ , namely spherical  $\text{Na}^+$  ions and pyramidal  $\text{ClO}_3^-$  ions (point group  $3m$ ), are not chiral, but their arrangement in the crystal is chiral. Both enantiomorphs adopt the same non-enantiomorphic Sohncke space group  $P2_1 3$  (Abrahams & Bernstein, 1977; Bruke-Laing & Trueblood, 1977).

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#### References

- Abrahams, S. C. & Bernstein, J. L. (1977). *Remeasurement of optically active  $\text{NaClO}_3$  and  $\text{NaBrO}_3$* . *Acta Cryst.* **B33**, 3601–3604.
- Alexander, L. E. (1969). *X-ray Diffraction Methods in Polymer Science*, pp. 19–22. New York: Wiley.
- Authier, A. (2014). *Introduction to the properties of tensors*. In *International Tables for Crystallography*, Vol. D, 2nd ed., edited by A. Authier, ch. 1.1, pp. 3–33. Chichester: Wiley.
- Barnett, S. A., Hulme, A. T. & Tocher, D. A. (2005). *A low-temperature redetermination of metaldehyde*. *Acta Cryst.* **E61**, o857–o859.
- Bhagavantam, S. (1966). *Crystal Symmetry and Physical Properties*. London: Academic Press.
- Bruke-Laing, M. E. & Trueblood, K. N. (1977). *Sodium chlorate. Precise dimensions for the  $\text{ClO}_3^-$  ion*. *Acta Cryst.* **B33**, 2698–2699.
- Buerger, M. J. (1956). *Elementary Crystallography*, especially chs. 10 and 11. New York: Wiley.
- Burzlaff, H. & Zimmermann, H. (1977). *Symmetriehre*, especially ch. II.3. Stuttgart: Thieme.
- Compendium of Polymer Terminology and Nomenclature* (2008). IUPAC Recommendations 2008, 2nd ed., edited by R. G. Jones, J. Kahovec, R. Stepto, E. S. Wilks, M. Hess, T. Kitayama & W. V. Metanomski, ch. 2. Cambridge: RSC Publications.
- Coxeter, H. S. M. (1973). *Regular Polytopes*, 3rd ed. New York: Dover.
- Curie, P. (1894). *Sur la symétrie dans les phénomènes physiques, symétrie d'un champ électrique et d'un champ magnétique*. *J. Phys. (Paris)*, **3**, 393–415.
- Dougherty, J. P. & Kurtz, S. K. (1976). *A second harmonic analyzer for the detection of non-centrosymmetry*. *J. Appl. Cryst.* **9**, 145–158.
- Fischer, W., Burzlaff, H., Hellner, E. & Donnay, J. D. H. (1973). *Space Groups and Lattice Complexes*. NBS Monograph No. 134, especially pp. 28–33. Washington, DC: National Bureau of Standards.
- Flack, H. D. (2003). *Chiral and achiral crystal structures*. *Helv. Chim. Acta*, **86**, 905–921.
- Friedel, G. (1926). *Leçons de cristallographie*. Nancy/Paris/Strasbourg: Berger-Levrault. [Reprinted (1964). Paris: Blanchard.]
- Groth, P. (1921). *Elemente der physikalischen und chemischen Kristallographie*. München: Oldenbourg.
- Hahn, Th. & Klapper, H. (2005). *Crystal symmetry*. In *Encyclopedia of Condensed Matter Physics*, Vol. 1, pp. 312–323. Amsterdam: Elsevier Academic Press.
- International Tables for Crystallography* (2010). Vol. A1, *Symmetry Relations Between Space Groups*, 2nd ed., edited by H. Wondratschek & U. Müller. Chichester: Wiley.

- International Tables for Crystallography* (2010). Vol. E, *Subperiodic Groups*, 2nd ed., edited by V. Kopský & D. B. Litvin. Chichester: Wiley.
- International Tables for Crystallography* (2014). Vol. D, *Physical Properties of Crystals*, 2nd ed., edited by A. Authier. Chichester: Wiley.
- International Tables for the Determination of Crystal Structures* (1935). First Volume. *Tables on the Theory of Groups*, edited by C. Hermann. Berlin: Gebrüder Borntraeger.
- International Tables for X-ray Crystallography* (1952). Vol. I. *Symmetry Groups*, edited by N. F. M. Henry & K. Lonsdale. Birmingham: The Kynoch Press.
- Joint Commission for Spectroscopy (1955). *Report on notation for the spectra of polyatomic molecules*. *J. Chem. Phys.* **23**, 1997–2011.
- Julian, M. M. (2015). *Foundations of Crystallography*, 2nd ed. Boca Raton: CRC Press.
- Klapper, H. & Hahn, Th. (2005). *Point groups*. In *Encyclopedia of Condensed Matter Physics*, Vol. 4, pp. 323–334. Amsterdam: Elsevier Academic Press.
- Klapper, H. & Hahn, Th. (2010). *The application of eigensymmetries of face forms to anomalous scattering and twinning by merohedry in X-ray diffraction*. *Acta Cryst.* **A66**, 327–346.
- Meille, S. V., Allegra, G., Geil, P. H., He, J., Hess, M., Jin, J.-I., Kratochvil, P., Mornmann, W. & Stepto, R. (2011). *Definitions and terms relating to crystalline polymers (IUPAC Recommendations 2011)*. *Pure Appl. Chem.* **83**, 1831–1871.
- Melcher, R. L. & Shiren, N. S. (1976). *Polarization echoes and long-time storage in piezoelectric powders*. *Phys. Rev. Lett.* **36**, 888–891.
- Moss, G. P. (1996). *Basic terminology of stereochemistry*. *Pure Appl. Chem.* **68**, 2193–2222. (IUPAC Recommendations for the Basic Terminology of Stereochemistry, <http://www.chem.qmul.ac.uk/iupac/stereo/>.)
- Müller, U. (1978). *Kristallisieren zentrosymmetrische Moleküle immer in zentrosymmetrischen Raumgruppen? – Eine statistische Übersicht*. *Acta Cryst.* **B34**, 1044–1046.
- Natta, G. & Corradini, P. (1960). *General consideration on the structure of crystalline polyhydrocarbons*. *Nuovo Cimento, Suppl.* **15**, 9–39.
- Neumann, F. (1885). *Vorlesungen über die Theorie der Elastizität der festen Körper und des Lichtäthers*, edited by O. E. Meyer. Leipzig: B. G. Teubner Verlag.
- Niggli, P. (1941). *Lehrbuch der Mineralogie und Kristallchemie*, 3rd ed. Berlin: Borntraeger.
- Niggli, A. (1963). *Zur Topologie, Metrik und Symmetrie der einfachen Kristallformen*. *Schweiz. Mineral. Petrogr. Mitt.* **43**, 49–58.
- Nowacki, W. (1933). *Die nichtkristallographischen Punktgruppen*. *Z. Kristallogr.* **86**, 19–31.
- Nye, J. F. (1957). *Physical Properties of Crystals*. Oxford: Clarendon Press. [Revised edition (1985).]
- Pauffer, P. (1986). *Physikalische Kristallographie*. Berlin: Akademie Verlag, and Weinheim: Verlag Chemie (VCH).
- Phillips, F. C. (1971). *An Introduction to Crystallography*, 4th ed., chs. 3, 4, 6 and 13. London: Longman.
- Pidcock, E., Motherwell, W. D. S. & Cole, J. C. (2003). *A database survey of molecular and crystallographic symmetry*. *Acta Cryst.* **B59**, 634–640.
- Rogers, D. (1975). *Some fundamental problems of relating tensorial properties to the chirality or polarity of crystals*. In *Anomalous Scattering*, edited by S. Ramaseshan & S. C. Abrahams, pp. 231–250. Copenhagen: Munksgaard.
- Schwarzenbach, D. & Chapuis, G. (2006). *Cristallographie*, 2nd ed. Lausanne: Presses Polytechniques et Universitaires Romandes. (In French.) [1st ed. in English (1996), Chichester: Wiley; in German (2001), Berlin: Springer].
- Shubnikov, A. V. & Koptsik, V. A. (1974). *Symmetry in Science and Art*, especially chs. 2 and 3. New York: Plenum.
- Shuvalov, L. A. (1988). Editor. *Modern Crystallography IV: Physical Properties of Crystals*. Berlin: Springer.
- Spruiell, J. E. & Clark, E. S. (1980). *Methods in Experimental Physics*, Vol. 16, *Polymers*, edited by R. A. Fava, Part B, ch. 6, pp. 19–22. New York: Academic Press.
- Vainshtein, B. K. (1994). *Fundamentals of Crystals. Symmetry, and Methods of Structural Crystallography*, 2nd ed., especially ch. 2.6 and 3. Berlin: Springer.
- Wooster, W. A. (1973). *Tensors and Group Theory for the Physical Properties of Crystals*. Oxford: Clarendon Press.
- Wooster, W. A. & Brenton, A. (1970). *Experimental Crystal Physics*, especially ch. 6. Oxford: Clarendon Press.