

9.7. The space-group distribution of molecular organic structures

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9.7.1. *A priori* classifications of space groups

The space group $P2_1/c$ accounts for about 1/3 of all known molecular organic structures, whereas the space group $P2/m$ has no certain example. Why? Ultimately, the space group of a crystal of a particular substance is determined by the minimum (or a local minimum) of the thermodynamic potential (Gibbs free energy) of the van der Waals and other forces, but a very simple model goes a long way towards 'explaining' the relative frequency of the various space groups within a crystal class or larger grouping. Nowacki (1943) discussed the basic idea that space-group frequency is determined by packing considerations, and had earlier (1942) given statistics for the structures known at the time. Nowacki's statistics were used by Kitajgorodskij* (1945), and recent writers tend to cite Kitajgorodskij as having originated the idea. Kitajgorodskij pointed out that the most frequent space groups are those that permit the close packing of triaxial ellipsoids. Later, Kitajgorodskij (1955) showed that the same space groups allowed close packing of objects of any reasonable shape, 'close packing' meaning packing with 12-point contact. Wilson (1988, 1990, 1993*d*) used the complementary idea that space groups are rare when they contain symmetry elements – notably mirror planes and rotation axes – that prevent the molecules from freely choosing their positions within the unit cell. A twofold axis excludes molecular centres from a column of diameter equal to some molecular diameter (say M), a mirror plane from a layer of thickness M , and a centre of symmetry from a sphere of diameter M . The volumes excluded by screw axes and glide planes are small in comparison.

9.7.1.1. Kitajgorodskij's categories

In his book† *Organicheskaya Kristallokhimiya*, Kitajgorodskij (1955) treated the triclinic, monoclinic and orthorhombic space groups in considerable detail, analysing the possibility of (a) forming close-packed layers (six-point contact), and (b) close stacking of the layers. On this basis, he divided the layers and the space groups into four categories each. For the layers they are:

- (1) *Coordination close-packed layers*. A coordination close-packed layer is one in which molecules of arbitrary shape and symmetry can be packed with six-point coordination.
- (2) *Closest-packed layers*. A closest-packed layer is one in which one can select the orientation of molecules of given shape and symmetry so as to produce a cell of minimal dimensions.
- (3) *Limitingly close-packed layers*. A limitingly close-packed layer for a given symmetry is a closest-packed layer in which a molecule retains inherent symmetry; in other words, in which it occupies a special position.
- (4) *Permissible layers*. A permissible layer is coordination close packed but *neither* closest packed *nor* limitingly close packed.

The categories of space groups are:

*Names in Cyrillic characters are transliterated in many ways in non-Russian languages. In this chapter, 'Kitajgorodskij' is used throughout the text, but the source transliteration is retained in the list of references. Similar complications arise with other names in Cyrillic characters.

†The US translation (Kitajgorodskij, 1961) differs from the original in several respects. Only relevant differences are noted in this chapter.

- (1) Closest-packed space groups are those that permit the closest stacking of closest-packed layers – the packing can be made no denser by varying the cell parameters and the orientation of the molecules. Closest stackings can be made by a monoclinic displacement (a translation making an arbitrary angle with the layer plane), a centre of symmetry, a glide plane, or a screw axis.
- (2) Limitingly close-packed space groups are those that contain limitingly close-packed layers stacked as closely as possible.
- (3) Permissible space groups fall into three subcategories: (a) Those containing closest-packed layers that can be closely stacked if the layer relief is suitable; this group contains layers stacked by centring (C, I, F) or by diad axes. (b) Those containing limitingly close-packed layers that can be most closely stacked if the layer relief is suitable. (c) Those containing permissible layers stacked in the densest fashion.
- (4) Impossible space groups fall into two subcategories: (a) Those containing any layers (even closest-packed layers) that are related by mirror planes and translations normal to the layer plane. (b) Those containing permissible coordination close-packed layers not stacked in the densest possible way.

Kitajgorodskij expected the frequency of space groups to decrease in the order (1) > (2) > (3) > (4). In particular, 'permissible space groups should be found but rarely, as exceptions'. The categorization is summarized in Table 9.7.1.1, based on Table 8 of Kitajgorodskij (1955).

Kitajgorodskij's categorization proved very successful in broad outline, but Wilson's (1993*b,c*) detailed statistics revealed about a dozen anomalous space-group types. The anomalies were of two kinds. The first was the frequent occurrence of molecules in general positions in space groups in which Kitajgorodskij expected molecules to use inherent symmetry in special positions. Wilson (1993*a*) pointed out that in such cases structural dimers* can be formed, with two molecules in general positions related by the required symmetry elements – both enantiomers would be required if the element were $\bar{1}$ or m . Such space groups could therefore be added to Kitajgorodskij's table, in the column for 'molecular symmetry 1'. The second kind of anomaly was the fairly frequent occurrence of structures with the 'impossible' space groups Pc and $P2/c$. These could be transferred from 'impossible' to 'permissible', subgroup (a), by the same packing argument that Kitajgorodskij had used for $P1$. These and a few other reclassifications are indicated in Table 9.7.1.1, the new entries being enclosed in square brackets for distinction. Where the change is a transfer to a higher category, the original position of the space group is indicated in round brackets.

9.7.1.2. Symmorphisms and antimorphism

Wilson (1993*d*) classified the space groups by degree of symmorphisms. A fully symmorphous space group contains only the 'syntropic' symmetry elements

$$2, 3, 4, 6; \bar{2} = m, \bar{3} = 3 + \bar{1}, \bar{4}, \bar{6} = 3/m$$

and a fully antimorphous space group contains only the 'antitropic' elements

*Empirically, only dimers involving a centre of symmetry or a diad axis are important in the systems under consideration. In principle, n -mers involving any point-group symmetry could be formed.

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Table 9.7.1.2. *Space groups arranged by arithmetic crystal class and degree of symmorphism (cont.)*

(b) Tetragonal space groups. For *, † see Subsection 9.7.4.1.

Arithmetic crystal class	Fully symmorphich	Tending to symmorphich	Equally balanced	Tending to antimorphich	Fully antimorphich
$4P$	$*P4^{(0)}$	$P4_2^{(1)}$	$P4_{1,3}\dagger^{(40)}$
$4I$	$I4_1\dagger^{(3)}$	$*I4^{(3)}$...
$\bar{4}P$	$*P\bar{4}\dagger^{(0)}$
$\bar{4}I$	$*I\bar{4}\dagger^{(7)}$
$4/mP$	$*P4/m^{(0)}$	$P4_2/m^{(0)}$ $P4/n^{(1)}$	$P4_2/n\dagger^{(20)}$
$4/mI$	$*I4/m^{(0)}$ $I4_1/a\dagger^{(29)}$...
$422P$...	$*P422^{(0)}$	$P42_12^{(0)}$	$P4_{1,3}2_12\dagger^{(49)}$...
		$P4_222^{(0)}$	$P4_{1,3}22^{(1)}$	$P4_22_12^{(1)}$	
$422I$	$I4_122\dagger^{(0)}$	$*I422^{(0)}$...
$4mmP$...	$*P4mm^{(0)}$	$P4bm^{(0)}$	$P4_2cm^{(0)}$...
				$P4_2nm^{(0)}$	
				$P4cc^{(0)}$	
				$P4nc^{(0)}$	
				$P4_2mc^{(0)}$	
				$P4_2bc\dagger^{(1)}$	
$4mmI$	$*I4mm^{(0)}$...
				$I4cm^{(0)}$	
				$I4_1md^{(0)}$	
				$I4_1cd\dagger^{(5)}$	
				$P\bar{4}2_1c\dagger^{(12)}$	
$\bar{4}2mP$...	$*P\bar{4}2m^{(0)}$	$P\bar{4}2c^{(0)}$...
			$P\bar{4}2_1m^{(0)}$		
$\bar{4}m2P$...	$*P\bar{4}m2^{(0)}$	$P\bar{4}c2^{(0)}$
			$P\bar{4}b2^{(0)}$		
			$P\bar{4}n2^{(0)}$		
$\bar{4}m2I$	$*I\bar{4}m2^{(0)}$	$I\bar{4}c2\dagger^{(0)}$...
$\bar{4}2mI$	$*I\bar{4}2m^{(0)}$	$I\bar{4}2\dagger^{(0)}$...
$4/mmmP$...	$*P4/mmm^{(0)}$	$P4/mcc^{(0)}$	$P4/nbm^{(0)}$...
		$P4_2/nmc^{(0)}$	$P4/nmm^{(0)}$	$P4/nnc^{(0)}$	
		$P4_2/mcm^{(0)}$		$P4/mbm^{(0)}$	
				$P4/mnc^{(0)}$	
				$P4/ncc^{(0)}$	
				$P4_2/nbc^{(0)}$	
				$P4_2/nmm^{(0)}$	
				$P4_2/mbc^{(0)}$	
				$P4_2/mnm^{(0)}$	
				$P4_2/nmc^{(0)}$	
				$P4_2/ncm^{(0)}$	
$4/mmmI$...	$*I4/mmm^{(0)}$...	$I4/mcm^{(0)}$...
				$I4_1/amd^{(0)}$	
				$I4_1/acd\dagger^{(0)}$	

empirical frequencies – it would be expected that there should be considerable correlation between them. All ‘closest-packed’ space groups are also ‘fully antimorphich’, and most of the ‘limitingly close packed’ and ‘permissible’ are ‘tending to antimorphich’; a few requiring high molecular symmetry (222 , $mm2$, mmm) and a couple of others are ‘equally balanced’. Two ‘fully antimorphich’ groups, Pc and Cc , are merely ‘permissible’. All ‘fully symmorphich’ space groups are ‘impossible’.

9.7.1.4. Relation to structural classes

Structural classes (Belsky & Zorky, 1977, and papers cited there and below) are not an *a priori* classification of space groups but are a classification of structures within a space-group type in accordance with the number and kind of Wyckoff positions occupied by the molecules. As a considerable knowledge of the structures is required before their structural classes can be

assigned, they form an *a posteriori* classification, and will be described (Section 9.7.5 below) after the empirical frequencies of space groups have been discussed.

9.7.2. Special positions of given symmetry

As noted by Kitajgorodskij, in many crystal structures molecules with inherent symmetry may occupy Wyckoff special positions, so that molecular and crystallographic symmetry elements coincide, and this may affect the relative frequencies of occurrence of structures with particular space groups. Tables of the frequency of occurrence of space groups have been published by many authors, from Nowacki (1942) onwards. Some typical recent papers are Brock & Dunitz (1994), Donohue (1985), Mighell, Himes & Rodgers (1983), Padmaya, Ramakumar & Viswamitra (1990), Wilson (1988, 1990,

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Table 9.7.1.2. Space groups arranged by arithmetic crystal class and degree of symmorphisms (cont.)

(c) Trigonal space groups. For *, † see Subsection 9.7.4.1.

Arithmetic crystal class	Fully symmorphic	Tending to symmorphisms	Equally balanced	Tending to antimorphism	Fully antimorphic
3P	*P3 ⁽⁰⁾	P3 _{1,2} † ⁽³³⁾
3R	*R3† ⁽¹¹⁾	...
$\bar{3}P$	*P $\bar{3}$ † ⁽¹⁾
$\bar{3}R$	*R $\bar{3}$ † ⁽³⁰⁾	...
312P 321P	...	*P312 ⁽⁰⁾ *P321 ⁽⁰⁾	...	P3 _{1,2} 12† ⁽⁰⁾ P3 _{1,2} 21† ⁽¹⁰⁾	...
32R	*R32† ⁽⁰⁾	...
3m1P 31mP	...	*P3m1 ⁽⁰⁾ *P31m ⁽⁰⁾	...	P3c1† ⁽⁰⁾ P31c† ⁽⁰⁾	...
3mR	*R3m ⁽⁰⁾ R3c† ⁽⁷⁾	...
$\bar{3}m1P$ $\bar{3}1mP$...	*P $\bar{3}m1$ ⁽⁰⁾ *P $\bar{3}1m$ ⁽⁰⁾	...	P $\bar{3}c1$ † ⁽⁰⁾ P $\bar{3}1c$ † ⁽⁰⁾	...
$\bar{3}mR$	*R $\bar{3}m$ ⁽⁰⁾ R $\bar{3}c$ † ⁽⁰⁾	...

(d) Hexagonal space groups. For *, † see Subsection 9.7.4.1.

Arithmetic crystal class	Fully symmorphic	Tending to symmorphisms	Equally balanced	Tending to antimorphism	Fully antimorphic
6P	*P6 ⁽⁰⁾	...	P6 _{2,4} ⁽¹⁾ P6 ₃ ⁽⁰⁾	...	P6 _{1,5} † ⁽²²⁾
$\bar{6}P$	*P $\bar{6}$ † ⁽⁰⁾
6/mP	*P6/m ⁽⁰⁾	...	P6 ₃ /m† ⁽⁰⁾
622P	...	*P622 ⁽⁰⁾ P6 _{2,4} 22 ⁽⁰⁾	...	P6 ₃ 22 ⁽¹⁾ P6 _{1,5} 22† ⁽²⁾	...
6mmP	...	*P6mm ⁽⁰⁾	...	P6cc ⁽⁰⁾	...
$\bar{6}m2P$ $\bar{6}2mP$...	*P $\bar{6}m2$ ⁽⁰⁾ *P $\bar{6}2m$ ⁽⁰⁾	...	P6 ₃ cm ⁽⁰⁾ P6 ₃ mc ⁽⁰⁾	...
6/mmmP	...	*P6/mmm ⁽⁰⁾	...	P $\bar{6}c2$ † ⁽⁰⁾ P $\bar{6}2c$ † ⁽⁰⁾	...
				P6/mcc† ⁽⁰⁾	...
				P6 ₃ /mcm ⁽⁰⁾ P6 ₃ /mmc ⁽⁰⁾	...

(e) Cubic space groups. For *, †, see Subsection 9.7.4.1. No examples with one molecule in general position were found, so the frequencies are omitted.

Arithmetic crystal class	Fully symmorphic	Tending to symmorphisms	Equally balanced	Tending to antimorphism	Antimorphic except for 3
23P	...	*P23	P2 ₁ 3†
23F	*F23†
23I	*I23 I2 ₁ 3†
$m\bar{3}P$...	*Pm $\bar{3}$	Pn $\bar{3}$...	Pa $\bar{3}$ †
$m\bar{3}F$	*Fm $\bar{3}$	Fd $\bar{3}$ †	...
$m\bar{3}I$	*Im $\bar{3}$	Ia $\bar{3}$ †	...
432P	...	*P432	...	P4 ₂ 32† P4 _{1,3} 32†	...
432F	*F432	F4 ₁ 32†	...
432I	*I432	I4 ₁ 32†	...
$\bar{4}3mP$...	*P $\bar{4}3m$...	P $\bar{4}3n$ †	...
$\bar{4}3mF$	*F $\bar{4}3m$	F $\bar{4}3c$ †	...
$\bar{4}3mI$	*I $\bar{4}3m$	I $\bar{4}3d$ †	...
$m\bar{3}mP$...	*Pm $\bar{3}m$	Pm $\bar{3}n$ Pn $\bar{3}m$	Pn $\bar{3}n$ †	...
$m\bar{3}mF$...	*Fm $\bar{3}m$...	Fm $\bar{3}c$ Fd $\bar{3}m$	Fd $\bar{3}c$ †
$m\bar{3}mI$...	*Im $\bar{3}m$...	Ia $\bar{3}d$ †	...

1993b,c), but many of them hardly go beyond recognizing the fact that structures frequently made use of molecular symmetry – Wilson (1988) explicitly chose to ignore it. The early work of Belsky, Zorky and their colleagues did not attract much attention outside Russian-speaking areas. Recently, however, there has been a spate of interest (Wilson, 1991, 1993b,c,d; Brock & Dunitz, 1994; Belsky, Zorkaya & Zorky, 1995). Earlier lack of results is partly due to the fact that the Cambridge Structural Database (Section 9.7.3) did not provide a search program that would distinguish between occupation of a general position and

multiple occupation of special positions of the required symmetry (Wilson, 1993d, Section 3). Belsky, Zorkaya & Zorky (1995) were able to make this distinction, and their paper is the source of many of the statistics quoted without special citation here.

It would be interesting to know which space groups possess positions with the symmetry of each of the 32 point groups 1, $\bar{1}$, 2, m , $2/m$, ..., $m\bar{3}m$. Volume A of *International Tables for Crystallography* (Hahn, 1995) enumerates the symmetry of all the special positions of a given space group, but does not readily

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answer the reverse question: which space groups contain special positions of given point group \mathcal{G} ? Some general points may be noted.

(i) Special positions of symmetry \mathcal{G} will be found in the symmorphic, but not other, space groups of the geometric class \mathcal{G} . Thus, for example, there are special positions of symmetry mmm in $Pnmm$, $Cmmm$, $Fmmm$, $Immm$, but not in any other space group in the geometric class mmm .

(ii) A 'family tree' of point groups is given in Fig. 10.3.2 of Volume A of *International Tables for Crystallography* (Hahn, 1995). Special positions of symmetry \mathcal{G} may be sought in space groups of the geometric classes linked to \mathcal{G} by a line (possibly zigzag) having a generally upwards direction. Thus, to take the same example, special positions of symmetry mmm are found in certain space groups of $4/mmm$ ($P4/mmm$, $P4/mbm$, $4_2/mmc$, $P4_2/mcm$, $P4_2/mmm$, $I4/mmm$, $I4/mcm$), in $6/mmm$ ($P6/mmm$), in $m\bar{3}$ ($Pm\bar{3}$, $Im\bar{3}$), and in $m\bar{3}m$ ($Pm\bar{3}m$, $Fm\bar{3}m$).

(iii) Obviously, the higher up the tree the symmetry \mathcal{G} is, the fewer will be the space groups in which it can occur – special positions of symmetry $m\bar{3}m$ can occur only in the three symmorphic space groups of the corresponding geometric class. The lower symmetries (2, m , $\bar{1}$, $\bar{3}$), with nothing below them but 1, can be traced upwards along many branches, and so can occur in many space groups, but not all are equally favoured. Special positions of symmetry 2 can be sought in all higher geometric classes except $\bar{6}$, $3m$, and $\bar{3}$, but those of symmetry 3 could occur only in the classes of the trigonal, hexagonal, and cubic systems. An approximate count* (Table 9.7.2.1) shows that special positions of symmetry 2 occur in 167 space groups, of m in 99, of $\bar{1}$ in 38, and of 3 in 57. The only other special positions with space-group frequencies of this order are $2/m$ (39), 222 (30), and mm (57).

9.7.3. Empirical space-group frequencies

Empirical space-group frequencies are based on two major collections of structural data for organic substances, in Cambridge and Moscow, respectively.

The Cambridge Structural Database (Allen *et al.*, 1991) contains assignments of space groups for a variety of different types of organic compounds. The file can be computer searched in many ways; it is easy, for example, to trace all structures having a particular space group, or those having a particular space group and a particular number of formula units per unit cell. For the present purpose, a selection has to be made, omitting space groups not substantiated by a full structure determination or dubious because of disorder in the crystal. The packing considerations discussed in previous paragraphs would not apply to crystals in which the intermolecular binding was ionic rather than van der Waals or the like, so that space groups of ionic structures (for example salts of organic acids) are also rejected. Unfortunately, as it is implemented at present (early 1995), it is not possible to search for structures with molecules occupying general positions or specified special positions, so that, in particular, the frequency data of Wilson (1993*d*) are inflated by the inability to distinguish between single occupation of a general position and multiple occupation of special positions.

The file compiled by V. A. Belsky at the L. Ya. Karpov Institute of Physical Chemistry in Moscow is the source of the data used by Belsky, Zorkaya & Zorky (1995). This file differs in objective from the Cambridge file; the latter includes all

* Such counts are tedious and subject to error, but the table should be correct within a few units.

reasonably established organic structures short of proteins and high polymers, whereas the former concentrates on structures containing only a single type of molecule ('homomolecular structures'). It thus contains appreciably fewer entries than the Cambridge file, even if structures of the types mentioned in the previous paragraph are excluded from the latter. The Moscow file is, of course, the primary source for the data of Belsky, Zorkaya & Zorky (1995), in which the occupation of general and special positions is explicitly presented.

9.7.4. Use of molecular symmetry

It has long been recognized that in many crystal structures molecules with inherent symmetry occupy Wyckoff special positions, so that molecular and crystallographic symmetry elements coincide, but until recently systematic data have been lacking. Now the occurrence of molecules of particular symmetry in structures of various space-group types can be traced in the data of Belsky, Zorkaya & Zorky (1995), and will be discussed briefly.

9.7.4.1. Positions with symmetry 1

The empirical results for 'homomolecular structures' with one molecule in the general position are given in Table 9.7.1.2. The classification by arithmetic crystal class and degree of symmorphism follows Wilson (1993*d*); the numerical data are taken from Belsky, Zorkaya & Zorky (1995). Space groups symmorphic in the technical sense (Wilson, 1993*d*) are prefixed by an asterisk (*), and in each arithmetic crystal class the space group most nearly antimorphic is followed by an obelus (†). The number of known structures having precisely one molecule in the general Wyckoff position is given as a superscript in brackets. It will be noticed immediately that structures with space groups 'fully symmorphic' or 'tending to symmorphism' are extremely rare. Most have no examples; three ($P4_2$, $P4/n$ and $P\bar{3}$) are credited with a single example each. The frequency of space groups increases rapidly with increasing antimorphism. In the monoclinic system, the 'fully symmorphic' space group $P2/m$ has no examples with one molecule in the general position, the 'equally balanced' $P2/c$ has 11 examples, the 'tending to antimorphism' $C2/c$ has 587, and the 'fully antimorphic' $P2_1/c$ has 5951. Other systems have fewer examples, but the trend is the same; the really popular space groups are the 'fully antimorphic' plus $P1$ and $P\bar{1}$.

All space groups, of course, possess general positions of symmetry 1, and the data in Table 9.7.2.1 show that 116 of them exhibit structures of some kind, and that 57 exhibit structures in which one or more general positions are used. 13 space groups ($P1$, $P2_1$, Pc , Cc , $P2_12_12_1$, $Pca2_1$, $Pna2_1$, $P4_{1,3}$, $P3_{1,2}$, $P6_{1,5}$) have no positions with symmetry higher than 1. These space groups contain no syntropic symmetry elements, and all are relatively popular.

9.7.4.2. Positions with symmetry $\bar{1}$

Many space groups are centrosymmetric (all those in the geometric classes $\bar{1}$, $2/m$, mmm , $4/m$, $4/mmm$, $\bar{3}$, $\bar{3}m$, $6/m$, $6/mmm$, $m\bar{3}$, $m\bar{3}m$), but comparatively few of them possess special positions of symmetry $\bar{1}$, as the centres of symmetry are often encumbered by other symmetry elements. All centres of symmetry in $P\bar{1}$, $P2_1/c$ and $Pbca$ are free, as are some of those in $P\bar{3}$ and $R\bar{3}$. When the encumbrance is an antitropic symmetry element, the special position can still be occupied by a molecule of symmetry $\bar{1}$ only, but when the encumbrance is syntropic or atropic the position cannot accommodate such a molecule. Table

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 Table 9.7.2.1. *Statistics of the use of Wyckoff positions of specified symmetry \mathcal{G} in the homomolecular organic crystals, based on the data by Belsky, Zorkaya & Zorky (1995)*

\mathcal{G}	Space groups with positions of symmetry \mathcal{G}	Space groups actually occurring	Space groups using such positions
1	230	116	57
2	167	79	38
m	99	42	25
$\bar{1}$	38	28	10
3	57	18	7
4	24	6	4
$\bar{4}$	29	17	8
222	50	15	5
$mm2$	57	18	5
$2/m$	39	21	6
6	5	1	0
$\bar{6}$	8	3	1
32	22	5	1
$3m$	22	8	5
$\bar{3}$	14	7	4
422	9	1	1
$\bar{4}2m, \bar{4}m2$	19	5	3
$4mm$	8	3	0
$4/m$	7	2	1
mmm	16	3	2
23	12	3	2
622	2	1	0
$\bar{6}2m, \bar{6}m2$	5	1	1
$6mm$	2	0	0
$6/m$	2	1	0
$\bar{3}m$	8	3	1
$4/mmm$	4	2	1
432	5	0	0
$\bar{4}3m$	6	2	1
$m\bar{3}$	5	2	1
$6/mmm$	1	0	0
$m\bar{3}m$	3	2	2

9.7.2.1 indicates that there are 38 space groups with special positions of symmetry $\bar{1}$, that 28 of them have examples of structures of some kind, and that ten have structures in which the centre of symmetry is actually used by a molecule.

The three space groups with no special positions except those of symmetry $\bar{1}$ are very popular, whether or not the centre of symmetry is actually used by the molecule. The single criterion 'no special positions except possibly free centres of symmetry' thus selects the space groups favoured by structures in which inherent molecular symmetry is not used.

 9.7.4.3. *Other symmetries*

Table 9.7.2.1 gives statistics for the number of space groups possessing Wyckoff positions of symmetry \mathcal{G} , where \mathcal{G} is one of the 32 point groups, the number exhibiting structures of some kind, and the number in which the special position of symmetry \mathcal{G} is actually used. It has to be remembered that this table represents the state of knowledge in 1994, that there may be small errors in the counts in the second column, and that new structures will gradually increase the numbers in the third and

fourth columns. Nevertheless, some trends are clear. The arrangement of the point groups is in ascending order of their 'order' (Hahn, 1995, p. 781), and all numbers show a general decrease with increasing order. When molecular symmetry is used, the favourite is the diad axis 2, closely followed by the mirror plane m , with the centre of symmetry $\bar{1}$, the triad axis 3 and the tetrad inversion axis $\bar{4}$ trailing. It must also be remembered that these data are for numbers of *space groups*, not numbers of *structures*.

 9.7.4.4. *Positions with the full symmetry of the geometric class*

The symmorphic space groups are in a one-to-one correspondence with the arithmetic crystal classes, and each has at least one Wyckoff position with the full symmetry of the geometric crystal class. It would thus be possible for each symmorphic space group to accommodate molecules with the full symmetry of the point group corresponding to the geometric crystal class. With the obvious exceptions of $P1$ and $P\bar{1}$, there seem to be no symmorphic space groups with primitive cells and one molecule only in the cell that do so, but the data of Belsky, Zorkaya &

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Zorky (1995) show that about half the possibilities are realized in symmorphic space groups with centred cells. The situation is set out in Table 9.7.4.1.

Although about half the point groups are not represented in symmorphic space groups with one molecule in the appropriate special position, it is interesting to look for molecules of these symmetries in space groups of higher symmetry. A few are in fact to be found in non-symmorphic space groups, but seven point groups have no established examples.

9.7.5. Structural classes

As developed so far (Belsky, Zorkaya & Zorky, 1995), structural classes relate primarily to homomolecular structures – structures in which all molecules are the same. Nevertheless, they are important in a study of the space-group distribution of molecular organic structures, as structures belonging to the same space-group type but to different structural classes are found to have very different frequencies. The germ of the idea is implicit in Kitajgorodskij's subdivision of his four categories by molecular symmetry.

In its general form, the symbol of a structural class has the form

$$SG, Z = n[(x)^a, (y)^b, \dots],$$

where SG is the standard space-group symbol, n is the number of molecules in the unit cell, x, y, \dots are the symbols of the point-group symmetries of the Wyckoff positions occupied, and a, b, \dots are the numbers of occupied Wyckoff positions of those symmetries. An example will make this clearer. There is a structural class

$$P\bar{4}m2, Z = 32[(mm)^4, m^4, 1].$$

This indicates that the space group is $P\bar{4}m2$ and that there are 32 molecules in the unit cell occupying four positions of symmetry mm , four of symmetry m , and one general position. On consulting the multiplicity of the special positions for this space group in Volume A of *International tables for crystallography* (Hahn, 1995), one finds that the 32 molecule total is accounted for as $(4 \times 2) + (4 \times 4) + (1 \times 8)$. If (as is usually the case) the square brackets are unnecessary, they are omitted, as in

$$P\bar{4}n2, Z = 2(222) \text{ and } P4/nnc, Z = 4(4).$$

Occasionally, two distinguishable structural classes will lead to the same symbol. As yet, Belsky, Zorkaya & Zorky prefer to deal with this problem on an *ad hoc* basis, rather than by attempting to devise any general rules.

Belsky, Zorkaya & Zorky divide the structural classes into six groups, in accordance with the number of examples found. The groups are 'anomalous' (up to five examples, 199 structural classes); 'rare' (up to 19 examples, 55 classes); 'small' (up to 49 examples, 24 classes); 'big' (13 classes); 'giant' (eight classes); and 'supergiant' (six classes). The last three are not explicitly defined, but examination of the tables shows that the dividing line between 'big' and 'giant' is about 250, and between 'giant' and 'supergiant' is about 750. All these statistics, of course, are subject to modification as the number of known structures increases.

9.7.6. A statistical model

Wilson (1988, 1990, 1991) has discussed the factors that, on statistical analysis, appear to govern the relative frequency of occurrence of the space groups of molecular organic crystals. In

its developed form (Wilson, 1990), the statistical model postulated that, within an arithmetic crystal class (see Chapter 1.4), the number of examples, N_{sg} , of a space-group type would depend exponentially on the numbers of symmetry elements within the unit cell, thus:

$$N_{sg} = A \exp \left\{ - \sum_j B_j [e_j]_{sg} \right\}. \quad (9.7.6.1)$$

In this equation, A is a normalizing constant depending on the arithmetic crystal class, $[e_j]_{sg}$ is the number of symmetry elements of type e_j within the unit cell in the space group, and B_j is a parameter depending on the arithmetic crystal class and the symmetry element e_j ; A and B_j are independent of the space group. Empirically, B_j has a positive sign for the syntropic symmetry elements (k and \bar{k} , where $n = 2, 3, 4, 6$) and a negative sign for l and the antitropic symmetry elements (glide planes and screw axes). Often, however, laws of 'conservation of symmetry elements', of the type

$$[2] + [2_1] = c, \quad (9.7.6.2)$$

or in general

$$\sum_j [e_j] = c, \quad (9.7.6.3)$$

where c is a constant for the crystal class, eliminate a separate dependence on one or more of the e_j 's (Wilson, 1990). Often a cohort larger than an arithmetic crystal class can be used, with arithmetic crystal class included as an additional factor.* With this adjustment, the model can be used for such cohorts as geometric crystal class or even crystal system, giving fits within the usual crystallographic range ($R_2 \lesssim 0.05$), but, for some classes (in particular mmm), statistical tests based on the scaled deviance indicated residual systematic error (Wilson, 1980). This was traced (Wilson, 1991) to the failure of an explicit postulate: 'The second possibility is that the distribution is seriously affected by molecular symmetry. Some molecules possess inherent symmetry . . . , and this symmetry could coincide with the corresponding crystallographic symmetry element, again increasing the variance and/or bias of the number of examples per space group. . . . The comparative rarity of utilization of molecular symmetry suggests that it can be ignored in an exploratory statistical survey . . .' (abbreviated from Wilson, 1988). This procedure was perhaps reasonable in a first 'exploratory' survey, and in fact agreement in the usual crystallographic range ($R_2 \lesssim 0.05$) was achieved (Wilson, 1988, 1990). However, the scaled deviance indicated that systematic errors still remained (Wilson, 1980), and the discrepancy was traced to the use of molecular symmetry in many structures (Wilson, 1990, 1992). If such structures are eliminated, R_2 falls to trivial values, and the agreement between observed and calculated frequencies becomes too good to be interesting.

9.7.7. Molecular packing

9.7.7.1. Relation to sphere packing

The effect of molecular symmetry cannot be ignored in overall statistical surveys as well as in structure prediction. However, in most structures, the molecular symmetry is low or it is not used

* Statistical modelling programs distinguish between variates and factors. The values of variates are ordinary numbers; $[2]$, $[m]$, . . . are variates. Factors are qualitative. In the immediate context, 'arithmetic crystal class' is a factor, but other categories, such as metal-organic compound, polypeptide, structural class (Belsky & Zorky, 1977), . . . , could be included if desired. The programs allow appropriately for both variates and factors; see Baker & Nelder (1978, Sections 1.2.1, 8.5.2, 22.1 and 22.2.1).

9.7. THE SPACE-GROUP DISTRIBUTION OF MOLECULAR ORGANIC STRUCTURES

Table 9.7.4.1. Occurrence of molecules with specified point group in centred symmorphic and other space groups, based on the statistics by Belsky, Zorkaya & Zorky (1995)

There is no entry in the 'other space group' column if examples are found in the centred symmorphic group.

Point group	Symmorphic space group	Other space group	Frequency
2	<i>C</i> 2	...	18
<i>m</i>	<i>C</i> <i>m</i>	...	6
2/ <i>m</i>	<i>C</i> 2/ <i>m</i>	...	20
222	None	<i>C</i> <i>c</i> <i>c</i> <i>a</i>	4
	...	<i>F</i> <i>d</i> <i>d</i>	2
	...	<i>P</i> $\bar{4}$ <i>n</i> 2	2
	...	<i>P</i> 4/ <i>n</i> <i>c</i> <i>c</i>	1
<i>mm</i> 2	<i>F</i> <i>m</i> <i>m</i> 2	<i>I</i> 4 ₁ / <i>a</i> <i>c</i> <i>d</i>	3
<i>mmm</i>	None	...	2
	...	<i>P</i> 4 ₂ / <i>m</i> <i>m</i> <i>m</i>	6
	...	<i>I</i> <i>m</i> $\bar{3}$	1
4	<i>I</i> 4	...	1
$\bar{4}$	None	<i>P</i> 4/ <i>n</i>	1
	...	<i>P</i> 4 ₂ / <i>n</i>	3
	...	<i>I</i> 4 ₁ / <i>a</i>	12
	...	<i>P</i> 4 ₂ 1/ <i>c</i>	17
	...	\bar{I} 4 ₂ <i>d</i>	1
	...	<i>I</i> 4 ₁ / <i>a</i> <i>c</i> <i>d</i>	1
4/ <i>m</i>	<i>I</i> 4/ <i>m</i>	...	1
422	None	<i>P</i> 4/ <i>n</i> <i>m</i> <i>c</i>	1
4 <i>mm</i>	None	None	None
$\bar{4}$ 2 <i>m</i>	\bar{I} 4 ₂ <i>m</i>	...	3
4/ <i>mmm</i>	<i>I</i> 4/ <i>mmm</i>	...	1
3	<i>R</i> 3	...	8
$\bar{3}$	<i>R</i> $\bar{3}$...	6
32	None	<i>R</i> $\bar{3}$ <i>c</i>	5
3 <i>m</i>	<i>R</i> 3 <i>m</i>	...	10
$\bar{3}$ <i>m</i>	<i>R</i> $\bar{3}$ <i>m</i>	...	2
6	None	None	None
$\bar{6}$	None	<i>P</i> 6 ₃ / <i>m</i>	12
6/ <i>m</i>	None	None	None
622	None	None	None
6 <i>mm</i>	None	None	None
$\bar{6}$ <i>m</i> 2	None	<i>P</i> 6 ₃ / <i>m</i> <i>m</i> <i>c</i>	1
6/ <i>mmm</i>	None	None	None
23	None	<i>F</i> 4 ₃ <i>c</i>	1
<i>m</i> $\bar{3}$	<i>F</i> <i>m</i> $\bar{3}$...	2
432	None	None	None
$\bar{4}$ 3 <i>m</i>	\bar{I} 4 ₃ <i>m</i>	...	4
<i>m</i> $\bar{3}$ <i>m</i>	<i>F</i> <i>m</i> $\bar{3}$ <i>m</i>	...	9
	<i>I</i> <i>m</i> $\bar{3}$ <i>m</i>	...	2

in the packing. In about 90% of crystalline compounds, the molecules crystallize in low-symmetry space groups, so that a given molecule has a 12-point contact with neighbouring molecules. As 12 corresponds to the number of nearest neighbours in cubic and hexagonal closest packing of spheres, the periodic assembly of most molecular structures can be regarded as the closest packing of distorted spheres, where symmetry ensures the interlocking of complex shapes (Gavez-zotti, 1994).

For the relatively infrequent cases where high molecular symmetry is reflected in high crystal symmetry, the packing of molecules can be derived from the appropriate, though not necessarily the densest, packing of spheres. For example, ten-point, eight-point and six-point molecular contacts can be

achieved, respectively, by tetragonal close packing (*I*4/*mmm*), by *I*-centred cubic packing (*I**m* $\bar{3}$ *m*), and by primitive cubic packing (*P**m* $\bar{3}$ *m*). For a review and some derivations of the densest packing of equal spheres, see Chapter 9.1 and Patterson & Kasper (1959), Coutanceau Clarke (1972), and Smith (1973); and for packing of clusters of unequal spheres, see Williams (1987).

With spheres having infinite point symmetry $\mathcal{K}_{\infty h}$, every sphere can be located on syntropic symmetry elements at special positions with high symmetry up to the symmetry of the lattice. The lattice translations, pertinent to the fully symmorphic space group, are then able to generate the entire crystal structure. When spheres are deformed, symmetry is removed and the non-lattice translations involved with antimorphic space groups

9. BASIC STRUCTURAL FEATURES

(which must be subgroups of the sphere-packing groups) become necessary to ensure space filling with the repetitive patterns of complex molecular shapes. In a similar manner, other objects with infinite elements of symmetry (*e.g.* rods; Lidin, Jacob & Andersson, 1995) can be subjected to a rigorous analysis of close packing.

9.7.7.2. *The hydrogen bond and the definition of the packing units*

The variously shaped molecular packing units of organic crystal structures are not necessarily identical with the individual molecule. The molecule (of a shape defined by chemical bonds on the inside and van der Waals forces on the outside) can be subjected to clustering under formation of intermolecular hydrogen bonds. Although far weaker than the chemical bond, hydrogen bonds are strong enough to alter the shape of the packing units of the crystal structure significantly. This may have far-reaching consequences for the adopted packing and symmetry. An extreme example is represented by the clustering of H₂O molecules, where two hydrogen bonds and two regular O—H bonds create a 43m point symmetry at each O atom, and a highly symmetrical structure emerges with an infinite bond network, similar to that in quartz, SiO₂. From the point of view of an individual H₂O molecule, the structure is very open. In contrast, a pseudo-close-packed structure of crystalline water, assuming an effective H₂O radius of 1.38 Å, would have specific density of 1.8 g cm⁻³.

Analogous principles apply to organic structures with hydrogen bonding. CH₃OH, for example, forms hydrogen-bonded zig-zag chains in its crystal structure. Obviously, the shape of the hydrogen-bonded cluster of molecules depends on the number and orientations of the hydrogen bonds relative to the size and shape of the molecule, causing three-dimensional, planar and linear 'polymers', or the formation of dimers and trimers. As in the example of water, this introduces additional symmetry elements and decreases the degree of space filling.

There is a general rule that ensures that this phenomenon is widespread. The principle of maximum hydrogen bonding states that all the H atoms in the active (polar) groups of a molecule are employed in hydrogen-bond formation (Evans, 1964). Therefore, as the O···HO and O···HN hydrogen bonds are both energetic and common, they are also of the greatest importance in this respect. Although most pronounced in smaller molecules, the symmetry-altering influence of hydrogen bonding also applies to relatively large molecules with a lower proportion of hydrogen bonding as, for example, in long-chain carboxylic acids that are linked in pairs. In large molecules with many active groups, however, the hydrogen bonds merely become the new delimiters of the shape of the individual molecule. The perils of the symmetry-statistical treatments of the hydrogen-bonded structures are well recognized and, for some purposes, the strategy adopted is to exclude such systems from the statistical pool (Filippini & Gavezzotti, 1992).

9.7.8. *A priori predictions of molecular crystal structures*

As physical properties of a molecular compound are a function of the spatial arrangement of molecules, an important goal of the

structural chemist is to predict the space group and crystal structure from the molecular shape. On the basis of the observation that many structures of organic compounds are formed on the principle of periodic close packing of variously shaped molecules, it seems that such prediction would be a more or less straightforward computational task. However, the task of predicting the crystal structure of a specific molecular solid is complicated owing to the occurrence of hydrogen bonding (Subsection 9.7.7.2) and the widespread phenomenon of polymorphism (Gavezzotti, 1994). With only subtle differences in their Gibbs free energies, the occurrence of the structural modifications can be influenced by various non-equilibrium factors during crystallization.

In spite of the above problems, experience has shown that prediction algorithms can often be used to generate several reasonable structures for any given molecule and that in many cases the correct structure is among them. There are two general strategies that have been adapted for structure prediction. In the first one, developed by Kitajgorodskij (1955, 1973), the molecular shape is physically constructed from models of atoms having van der Waals radii, resulting in the calot model. The physical calot model is then used for an analogue calculation of the space filling using a mechanical instrument that relates the molecules in three-dimensional space so that the projection of one molecule fits into the voids of other molecules. When the unit-cell dimensions are known, the entire crystal structure can be derived in this way. In the second approach, the same yet abstract 'fused sphere model' is analysed for its symmetry by what can be called a 'morphic' (as opposed to metric) transformation by the methods of molecular topology (Mezey, 1993). The abstract topological molecular shapes can in principle be treated more rigorously and are computable into probable crystal structures.

Such *a priori* predictions of molecular structures are still in a relatively early stage of development. Several recent studies are indicative of the current progress in the field. For layered structures, good predictions can be obtained using construction techniques, symmetry probabilities, and potential energy functions (Scaringe, 1991). An algorithm for the generation of crystal structures by the optimization of packing potential energy over several possible space groups has been devised by Gavezzotti (1991, 1994). In a third approach, energy minimization without symmetry constraints is used for determining molecular crystal structures (Gibson & Scheraga, 1995).

In spite of recent progress, the conceptual link between the molecular and crystal structures still relies to a large extent on the chemical intuition of scientists. The space-group statistics have played a critical role, as they provide the researcher with a summary of what happens in nature. It is likely that the prediction process can be enhanced by calculating statistics of the space-group frequencies and symmetry for molecules that are the most closely related to the shape or chemistry of the molecule under study. As such statistical subsets are often significantly different from the overall statistics, they may prove more valuable in the *a priori* prediction of the crystal structure for a specific molecule. The space-group frequencies and symmetry statistics remain one of the important strings in this link.

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