Space Groups Rare for Organic Structures. III. Symmorphism and Inherent Molecular Symmetry

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Abstract

To a close approximation, the relative frequency of the space groups of molecular organic compounds is determined by ease of packing. When the molecules are in general Wyckoff positions, the relative frequency anticorrelates with the degree of symmorphism. Somewhat different considerations apply if the molecule possesses and uses some inherent symmetry ($\bar{1}$, 2, m, $2/m$, 222, mm, ...) [Китайгородский (1955). Органическая Кристаллохимия. Москва: Изд. Акад. Наук; Kitaigorodskii (1961). *Organic Chemical Crystallography.* New York: Consultants Bureau]. The observed frequencies are analysed in the light of the degree of symmorphism and molecular symmetry.

1. Symmorphism

1.1. *Symmorphic space groups*

The 73 symmorphic space groups are in one-to-one correspondence with the arithmetic crystal classes, and in fact conventional crystallographic symbolism did not distinguish between them until recently (de Wolff *et al.,* 1985). The symmorphic space groups are defined in various ways, of which three examples are:

1. the space group corresponding to the zero solution of the Frobenius congruences is called a symmorphic space group (Engel, 1986, p. 155);

2. a space group F is called *symmorphic* if one of its finite subgroups (and therefore an infinity of them) is of an order equal to the order of the point group R_r (Opechowski, 1986, p. 255);

3. a space group is called *symmorphic* if the coset representatives W_j can be chosen in such a way that they leave one common point fixed (Wondratschek, 1989, p. 717).

Even in context, these are pretty opaque. Fortunately, however, there is a rule of thumb by which the symmorphic space groups can be recognized immediately from their standard Hermann–Mauguin symbols. Before the rule is stated (§ 1.1.1), it is necessary to consider some of the conventions governing the construction of the space-group symbols from the symbols of the symmetry elements constituting the space group.

Volume A of *International Tables for Crystallography* distinguishes (Bertaut, 1989, pp. 49–68) three types of space-group symbols: (i) *standard* (*short*), (ii) *full* and (iii) *extended*, depending on the amount of symmetry information included. In forming the symbols, priority is given to reflection planes and rotation (including rotation-inversion) axes. Screw axes and glide planes occur in the standard symbols only when their use is unavoidable; as far as possible, they are relegated to the full symbols and the extended symbols. The centre of symmetry is indicated only in one space-group symbol, $P\bar{1}$. The rule of thumb can now be enunciated.

1.1.1. *The rule of thumb. Symmorphic space groups are those whose standard (short) symbols do not contain glide planes or screw axes.*

Although the *standard* symbols of the symmorphic space groups do not contain screw axes or glide planes, this is a result of the manner in which the space-group symbols have been devised. Most symmorphic space groups do in fact contain screw axes and/or glide planes. This is immediately obvious for the symmorphic space groups based on centred cells; $C2$ contains equal numbers of diad rotation axes and diad screw axes, and Cm contains equal numbers of reflection planes and glide planes. In the more symmetric crystal systems, even symmorphic space groups with primitive cells contain screw axes and/or glide planes; for example, $P422$ contains many diad screw axes and $P4mm$ contains many glide planes. Such screw axes and glide planes can be regarded as resulting from the interactions of the symmetry operations indicated in the standard symbol with the translations of the unit cell. Bertaut (1989, Tables 4.1.2 and 4.1.3) gives representative examples but not a complete enumeration.

1.1.2. *Definitions.* For brevity, throughout the remainder of this paper, the symmetry elements

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

will be called *syntropic*; the elements

$$2_1, \ 3_{1,2}, \ 4_{1,3}, \ 6_{1,5}; \quad \text{any glide plane}$$

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will be called *antitropic*; and the remaining elements

$$1, \bar{1}; \quad 4_2 = 2 + 2_1; \quad 6_{2,4} = 2 + 3_{1,2}, \quad 6_3 = 2_1 + 3$$

will be called *atropic*. These or similar words are already in use in botanical contexts, but no confusion can arise.

In space groups with several symmetry elements, the elements may avoid each other or intersect or coincide. A symmetry element that lies fully in one or more others is called 'encumbered'; one that avoids, or at most intersects, others is called 'free' (Wilson, 1988, § 5). For example, in the space group $Pmm2$, the diad axis lies in the intersection of the mirror planes and is 'encumbered', whereas, in $Pna2_1$, the diad screw axis avoids the glide planes and is thus 'free'. 'Free' centres of symmetry occur in only three space groups ($P\bar{1}$, $P2_1/c$, $Pbca$).

Adjectives like 'rare', 'common', 'frequent' are to be taken as relative to space groups in the immediate neighbourhood of the space group under discussion.

1.2. 'Antimorphic' space groups

It would be nice to define in each arithmetic crystal class (Wilson, 1992a) an 'antimorphic' space group, one that departs as far as possible from full symmorphism – one that contains no syntropic symmetry elements. This is often possible; familiar examples are $P2_1$, Pc, $P2_1/c$, $Pbca$. The only fully 'antimorphic' space group with a centred cell is Cc. There is no formal definition of 'antimorphic' and occasionally there may be more than one 'antimorphic' candidate; the most obvious example is the pair $Pca2_1$ and $Pna2_1$. It is reasonable to choose $Pna2_1$ as in it the diad axis is 'free' (§ 1.1.2).

1.3. Degrees of symmorphism

Space groups can be classified by the extent to which they tend to symmorphism or antimorphism. If they contain only the syntropic elements k and/or $\bar{k}$, where $k = 2$, 3, 4 or 6, they are fully symmorphic. The fully antimorphic space groups contain only antitropic glide planes and/or simple screw axes k_1 or k_{k-1} – and, in centrosymmetric crystal classes, 'free' centres of symmetry (Wilson, 1988, § 5.1). When the two types are mixed, the space groups can be classified as 'tending to symmorphic', 'equally balanced' or 'tending to antimorphic'. There is obviously the possibility of some ambiguity about the intermediate classes: are planes and axes to be given equal weight? Does 2_1 exactly cancel m in $P2_1/m$ or 2 exactly cancel c in $P2/c$? Sometimes there is no doubt, for example when the cancellation is glide plane *versus* reflection plane or diad *versus* screw diad. All space groups with centred lattices except Cc are in the intermediate classes.

1.3.1. A numerical index. If the cancellation just discussed is accepted, a numerical index of degree of symmorphism can be constructed. An index that corresponds well with the subjective concept is the syntropic-symmetry fraction

$$S = N_{\text{syn}}/(N_{\text{syn}} + N_{\text{anti}}),   (1)$$

where N_{syn} is the number of syntropic symmetry elements in the unit cell and N_{anti} is the number of antitropic elements. This takes the value unity for the fully symmorphic space groups and the value zero for the fully antisymmorphic; the rest give fractional values in the intervening range. In the monoclinic and orthorhombic systems, the same values are obtained by taking the N's (with a little care in counting!) from the tabulations of symmetry operations in the space-group entries in *International Tables for Crystallography* (Hahn, 1989) but it is difficult to extend the latter procedure to the space groups of higher symmetry. For four space groups ($P4_2$, $P6_{2,3,4}$), the composite atropic screw axes must be broken down into their syntropic and antitropic components, as indicated in § 1.1.2.

The index could be modified in various ways, such as by including the atropic screw axes in both the numerator and the denominator of (1) for all space groups in which they occur, but there is no obvious advantage. Numerical indices of symmorphism are not used explicitly in this paper, but they have sometimes influenced the placing of a space group in Tables 1 to 7.

When two related space groups are assigned to the same column in the tables, they are sometimes printed with the more nearly symmorphic one to the left and the more nearly antimorphic one to the right of the column.

1.3.2. Single-member arithmetic crystal classes. 12 arithmetic crystal classes contain only one space group each, and this gives rise to a paradox in nomenclature – the single member is symmorphic and it is also the only candidate for the title of 'antimorphic'. This is reasonable enough for space groups like $C2$ and $R3$, which contain both syntropic and antitropic symmetry elements, but paradoxical for $P\bar{3}$, $P\bar{4}$ and $P\bar{6}$, which contain only syntropic symmetry elements. The space groups of the single-member classes are arranged by degree of symmorphism in Table 1.

1.3.3. Symmorphism and special positions. Inspection of *International Tables for Crystallography* shows that the space groups can be divided into four types on the basis of their special positions.

1. Three space groups whose only special positions have symmetry $\bar{1}$ ($P\bar{1}$, $P2_1/c$, $Pbca$). For $P\bar{1}$, see the heading of Table 1; P_1/c and $Pbca$ are fully antimorphic.

2. 13 space groups with no special positions ($P1$, $P2_1$, Pc, Cc, $P2_12_12_1$, $Pca2_1$, $Pna2_1$, $P4_1$, $P4_3$, $P3_1$, $P3_2$, $P6_1$, $P6_5$). All are fully antimorphic.

3. 39 space groups, not included in 1 or 2, with at least one position of multiplicity unity. All have primitive cells (P or R) and are symmorphic in the sense of § 1.1. However, those with R cells 'tend to antimorphism', and only the space groups with few symmetry elements and P cells

Table 1. *The space groups of the single-member arithmetic crystal classes arranged by degree of symmorphism*

For *, † and the superscript numerals, see § 1.3.4. The triclinic space groups are a special case, with 'syntropic-symmetry fraction' undefined ($S = 0/0$), and they are not assigned to any particular column.

Arithmetic crystal class	Fully symmorphic	Tending to symmorphism	Equally balanced	Tending to antimorphism	Fully antimorphic
1P $\overline{1}P$			$*P1†^{189}$ $*P\overline{1}†^{5946}$		
2C			$*C2†^{260}$		
222F			$*F222†^{0}$		
$\overline{4}P$ $\overline{4}I$	$*P\overline{4}†^{0}$		$*I\overline{4}†^{19}$		
3R $\overline{3}P$ $\overline{3}R$ 32R $\overline{6}P$	$*P\overline{3}†^{6}$ $*P\overline{6}†^{0}$			$*R3†^{15}$ $*R\overline{3}†^{53}$ $*R32†^{0}$	
23F			$*F23†^{0}$		

Table 2. *Monoclinic space groups classified by degree of symmorphism*

For *, † and the superscript numerals, see § 1.3.4.

Arithmetic crystal class	Fully symmorphic	Tending to symmorphism	Equally balanced	Tending to antimorphism	Fully antimorphic
2P	$*P2^{3}$	...	...	...	$P2_{1}†^{2552}$
2C	...	...	$*C2†^{260}$	...	...
mP	$*Pm^{1}$	...	...	...	$Pc†^{138}$
mC	...	...	$*Cm^{1}$	...	$Cc†^{371}$
2/mP	$*P2/m^{0}$	...	$P2_{1}/m^{16}$ $P2/c^{74}$	...	$P2_{1}/c†^{13131}$
2/mC	...	...	$*C2/m^{0}$	$C2/c†^{1456}$	...

are 'fully symmorphic'. The others with P cells 'tend to symmorphism'.

4. The remaining space groups; they are neither fully symmorphic nor fully antimorphic.

Examples of type (1) are very frequent, of type (2) are frequent and of type (3), except $R3$, are not common. The frequency of examples of type (4) has been discussed semi-seriously by Wilson (1992b) in terms of two sub-types; see also § 3.2 below.

1.3.4. *Asterisk, obelus, superscript.* In many tables of this paper, the symmorphic space groups are marked with an asterisk * and the antimorphic with an obelus †. The superscript numbers following the space-group symbols approximate to the number of molecular organic structures with a single molecule in the general position of the space group; their exact significance is explained in § 3, but they are indicated at this stage in order to give an impression of the relative frequencies of the space groups of

structures governed primarily by packing considerations. A glance at the tables shows that organic molecules avoid the general positions in the space groups on the left (symmorphic or tending to symmorphic) and prefer the general positions in the space groups on the right (antimorphic or tending to antimorphic).

2. Symmorphism in the crystal systems

2.1. *The triclinic system*

The two triclinic space groups are included in Table 1. Neither is 'fully symmorphic' nor 'fully antimorphic' in the senses described above. Unlike the fully symmorphic space groups with $k > 1$, $P\overline{1}$ is very frequent and $P1$ is not rare among molecular organic compounds. The above discussion gives no basis for assigning them to any particular column in Table 1, so the vertical divisions are omitted in the triclinic section of the table.

Table 3. *Orthorhombic space groups classified by degree of symmorphism*

For *, † and the superscript numerals, see § 1.3.4.

Arithmetic crystal class	Fully symmorphic	Tending to symmorphism	Equally balanced	Tending to antimorphism	Fully antimorphic
222P	$*P222^1$	$P222_1^0$	...	$P22_12_1^{114}$	$P2_12_12_1\dagger^{5410}$
222C	....	$*C222^0$	...	$C222_1\dagger^{27}$	...
222F	...	...	$*F222^0$	...	...
222I	...	...	$*I222^3$	...	...
			$I2_12_12_1\dagger^0$		
mm2P	$*Pmm2^0$	$Pma2^0$	...	$Pmc2_1^1$	$Pca2_1^{289}$
				$Pcc2^0$	$Pna2_1\dagger^{748}$
				$Pnc2^2$	
				$Pmn2_1^0$	
				$Pba2^3$	
				$Pnn2^3$	
mm2C	...	$*Cmm2^0$	...	$Cmc2_1\dagger^2$	...
				$Ccc2^2$	
2mmC	...	$*C2mm^0$	...	$C2mb^1$	...
				$C2cm^0$	
				$C2cb\dagger^{19}$	
mm2F			$*Fmm2^0$	$Fdd2\dagger^{86}$	
mm2I	...	...	$*Imm2^0$	$Iba2\dagger^{28}$	
				$Ima2^0$	
mmmP	$*Pmmm^0$	$Pccm^0$	$Pnnn^0$	$Pnna^9$	$Pbca\dagger^{1798}$
		$Pmma^0$	$Pban^0$	$Pcca^8$	
			$Pmna^0$	$Pbam^2$	
			$Pmmn^0$	$Pccn^{96}$	
				$Pbcm^4$	
				$Pnnm^0$	
				$Pbcn^{158}$	
				$Pnma^{13}$	
mmmC	...	$*Cmmm^0$	$Cmma^0$	$Cmcm^0$	...
				$Cmca^0$	
				$Cccm^0$	
				$Ccca\dagger^1$	
mmmF	...	...	$*Fmmm^0$	$Fddd\dagger^2$	...
mmmI	...	...	$*Immm^0$	$Ibam^0$	
				$Ibca^0$	
				$Imma^0$	

2.2. The monoclinic system

The classification of the space groups in the monoclinic system is given in Table 2. The system contains six symmorphic space groups (indicated by asterisks), corresponding to its six arithmetic crystal classes, of which three ($P2$, Pm, $P2/m$) are fully symmorphic and three ($C2$, Cm, $C2/m$) are equally balanced. The fully symmorphic space groups are all rare and the equally balanced ones are at best of moderate frequency. There are four fully antimorphic space groups ($P2_1$, Pc, Cc, $P2_1/c$); none are rare and one, $P2_1/c$, is the commonest organic space group.

2.3. The orthorhombic system

The classification of the space groups in the orthorhombic system is given in Table 3. The system contains 13 symmorphic space groups, corresponding to its 13 arithmetic crystal classes, of which three ($P222$, $Pmm2$, $Pmmm$) are fully symmorphic and seven ($F222$, $I222$, $C2mm$, $Imm2$, $Immm$, $Fmmm$) are equally balanced. Three ($C222$, $Cmm2$, $Cmmm$) 'tend to sym-

morphism'. The fully symmorphic space groups and those tending to symmorphism are all rare and the equally balanced ones are at best of moderate frequency. There are four fully antimorphic space groups ($P2_12_12_1$, $Pna2_1$, $Pca2_1$, $Pbca$), all common. In some cases, there is an appreciable difference in the 'degree of symmorphism' between space groups in the same column, sometimes indicated by displacing the symbol to the left or to the right of the column.

2.4. The tetragonal system

The classification of the space groups in the tetragonal system is given in Table 4. There are no really frequent space groups.

2.5. The trigonal system

The classification of the space groups in the trigonal system is given in Table 5. The system contains 13 symmorphic space groups, of which two ($P3$ and $P\overline{3}$) are fully symmorphic and six ($P312$, $P321$, $P3m1$, $P31m$, $P\overline{3}m1$ and $P\overline{3}1m$) 'tend to symmorphism'. All space groups

Table 4. *Tetragonal space groups classified by degree of symmorphism*

For *, † and the superscript numerals, see § 1.3.4.

Arithmetic crystal class	Fully symmorphic	Tending to symmorphism	Equally Balanced	Tending to antimorphism	Fully antimorphic
4P	*$P4$[0]	$P4_2$[3]	...	...	$P4_{1,3}$†[89]
4I	...	...	$I4_1$†[4]	*$I4$[7]	...
$\bar{4}P$	*$P\bar{4}$†[0]	...	...	...	...
$\bar{4}I$	...	...	*$I\bar{4}$†[19]	...	...
4/mP	*$P4/m$[0]	$P4_2/m$[0] $P4/n$[2]	$P4_2/n$†[30]	...	...
4/mI	...	...	...	*$I4/m$[0] $I4_1/a$†[59]	...
422P	...	*$P422$[0] $P4_222$[0]	$P42_12$[0] $P4_{1,3}22$[3]	$P4_{1,3}2_12$†[92] $P4_22_12$[2]	...
422I	...	...	$I4_122$†[0]	*$I422$[0]	...
4mmP	...	*$P4mm$[0]	$P4bm$[0]	$P4_2cm$[0] $P4_2cm$[0] $P4cc$[0] $P4nc$[0] $P4mc$[0] $P4_2bc$†[0]	...
4mmI	...	...	...	*$I4mm$[0] $I4cm$[0] $I4_1md$[0] $I4_1cd$†[11]	...
$\bar{4}2mP$	...	*$P\bar{4}2m$[0]	$P\bar{4}2c$[0] $P\bar{4}2_1m$[0]	$P\bar{4}2_1c$†[27]	...
$\bar{4}m2P$	...	*$P\bar{4}m2$[0]	$P\bar{4}c2$[0] $P\bar{4}b2$[0] $P\bar{4}n2$[0]	...	...
$\bar{4}m2I$	...	...	*$I\bar{4}m2$[0]	$I\bar{4}c2$†[0]	...
$\bar{4}2mI$	...	...	*$I\bar{4}2m$[0]	$I\bar{4}2d$†[1]	...
4/mmmP	...	*$P4/mmm$[0] $P4_2/mmc$[0] $P4_2/mcm$[0]	$P4/mmc$[0] $P4/nmm$[0]	$P4/nbm$[0] $P4/nnc$[0] $P4/mbn$[0] $P4/ncc$[0] $P4_2/nbc$[1] $P4_2/mbc$[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] $I4_1/acd$†[2]	

Table 5. *Trigonal space groups classified by degree of symmorphism*

For *, † and the superscript numerals, see § 1.3.4.

Arithmetic crystal class	Fully symmorphic	Tending to symmorphism	Equally balanced	Tending to antimorphism	Fully antimorphic
3P	*$P3$[9]	...	...	...	$P3_{1,2}$†[58]
3R	...	...	...	*$R3$†[15]	...
$\bar{3}P$	*$P\bar{3}$†[6]	...	...	...	...
$\bar{3}R$	...	...	...	*$R\bar{3}$†[53]	...
312P 321P	...	*$P312$[0] *$P321$[1]	...	$P3_{1,2}12$†[1] $P3_{1,2}21$†[17]	...
32R	...	...	...	*$R32$†[0]	...
3m1P 31mP	...	*$P3m1$[0] *$P31m$[0]	...	$P3c1$†[0] $P31c$†[0]	...
3mR	...	...	...	*$R3m$[0] $R3c$†[12]	...
$\bar{3}m1P$ $\bar{3}1mP$	...	*$P\bar{3}m1$[0] *$P\bar{3}1m$[0]	...	$P\bar{3}c1$†[0] $P\bar{3}1c$†[0]	...
$\bar{3}mR$	...	...	...	*$R\bar{3}m$[0] $R\bar{3}c$†[1]	...

Table 6. *Hexagonal space groups classified by degree of symmorphism*

For *, † and the superscript numerals, see § 1.3.4.

Arithmetic crystal class	Fully symmorphic	Tending to symmorphism	Equally balanced	Tending to antimorphism	Fully antimorphic
$6P$	$*P6^0$	...	$P6_{2,4}{}^2$ $P6_3{}^3$	...	$P6_{1,5}†^{46}$
$\bar{6}P$	$*P\bar{6}†^0$	...	...	...	...
$6/mP$	$*P6/m^0$	...	$P6_3/m†^0$	...	...
$622P$	...	$*P622^0$ $P6_{2,4}22^0$	...	$P6_322^2$ $P6_{1,5}22†^2$	...
$6mmP$	...	$*P6mm^0$	...	$P6cc^0$ $P6_3cc^0$; $P6_3cm^0$ $P6_3mc^0$	...
$\bar{6}m2P$ $\bar{6}2mP$	...	$*P\bar{6}m2^0$ $*P\bar{6}2m^0$	...	$P\bar{6}c2†^0$ $P\bar{6}2c†^0$	...
$6/mmmP$	...	$*P6/mmm^0$	...	$P6/mcc†^0$; $P6_3/mcm^0$ $P6_3/mmc^0$	...

with R cells possess one triad axis and two triad screw axes, which exclude them from all columns except 'Tending to antimorphic', though $R32$ comes close to being 'Equally balanced'. The only fully antimorphic groups are the enantiomorphic pair $P3_{1,2}$. Only a few have many examples with Z' (§ 3) equal to unity; $P3_{1,2}{}^{58}$, $R3^{15}$, $R\bar{3}^{53}$, $P3_{1,2}21^{17}$ and $R3c^{12}$ are appreciably represented. All are in the antimorphic part of Table 5.

2.6. The hexagonal system

The classification of the space groups in the hexagonal system is given in Table 6. Only the fully antimorphic pair $P6_{1,5}†^{46}$ has an appreciable number of examples.

2.7. The cubic system

There are no space groups in the cubic system that are fully one or the other. The symmorphic space groups all have triad screw axes parallel to the cube diagonals and sometimes other antitropic elements. The situation is similar to that of the space groups with R cells (§ 2.5). Similarly, the antimorphic space groups have simple triad axes in the same orientation and sometimes other syntropic elements.

The column headings in Table 7 have been adjusted accordingly. No structures with $Z' = 1$ were found and thus the superscript numbers (§ 3.1) are omitted.

3. The Cambridge Structural Database

The Cambridge Structural Database (Allen, Kennard & Taylor, 1983) contains a data file of organic structures, broadly defined, but stopping short of high-molecular-weight polypeptides and proteins. The data used here refer to the file as it was in January 1992, when it contained 106 694 entries. The data vary widely in quality. For the present purpose, a selection was made, rejecting space groups not substantiated by a complete structure determination or dubious because of disorder in the crystal. Structures in which the binding was likely to have a large ionic

component were rejected, as were duplicate determinations of the same structure. The numbers used here thus represent, as closely as the search programs allow, molecular organic structures with predominantly non-directive bonding between the molecules and thus structures likely to be determined predominantly by packing considerations.

The database can be searched for the space group and for the number of formula units in the unit cell; unfortunately, the Wyckoff position is not explicitly recorded in the file. However, the file can be searched for the relative multiplicity

$$Z' = Z_{\text{actual}}/Z_{\text{general}}, \qquad (2)$$

where Z_{actual} is the actual number of formula units in the unit cell and Z_{general} is the multiplicity of the general Wyckoff position. If Z' is not an integer, some molecules must be in special positions. In general, $Z' = 1$ corresponds to one molecule in the general position but it may also correspond to n molecules in special positions of multiplicity Z/n. In well populated space groups, the numbers thrown up by the search for $Z' = 1$ were accepted but when the space group had few examples these were individually checked and if fractional molecules in multiple positions were involved a comment is made in the relevant paragraph.

Similar considerations apply to non-integral values of Z'. An apparent value of $Z' = 1/m$ may result from n molecules in positions of multiplicity Z_{general}/nm. The molecular symmetry implied by any value of Z' must, therefore, be interpreted as the *minimum* symmetry of the molecule unless the actual structure determination has been consulted.

Relative multiplicities in the ranges $0.5 < Z' < 1.0$ and $Z' > 1.0$ result from molecules occupying more than one Wyckoff position.

3.1. Superscript numbers in the tables

The number of structures with one formula unit in the unit cell is given as a superscript to the space-group sym-

Table 7. *Cubic space groups classified by degree of symmorphism*

For * and †, see § 1.3.4 and, for the column headings, § 2.7. No examples with $Z' = 1$ were found, so the superscript numerals are omitted.

Arithmetic crystal class	Symmorphic except for 3_1	Tending to symmorphism	Equally balanced	Tending to antimorphism	Antimorphic except for 3
$23P$	$*P23$	...	...	...	$P2_13$†
$23F$	...	...	$*F23$†	...	...
$23I$	...	...	$*I23\ I2_13$†	...	...
$m\bar{3}P$	$*Pm\bar{3}$	...	$Pn\bar{3}$	...	$Pa\bar{3}$†
$m\bar{3}F$	...	...	$*Fm\bar{3}$	$Fd\bar{3}$†	...
$m\bar{3}I$	...	...	$*Im\bar{3}$	$Id\bar{3}$†	...
$432P$	...	$*P432$	...	$P3_{1,2}$†	...
$432F$	...	...	$*F432$	$F4_132$†	...
$432I$	...	...	$*I432$	$I4_132$†	...
$\bar{4}3mP$	...	$*P\bar{4}3m$	...	$P\bar{4}3n$†	...
$\bar{4}3mF$	...	...	$*F\bar{4}3m$	$F\bar{4}3c$†	...
$\bar{4}3mI$	...	...	$*I\bar{4}3m$	$I\bar{4}3d$†	...
$m\bar{3}mP$	...	$*Pm\bar{3}m$	$Pm\bar{3}n\ Pn\bar{3}m$	$Pn\bar{3}n$†	...
$m\bar{3}mF$	...	$*Fm\bar{3}m$	...	$Fm\bar{3}c\ Fd\bar{3}m$	$Fd\bar{3}c$†
$m\bar{3}mI$	...	$*Im\bar{3}m$	...	$Ia\bar{3}d$†	...

bol in Tables 1 to 7. In Tables 8 to 15, the superscript indicates the number of molecules with the relevant value of the relative multiplicity Z'.

3.2. Molecules in special positions

If Z' [(2)] is less than unity, some molecules must occupy special positions and have the symmetry of those positions. In principle, the number of possible molecular symmetries is indefinitely large (Hahn & Klapper, 1989, pp. 780–786) but only the 32 symmetries of the geometric crystal classes can in fact be used by finite molecules in a crystal. If the free molecule has potentially a higher symmetry, its actual symmetry will be degraded to a greater or a lesser extent by the intermolecular forces. In particular, if two inherently centrosymmetric molecules are related by a crystallographic centre of symmetry, they will be distorted to form a pair of non-centrosymmetric enantiomers and the resultant will be a dimer in a structural sense, though possibly not in a chemical sense.

Examples of nearly all the geometric crystal classes can be found. The simpler ones, of multiplicity two ($\bar{1}, 2, m$), are frequent; those with multiplicities three, four or six ($2/m$, 222, mm, 4, $\bar{4}$, 3, $\bar{3}$, ...) are fairly frequent; and those with higher multiplicities (mmm, ...) are rare.

In a loose sense, if a crystal consists of molecules occupying a special position, the packing is 'roughly as if' the symmetry of the space group were degraded to that of a subgroup lacking the molecular symmetry in question (Wilson, 1992b). The subgroup can usually be identified without difficulty by the entry 'Maximal non-isomorphous subgroups' in the space-group entries in *International Tables for Crystallography*, Volume A (Hahn, 1989); in non-obvious cases, Fig. 10.3.2 is helpful.

The analysis of numbers of examples of space groups classified by Z' is given in Tables 8 to 15.

Table 8. *The space groups of the triclinic and monoclinic crystal classes arranged by relative multiplicity* Z'

In this and the following tables, a dash (-) indicates that the multiplicity is inconsistent with the space group; the numeral zero (0) indicates that the multiplicity is theoretically possible but that no examples were found.

Space group	Relative multiplicity Z'							
	1/4 $2/m$	1/2 $\bar{1},2,m$	1	3/2	2	5/2	3	≥ 4
1 $P1$	-	-	189	-	172	-	0	30
2 $P\bar{1}$	-	1477	5946	24	996	1	37	28
3 $P2$	-	0	0	3	0	0	0	0
4 $P2_1$	-	-	2552	-	576	0	18	24
5 $C2$	-	87	260	4	39	0	1	3
6 Pm	-	0	1	0	1	0	0	0
7 Pc	-	-	138	-	28	-	3	3
8 Cm	-	18	1	3	0	0	0	0
9 Cc	-	-	371	-	45	-	7	5
10 $P2/m$	0	0	0	0	0	0	0	0
11 $P2_1/m$	-	215	16	2	0	0	0	0
13 $P2/c$	-	66	74	2	22	0	0	0
14 $P2_1/c$	-	2658	13131	28	1108	0	42	17
12 $C2/m$	107	45	0	0	0	0	0	0
15 $C2/c$	-	1626	1456	27	49	0	7	1

4. Utilization of special positions

4.1. The triclinic system

The numbers of structures in the two triclinic space groups, arranged by relative multiplicity Z', are given in Table 8. As noted in the heading, in this and the following tables a dash (-) indicates that the multiplicity is inconsistent with the space group and a zero (0) indicates

Table 9. *The space groups of the orthorhombic crystal class 222 arranged by relative multiplicity Z'*

For the dash (-) and zero (0), see § 4.1. Relative multiplicity $Z' = 1/4$ implies molecular symmetry 222; $Z' = 1/2$ implies symmetry 2.

Space group	Relative multiplicity Z'							
	1/4	1/2	1	3/2	2	5/2	3	≥ 4
16 $P222$	0	0	1	0	0	0	0	0
17 $P222_1$	-	0	0	1	0	0	0	0
18 $P2_12_12$	-	69	114	2	13	0	0	0
19 $P2_12_12_1$	-	-	5410	-	329	-	16	10
20 $C222_1$	-	33	27	1	0	0	1	0
21 $C222$	0	0	0	0	1	0	0	0
22 $F222$	0	0	0	0	0	0	0	0
23 $I222$	1	0	3	0	0	0	0	0
24 $I2_12_12_1$	-	1	0	0	0	0	0	0

Table 10. *The space groups of the orthorhombic crystal class mm arranged by relative multiplicity Z'*

For the dash (-) and zero (0), see § 4.1.

Space group	Relative multiplicity Z'							
	1/4 mm	1/2 $2,m$	1	3/2	2	5/2	3	≥ 4
25 $Pmm2$	0	0	0	0	0	0	0	0
26 $Pmc2_1$	-	3	7	0	0	0	0	0
27 $Pcc2$	-	0	1	0	0	0	0	0
28 $Pma2$	-	0	0	0	0	0	0	0
29 $Pca2_1$	-	-	289	-	97	-	1	2
30 $Pnc2$	-	2	2	0	0	0	0	0
31 $Pmn2_1$	-	36	0	0	0	0	0	0
32 $Pba2$	-	9	3	0	2	0	0	0
33 $Pna2_1$	-	-	748	-	83	-	3	1
34 $Pnn2$	-	9	3	0	3	0	0	0
35 $Cmm2$	0	0	0	0	0	0	0	0
36 $Cmc2_1$	-	71	2	0	0	0	0	0
37 $Ccc2$	-	4	0	0	0	0	0	0
38 $C2mm$	2	3	0	0	0	0	0	0
39 $C2mb$	-	3	1	0	0	0	0	0
40 $C2cm$	-	6	0	2	0	0	0	0
41 $C2cb$	-	32	19	2	0	0	0	0
42 $Fmm2$	6	0	0	0	0	0	0	0
43 $Fdd2$	-	99	86	1	1	0	0	0
44 $Imm2$	1	0	0	0	0	0	0	0
45 $Iba2$	-	11	28	0	3	0	0	1
46 $Ima2$	-	3	0	0	0	0	0	0

Table 11. *The space groups of the orthorhombic crystal class mmm arranged by relative multiplicity Z'*

For the dash (-) and zero (0), see § 1.4. Space groups 47, 65, 69 and 71 have the possibility of $Z' = 1/8$; $Fmmm$ (69) has a single example.

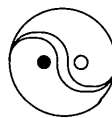| Space group	Relative multiplicity Z'							
	1/4	1/2	1	3/2	2	5/2	3	≥ 4
47 $Pmmm$	0	0	0	0	0	0	0	0
48 $Pnnn$	222 2	0	0	0	0	0	0	0
49 $Pccm$	0	0	0	0	0	0	0	0
50 $Pban$	222 2	0	0	0	0	0	0	0
51 $Pmma$	0	0	0	0	0	0	0	0
52 $Pnna$	-	$\bar{1},2$ 25	9	0	0	0	0	0
53 $Pmna$	$2/m$ 4	$2,m$ 1	0	0	0	0	0	0
54 $Pcca$	-	$\bar{1},2$ 10	8	0	0	0	0	0
55 $Pbam$	$2/m$ 1	$2,m$ 4	2	0	0	0	0	0
56 $Pccn$	-	$\bar{1},2$ 90	96	0	5	0	0	0
57 $Pbcm$	-	$\bar{1},2,m$ 44	4	0	0	0	0	0
58 $Pnnm$	$2/m$ 13	$\bar{1},m$ 5	0	0	0	0	0	0
59 $Pmmn$	mm 11	$\bar{1},m$ 1	0	0	0	0	0	0
60 $Pbcn$	-	$\bar{1},2$ 276	158	2	5	0	2	0
61 $Pbca$	-	$\bar{1}$ 268	1798	0	78	0	1	1
62 $Pnma$	-	$\bar{1},m$ 673	13	0	1	0	0	0
63 $Cmcm$	$2/m,mm$ 43	0	0	0	0	0	0	0
64 $Cmca$	$2/m$ 35	$\bar{1},2,m$ 18	0	0	0	0	0	0
65 $Cmmm$	0	0	0	0	0	0	0	0
66 $Cccm$	0	$2,m$ 2	0	0	0	0	0	0
67 $Cmma$	$222,2/m$ 1	0	0	0	0	0	0	0
68 $Ccca$	222 8	$\bar{1},2$ 2	1	0	0	0	0	0
69 $Fmmm$	0	0	0	0	0	0	0	0
70 $Fddd$	222 9	$\bar{1},2$ 6	2	0	0	0	0	0
71 $Immm$	0	0	0	0	0	0	0	0
72 $Ibam$	$222,2/m$ 17	$\bar{1},2,m$ 4	0	0	0	0	0	0
73 $Ibca$	-	$\bar{1},2$ 3	0	0	0	0	0	0
74 $Imma$	$2/m,mm$ 4	0	0	0	0	0	0	0

that the multiplicity is possible but that no examples were found. Space group $P1$ cannot have Z' fractional; it has 189 examples with $Z' = 1$ and over 200 with $Z' \geq 2$. The obvious suspicion is that there are printing or other errors and that the examples with $Z' = 2$ really belong to $P\bar{1}$. A check of the structures reported in *Acta Crystallographica* Sections B and C showed only two for which such an er-

ror would be plausible but a high proportion of the papers commented that the molecules were related by some kind of pseudosymmetry such as 2 or $\bar{1}$. A full study of such structures might be interesting, but it has not been undertaken. One possible explanation is that two fairly unsymmetrical objects can be combined into a less unsymmetrical structural dimer by these symmetry elements and thus facilitate packing. A simple example is the *yin/yang* circle:

Roughly equidimensional pseudodimers can be arranged more compactly than if the monomers all had the same orientation.

4.2. *The monoclinic system*

The relative multiplicities for the monoclinic system are given in Table 8. For most space groups, $Z' = 1$ is the commonest relative multiplicity. The exceptions are

Table 12. *Use of molecular symmetry in the tetragonal system*

Space groups for which no examples were found are omitted. The minimum symmetry implied by the multiplicity is indicated. For the dash (-) and zero (0), see § 4.1.

Space group	Relative multiplicity Z'								
	1/16 $4/mmm$	1/8 $4/m$	1/4 $4,\bar{4}$	1/2 2	1	5/4 3	3/2	2	4
75 $P4$	-	-	1	1	0	0	0	1	0
76,78 $P4_{1,3}$	-	-	-	-	89	-	-	7	1
77 $P4_2$	-	-	-	3	3	0	0	0	0
79 $I4$	-	-	2	0	7	0	0	0	0
80 $I4_1$	-	-	-	8	4	0	0	2	1
81 $P\bar{4}$	-	-	0	4	0	0	0	2	0
82 $I\bar{4}$	-	-	18	2	19	0	0	1	0
83 $P4/m$	-	1	0	0	0	0	0	0	0
84 $P4_2/m$	-	-	1	0	0	0	0	0	0
85 $P4/n$	-	-	4	1	2	0	0	0	0
86 $P4_2/n$	-	-	20	28	30	1	0	0	0
87 $I4/m$	-	12	0	1	0	0	0	0	0
88 $I4_1/a$	-	-	39	38	59	1	0	1	0
91,95 $P4_{1,3}22$	-	-	-	0	3	0	0	0	0
92,96 $P4_{1,3}2_12$	-	-	-	108	92	0	0	3	1
94 $P4_22_12$	-	-	2	2	2	0	0	0	0
98 $I4_122$	-	-	0	1	0	0	0	0	0
101 $P4_2cm$	-	-	-	1	0	0	0	0	0
102 $P4_2nm$	-	-	2	2	0	0	0	0	0
104 $P4nc$	-	-	3	-	0	0	0	0	0
106 $P4_2bc$	-	-	-	1	0	0	0	0	0
107 $I4mm$	-	2	-	-	0	0	0	0	0
109 $I4_1md$	-	-	1	2	0	0	0	0	0
110 $I4_1cd$	-	-	-	8	11	0	0	0	0
112 $P\bar{4}2c$	-	-	-	1	0	0	0	0	0
113 $P\bar{4}2_1m$	-	-	7	2	0	0	0	0	0
114 $P\bar{4}2_1c$	-	-	38	5	27	0	1	1	0
117 $P\bar{4}b2$	-	-	1	1	0	0	0	0	0
118 $P\bar{4}n2$	-	-	3	3	0	0	0	0	0
120 $I\bar{4}c2$	-	-	-	1	0	0	0	0	0
121 $I\bar{4}2m$	-	7	1	-	0	0	0	0	0
122 $I\bar{4}2d$	-	-	7	9	1	0	0	0	0
124 $P4/mcc$	-	-	1	1	0	0	0	0	0
126 $P4/nnc$	-	2	2	1	0	0	0	0	0
128 $P4/mnc$	-	-	-	1	0	0	0	0	0
130 $P4/ncc$	-	-	3	2	0	0	0	0	0
132 $P4_2/mcm$	-	1	-	-	0	0	0	0	0
133 $P4_2/nbc$	-	-	-	-	1	0	0	0	0
134 $P4_2/nnm$	-	1	-	-	0	0	0	0	0
135 $P4_2/mbc$	-	-	1	-	0	0	0	0	0
136 $P4_2/mnm$	-	6	-	-	0	0	0	0	0
137 $P4_2/nmc$	-	2	-	-	0	0	0	0	0
139 $I4/mmm$	1	-	-	-	0	0	0	0	0
141 $I4_1/amd$	-	6	1	-	0	0	0	0	0
142 $I4_1/acd$	-	-	11	6	2	0	0	0	0

the space groups with mirror planes (Pm, Cm, $P2/m$, $P2_1/m$, $C2/m$); for these either the mirror plane is used or the space group has few examples.

4.3. The orthorhombic system

The relative multiplicities for the orthorhombic space groups are given in Tables 9–11. The assumption that most structures have molecules in general positions is confirmed only for the fully antimorphic space groups,

Table 13. *Use of molecular symmetry in the trigonal system*

Space groups for which no examples were found are omitted. The minimum symmetry implied by the multiplicity is indicated. For the dash (-) and zero (0), see § 4.1.

Space group	Relative multiplicity Z'								
	1/12 $\bar{3}m$	1/6 $\bar{3},32,3m$	1/3 3	1/2 $\bar{1},2,m$	2/3 3	1	4/3	2	≥ 3
143 $P3$	-	-	0	-	1	9	0	0	0
144,145 $P3_{1,2}$	-	-	-	-	-	58	-	2	2
146 $R3$	-	-	28	-	3	15	0	7	0
147 $P\bar{3}$	-	0	20	3	0	6	0	0	0
148 $R\bar{3}$	-	37	41	18	2	53	0	1	2
151,153 $P3_{1,2}12$	-	-	-	0	-	1	-	0	0
152,154 $P3_{1,2}21$	-	-	-	32	-	17	-	1	0
156 $P3m1$	-	-	0	1	0	0	0	0	0
159 $P31c$	-	-	0	-	1	0	0	0	0
160 $R3m$	-	10	-	0	-	0	-	0	0
161 $R3c$	-	-	39	-	1	12	1	0	1
163 $P\bar{3}1c$	-	4	0	0	0	0	0	0	0
165 $P\bar{3}c1$	-	1	0	6	0	0	0	0	0
166 $R\bar{3}m$	2	2	-	0	-	0	-	0	0
167 $R\bar{3}c$	-	15	2	1	0	1	0	0	0

($P2_12_12_1$, $Pca2_1$, $Pna2_1$, $Pbca$), plus one tending to antimorphism ($P2_12_12$). For most other space groups, $Z' = 1/2$ or $1/4$ is more frequent; for $Pccn$, $Z' = 1$ is marginally more frequent than $Z' = 1/2$. The frequencies in the arithmetic crystal classs $mmmP$ have already been discussed (Wilson, 1991). Those given here are mostly slightly higher because of the growth of the database in the two years 1990–1992 but the overall picture is unchanged.

4.4. The tetragonal system

The relative multiplicities for the tetragonal space groups are given in Table 12. Molecular symmetries 2, 4 and $\bar{4}$ are frequently used.

4.5. The trigonal system

The relative multiplicities for the trigonal space groups are given in Table 13. The only special positions in the space group $P3$ (143) have symmetry 3. All nine structures with $Z' = 1$ turn out to have three molecules of symmetry 3 in three special positions and the single structure with $Z' = 2/3$ has two such molecules. The situation for $P\bar{3}$ (147) is more complex as it has special positions of symmetry $\bar{1}$, 3 and $\bar{3}$. That of symmetry 3 is the most frequent; the 20 examples with $Z' = 1/3$ all contain two molecules with this symmetry. Three examples with $Z' = 1/2$ have three molecules of symmetry $\bar{1}$.

4.6. The hexagonal system

The relative multiplicities for the hexagonal space groups are given in Table 14. The system is relatively rare; 3 and $\bar{3}$ are the molecular symmetries frequently used.

Table 14. *Use of molecular symmetry in the hexagonal system*

Space groups for which no examples were found are omitted. The minimum symmetry implied by the multiplicity is indicated. For the dash (-) and zero (0), see § 4.1.

Space group	Relative multiplicity Z'							
	1/12 $6̄2m,3̄m$	1/6 $6̄,3̄$	1/4 222	1/3 3	1/2 $1̄,2,m$	1	4/3	3/2
169,170 $P6_{1,5}$	-	-	-	-	-	46	-	-
171,172 $P6_{2,4}$	-	-	-	-	0	2	-	0
173 $P6_3$	-	-	-	16	-	3	1	-
174 $P6̄$	-	0	-	1	0	0	0	0
176 $P6_3/m$	1	21	-	0	6	0	0	0
178,179 $P6_{1,5}22$	-	-	-	-	6	2	-	0
180,181 $P6_{2,4}22$	-	-	1	-	0	0	-	0
182 $P6_322$	-	0	-	0	0	2	0	0
185 $P6_3cm$	-	1	-	0	0	0	0	0
186 $P6_3mc$	-	5	-	-	0	0	-	0
190 $P6̄2c$	-	1	-	0	1	0	-	0
192 $P6/mcc$	0	0	0	0	0	0	0	1
193 $P6_3/mcm$	1	0	0	0	0	0	0	0

Table 15. *Use of molecular symmetry in the cubic system*

Space groups for whch no examples were found are omitted. For the dash (-) and zero (0), see § 4.1. Implied minimum symmetries are indicated.

Space group	Relative multiplicity Z'						
	1/24 $4̄3m$	1/12 23	1/8 $mmm,42.2$	1/6 $3̄$	1/4 $4̄,222$	1/3 3	1/2 $1̄,2$
197 $I23$	1	0	-	-	0	-	0
198 $P2_13$	-	-	-	-	-	4	0
204 $Im3$	0	-	mmm 4	0	-	-	0
205 $Pa3$	-	-	-	11	-	10	-
206 $Ia3$	-	-	-	0	-	3	0
212,213 $P4_{1,3}32$	-	-	-	1	-	1	0
217 $I4̄3m$	4	0	0	0	0	-	0
218 $P4̄3n$	-	0	-	-	1	1	0
219 $F4̄3c$	-	3	-	-	0	0	0
220 $I4̄3d$	-	-	-	-	$4̄2$	5	-
222 $Pn3n$	0	-	422 3	2	0	0	0
224 $Pn3m$	1	0	0	0	0	-	0
227 $Fd3m$	3	0	-	0	0	-	0
230 $Ia3d$	-	-	-	0	0	0	2 1

4.7. *The cubic system*

The relative multiplicities for the cubic space groups are given in Table 15. Molecular symmetries 3 and $3̄$ are frequently used; the absence of any examples with $Z' = 1$ is notable.

5. Status of the statistical model

In previous papers, 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 (Wilson, 1992a), the number of examples, N_{sg}, of a space-group type depended exponentially on the numbers of symmetry elements within the unit cell, thus:

$$N_{sg} = A \exp\left\{ -\sum_j B_j[e_j]_{sg} \right\}.$$ (3)

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. The program *GLIM* (Baker & Nelder, 1978) was used to evaluate the parameters. 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 the antitropic symmetry elements (glide

planes and screw axes). Often, however, laws of 'conservation of symmetry elements', of the type

$$[2] + [2_1] = c,$$ (4)

or, in general,

$$\sum_j [e_j] = c,$$ (5)

where c is a constant for the crystal class, eliminate a separate dependence on one or more of the e_j's (Wilson, 1990, §§ 1.1, 5.1).

The model fitted the observed frequencies of the space groups 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 (abbreviated from Wilson, 1988, § 4.2):

'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 ... .'

This procedure was perhaps reasonable in a first 'exploratory' survey but the use of inherent symmetry has been found to be very frequent in some space groups, as discussed in § 4 above. It is therefore necessary to ask if the statistical model is still useful if applied to the frequencies of space groups with $Z' = 1$ - the situation

Table 16. *Observed and calculated frequencies of structures with $Z' = 1$ in the geometric class mm*

The values of the parameters of the fit are also given, along with those found for structures unsorted by Z (Table 4 of Wilson, 1990).

Arithmetic crystal class	Space group	Frequency observed	Frequency calculated	E.s.d.
mm2P	25 Pmm2	0	0	1
	26 Pmc2₁	7	0	2
	27 Pcc2	1	1	1
	28 Pma2	0	0	1
	29 Pca2₁	289	289	15
	30 Pnc2	2	1	2
	31 Pmn2₁	0	0	1
	32 Pba2	3	3	2
	33 Pna2₁	748	748	17
	34 Pnn2	3	3	2
mm2C	35 Cmm2	0	0	1
	36 Cmc2₁	2	2	2
	37 Ccc2	0	0	1
2mmC	38 C2mm	0	0	1
	39 C2mb	1	0	1
	40 C2cm	0	0	1
	41 C2cb	19	19	4
mm2F	42 Fmm2	0	1	1
	43 Fdd2	86	86	9
mm2I	44 Imm2	0	0	1
	45 Iba2	28	28	5
	46 Ima2	0	0	1

Parameter	Value	E.s.d.	Value (1990)	E.s.d.
Free diad	−4.54	0.47	−3.32	0.52
Encumbered diad	−5.50	0.85	−4.99	0.44
Free screw diad	0.95	0.06	0.77	0.06
Mirror plane	−8.13	2.29	−3.15	0.20
mm2P	Set to zero			
mm2C	−1.03	1.36	0.06	0.15
2mmC	0.03	0.48	0.43	0.26
mm2F	0.58	0.25	0.55	0.14
mm2I	0.41	0.46	0.22	0.28
Scaled deviance	11.8	5.1	24.1	5.1
R_2	0.009	–	0.40	–
Degrees of freedom	13	–	13	–

postulated when the model was first developed. In this context, 'useful' means (1) that the model fits the data within the limits to be expected from sampling fluctuations and (2) that the parameters of the fit are not small in comparison with their program-estimated standard deviations. Condition (1) is fulfilled throughout the monoclinic and orthorhombic crystal systems. As already noted for the arithmetic class $mmmP$ (Wilson, 1991), condition (1) is better fulfilled for the examples with $Z' = 1$ than for examples not sorted by Z'; R_2 falls to trivial values (0.000 for the monoclinic cohort, 0.001 for 222, 0.009 for mm and 0.003 for mmm). The discrepancy between the observed and calculated frequencies rarely exceeds two units. In view of the small observed frequencies, it has not been thought worth while to attempt fits for the more symmetric crystal systems. Even for the less-symmetric systems, it would be tedious to reproduce tables equivalent to Tables 1, 3, 4 and 5 of Wilson (1990) but as an example the equivalent of Table 4 (geometric class mm)

is given in Table 16; the parameters from the earlier paper are included for comparison. Table 16 exhibits some features worth discussing.

1. The parameter corresponding to $[m]$ has more than doubled and it has become less well defined.

2. The parameters corresponding to the three types of diad are of the same order of magnitude as they were for the unsorted cohort.

3. With the possible exception of $mm2F$, the parameters corresponding to the arithmetic crystal classes are not significantly different from zero.

4. Except for $Pmc2_1$, the observed and calculated frequencies agree within one unit.

The large negative value of the parameter corresponding to $[m]$ is practically equivalent to the Китайгородский (1955) criterion that structures involving stacking of layers by mirror planes are 'impossible'. The more moderate negative value of the parameters corresponding to [2] is equivalent to his criterion that stacking of layers related by diad axes is 'permissible' (possible but rare) but, in addition, they give numerical estimates of the inhibiting effect. Though the parameters corresponding to the arithmetic crystal classes are not large, equating them to zero markedly worsens the agreement; the largest discrepancy rises to 16, though R_2 and the scaled deviance still have tolerable values (0.025; 22.9 with 17 degrees of freedom).

The large discrepancy (seven units) for $Pmc2_1$ is readily explained by the consideration following equation (2). One reference was not readily accessible but the six consulted all showed two independent molecules using mirror symmetry. Though not directly relevant, the consultation of the original papers showed that a remarkably high proportion of the structures in this space group with $Z' = 0.5$ and $Z' = 1$ formed chains or polymers parallel to the 2_1 axis.

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The Classification of Face-Transitive Periodic Three-Dimensional Tilings

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Abstract

It has long been known that there exists an infinite number of types of *tile*-transitive periodic three-dimensional tilings. Here, it is shown that, by contrast, the number of types of *face*-transitive periodic three-dimensional tilings is finite. The method of Delaney symbols and the properties of the 219 isomorphism classes of crystallographic space groups are used to find exactly 88 *equivariant* types that fall into seven topological families.

0. Introduction

Consider the three-dimensional Euclidean space $\mathbb{E}^3$. A point-set $P \subseteq \mathbb{E}^3$, together with a finite family $F(P)$ of *faces* $f \subset P$, is called a *topological polyhedron* if it satisfies the following conditions:

(*P*1) the set P is homeomorphic to the unit ball $B_3 := \{x \in \mathbb{R}^3 \mid |x| \leq 1\}$;

(*P*2) the union of faces covers the boundary of P, *i.e.* $\bigcup_{f \in F(P)} f = \partial P$;

(*P*3) each face $f \in F(P)$ is homeomorphic to the disc $D := \{x \in \mathbb{R}^2 \mid |x| \leq 1\}$;

(*P*4) the intersection of any number of distinct faces is either empty, a point (called a *vertex*) or an arc (called an *edge*), that is, homeomorphic to the interval $I := \{x \in \mathbb{R} \mid |x| \leq 1\}$;

(*P*5) each face contains at least three vertices.

Note that it follows from these conditions that – dually to (*P*5) – each vertex is contained in at least three edges.

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A system $\mathscr{T} = \{P_1, P_2, P_3, \ldots\}$ of topological polyhedra (called *tiles*) is called a (face-to-face) *tiling* of $\mathbb{E}^3$, or *three-dimensional tiling*, if it satisfies the following conditions:

(*T*1) the tiling covers space, *i.e.* $\bigcup_{P \in \mathscr{T}} P = \mathbb{E}^3$;

(*T*2) the intersection of any two distinct tiles P and P' is either empty, a common vertex, a common edge or a common face. The tiles, faces, edges and vertices associated with $\mathscr{T}$ are called the *constituents* of $\mathscr{T}$ (of dimension 3, 2, 1 and 0, respectively).

A three-dimensional tiling $\mathscr{T}$ is called *periodic* if there exists a discrete group Γ of isometries of $\mathbb{E}^3$, containing three linearly independent translations, *i.e.* a *crystallographic space group*, such that $\mathscr{T} = \gamma \cdot \mathscr{T} := \{\gamma P \mid P \in \mathscr{T}\}$ for all $\gamma \in \Gamma$ (with $\gamma P := \{\gamma p \mid p \in P\}$, of course) and $F(\gamma P) = \gamma F(P)$ for all $P \in \mathscr{T}$ and $\gamma \in \Gamma$. In this case, the pair $(\mathscr{T}, \Gamma)$ is an *equivariant tiling* as defined by Dress (1984, 1987).

More specifically, if – as above – $\mathscr{T}$ is a three-dimensional tiling and if Γ is a crystallographic group, then we call the pair $(\mathscr{T}, \Gamma)$ an *equivariant three-dimensional tiling*.‡ Two equivariant three-dimensional tilings $(\mathscr{T}, \Gamma)$ and $(\mathscr{T}', \Gamma')$ are called *topologically equivalent* (or are described as being in the same *topological family*) if there exists a homeomorphism $\varphi: \mathbb{E}^3 \to \mathbb{E}^3$ that maps the tiles of one tiling onto the tiles of the other, *i.e.* if $\varphi \mathscr{T} = \mathscr{T}'$. If, additionally, $\Gamma' = \varphi \Gamma \varphi^{-1}$ holds, then the two are called *equivariantly equivalent*.

‡ Even more specifically, such a pair should be called an equivariant *Euclidean* three-dimensional tiling, where the term Euclidean indicates that the group Γ is supposed to consist of isometries with respect to the Euclidean metric of $\mathbb{E}^3$ (as opposed to arbitrary groups of homeomorphisms of $\mathbb{E}^3$).