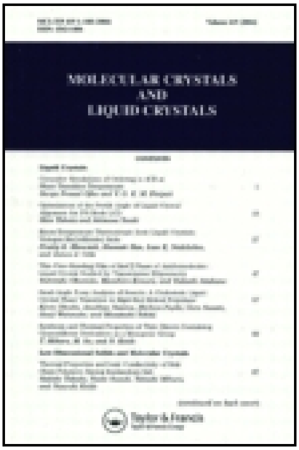

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On the Prevalence of polar and Chiral Space Groups

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ON THE PREVALENCE OF POLAR AND CHIRAL SPACE GROUPS

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Abstract Previous compilations of space-group frequencies have largely ignored differences in the number of molecules or formula units in the asymmetric unit, *i.e.*, differences in $Z' = Z/N$, where N is the number of general positions in the space group. This study demonstrates the importance of the variable Z'. Crystals with space groups that include mirror planes nearly always contain mirror-symmetric molecules located at these special positions; likewise, crystals with space groups that include threefold rotation axes usually contain molecules with threefold symmetry. The relative occurrence of polar and chiral space groups is discussed.

INTRODUCTION

A commonly stated aim of the several available compilations of space-group frequencies[1-12] is to provide a basis for a better understanding of molecular packing in crystals, *i.e.*, of the general principles of molecular aggregation. It has been found that neighboring molecules in crystals tend to be related by screw axes, glide planes, inversion centers, and translations rather than by pure rotation axes or mirror planes. There are obvious reasons why these "pure" symmetry elements lead to unfavorable packing arrangements, but nevertheless, a number of common space groups (*e.g.*, C2/c and Pnma) do include them. One flaw in previous compilations is the failure to take full account of the ratio (hereafter, Z') between the number of molecules or formula units in the unit cell (Z) and the number of general positions (*i.e.*, the order of the symmetry group). In other words, does the asymmetric unit of the crystal structure consist of one molecule, a fraction of a molecule, or more than one molecule? Kitaigorodskii[4] recognized the importance of Z'; he made predictions about the retention in the crystal of molecular symmetry elements and about the space groups most probable for symmetric molecules. Padmaja, Ramakumar & Viswamitra[10] compared space-group frequencies for structures with Z' = 1 and Z' > 1. Scaringe[13] provided a brief table comparing frequencies for Z' = 1 and Z' < 1 for the most common space groups. Wilson[11,12] has considered the importance of Z' to his mathematical models of the distribution of space groups for organic crystals. In this paper we report a preliminary, but more extensive, study of the importance of the variable Z'.

METHODOLOGY

Searches of the July 1991 version of the Cambridge Structural Database[14] (hereafter, the CSD) included the following acceptance criteria: RFAC 0.010-0.070; COOR ≥ 2 (coordinates present for at least two atoms); SIGF ≤ 2 (average standard deviation for a C-C bond ≤ 0.010 Å); ZVAL ≥ 0. These criteria, which are somewhat more stringent than those in previous compilations, are intended to eliminate structures for which the space group may be in doubt. Of the 33586 entries (37% of the file) that satisfy these criteria, 99% were published after 1969 and 82% after 1979. Duplicate REFCODEs were discarded because they usually refer to the same structure; one statistically insignificant consequence of this step is that polymorphs with the same space group and the same REFCODE may have been counted incorrectly. Calculations of Z' values for triclinic, monoclinic, and rhombohedral groups allowed for possible variation in the number of lattice points per unit cell (*e.g.*, for space group #2: $P\bar{1}$, Z'=Z; $C\bar{1}$, Z'=Z/2; and $F\bar{1}$, Z'=Z/4).

RESULTS AND DISCUSSION

Table I shows Z' statistics for selected space groups that have special positions [$\bar{1}$ and 2 in Table I(a); 3, $\bar{3}$, and $\bar{1}$ in Table I(b); and m, $\bar{1}$, and m × $\bar{1}$ = 2 in Table I(c)]. While the majority of the space groups in Table I(a) show a preponderance of Z' = 1, P2/c, C2/c, Fdd2, Pccn, and Pbcn do not fit the pattern. Retention of molecular $\bar{1}$ or 2 symmetry in crystals is fairly common.* The space groups in Table I(b) and I(c), however, show an *overwhelming* preference for Z' < 1. Retention of molecular symmetries 3 and m is the rule rather than the exception. Moreover, Z' = 1 is no

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*Preliminary results from a collaborative study with F.H. Allen and D. G. Watson of the Cambridge Crystallographic Data Centre and J. A. K. Howard and J. C. Cole of Durham University show that the positions with symmetry 2 are much more likely to be occupied than are the positions with symmetry $\bar{1}$.

guarantee that the molecules occupy a set of general positions: most of the $Z' = 1$ structures in Table I(c) contain two independent sets of mirror-symmetric molecules.*

Table II shows Z' statistics for the space groups that have no special positions. Several of these groups show a high incidence of structures with $Z' = 2$ or more. For technical reasons, structures with $Z' > 1$ are often difficult to solve and refine, so their true incidence is almost certainly higher than is reported here. Especially noteworthy is the large proportion of $Z' = 2$ structures in group P1.¶

The space-group classification is not necessarily enlightening as far as discerning similarities and differences in packing of a series of related molecules. Consider the aromatic hydrocarbons. Although naphthalene, anthracene, tetracene and pentacene all have essentially the same herringbone packing, the first two compounds crystallize in space group $P2_1/c$ with $Z' = 1/2$ and the latter two in $P\bar{1}$ with $Z' = 1 = 2*(1/2)$. While a number of larger planar aromatic hydrocarbons also crystallize in $P2_1/c$ with $Z' = 1/2$, their structures are characterized by molecular stacking along a short translation direction rather than by herringbone packing.[17]

There is also the problem of choosing an appropriate "molecule" in a complex structural unit. Is a hydrogen-bonded carboxylic acid dimer to be regarded as one molecule or as two? How should we classify the sodium hydrogen bis(acetate) structure, $NaH(CH_3COO)_2$, space group $Ia\bar{3}$, $Z = 24$? The 48 acetates are in general positions, and the 24 sodiums are distributed over two sets of special positions, one sixfold ($\bar{3}$), the other threefold (3).[18] Compare this compound with basic beryllium acetate, $Be_4O(CH_3COO)_6$, space group $Fd\bar{3}$, $Z = 8$.[19,20] In this molecular complex six acetates span the edges of a tetrahedron of berylliums with an oxygen at the center. The 48 acetates sit on dyad axes, *i.e.*, only the 96 carboxylate oxygens are in general positions. Chemical tradition would tend to treat the acetate ions as the structural units

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*Molecules with apparent crystallographic mirror symmetry often show large displacement parameters in the direction perpendicular to the mirror plane; these parameters may indicate disorder or twinning of a lower symmetry structure. Unfortunately, since displacement parameters are still not included in the CSD, it is not possible to detect such behavior without recourse to the original literature.

¶There seems to be a persistent notion that crystals with $Z'>1$ are disfavored entropically. As Pauling and Tolman pointed out in 1925[15] and as we reiterated for the specific case of spontaneous resolution,[16] the entropy of all *ordered* crystals is zero at 0 K — as it must be according to the third law of thermodynamics. As far as we are aware, there is no evidence that the vibrational entropy of a crystal with $Z'>1$ is necessarily greater than that of a crystal with $Z' \leq 1$.

in the first case (Z' = 1) and the tetrahedral complex as the structural unit in the second (Z' = 1/12). Problems of this kind abound; we simply adopted the Z values given in the CSD.

POLAR AND CHIRAL SPACE GROUPS

The overall frequency of polar* and chiral space groups is low because the two most common space groups ($P2_1/c$ and $P\bar{1}$), which together account for 60% of all known molecular crystals, are both centrosymmetric. About half of all chiral structures occur in the space group $P2_12_12_1$, the third most common one, which accounts for about 11% of the total.

Molecules containing improper symmetry elements (inversion centers, mirror planes, rotation-inversion axes) often occupy the corresponding special positions in their crystal structures. There is no doubt that if these molecules were removed from space-group compilations, the resulting increase in the proportion of crystal structures in chiral and polar space groups would be considerable. This should encourage scientists seeking to synthesize non-linear optical materials (for which a noncentrosymmetric space group is required) or to resolve racemic products by crystallization.

As Table III shows, the relative frequency of polar or chiral space groups increases in higher crystal systems. Crystallization in trigonal, hexagonal, and cubic systems seems to be favored by the presence of a molecular threefold rotation axis; of the 509 structures in these systems at least 316 (62%) contain molecules on sites that include a threefold rotation axis (symmetry 3, $\bar{3}$, $\bar{6}$, *etc.*). Indeed, of the 125 structures with Z' = 1/3 or 2/3 (molecular symmetry 3) determined for racemic or achiral starting material, 48% are noncentrosymmetric and 24% are chiral. These fractions are substantially higher than the corresponding fractions for the whole file, and would be relatively even higher if the overall values could be corrected for resolution of the starting material prior to crystallization.

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*The term polar is used here to designate space groups that are noncentrosymmetric. These groups have at least one polar direction.

TABLE I Frequency of occurrence *vs*. Z' for some space groups with special positions (Z = Z' * Mult).

(a) Space groups with inversion centers and/or two-fold rotation axes

Num	Space Group	Mult	Z' = 1/2	**Z' = 1**	Z' = 3/2	Z' = 2	Z' > 2
2	P$\bar{1}$	2	1295 ($\bar{1}$)	**4460**	19	566	32
5	C2	4	50 (2)	**163**	0	22	0
13	P2/c	4	74 (2 or $\bar{1}$)	**49**	2	8	0
14	P2_1/c	4	1897 ($\bar{1}$)	**9702**	15	560	27
15	C2/c	8	1270 (2 or $\bar{1}$)	**1023**	16	32	10
18	P$2_12_1$2	4	41 (2)	**67**	0	5	0
20	C222_1	8	12 (2)	**15**	0	0	0
43	Fdd2	16	56 (2)	**48**	0	0	0
56	Pccn	8	49 (2 or $\bar{1}$)	**41**	1	1	0
60	Pbcn	8	192 (2 or $\bar{1}$)	**101**	2	1	0
61	Pbca	8	187 ($\bar{1}$)	**1143**	0	37	1

(b) Space groups with three-fold rotation axes

Num	Space Group	Mult	Z' = 1/6	Z' = 1/3	Z' = 2/3	**Z' = 1**	Z' > 1
146	R3	3*		13 (3)	4	**6**	5
148	$R\bar{3}$	6*	57 $(\bar{3})$	38 (3)	0	**38¶**	1
161	R3c	6*		23 (3)	2	**3**	1
198	$P2_13$	12		12 (3)	0	**0**	0
205	$Pa\bar{3}$	24		8 $(\bar{3})$	5 (3)	**1**	0

*The multiplicity is given for the rhombohedral (rather than the hexagonal) cell.
¶There are also 8 structures with Z' = 1/2 (symmetry $\bar{1}$).

(c) Space groups with mirror planes

Num	Space Group	Mult	Z' = 1/4	Z' = 1/2	**Z' = 1**	Z' = 3/2	Z' = 2	Z' > 2
11	$P2_1/m$	4		180 (m or $\bar{1}$)	**10***	1	0	0
12	C2/m	8	102 (2/m)	38 (m, 2, or $\bar{1}$)	**1¶**	0	0	0
26	$Pmc2_1$	4		0 (m)	**5¶**	0	0	0
36	$Cmc2_1$	8		37 (m)	**2¶**	0	0	0
62	Pnma	8		450 (m or $\bar{1}$)	**12***	1	0	1

*The majority of these structures contain two independent, mirror-symmetric molecules.
¶All of these structures contain two independent, mirror-symmetric molecules.

Table I(c), con't.

63	Cmcm	16	25 (mm2 or 2/m)	0	**0**	0	0	0
64	Cmca	16	27 (2/m)	17 (m, 2 or $\bar{1}$)	**0**	0	0	0

TABLE II Frequency of occurrence *vs.* Z' for space groups without special positions (Z = Z' * Mult).

Num	Group	Mult	**Z' = 1**	Z' = 2	Z' = 3	Z' = 4	Z' > 4
1	P1	1	**120**	93	2	4	1
4	$P2_1$	2	**1556**	256	9	7	0
7	Pc	2	**61**	17	1	1	1
9	Cc	4	**192**	19	2	3	0
19	$P2_12_12_1$	4	**3215**	139	7	5	0
29	$Pca2_1$	4	**148**	40	1	1	0
33	$Pna2_1$	4	**337**	23	4	1	0
76 78	$P4_1$ * $P4_3$	4	**57**	3	0	0	0
144 145	$P3_1$ * $P3_2$	3	**37**	0	0	0	0
169 170	$P6_1$ * $P6_5$	6	**15**	0	0	0	0

*Enantiomorphic space groups (*e.g.*, $P3_1$and $P3_2$)[21-23] have been grouped.[24]

TABLE III Noncentrosymmetric and Chiral Space Groups

System	% of total entries in CSD	% of structures in this system in noncentrosymmetric groups	% of structures in this system in chiral groups
triclinic	21	3	3
monoclinic	55	14	12
orthorhombic	21	64	52
tetragonal	2	55	36
trigonal	1	42	32
hexagonal	<1	52	44
cubic	<1	49	31
all	(100)	23	19

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