Acta Cryst. (1999). A**55**, 621–627

Molecular packing groups and *ab initio* crystal-structure prediction

Daquan Gao and Donald E. Williams*

Department of Chemistry, University of Louisville, Louisville, KY 40292, USA.
E-mail: dew01@xray5.chem.louisville.edu

(*Received 9 July 1998; accepted 30 November 1998*)

Abstract

Ab initio crystal structure prediction can proceed by minimization of the packing energy of Z independent molecules per cell, or alternatively by energy minimization taking one molecule as independent and $Z-1$ molecules as related by assumed space-group symmetry. In the former method, a large number of positional variables must be considered. In the latter method, a large number of space groups must be considered. An alternative, more efficient, procedure is proposed, where it is recognized that values of Z and the number of molecules in the asymmetric unit, Z', impose restrictions on possible space groups. Examples of application of this method to crystal structure prediction are given.

1. Introduction

Prediction of crystal structures favored by a molecule of known molecular structure may be termed *ab initio* if the starting model for energy minimization is a structure with arbitrary initial lattice constants, molecular orientations and positions without reference to any experimental crystal structure information. The initial array of molecules is normally taken as being less dense than the crystal and, since it consists of arbitrarily positioned molecules, may be compared to a dense gas with lattice properties. A crystal structure prediction program is expected to pack the separated molecules together to reproduce accurately the experimental unit cell, molecular orientations and positions. This process is controlled by the intermolecular force field, which operates between atoms (or sites) of the separate molecules. Energy surfaces defined by intermolecular force fields are known to have many subsidiary minima, in addition to the global minimum sought by energy minimization.

The most general way to construct the starting model is to place Z molecules in random orientations and separated positions in a large cell; we call this the $P1$ packing method, since the cell has no imposed symmetry. The number of molecules in the asymmetric unit, Z', is initially set equal to Z. Since there is no restriction on the value of Z, separate energy minimization runs must be made for each assumed value of Z. Analysis of 31 770 observed crystal structures showed an average Z of 3.85 (Brock & Dunitz, 1994); even cubic groups, with up to 192 general positions, have an average Z of only 6.7. Thus small values of Z, say $Z \leq 8$, account for the great majority of observed crystal structures. The $P1$ method can predict higher cell symmetry, as has been shown for the $P2_1/c$ and $Pbca$ crystal structures of benzene, and the $P\bar{4}2_1m$ structure of urea (Williams, 1996*a*). The $P1$ method also automatically includes the possibility that $Z' > 1$, *i.e.* more than one molecule in the asymmetric unit. Often the $P1$ method fails to predict the correct global energy minimum or symmetry, probably because of the large number of independent variables required.

Alternatively, space-group symmetry may be assumed at the beginning, which we call the space-group-constrained method. For a space group of order N, Z is taken as equal to N and only the position of one molecule is variable; in addition, the space group may impose constraints on the unit-cell constants. The space-group-symmetry method can in principle consider $Z > N$, but that is not normally included since it greatly complicates the calculation. The method automatically considers the case of $Z < N$, where $Z' < 1$ and the asymmetric unit is a fraction of a molecule. In this case, the molecule resides on a special position of a supergroup which has the assumed space group as a subgroup.

The large number of possible space groups creates difficulties for this method. A widely used approach is to perform calculations in popular space groups only. Mighell *et al.* (1983) report that 90% of organic crystals occur in only 17 space groups. Of course, if a particular molecule crystallizes in an unpopular space group, the method would fail; the urea example cited above illustrates this, since $P\bar{4}2_1m$ is not a popular space group.

In this paper, we report an improved approach to *ab initio* crystal structure prediction, which extends the symmetry-constrained method to consider all possible molecular packing groups with given Z. This method takes advantage of the structure of the space groups. We call this the molecular packing-group method.

2. Molecular packing-group method

Molecular packing in crystals may be subdivided into three types: one molecule in the asymmetric unit

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ISSN 0108-7673 © 1999

Table 1. *Number of space groups of a particular order N*

N	Number of groups	N	Number of groups
1	1	16	41
2	5	18	4
3	3	24	15
4	26	32	6
6	18	36	2
8	63	48	11
9	1	96	8
12	22	192	4

($Z' = 1$, the most straightforward case), a fraction of a molecule in the asymmetric unit ($Z' < 1$, in which case the molecule has site symmetry), or several molecules in the asymmetric unit ($Z' > 1$). Only a small fraction of crystal structures have $Z' > 1$ (Brock & Dunitz, 1994). In the molecular packing-group method, we consider only $Z' \leq 1$, which is suitable for the great majority of molecules.

Wilson (1993) points out that the molecular packing group contains only symmetry operations applied to the entire molecule; the molecular packing group is either identical with the space group or is a subgroup of it. By this definition, and by the assumption that $Z' \leq 1$, we point out that the possible packing groups for a certain Z value are limited to those with $N = Z$. For example, when $Z = 1$, there is only one such packing group, $P1$. When $Z = 2$, there are five such packing groups, $P\bar{1}$, $P2$, $P2_1$, Pc and Pm. Consider a $Z = 2$ structure in space group $P2_1/c$ with molecules placed at site symmetry $\bar{1}$. If the $\bar{1}$ operation is deleted from $P2_1/c$, one obtains molecular packing groups $P2_1$ or Pc. The number of packing groups for each possible value of N is given in Table 1.

3. Molecular packing groups for $Z = 2$

The packing-group method is introduced here for the computational problem of *ab initio* molecular packing analysis. Consider the $Z = 2$ case. If the molecules do not have any point symmetry, or the molecules do not occupy any special positions even if they have symmetry, then the five space groups with $N = 2$ are the only possible molecular packing groups. Otherwise, if the molecules have some symmetry and the symmetry is expressed on some special site as listed in *International Tables for Crystallography* (Hahn, 1992), then the true space group can be obtained by examining the atomic coordinates of the asymmetric unit. The true space group is a supergroup and is simply the product of the site-symmetry operations and the molecular packing-group operations. Using information from *International Tables for Crystallography*, it is possible to prepare convenient tables of molecular site symmetry, molecular packing group and the true space group. However, these tables can be quite lengthy, so only an example is given herein (see Appendix *A*) for $Z = 2$. For molecular packing groups with $Z > 2$, it is probably best to treat the specific symmetry situation of interest.

Table 2. *Molecular packing of urea, Z = 2, in all possible molecular packing groups*

Space group	Degrees of freedom	Minimum energy (kJ mol^{-1})
$P\bar{1}$	12	−95.7
$P2$	10	−75.1
$P2_1$	10	−103.6
Pm	10	−77.6
Pc	10	−95.2

According to the above considerations, a $Z = 2$ crystal structure may be predicted *ab initio* by searching for minimum-energy structures in only five possible molecular packing groups, starting from random trial models. Enough models must be tried in order to locate the global energy minimum in each packing group. After the minimization, the packing group that has the lowest energy is the predicted packing group. The true space group is either the molecular packing group or a supergroup of it.

4. Application to the urea crystal

To illustrate the usefulness of the method, consider the case of the urea crystal, where $Z = 2$, the symmetry of the isolated molecule is $2mm$, and the observed space group is $P\bar{4}2_1m$. Previously, a prediction of the crystal structure of urea, including prediction of the correct space group, was successful using the $P1$ method (Williams, 1996*a*). In that calculation, $Z = 2$ and $Z' = 2$ (two identical molecules in the asymmetric unit) and there were 15 degrees of freedom: six cell constants, six molecular rotations and three molecular translations. The translational position of one molecule fixed the origin.

Since only five molecular packing groups for $Z = 2$ are possible, an alternative approach to predict the crystal structure of urea would be to find minimum-energy structures in each of the space groups $P\bar{1}$, $P2$, $P2_1$, Pm and Pc. The correct structure would be the one in the molecular packing group that shows the lowest energy. This assumes, of course, that the intermolecular force field is sufficiently accurate and that enough random trials are made to find the global minimum energy in each molecular packing group. Since in molecular packing groups there is only one molecule in the asymmetric unit, the calculations are fast. In fact, the exploration of all five molecular packing groups for $Z = 2$ and $Z' = 1$ takes about an order of magnitude less computer time than exploration of $P1$ with $Z' = 2$. Calculations were carried out with the computer program *MPA* (Williams, 1996*b*) using the Biosym (1989) force field with net atomic charges obtained with the computer program *PDM*97 (Williams, 1997).

Table 3. *Ab initio crystal-structure prediction using molecular packing groups*

Name		*n*-Hexane					
Formula		C_6H_{14}					
Crystal structure		Norman & Mathisen (1961)					
Intermolecular force field		Williams & Houpt (1986)					
Molecular packing group		*P*1					
Space group		$P\bar{1}$					
Cell constants and lattice energy							
	a (Å)	*b* (Å)	*c* (Å)	*α* (°)	*β* (°)	*γ* (°)	*E* (kJ mol^{-1})
Observed	4.17	4.70	8.57	96.0	87.2	105.0	−52.53
Relaxed	4.21	4.54	8.69	96.7	88.3	103.4	−53.26
Predicted	4.21	4.54	8.69	83.3	88.3	76.6	−53.26
Name		*n*-Octane					
Formula		C_8H_{18}					
Crystal structure		Mathisen *et al.* (1967)					
Intermolecular force field		Williams & Houpt (1986)					
Molecular packing group		*P*1					
Space group		$P\bar{1}$					
Cell constants and lattice energy							
	a (Å)	*b* (Å)	*c* (Å)	*α* (°)	*β* (°)	*γ* (°)	*E* (kJ mol^{-1})
Observed	4.22	4.79	11.02	94.7	84.3	105.8	−69.70
Relaxed	4.18	4.53	11.08	94.6	84.4	103.5	−72.06
Predicted	4.18	4.53	11.08	85.4	84.4	76.5	−72.06
Name		3,6-Bis(diazo)cyclohexanetetraone					
Formula		$C_6N_4O_4$					
Crystal structure		Ansell (1969)					
Intermolecular force field		Williams & Houpt (1986)					
Molecular packing group		$P2_1$ indicated out of five possible groups					
Space group		$P2_1/c$					
Cell constants and lattice energy							
	a (Å)	*b* (Å)	*c* (Å)	*α* (°)	*β* (°)	*γ* (°)	*E* (kJ mol^{-1})
Observed	8.439	7.093	6.553	90	111.7	90	−138.8
Relaxed	8.14	7.36	6.21	90	111.7	90	−142.17
Predicted	8.14	7.36	6.21	90	111.7	90	−142.17
Name		Adamantane					
Formula		$C_{10}H_{16}$					
Crystal structure		Amoureux & Foulon (1987)					
Intermolecular force field		See note†					
Packing group		$P2_1$ indicated out of five possible groups					
Space group		$P\bar{4}2_1/c$					
Cell constants and lattice energy							
	a (Å)	*b* (Å)	*c* (Å)	*α* (°)	*β* (°)	*γ* (°)	*E* (kJ mol^{-1})
Observed	6.639	6.639	8.918	90	90	90	−70.84
Relaxed	6.64	6.64	8.85	90	90	90	−70.94
Predicted	6.64	6.64	8.83	90	90	90	−70.82
Name		Iceane					
Formula		$C_{12}H_{18}$					
Crystal structure		Hamon *et al.* (1977)					
Intermolecular force field		See note†					
Packing group		$P2_1$ indicated out of five possible groups					
Space group		$P6_3/m$					
Cell constants and lattice energy							
	a (Å)	*b* (Å)	*c* (Å)	*α* (°)	*β* (°)	*γ* (°)	*E* (kJ mol^{-1})
Observed	6.582	6.582	11.843	90	90	120	−82.44
Relaxed	6.57	6.57	11.6105	90	90	120	−83.07
Predicted	6.58	6.58	11.5575	90	90	120	−83.78

Table 2 shows global minimum energies found for urea in these five space groups, using 20 random starting models in each. As can be seen from the calculated intermolecular energies, the predicted molecular packing group for urea, $Z = 2$, is $P2_1$. Analysis of unit-cell dimensions and fractional atomic coordinates led to identification of the space group, $P\bar{4}2_1m$. In this space group, the molecule is located on symmetry site *mm*2.

Table 3 (*cont.*)

Name		Pentaspiro[2.0.0.2.0.2.0.0.2.0]tridecane					
Formula:		$C_{13}H_{16}$					
Crystal structure		Zefirov *et al.* (1992)					
Intermolecular force field		See note†					
Packing group		$Pca2_1$ indicated out of 26 possible groups					
Space group		*Pbcn*					
Cell constants and lattice energy							
	a (Å)	*b* (Å)	*c* (Å)	α (°)	β (°)	γ (°)	*E* (kJ mol^{-1})
Observed	9.466	7.601	14.44	90	90	90	−76.33
Relaxed	9.45	7.62	14.72	90	90	90	−77.25
Predicted	7.65	9.46	14.69	90	90	90	−77.42
Name		*n*-Pentane					
Formula		C_5H_{12}					
Crystal structure		Mathisen *et al.* (1967)					
Intermolecular force field		See note†					
Packing group		$Pca2_1$ indicated out of 26 possible groups					
Space group:		*Pbcn*					
Cell constants and lattice energy							
	a (Å)	*b* (Å)	*c* (Å)	α (°)	β (°)	γ (°)	*E* (kJ mol^{-1})
Observed	4.10	9.04	14.70	90	90	90	−42.94
Relaxed	4.19	8.93	14.93	90	90	90	−43.57
Predicted	4.19	8.93	14.93	90	90	90	−43.57

† Unpublished intermolecular force field using methylene bisector charge sites (Williams, 1994).

Thus the product of the symmetry operations of $P2_1$ and *mm*2 yields the true space group $P\bar{4}2_1m$.

In the urea example, the site symmetry and space group led to a unique specification for the molecular packing group. When site symmetry is present, the specification of the molecular packing group may not be unique. For example, consider a case in which the molecule resides on site symmetry 32 in space group $R\bar{3}c$. It can be shown that the molecular packing group can be specified either as $P\bar{1}$ or *Pc* (see Appendix *A*). This situation prevails because the product of either $P\bar{1}$ or *Pc* with symmetry 32 yields $R\bar{3}c$.

Besides restriction of the number of possible space groups and specification of fewer degrees of freedom, there is another calculational advantage in searching molecular packing groups instead of using $Z' = 2$ in *P*1. Consider random rotational orientations of one or two molecules using a Lattman angle grid (Williams, 1973). If $Z' = 1$ and rotational grid spacing is about 30°, there are 536 points to be sampled. On the other hand, if $Z' = 2$, there are $536^2 = 287\,296$ rotational grid points to be sampled, a very much larger number. Thus, for $Z' = 2$, many more points in six-dimensional rotation space need be considered. In fact, successes of *ab initio* crystal structure prediction for $Z' > 1$ are no doubt abetted by the presence of much molecular symmetry, which effectively creates additional rotational sampling points. This is illustrated by successful *ab initio* predictions of the crystal structures of urea (*mm*2 symmetry) with $Z = 2$ and $Z' = 2$, and benzene (6/*mmm* symmetry) with $Z = 4$ and $Z' = 4$ (Williams, 1996*a*).

5. Examples of the use of molecular packing groups

The example of urea was discussed above. Here additional examples are given: two $Z = 1$ structures, three $Z = 2$ structures and two $Z = 4$ structures. The computer program *MPA* (Williams, 1972, 1996*b*) was used to carry out the crystal energy minimizations. The program *GAUSSIAN*94 (Frisch *et al.*, 1995) was used to calculate the molecular electric potential using the 6-31G** basis set. The program *PDM*97 (Williams, 1997) was used to obtain net atomic charges for the molecules. In some cases, additional nonatomic charge sites were used to represent the molecular electric potential better. Several intermolecular force fields were used, as indicated in Table 3. The accuracy of the force field was checked by performing energy minimization in the observed space group, starting from the observed coordinates. The structural shifts obtained were small; this energy-relaxed structure was then used as the target structure for *ab initio* crystal structure prediction.

Ab initio crystal structure prediction by searching molecular packing groups requires four assumptions. Firstly, the molecule must have known structure and conformation. The molecular structure may be obtained, for example, with use of standard bond lengths and angles, by observations on gas-phase molecules, or from quantum-mechanical theory. If the molecule has several low-energy conformations, each conformation may be treated as a distinct rigid molecule. Secondly, sufficiently accurate force-field parameters must be available. Thirdly, only one molecule or a portion of a molecule comprises the asymmetric unit ($Z' \leq 1$). Finally, the *Z*

Table 4. *The 26 molecular packing groups for Z = 4*

The sequence number of the space group in *International Tables for Crystallography* Vol. A is given in parentheses.

$C2$ (5)	Cm (8)	Cc (9)	$P2/m$ (10)	$P2_1/m$ (11)
$P2/c$ (13)	$P2/c$ (14)	$P222$ (16)	$P222_1$ (17)	$P2_12_12$ (18)
$P2_12_12_1$ (19)	$Pmm2$ (25)	$Pmc2_1$ (26)	$Pcc2$ (27)	$Pma2$ (28)
$Pca2_1$ (29)	$Pnc2$ (30)	$Pmn2_1$ (31)	$Pba2$ (32)	$Pna2_1$ (33)
$Pnn2$ (34)	$P4$ (75)	$P4_1$ (76)	$P4_2$ (77)	$P4_3$ (78)
$P\bar{4}$ (81)				

value must be known (if Z is not known, several Z values may be tried). Without the assumption $Z' \leq 1$, there can be any number of molecules in the asymmetric unit; $P1$ is then always a possible packing group for any Z value.

These four conditions were utilized in the prediction of the structures listed in Table 3 with the procedures described for the urea example. When $Z = 2$, as in the urea example, the five packing groups were searched. When $Z = 1$, as in the first two examples listed in Table 3, only $P1$ was searched. When $Z = 4$, as in the sixth and seventh examples listed in Table 3, 26 packing groups were searched (Table 4).

In the prediction runs, the reference molecule was initially placed in a large cubic cell (say $14 \times 14 \times 14$ Å) in a randomly selected orientation. The intermolecular energy was minimized by allowing the molecule to rotate and translate, while maintaining the molecular packing-group symmetry. The cell constants were also allowed to vary, again retaining the symmetry of the molecular packing group. The size of the initial cell was generally set as large as permitted by the lattice summation limit cutoff. Table 3 summarizes the results.

For each example, Table 3 shows observed cell constants and lattice energy for the observed structure, relaxed cell constants and the corresponding energy, and predicted cell constants obtained by lattice-energy minimization. If the *ab initio* prediction is successful, relaxed and predicted cell constants, and the corresponding energies, should agree within close tolerance, which they did.

6. Conclusions

The relationships of molecular packing groups to the number of molecules per cell, space group and site symmetry have been described. The number of molecules per cell places restrictions on possible space groups and molecular packing groups. The use of molecular packing groups for *ab initio* crystal-structure prediction was successful for several examples, leading to the suggestion that the molecular packing-group method is generally capable of predicting crystal structures that contain one independent molecule per cell. An indirect result of *ab initio* crystal-structure prediction is verification of the intermolecular force fields for the molecules considered.

Table 5. *Molecular packing groups for Z = 2 and the corresponding space groups, for each site symmetry*

A × indicates a molecular packing group that is compatible with the space group.

Site	Molecular packing group					Space	
symmetry	$P\bar{1}$	$P2$	$P2_1$	Pm	Pc	group	Z'
$\bar{1}$			×	×		$P2_1/m$	1/2
		×			×	$P2/c$	
			×		×	$P2_1/c$	
2			×			$C2$	1/2
	×			×		$P2/m$	
	×				×	$P2/c$	
		×				$P222$	
		×	×			$P222_1$	
			×			$P2_12_12$	
					×	$Pcc2$	
				×	×	$Pma2$	
					×	$Pnc2$	
					×	$Pba2$	
					×	$Pnn2$	
m					×	Cm	1/2
	×	×				$P2/m$	
	×		×			$P2_1/m$	
		×		×		$Pmm2$	
			×		×	$Pmc2_1$	
		×			×	$Pma2$	
			×		×	$Pmn2_1$	
$2/m$	×		×		×	$C2/m$	1/4
		×			×	$Pccm$	
		×	×	×	×	$Pmma$	
		×	×		×	$Pmna$	
			×		×	$Pbam$	
			×		×	$Pnnm$	
222		×	×			$C222$	1/4
			×			$I222$	
	×				×	$Pnnn$	
	×			×	×	$Pccm$	
	×				×	$Pban$	
		×				$P422$	
			×			$P42_12$	
		×				$P4222$	
			×			$P422_12$	
				×		$P\bar{4}2m$	
					×	$P\bar{4}2c$	
					×	$P\bar{4}c2$	
					×	$P\bar{4}b2$	
					×	$P\bar{4}n2$	
$mm2$		×			×	$Cmm2$	1/4
			×		×	$Amm2$	
			×		×	$Imm2$	
	×	×		×		$Pmmm$	
	×	×	×		×	$Pmma$	
	×		×		×	$Pmmn$	
				×		$P4nm$	
					×	$P4_2cm$	
					×	$P4_2nm$	
					×	$P4_2mc$	
		×				$P\bar{4}2$	
			×			$P\bar{4}2_1m$	
		×				$P\bar{4}m2$	
mmm	×	×	×		×	$Cmmm$	1/8
	×		×		×	$Immm$	
		×		×		$P4/mmm$	
			×		×	$P4/mbm$	
		×			×	$P4_2/mmc$	
		×			×	$P4_2/mcm$	

Table 5 (*cont.*)

Site symmetry	Molecular packing group $P\bar{1}$	$P2$	$P2_1$	Pm	Pc	Space group	Z'
			×		×	$P4_2/mnm$	
4			×			$I4$	1/4
	×				×	$P4/n$	
		×				$P422$	
		×	×			$P42_12$	
				×	×	$P4bm$	
					×	$P4cc$	
					×	$P4nc$	
$\bar{4}$			×			$I\bar{4}$	1/4
	×			×		$P4_2/m$	
	×				×	$P4/n$	
	×				×	$P4_2/n$	
		×			×	$P\bar{4}2c$	
			×	×	×	$P\bar{4}2_1m$	
			×		×	$P\bar{4}2_1c$	
		×			×	$P\bar{4}c2$	
		×	×		×	$P\bar{4}b2$	
		×	×		×	$P\bar{4}n2$	
4/m	×		×		×	$I4/m$	1/8
		×			×	$P4/mcc$	
		×	×	×	×	$P4/mbm$	
		×	×		×	$P4/mnc$	
422		×	×			$I422$	1/8
	×			×	×	$P4/mcc$	
	×			×	×	$P4/nbm$	
	×				×	$P4/nnc$	
4mm			×		×	$I4mm$	1/8
	×	×		×		$P4/mmm$	
	×	×	×		×	$P4/nmm$	
$\bar{4}2m$			×		×	$I\bar{4}2m$	1/8
	×	×			×	$P4/nbm$	
	×	×		×	×	$P4_2/mcm$	
	×	×	×		×	$P4_2/nnm$	
$\bar{4}m2$	×	×		×	×	$P4_2/mmc$	1/8
	×		×		×	$P4_2/nmc$	
4/mmm	×	×	×		×	$I4/mmm$	1/16
3	×					$P\bar{3}$	1/3
	×					$R\bar{3}, r$	
		×				$P312$	
		×				$P321$	
		×				$R32, r$	
				×		$P31m$	
					×	$P3c1$	
					×	$P31c$	
					×	$R3c, r$	
		×				$P6$	
			×			$P6_3$	
				×		$P\bar{6}$	
$\bar{3}$		×			×	$P\bar{3}1c$	1/6
		×			×	$P\bar{3}c1$	
		×			×	$R\bar{3}c, r$	
			×	×		$P6_3/m$	
32	×			×		$P\bar{3}1m$	1/6
	×				×	$P\bar{3}1c$	
	×				×	$P\bar{3}c1$	
	×				×	$R\bar{3}c, r$	
		×				$P622$	
		×	×			$P6_322$	
				×	×	$P\bar{6}c2$	
				×	×	$P\bar{6}2c$	
3m	×	×				$P\bar{3}1m$	1/6
	×	×				$P\bar{3}m1$	
	×	×				$R\bar{3}m, r$	
		×		×		$P6mm$	
			×		×	$P6_3cm$	

Table 5 (*cont.*)

Site symmetry	Molecular packing group $P\bar{1}$	$P2$	$P2_1$	Pm	Pc	Space group	Z'
			×		×	$P6_3mc$	
		×		×		$P\bar{6}m2$	
		×		×		$P\bar{6}2m$	
6	×			×		$P6/m$	1/6
					×	$P6cc$	
$\bar{6}$	×	×		×		$P6/m$	1/6
	×		×			$P6_3/m$	
		×			×	$P\bar{6}c2$	
		×		×		$P\bar{6}2m$	
		×			×	$P\bar{6}2c$	
6/m		×			×	$P6/mcc$	1/12
622	×			×	×	$P6/mcc$	1/12
6mm	×	×		×		$P6/mmm$	1/12
$\bar{6}m2$	×	×		×		$P6/mmm$	1/12
	×	×	×		×	$P6_3/mmc$	
$\bar{6}2m$	×	×	×		×	$P6_3/mcm$	1/12
23			×			$I23$	1/12
	×				×	$Pn\bar{3}$	
		×	×			$P4_232$	
					×	$P\bar{4}3n$	
$m\bar{3}$	×		×		×	$Im\bar{3}$	1/24
		×	×		×	$Pm\bar{3}n$	
432		×	×			$I432$	1/24
	×				×	$Pn\bar{3}n$	
$\bar{4}3m$			×		×	$I\bar{4}3m$	1/24
	×	×	×		×	$Pn\bar{3}m$	
$m\bar{3}m$	×	×	×		×	$Im\bar{3}m$	1/48

APPENDIX *A*

Consider possible space groups for the case of $Z = 2$ and $Z' \leq 1$. It is obvious that $P1$ is excluded from this list, since $N \geq 2$. All space groups with $N = 2$ are possible, in which case $Z' = 1$; space groups with $N > 2$ are also possible, but only if they have special positions of multiplicity 2, in which case $Z' = 2/N$. *These conditions eliminate 104 space groups from consideration*. Table 5 lists the 126 space groups that will accommodate $Z = 2$ and $Z' \leq 1$. Note that the twofold sites in space groups $P4$, $P4_2$ and $P\bar{4}$, as well as the $2/m$ sites in $P4/m$ and $P4_2/m$, do not have nontrivial molecular packing groups.

If $Z = 2$, $Z' < 1$ and $N > 2$, the molecule must occupy a special position. The possible special positions (with site symmetry indicated) available in each possible space group are given in Table 5. To obtain the molecular packing group, the site point symmetry operations must be deleted from the space-group symmetry operations. This process nearly always leads to one or more of the five possible molecular packing groups for $Z = 2$ as indicated on the right-hand side of the table. Only a few space groups lead to the $P1$ molecular packing group for $Z = 2$; some space groups allow only a single molecular packing group, others allow several, and some are compatible with four of the five possible molecular packing groups for $Z = 2$.

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