

Two-dimensional packing and pseudosymmetry

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It is possible to understand, or at least rationalize, the occurrence of pseudosymmetry elements in some crystals as a consequence of a higher symmetry in a two-dimensional layer being obscured by the three-dimensional packing of the layers. Six examples, including both simple compounds and co-crystals and involving six different symmetries, are described.

1. Introduction

There is a growing interest in structures with $Z' > 1$, or, more specifically, structures where more than one, or parts of more than one, molecule are included in the asymmetric unit. For example, Padmaja *et al.* (1990) have looked at the distribution of such structures among the space groups. Desiraju *et al.* (1991) have discussed pseudoinversion centers in $P\bar{1}$. Karthe *et al.* (1993) have looked at the packing energies in 18 such structures. Brock (1996) has discussed problems in solving such structures. Kalman & Argay (1998) have discussed the pseudosymmetries in structures in $P\bar{1}$ with $Z = 8$. Marsh *et al.* (1998) have discussed pseudoinversion in $Pca2_1$ and $Pna2_1$. Much earlier, Templeton (1956) showed that pseudosymmetry could cause misleading systematic absences.

There is no single explanation for this phenomenon, except, of course, that in the cases where it occurs it may lower the free energy. Kitaigorodskii (1970) suggested¹ that two or more molecules per asymmetric unit '...can ensure an increase in the number of degrees of freedom per cell, and, consequently, can ensure packing of the highest density'. Indeed, one might raise the question why $Z' = 1$ as often as it does.

There is, however, a sub-set of structures where this can be explained or understood by recognizing that the molecules have packed so that a two-dimensional translational pattern has formed in which $Z' \leq 1$ in a two-dimensional plane group, or, more accurately, in a layer group, but that some or all of the symmetry elements in this simple pattern are lost when the two-dimensional layers pack in three dimensions.

The earliest example known to the author of such a structure and the one that started his interest is that of boric acid (Zachariasen, 1954). Without particularly trying, about 20 more such structures have been found over the years. Six of these are discussed here as illustrative examples. In each case we will expand Z to include the symmetry class as suggested by Zorky and coworkers (Zorky *et al.*, 1967; Belsky *et al.*, 1995; Zorky, 1996), so that, for example, we can distinguish between

¹ The author is indebted to a referee for pointing out that this suggestion is not necessarily true. A polymorph whose growth is kinetically controlled would not have a lower free energy than the thermodynamically stable form. However, no polymorphs have been discovered, as yet, for any of the six examples quoted here.

$P2_1/c$, $Z = 4(1)$, with four molecules in general positions, and $Z = 4(\bar{1}^2)$, with two independent molecules each on a center of symmetry.

2. Background

Shubnikov & Koptsik (1974) identify seven categories of symmetry lower than the symmetry of three-dimensional spaces. These are the symmetries of one-sided rosettes, of figures with a singular point (at least one point is left unchanged by all of the symmetry operations), of one-sided bands (border groups), of two-sided bands, of rods, of network patterns (plane groups) and of layers. These are not all independent: rosettes are a subset of figures with a singular point; one-sided bands are a subset of two-sided bands, which in turn are a subset of rods; network patterns are a subset of layers. Molecules or aggregates of molecules that would be expected to have a particular symmetry in isolation or semi-isolation sometimes retain that particular symmetry in a three dimensional structure, but sometimes lose all or part of that symmetry when packed in three dimensions. This is well known with some of these symmetry categories, but less well known in others.

The loss of symmetry elements in molecules (figures with a singular point) is very familiar. If a molecule has an ideal symmetry that is not one of the 32 allowable point groups of crystallography, it cannot retain all of its symmetry in the crystal. For example, ferrocene, whether its actual symmetry is D_{5d} , D_{5h} or D_5 , must lose the fivefold axis as a true symmetry element. However, even if the molecular symmetry is an allowed crystal symmetry, it may be lost in the crystal. As only one example, an isolated molecule of 1,3,5-trichlorobenzene would be expected to have D_{3h} symmetry, but in the crystal, in

space group $P2_12_12_1$, it has no crystallographic symmetry at all, although metrically it is quite close to D_{3h} .

Molecular aggregates with translational symmetry in only one dimension that might be expected to have one- or two-sided or rod symmetry may have it approximately but not crystallographically. As an example, isophthalic acid might be expected to have the band symmetry $pbmm$ (in the notation of Smith, 1982) and does approximate this very closely in the crystal (Derissen, 1974), but has only 2_1 crystallographic symmetry.

Aggregates with translational symmetry in two dimensions that might be expected to have plane symmetry or layer symmetry may also have it approximately but not crystallographically. While layer symmetry groups are more appropriate, we will also use plane groups to describe these cases, since plane groups are more familiar, even though the layers are not exactly planar. As an example here, guanidinium nitrate might be expected to occur in two-dimensional sheets with layer symmetry $p\bar{6}m2$.² The observed low-temperature structure (Katrusiak & Svafranski, 1994), shown in Fig. 1, has sheets of crystallographic symmetry $c1m1$ that are very close metrically to $p\bar{6}m2$. If the conventional unit cell with Cm symmetry is converted to a primitive cell by the matrix $1/2, 1/2, 0 // -1/2, 1/2, 0 // 0, 0, 1$, the new cell has $a = b$ and $\gamma = 120.34^\circ$; $\gamma = 120^\circ$ would be expected for exact $p\bar{6}m2$ symmetry. The observed symmetry is lower than the ideal because successive layers stack in such a way that the threefold axes and two of the mirror planes do not coincide between layers, although the C -centering, which is observed is a consequence of the pseudothreefold symmetry. This is presumably because the layers have shifted to improve the layer-to-layer interactions. Another consequence of this is that the layers are not exactly planar. Their non-planarity, however, does not negate the general argument.

Its packing arrangements similar to the last, but with $Z' > 1$ in the conventional cell that are the main concern of this paper.

3. Examples

3.1. General

In each of the following examples one layer will be shown in the figure along with the originally reported unit cell. The deviations from planarity within the layer will be ignored and the pseudosymmetry described so that it includes a pseudomirror in the plane of the layer. The crystallographically independent molecules are labelled *A* and *B* in each case. If the structure involves a co-crystal, then one molecule of each type will be labelled *A* and the others *B*; there is no significance to which two are labelled *A*.

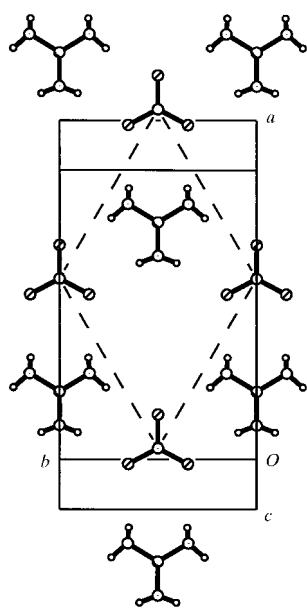


Figure 1
One layer of guanidinium nitrate; view perpendicular to (001). The conventional three-dimensional unit cell is shown with solid lines. The two-dimensional pseudocell in $p\bar{6}m2$ is shown with dotted lines.

² The layer group $p\bar{6}m2$ can be derived from the plane group $p3m1$ and is listed as No. 78 in the forthcoming Volume E of *International Tables of Crystallography* (2000). Henceforth, this will be summarized as $p\bar{6}m2$ (No. 78, $p3m1$). The layer groups are also described by Shubnikov & Koptsik (1974) and Smith (1982), but the numbering in the former and some of the labelling in both differ from the IUCr recommendations.

3.2. Diacetamide–4-hydroxybenzamide (1/1): pseudosymmetry $p12/m1$ (No. 6, $p2$)

The crystal structure of the diacetamide–4-hydroxybenzamide (1/1) cocrystal was determined by Etter & Reutzel (1991). The crystals are monoclinic, space group $P2_1/n$, with $Z = 8(1^2)$ and two independent molecules of each type in the asymmetric unit. There was no mention of the pseudosymmetry in the original report. Examination of the structure shows that the molecules lie in almost planar sheets, which contain no real symmetry elements, but which do contain both sets of crystallographically independent molecules. A portion of a planar layer is shown in Fig. 2. The pattern as a whole is close to $p12/m1$ symmetry with a pseudocenter at $x = 0.24$, $y = 0.15$, $z = 0.36$. Successive, identical layers are related by the usual symmetry elements of $P2_1/n$. The interlayer interactions lead to a mean deviation from the mean plane of 0.21 Å.

3.3. 2,4,6-Tribromobenzoisonitrile: pseudosymmetry $pmam$ (No. 40, pmg)

The crystal structure of 2,4,6-tribromobenzoisonitrile was determined by Carter *et al.* (1977). The crystals are orthorhombic, space group $Pnam$, with $Z = 8(m^2)$ and two independent half-molecules in the asymmetric unit, each lying on a mirror plane. In the original report it was noted that the two molecules are nearly coplanar, but no other relationship between them was mentioned. Examination of the extended structure, Fig. 3, shows that the molecules lie in nearly planar sheets, which are intersected by the crystallographic mirror planes and contain both types of crystallographically independent molecules. The pattern as a whole is close to $pmam$ symmetry. The atoms in the two molecules all have x near 1/8; the average deviation from the mean plane is 0.17 Å. The crystallographic glide planes produce new layers which are displaced so that the glide plane in $pmam$ is lost.

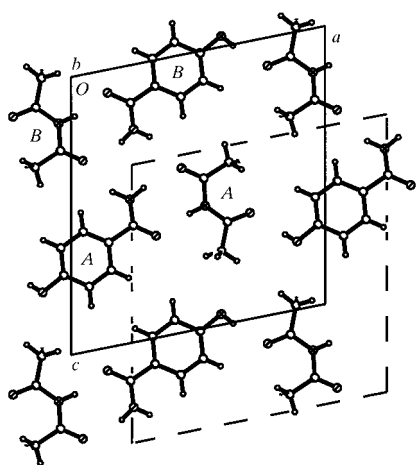


Figure 2
One layer of diacetamide–4-hydroxybenzamide (1/1); view perpendicular to (010). The molecules labelled A and B are crystallographically independent. The conventional three-dimensional unit cell is shown with solid lines. The two-dimensional pseudocell in $p12/m1$ is shown with dotted lines.

It is worth noting that the isosteric isomer of this compound, 2,4,6-tribromobenzonitrile, occurs in the space group $P2_1/m$, $Z = 2(m)$, with virtually identical planar layers (Carter & Britton, 1972). In this case the layer, in projection, has exact $pmam$ symmetry as a consequence of m plus 2_1 symmetry elements in three dimensions.

3.4. 3,5-Dibromo-4-hydroxybenzonitrile (Bromoxynil): pseudosymmetry $pbam$ (No. 44, pgg)

The crystal structure of bromoxynil was determined by Baughman *et al.* (1981). The crystals are triclinic, space group $P\bar{1}$, with $Z = 4(1^2)$ and two independent molecules in the asymmetric unit. In the original report it was noted that the two molecules are nearly coplanar, but no other relationship between them was mentioned. Examination of the extended structure shows that the molecules lie in almost planar sheets, which include real centers of symmetry and both types of crystallographically independent molecules. If the original cell is transformed by the matrix $100/110/\bar{1}11$, a new cell is obtained with $a = 9.154$, $b = 14.139$, $c = 17.051$ Å, $\alpha = 89.58$, $\beta = 157.66$, $\gamma = 55.78^\circ$; $\alpha = 90^\circ$ would be expected for perfect pgg symmetry. A portion of a planar layer plus the new unit cell is shown in Fig. 4. The pattern as a whole is close to pgg symmetry with the molecules all having an x coordinate near zero in the new cell; the maximum deviation from the mean plane is 0.29 Å. The centers that occur in $pbam$ (these are twofold axes in pgg) coincide with the centers in $P\bar{1}$, but the glide planes that are present in $pbam$ are lost in the real cell because the next layer along \mathbf{a} is translated to a position that does not align with either glide plane.

3.5. Bis-imidazolium squarate: pseudosymmetry $p4/m$ (No. 51, $p4$)

The crystal structure of bis-imidazolium squarate was determined by MacDonald & Etter (1991). The crystals are

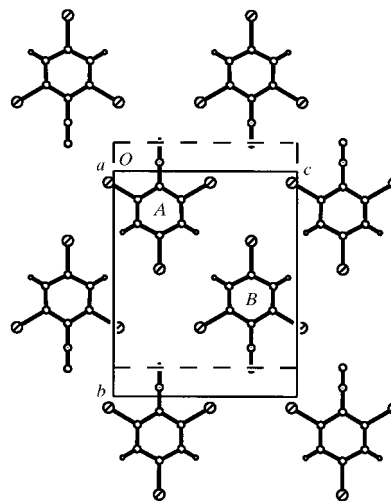


Figure 3
One layer of 2,4,6-tribromobenzoisonitrile; view perpendicular to (100). The molecules labelled A and B are crystallographically independent. The conventional three-dimensional unit cell is shown with solid lines. The two-dimensional pseudocell in $pmam$ is shown with dotted lines.

triclinic, space group $P\bar{1}$, with $Z = 4$ (imidazolium, 1^2 ; squarate, $\bar{1}^2$), two independent imidazolium ions and two half squarate ions in the asymmetric unit. Examination of the structure shows that the molecules lie in nearly planar sheets, which contain crystallographic inversion centers, but no other symmetry, and which do contain all the crystallographically independent ions. A portion of a planar layer is shown in Fig. 5. The pattern as a whole is close to $p4/m$ symmetry. Successive, identical layers are related by translation, but the shift in the layers is such that the fourfold symmetry is lost. If the conventional cell, $a = 4.810$, $b = 8.763$, $c = 13.975$ Å, $\alpha = 91.17$, $\beta = 91.39$, $\gamma = 98.13^\circ$, is transformed by the matrix $1, 0, 0 / -2, 1, 0 / 0, 0, 1$, the new cell has $a = 4.810$, $b = 13.897$, $c = 13.975$ Å, $\alpha = 89.78$, $\beta = 91.39$, $\gamma = 141.38^\circ$; $b = c$ and $\alpha = 90^\circ$ would be expected for exact $p4/m$ symmetry.

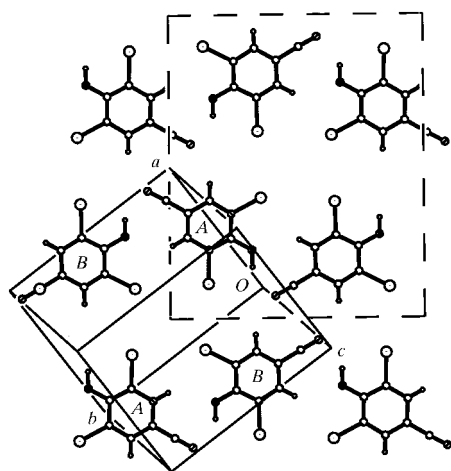


Figure 4
One layer of 3,5-dibromo-4-hydroxybenzonitrile; view perpendicular to $(1, -1, 2)$. The molecules labelled *A* and *B* are crystallographically independent. The conventional three-dimensional unit cell is shown with solid lines. The two-dimensional pseudocell in $pbam$ is shown with dotted lines.

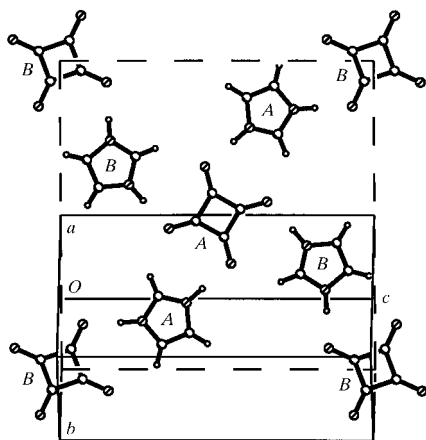


Figure 5
One layer of bis-imidazolium squarate; view perpendicular to (120) . The molecules labelled *A* and *B* are crystallographically independent. The conventional three-dimensional unit cell is shown with solid lines. The two-dimensional pseudocell in $p4/m$ is shown with dotted lines. While the four imidazolium ions shown are equivalent under the pseudosymmetry, the squarate ions *A* and *B* are not (see text).

The pseudosymmetry here is different from the previous cases in that the two independent squarate ions are still independent, but the two independent imidazolium ions are related by the pseudorotation. That is, the pseudosymmetric $p4/m$ layer has $Z = 1/2$ (imidazolium, 1; squarate, 4^2).

A referee has pointed out that the squarates alone have pseudosymmetry $p4mbm$ (No. 63, $p4gm$), but this would require the imidazolium ions to lie on a diagonal mirror, which they do not. They do lie close to a diagonal mirror position if the C and N are regarded as equivalent. Perhaps this is an example of pseudopseudosymmetry.

3.6. 2,6-Dibromobenzonitrile: pseudosymmetry $p4/mbm$ (No. 63, $p4gm$)

The crystal structure of 2,6-dibromobenzonitrile was determined by Britton *et al.* (2000). The crystals are monoclinic, space group $C2/m$, with $Z = 8(2, m)$ and two independent half molecules in the asymmetric unit, one lying on a twofold axis and the other lying on a mirror plane (see Fig. 6). The molecules lie in sheets parallel to (201) . Within the sheets the molecules have close to $p4/mbm$ symmetry. If the original cell is transformed by the matrix $1/2, 1/2, -1 // -1/2, 1/2, 1 // 0, 0, 1$, the new unit-cell dimensions are $a = 15.069$, $b = 15.069$, $c = 3.966$ Å, $\alpha = 67.47$, $\beta = 112.53$, $\gamma = 89.80^\circ$; for exact $p4g$ symmetry $a = b$ and $\gamma = 90^\circ$ would be expected. The fourfold axes and the exact planarity of the layer are lost as a consequence of the packing of adjacent layers.

3.7. Orthoboric acid: pseudosymmetry $p6/m$ (No. 75, $p6$)

The structure of orthoboric acid was determined approximately and later refined by Zachariasen (1934, 1954) and studied further by neutron diffraction of the deuterated acid (Craven & Sabine, 1966). The crystals are triclinic, space group $P\bar{1}$, with $Z = 4(1^2)$ and two independent molecules in the asymmetric unit. The molecules pack in sheets parallel to

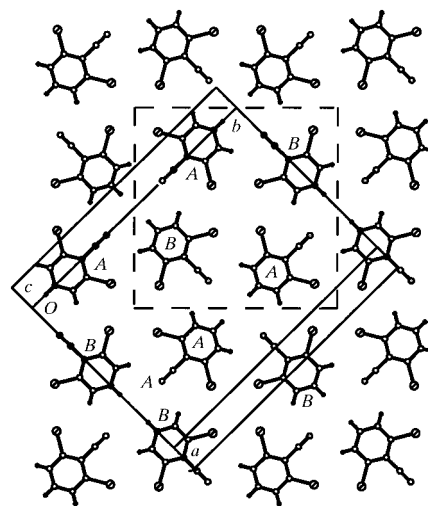


Figure 6
One layer of 2,6-dibromobenzonitrile; view perpendicular to (201) . The molecules labelled *A* and *B* are crystallographically independent. The conventional three-dimensional unit cell is shown with solid lines. The two-dimensional pseudocell in $p4mbm$ is shown with dotted lines.

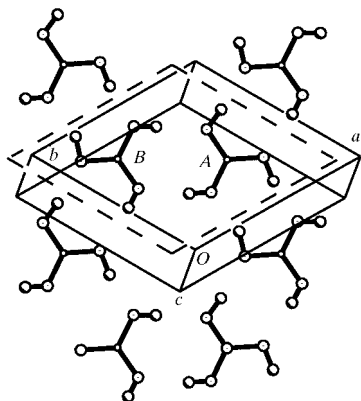


Figure 7

One layer of orthoboric acid. View perpendicular to (010). The molecules labelled *A* and *B* are crystallographically independent. The conventional three-dimensional unit cell is shown with solid lines. The two-dimensional pseudo-cell in *p6/m* is shown with dotted lines.

(001). A portion of a sheet is shown in Fig. 7. The two molecules inside the unit-cell boundaries in the figure are crystallographically independent, related by a pseudocenter of symmetry, but clearly the pattern as a whole is very close to *p6/m* symmetry. One could imagine a three-dimensional structure where successive sheets have equivalent atoms perpendicularly above one another; such an arrangement would have space group *P6/m* with one-third of a molecule in the asymmetric unit. As Zachariasen pointed out, in the actual structure successive sheets are displaced, so that O atoms in one sheet are above or below B or H atoms in the next sheet. This displacement obscures all the symmetry elements and leads, among other things, to all of the centers of symmetry in a sheet being turned into pseudocenters. The centers in the actual structure relate adjacent sheets.

Once the symmetry has been lost there is no requirement that the sheets be exactly planar, and they are not. Zachariasen suggested that the deviations from planarity are a consequence of the inter-sheet contacts, and Craven and Sabine pointed out that small deviations from planarity within the sheets allowed the O—H...O angle in the hydrogen bonds to come closer to being linear.

As a final observation on the pseudosymmetry, if the sheet did have *p6/m* symmetry, this would require that $a = b$ and $\gamma =$

120° . The unit cell reported by Zachariasen has $a = 7.039$ (2), $b = 7.053$ (2) and $\gamma = 119.83$ (2)°.

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