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Crystals of the recently published [Bolotina, Kirschbaum & Pinkerton (2005). *Acta Cryst.* B**61**, 577–584] triclinic ($P\bar{1}$) structure of 5-nitro-2,4-dihydro-1,2,4-triazol-3-one (α-NTO) occur as fourfold twins. There are $Z' = 4$ independent molecules per asymmetric unit. We show that the structure contains layers with 2-periodic layer-group symmetry $p2_1/b\ 1$ (1). This symmetry is lost through the stacking of the layers, which is a possible explanation for $Z' = 4$. A layer can assume four different but equivalent positions with respect to its nearest neighbor. Twinning arises through stacking faults and is an instructive example of the application of order–disorder theory using local symmetry operations. The near-neighbor relations between molecules remain unchanged through all twin boundaries. The four structures with maximum degree of order, one of which is the observed one, and the family reflections common to all domains are identified. Rods of weak diffuse scattering confirm the stacking model.

1. Introduction

The structure and twinning of the energetic material 5-nitro-2,4-dihydro-1,2,4-triazol-3-one (α-NTO) has recently been published by Bolotina *et al.* (2005), in the following referred to as BKP. The space group is $P\bar{1}$ with four molecules of identical dimensions in the asymmetric unit, $Z' = 4$, $Z = 8$. The transformation of the triclinic primitive cell by $\mathbf{a} = \mathbf{a}_t$, $\mathbf{b} = \mathbf{b}_t$, $\mathbf{c} = \mathbf{a}_t + \mathbf{b}_t + 2\mathbf{c}_t$ gives an I-centered cell (cell 5 of BKP) with near-orthorhombic metric, $\alpha = 90.030$, $\beta = 89.600$, $\gamma = 89.848°$. For this cell, we use the non-standard space-group symbol $I\bar{1}$, $Z = 16$. The two investigated crystals were both four-component twins. Twin elements with respect to the I-cell are twofold rotations about [100], [010] and [001], or equivalently reflections on (100), (010) and (001). The volume ratios of the domains in two crystals were refined to 55:9:20:16 and 27:19:29:25. Other volume ratios, including nearly equal domain sizes, were found for other crystals in subsequent work.

The importance of twinning has been rediscovered in the past decade (Le Page, 2002; Hahn & Klapper, 2003). Rules have been formulated for the detection of the effects of twinning during structure determination (Cooper *et al.*, 2002; Parsons, 2003), and easy-to-use software is available for the refinement of volume ratios of merohedral and non-merohedral twin domains, such as *SHELXTL* (Sheldrick, 1997) and *JANA2000* (Petricek *et al.*, 2000). If the twin elements relating the orientations of the domains (reflections, rotations) are known, these programs allow one to obtain reliable structural parameters for twinned crystals. However, the twin elements are a purely formal description in terms of symmetry and give no answer to important questions such as the origin of twin-

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Table 1
Coordinates of molecule 2 in the idealized structure (see text).

The center of the five-membered ring is the average of the coordinates of N1, N2, C3, N4 and C5.

Atom	x	y	z
N1	−0.1466	0.0143	0.0536
N2	−0.0320	0.1125	0.0329
C3	0.2330	0.1096	0.0341
N4	0.2847	0.0018	0.0568
C5	0.0516	−0.0475	0.0671
O3	0.3904	0.1830	0.0188
N5	0.0237	−0.1618	0.0912
O5	0.2261	−0.2097	0.1031
O6	−0.1966	−0.1998	0.0978
Center	0.07742	0.03814	0.04890

ning and the interfaces between domains. Among the vast variety of twins (Hahn & Klapper, 2003), one mechanism of twinning appears to us to be particularly easy both to identify and to interpret, and to occur particularly frequently, namely twinning by faults in layer stackings. This type of twinning is best described by OD theory (Dornberger-Schiff & Grell-Niemann, 1961; Dornberger-Schiff & Dunitz, 1965; Dornberger-Schiff, 1982), *i.e.* the theory of one-dimensional order–disorder. A single isolated stacking fault may lead to a twinned domain while the nearest-neighbor environment of the layers remains unchanged across the planar twin boundary, giving an intuitive explanation for the origin of twinning. Some examples with complete descriptions of this mechanism are given by Bürgi *et al.* (2005). The remarkable twinning in piperazine hexahydrate (Schwarzenbach, 1968) can also be formulated in terms of OD theory.

We show that α-NTO is a layer structure and that its twinning is a non-trivial, instructive example of the application of OD theory providing a qualitative explanation of the occurrence of twinning and of the presence of four independent molecules per asymmetric unit, $Z' = 4$. Faint rods of diffuse scattering confirm this interpretation.

2. OD theory applied to the structure of α-NTO

In the following, we use exclusively the I-centered cell 5 of BKP, idealized to show an exact orthorhombic metric, $a = 5.1233$, $b = 10.314$, $c = 34.143$ Å, $\alpha = \beta = \gamma = 90°$. The atomic coordinates x_o, y_o, z_o in the setting $I\bar{1}$ are obtained from the published coordinates x_t, y_t, z_t with $x_o = x_t - z_t/2$, $y_o = y_t - z_t/2$, $z_o = z_t/2$. For aesthetic reasons, we invert the signs of these coordinates and transfer the origin to $(1/2, 0, 1/2)$: $x = 1/2 - x_o$, $y = -y_o$, $z = 1/2 - z_o$. The results show intriguing relations between the coordinates of different NTO molecules. Very minor shifts of the molecules by less than 0.06 Å result in the following idealized structure:

$(0, 0, 0)+$ $(1/2, 1/2, 1/2)+$

molecule 1: $\pm[1/2 - x, 1/2 + y, z]$

molecule 2: $\pm[x, y, z]$, coordinates reported in Table 1

molecule 3: $\pm[3/4 - x, 1/4 + y, 1/4 - z]$

molecule 4: $\pm[1/4 + x, 3/4 + y, 1/4 - z]$.

The molecules are numbered as in BKP. The molecular dimensions agree to within less than 1 s.u. with the average distances and angles of BKP. The relations are local symmetry operations; they cannot be applied repeatedly and are valid only for a single molecule. BKP show in their Fig. 4 that molecules 1 and 2, and likewise molecules 3 and 4, form infinite flat hydrogen-bonded ribbons along **a**. The relations between molecules 1 and molecules 2 are those of the 2-periodic layer group $p2_1/b$ 1 (1), the non-periodic direction being parallel to **c** and the center of symmetry $\bar{1}$ at $(0, 0, 0)$. The molecules 3 and 4 at $1/4 - z$ and those at $1/4 + z$ (obtained with the $-$ sign and the translation $1/2, 1/2, 1/2$) conform to the same layer group with $\bar{1}$ at $(1/4, 1/4, 1/4)$. Fig. 1 shows a plot of these two layers where the 'atoms' represent the centers of the five-membered rings (Table 1). Fig. 2 shows the herringbone packing of the layers looking down the ribbon axis. The following arguments are independent of the details of the molecular shape and the hydrogen-bonding scheme for which the reader is referred to Fig. 4 of BKP.

Order–disorder structures arise when the layer symmetry is local and adjacent layers are related by local symmetry operations that cannot be repeated simultaneously to become elements of a space group. This means that there are alternative positions of two adjacent layers with exactly the same contacts (as is well known in the closest sphere packings). The local symmetry operations relating the layer at 0 to the layer at 1/4 (Figs. 1 and 2) are:
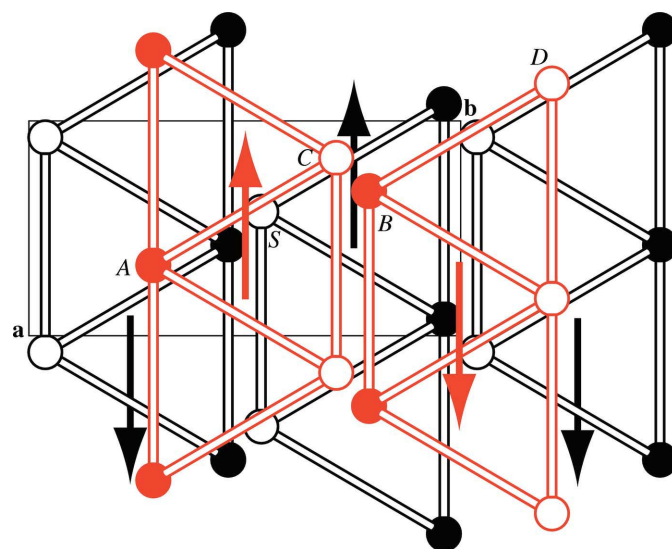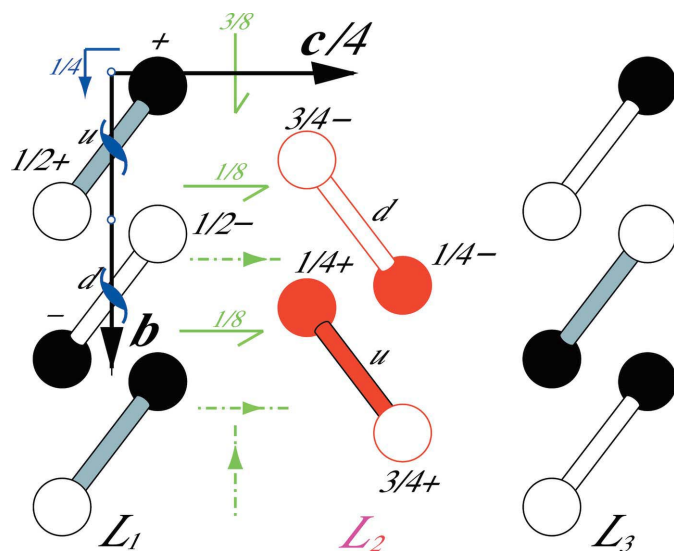

Figure 1
Projection of two adjacent layers of the structure onto (001), looking down [001]. The molecules are represented by their centers; the bonds represent the hydrogen-bonded ribbons whose planes are closely parallel to $(0 \pm 3\ 13)$ and form an angle of 37.39° with (001). Filled and empty circles indicate the lower and upper sides of the layers, respectively. The layer contact is thus between empty circles of the lower layer formed by molecules 1 and 2 at coordinate z, and the filled circles of the upper layer formed by molecules 3 and 4 at $1/4 - z$. The arrows show the polar orientation of the ribbons, which corresponds to the direction from left to right in Fig. 4 of BKP. The letters S, A, B, C, D indicate the local symmetry operations relating the two layers (see text).

(i) n glide plane at $z = 1/8$ between layers, translation [1/4, −1/4, 0], moving S to A,

(ii) 2_1 screw at x, $z = 3/8$, 1/8 between layers, translation [0, 1/4, 0], moving S to B,

(iii) n-glide plane perpendicular to $\mathbf{b}$ at $y = 5/8$, translation [−1/4, 0 1/4], moving S to C,

(iv) 2_1 screw parallel to $\mathbf{c}$ at x, $y = 1/8$, 7/8, translation [0, 0, 1/4], moving S to D.

Remember that the c axis spans four layers. Maximum-degree-of-order (MDO) structures are periodic structures with maximal space-group symmetries and are obtained by continually repeating one local operation to the detriment of the others (for an exact definition see Dornberger-Schiff, 1982). All interfaces between the layers in the MDOs of α-NTO are equivalent under the resulting space-group symmetry. Two repeatable operations to give layers at $z = 1/2$, 3/4, ... are part of the layer symmetry and two relate adjacent layers: $\overline{1}$, 2_1 along $\mathbf{a}$, n perpendicular to $\mathbf{b}$ and 2_1 along $\mathbf{c}$. The other operations are not repeatable. The MDOs and twin laws created by a single stacking fault are in the above order:

(i) $I\overline{1}$, $Z' = 4$, the observed structure. The layer symmetry group is reduced to $p\overline{1}\,1\,(1)$. All interfaces between layers are equivalent through the centers $\overline{1}$ at (0, 0, 0) and (1/4, 1/4, 1/4). In contrast, the layers are not symmetry-equivalent because of the alternating polarity of the interfaces, although they are geometrically identical.

Figure 2
Projection of the observed structure MDO1 ($I\overline{1}$) down the ribbon axis $\mathbf{a}$ on to (100). Filled and empty circles are at heights $\pm x$, $1/4 \pm x$ and $1/2 \pm x$, $3/4 \pm x$, respectively. Filled and empty bonds symbolize the polar directions *up* (u) and *down* (d), respectively. Partial symmetry elements of a single layer (L_1) are shown in blue, and those relating adjacent layers (L_1 and L_2) in green. Layers L_1 and L_3 are related by the I-translation which when applied to the red layer L_2 continues the structure along $\mathbf{c}$. The alternative positions of a layer equivalent with respect to its nearest neighbors are obtained by swapping filled with empty circles (add 1/2 to x), or/and swapping filled with empty bonds (swap + with −). Generating subsequent layers along $\pm\mathbf{c}$ with the I-translation gives domains of MDO1 related by the twin laws (100), (001) and (010).

(ii) $A2_1 11$, $Z' = 4$. The layer symmetry becomes $p2_1\,1\,(1)$. The standard space-group symbol $P12_11$ is obtained with the transformation $\mathbf{a}' = (\mathbf{b} + \mathbf{c})/2$, $\mathbf{b}' = \mathbf{a}$, $\mathbf{c}' = -\mathbf{c}$. The layers are again not symmetry-equivalent, but the interfaces are equivalent through the 2_1 screws. A stacking fault of this type displaces a layer with respect to the published structure by $\mathbf{a}/2$. It is easy to show by generating the coordinates of the twin domains that a single stacking fault results in a [100] twin.

(iii) $B1d1$, $Z' = 4$. The standard space-group symbol $P1c1$ is obtained with $\mathbf{a}' = \mathbf{c}$, $\mathbf{b}' = -\mathbf{b}$, $\mathbf{c}' = (\mathbf{a} - \mathbf{c})/2$. Layers and interfaces are symmetry-equivalent, the layer group being $p1\,1\,(1)$. A stacking fault of this type displaces a layer by $\mathbf{b}/2$ and results in a [010] twin.

(iv) $P112_1$ with $\mathbf{c}' = \mathbf{c}/2$, $Z' = 4$. Again, layers and interfaces are symmetry-equivalent, the layer group being $p1\,1\,(1)$. A stacking fault of this type displaces a layer by $(\mathbf{a} + \mathbf{b})/2$ and results in a [001] twin.

Clearly, any two of the three twin laws imply the remaining law. Diffraction patterns from OD structures contain family reflections whose structure factors do not depend on the stacking order. In the case of α-NTO, their indices h, k, l are all even. In direct space, the family reflections correspond to a superposition structure with space group $Pmnn$ (standard setting $Pnnm$) and axial lengths $a/2$, $b/2$, $c/2$. The reflections with h, k, l even in the *Supplementary Material* of BKP indeed show approximately the corresponding absence rules: they are weak for $hk0$, $(h + k)/2$ odd, and for $h0l$, $(h + l)/2$ odd. These indices refer to the orthorhombic cell and are obtained from the triclinic indices of BKP by the transformation $h = h_t$, $k = k_t$, $l = h_t + k_t$. In addition, a sufficiently disordered OD structure may show rods of diffuse scattering through the non-family reflections, in the present case along $\mathbf{c}^*$ through reflections with at least one odd index h, k. Such rods have indeed been found for all investigated crystals. Fig. 3 shows an example from a crystal with nearly equal volume ratios of the four domains. This observation is a convincing argument that the OD interpretation of the structure is correct.

3. Discussion

The OD family of the layer stacking belongs to category I_b and its symbol (Dornberger-Schiff, 1982) is

$$p \quad \begin{matrix} 2_1/b & 1 & (1) \\ \{ \quad 1 & 2_{1/2}/n_{2,\overline{1/2}} & 2_2/n_{1/2,\overline{1/2}} \} \end{matrix},$$

where the glide-components along $\mathbf{c}$ are given in units of the distance between layers, $c' = c/4$. This family appears to be unusual because it comprises four MDO structures (Dornberger-Schiff, 1982). Fig. 2 gives a recipe for drawing the twin boundaries. Twin domains should alternate along a single direction with planar interfaces. All layers in the idealized structure have identical nearest-neighbor contacts through all twin boundaries.

The observed volume ratios of twin domains do not suggest a marked preference for any particular twin law. However, they are not all equal to 0.25, and they depend on the specimen. This observation indicates that there are few

isolated stacking faults resulting in relatively large twin domains. On the other hand, the observation of diffuse scattering implies the presence of many stacking faults, which in turn should result in equal volume ratios of the twin domains. Therefore, the crystals might exhibit not only relatively large ordered twin domains but also very disordered layer sequences. Indeed, the calculation of the diffuse intensities in close analogy to the method described by Bürgi *et al.* (2005) gives a qualitative indication of the presence of disordered domains. Assuming nearest- and next-nearest-neighbor interactions defined by the four probabilities p_1, p_2, p_3 and p_4 with $p_1 + p_2 + p_3 + p_4 = 1$ to find stacks of three neighboring layers according to MDO1, MDO2, MDO3 and MDO4, respectively, gives an intensity variation of

$$I(l) = (N/2)[|F(l)|^2 + |F(-l)|^2][(1 - w^2)/(1 + w^2 - 2w \cos \pi l)],$$

$$w = (-1)^{h+k}p_1 + (-1)^k p_2 + (-1)^h p_3 + p_4.$$

N is the number of layers, $|F|$ is the structure amplitude of a single layer and l is the continuous coordinate along $\mathbf{c}^*$ referring to the distance c of four layers. The extrema of $I(l)$ are at l integral. The larger the maxima, the smaller are the minima. In Fig. 3, the diffuse intensities between reflections at l integer ($h + k + l = 2n$) are nearly constant but too strong to be compatible with the high maxima. They suggest a completely disordered structure with $p_1 = p_2 = p_3 = p_4 = 1/4$, $w = 0$, and therefore negligible second-neighbor interactions. $I(l)$ depends then only on the diffraction by a single layer and varies slowly.
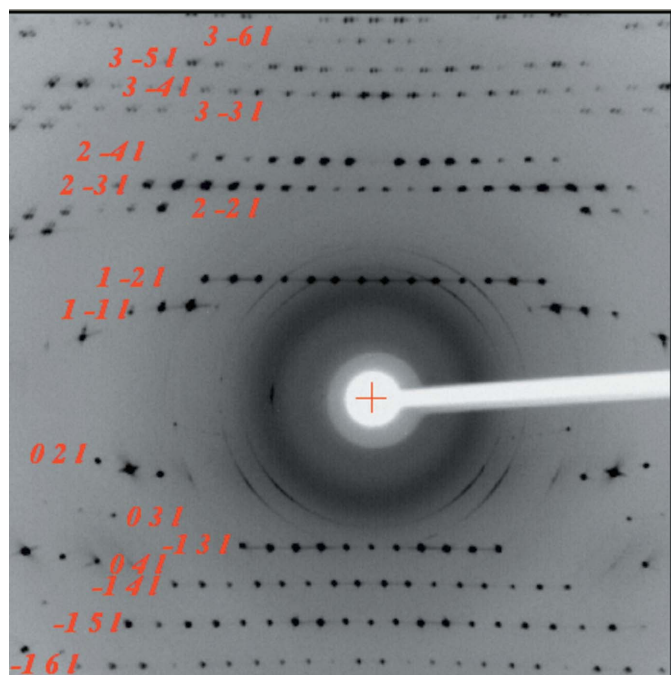
Figure 3
Faint rods of diffuse intensity along $\mathbf{c}^*$ with indices h, k not both even for a crystal with nearly equal volume fractions for the four twin orientations. $\mathbf{c}^*$ is horizontal.

The reason for the occurrence of ordered domains is surely the fact that the observed structure is 'relaxed', *i.e.* deviates by small shifts from the ideal model [in analogy to a proposition for tris(bicyclo[2.1.1]hexeno)benzene by Bürgi *et al.* (2005)]. These relaxations may be responsible for the correlations between second-nearest layers, rather than long-range van der Waals interactions. One can imagine that the disordered domains grew too fast for the structure to relax. The formation of the observed structure in preference to the other three MDOs is not easily explained. The center of symmetry in the observed structure ensures that the planes of the ribbons in a layer remain strictly parallel for any amount of relaxation, which is not necessarily the case for the structures with screw axes or glide planes.

Under the polarizing microscope, the domains are invisible. The crystals look like single crystals. They are transparent only in the $\mathbf{c}$ direction, looking onto the dominant faces $\pm(001)$ parallel to the layer plane. The lateral faces, principally $\pm(100)$ and $\pm(010)$, have a frosted appearance. In polarized light, the extinctions on (001) and freshly cleaved (010) are sharp. This is not incompatible with the proposed large ordered domains. Extinctions are sharp if the principal axes of the optical indicatrix are parallel to the local symmetry elements, *i.e.* the pseudo-orthorhombic axes a, b and c, and thus closely parallel in all domains.

All MDOs have four independent molecules per asymmetric unit. The reason for this is evident in this case: the molecules in a single layer are indeed related by symmetry, but this symmetry is lost by the stacking of the layers into the herringbone packing of the ribbons. However, the layer symmetry persists as local symmetry. Each molecule has two contacts with the neighboring layer, at distances between the centers in the idealized structure of 5.822 (1–4), 5.941 (1–3), 5.941 (2–4) and 6.161 Å (2–3), where the numbers (a–b) designate the molecules. The distances of 5.941 Å are between ribbons of the same polarity; the other two are between ribbons of opposite polarity. These four contacts, involving of course all atoms and not just the centers of the molecules, are inequivalent and cannot be made identical by any idealization of the structure (short of modifying the shape of the NTO molecule). They are, however, very similar; one O atom of the nitro group O5(b) or O6(b) of molecule b is located roughly above the mid-point of the C5(a)–N5(a) bond of the nitro moiety of molecule a, on a line perpendicular to the molecular plane of a (see Fig. 3 of BKP). The distances O5(b)–N5(a) and O5(b)–C5(a) are shorter (in the idealized structure, 2.82, 2.83 and 2.88, 2.90 Å, respectively) than the distances O6(b)–N5(a) and O6(b)–C5(a) (3.02, 3.05 and 3.08, 3.12 Å, respectively).

4. Conclusions

We have shown that the multiple twinning of α-NTO can be rationalized by stacking faults of identical layers. In addition to the four domain types with different twin orientations, the rods of diffuse intensity suggest the presence of domains with completely disordered stacking. It is an intrinsic property of the layer stacking that the four molecules become symme-

trically inequivalent even in the idealized structure. It is a wonder of nature that the intermolecular contacts remain closely similar. The symmetry of a single ribbon is $p2_1$ (a) (m), but only the 2_1 axis is part of the symmetry of a layer. We have not been able to imagine a generalized OD structure exploiting the additional mirror symmetry where all ribbons would have identical nearest-neighbor environments.

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