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1-Nitronaphthalene, a non-OD, non-MDO polytype

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Abstract: Crystals of 1-nitronaphthalene were grown by evaporation of a methanol solution. The structure [$P2_1/c$, a = 13.2780(13) Å, b = 3.8131(3)° Å, c = 31.851(3) Å, β = 91.173(8), V = 1,612.3 Å^3] was solved from a crystal twinned by twofold rotation about [100]. Twinning is explained by the polytype character: layers with (idealized) $p2_111$ symmetry can connect via either $\bar{1}$ or 2_1 operations, leading to geometrically distinct pairs of layers. In the twin individuals, the two kinds of contacts alternate, at the composition plane two subsequent contacts of the same type are realized.

Keywords: order-disorder theory; polytypism; twinning

1 Introduction

Performing a literature search on the crystal chemistry of nitrated polycyclic aromatics, we were surprised that no crystal structure of *1-nitronaphthalene* has been deposited in the *Chemical Structure Database* (CSD).[1] Apparently, only a few co-crystals have been successfully structurally characterized so far. 1-Nitronaphthalene is a common chemical and we would have expected at least unintentional crystallization from reaction mixtures, leading to an opportunistic crystal structure determination.

Since crystalline commercial 1-nitronaphthalene was available on-site, we decided to investigate the matter. A few preliminary diffraction experiments of the commercial material solved the riddle of the lack of structural data: intensities were invariably diffuse and weak making indexation difficult. Therefore, we recrystallized a small amount from methanol, growing long (>1 cm) needle-shaped crystals. Here likewise, large crystals featured subpar diffraction patterns plagued by systematic twinning and pronounced mosaicity. However, by collecting data of a rather small crystal on a modern diffractometer system with large detector distance and fine slicing, we were able to satisfactorily solve and refine the structure from a twinned crystal.

From a crystallographic point of view, *1-nitronaphthalene* piqued our interest owing to its polytypism (the ability of layer structures being arranged in different ways). Polytypes can be classified into OD polytypes and non-OD polytypes. OD originally stands for *order-disorder*, though the name is unfortunate, since OD polytypism is unrelated to order-disorder phase transformations. In OD polytypes, for which a comprehensive and very useful theory has been developed,[2] the different ways of connecting layers are geometrically equivalent. This means that there are an infinity of possible polytypes, which are all locally equivalent. The set of these polytypes is called an *OD family*. In contrast, in the case of non-OD polytypes, the layers of members of a *polytype family* can connect in geometrically different ways.

1-nitronaphthalene is of the rarer non-OD type. We will show how to apply the formalism developed in the context of OD theory also in such a case and thus demonstrate its generality.

2 Experimental

2.1 Crystallization

Needles of 1-nitronaphthalene were grown by dissolving 100 mg of commercial material (Fluka, *purum*) in 10 ml methanol followed by evaporation of the solvent at room temperature over night.

2.2 Data collection and refinement

Multiple crystals were selected under a polarizing microscope and checked for diffraction quality using CuKα radiation on an STOE StadiVari diffractometer system equipped with a Dectris Eiger CdTe hybrid photon counting detector. Crystals were systematically twinned with a high degree of reflection overlap and featured pronounced mosaicity. Generally, small crystals were of better diffraction quality. Intensity data of the crystal with the least mosaicity were then collected at 200 K in a dry stream of nitrogen up to 2θ = 140° using fine-sliced (0.3°) ω-scans.

Data were processed with X-Area.[3] Two domains were identified and integrated concurrently using overlap information (HKLF5 format). Periodic refinement of the orientation matrix from reflection positions had to be turned off for

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reliable results. This proved to be a non-issue owing to the stability of the goniometer. A correction for absorption and beam inhomogeneity was applied using the multi-scan approach implemented in LANA.[3]

The structure was solved using the dual-space approach implemented in SHELXT[4] and refined against F^2 using SHELXL.[5] C, N and O atoms were refined using anisotropic atomic displacement parameters (ADPs). H atoms were placed at calculated positions and refined as riding on the parent C atom. More data collection and refinement details are collected in Table 1.

3 Results and discussion

3.1 Crystal and molecular structure

1-Nitronaphthalene crystallizes in a space group of type $P2_1/c$ with $Z' = 2$ molecules in the asymmetric unit. The crystallographically independent molecules are indicated by different shading in Figure 1. The atoms in both molecules are labeled equivalently up to an added *A* or *B* letter. The molecules are accordingly called the *A* and *B* molecule, respectively.

Table 1: Data collection and structure refinement details.

	1-nitronaphthalene
Crystal data	
Formula	$C_{10}H_7NO_2$
M_r	173.17
Temperature (K)	200
Crystal system, space group	Monoclinic, $P2_1/c$
a, b, c (Å)	13.2780(13), 3.8131(3), 31.851(3)
β (°)	91.173(8)
V (Å^3)	1612.3(3)
Z	8
Radiation type	CuK$\bar{\alpha}$
μ (mm^{-1})	0.836
Crystal shape	Rod
Crystal size (mm)	0.13 × 0.04 × 0.02
Data collection	
Diffractometer	STOE StadiVari
Absorption correction	Multi-scan (LANA)
T_{min}, T_{max}	0.694, 0.962
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	26214, 14623, 9524
R_{int}	0.0417
Refinement	
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.61
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$	0.0736, 0.2558
S	1.073
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.260, −0.301
Twin operation	Twofold rotation about [100]
Twin volume ratio	0.599:0.401(3)
CSD number	2358669

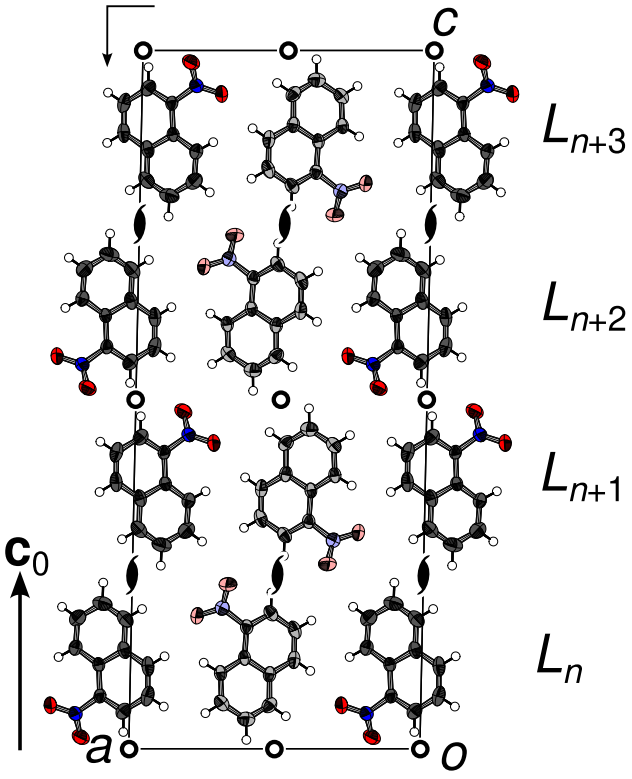

Figure 1: The crystal structure of 1-nitronaphthalene viewed along [010]. C (gray), N (blue) and O (red) atoms are represented by ellipsoids drawn at the 75 % probability levels, H atoms by white spheres of arbitrary radius (0.2 Å). The crystallographically distinct *A* (light) and *B* (dark) molecules are differentiated by brightness. Symmetry elements of the $P2_1/c$ space group are indicated using the usual graphical symbols.[6]

The molecules are arranged in layers extending parallel to (001), which are called L_n, where n is a sequential number (Figure 1). Adjacent layers L_n and L_{n+1} are alternately related by the $\bar{1}$ and $[-2_1-]$ operations of the $P2_1/c$ space group. Note: For symmetry operations with a directional element, we use a notation with places to indicate the direction (e.g. $[--2_1]$ is a screw rotation in the [001] direction, etc.).[7] Layers L_n and L_{n+2} are mapped by *c*-glides reflections, which arise from a combination of the $[-2_1-]$ and $\bar{1}$ operations. Four layers form a translation period in the [001] direction.

The two distinct molecules are geometrically practically equivalent (see below for quantification). The nitro group is tilted with respect to the naphthalene ring system (Figure 2), owing to steric interaction with C9's hydrogen atom. The torsion angle between the respective least squares planes is 40.1(6)° and 38.1(6)° for the *A* and *B* molecule, respectively.

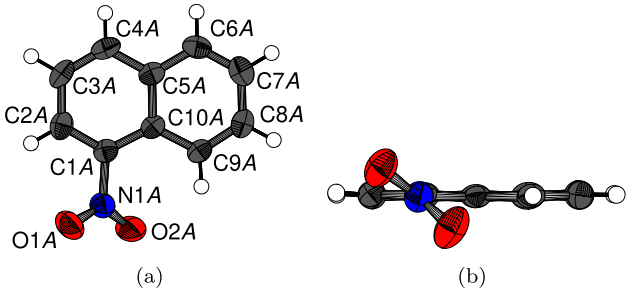

Figure 2: The *A* molecule (a) projected on the plane of the naphthalene system and (b) viewed along the bond connecting the nitro group the naphthalene moiety. Atoms as in Figure 1. The *B* molecule is geometrically practically equivalent and therefore not shown.

3.2 Pseudo-symmetry of layers

Our argument that the crystal structure of 1-nitronaphthalene possesses polytype character is based on the pseudo-symmetry of the L_n layers. In fact, the layers can be considered as having (pseudo) $p2_111$ symmetry (see Figure 3). According to the *International Tables of Crystallography*, the lower case Bravais symbol indicates the two-dimensionality of the translation lattice and it is implicitly assumed that the layer extends in the (001) plane.[8] The *A* and *B* molecules, which are distinct according to the space group symmetry, are related by pseudo-$[2_1 - -]$ screw rotations.

To prove the validity of our interpretation, it is crucial to quantify the deviation from this idealized symmetry. Thereto, the atom coordinates were transformed into a Cartesian coordinate system and the location of the screw axis determined by averaging the *y* and *z* coordinates of the C, N and O atoms. The intrinsic translation of the screw rotation was derived by halving the **a** basis vector. This, now well defined, screw rotation was then applied to the *A* molecule, to map it onto the *B* molecule. An overlay of the molecules is shown in Figure 2 and the distance between atoms is given in Table 2. A maximum distance of 0.233 Å for the C7A/C7B pair confirms the pseudo-symmetry and henceforth we will consider (slightly) idealized L_n layers

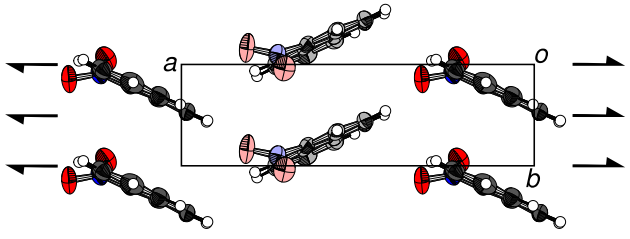

Figure 3: L_n layer in 1-nitronaphthalene projected on the layer plane (001). Atoms as in Figure 1. The locations of the pseudo $[2_1 - -]$ axes are represented by the usual symbols.

Table 2: Distance *d* between atoms of the image of the *A*-molecule by the $[2_1 - -]$ layer symmetry to the atoms of the *B*-molecule.

Atoms	*d* (Å)	Atoms	*d* (Å)
C1	0.087	C8	0.177
C2	0.144	C9	0.109
C4	0.153	C10	0.027
C4	0.155	N1	0.166
C5	0.097	O1	0.211
C6	0.185	O2	0.218
C7	0.233		

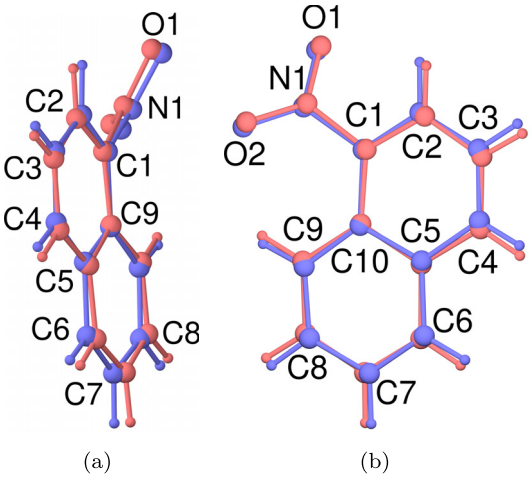

Figure 4: Overlay of the image of the *A*-molecule by the pseudo-$[2_1 - -]$ screw rotation (red) and the *B*-molecule (blue), viewed along (a) [100] and (b) [010].

with $p2_111$ symmetry.[8] The slight deviation is mostly due to a rotation about an axis parallel to [100], as seen in Figure 4(a).

3.3 Polytypism

According to the $p2_111$ symmetry,[8] the L_n layers are *non-polar*, which means that both sides are related by symmetry. However, in the crystal structure of 1-nitronaphthalene, both sides connect in non-equivalent ways to adjacent layers: by $\bar{1}$, resulting in (L_n, L_{n+1}) pairs of layers with $p\bar{1}$ layer symmetry, and by $[-2_1-]$ resulting in pairs with $p12_11$ symmetry. Since these pairs feature distinct symmetry, notably the orientation relation of the adjacent layers are different, they are geometrically different. The two distinct layer contacts will be designated according to the operations relating the adjacent layers as $\bar{1}$- and $[-2_1-]$-contact, respectively.

This proves the polytype character of 1-nitronaphthalene, since a layer can contact in different ways to adjacent layers.

Moreover, it violates the *vicinity condition* of OD theory,[9] which states that *equivalent sides of equivalent layers connect in such a way to adjacent layers that the resulting pairs are equivalent*. 1-Nitronaphthalene is therefore a *non-OD* polytype. Note that the non-OD character stems from different sets of operations that relate layers of the *same* kind. An alternative way of achieving non-OD polytypes is a layer that can contact to two (or more) layers of different kind. If this leads to structures composed of distinct sets of layers, one also speaks of *merotypes* instead of *polytypes*.[7]

In OD polytypes, layer contacts are equivalent and therefore it is reasonable to associate a 'width' or 'thickness' to layers. The vector perpendicular to the layer plane and of the length of one layer width is typically called $\mathbf{c}_0$ (for stacking direction [001]). In contrast, in non-OD polytypes, the distinct layer contacts may lead to structures with different density and there may therefore be a distinct $\mathbf{c}_0$ for each layer contact.

Interestingly, for 1-nitronaphthalene, the $[2_1 - -]$ axis (see above for determination) of the layer symmetry is located a negligible 0.003 Å away from the $z = \frac{1}{8}$ (with respect to the basis of the $P2_1/c$ structure) plane. That is, it is equidistant to the $\bar{1}$ and $[-2_1-]$ symmetry elements of the $P2_1/c$ space group. Thus, in both kinds of layer contacts, the layer planes are equidistant, which means that we can define a common $\mathbf{c}_0$ vector, with the length $c \sin(\beta)/4 = 7.961$ Å. It is indicated in Figure 1.

3.4 Comparison of layer contacts

Even if adjacent layers do not form equivalent pairs, it is sometimes possible to construe an OD interpretation by (formally) 'cutting' the molecules and considering the layer contact as a distinct OD layer with higher symmetry (see for example Ref 10).

To rule out such an interpretation and to show that the layer contacts are indeed chemically different, we performed a Hirshfeld surface analysis[11] using *Crystal Explorer*.[12] Figure 5 shows the Hirshfeld surface of both sides of an L_n layer decorated with d_{norm} values. For the $\bar{1}$-contact, large d_{norm} values (red spots in Figure 5(a)) show that the most prominent interlayer interactions are O3B–H8A contacts. In contrast, there are no such prominent interactions for the $[-2_1-]$-contact (Figure 5(b)).

While these results shouldn't be over-interpreted, since Hirshfeld surfaces analyses are sensitive to small distortions, it shows that the contacts *are* chemically different and that the crucial contact is from the O atom of the nitro-group to an H atom in the adjacent layer.

To get a clearer picture of the different layer contacts, we applied the $[-2_1-]$ screw rotation of the L_n layer to a (L_{n-1}, L_n) pair of layers and overlaid it with the (L_n, L_{n+1}) pair. The result is shown in Figure 6(a). As described above, the L_n layer and its image overlap nearly perfectly. The overlay of

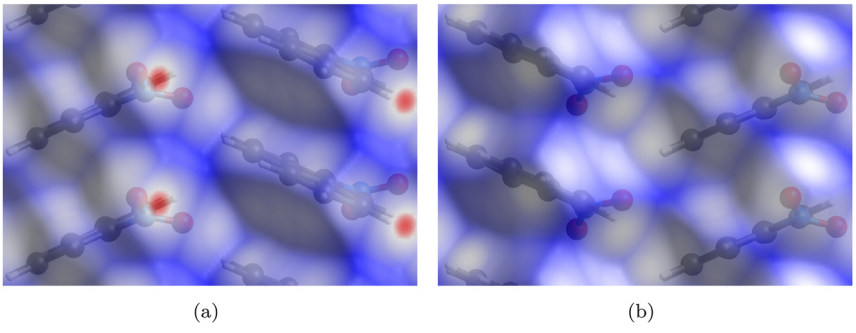

Figure 5: Hirshfeld surfaces of an L_n layer decorated with d_{norm} values for the (a) $\bar{1}$- and the (b) $[-2_1-]$-contact.

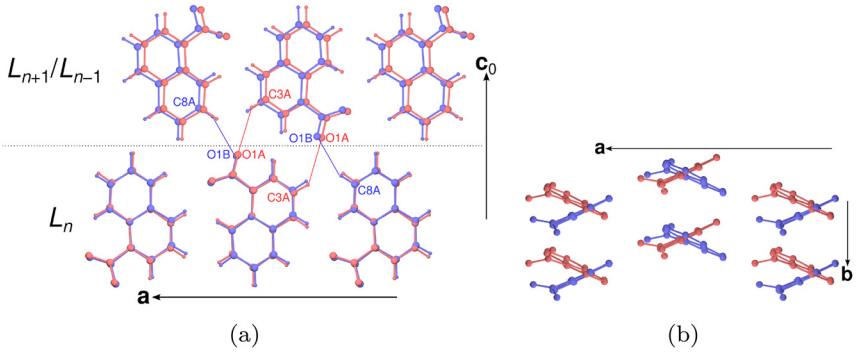

Figure 6: Comparison of the two kinds of layer contacts. (a) Overlay of an (L_n, L_{n+1}) pair (red) and the image of the (L_{n-1}, L_n) pair (blue) by the $[2_1 - -]$ operation of the L_n layer viewed along [010]. A dotted line represents the interface between the layers, short O1–H contacts are indicated by solid lines. (b) Overlay of the L_{n+1} layer (red) and the image of the L_{n-1} layer (blue) by the $[2_1 - -]$ operation of the L_n layer. H atoms are omitted for clarity.

the image of L_{n-1} and L_{n+1} quantifies the difference of the two contacts.

First observe that, as noted above, the [001] components of the layer origins are virtually identical, which justifies the choice of a single $\mathbf{c}_0$ vector connecting the planes of adjacent layers. However, in the [100] direction, there is a small, but distinct difference in the origin shift. Apart from that, both layer contacts look very similar in the [010] projection. However, a projection along [001] (Figure 6(b)) reveals that their orientation is reflected with respect to [010], which follows from the fact that $[-2_1-]$ retains, but $\bar{1}$ inverses the orientation with respect to [010].

This results in entirely different inter-layer O–H contacts. As noted above, at the $\bar{1}$-contact, two molecules 'touch' via short O1*A*–H3*B* contacts (2.55 Å, red lines in Figure 6(a)). The two connected molecules feature the same orientation with respect to [001] (the nitro group points in the same direction).

In the $[-2_1-]$-contact, on the other hand, the shortest inter-layer O–H contact is significantly longer (O1*A*–H8A, 2.70 Å, blue lines in Figure 6(a)). Here, the connected molecules are related by $\bar{1}$ and thus feature different orientation with respect to [001].

Ultimately, we note that the layer interfaces are chemically distinct and there are two ways of placing the L_{n+1} layer into the mold of the L_n layer's interface. We see no reasonable way of forcing an OD interpretation in this case.

3.5 Application of the OD formalism

In the context of OD theory a rich formalism for analyzing OD polytypes has been developed, which can however also be applied to non-OD polytypes with small adaptations, as we will do in the upcoming sections.

3.5.1 NFZ relationship

The central point of OD theory is that, given a layer, distinct placements of adjacent layers can lead to geometrically equivalent layer pairs. Given the layer L_n, the number of ways of placing the adjacent layer L_{n+1} is called Z and is calculated using the *NFZ relationship*.[13] Since in 1-nitronaphthalene layers can contact in two non-equivalent ways, the NFZ relationship is applied to both separately. Accordingly, the number of ways of placing the adjacent layer will be called $Z_{\bar{1}}$ and $Z_{[-2_1-]}$, respectively.

To calculate Z, for each layer L_n one has to determine the subgroup $\mathcal{G}_n$ of symmetry operations that do not invert its orientation with respect to the stacking direction. In 1-nitronaphthalene, $\mathcal{G}_n = p1$ for all L_n, because $[2_1 - -]$ *does* invert the orientation and all that remains are pure translations.

Then, one needs to know the partial operations (POs, operations that apply for distinct layers, not the whole structure) relating the adjacent layers. These are obtained by forming the coset of the layer group of L_n and a representative operation mapping L_n onto L_{n+1}. We obtain, up to lattice translations, $\{[c_2 \; - \; -], \bar{1}\}$ ($\bar{1}$-contact) and $\{[-2_1-], [- \; - \; 2_2]\}$ ($[-2_1-]$-contact). c_2 and 2_2 are generalizations of the Hermann-Mauguin notation used in OD theory, indicating intrinsic translations of one layer width.

In both layer contacts, there is a PO inverting the orientation of the layers with respect to the stacking direction (called σ-ρ-POs in the OD literature): $[-2_1-]$ and $\bar{1}$, which are also symmetry operations of the resulting layer pairs. In such a case, the number of ways of placing the adjacent layer is obtained by coset decomposition of the subgroup $\mathcal{G}_n \cap \mathcal{G}_{n+1}$ in $\mathcal{G}_n$. I.e. one considers the operations that map L_n onto itself, but not L_{n+1} onto L_{n+1}. In both cases, $\mathcal{G}_n \cap \mathcal{G}_{n+1} = \mathcal{G}_n = p1$ and therefore there is only $Z_{\bar{1}} = Z_{[-2_1-]} = [p1 : p1] = 1$ way of placing the adjacent layer.

We conclude that not only is 1-nitronaphthalene of the non-OD type, but also *both* layer contacts do *not* possess *OD character*. Note however, that given a layer L_n, the total number of ways of placing the adjacent L_{n+1} layer is $Z = Z_{\bar{1}} + Z_{[-2_1-]} = 2$, *i.e.* there *is* an ambiguity in the stacking arrangement.

A different situtation would arise if the $[-2_1-]$ PO relating two layers would have an intrinsic translation of $r\mathbf{b}$ with $0 < r < \frac{1}{2}$. Then, it would not be a symmetry operation of the (L_n, L_{n+1}) pair and application of the inverse operation to that pair would lead to a pair with the same L_n layer, but a different L_{n+1} layer. Since there would be two ways of placing L_{n+1}, this layer contact would have OD character. In contrast, the $\bar{1}$ contact can *never* possess OD character, because $\bar{1}$ is always a symmetry operation of the pair. The described situation would correspond to a non-OD polytype, where one contact does and the other doesn't possess OD character.

3.5.2 MDO polytypes

A further crucial concept is that of polytypes of a *maximum degree of order* (MDO).[14] The definition was originally given only for OD structures. However, it is just as useful in the non-OD case. In a family of polytypes, the MDO polytypes are those that cannot be decomposed into fragments of simpler polytypes. Here, there are two distinct kinds of pairs of layers (the $\bar{1}$- and $[-2_1-]$-contacts) and the MDO polytypes are those that consist of only one type of these pairs. MDO_1

(all adjacent layers related by $\bar{1}$) has $P2_1/c11$ symmetry and MDO_2 (all adjacent layers related by $[-2_1-]$) has $P2_12_12_1$ symmetry. In both cases, there is one 1-nitronaphthalene molecule in the asymmetric unit and the L_n layers retain their idealized $p2_111$ symmetry.[8] Though not necessary, it is often the case that layers retain there idealized symmetry in non-OD MDO polytypes, see for example Ref 15 In contrast, in OD MDO polytypes the symmetry is typically reduced.

The polytype under investigation is not of the MDO kind, as it is built of an alternation of MDO_1 and MDO_2 fragments. Here, the symmetry of the L_n layers *is* reduced by a *translationengleiche* (loss of point symmetry) transformation of index 2 from $p2_111$ to $p1$.

3.5.3 Space groupoid

The full symmetry of a polytype is given by the POs that map individual layers onto each others (including those mapping layers onto themselves). These form an algebraic structure called a *space groupoid*.[16,17]

The sets of POs mapping a layer onto itself correspond to the layer symmetry groups. As noted above, in the polytype under investigation, layers L_n are related to L_{n+1} alternately by $\{[c_2\ -\ -], \bar{1}\}$ and $\{[-2_1-],\ [-\ -\ 2_1]\}$ (up to layer lattice translation). By combination of these cosets, L_n and L_{n+2} are related by $\{[\ -g\,(r,0,2)\,-],\ [\ -\ -\,g\,(r+\frac{1}{2},0,2)]\}$. Here, $g(r,0,2)$ denotes a glide with intrinsic translation component $r\mathbf{a}/2 + 2\mathbf{c}_0$. This operation corresponds to the c-glide of the $P2_1/c$ symmetry of the polytype. Thus, the groupoid is fully determined up to lattice translation.

Interestingly, a closely related groupoid description has recently been given for the polytypes of pyroxene.[18] There, layers are either related by translations or by glide reflections with a plane parallel to the layers. The two MDO polytypes are clino-pyroxene (only translations) and proto-pyroxenes (only glide reflections). Orthopyroxenes are non-MDO polytyoe constructed by an alternation of both layer-contacts. In contrast to 1-nitronaphthalene, the pyroxene family of compounds can be described as a family of OD structures by a finer slicing of layers.

3.5.4 Point group and family structure

In analogy to point groups associated to space group types, it is reasonable to associate a point group to families of polytypes, which can for example be used to derive the expected twin laws. These point groups are not necessarily crystallographic.[19] The point group of the family is the group generated by the linear parts of the POs of the space groupoids all members of the family. For 1-nitronaphthalene, the point group is *mmm*, *i.e.* we can say that the point symmetry of the polytype family is *orthorhombic*.

The *family structure* is informally defined as an equal overlay of all polytypes in a family. A more rigorous definition in the context of OD theory has been given by Fichtner.[19] It is crucial for analyzing diffraction patterns of polytype families, as the reflections corresponding the family structure are sharp even in non-periodic layer arrangements. For OD families, the family structure can often be considered as being three-dimensionally discretely periodic (or *crystallographic*), notably if the intrinsic translations of the POs are all commensurate with the layer lattice.

As noted above, there is a common $\mathbf{c}_0$ vector for both layer contacts. Therefore, the origin of the L_n layer is located at $r\mathbf{a} + s\mathbf{b} + n\mathbf{c}_0$, $r, s \in \mathbb{R}$. Moreover, by suitable choice of the layer origin in the [010] direction, the $\bar{1}$-contact retains the y-component of the layer origin and the $[-2_1-]$-contact increases it by $\frac{1}{2}$. Thus, the position of the L_n layer can be refined to $r\mathbf{a}, \frac{m}{2}\mathbf{b} + n\mathbf{c}_0$, $m = 0, 1$.

Concerning the x-component, observe that MDO_1 ($P2_12_12_1$) and MDO_2 ($P2_1/c11$) fragments leave the x-component unchanged, but a four-layer fragment of the $P2_1/c$ polytype under investigation adds $c\cos(\beta)/a = -0.049 \approx -\frac{3}{61}$ to the x-component of the origin. This is due to the different origin shifts seen in Figure 6(a). If, given the large denominator, we consider this value as irrational, then for large n the x-coordinate of the origin of L_n can approach any value in the [0,1) interval by choosing the appropriate number of $P2_1/c$ fragments and filling up the rest with MDO_1 and MDO_2 fragments. Thus, the translation lattice of the family structure, but not individual ordered polytypes, collapses in the [100] direction. One can say that there is a structural decoherence in the [100] direction. In summary, the translation lattice of the family structure is discrete in [010] and [001], but dense in [100] direction. For disordered polytypes, we therefore expect sharp reflections only for $h = 0$.

An alternative interpretation might be that the deviation of β from 90° is an effect of *desymmetrization*[20] and negligible. Then, the family structure would retain the translation symmetry in the [100] direction and consist of an overlay of layers as shown in Figure 6(b). However, we prefer the former interpretation, because both layer contacts possess chemically different connectivities and therefore equal origin shifts would be a strange coincidence. Moreover, even though the difference is nominally small, the decoherence shown in Figure 6(a) is significant. Finally, we suspect that this structural deconherence is responsible for the mediocre crystal quality and it has an pronounced effect on the diffraction pattern, as described below.

However, it must be stressed that, as noted by Ďurovič,[20] deciding whether the observed effect is a matter of

desymmetrization or a 'real' structural phenomenon, requires the structural determination of at least another (ordered) polytype.

3.6 Twinning

The twin laws (*i.e.* the symmetry relationships between the orientations of the twin individuals[21]) are derived by coset decomposition of the point group of a polytype in the point group of the polytype family (*mmm*, see above). For the $P2_1/c$ polytype (point group 2/*m*), we obtain, besides the point group itself, a second coset {[2 – –], [*m* – –], [– – 2], [– – *m*]}. This corresponds precisely to the observed two-domain twinning (see Table 1) and thus shows the predictive power of the polytype theory. At the twin interface is probably located either a fragment of the MDO_1 polytype or the MDO_2 polytype, since in both cases their point groups (222 and 2/*m*11, respectively) contain operations of the twin law. However, theoretically between the twin individuals could also be located a different polytype or a disordered region of layers. In any case, the twin interface is at least one, though possibly more, layers wide. One therefore should speak of an composition *region* or *slab* instead of a composition *plane*. The precise nature of this region cannot be derived from routine diffraction experiments.

The slight deviation from orthorhombic metrics (β = 91.173°) makes this twinning a problematic case *for structure elucidation*, as most reflections overlap, yet the twin obliquity is too large to integrate data using a single domain (Figure 7). Faint streaking along $\mathbf{c}^*$ (exemplarily indicated by red arrows in Figure 7) suggests either disordered domains or small twin domains.

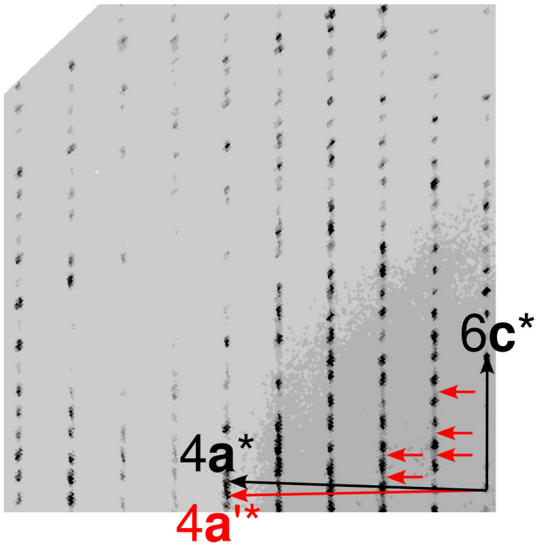

Figure 7: (*h*2*l*)* section of reciprocal space of the 1-nitronaphthalene twin under investigation. Multiples of reciprocal lattice basis vectors of the major domain are indicated in black, the 4**a*** vector of the minor domain in red.

4 Conclusion and outlook

The OD character of polytypes (all members of a family being locally equivalent) has often been used to rationalize the common occurrence of polytypism. Ordered domains of a polytypic compound are often of the MDO kind, because even though of similar energy, the fragment of one MDO polytype may be preferred during crystallization.

However, exceptions exist and in the case of the title compound both 'rules of thumb' are broken. We have shown that many of the core concepts of OD theory are just as useful in the context of non-OD polytypes and need only slight adjustments. We therefore suggest a generalized theory of polytypism, which can for example also describe 'mixed' polytypes where some layer contacts possess and others do not possess OD character.

The existence of non-MDO polytypes means that there is 'communication' of *structural information* beyond one MDO fragment during crystallization, for example by tilting of molecules or by propagation of ledge or screw dislocations.

A final question to answer is whether it is possible to grow the MDO polytypes or other non-MDO polytypes of the title compound.

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