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Polytypism, Twinning, and Disorder in 2,2-Aziridinedicarboxamide

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Abstract

Some phenomena of $C_4H_7N_3O_2$ [Brückner (1982). *Acta Cryst.* **B38**, 2405–2408] are explained on the basis of the OD theory of Dornberger-Schiff. The symbol of the OD groupoid family is $Pba(2)|(n)x, y|(\bar{4})x', y'$ with parameters $x \approx \pm\frac{1}{6}$, $y \approx 0$ (or $x \approx 0$, $y \approx \pm\frac{1}{6}$); $x' \approx \pm\frac{1}{4}$, $y' \approx \pm\frac{1}{4}$. The net constants are $a = b \approx 12.38 \text{ \AA}$; the distance between next-but-one layers is $c_0 \approx 7.55 \text{ \AA}$.

Introduction

The structures of two crystalline forms of the title compound have been reported by Brückner (1982): form A, $P4_212$, $a = 12.382(2)$, $c = 30.211(3) \text{ \AA}$, $V = 4632 \text{ \AA}^3$, $Z = 32$; form B, $P1$, $a = 12.381(2)$, $b = 12.391(2)$, $c = 15.829(2) \text{ \AA}$, $\alpha = 74.3(1)$, $\beta = 83.1(1)$, $\gamma = 90.0(1)^\circ$, $V = 2312 \text{ \AA}^3$, $Z = 16$ (axes of form B interchanged for better comparison with form A). The two crystals are formed by different stacking of layers; the layer symmetry is not extended to the whole packing (Brückner, 1982, p. 2405).

These are strong indications that the two crystals are order-disorder (OD) structures. The OD theory

of Dornberger-Schiff (Dornberger-Schiff, 1956, 1979, 1982; Dornberger-Schiff & Grell-Niemann, 1961) explains the existence of different stacking variants of a layered structure by partial symmetry operations, which are valid for any single layer but do not extend to its adjacent layers. The different structures are built up of the same kind of layer and the same pairs of layers; they differ, however, in triples and higher n -tuples of layers.

The aim of this paper is to explain polymorphism, twinning and apparent disorder and to describe the stacking possibilities of $C_4H_7N_3O_2$.

The family of OD structures according to form A

Fig. 1 shows a layer of form A consisting of hydrogen-bonded molecules arranged in rows along the x direction (P layer). There are also layers with rows along the y direction (Q layer). The unit cell consists of eight layers with the following sequences in the z direction: $P_1P_2Q_3Q_4P_5P_6Q_7Q_8$. Obviously, there are two types of layer pairs: PP and QQ on the one hand, and PQ and QP on the other. Consecutive pairs of the same type are transformed into each other by the 4, space-group transformation. The layers have a square net,

although the layer group $Pba(2)$ (notation according to Dornberger-Schiff, 1956) requires only a rectangular net.

The b glide plane of P_1 is not extended to P_2 . Therefore, according to OD theory, for P_2 there is an alternative position to that actually existing in form A. These two possible positions of P_2 relative to P_1 (Fig. 2a) are described by non-space-group transformations: glide planes perpendicular to the z direction with components $x = \frac{1}{6}, y = 0$ or $x = -\frac{1}{6}, y = 0$, respectively. Thus any PP pair is concisely characterized by

$$PP: (n)x, y \quad (x, y) = (\frac{1}{6}, 0); (-\frac{1}{6}, 0). \quad (1)$$

Accordingly, for any QQ pair results:

$$QQ: (n)x, y \quad (x, y) = (0, \frac{1}{6}); (0, -\frac{1}{6}). \quad (2)$$

None of the glide planes of P_2 are extended to Q_3 . Thus, in addition to the position of Q_3 in form A, three alternative positions of Q_3 relative to P_2 are possible. In Fig. 2(b), each of these possible positions is characterized by a fragment of a molecule and a vector from a twofold axis of P_2 to a twofold axis of the respective Q_3 position. For a unique description of these positions a convention on symbols of OD groupoid families (Fichtner, 1984) is used: Any position of Q_3 results from the application of a non-space-group $\bar{4}$ operation to P_2 . Any of these $\bar{4}$ operations may be considered as a result of two consecutive space transformations: a clockwise rotation of 90° around an axis parallel to the z direction through the origin of P_2 (twofold axis) and a glide reflexion in a plane perpendicular to the z direction.* The different

* Neither the rotation nor the glide reflexion is a symmetry operation of the structure or of the layers.

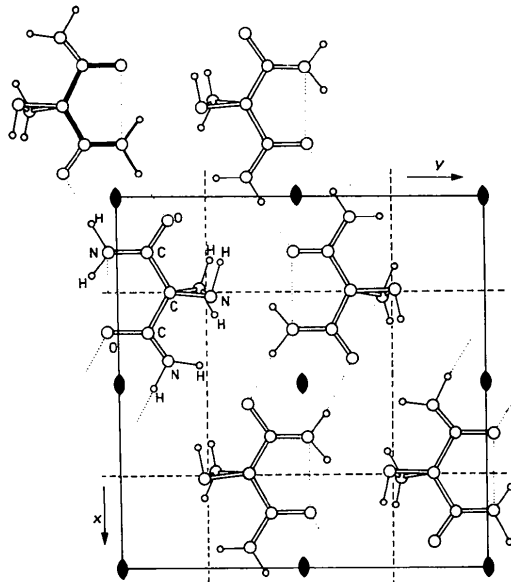


Fig. 1. A layer P in crystal form A. The fragment of a molecule used in Fig. 2 is indicated by filled bonds.

positions of Q_3 are then uniquely described by the respective glide components. Any pair QP may be characterized in the same way,

$$PQ, QP: (\bar{4})x', y'$$

$$(x', y') = (\frac{1}{4}, \frac{1}{4}); (-\frac{1}{4}, \frac{1}{4}); (-\frac{1}{4}, -\frac{1}{4}); (\frac{1}{4}, -\frac{1}{4}). \quad (3)$$

In summary, the OD groupoid family as given in the *Abstract* results. Special features are:

–For a PQ pair the first two variants of (3) on the one hand and the second two variants on the other are almost identical, because in any Q layer ‘along x is an approximate repeat vector $a/2$ ’ (Brückner, 1982, p. 2407).

–Form A is an OD structure of maximum degree of order; only one kind of triple of layers occurs (compare Fig. 3a). It may be supposed that this triple is energetically more favourable than the alternative triple.

Discussion of form B

From the hypothesis that forms A and B belong to the same family of OD structures, it follows that B contains the same layers and layer pairs as form A. There are four layers per unit cell in form B, as may be seen from the volumes of the unit cells of A and B. In order to determine possible structures in accordance with the lattice parameters given for form B, five consecutive layers $P_1P_2Q_3Q_4P_5$ are considered. P_1 and P_5 are related by the translational vector c . The projection of c along c^* has the components $x \approx \frac{1}{6}, y \approx \frac{1}{3}$ (Fig. 3b). The positions of P_2, Q_3 and Q_4 may be determined using formulae (1), (2) and (3). P_2 is

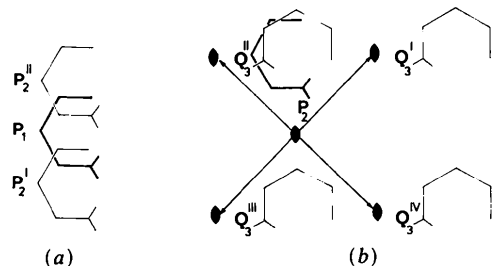


Fig. 2. Possible positions for next layers. Possible positions of (a) P_2 for fixed layer P_1 , and (b) Q_3 for fixed layer P_2 . Any layer is characterized by a fragment of one molecule.

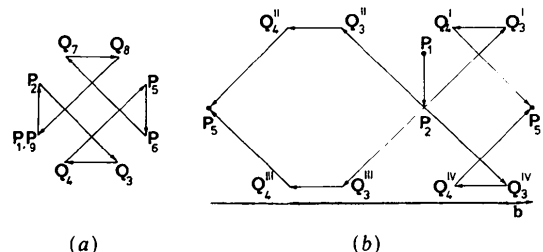


Fig. 3. Schematic representation of stacking variants. (a) Sequence of layers in form A. (b) The four possibilities of form B as concluded from the lattice constants. Any layer is characterized by the position of its origin in projection along c^* .

uniquely determined, because the alternative position is not compatible with the position of P_5 . Q_3 may have one of four positions indicated by Q_3^i , Q_3^{ii} , Q_3^{iii} , Q_3^{iv} . If Q_3 and P_5 are fixed, Q_4 is uniquely determined. Thus, only four stacking variants are in agreement with the observed lattice constants of form *B*.

The atomic coordinates of form *B* (Brückner, 1982, deposited data) show that the variants (ii) and (iii) do not exist in form *B*, whereas both the variants (i) and (iv) are present. This results because:

–it was impossible to decide between N and O atoms in the Fourier map;

–variants (i) and (iv) are almost identical and may be transformed into each other by interchanging O atoms and NH_2 groups.

More precise information on the occurrence of (i) and (iv) in form *B* could be obtained from a detailed investigation of the distribution of the intensities in reciprocal space. Possible results are, for instance:

–statistical occurrence of (i) and (iv) with approximately equal probabilities;

–alternating occurrence of (i) and (iv);

–the crystal consists of regions containing either

only (i) or only (iv). The volume of the regions of type (i) and the volume of the regions of type (iv) are about the same.

In both variants (i) and (iv) the two possible kinds of triples of layers are present. In (i) as well as in (iv) their proportion is 3:1 in favour of the triple existing in form *A* (see Fig. 3*b*).

Concluding remark. The example discussed is also of interest in OD theory. No structure with a similar stacking of layers has been found so far. The combination of pairs of layers related by a centre of symmetry and pairs of layers related by a fourfold inversion axis is rather unusual.

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Structure–Potency Relationships for Three Isomers of (±)-1,2,3-Trimethyl-4-phenyl-4-piperidinol*

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Abstract

The three isomers of the title compound, $\text{C}_{14}\text{H}_{21}\text{NO}$, are known to have propionate esters with potency rankings $\gamma > \alpha > \beta$. The present X-ray analyses have shown their configurations to be: α -base, *t*-2- CH_3 , *t*-3- CH_3 , *r*-4- C_6H_5 ; β -base, *c*-2- CH_3 , *t*-3- CH_3 , *r*-4- C_6H_5 ; γ -HCl, *t*-2- CH_3 , *c*-3- CH_3 , *r*-4- C_6H_5 , as deduced also from an independent NMR study. In the solid state, the three isomers have the piperidine ring in the chair conformation with the 1-methyl and 4-phenyl in equatorial positions. Intermolecular hydrogen bonding is present, as $\text{O}-\text{H}\cdots\text{N}'$ in the α -base and β -base structures, and as $\text{O}-\text{H}\cdots\text{Cl}\cdots\text{H}-\text{N}'$ in the γ -HCl. Comparison of the isomers of prodine, promedol alcohol, and the present compound

shows that the potency is highest for the isomers with the configuration *c*-3- CH_3 (or *c*-5- CH_3), *r*-4- C_6H_5 . Also, activity is most inhibited for the present β -2,3-dimethyl isomer, where 2- CH_3 is *cis* and 3- CH_3 is *trans* to 4- C_6H_5 . Preliminary interpretation of the structure–potency relationships indicates that the degree of potency of these analgesics may be dependent on the preferred orientations of the 4-phenyl and/or 4-hydroxyl relative to the piperidine ring. [Crystal data: α -base: $M_r = 219.33$, $Pna2_1$, $a = 10.137(1)$, $b = 11.446(1)$, $c = 10.815(1)$ Å, $V = 1254.8$ Å³, $Z = 4$, $D_m = 1.162$, $D_x = 1.161$ g cm⁻³, $F(000) = 480$, $T = 294$ K, $\lambda(\text{Cu } K\alpha_1) = 1.54056$ Å, $\mu = 5.26$ cm⁻¹, $R = 0.032$ for 1294 observed reflexions; β -base: $M_r = 219.33$, $P2_1/a$, $a = 18.434(1)$, $b = 9.391(1)$, $c = 7.445(2)$ Å, $\beta = 91.27(1)^\circ$, $V = 1288.5$ Å³, $Z = 4$, $D_m = 1.130$, $D_x = 1.130$ g cm⁻³, $F(000) = 480$, $T = 294$ K, $\lambda(\text{Cu } K\alpha_1) = 1.54056$ Å, $\mu = 5.12$ cm⁻¹, $R = 0.043$ for 1617 observed reflexions; γ -HCl: $M_r = 255.80$, $P2_1/a$, $a =$

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