

1,5-Dianilinopentane-1,3,5-trione:  
a crystal structure containing two  
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Received 28 February 2011

Accepted 9 May 2011

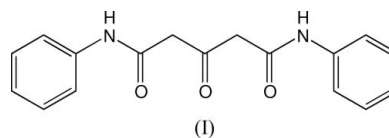
Online 24 May 2011

Single crystals of the title compound, C<sub>17</sub>H<sub>16</sub>N<sub>2</sub>O<sub>3</sub>, were obtained by gas diffusion. The observed diffraction pattern is compatible with a superposition of reflections from two monoclinic unit cells with the space group *C2/c*. The two cells share the *a* and *b* axes but not the *c* axis. Both structures contain layers parallel to (001), with molecules connected by intermolecular N—H···O=C hydrogen bonds. The bonding between adjacent layers is weak. Layer displacements result in a crystal structure containing two closely related polymorphic domains. The structure of one polymorph can be derived from the structure of the other if subsequent layers are displaced by (*a*/*4*, *b*/*4*, 0) for odd-numbered layers and by (*a*/*4*, −*b*/*4*, 0) for even-numbered layers. Three different crystals were analysed and their observed diffraction patterns were similar, showing all three crystals to contain the polymorphic domain structure.

## Comment

Polymorphism in molecular crystals is a well known phenomenon (Bernstein, 2002, 2011). However, the occurrence of two polymorphic domains in a single crystal is very rare. For organic compounds it was first reported by Freer & Kraut (1965) in crystals of D,L-homocysteine thiolactone hydrochloride, which were described as hybrids of *Pbca* and *Pbc*<sub>2</sub> polymorphs with coincidence of the unit-cell axes. More recently, Bond *et al.* (2007) showed aspirin crystals to contain intergrowths of two polymorphic domains with very similar crystal structures. Yufit *et al.* (2002) reported two polymorphs with closely related orthorhombic and monoclinic unit cells within a single crystal of 5-oxatricyclo[5.1.0.0<sup>1,3</sup>]octan-4-one, although according to Herbstein (2003) this structure is better described as a composite crystal containing an enantiomorph and a racemate rather than two polymorphs. Bats *et al.* (2005) found polymorphic domains in crystals of (*Z*)-4-bromo-*N*-

(pent-2-enyl)-*N*-(3-phenylprop-2-ynyl)benzenesulfonamide. Both polymorphs correspond to the space group *P2<sub>1</sub>/c* and have very similar lattice constants. Furthermore, a *P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>* polymorph of tetrakis(acetonitrile-*κN*)copper(I) tetrafluoroborate was reported to contain a volume fraction of 0.088 (7) of a *Pna*2<sub>1</sub> polymorph with a closely related crystal structure (Bats *et al.*, 2009). The crystal structures of all these compounds contain layers and the arrangement of the molecules in the layers is slightly different for the two polymorphs. During the structure determination of the title compound, (I), we noticed that the observed diffraction pattern could also be described by a superposition of reflections from two polymorphic domains.

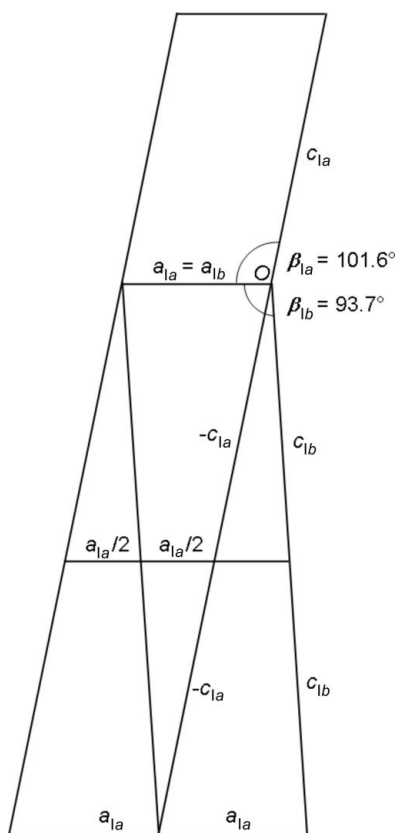


1,5-Dianilinopentane-1,3,5-trione (Junek *et al.*, 1967; Patev, 1969; Ali & El-Morsy, 1979) is also known as acetonedicarboxylic acid dianilide. In order to search for different crystallographic phases, hydrates or solvates of this compound, a polymorph screen was performed. Different crystallization methods included: (i) recrystallization from various solvents and solvent mixtures by heating and subsequent slow cooling; (ii) overlaying a solution of the compound with an antisolvent; (iii) diffusion of an antisolvent into a solution of the compound *via* the gas phase. The solvents included the most common organic solvents, *e.g.* dimethyl sulfoxide, ethers, esters and alcohols, as well as acids, bases and water. X-ray powder diffraction diagrams showed all crystalline products to correspond to the phase reported in this study.

1,5-Dianilinopentane-1,3,5-trione has a rather peculiar diffraction pattern. The observable reflections could be indexed with a *C*-centred monoclinic unit cell (cell I) with *a* = 17.6547 (5) Å, *b* = 9.8640 (3) Å, *c* = 65.5807 (15) Å and  $\beta$  = 93.733 (1)°. The reflections with even values of *h*, *k* and *l* and *h*+*k* = 4*n* had normal intensities, but reflections with odd values of *h*, *k* or *l* were extremely weak. The reflections with *h* and *k* even and *h*+*k* = 4*n*+2 were also very weak. This means that the crystal structure deviates only slightly from an average structure having a *C*-centred unit cell with dimensions *a*/*2*, *b*/*2* and *c*/*2*. The structure could easily be determined in this smaller unit cell. The resulting space group was *C2/c* and the structure had  $Z' = \frac{1}{2}$ , with the central C=O bond positioned on a twofold axis. However, the phenyl group was disordered over two possible orientations with occupancy factors of 0.5. There were unusually short intermolecular distances along the *b* direction between neighbouring phenyl groups having the same orientation. These short contacts can be avoided if neighbouring phenyl groups along the *b* direction have alternating orientations, resulting in a doubling of the length of the *b* axis. Thus, a larger unit cell is required and the occurrence of the weak reflections may result from an ordered arrangement of the phenyl groups.

For the large unit cell [cell (I)], the crystal structure could only be determined for the space group *C2*, but not for *Cm*,

<sup>1</sup> Dedicated to Dr Jürgen Glinnemann on the occasion of his 60th birthday.

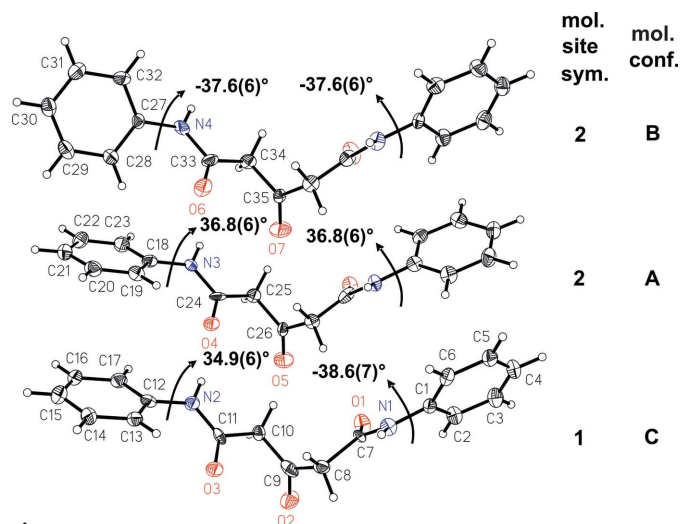


**Figure 1**  
The relationship between the unit cells of structures (Ia) and (Ib).

$C2/m$ ,  $Cc$  or  $C2/c$  (see *Refinement* section). The resulting structure had  $Z' = 8$  and all phenyl groups were disordered. Therefore, a different and possibly smaller unit cell was sought, which would represent the observed reflection pattern either through twinning or through a superposition of two closely related structures with slightly different packing arrangements. Moreover, it was observed that all reflections with  $h$  and  $k$  even and  $l$  odd were absent. This could also indicate that cell I is too large.

In order to find alternative unit cells, the following procedure was used. The  $C$ -centred unit cell corresponding to the average structure was reduced to a primitive cell. The additional weak reflections were then found to belong to four different parity groups: (a)  $h+\frac{1}{2}, k, l$ ; (b)  $h+\frac{1}{2}, k, l+\frac{1}{2}$ ; (c)  $h+\frac{1}{2}, k+\frac{1}{2}, l$ ; (d)  $h+\frac{1}{2}, k+\frac{1}{2}, l+\frac{1}{2}$ . Indexing of the strong reflections in combination with the reflections of one of the parity groups (a), (b), (c) or (d) resulted in four triclinic unit cells with two different sets of cell constants. All four cells had a short axis of  $5.0559(1) \text{ \AA}$ , which is too short to allow for an ordered arrangement of the phenyl groups. Thus, these triclinic cells were discarded.

Indexing the strong reflections, either in combination with the reflections of parity groups (b) and (d) or in combination with the reflections of parity groups (a) and (c), gave two new unit cells: (Ia) with  $a_{1a} = a_1$ ,  $b_{1a} = -b_1$  and  $c_{1a} = -(a_1 + c_1)/2$ , resulting in  $a = 17.6547(5) \text{ \AA}$ ,  $b = 9.8640(3) \text{ \AA}$ ,  $c = 33.3982(8) \text{ \AA}$  and  $\beta = 101.560(1)^\circ$ ; (Ib) with  $a_{1b} = a_1$ ,  $b_{1b} = b_1$  and  $c_{1b} = c_1/2$ , resulting in  $a = 17.6547(5) \text{ \AA}$ ,  $b = 9.8640(3) \text{ \AA}$ ,



**Figure 2**  
The molecular structure of polymorph (Ia), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. Unlabelled atoms are related to labelled atoms by a twofold rotation axis through the central  $C=O$  bond of the corresponding molecule. For the corresponding structure of polymorph (Ib), see the *Supplementary material*.

$c = 32.7904(8) \text{ \AA}$  and  $\beta = 93.733(1)^\circ$ . [For other combinations of (a), (b), (c) and (d), see below.] The observed diffraction pattern is a superposition of reflections of structures (Ia) and (Ib). The reflections of (Ia) and (Ib) with even values of  $h$  and  $k$  coincide. The latter reflections correspond to the average structure with the phenyl group equally distributed over two orientations, and thus should have the same intensities for (Ia) and (Ib). The fractional contributions of the two structures to the total scattering could be derived by refinement of a separate scale factor assigned to the reflections with odd values of  $h$  and  $k$ . Values of 0.5219(19) and 0.3817(7) were obtained, respectively, for (Ia) and (Ib). One would expect the sum of the two contributions to be equal to 1.0. The somewhat smaller value of 0.904 could mean that about 10% of the structural units are randomly disordered and therefore do not contribute to the weak reflections with odd values of  $h$  and  $k$ . Disorder could result in diffuse scattering parallel to the  $c^*$  direction. However, the long dimension of the  $c$  axis [ $c = 65.5807(15) \text{ \AA}$  for cell (I)] prevents the background area between the reflections along this direction from being observed.

The crystal structures of (Ia) and (Ib) are closely related (Fig. 1). The unit cell of (Ib) can be derived from the unit cell of (Ia) by the transformation  $a_{1b} = a_{1a}$ ,  $b_{1b} = -b_{1a}$  and  $c_{1b} = -0.5a_{1a} - c_{1a}$ . The fractional coordinates in the asymmetric unit of the two structures are related by  $x_{1b} = 0.125 + x_{1a} - 0.5z_{1a}$ ,  $y_{1b} = 0.875 - y_{1a}$  and  $z_{1b} = 0.5 - z_{1a}$ .

Refinement of the lattice constants using subsets of reflections belonging only to either setting (Ia) or setting (Ib) resulted in values which did not deviate significantly from the lattice constants derived directly from the supercell. Moreover, the reflections with contributions from both lattices showed narrow reflection profiles and no signs of splitting. Thus, all reflections fit perfectly into the supercell (I).

In both (*Ia*) and (*Ib*), the asymmetric unit contains one molecule in a general position and two half molecules, each with the central C=O bond on a twofold axis. Fig. 2 shows the molecular structure of (*Ia*) and the numbering scheme used in both structures. The molecular structure of (*Ib*) is very similar. The central 1,5-dianilino-pentane-1,3,5-trione fragments have very similar conformations in all independent molecules. For molecules in general positions, this fragment exhibits approximately twofold symmetry, while the molecules with the central C=O groups in special positions have exact twofold symmetry. For the phenyl rings, two orientations are possible, with  $C_{\text{keto}}-\text{N}-\text{C}-\text{C}_{\text{phenyl}}$  torsion angles of approximately  $-36$  or  $36^\circ$ . The molecules at general positions have nonsymmetric orientations of the two phenyl groups [torsion angles in (*Ia*):  $\text{C}7-\text{N}1-\text{C}1-\text{C}2 = -38.6 (7)^\circ$  and  $\text{C}11-\text{N}2-\text{C}12-\text{C}13 = 34.9 (6)^\circ$ ]. The two molecules with crystallographic twofold rotation symmetry differ only with respect to the orientation of the phenyl group [torsion angles in (*Ia*):  $\text{C}24-\text{N}3-\text{C}18-\text{C}19 = 36.8 (6)^\circ$  and  $\text{C}33-\text{N}4-\text{C}27-\text{C}28 = -37.6 (6)^\circ$ ] (Fig. 2).

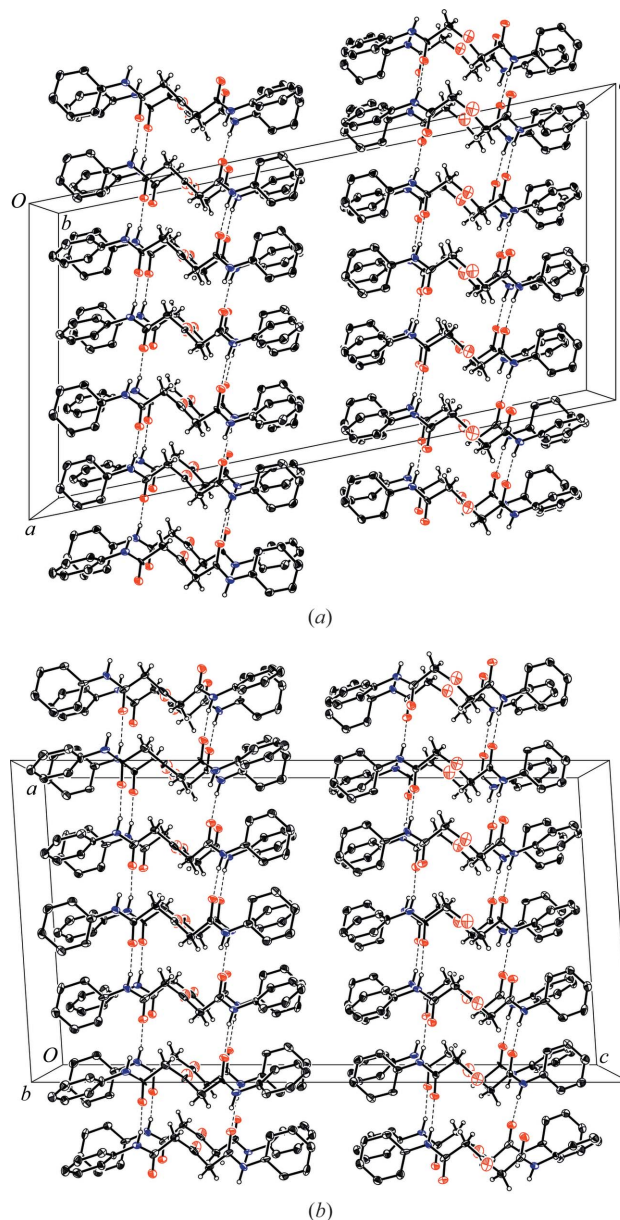
Each molecule is connected by intermolecular  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds to four neighbouring molecules (Tables 1 and 2). This results in layers parallel to the (001) plane (Fig. 3). The molecular arrangement inside a layer also shows four different additional weak intermolecular methylene-carbonyl  $\text{C}-\text{H}\cdots\text{O}$  contacts, with  $\text{H}\cdots\text{O}$  distances between 2.52 and 2.61 Å, and four different weak intermolecular phenyl-phenyl  $\text{C}-\text{H}\cdots\pi$  contacts, with  $\text{H}\cdots\text{C}_g$  distances between 2.93 and 2.97 Å ( $\text{C}_g$  represents the mid-point of the acceptor phenyl ring).

The terminal phenyl groups of each layer show a herringbone arrangement. The arrangement of the phenyl groups in the segment at  $0 < z < 0.1$  of (*Ia*) is shown in Fig. 4(*a*). The figure shows a pseudo-translation vector of  $(a/4, b/4, 0)$ . The phenyl rings in the segment at  $0.4 < z < 0.5$  form a herringbone arrangement also, but with a pseudo-translation vector of  $(a/4, -b/4, 0)$  (Fig. 4*b*).

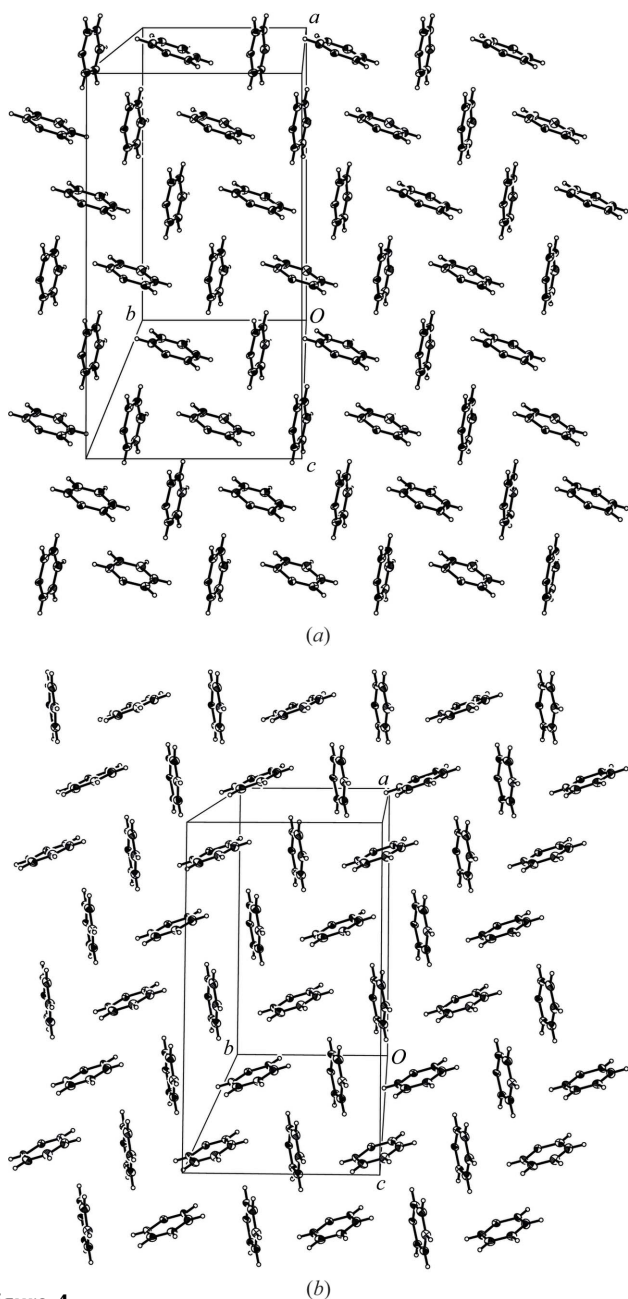
The layers in (*Ia*) and (*Ib*) are similar. In both structures, the molecules within a single layer are related by twofold rotation and screw axes and by *C*-centring. They are related to the molecules in the adjacent layers by *c*- and *n*-glide planes and inversion centres. A close comparison of the packing arrangements of (*Ia*) and (*Ib*) shows that the layer arrangement of (*Ib*) can be derived from that of (*Ia*) if the layer at  $-0.5 < z < 0.0$  is translated by  $(a/4, b/4, 0)$  with respect to the layer at  $0.0 < z < 0.5$ , and both layers are translated by  $(a/4, -b/4, 0)$  with respect to the layer at  $0.5 < z < 1.0$ . Thus, after a translation of one unit cell along the *c* axis, the origin of (*Ib*) is shifted by  $a/2$  compared with the origin of (*Ia*), in agreement with the observed unit-cell transformation.

The remarkable structure of 1,5-dianilino-pentane-1,3,5-trione can be explained in terms of the intermolecular interactions. As mentioned above, each molecule is connected to four neighbouring molecules by hydrogen bonds. The *C*(4) hydrogen-bond chains [for graph-set notation, see Bernstein *et al.* (1995)]  $-\text{N}-\text{H}\cdots\text{O}=\text{C}-\text{N}-\text{H}\cdots\text{O}=\text{C}-$  align in two different directions, *viz.*  $[110]$  and  $[1\bar{1}0]$ . Each molecule is

involved in both chain directions: if the front hydrogen bond runs along  $[110]$  (Fig. 5, black), then the back hydrogen bond runs along  $[1\bar{1}0]$  (Fig. 5, blue). Correspondingly, the CONH groups are also aligned in the  $[110]$  and  $[1\bar{1}0]$  directions. The phenyl rings cannot be coplanar with the adjacent CONH groups, because this would cause too close contacts between neighbouring phenyl groups in the  $[110]$  and  $[1\bar{1}0]$  directions. Therefore, the phenyl rings are rotated by *ca*  $\pm 36^\circ$ , which makes them either parallel to *a* or almost parallel to *b*. Each molecule has two phenyl rings, the orientations of which are independent of each other. This leads to three different molecular conformations: either both rings are parallel to *a* (Fig. 5, molecule *A*) or both rings are almost parallel to *b* (molecule



**Figure 3**  
The crystal packing of (*a*) polymorph (*Ia*) and (*b*) polymorph (*Ib*), viewed down  $[010]$ . Hydrogen bonds are represented by dotted lines and H atoms on the phenyl groups have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

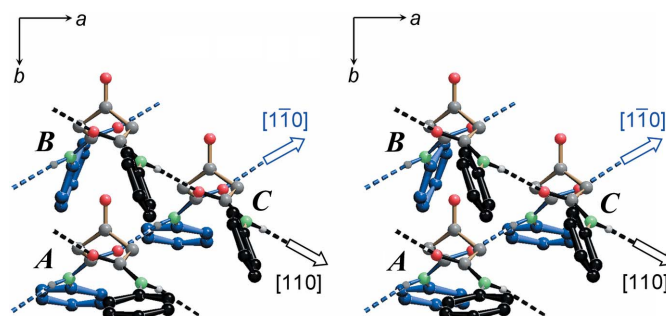


**Figure 4**  
The mutual orientations of the terminal phenyl groups in a layer of molecules of polymorph (Ia), showing (a) the section with  $0 < z < 0.1$  and (b) the section with  $0.4 < z < 0.5$ , viewed down [001]. Displacement ellipsoids are drawn at the 50% probability level.

*B*) or the rings are almost orthogonal to each other, one being parallel to *a*, the other almost parallel to *b* (molecule *C*).

In the *b* direction, the molecules are stacked on top of each other. Along the stack, the phenyl rings of neighbouring molecules are in alternating orientations (Fig. 5, molecules *A* and *B*). This arrangement results in weak intermolecular phenyl–phenyl  $C-H \cdots \pi$  interactions and thus may have a stabilizing effect on the crystal packing.

Along the hydrogen-bond chains, all the phenyl rings are in a parallel orientation because of steric requirements. If a molecule *B* (with phenyl rings almost parallel to *b*) is



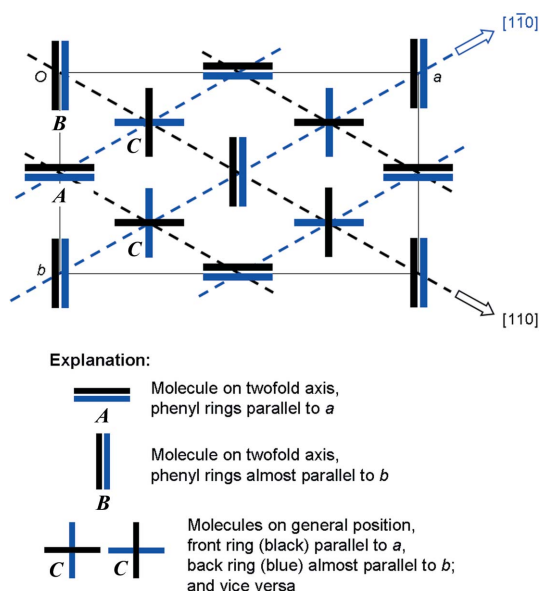
**Figure 5**  
A stereoview of the molecular conformation and hydrogen-bond network in (Ia) [which is the same for (Ib); the view direction is approximately [001]]. Molecules *A*, *B* and *C* are symmetry independent. (In the electronic version of the paper, phenyl rings in front are drawn in black and those at the back in blue.)

connected to a molecule *C* by the front hydrogen bond, the front phenyl ring of molecule *C* must also be almost parallel to *b* (Fig. 5, black). Similarly, the rear hydrogen bond from molecule *A* to molecule *C* requires the rear phenyl ring of *C* to be parallel to *a* (Fig. 5, blue). Hence, the two phenyl rings of molecule *C* must be oriented in almost orthogonal orientations. It is this hydrogen-bond pattern which is the reason that the structure contains three different molecules, *viz.* *A*, *B* and *C*, with a ratio of 1:1:2.

The hydrogen bonds form a two-dimensional network, leading to a layer of molecules parallel to (001). The surfaces of the layers are formed by the phenyl rings. The bonding between the layers is quite weak, because only van der Waals interactions are present. Indeed, an inspection of the crystal packing of (Ia) and (Ib) shows that there are no short intermolecular contacts between adjacent layers. The shortest contacts are intermolecular phenyl–phenyl  $C-H \cdots H-C$  distances of 2.53 Å in (Ia) and 2.52 Å in (Ib).

The front surface of the first layer, formed by the phenyl rings at  $0 < z < 0.1$ , exhibits a herringbone pattern in the [110] direction (Fig. 4a, black sticks in Fig. 6), because the underlying hydrogen-bond chain runs in the [110] direction. Correspondingly, the phenyl rings at the rear surface of this layer, at  $0.4 < z < 0.5$ , form a herringbone pattern in the  $[1\bar{1}0]$  direction (Fig. 4b, blue sticks in Fig. 6). Since the translation periodicity of the front hydrogen bond is  $(a/4, b/4, 0)$ , the front surface also shows a pseudo-translation vector of  $(a/4, b/4, 0)$ . At the back surface, with the phenyl rings in the segments at  $0.4 < z < 0.5$ , the pseudo-translation vector of the herringbone arrangement is  $(a/4, -b/4, 0)$ . The maximum deviation from pseudosymmetry is as small as 0.03 Å. Hence, from the positions and orientations of the phenyl rings, it cannot be deduced if they belong to a molecule of type *A* or *C* (or of type *B* or *C*, respectively). A layer translation by  $(a/4, b/4, 0)$ , or by  $(a/4, -b/4, 0)$ , respectively, would not greatly change the intermolecular contacts. However, such a translation leads to a different structure, because the interior of the layer only has a periodicity of  $(a/2, b/2, 0)$ . The surface of the layer has a higher pseudosymmetry than the layer itself, which is the reason for the disorder. A similar effect is known for pseudosymmetric




**Figure 6**

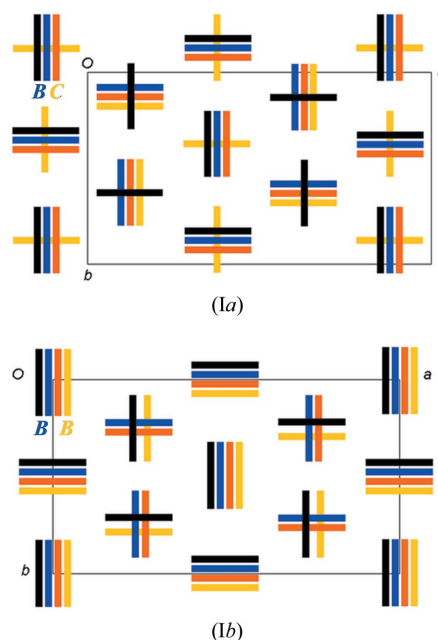
The orientation of the phenyl rings within a layer, viewed down [001]. Hydrogen bonds are drawn as dashed lines. (In the electronic version of the paper, phenyl rings in the front surface of the layer are drawn as black sticks and those in the rear surface as blue sticks.)

molecules, in that molecules with a pseudosymmetric molecular shape (*i.e.* a molecular shape close to being more symmetrical than the molecule itself) are frequently disordered in the solid state (Hörnig *et al.*, 1993).

In subsequent layers, the pattern of the front phenyl rings of the second layer (phenyl rings at  $0.5 < z < 0.6$ ) resembles the structure of the back surface of the first layer (phenyl rings at  $0.4 < z < 0.5$ ). Both have a herringbone arrangement with a pseudo-translation vector of  $(a/4, -b/4, 0)$ . There are two possible lateral positions for the second layer. If a molecule *B* is followed by another molecule *B* in the next layer, polymorph (*Ib*) is the result (bottom part of Fig. 7). If *B* is followed by *C*, polymorph (*Ia*) is formed (top part of Fig. 7). Due to the pseudosymmetry of the layer surface, both lateral positions have very similar interaction energies, which causes stacking disorder. Apparently, the stacking sequence is not completely random; there are ordered domains of polymorphs (*Ia*) and (*Ib*) and disordered regions of short-range stacking order.

It can be assumed that the distribution of the individual domains in the crystal is not correlated. The observed intensities are then the sum of the contributions from the two polymorphs. The structures of the two polymorphs have to be refined separately, as applied in this study. A refinement of the complete structure in supercell I is not realistic.

The structures of (*Ia*) and (*Ib*) were derived by indexing the strong reflections, either in combination with reflections of parity groups (*b*) and (*d*) or in combination with reflections of parity groups (*a*) and (*c*). A search for other possible unit cells which could describe the observed reflection pattern resulted in two different twinned triclinic cells. Indexing of the strong reflections, either in combination with reflections from parity groups (*a*) and (*b*) or from (*c*) and (*d*), resulted in two unit


**Figure 7**

The orientation of phenyl rings in two subsequent layers of polymorphs (*Ia*) (top) and (*Ib*) (bottom). 'B' and 'C' denote molecules contacting at the interface between the two layers.

cells (*Ic*) with identical cell constants:  $a = 5.0559(1) \text{ \AA}$ ,  $b = 8.6146(3) \text{ \AA}$ ,  $c = 65.4882(15) \text{ \AA}$ ,  $\alpha = 91.788(1)^\circ$ ,  $\beta = 91.163(1)^\circ$  and  $\gamma = 91.628(1)^\circ$ . Structure determination in  $P\bar{1}$  [15564 reflections, 776 parameters,  $wR(F^2) = 0.332$ ,  $R[F^2 > 2\sigma(F^2)] = 0.100$ ,  $\Delta\rho_{\text{max}} = 0.66 \text{ e \AA}^{-3}$ ] resulted in an asymmetric unit with four independent molecules. Six of the eight phenyl groups were disordered. The short dimension of the *a* axis resulted in four short phenyl–phenyl C...C distances of 2.64–2.78 Å. Thus, cell (*Ic*) can be discarded.

Similarly, indexing the strong reflections either in combination with reflections from parity groups (*a*) and (*d*) or from (*b*) and (*c*) resulted in two cells (*Id*) with identical cell constants:  $a = 9.8640(3) \text{ \AA}$ ,  $b = 10.1117(3) \text{ \AA}$ ,  $c = 32.8926(8) \text{ \AA}$ ,  $\alpha = 91.370(1)^\circ$ ,  $\beta = 94.300(1)^\circ$  and  $\gamma = 119.193(1)^\circ$ . Structure determination in  $P\bar{1}$  [15639 reflections, 766 parameters,  $wR(F^2) = 0.277$ ,  $R[F^2 > 2\sigma(F^2)] = 0.069$ ,  $\Delta\rho_{\text{max}} = 0.85 \text{ e \AA}^{-3}$ ] again resulted in four independent molecules in the asymmetric unit. Four of the eight phenyl groups were disordered, with an occupancy ratio of approximately 0.875:0.125.

The crystal structures of the settings (*I*), (*Ia*), (*Ib*), (*Ic*) and (*Id*) are essentially similar. The structures differ only in the amount of disorder of the phenyl groups and the number of

independent molecules. A criterion for the most likely structure would be the smallest value of  $Z'$ , the smallest amount of disorder and the lowest  $R$  values. Thus, a superposition of structures (Ia) and (Ib) is clearly preferred over the other three possibilities. The crystal structures of (Ia) and (Ib) are polymorphs. Thus, the crystal is an intergrowth of two polymorphs. Measurements of two additional crystals of 1,5-dianilinopentane-1,3,5-trione showed diffraction patterns similar to that observed in this study. All three crystals had the polymorphic domain structure. The data set with the lowest  $R$  values was used for the present work.

## Experimental

1,5-Dianilinopentane-1,3,5-trione, (I), was synthesized according to the procedure of Ali & El-Morsy (1979) by heating a mixture of acetonedicarboxylic acid diethyl ester (20.2 g), aniline (20 g) and pyridine (30 ml) to 403 K for 4 h. For extraction, the hot solution was poured into concentrated hydrochloric acid and ice. Single crystals of (I) were grown by gas diffusion. The compound (30 mg) was dissolved in acetone in a small flask, which was placed inside a larger flask. Diisopropyl ether (2 ml) was poured into the larger container, which was then sealed and left to stand for crystallization. Colourless single crystals of (I) were obtained after 3 d. Data collection was performed at 167 K. No phase transition was observed on cooling the crystal from room temperature to 167 K.

### Polymorph (Ia)

#### Crystal data

$C_{17}H_{16}N_2O_3$	$V = 5698.2 (3) \text{ \AA}^3$
$M_r = 296.32$	$Z = 16$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 17.6547 (5) \text{ \AA}$	$\mu = 0.10 \text{ mm}^{-1}$
$b = 9.8640 (3) \text{ \AA}$	$T = 167 \text{ K}$
$c = 33.3982 (8) \text{ \AA}$	$0.60 \times 0.16 \times 0.16 \text{ mm}$
$\beta = 101.560 (1)^\circ$	

#### Data collection

Siemens SMART 1K CCD area-detector diffractometer	41943 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2000)	8099 independent reflections
$T_{\min} = 0.924$ , $T_{\max} = 0.985$	1972 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.141$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.048$	399 parameters
$wR(F^2) = 0.111$	H-atom parameters constrained
$S = 0.81$	$\Delta\rho_{\text{max}} = 0.29 \text{ e \AA}^{-3}$
8099 reflections	$\Delta\rho_{\text{min}} = -0.26 \text{ e \AA}^{-3}$

**Table 1**

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ) for polymorph (Ia).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N1-H1A\cdots O6^i$	0.88	2.08	2.940 (5)	168
$N2-H2B\cdots O4$	0.88	2.07	2.929 (5)	166
$N3-H3B\cdots O3^{ii}$	0.88	2.08	2.944 (5)	167
$N4-H4B\cdots O1^{iii}$	0.88	2.07	2.938 (5)	168

Symmetry codes: (i)  $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$ ; (ii)  $x - \frac{1}{2}, y - \frac{1}{2}, z$ ; (iii)  $-x, y - 1, -z + \frac{1}{2}$ .

### Polymorph (Ib)

#### Crystal data

$C_{17}H_{16}N_2O_3$	$V = 5698.2 (3) \text{ \AA}^3$
$M_r = 296.32$	$Z = 16$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 17.6547 (5) \text{ \AA}$	$\mu = 0.10 \text{ mm}^{-1}$
$b = 9.8640 (3) \text{ \AA}$	$T = 167 \text{ K}$
$c = 32.7904 (8) \text{ \AA}$	$0.60 \times 0.16 \times 0.16 \text{ mm}$
$\beta = 93.733 (1)^\circ$	

#### Data collection

Siemens SMART 1K CCD area-detector diffractometer	41837 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2000)	8093 independent reflections
$T_{\min} = 0.924$ , $T_{\max} = 0.985$	1858 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.176$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.052$	399 parameters
$wR(F^2) = 0.115$	H-atom parameters constrained
$S = 0.83$	$\Delta\rho_{\text{max}} = 0.31 \text{ e \AA}^{-3}$
8093 reflections	$\Delta\rho_{\text{min}} = -0.28 \text{ e \AA}^{-3}$

Reflections were measured using a  $C$ -centred monoclinic unit cell, with  $a = 17.6547 (5) \text{ \AA}$ ,  $b = 9.8640 (3) \text{ \AA}$ ,  $c = 65.5807 (15) \text{ \AA}$  and  $\beta = 93.733 (1)^\circ$ . A possible crystal structure could be determined for the space group  $C2$ . The resulting structure had  $Z' = 8$ , with all phenyl groups disordered over two possible orientations. The unit cell of model (Ia) was derived from the original data by the transformation  $a_{1a} = a$ ,  $b_{1a} = -b$  and  $c_{1a} = -(a + c)/2$ . The unit cell of model (Ib) was derived from the original data by the transformation  $a_{1b} = a$ ,  $b_{1b} = b$  and  $c_{1b} = c/2$ . The same transformation was used to transform the Miller indices  $hkl$ . Structure determination of both (Ia) and (Ib) was successful in the space group  $C2/c$ . The H atoms were positioned geometrically and treated as riding, with nonplanar C—H = 0.99  $\text{\AA}$ , planar C—H = 0.95  $\text{\AA}$  and N—H = 0.88  $\text{\AA}$ , and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$ . The structure factors for reflections with even values of  $h$  were multiplied by 0.522 [structure (Ia)] or by 0.382 [structure (Ib)].

Reflections with even values of  $h$  and  $k$  originate from the average structure and have normal intensities for  $h+k = 4n$ , but are almost absent for  $h+k = 4n+2$ . Reflections with odd values of  $h$  and  $k$  depend only on the relative orientations of the terminal phenyl groups. Therefore, these reflections are rather weak. Approximately 75% of all reflections are weak, resulting in a low ratio of observed to unique reflections. Consequently, the  $R_{\text{int}}$  values are rather large [0.141 for (Ia) and 0.176 for (Ib)]. Based only on the observed reflections with  $I > 2\sigma(I)$ , the  $R_{\text{int}}$  value is 0.054 for (Ia) and 0.064 for (Ib).

Analysis of the variances for the reflections employed in the refinements showed the average value of  $F_o^2/F_c^2$  to be larger than the expected value of 1.0 for the very weak reflections with  $F_c < 0.005I_{c,\text{max}}$ . This may result from inconsistencies in the background estimation of the weakest reflections due to the long dimension of the

**Table 2**

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ) for polymorph (Ib).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N1-H1A\cdots O6^i$	0.88	2.07	2.936 (5)	168
$N2-H2B\cdots O4$	0.88	2.06	2.922 (5)	168
$N3-H3B\cdots O3^{ii}$	0.88	2.09	2.952 (5)	165
$N4-H4B\cdots O1^{iii}$	0.88	2.08	2.942 (5)	167

Symmetry codes: (i)  $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$ ; (ii)  $x - \frac{1}{2}, y + \frac{1}{2}, z$ ; (iii)  $-x, y + 1, -z + \frac{1}{2}$ .

*c* axis. As only the weakest reflections were involved, the refined atomic parameters were not affected.

For both polymorphs, data collection: *SMART* (Siemens, 1995); cell refinement: *SAINTE* (Siemens, 1995); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

The authors thank Drs Carsten Plüg and Hans Joachim Metz (Clariant GmbH, Frankfurt am Main) for the supply of the raw material, and Clariant GmbH, Germany, for financial support.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG3256). Services for accessing these data are described at the back of the journal.

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