

3-Nitrobenzaldehyde isonicotinoyl-hydrazone monohydrate redetermined at 120 K: sheets built from O—H...O, O—H...N, N—H...O and C—H...O hydrogen bonds

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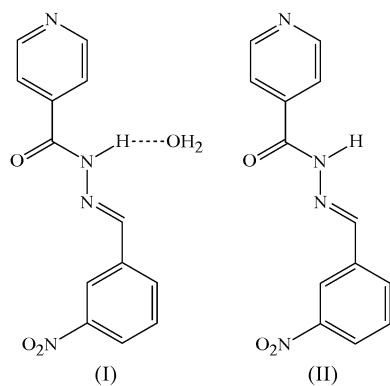
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In the title compound, C₁₃H₁₀N₄O₃·H₂O, the molecular components are linked into complex sheets by a combination of four types of hydrogen bonds.

Comment

The structure of the title compound, (I), has recently been determined using diffraction data measured at 294 K (Guo *et al.*, 2006). Although a number of hydrogen bonds were identified and listed in this report, no indication of their action was given beyond the rather terse comment that the water of crystallization interacts with the organic molecules through hydrogen bonds. We report here a redetermination of the structure of (I) from diffraction data collected at 120 K,



undertaken as part of a more general study of isonicotinoyl-hydrazones (Wardell, de Souza, Ferreira *et al.*, 2005; Wardell, de Souza, Wardell *et al.*, 2005; Wardell *et al.*, 2006; Low *et al.*,

2006) and we provide a full description of the supramolecular aggregation, along with a brief comparison of the crystal structure of this monohydrate, obtained by crystallization of the anhydrous form from ethanol, with that of the anhydrous compound, (II), crystals of which were obtained from a solution in methanol (Wardell, de Souza, Wardell *et al.*, 2005).

The space group and unit-cell dimensions at 120 and 294 K indicate that no phase change occurs between these temperatures, although we note a marked difference between the values of *b* at these two temperatures, while the value of *c* is in fact larger at 120 K than that reported at 294 K (Guo *et*

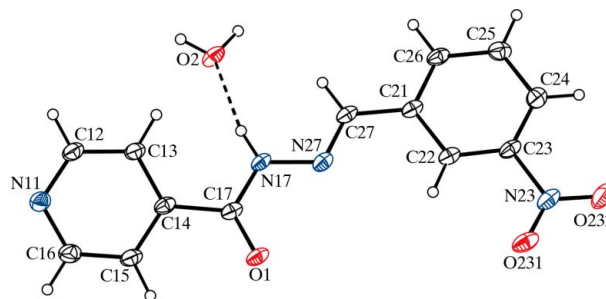


Figure 1

The independent molecular components of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

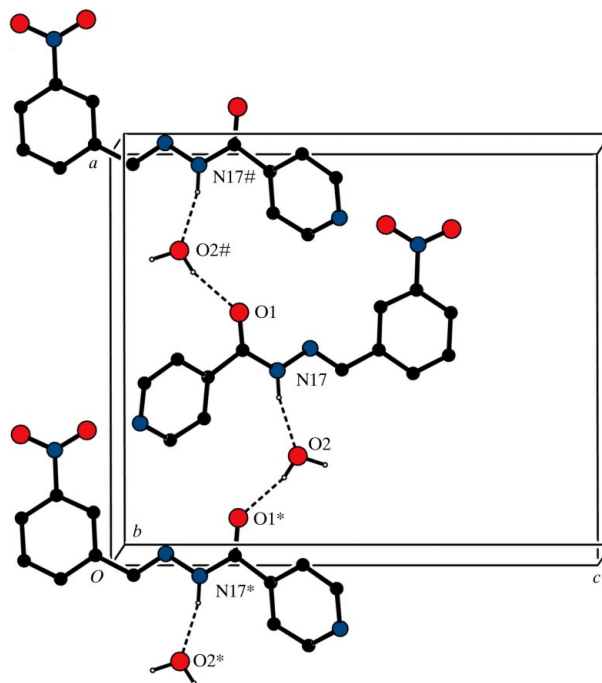


Figure 2

Part of the crystal structure of compound (I), showing the formation of a hydrogen-bonded C₂(6) chain along [100]. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(-\frac{1}{2} + x, y, \frac{1}{2} - z)$ and $(\frac{1}{2} + x, y, \frac{1}{2} - z)$, respectively.

al., 2006). The conformation of the organic component, as defined by the leading torsion angles (Table 1), shows a significant twist about the C14–C17 bond, removing the isonicotinoyl ring from the plane of the central spacer unit, and a modest rotation of the nitro group around the C23–N23

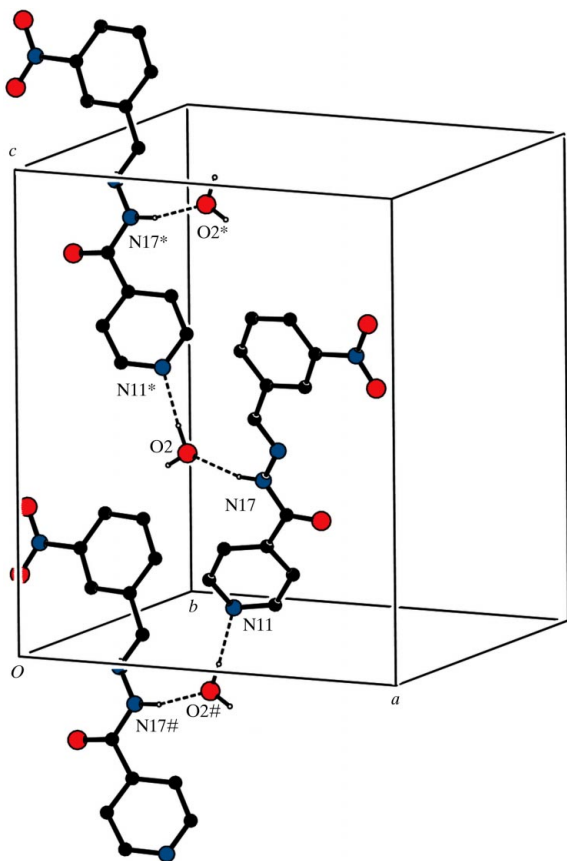


Figure 3
Part of the crystal structure of compound (I), showing the formation of a hydrogen-bonded $C_2^2(9)$ chain along [001]. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(\frac{1}{2} - x, 1 - y, \frac{1}{2} + z)$ and $(\frac{1}{2} - x, 1 - y, -\frac{1}{2} + z)$, respectively.

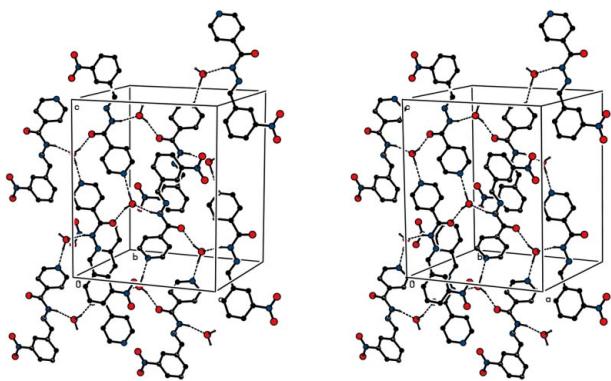


Figure 4
A stereoview of part of the crystal structure of compound (I), showing the formation of a hydrogen-bonded sheet parallel to (010). For the sake of clarity, H atoms bonded to C atoms have been omitted.

bond, taking it away from the plane of the adjacent aryl ring. We note that the molecular conformation was not mentioned in the earlier report on (I) (Guo *et al.*, 2006).

The independent molecular components are linked into sheets by four structurally significant hydrogen bonds, one each of types O–H···O, O–H···N, N–H···O and C–H···O (Table 2). These correspond with the intermolecular interactions reported earlier, although comparison is not eased by the unsystematic atom labelling adopted in the earlier report. There is an N–H···O hydrogen bond within the selected asymmetric unit (Fig. 1), and the formation of the hydrogen-bonded sheet is readily analysed in terms of two simple substructures, each one-dimensional. In the first of these substructures, water atom O2 at (x, y, z) acts as a hydrogen-bond donor, *via* atom H2A, to carbonyl atom O1 at $(-\frac{1}{2} + x, y, \frac{1}{2} - z)$, so forming a $C_2^2(6)$ (Bernstein *et al.*, 1995) chain running parallel to the [100] direction and generated by the *a*-glide plane at $z = \frac{1}{4}$ (Fig. 2). In the second substructure, water atom O2 at (x, y, z) acts as a hydrogen-bond donor, this time *via* atom H2B, to pyridyl atom N11 at $(\frac{1}{2} - x, 1 - y, \frac{1}{2} + z)$, so forming a $C_2^2(9)$ chain running parallel to the [001] direction and generated by the 2_1 screw axis along $(\frac{1}{4}, \frac{1}{2}, z)$ (Fig. 3). The combination of these two motifs then generates a sheet parallel to (010) lying in the domain $0.28 < y < 0.72$ (Fig. 4). The sheet formation is modestly reinforced by the C–H···O hydrogen bond. A second sheet containing 2_1 screw axes at $y = 0$ lies in the domain $-0.22 < y < 0.22$, but there are no direction-specific interactions between adjacent sheets. In particular, C–H··· π hydrogen bonds and π – π stacking interactions are absent.

Although the original report on compound (I) (Guo *et al.*, 2006) gave no descriptive analysis of the actions of the hydrogen bonds, it did contain a packing diagram. However, this diagram shows an edge-on view of several (010) sheets, such that it is not possible, in the absence of any descriptive text, to discern from this diagram whether the supramolecular structure is actually composed of chains or of sheets.

In the structure of the anhydrous compound, (II), which crystallizes in the space group $P2_1/c$, the molecules are again linked into sheets. However, as the strong hydrogen bonds of types O–H···O and N–H···O are both absent, their place is taken by the less favourable N–H···N and C–H···N types, along with a C–H···O hydrogen bond.

Experimental

The anhydrous compound, (II), was obtained as described previously (Wardell, de Souza, Wardell *et al.*, 2005). The title compound, (I), was obtained by slow evaporation of a solution of (II) in reagent grade ethanol (ethanol–water, 97:3 *v/v*).

Crystal data

$C_{13}H_{10}N_4O_3 \cdot H_2O$
 $M_r = 288.27$
Orthorhombic, $Pbca$
 $a = 13.3271$ (5) Å
 $b = 12.7054$ (5) Å
 $c = 15.7748$ (6) Å
 $V = 2671.09$ (18) Å³

$Z = 8$
 $D_x = 1.434$ Mg m⁻³
Mo $K\alpha$ radiation
 $\mu = 0.11$ mm⁻¹
 $T = 120$ (2) K
Plate, colourless
 $0.24 \times 0.20 \times 0.04$ mm

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
 $T_{\min} = 0.947$, $T_{\max} = 0.996$

25385 measured reflections
 3036 independent reflections
 2037 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.077$
 $\theta_{\text{max}} = 27.5^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.053$
 $wR(F^2) = 0.155$
 $S = 1.14$
 3036 reflections
 191 parameters
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0547P)^2 + 1.8808P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.23 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.23 \text{ e } \text{\AA}^{-3}$
 Extinction correction: SHELXL97 (Sheldrick, 1997)
 Extinction coefficient: 0.0056 (11)

Table 1

Selected torsion angles ($^\circ$).

C13–C14–C17–N17	–22.6 (3)	N17–N27–C27–C21	–179.87 (19)
C14–C17–N17–N27	176.80 (18)	N27–C27–C21–C22	2.1 (3)
C17–N17–N27–C27	179.2 (2)	C22–C23–N23–O231	–8.2 (3)

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N17–H17 \cdots O2	0.88	2.00	2.865 (2)	166
O2–H2A \cdots O1 ⁱ	0.83	1.99	2.798 (2)	164
O2–H2B \cdots N11 ⁱⁱ	0.93	1.93	2.860 (3)	177
C25–H25 \cdots O232 ⁱⁱⁱ	0.95	2.35	3.195 (3)	148

Symmetry codes: (i) $x - \frac{1}{2}, y, -z + \frac{1}{2}$; (ii) $-x + \frac{1}{2}, -y + 1, z + \frac{1}{2}$; (iii) $x - \frac{1}{2}, y, -z + \frac{3}{2}$.

The space group $Pbca$ was uniquely assigned from the systematic absences. All H atoms were located in difference maps and then treated as riding atoms, with distances C–H = 0.95 Å, N–H = 0.88 Å and O–H = 0.83–0.93 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,N,O})$.

Data collection: COLLECT (Nonius, 1999); cell refinement: DENZO (Otwinowski & Minor, 1997) and COLLECT; data reduction: DENZO and COLLECT; program(s) used to solve structure: OSCAIL (McArdle, 2003) and SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: OSCAIL and SHELXL97 (Sheldrick, 1997); molecular graphics: PLATON (Spek, 2003); software used to prepare material for publication: SHELXL97 and PRPKAPPA (Ferguson, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3078). Services for accessing these data are described at the back of the journal.

References

- Bernstein, J., Davis, R. E., Shimon, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
 Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.
 Guo, M.-J., Sun, J.-C., Jing, Z.-L., Yu, M. & Chen, X. (2006). *Acta Cryst.* **E62**, o820–o821.
 Low, J. N., Wardell, S. M. S. V., de Souza, M. V. N., Wardell, J. L. & Glidewell, C. (2006). *Acta Cryst.* **C62**, o444–o446.
 McArdle, P. (2003). *OSCAIL for Windows*. Version 10. Crystallography Centre, Chemistry Department, NUI Galway, Ireland.
 Nonius (1999). *COLLECT*. Nonius BV, Delft, The Netherlands.
 Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
 Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
 Sheldrick, G. M. (2003). *SADABS*. Version 2.10. University of Göttingen, Germany.
 Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
 Wardell, S. M. S. V., de Souza, M. V. N., Ferreira, M. de L., Vasconcelos, T. R. A., Low, J. N. & Glidewell, C. (2005). *Acta Cryst.* **C61**, o617–o620.
 Wardell, S. M. S. V., de Souza, M. V. N., Wardell, J. L., Low, J. N. & Glidewell, C. (2005). *Acta Cryst.* **C61**, o683–o689.
 Wardell, S. M. S. V., de Souza, M. V. N., Wardell, J. L., Low, J. N. & Glidewell, C. (2006). *Acta Cryst.* **E62**, o3361–o3363.