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4-Cyanobenzaldehyde isonicotinoylhydrazone monohydrate: a three-dimensional hydrogen-bonded framework structure

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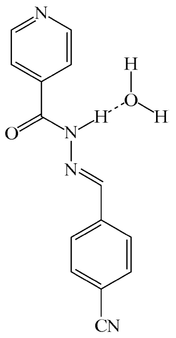
In the title compound, $C_{14}H_{10}N_4O\cdot H_2O$, the molecular components are linked into a three-dimensional framework by three hydrogen bonds, one each of the O—H···O, O—H···N and N—H···O types, weakly augmented by two C—H···O hydrogen bonds.

Comment

As part of a more general study of isonicotinoylhydrazones (Wardell, de Souza, Ferreira *et al.*, 2005; Wardell, de Souza, Wardell *et al.*, 2005; Wardell *et al.*, 2006; Low *et al.*, 2006), we report here the molecular and supramolecular structure of the title compound, (I) (Fig. 1), which was crystallized from damp ethanol as a stoichiometric monohydrate.



(I)

The central spacer unit of the hydrazone component, between atoms C14 and C21 (Fig. 1), is effectively planar with an all-*trans* extended-chain conformation, as shown by the key torsion angles (Table 1); the two rings, on the other hand, are each rotated out of this plane, so that the hydrazone molecules have no internal symmetry and thus are chiral. While the bulk sample is racemic, in the absence of any inversion twinning, each crystal contains only a single enantiomer.

Within the selected asymmetric unit, the two independent molecular components are linked by an almost linear N—H···O hydrogen bond, weakly augmented by a C—H···O hydrogen bond (Fig. 1 and Table 2). These bimolecular units are then linked into a three-dimensional framework by one O—H···N and one O—H···O hydrogen bond, whose action may be weakly augmented by a second C—H···O hydrogen bond, although this augmentation is not essential to the framework formation. The formation of the framework is readily analysed in terms of three one-dimensional substructures, one formed by the inter-aggregate O—H···O hydrogen bond, one formed by the inter-aggregate O—H···N hydrogen bond and one involving both of these interactions. For the sake of simplicity, we shall omit any further consideration of the C—H···O hydrogen bonds, which are both likely to be weak, and which do not influence the overall dimensionality of the supramolecular structure.

In the first substructure, water atom O2 at (x, y, z) acts as a hydrogen-bond donor, *via* H2*A*, to carbonyl atom O1 at ($1 - x$, $-\frac{1}{2} + y$, $\frac{1}{2} - z$), so forming a $C_2^2(6)$ (Bernstein *et al.*, 1995) chain running parallel to the [010] direction and generated by the 2_1 screw axis along ($\frac{1}{2}$, y, $\frac{1}{4}$) (Fig. 2). In the second substructure, water atom O2 at (x, y, z) acts as a hydrogen-bond donor, this time *via* H2*B*, to pyridyl atom N11 at ($\frac{3}{2} - x$, $1 - y$, $\frac{1}{2} + z$), so forming a $C_2^2(9)$ chain running parallel to the [001] direction

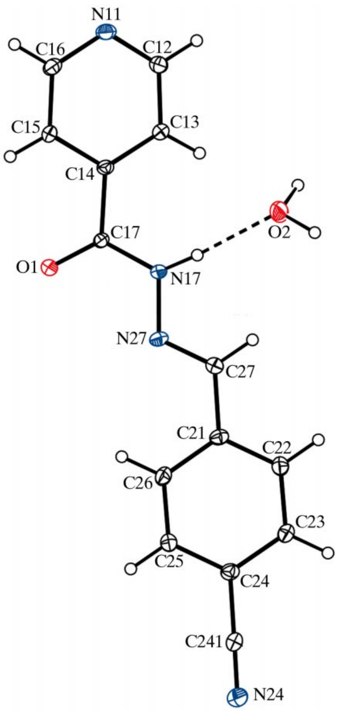


Figure 1
The independent molecular components of compound (I), showing the atom-labelling scheme and the N—H···O hydrogen bond within the selected asymmetric unit. Displacement ellipsoids are drawn at the 30% probability level.

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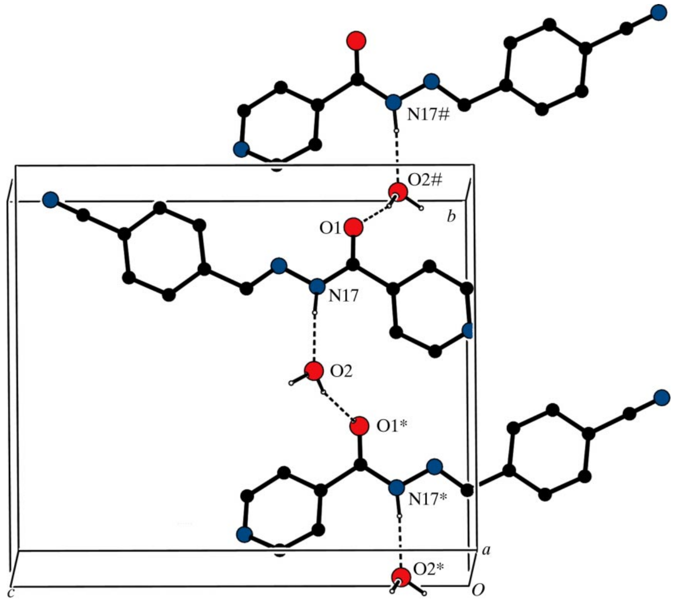

Figure 2
Part of the crystal structure of compound (I), showing the formation of a $C_2^2(6)$ chain along [010] built from N—H···O and O—H···O hydrogen bonds only. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(1 - x, -\frac{1}{2} + y, \frac{1}{2} - z)$ and $(1 - x, \frac{1}{2} + y, \frac{1}{2} - z)$, respectively.

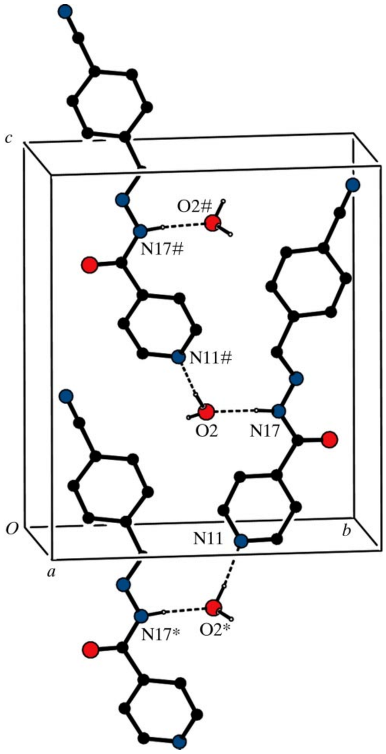

Figure 3
Part of the crystal structure of compound (I), showing the formation of a $C_2^2(9)$ chain along [001] built from N—H···O and O—H···N hydrogen bonds only. For the sake of clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry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

and generated by the 2_1 screw axis along $(\frac{3}{4}, \frac{1}{2}, z)$ (Fig. 3). Each of these two chains involves only one type of inter-aggregate hydrogen bond; the alternation of the two types of inter-aggregate hydrogen bond generates a $C_4^4(15)$ chain running parallel to the [100] direction (Fig. 4). The combination of the two chain motifs, along [100], [010] and [001], is sufficient to link all the molecules into a single three-dimensional framework structure.

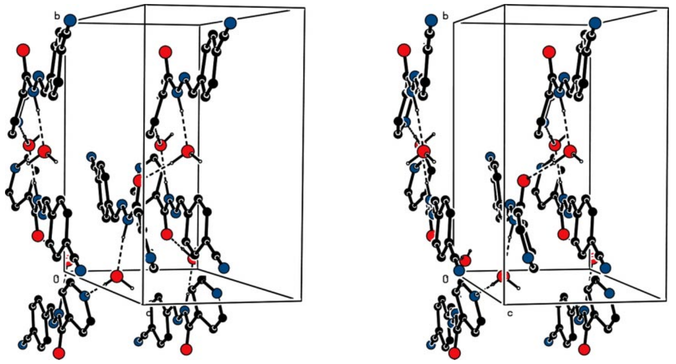

Figure 4
A stereoview of part of the crystal structure of compound (I), showing the formation of a $C_4^4(15)$ chain along [100] built from N—H···O, O—H···O and O—H···N hydrogen bonds. For the sake of clarity, H atoms bonded to C atoms have been omitted.

Experimental

A mixture of 4-cyanobenzaldehyde and isonicotinoylhydrazine (10 mmol of each) in tetrahydrofuran (20 ml) was heated under reflux until thin-layer chromatography (on silica gel, with a chloroform/methanol mixture as eluant) indicated complete reaction (*ca* 4 h reaction time). The solution was cooled and the solvent was removed under reduced pressure; the residue was washed successively with cold ethanol and then diethyl ether, and the resulting solid product was recrystallized from reagent-grade ethanol (ethanol/water, 97:3 *v*/*v*) to give crystals of the monohydrate (I) suitable for single-crystal X-ray diffraction (yield 76%; m.p. 498–499 K). GC/MS *m*/*z* 250 $[M]^+$. NMR (DMSO-d_6): δ(H) 7.83 (2H, *d*, *J* = 5.5 Hz, H13 and H15), 7.94 (4H, *m*, H22, H23, H25 and H26), 8.52 (1H, *s*, N=C—H), 8.80 (2H, *d*, *J* = 5.5 Hz, H12 and H16), 12.31 (1H, *s*, NH); δ(C) 161.9, 150.4, 147.0, 140.2, 138.4, 132.8, 127.8, 121.5, 118.6, 112.2. IR (KBr pellets, cm^{-1}): 3163 (NH), 2223 (CN), 1668 (C=O).

Crystal data

$C_{14}H_{10}N_4O\cdot H_2O$
$M_r = 268.28$
Orthorhombic, $P2_12_12_1$
$a = 6.9692$ (2) Å
$b = 12.3802$ (5) Å
$c = 14.5513$ (7) Å
$V = 1255.49$ (9) Å^3
$Z = 4$
$D_x = 1.419$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.10$ mm^{-1}
$T = 120$ (2) K
Needle, colourless
0.62 × 0.04 × 0.03 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{\min} = 0.956$, $T_{\max} = 0.997$
14838 measured reflections
1664 independent reflections
1437 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.069$
$\theta_{\max} = 27.5°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.107$
$S = 1.06$
1664 reflections
181 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0426P)^2 + 0.6011P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.25$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ e Å^{-3}

Table 1
Selected torsion angles (°).

C13—C14—C17—N17	28.8 (3)	N17—N27—C27—C21	179.9 (2)
C14—C17—N17—N27	176.7 (2)	N27—C27—C21—C22	168.0 (3)
C17—N17—N27—C27	179.0 (2)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N17—H17···O2	0.90	1.95	2.845 (3)	174
O2—H2*A*···O1^{i}	0.95	1.94	2.858 (3)	162
O2—H2*B*···N11^{ii}	0.95	1.85	2.801 (3)	174
C13—H13···O2	0.95	2.44	3.122 (3)	129
C13—H13···O1^{i}	0.95	2.51	3.243 (3)	134

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

The space group $P2_12_12_1$ was uniquely assigned from the systematic absences. All H atoms were located in difference maps and then treated as riding atoms. H atoms bonded to C or N atoms were assigned C—H distances of 0.95 Å and N—H distances of 0.90 Å [U_{iso}(H) = 1.2U_{eq}(C,N)]; H atoms bonded to O atoms were permitted to ride at the positions derived from the difference maps, with O—H distances of 0.95 Å and U_{iso}(H) values of 1.5U_{eq}(O). In the absence of significant resonance scattering it was not possible to establish the absolute configuration of the molecules in the crystal selected for data collection, although this configuration has no chemical significance; accordingly, the Friedel equivalent reflections were merged prior to the final refinements.

Data collection: *COLLECT* (Hooft, 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: AV3063). Services for accessing these data are described at the back of the journal.

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