organic compounds

2,4-Dimethylbenzaldehyde isonicotinoylhydrazone trihydrate: a three-dimensional hydrogen-bonded framework structure

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In the title compound, $C_{15}H_{15}N_3O\cdot 3H_2O$, two of the three water molecules exhibit disorder. The molecular components are linked into a three-dimensional framework by a combination of N—H⋯O, O—H⋯N and O—H⋯O hydrogen bonds.

Comment

We report here the structure of the title compound, (I), which is a stoichiometric trihydrate (Fig. 1), and we compare the supramolecular aggregation in (I) with that in the analogous compounds (II), which crystallizes in an anhydrous form (Wardell, de Souza, Ferreira *et al.*, 2005), and (III), which crystallizes as a stoichiometric monohydrate (Wardell, de Souza, Wardell *et al.*, 2005).
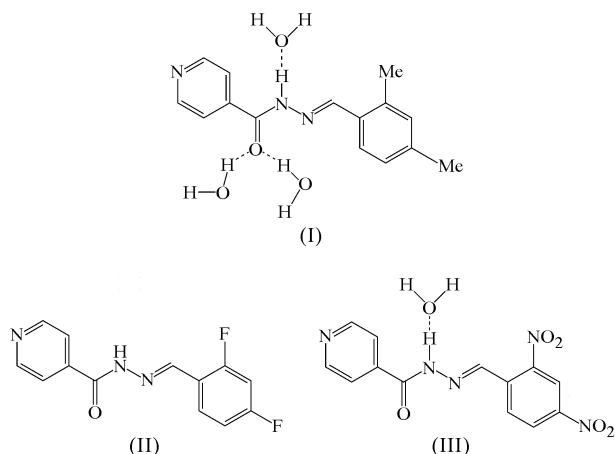
The conformation of (I) is very similar to those of (II) and (III). The central spacer unit is nearly coplanar with the

substituted phenyl ring, with only the pyridyl ring significantly twisted away from coplanarity with the remainder of the molecule (Table 1). The bond lengths and angles show no unexpected features.

In two of the three water molecules in the structure of (I), *viz.* those containing atoms O2 and O3, the H atoms exhibit some disorder. This was modelled in each molecule in terms of one hydrogen site of full occupancy (labelled H2A and H3A) and two others each of 0.5 occupancy (labelled H2B/H2C and H3B/H3C). This disorder materially complicates the analysis of the supramolecular aggregation and, for the sake of convenience, we consider first the effect of those hydrogen bonds involving H-atom sites of unit occupancy, and then the disordered H-atom sites.

Within the selected asymmetric unit (Fig. 1) there are three hydrogen bonds, two of O—H⋯O type and one of N—H⋯O type, all involving fully occupied H-atom sites (Table 2). Two further hydrogen bonds with full-occupancy H atoms then link these aggregates into a chain of edge-fused rings. Water atom O2 at (x, y, z) acts as hydrogen-bond donor, *via* atom H2A, to water atom O4 at $(-1 + x, y, z)$, so generating by translation a $C_2^2(8)$ (Bernstein *et al.*, 1995) chain running parallel to the [100] direction. At the same time, water atom O4 at (x, y, z) acts as hydrogen-bond donor to ring atom N11 at $(1 - x, 2 - y, 2 - z)$, so forming by inversion an $R_4^4(18)$ ring centred at
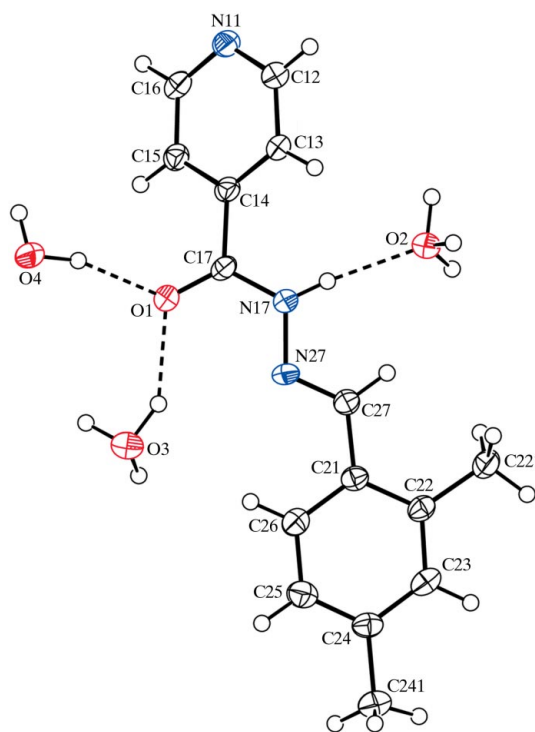

Figure 1
The independent molecular components of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Hydrogen bonds within the selected asymmetric unit are indicated by dashed lines. The H atoms bonded to atoms O2 and O3 are disordered (see *Comment*).

$(\frac{1}{2}, 1, 1)$. The combination of these two motifs then generates a chain of edge-fused rings along $(x, 1, 1)$, with $R_4^4(18)$ rings centred at $(n + \frac{1}{2}, 1, 1)$ (n = zero or integer) and $R_6^6(22)$ rings centred at $(n, 1, 1)$ (n = zero or integer) (Fig. 2).

Pairs of O2 water atoms and pairs of O3 water atoms are each related by centres of inversion, at $(0, 1, \frac{1}{2})$ and $(1, \frac{1}{2}, \frac{1}{2})$, respectively (Table 2), and for each pair of such O atoms the O—H···O contacts involving atoms H2C and H3C are almost linear. Hence, in each case, only one of the symmetry-related H-atom sites can be occupied; if both such sites were occupied, the corresponding H···H distances would be similar to the covalent bonding distance in molecular H₂. Thus, for example, if the site H2C at (x, y, z) is occupied, the sites H2B at (x, y, z) and H2C at $(-x, 2 - y, 1 - z)$ must both be vacant, and conversely. Similar considerations apply to the sites H3B and H3C. To the extent that the sites H2B and H3B are occupied, they reinforce the [100] chain of rings. To the extent that the sites H2C and H3C are occupied, they link the [100] chains into a three-dimensional framework structure.

Water atoms O2 and O3 at (x, y, z) are each part of the [100] chain along $(x, 1, 1)$. These atoms act as hydrogen-bond donors, *via* atoms H2C and H3C, respectively, to water atoms O2 at $(-x, 2 - y, 1 - z)$ and O3 at $(2 - x, 1 - y, 1 - z)$, which themselves lie in the [100] chains along $(x, 1, 0)$ and $(x, 0, 0)$, respectively. Hence, propagation by translation and inversion of these two hydrogen bonds links all of the [100] chains into a three-dimensional framework structure. Although each of the H-atom sites involved has only 0.5 occupancy, averaged over the entire crystal, there is no necessary correlation between the H-atom occupancies at different local sites related by translation along [100]. Hence each [100] chain will be linked, at some points along its length, to four adjacent chains, so forming the framework structure.

In the anhydrous 2,4-difluoro analogue, (II), the molecules are linked by a combination of N—H···O and C—H···O hydrogen bonds, one of each type, into chains of rings, which are themselves further linked into sheets by a single π–π stacking interaction (Wardell, de Souza, Ferreira *et al.*, 2005). In the 2,4-dinitro analogue, (IV), which crystallizes as a stoichiometric monohydrate with fully ordered H-atom sites, a combination of O—H···O, O—H···N, N–H···O and C—H···O hydrogen bonds links the molecular components into a three-dimensional framework structure (Wardell, de Souza, Wardell *et al.*, 2005). The substituents in the aryl ring thus exert a considerable influence, not only upon the crystallization characteristics of the compounds, but also upon the supramolecular aggregation, even when, as in compounds (I) and (II), those substituents play no direct role in that aggregation.

Experimental

A mixture of equimolar quantities (10 mmol of each component) of 2,4-dimethylbenzaldehyde and isonicotinoylhydrazine (isoniazid) in tetrahydrofuran (20 ml) was heated under reflux for 6 h. The mixture was cooled and the solvent was removed under reduced pressure. The solid product was washed successively with cold ethanol and diethyl ether, and then recrystallized from ethanol (m.p. 426–428 K). CG/MS: m/z 253 $[M]^+$; ^{1}H NMR (DMSO-d_6): δ 12.00 (1H, s, NH), 8.80 (2H, d, J = 5.5 Hz), 8.72 (1H, s, N=C—H), 7.84 (2H, d, J = 5.5 Hz), 7.77 (1H, d, J = 8.0 Hz), 7.12 (1H, d, J = 8.0 Hz), 7.09 (1H, s); ^{13}C NMR (DMSO-d_6): δ 161.2, 150.2, 147.6, 140.4, 139.8, 136.9, 131.4, 129.2, 126.9, 126.4, 121.4, 20.8, 18.9; IR (KBr disk, ν, cm^{-1}): 3195 (NH), 1653 (CO).

Crystal data

$C_{15}H_{15}N_3O\cdot3H_2O$	$V = 775.41\ (10)$ Å^3
$M_r = 307.35$	$Z = 2$
Triclinic, $P\bar{1}$	$D_x = 1.316$ Mg m^{-3}
$a = 8.6765\ (7)$ Å	Mo $K\alpha$ radiation
$b = 9.0833\ (6)$ Å	$\mu = 0.10$ mm^{-1}
$c = 11.2901\ (9)$ Å	$T = 120\ (2)$ K
$\alpha = 73.870\ (5)°$	Plate, colourless
$\beta = 82.182\ (4)°$	$0.20 \times 0.05 \times 0.02$ mm
$\gamma = 65.147\ (3)°$	

Data collection

Nonius KappaCCD area-detector diffractometer	14799 measured reflections
φ and ω scans	3563 independent reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)	1982 reflections with $I > 2\sigma(I)$
$T_{min} = 0.949$, $T_{max} = 0.998$	$R_{int} = 0.093$
	$\theta_{max} = 27.6°$

Refinement

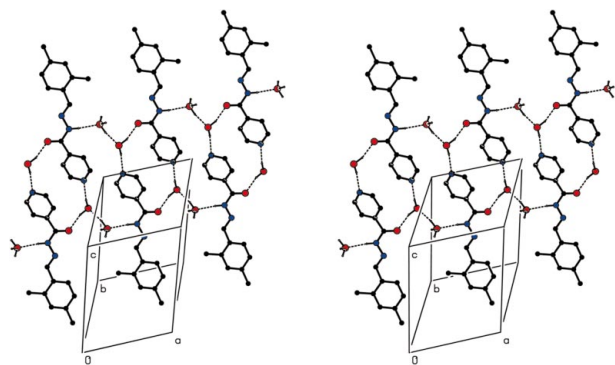|	
Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.073P)^2 + 0.1388P]$
$R[F^2 > 2\sigma(F^2)] = 0.064$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.173$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.03$	$\Delta\rho_{max} = 0.32$ e Å^{-3}
3563 reflections	$\Delta\rho_{min} = -0.30$ e Å^{-3}
200 parameters	
H-atom parameters constrained	

Figure 2
A stereoview of part of the crystal structure of compound (I), showing the formation of a chain of edge-fused $R_4^4(18)$ and $R_6^6(22)$ rings lying along [100]. For the sake of clarity, the water molecule containing atom O3 and the H atoms bonded to C atoms have been omitted. The H atoms bonded to atom O2 are disordered (see *Comment*).

Table 1
Selected torsion angles (°).

C13—C14—C17—N17	−32.8 (3)	N17—N27—C27—C21	−176.9 (2)
C14—C17—N17—N27	−174.39 (19)	N27—C27—C21—C22	176.1 (2)
C17—N17—N27—C27	168.3 (2)		

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$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N17—H17$\cdots$O2	0.88	2.00	2.878 (3)	172
O2—H2$A\cdots$O4^{i}	0.95	1.77	2.711 (2)	168
O2—H2$B\cdots$O3^{i}	0.96	2.08	2.877 (3)	139
O2—H2$C\cdots$O2^{ii}	0.96	1.86	2.801 (3)	167
O3—H3$A\cdots$O1	1.00	2.02	2.900 (3)	146
O3—H3$B\cdots$O2^{iii}	0.95	2.26	2.877 (3)	122
O3—H3$C\cdots$O3^{iv}	1.03	1.89	2.917 (4)	174
O4—H4$A\cdots$O1	0.97	1.87	2.811 (3)	163
O4—H4$B\cdots$N11^{v}	0.87	2.01	2.872 (3)	172

Symmetry codes: (i) $x-1, y, z$; (ii) $-x, -y+2, -z+1$; (iii) $x+1, y, z$; (iv) $-x+2, -y+1, -z+1$; (v) $-x+1, -y+2, -z+2$.

Crystals of compound (I) are triclinic; the space group $P\bar{1}$ was selected and confirmed by the structure analysis. H atoms bonded to C or N atoms were located in a difference map and then treated as riding atoms, with C—H = 0.95 (aromatic) or 0.98 Å (methyl), and N—H = 0.88 Å, and with $U_{iso}(H) = xU_{eq}(C,N)$, where $x = 1.5$ for the methyl groups and 1.2 for all other H atoms bonded to C or N atoms. The H atoms of the water molecules were located in a difference map, and those bonded to atoms O2 and O3 were modelled as two H atoms of full occupancy (H2A and H3A) and four with occupancy 0.5 (H2B/H2C and H3B/H3C). These H atoms were all permitted to ride at the O—H distances (0.87–1.03 Å) found from the difference map, with $U_{iso}(H) = 1.2U_{eq}(O)$.

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 macro *PRPKAPPA* (Ferguson, 1999).

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