

N,N'-Bis(2-chloronicotinoyl)-*N*-(3-nitrophenyl)hydrazine monohydrate: complex sheets built from O—H···N, N—H···O and C—H···O hydrogen bonds

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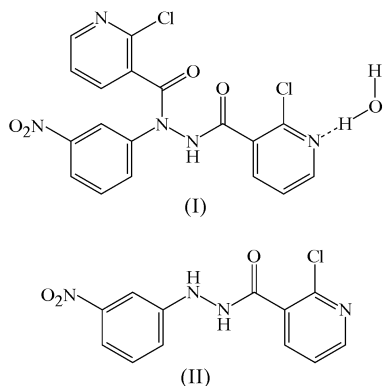
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In the title compound, C₁₈H₁₁Cl₂N₅O₄·H₂O, the two components are linked into complex sheets by a combination of five independent hydrogen bonds, *viz.* one of N—H···O type and two each of O—H···N and C—H···O types.

Comment

The title compound, (I) (Fig. 1), was obtained as an adventitious by-product, in low yield, during the attempted preparation of *N*-(2-chloronicotinoyl)-3-nitrophenylhydrazine, (II).



Within the hydrazine component in (I), both N atoms (N17 and N21) have effectively planar coordination, and the N—N bond distance (Table 1) is typical of the value in hydrazines with both N atoms having planar coordination (the mean value is 1.401 Å; Allen *et al.*, 1987). The fragment C13—C17(=O1)—N17—N21 is effectively planar, as shown by the key torsion angles, but the corresponding fragment encompassing atoms N21 and C37 shows a markedly non-planar

conformation. The molecule overall has no internal symmetry and hence it is chiral.

The independent molecular components in (I) are linked into sheets of considerable complexity by a combination of five independent hydrogen bonds, of O—H···N, N—H···O and C—H···O types (Table 2). Within the selected asymmetric unit (Fig. 1) the components are linked by an O—H···N hydrogen bond, and four further hydrogen bonds generate the sheet. The formation of the sheet is readily analysed in terms of three substructures, *viz.* one finite (zero-

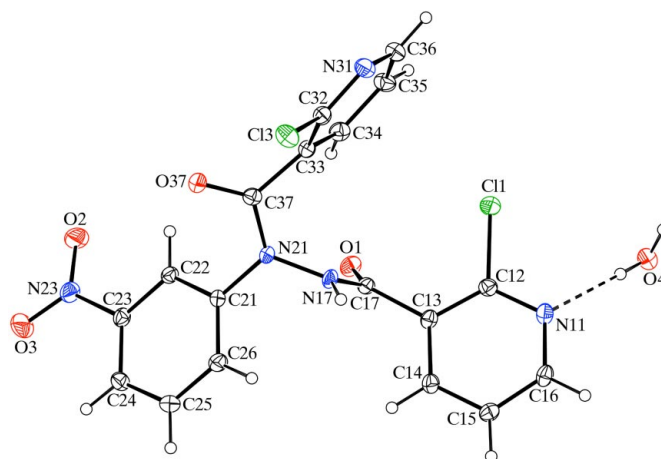


Figure 1
The molecular components of (I), showing the atom-labelling scheme and the O—H···N hydrogen bond (dashed line) within the asymmetric unit. Displacement ellipsoids are drawn at the 30% probability level.

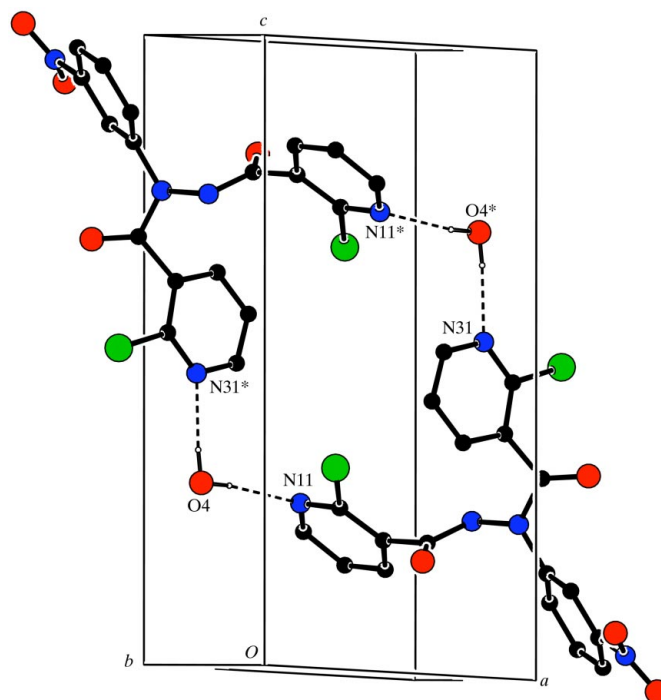


Figure 2
Part of the crystal structure of (I), showing the formation of a centrosymmetric $R_4^2(26)$ aggregate of four molecules. For the sake of clarity, H atoms bonded to C and N atoms have been omitted. Atoms marked with an asterisk (*) are at the symmetry position ($-x + 1, -y + 1, -z + 1$).

dimensional) substructure and two distinct one-dimensional substructures.

The finite substructure is built from the two O—H···N hydrogen bonds. Water atom O4 at (x, y, z) acts as a hydrogen-bond donor, *via* H4A and H4B, respectively, to atoms N11 at (x, y, z) and N31 at $(-x + 1, -y + 1, -z + 1)$, thereby generating a cyclic centrosymmetric four-molecule aggregate of $R_4^4(26)$ type (Bernstein *et al.*, 1995) and centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (Fig. 2). The two independent one-dimensional substructures result from two different modes of linking of these $R_4^4(26)$ aggregates; one mode utilizes the single N—H···O hydrogen bond, while the other utilizes the concerted action of the two C—H···O hydrogen bonds.

In the simpler of the two one-dimensional substructures, atoms N17 in the hydrazine molecules at (x, y, z) and $(-x + 1, -y + 1, -z + 1)$, which form part of the $R_4^4(26)$ aggregate centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, act as hydrogen-bond donors, respectively, to water atoms O4 at $(x + 1, y, z)$ and $(x - 1, y, z)$, which themselves lie in the $R_4^4(26)$ aggregates centred at $(\frac{3}{2}, \frac{1}{2}, \frac{1}{2})$ and $(-\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, respectively. Propagation of this hydrogen bond by

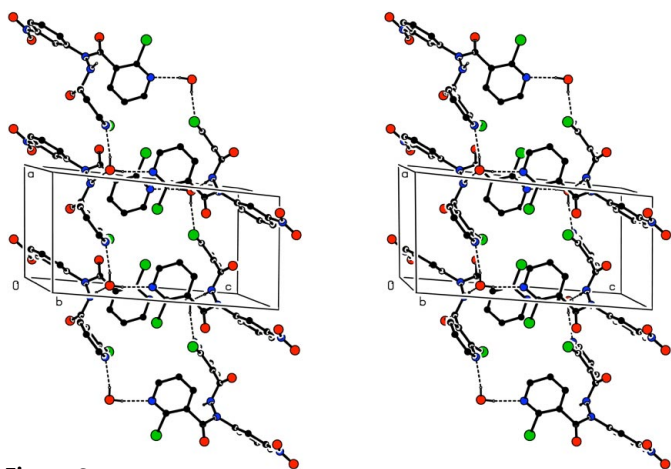


Figure 3
A stereoview of part of the crystal structure of (I), showing the formation of a [100] chain of edge-fused $R_4^4(18)$ and $R_4^4(26)$ rings. For the sake of clarity, H atoms bonded to C atoms have been omitted.

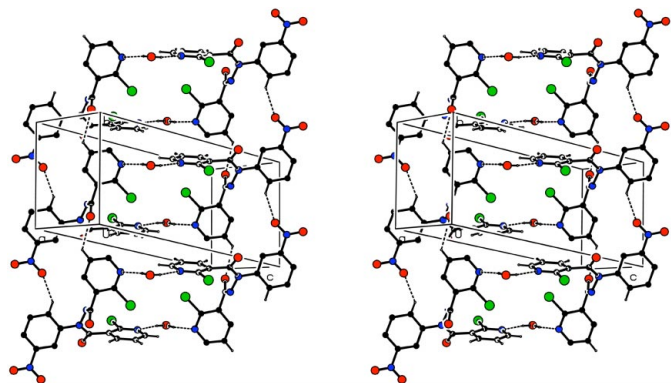


Figure 4
A stereoview of part of the crystal structure of (I), showing the formation of a [010] ribbon containing edge-fused $R_2^2(19)$, $R_4^4(26)$ and $R_6^6(30)$ rings. For the sake of clarity, H atoms not involved in the hydrogen bonds shown have been omitted.

translation and inversion then generates a chain of edge-fused rings running parallel to the [100] direction, with $R_4^4(26)$ rings centred at $(n + \frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ ($n = \text{zero or integer}$) and $R_4^4(18)$ rings centred at $(n, \frac{1}{2}, \frac{1}{2})$ ($n = \text{zero or integer}$) (Fig. 3).

In the second of the one-dimensional substructures, atoms C15 and C26 at (x, y, z) act as hydrogen-bond donors, respectively, to atoms O1 and O2, both at $(x, y + 1, z)$, thereby generating by translation a $C(6)C(7)[R_2^2(19)]$ chain of rings running parallel to the [010] direction (Fig. 4). In combination with the $R_4^4(26)$ aggregates (Fig. 2), these C—H···O hydrogen bonds then generate a complex ribbon containing three distinct types of ring. The central strip of the ribbon consists of edge-fused centrosymmetric $R_2^2(26)$ and $R_6^6(30)$ rings generated by inversion, with the $R_4^4(26)$ rings centred at $(\frac{1}{2}, n + \frac{1}{2}, \frac{1}{2})$ ($n = \text{zero or integer}$) and the $R_6^6(30)$ rings centred at $(\frac{1}{2}, n, \frac{1}{2})$ ($n = \text{zero or integer}$), while there are two antiparallel chains of edge-fused $R_2^2(19)$ rings, generated by translation, along the two edges of the ribbon (Fig. 4).

The combination of the [100] and [010] chains of rings, containing two and three distinct types of ring, respectively, then generates a complex (001) sheet. A single sheet of this type passes through each unit cell, but there are no direction-specific interactions between adjacent sheets.

Experimental

A solution of 2-chloronicotinoyl chloride (2 mmol), 3-nitrophenylhydrazine hydrochloride (2 mmol) and triethylamine (1 ml) in 1,2-dichloroethane (30 ml) was boiled under reflux for 60 min; the solution was cooled to ambient temperature and filtered to remove the precipitate of triethylammonium chloride. The filtrate was left to stand overnight at ambient temperature and crystals of (I), which had formed in very low yield, were collected by filtration. These were found to be suitable for single-crystal X-ray diffraction analysis. IR (cm^{-1} , KBr pellet): 3230 (NH), 1684 (CO).

Crystal data

$\text{C}_{18}\text{H}_{11}\text{Cl}_2\text{N}_5\text{O}_4 \cdot \text{H}_2\text{O}$
 $M_r = 450.23$
 Triclinic, $P\bar{1}$
 $a = 7.4435$ (3) Å
 $b = 7.8829$ (5) Å
 $c = 16.2657$ (10) Å
 $\alpha = 99.564$ (2)°
 $\beta = 96.806$ (3)°
 $\gamma = 90.842$ (3)°
 $V = 933.94$ (9) Å³

$Z = 2$
 $D_x = 1.601$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 4263 reflections
 $\theta = 3.1\text{--}27.5^\circ$
 $\mu = 0.39$ mm⁻¹
 $T = 120$ (2) K
 Plate, yellow
 $0.16 \times 0.14 \times 0.03$ mm

Data collection

Bruker KappaCCD diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
 $T_{\min} = 0.960$, $T_{\max} = 0.988$
 19029 measured reflections
 4263 independent reflections

2991 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.076$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -9 \rightarrow 9$
 $k = -10 \rightarrow 10$
 $l = -21 \rightarrow 21$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.050$
 $wR(F^2) = 0.120$
 $S = 1.04$
 4263 reflections
 271 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0464P)^2 + 0.5704P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.31$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.37$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

N17—N21	1.399 (3)		
C13—C17—N17—N21	−173.63 (19)	C12—C13—C17—N17	−110.2 (3)
C17—N17—N21—C21	78.5 (3)	N17—N21—C21—C22	−142.1 (2)
C17—N17—N21—C37	−116.7 (2)	N21—C37—C33—C32	−133.4 (2)
N17—N21—C37—C33	30.2 (3)	C21—N21—C37—O37	8.0 (3)
N17—N21—C37—O37	−156.2 (2)	C21—N21—C37—C33	−165.7 (2)

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O4—H4A...N11	0.84	2.06	2.891 (3)	170
O4—H4B...N31 ⁱ	0.84	1.97	2.805 (3)	171
N17—H17...O4 ⁱⁱ	0.87	1.88	2.747 (3)	175
C15—H15...O1 ⁱⁱⁱ	0.95	2.56	3.228 (3)	127
C26—H26...O2 ⁱⁱⁱ	0.95	2.42	3.158 (3)	134

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

Crystals of (I) are triclinic; the space group $P\bar{1}$ was selected and confirmed by the successful structure analysis. All H atoms were located in difference maps and then treated as riding atoms, with C—H distances of 0.95 Å, N—H distances of 0.87 Å and O—H distances of 0.84 Å, and with $U_{\text{iso}}(\text{H})$ values set at $1.2U_{\text{eq}}(\text{C,N,O})$.

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: SK3004). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
- Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.
- Hooft, R. W. W. (1999). *COLLECT*. Nonius BV, Delft, The Netherlands.
- McArdle, P. (2003). *OSCAIL for Windows*. Version 10. Crystallography Centre, Chemistry Department, NUI Galway, Ireland.
- 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.