

Hydrogen-bonded framework structures in 4-[(4-chloro-3-nitrobenzoyl)hydrazinocarbonyl]pyridinium chloride and *N*-3,5-dinitrobenzoyl-*N'*-isonicotinoylhydrazine

Thatyana R. A. Vasconcelos,^a Marcus V. N. de Souza,^a
Solange M. S. V. Wardell,^b James L. Wardell,^c John N.
Low^d and Christopher Glidewell^{e*}

^aComplexo Tecnológico de Medicamentos Farmanguinhos, Av. Comandante Guarany 447, Jacarepaguá, Rio de Janeiro, RJ, Brazil, ^bFundação Oswaldo Cruz, Far Manguinhos, Rua Sizenando Nabuco, 100 Manguinhos, 21041-250 Rio de Janeiro, RJ, Brazil, ^cInstituto de Química, Departamento de Química Inorgânica, Universidade Federal do Rio de Janeiro, CP 68563, 21945-970 Rio de Janeiro, RJ, Brazil, ^dDepartment of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB24 3UE, Scotland, and ^eSchool of Chemistry, University of St Andrews, Fife KY16 9ST, Scotland

Correspondence e-mail: cg@st-andrews.ac.uk

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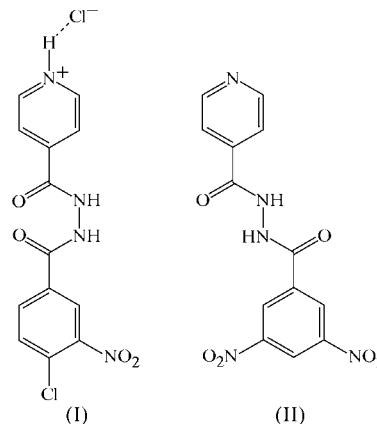
In 4-[(4-chloro-3-nitrobenzoyl)hydrazinocarbonyl]pyridinium chloride, $C_{13}H_{10}ClN_4O_4^+ \cdot Cl^-$, the component ions are linked into a three-dimensional framework structure by a combination of three $N-H \cdots Cl$ and five $C-H \cdots O$ hydrogen bonds. In *N*-3,5-dinitrobenzoyl-*N'*-isonicotinoylhydrazine, $C_{13}H_9N_5O_6$, the molecules are linked into a three-dimensional framework structure by one $N-H \cdots O$ and three $C-H \cdots O$ hydrogen bonds, augmented by an aromatic $\pi-\pi$ stacking interaction.

Comment

As part of our continuing studies of the supramolecular structures of hydrazones, we now report the structures of the title compounds, (I) and (II). These compounds were initially prepared as part of a programme to test their bactericidal activities, especially towards the *Mycobacterium tuberculosis* bacterium. Both compounds were found to exhibit significant activities, which will be reported elsewhere.

In each compound (Figs. 1 and 2), the N atoms of the hydrazine unit exhibit only very modest pyramidalization; however, the overall conformations are very far from being planar, as the leading torsion angles (Table 3) readily show. The most striking difference between the two conformations is provided by the $C17-N17-N27-C27$ torsion angles; in both compounds, the nitro groups are also twisted out of the planes of the adjacent aryl rings. Hence, each molecule exhibits no internal symmetry, so that the molecules are chiral. However,

in each of (I) and (II), the space group accommodates equal numbers of the two enantiomers



Compound (I) is a salt in which the pyridyl N atom is protonated. The component ions are linked into a three-dimensional framework by three $N-H \cdots Cl$ hydrogen bonds, all involving the $Cl1$ anion as the acceptor, and five independent $C-H \cdots O$ hydrogen bonds (Table 1). The structure also contains two fairly short $C-H \cdots Cl$ contacts, again both involving the $Cl1$ anion. The three-dimensional nature of the supramolecular structure can be demonstrated most simply in terms of a sheet formed by the three $N-H \cdots Cl$ hydrogen bonds only, and the linking of adjacent sheets *via* a cyclic motif involving just one of the $C-H \cdots O$ hydrogen bonds.

Within the selected asymmetric unit (Fig. 1), pyridinium atom $N11$ acts as a hydrogen-bond donor to the $Cl1$ anion.

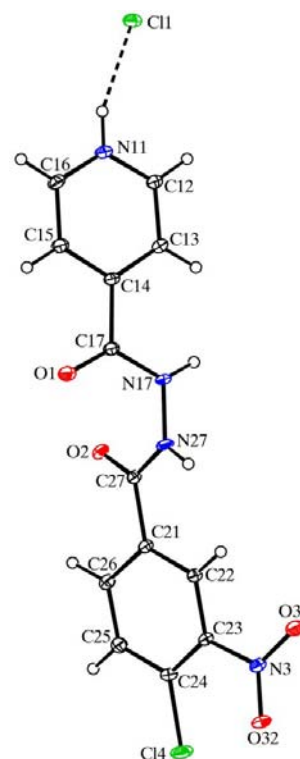


Figure 1
The independent components of (I), showing the atom-labelling scheme and the $N-H \cdots Cl$ hydrogen bond within the asymmetric unit. Displacement ellipsoids are drawn at the 30% probability level.

Hydrazine atom N17 in the cation at (x, y, z) acts as a hydrogen-bond donor to the anion at $(\frac{1}{2} + x, \frac{3}{2} - y, z)$, so forming a $C_2^1(9)$ (Bernstein *et al.*, 1995) chain of alternating cations and anions running parallel to the [100] direction and generated by the a -glide plane at $y = \frac{3}{4}$. In addition, hydrazine atom N27 in the cation at (x, y, z) acts as a hydrogen-bond donor to the anion at $(\frac{1}{2} - x, y, \frac{1}{2} + z)$, forming a $C_2^1(5)$ chain of alternating cations and anions running parallel to the [001] direction and generated by the effective c -glide plane at $x = \frac{1}{4}$ arising from the combination of the A -face centring and the explicit b -glide plane at $x = \frac{1}{4}$. The combination of the [100] and [001] chains generates a (010) sheet built from a single type of $R_6^6(24)$ ring (Fig. 3).

Two (010) sheets pass through each unit cell, generated, respectively, by the a -glide planes at $y = \frac{1}{4}$ and $y = \frac{3}{4}$, and adjacent sheets are linked by pairs of short $C-H \cdots O$ hydrogen bonds forming a cyclic motif. Aryl atom C26 in the cation at (x, y, z) acts as a hydrogen-bond donor to carbonyl atom O2 in the cation at $(1 - x, 1 - y, z)$, thus generating an $R_2^2(10)$ ring centred at $(\frac{1}{2}, \frac{1}{2}, 0)$ (Fig. 4). Propagation of this hydrogen bond then links all of the (010) sheets into a single

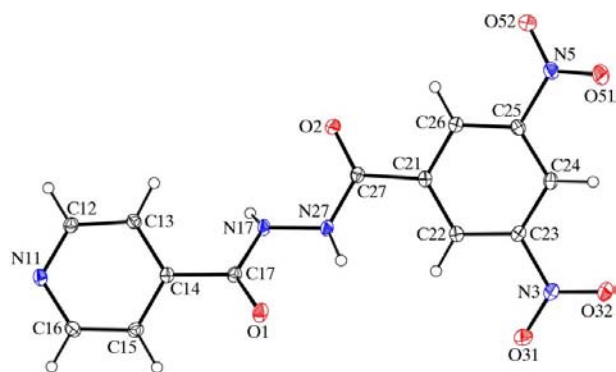


Figure 2
The molecule of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

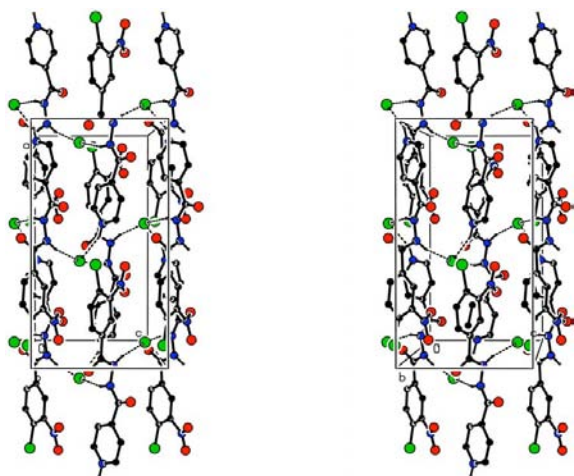


Figure 3
A stereoview of part of the crystal structure of (I), showing the formation of a (010) sheet of $R_6^6(24)$ rings constructed from three independent $N-H \cdots Cl$ hydrogen bonds. For the sake of clarity, H atoms bonded to C atoms have been omitted.

framework structure, which is further reinforced by the other $C-H \cdots O$ hydrogen bonds to give a three-dimensional structure of considerable complexity.

Since there are also two short $C-H \cdots Cl$ contacts within the structure (Table 1), the Cl1 anion at (x, y, z) is surrounded

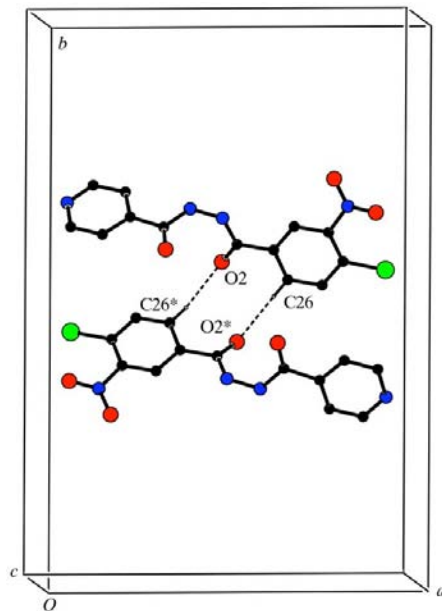


Figure 4
Part of the crystal structure of (I), showing the formation of an $R_2^2(10)$ ring linking the cations in adjacent sheets. For the sake of clarity, the anions, and H atoms not involved in the motif shown, have been omitted. Atoms marked with an asterisk (*) are at the symmetry position $(1 - x, 1 - y, z)$.

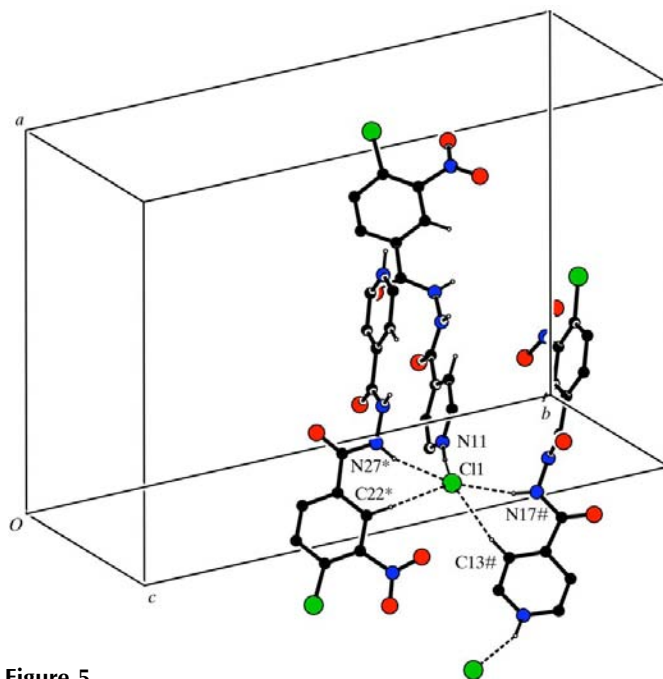


Figure 5
Part of the crystal structure of (I), showing the coordination of the anion at (x, y, z) . For the sake of clarity, H atoms that are bonded to C atoms but are not involved in the interactions shown have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(\frac{1}{2} - x, y, -\frac{1}{2} + z)$ and $(-\frac{1}{2} + x, \frac{3}{2} - y, z)$, respectively.

by atoms N11 at (x, y, z) , N17 and C13 both at $(-\frac{1}{2} + x, \frac{3}{2} - y, z)$, and N27 and C22 both at $(\frac{1}{2} - x, y, -\frac{1}{2} + z)$. The H \cdots Cl distances are within the sums of the van der Waals radii, although the interaction energies are probably small. Atoms C11, N17^{vii}, N27^{viii} and C22^{viii} [symmetry codes: (vii) $x - \frac{1}{2}, -y + \frac{3}{2}, z$; (viii) $-x + \frac{1}{2}, y, z - \frac{1}{2}$] are effectively coplanar, and the overall coordination of atom C11 can be regarded as a distorted trigonal bipyramid, with atoms N11 and C13^{vii} occupying the axial sites (Fig. 5).

The molecules of compound (II) (Fig. 2) are linked into a three-dimensional framework by a combination of one N—H \cdots N hydrogen bond and three C—H \cdots O hydrogen bonds (Table 2), augmented by an aromatic π – π stacking interaction. The formation of this rather complex framework can readily be analysed in terms of two one-dimensional substructures, each in the form of a chain of rings built from the co-operative interaction of two hydrogen bonds.

Hydrazine atom N17 in the molecule at (x, y, z) acts as a hydrogen-bond donor to the ring atom N11 in the molecule at

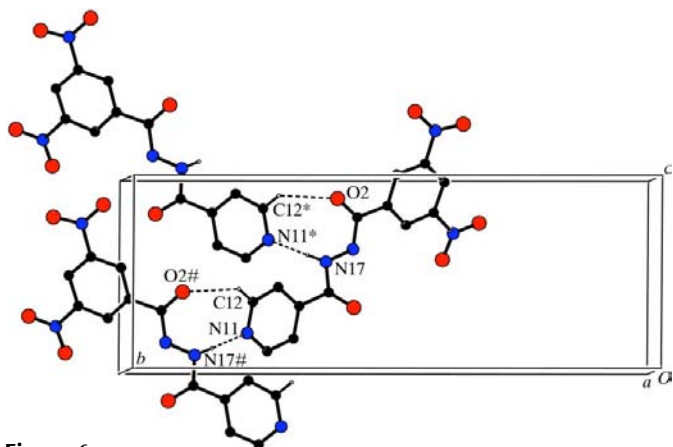


Figure 6

Part of the crystal structure of (II), showing the formation of a $C(7)C(9)[R_2^2(8)]$ chain of rings along [101]. For the sake of clarity, H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$ and $(-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z)$, respectively.

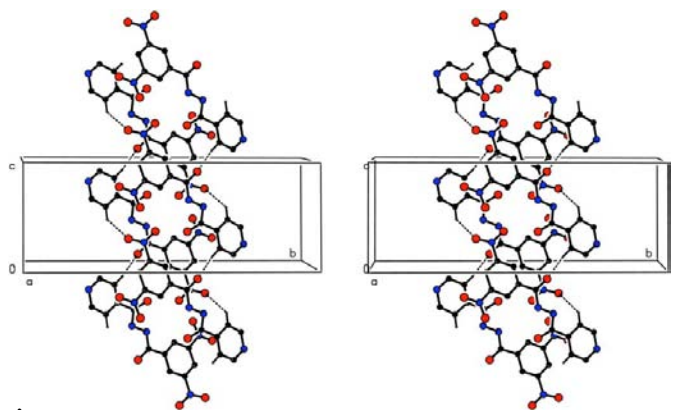


Figure 7

A stereoview of part of the crystal structure of (II), showing the formation of a chain of edge-fused $R_2^2(24)$ and $R_4^4(24)$ rings along [001]. For the sake of clarity, H atoms not involved in the motif shown have been omitted.

$(\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z)$, so forming a $C(7)$ chain running parallel to the [101] direction and generated by the n -glide plane at $y = \frac{3}{4}$. At the same time, pyridyl atom C12 in the molecule at $(\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z)$ acts as a hydrogen-bond donor to carbonyl atom O2 in the molecule at (x, y, z) , thereby forming a $C(9)$ chain along [101]. The combination of these two hydrogen bonds then generates a $C(7)C(9)[R_2^2(8)]$ chain of rings along [101] (Fig. 6).

The [101] chains of rings are linked into sheets by a simple chain motif running parallel to the [001] direction. Pyridyl atom C15 in the molecule at (x, y, z) acts as a donor to carbonyl atom O2 in the molecule at $(x, y, -1 + z)$ in a nearly linear hydrogen bond, so generating by translation a $C(8)$ chain running parallel to the [001] direction. The combination of the [101] chain of rings and the [001] chain generates a (010) sheet, whose formation is further augmented by a single π – π stacking interaction. The nitrated C21–C26 aryl rings in the molecules at (x, y, z) and $(2 - x, 1 - y, 2 - z)$, which lie in adjacent [101] chains offset along [100], are strictly parallel, with an interplanar spacing of 3.342 (2) Å; the ring-centroid separation is 3.519 (2) Å, corresponding to a ring offset of 1.102 (2) Å.

Two (010) sheets pass through each unit cell; they are related to one another by inversion and are generated by the n -glide planes at $y = \frac{1}{4}$ and $y = \frac{3}{4}$, respectively. Adjacent sheets are linked into a single continuous three-dimensional framework structure by the final C—H \cdots O hydrogen bond. Pyridyl atom C13 in the molecule at (x, y, z) , which lies in the (010) sheet generated by the n -glide plane at $y = \frac{3}{4}$, acts as a hydrogen-bond donor to nitro atom O51 in the molecule at $(1 - x, 1 - y, 2 - z)$, which forms part of the (010) sheet generated by the n -glide plane at $y = \frac{1}{4}$, so generating by inversion an $R_2^2(24)$ ring centred at $(\frac{1}{2}, \frac{1}{2}, 1)$. The combination of the two hydrogen bonds having atoms C13 and C15 as the donors then generates a chain of edge-fused centrosymmetric rings having $R_2^2(24)$ rings centred at $(\frac{1}{2}, \frac{1}{2}, n)$ ($n =$ zero or integer) and $R_4^4(24)$ rings centred at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2} + n)$ ($n =$ zero or integer) (Fig. 7).

Experimental

Substituted nitrobenzoyl chlorides were prepared by treating the appropriate carboxylic acid (1 g) with thionyl chloride (3 equivalents), *N,N*-dimethylformamide (0.1 equivalent) and dichloromethane (20 ml) at room temperature, under stirring and in a dinitrogen atmosphere. After 6–8 h, the excess of thionyl chloride was removed under reduced pressure to leave the crude acyl chloride, which was used without purification in a reaction with isonicotinoylhydrazine (isoniazid, 1 equivalent) and, in the preparation of (II) only, triethylamine (1 equivalent) in tetrahydrofuran (20 ml) at 340 K. Compound (I) was purified by recrystallization from ethanol (m.p. 510–511 K, yield 88%). MS m/z : 320 $[M - HCl]^+$. NMR (DMSO- d_6): δ (H) 11.48 (1H, s, NH), 11.30 (1H, s, NH), 9.06 (2H, d, $J = 4.5$ Hz, H2 and H6), 8.63 (1H, s, H2'), 8.28 (1H, d, $J = 5.5$ Hz, H3 and H5), 8.27 (1H, d, $J = 8.5$ Hz, H6'), 8.01 (1H, d, $J = 8.5$ Hz, H5'); δ (C) 162.7, 162.6, 147.3, 145.8, 143.9, 132.5, 132.3, 132.0, 128.7, 124.8, 123.7. IR (KBr disk, cm^{-1}): 3171 (NH), 1710 (CO), 1677 (CO). Compound (II) was purified by column chromatography on silica gel, using as eluant a hexane/ethyl acetate gradient, followed by recryst-

tallization from ethanol (m.p. 531–533 K, yield 81%). MS m/z : 331 (M^+). NMR (DMSO- d_6): δ (H) 11.67 (1H, s, NH), 11.61 (1H, s, NH), 9.15 (2H, s, H2 and H6 or H3 and H5), 9.05 (2H, d, $J = 6.0$ Hz, H2 and H6 or H3 and H5), 8.98 (1H, d, $J = 5.5$ Hz, H4'), 8.28 (1H, d, $J = 5.5$ Hz, H2' or H6'), 8.19 (1H, d, $J = 5.5$ Hz, H2' or H6'); δ (C) 162.6, 161.6, 148.3, 146.0, 143.6, 134.4, 127.7, 123.7, 121.6. IR (KBr disk, cm^{-1}): 3153 (NH), 1718 (CO), 1683 (CO).

Compound (I)

Crystal data

$\text{C}_{13}\text{H}_{10}\text{ClN}_4\text{O}_4^+\cdot\text{Cl}^-$ Mo $K\alpha$ radiation
 $M_r = 357.15$ Cell parameters from 3204 reflections
 Orthorhombic, $Aba2$ reflections
 $a = 15.2414$ (2) Å $\theta = 2.9$ – 27.5°
 $b = 22.6430$ (9) Å $\mu = 0.48$ mm $^{-1}$
 $c = 8.3783$ (5) Å $T = 120$ (2) K
 $V = 2891.4$ (2) Å 3 Plate, yellow
 $Z = 8$ $0.30 \times 0.10 \times 0.10$ mm
 $D_x = 1.641$ Mg m $^{-3}$

Data collection

Nonius KappaCCD diffractometer 3013 reflections with $I > 2\sigma(I)$
 φ and ω scans $R_{\text{int}} = 0.044$
 Absorption correction: multi-scan $\theta_{\text{max}} = 27.5^\circ$
 (SADABS; Sheldrick, 2003) $h = -17 \rightarrow 19$
 $T_{\text{min}} = 0.870$, $T_{\text{max}} = 0.954$ $k = -29 \rightarrow 29$
 14651 measured reflections $l = -10 \rightarrow 9$
 3204 independent reflections

Refinement

Refinement on F^2 $w = 1/[\sigma^2(F_o^2) + (0.035P)^2 + 2.5382P]$
 $R[F^2 > 2\sigma(F^2)] = 0.030$ where $P = (F_o^2 + 2F_c^2)/3$
 $wR(F^2) = 0.074$ $(\Delta/\sigma)_{\text{max}} < 0.001$
 $S = 1.05$ $\Delta\rho_{\text{max}} = 0.25$ e Å $^{-3}$
 3204 reflections $\Delta\rho_{\text{min}} = -0.36$ e Å $^{-3}$
 208 parameters Absolute structure: Flack (1983),
 H-atom parameters constrained 1424 Friedel pairs
 Flack parameter: 0.01 (5)

Table 1

Hydrogen-bond geometry (Å, °) for (I).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N11–H11 \cdots C11	0.88	2.26	3.078 (2)	153
N17–H17 \cdots C11 ⁱ	0.88	2.31	3.161 (2)	163
N27–H27 \cdots C11 ⁱⁱ	0.88	2.33	3.176 (2)	162
C12–H12 \cdots O31 ⁱⁱⁱ	0.95	2.39	3.127 (3)	134
C16–H16 \cdots O2 ^{iv}	0.95	2.27	2.988 (3)	132
C16–H16 \cdots O32 ^v	0.95	2.42	3.018 (2)	121
C25–H25 \cdots O1 ^{vi}	0.95	2.50	3.439 (3)	168
C26–H26 \cdots O2 ^{vi}	0.95	2.33	3.204 (2)	152
C13–H13 \cdots C11 ⁱ	0.95	2.67	3.607 (2)	170
C22–H22 \cdots C11 ⁱⁱ	0.95	2.67	3.589 (2)	162

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

Compound (II)

Crystal data

$\text{C}_{13}\text{H}_9\text{N}_5\text{O}_6$ $D_x = 1.654$ Mg m $^{-3}$
 $M_r = 331.25$ Mo $K\alpha$ radiation
 Monoclinic, $P2_1/n$ Cell parameters from 3028 reflections
 $a = 7.4534$ (2) Å $\theta = 3.1$ – 27.5°
 $b = 22.1762$ (6) Å $\mu = 0.14$ mm $^{-1}$
 $c = 8.1006$ (2) Å $T = 120$ (2) K
 $\beta = 96.4890$ (16)° Block, yellow
 $V = 1330.35$ (6) Å 3 $0.28 \times 0.16 \times 0.16$ mm
 $Z = 4$

Data collection

Nonius KappaCCD diffractometer 2754 reflections with $I > 2\sigma(I)$
 φ and ω scans $R_{\text{int}} = 0.035$
 Absorption correction: multi-scan $\theta_{\text{max}} = 27.5^\circ$
 (SADABS; Sheldrick, 2003) $h = -9 \rightarrow 8$
 $T_{\text{min}} = 0.932$, $T_{\text{max}} = 0.979$ $k = -28 \rightarrow 26$
 16762 measured reflections $l = -10 \rightarrow 10$
 3028 independent reflections

Refinement

Refinement on F^2 $w = 1/[\sigma^2(F_o^2) + (0.0419P)^2 + 0.7643P]$
 $R[F^2 > 2\sigma(F^2)] = 0.037$ where $P = (F_o^2 + 2F_c^2)/3$
 $wR(F^2) = 0.099$ $(\Delta/\sigma)_{\text{max}} = 0.001$
 $S = 1.06$ $\Delta\rho_{\text{max}} = 0.30$ e Å $^{-3}$
 3028 reflections $\Delta\rho_{\text{min}} = -0.22$ e Å $^{-3}$
 217 parameters
 H-atom parameters constrained

Table 2

Hydrogen-bond geometry (Å, °) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N17–H17 \cdots N11 ^{ix}	0.88	1.94	2.8194 (16)	175
C12–H12 \cdots O2 ^x	0.95	2.50	3.2615 (16)	137
C13–H13 \cdots O51 ^{xi}	0.95	2.49	3.1956 (17)	131
C15–H15 \cdots O2 ^{xii}	0.95	2.40	3.3415 (16)	172

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

Table 3

Selected torsion angles (°) for compounds (I) and (II).

	(I)	(II)
C13–C14–C17–N17	1.8 (3)	–32.02 (17)
C14–C17–N17–N27	–172.91 (17)	–177.39 (10)
C17–N17–N27–C27	77.4 (3)	–156.24 (12)
N17–N27–C27–C21	170.59 (16)	177.66 (10)
N27–C27–C21–C22	–14.3 (3)	15.36 (17)
C22–C23–N3–O31	–15.8 (3)	5.25 (18)
C24–C25–N5–O51	–	–18.90 (18)

For (I), the systematic absences permitted $Aba2$ (= $C2ca$) or $Cmca$ as possible space groups; $Aba2$ was selected and confirmed by the subsequent structure analysis. For (II), the space group $P2_1/n$ 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 atoms were positioned geometrically, with C–H distances of 0.95 Å and $U_{\text{iso}}(\text{H})$ values of $1.2U_{\text{eq}}(\text{C})$. H atoms bonded to N atoms were allowed to ride at the sites located from the difference maps, with N–H distances of 0.88 Å and $U_{\text{iso}}(\text{H})$ values of $1.2U_{\text{eq}}(\text{N})$. The correct orientation of the structure of (I) with respect to the polar axis direction was established by means of the Flack (1983) parameter.

For both compounds, 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).

X-ray data were collected at the EPSRC X-ray Crystallographic Service, University of Southampton, England; the

authors thank the staff of the Service for all their help and advice. JLW thanks CNPq and FAPERJ for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG3003). Services for accessing these data are described at the back of the journal.

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