

## Four nitrobenzaldehyde isonicotinoylhydrazones at 120 K: four different supramolecular structures in two and three dimensions

Solange M. S. V. Wardell,<sup>a</sup> Marcus V. N. de Souza,<sup>a</sup>  
James L. Wardell,<sup>b</sup> John N. Low<sup>c</sup> and Christopher  
Glidewell<sup>d\*</sup>

<sup>a</sup>Fundação Oswaldo Cruz, Far Manguinhos, Rua Sizenando Nabuco, 100 Manguinhos, 21041-250 Rio de Janeiro, RJ, Brazil, <sup>b</sup>Instituto de Química, Departamento de Química Inorgânica, Universidade Federal do Rio de Janeiro, CP 68563, 21945-970 Rio de Janeiro, RJ, Brazil, <sup>c</sup>Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB24 3UE, Scotland, and <sup>d</sup>School of Chemistry, University of St Andrews, Fife KY16 9ST, Scotland  
Correspondence e-mail: cg@st-andrews.ac.uk

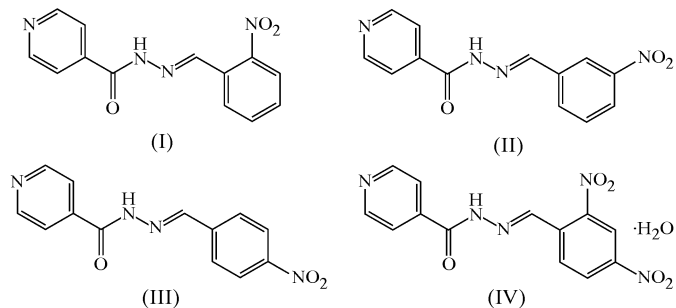
Received 21 September 2005  
Accepted 11 October 2005  
Online 11 November 2005

The molecules of 2-nitrobenzaldehyde isonicotinoylhydrazone,  $C_{13}H_{10}N_4O_3$ , (I), are linked into a three-dimensional framework by a combination of one  $N-H\cdots N$  and three  $C-H\cdots O$  hydrogen bonds. In the isomeric compound 3-nitrobenzaldehyde isonicotinoylhydrazone, (II), the molecules are linked into complex sheets by a combination of three hydrogen bonds, one each of the  $N-H\cdots N$ ,  $C-H\cdots N$  and  $C-H\cdots O$  types. The molecules of the third isomer, namely 4-nitrobenzaldehyde isonicotinoylhydrazone, (III), are linked into bilayers by a combination of one  $N-H\cdots N$ , one  $C-H\cdots N$  and two  $C-H\cdots O$  hydrogen bonds. 2,4-Dinitrobenzaldehyde isonicotinoylhydrazone, (IV), crystallizes as a stoichiometric monohydrate,  $C_{13}H_9N_5O_5\cdot H_2O$ , and the molecular components are linked into a three-dimensional framework by a combination of  $O-H\cdots O$ ,  $O-H\cdots N$ ,  $N-H\cdots O$  and three independent  $C-H\cdots O$  hydrogen bonds.

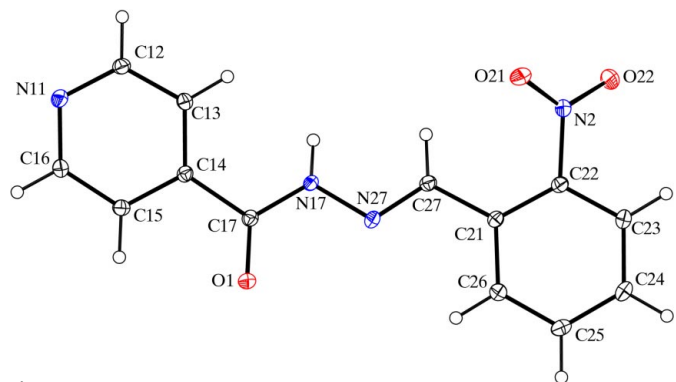
### Comment

As part of our structural studies of imines and hydrazones, we report here the molecular and supramolecular structures of four *N*-(isonicotinoyl)-nitrobenzaldehyde hydrazones, *viz.* 2-nitrobenzaldehyde isonicotinoylhydrazone, (I), 3-nitrobenzaldehyde isonicotinoylhydrazone, (II), 4-nitrobenzaldehyde isonicotinoylhydrazone, (III), and 2,4-dinitrobenzaldehyde isonicotinoylhydrazone, (IV), all at 120 K. The structures of compounds (I)–(III) have been reported previously at ambient temperature (Chuev *et al.*, 1996; Fun *et al.*, 1997; Liu *et al.*, 1998; Atovmyan *et al.*, 2002). For each compound it is clear from the cell dimensions that no phase changes have occurred between ambient temperature and 120 K, but also that the

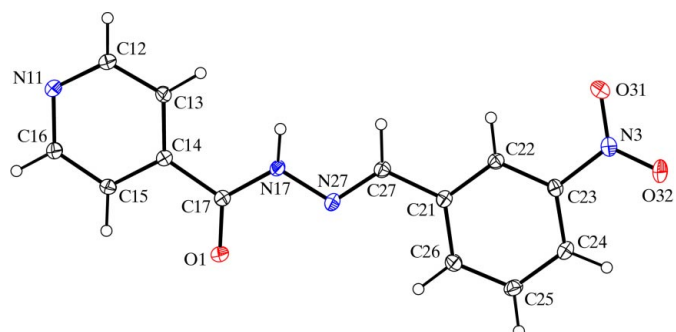
low-temperature determinations are of significantly higher precision. In their discussion of the supramolecular structures of compounds (I)–(III), Atovmyan *et al.* (2002) considered only  $N-H\cdots N$  hydrogen bonds and stated that ‘the position of the nitro group has no effect on the type of the crystal structure’.



By contrast, we have found that when the  $C-H\cdots O$  and  $C-H\cdots N$  hydrogen bonds are properly taken into consideration, the supramolecular structures of compounds (I)–(III) are all entirely different: *viz.* a three-dimensional framework structure in (I), single sheets in (II) and bilayers in (III). In an earlier report restricted to compound (III) only (Fun *et al.*, 1997), the  $D\cdots A$  and  $D-H\cdots A$  parameters were listed for a number of intermolecular  $C-H\cdots O$  and  $C-H\cdots N$  contacts, including some not identified as hydrogen bonds by *PLATON*

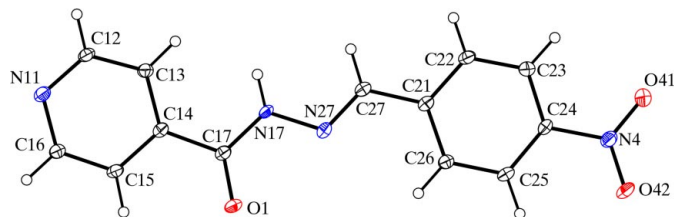


**Figure 1**  
The molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

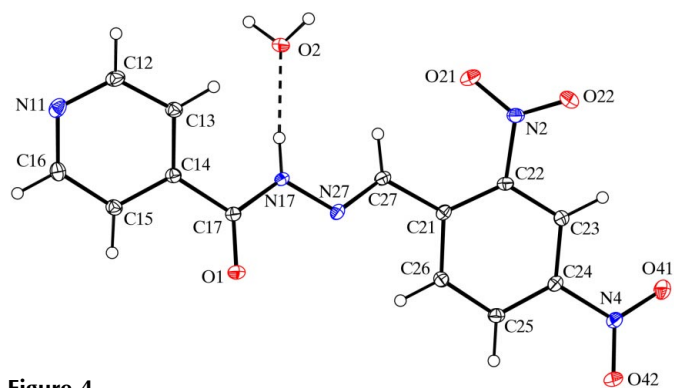


**Figure 2**  
The molecule of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

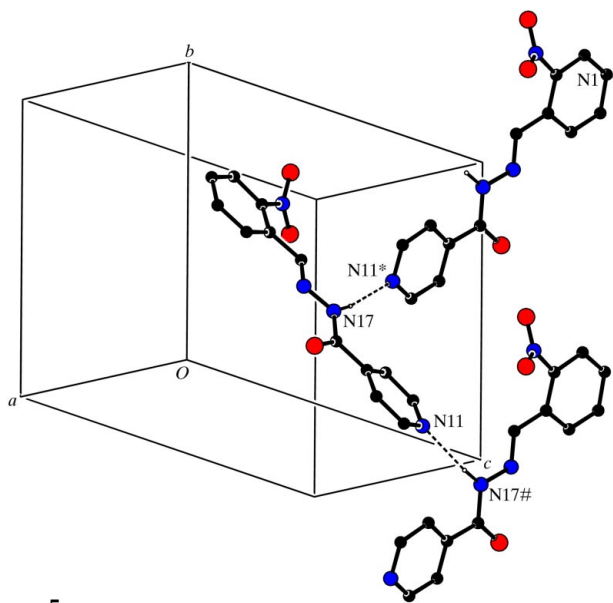
(Spek, 2003), but no descriptive analysis of the structural consequences of these interactions was provided beyond the statement that ‘the molecules pack as a network structure through hydrogen bonds’, and no packing diagrams were



**Figure 3**  
The molecule of (III), 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 4**  
The independent components in (IV), showing the atom-labelling scheme and the hydrogen bond within the asymmetric unit. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.



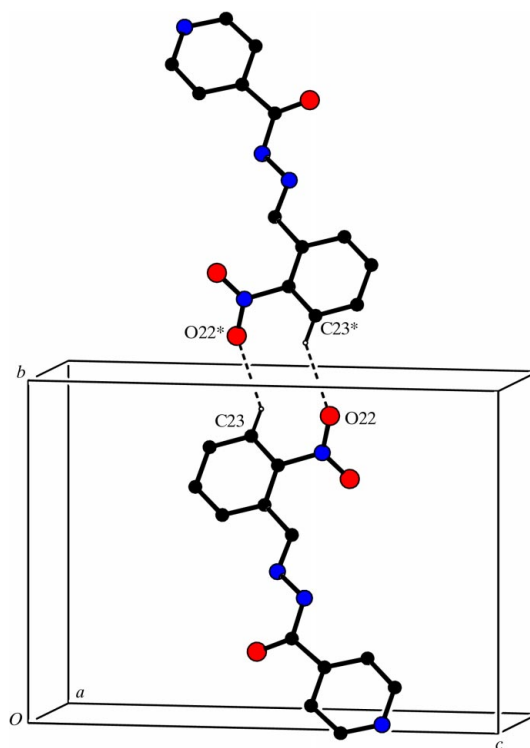
**Figure 5**  
Part of the crystal structure of (I), showing the formation of a C(7) chain along [010]. For the sake of clarity, H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (\*) or a hash (#) are at the symmetry positions  $(-x, \frac{1}{2} + y, \frac{3}{2} - z)$  and  $(-x, -\frac{1}{2} + y, \frac{3}{2} - z)$ , respectively.

provided. Similarly, in a report on compound (I) only (Liu *et al.*, 1998), the presence of just two intermolecular hydrogen bonds was mentioned, one each of the N–H···N and C–H···O types, as opposed to the four such bonds found here, but again without any indication of their structural consequences and again without any packing diagrams. Accordingly, we thought it important to repeat these determinations using low-temperature diffraction data and to report a thorough analysis of the supramolecular structures of compounds (I)–(III), as well as that of compound (IV).

In each of compounds (I)–(IV), the central spacer unit between atoms C14 and C21 (Figs. 1–4) adopts a nearly planar all-*trans* conformation, as shown by the key torsion angles (Table 1). The pyridyl ring is effectively coplanar with the spacer unit in compounds (II) and (III), although not in (I) and (IV). The aryl ring is effectively coplanar with this spacer unit in all compounds except (IV), while there is no clear pattern of behaviour for the nitro-group conformations. The bond lengths and angles show no unexpected features.

The supramolecular structures of compounds (I)–(IV) all differ, and all depend on different combinations of hydrogen bonds (Tables 2–5).

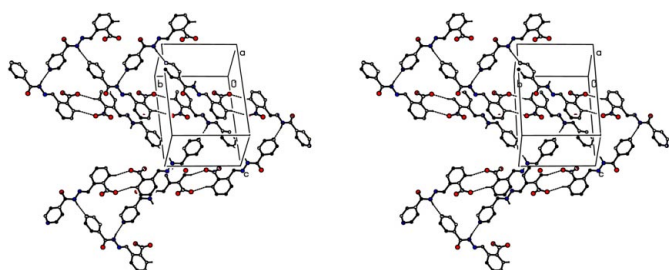
The molecules of compound (I) (Fig. 1) are linked into chains by a rather short and nearly linear N–H···N hydrogen bond, and these chains are linked into a three-dimensional framework structure by C–H···O hydrogen bonds (Table 2). Amide atom N17 in the molecule at  $(x, y, z)$  acts as hydrogen-bond donor to pyridyl atom N11 in the molecule at  $(-x, \frac{1}{2} + y,$



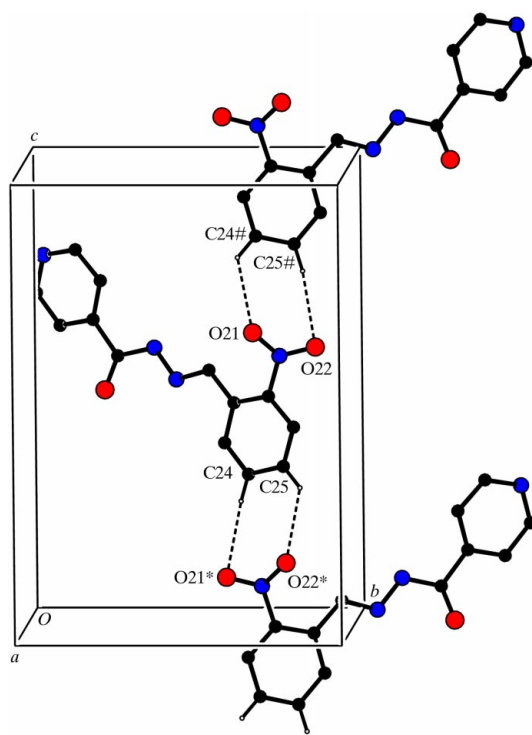
**Figure 6**  
Part of the crystal structure of (I), showing the formation of a centrosymmetric  $R_2^2(10)$  dimer. For the sake of clarity, H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (\*) are at the symmetry position  $(1 - x, 2 - y, 1 - z)$ .

$\frac{3}{2} - z$ ), so forming a  $C(7)$  chain running parallel to the  $[010]$  direction and generated by the  $2_1$  screw axis along  $(0, y, \frac{3}{4})$  (Fig. 5).

Of the three  $C-H \cdots O$  hydrogen bonds, the shortest links the molecules into centrosymmetric pairs. Aryl atom C23 in the molecule at  $(x, y, z)$  acts as donor to nitro atom O22 in the molecule at  $(1 - x, 2 - y, 1 - z)$ , so generating a centrosymmetric  $R_2^2(10)$  dimer (Fig. 6). For the hydrogen-bond motif descriptor, see Bernstein *et al.* (1995). The molecule at  $(1 - x, 2 - y, 1 - z)$  forms part of the  $C(7)$  chain generated by the  $2_1$  screw axis along  $(1, -y, \frac{1}{4})$ , and hence the effect of the  $R_2^2(10)$  dimer motif is to link the  $[010]$  chains into  $(102)$  sheets built from alternating  $R_2^2(10)$  and  $R_6^0(54)$  rings (Fig. 7). The other two  $C-H \cdots O$  hydrogen bonds in the structure of (I) are both



**Figure 7**  
Stereoview of part of the crystal structure of (I), showing the formation of a  $(102)$  sheet built from alternating  $R_2^2(10)$  and  $R_6^0(54)$  rings. For the sake of clarity, H atoms not involved in the motifs shown have been omitted.

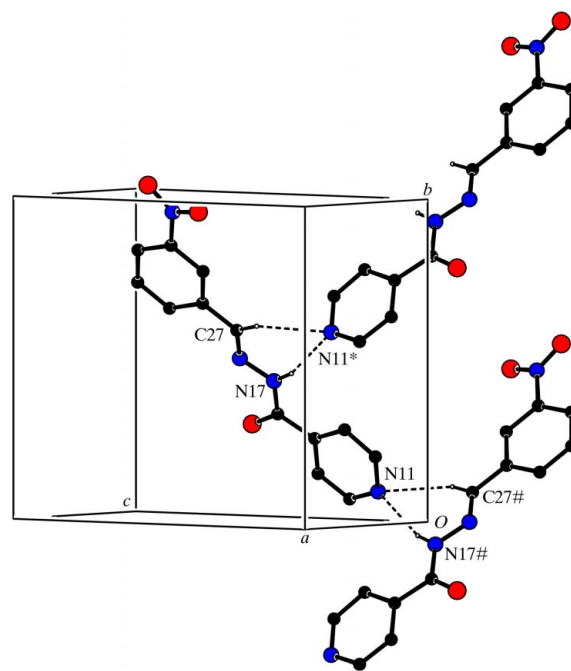


**Figure 8**  
Part of the crystal structure of (I), showing the formation of a  $C(6)C(7)[R_2^2(6)]$  chain of rings along  $[001]$ . For the sake of clarity, H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (\*) or a hash (#) are at the symmetry positions  $(x, \frac{3}{2} - y, -\frac{1}{2} + z)$  and  $(x, \frac{3}{2} - y, \frac{1}{2} + z)$ , respectively.

fairly weak, but they act in concert to generate a chain of rings parallel to the  $[001]$  direction, the effect of which is to link the  $(102)$  sheets. The adjacent aryl atoms C24 and C25 in the molecule at  $(x, y, z)$  act as donors to, respectively, nitro atoms O21 and O22, both in the molecule at  $(x, \frac{3}{2} - y, -\frac{1}{2} + z)$ , so forming a  $C(6)C(7)[R_2^2(6)]$  chain of rings along  $[001]$  generated by the  $c$ -glide plane at  $y = \frac{3}{4}$  (Fig. 8)

As in compound (I), the molecules of compound (II) (Fig. 2) are linked into chains by an  $N-H \cdots N$  hydrogen bond (Table 3), but this is now augmented, albeit rather weakly, by a  $C-H \cdots N$  interaction. Both amide atom N17 and nearby methine atom C27 in the molecule at  $(x, y, z)$  act as donors to pyridyl atom N11 in the molecule at  $(-x, \frac{1}{2} + y, \frac{1}{2} - z)$ , so generating a  $C(7)C(9)[R_2^1(6)]$  chain of rings running parallel to the  $[010]$  direction and generated by the  $2_1$  screw axis along  $(0, y, \frac{1}{4})$  (Fig. 9). The  $N-H \cdots N$  component thus mimics precisely the action of the corresponding bond in compound (I), where the  $C27-H27$  bond is effectively shielded from intermolecular interactions by the presence of the 2-nitro group, forming a short intramolecular  $C-H \cdots O$  contact.

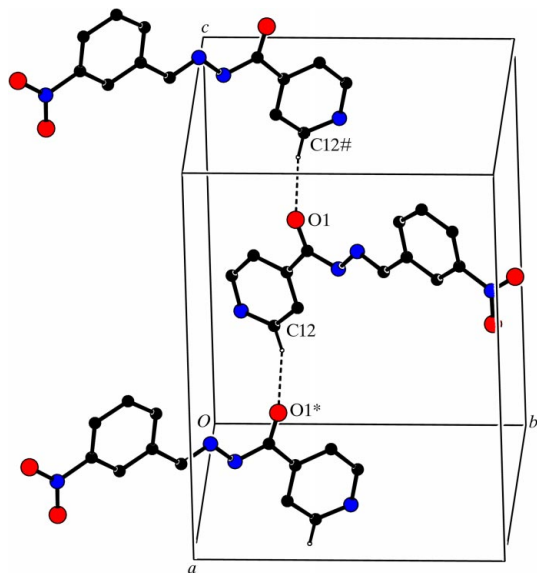
The structure of compound (II) also contains a single  $C-H \cdots O$  hydrogen bond, but unlike the  $C-H \cdots O$  bonds in (I), that in (II) involves amide atom O1 as the acceptor. Pyridyl atom C12 in the molecule at  $(x, y, z)$  acts as donor to atom O1 in the molecule at  $(x, \frac{1}{2} - y, -\frac{1}{2} + z)$ , so forming a  $C(6)$  chain running parallel to the  $[001]$  direction and generated by the  $c$ -glide plane at  $y = \frac{1}{4}$  (Fig. 10). The combination of the  $[010]$  and  $[001]$  motifs then generates a  $(100)$  sheet containing  $R_2^1(6)$ ,  $R_4^4(14)$  and  $R_4^4(26)$  rings (Fig. 11).



**Figure 9**  
Part of the crystal structure of (II), showing the formation of a  $C(7)C(9)[R_2^1(6)]$  chain of rings along  $[010]$ . 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  $(-x, \frac{1}{2} + y, \frac{1}{2} - z)$  and  $(-x, -\frac{1}{2} + y, \frac{1}{2} - z)$ , respectively.

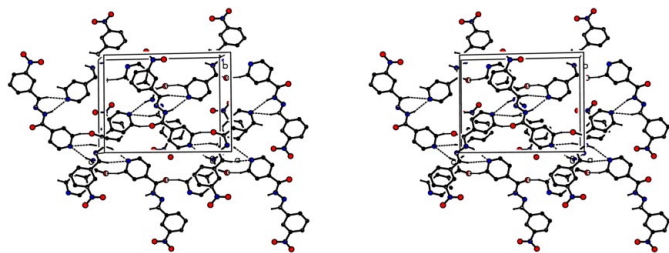
In compound (III) (Fig. 3), the molecules are linked into complex sheets by a combination of one N—H···N, one C—H···N and two C—H···O hydrogen bonds (Table 3), and the structure is most readily analysed in terms of two rather simple substructures. In the first of these substructures, which is one-dimensional, the molecules are linked into a  $C(4)C(7)[R_2^1(6)]$  chain of rings utilizing a combination of N—H···N and C—H···N hydrogen bonds, much as in compound (II), but in (III) the C—H···N hydrogen bond has as donor pyridyl atom C13 rather than methine atom C27. This chain runs parallel to the [010] direction and is generated by the  $2_1$  screw axis along  $(\frac{1}{2}, y, \frac{3}{4})$  (Fig. 12).

The second substructure in compound (III) is two-dimensional and is built using two independent C—H···O hydrogen bonds, one of which utilizes the amide O atom as acceptor, while the other utilizes a nitro O atom as acceptor. Pyridyl atom C12 in the molecule at  $(x, y, z)$  acts as donor to amide atom O1 in the molecule at  $(x, \frac{1}{2} - y, \frac{1}{2} + z)$ , so forming a  $C(6)$  chain running parallel to the [001] direction and generated by



**Figure 10**

Part of the crystal structure of (II), showing the formation of a  $C(6)$  chain along [001]. 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  $(x, \frac{1}{2} - y, -\frac{1}{2} + z)$  and  $(x, \frac{1}{2} - y, \frac{1}{2} + z)$ , respectively.

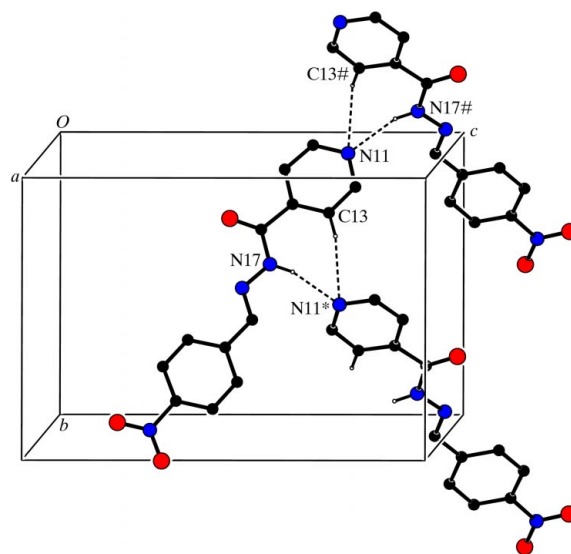


**Figure 11**

Stereoview of part of the crystal structure of (II), showing the formation of a (100) sheet built from  $R_2^1(6)$ ,  $R_4^1(14)$  and  $R_4^1(26)$  rings. For the sake of clarity, the weak C—H···N hydrogen bond and all H atoms not involved in the motifs shown have been omitted.

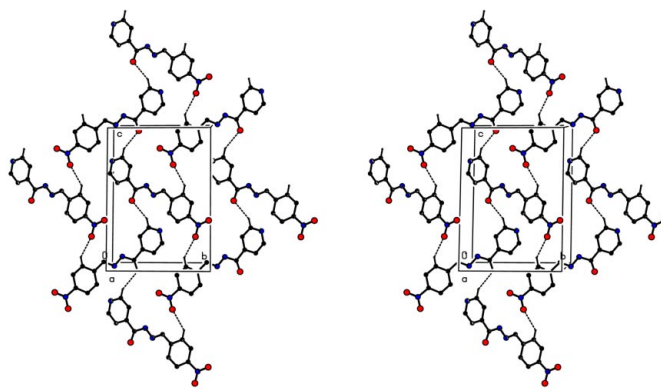
the  $c$ -glide plane at  $y = \frac{1}{4}$  (Fig. 13). In a similar manner, aryl atom C22 in the molecule at  $(x, y, z)$  acts as donor to nitro atom O42 in the molecule at  $(x, \frac{3}{2} - y, \frac{1}{2} + z)$ , so forming a second  $C(6)$  chain parallel to [001], but this time generated by the  $c$ -glide plane at  $y = \frac{3}{4}$ . The combination of these two  $C(6)$  chains then generates a (100) sheet in the form of a (4,4)-net (Batten & Robson, 1998) built from a single type of  $R_4^1(34)$  ring (Fig. 13). Two sheets of this type, related to one another by inversion, pass through each unit cell in the domains  $0.35 < x < 1.11$  and  $-0.11 < x < 0.65$ , and this pair of sheets is linked into a bilayer by the [010] chain of rings. There are no direction-specific interactions between adjacent bilayers.

The 2,4-dinitrophenylhydrazone derivative crystallizes as a stoichiometric monohydrate, (IV), and the two molecular components are linked within the selected asymmetric unit by a nearly linear N—H···O hydrogen bond (Fig. 4 and Table 5).



**Figure 12**

Part of the crystal structure of (III), showing the formation of a  $C(4)C(9)[R_2^1(6)]$  chain of rings along [010]. 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  $(1 - x, \frac{1}{2} + y, \frac{3}{2} - z)$  and  $(1 - x, -\frac{1}{2} + y, \frac{3}{2} - z)$ , respectively.

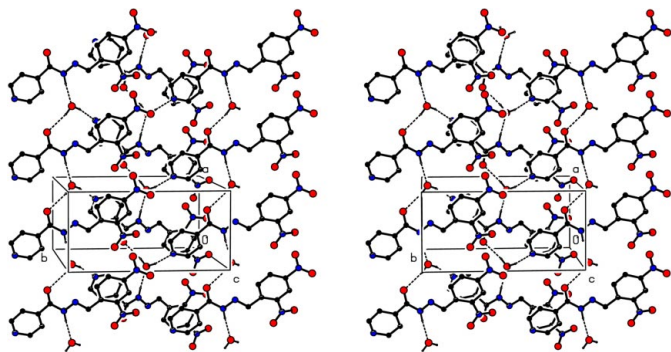


**Figure 13**

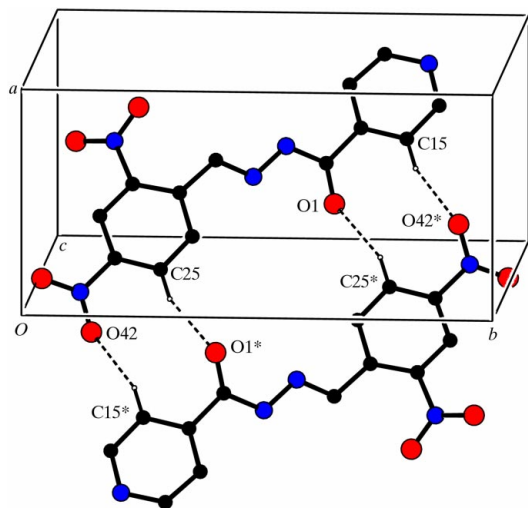
Stereoview of part of the crystal structure of (III), showing the combination of two independent  $C(6)$  chains along [001] to form a (100) sheet built from  $R_4^1(34)$  rings. For the sake of clarity, H atoms not involved in the motifs shown have been omitted.

The bimolecular aggregates are linked into sheets by a combination of O—H···O and O—H···N hydrogen bonds, and these sheets are further linked into a continuous three-dimensional framework by the concerted action of two C—H···O hydrogen bonds (Table 5).

Water atom O2 at  $(x, y, z)$  acts as hydrogen-bond donor, *via* atoms H2A and H2B, respectively, to amide atom O1 at  $(1 + x, y, z)$  and pyridyl atom N11 at  $(2 - x, -\frac{1}{2} + y, \frac{3}{2} - z)$ . These two hydrogen bonds thus produce a  $C_2^2(6)$  chain running parallel to the [100] direction and generated by translation, and a  $C_2^2(9)$  chain parallel to [010] and generated by the  $2_1$  screw axis along  $(1, y, \frac{3}{4})$ . The combination of these two chains then generates an (001) sheet built from a single type of  $R_6^6(24)$  ring (Fig. 14). Two sheets of this type pass through each unit cell, generated by, respectively, the  $2_1$  screw axes at  $z = \frac{1}{4}$  and  $z = \frac{3}{4}$ . Adjacent sheets are linked by a centrosymmetric motif involving two independent C—H···O hydrogen bonds. Atoms C15 and C25 at  $(x, y, z)$  act as hydrogen-bond donors to, respectively, nitro atom O42 and amide atom O1, both at  $(-x,$



**Figure 14**  
Stereoview of part of the crystal structure of (IV), showing the formation of an (001) sheet built from  $R_6^6(24)$  rings. For the sake of clarity, H atoms not involved in the motifs shown have been omitted.



**Figure 15**  
Part of the crystal structure of (IV), showing the formation of the cyclic centrosymmetric motif which links adjacent (001) sheets. For the sake of clarity, H atoms not involved in the motifs shown have been omitted. Atoms marked with an asterisk (\*) are at the symmetry position  $(-x, 1 - y, 1 - z)$ .

$1 - y, 1 - z)$ . The first of these hydrogen bonds generates an  $R_2^2(26)$  ring, while the second generates an  $R_2^2(18)$  ring (Fig. 15).

## Experimental

For the preparation of compounds (I)–(IV), equimolar mixtures (2 mmol of each component) of isoniazid and the appropriate nitrobenzaldehyde in tetrahydrofuran (20 ml) containing a catalytic quantity of triethylamine were heated under reflux for 6 h. After cooling, the solvent was removed under reduced pressure and the solid residues were chromatographed on silica gel, eluting with a hexane–ethyl acetate gradient, to provide the pure products. Crystals suitable for single-crystal X-ray diffraction were obtained upon recrystallization from methanol. Melting points: for (I), 506–508 K; for (II), 571–573 K; for (III), 553–555 K; for (IV), 504–506 K. Spectroscopic analyses:  $^1\text{H}$  NMR (DMSO- $d_6$ ,  $\delta$ , p.p.m.): (I) (major conformer) 12.44 (1H, s, NH), 8.89 (1H, s), 8.81 (2H, d,  $J = 5.5$  Hz), 8.13 (2H, t,  $J = 8$  Hz), 7.85 (3H, m), 7.73 (1H, m); (I) (minor conformer) 12.33 (1H, s, NH), 8.73 (2H, d,  $J = 5.0$  Hz), 8.50 (1H, s), 8.04 (1H, m), 7.72 (2H, m), 7.65 (3H, m); ratio of major to minor conformers = 6:1; for (II) (major conformer) 12.38 (1H, s, NH), 8.81 (2H, d,  $J = 6$  Hz), 8.57 (2H, s), 8.31 (1H, d,  $J = 7.5$  Hz), 8.20 (1H, d,  $J = 7.5$  Hz), 7.85 (2H, d,  $J = 6$  Hz), 7.78 (1H, t,  $J = 7.5$  Hz); (II) (minor conformer) 12.32 (1H, s, NH), 8.75 (2H, d,  $J = 6$  Hz), 8.32 (1H, m), 8.22 (1H, m), 7.96 (1H, d,  $J = 7$  Hz), 7.67 (1H, m), 7.67 (3H, m); ratio of major to minor conformers = 6:1; (III) (major conformer) 12.40 (1H, s, NH), 8.82 (2H, d,  $J = 6$  Hz), 8.57 (1H, s), 8.33 (2H, d,  $J = 8.5$  Hz), 8.03 (2H, d,  $J = 8.5$  Hz), 7.85 (2H, d,  $J = 6$  Hz); (III) (minor conformer) 12.36 (1H, s, NH), 8.76 (2H, d,  $J = 5$  Hz), 8.25 (2H, d,  $J = 8$  Hz), 8.22 (1H, s), 7.77 (2H, d,  $J = 8$  Hz), 7.67 (2H, d,  $J = 5$  Hz); ratio of major to minor conformers = 6:1; (IV) (major conformer) 12.65 (1H, s, NH), 8.92–8.76 (4H, m), 8.61–8.38 (2H, m), 7.84 (2H, s);  $^{13}\text{C}$  NMR (DMSO- $d_6$ ,  $\delta$ , p.p.m.): (II) 121.1, 121.5, 124.4, 130.4, 133.4, 135.8, 140.1, 146.5, 148.2, 150.3, 161.4; (III) 121.5, 124.0, 128.1, 130.4, 140.1, 140.2, 146.5, 148.0, 150.3, 161.9; (IV) 120.3, 121.5, 127.7, 129.4, 134.0, 139.6, 142.6, 147.4, 147.8, 150.4, 162.0; IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): (I) 3337, 3100–2800, 1681, 1603; (II) 3360, 3200–2800, 1693, 1619, 1610, 1601; (III) 3349, 3100–2800, 1685; (IV) 3161, 1664.

**Table 1**

Selected torsion angles ( $^\circ$ ) for compounds (I)–(IV).

	(I)	(II)	(III)	(IV)
C13–C14–C17–N17	–16.33 (19)	–0.6 (2)	–9.2 (2)	–29.69 (18)
C14–C17–N17–N27	173.53 (1)	–177.29 (11)	176.77 (12)	–179.13 (10)
C17–N17–N27–C27	–175.01 (12)	173.52 (12)	–175.78 (14)	–179.53 (11)
N17–N27–C27–C21	179.85 (11)	179.15 (11)	179.69 (13)	177.97 (10)
N27–C27–C21–C22	–174.50 (12)	–174.50 (13)	178.61 (15)	150.33 (13)
C21–C22–N2–O21	38.40 (18)			–24.41 (18)
C22–C23–N3–O31		–12.01 (19)		
C23–C24–N4–O41			–4.8 (2)	–18.96 (18)

## Compound (I)

### Crystal data

$\text{C}_{13}\text{H}_{10}\text{N}_4\text{O}_3$   
 $M_r = 270.25$   
 Monoclinic,  $P2_1/c$   
 $a = 7.3096$  (2) Å  
 $b = 10.9305$  (4) Å  
 $c = 15.3801$  (5) Å  
 $\beta = 94.569$  (2) $^\circ$   
 $V = 1224.93$  (7) Å $^3$   
 $Z = 4$

$D_x = 1.465$  Mg m $^{-3}$   
 Mo  $K\alpha$  radiation  
 Cell parameters from 2802 reflections  
 $\theta = 3.3$ – $27.5$  $^\circ$   
 $\mu = 0.11$  mm $^{-1}$   
 $T = 120$  (2) K  
 Block, colourless  
 $0.38 \times 0.14 \times 0.12$  mm

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)  
 $T_{\min} = 0.967$ ,  $T_{\max} = 0.987$   
 14989 measured reflections

2802 independent reflections  
 2401 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.038$   
 $\theta_{\text{max}} = 27.5^\circ$   
 $h = -9 \rightarrow 9$   
 $k = -14 \rightarrow 14$   
 $l = -19 \rightarrow 19$

Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.041$   
 $wR(F^2) = 0.112$   
 $S = 1.06$   
 2802 reflections  
 181 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0492P)^2 + 0.6309P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.34 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.26 \text{ e } \text{Å}^{-3}$

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

D—H...A	D—H	H...A	D...A	D—H...A
N17—H17...N11 <sup>i</sup>	0.86	2.23	3.0776 (16)	169
C23—H23...O22 <sup>ii</sup>	0.95	2.45	3.2294 (18)	139
C24—H24...O21 <sup>iii</sup>	0.95	2.55	3.2147 (18)	127
C25—H25...O22 <sup>iii</sup>	0.95	2.59	3.5052 (18)	163

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

**Compound (II)**

Crystal data

$\text{C}_{13}\text{H}_{10}\text{N}_4\text{O}_3$   
 $M_r = 270.25$   
 Monoclinic,  $P2_1/c$   
 $a = 8.2161$  (3) Å  
 $b = 10.8475$  (3) Å  
 $c = 14.1397$  (4) Å  
 $\beta = 106.2920$  (18)°  
 $V = 1209.58$  (7) Å<sup>3</sup>  
 $Z = 4$

$D_x = 1.484 \text{ Mg m}^{-3}$   
 Mo  $K\alpha$  radiation  
 Cell parameters from 2767 reflections  
 $\theta = 3.2\text{--}27.5^\circ$   
 $\mu = 0.11 \text{ mm}^{-1}$   
 $T = 120$  (2) K  
 Block, colourless  
 $0.28 \times 0.26 \times 0.22 \text{ mm}$

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)  
 $T_{\min} = 0.954$ ,  $T_{\max} = 0.976$   
 16374 measured reflections

2767 independent reflections  
 2118 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.049$   
 $\theta_{\text{max}} = 27.5^\circ$   
 $h = -10 \rightarrow 10$   
 $k = -14 \rightarrow 14$   
 $l = -18 \rightarrow 18$

Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.045$   
 $wR(F^2) = 0.132$   
 $S = 1.07$   
 2767 reflections  
 181 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0784P)^2 + 0.12P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.21 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.36 \text{ e } \text{Å}^{-3}$

**Table 3**  
 Hydrogen-bond geometry (Å, °) for (II).

D—H...A	D—H	H...A	D...A	D—H...A
N17—H17...N11 <sup>i</sup>	0.86	2.41	3.2382 (16)	162
C12—H12...O1 <sup>ii</sup>	0.95	2.36	3.0735 (18)	132
C27—H27...N11 <sup>i</sup>	0.97	2.58	3.4154 (17)	145

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

**Compound (III)**

Crystal data

$\text{C}_{13}\text{H}_{10}\text{N}_4\text{O}_3$   
 $M_r = 270.25$   
 Monoclinic,  $P2_1/c$   
 $a = 7.7821$  (3) Å  
 $b = 10.6633$  (4) Å  
 $c = 14.8417$  (6) Å  
 $\beta = 100.799$  (2)°  
 $V = 1209.80$  (8) Å<sup>3</sup>  
 $Z = 4$   
 $D_x = 1.484 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation  
 Cell parameters from 2777 reflections  
 $\theta = 3.3\text{--}27.6^\circ$   
 $\mu = 0.11 \text{ mm}^{-1}$   
 $T = 120$  (2) K  
 Block, yellow  
 $0.26 \times 0.18 \times 0.12 \text{ mm}$

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)  
 $T_{\min} = 0.966$ ,  $T_{\max} = 0.987$   
 14033 measured reflections

2777 independent reflections  
 1863 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.074$   
 $\theta_{\text{max}} = 27.6^\circ$   
 $h = -10 \rightarrow 10$   
 $k = -13 \rightarrow 12$   
 $l = -19 \rightarrow 19$

Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.051$   
 $wR(F^2) = 0.139$   
 $S = 1.02$   
 2777 reflections  
 181 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0763P)^2 + 0.0753P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.22 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.39 \text{ e } \text{Å}^{-3}$

**Table 4**  
 Hydrogen-bond geometry (Å, °) for (III).

D—H...A	D—H	H...A	D...A	D—H...A
N17—H17...N11 <sup>i</sup>	0.88	2.15	3.005 (2)	162
C12—H12...O1 <sup>ii</sup>	0.95	2.47	3.340 (2)	151
C13—H13...N11 <sup>i</sup>	0.95	2.58	3.409 (2)	146
C22—H22...O42 <sup>iii</sup>	0.95	2.52	3.294 (2)	138

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

**Compound (IV)**

Crystal data

$\text{C}_{13}\text{H}_9\text{N}_5\text{O}_5 \cdot \text{H}_2\text{O}$   
 $M_r = 333.27$   
 Monoclinic,  $P2_1/c$   
 $a = 6.7545$  (2) Å  
 $b = 13.8578$  (5) Å  
 $c = 15.2311$  (5) Å  
 $\beta = 91.098$  (2)°  
 $V = 1425.41$  (8) Å<sup>3</sup>  
 $Z = 4$   
 $D_x = 1.553 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation  
 Cell parameters from 3252 reflections  
 $\theta = 3.1\text{--}27.5^\circ$   
 $\mu = 0.13 \text{ mm}^{-1}$   
 $T = 120$  (2) K  
 Block, colourless  
 $0.50 \times 0.40 \times 0.35 \text{ mm}$

**Table 5**  
 Hydrogen-bond geometry (Å, °) for (IV).

D—H...A	D—H	H...A	D...A	D—H...A
N17—H17...O2	0.87	1.98	2.8521 (14)	174
O2—H2A...O1 <sup>i</sup>	0.85	2.24	3.0648 (13)	165
O2—H2B...N11 <sup>ii</sup>	0.86	2.02	2.8716 (15)	169
C12—H12...O21 <sup>iii</sup>	0.95	2.34	3.2326 (18)	157
C15—H15...O42 <sup>iv</sup>	0.95	2.31	3.2113 (17)	158
C25—H25...O1 <sup>iv</sup>	0.95	2.39	3.2742 (16)	155

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

*Data collection*

Bruker–Nonius KappaCCD area-detector diffractometer	3252 independent reflections
$\varphi$ and $\omega$ scans	2621 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	$R_{\text{int}} = 0.029$
$T_{\text{min}} = 0.946$ , $T_{\text{max}} = 0.957$	$\theta_{\text{max}} = 27.5^\circ$
15552 measured reflections	$h = -8 \rightarrow 8$
	$k = -17 \rightarrow 17$
	$l = -18 \rightarrow 19$

*Refinement*

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0652P)^2 + 0.3739P]$
$R[F^2 > 2\sigma(F^2)] = 0.039$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.116$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.07$	$\Delta\rho_{\text{max}} = 0.29 \text{ e } \text{\AA}^{-3}$
3252 reflections	$\Delta\rho_{\text{min}} = -0.29 \text{ e } \text{\AA}^{-3}$
217 parameters	
H-atom parameters constrained	

For each of (I)–(IV), the space group  $P2_1/c$  was uniquely assigned from the systematic absences. All H atoms were located in difference maps. H atoms in aryl or pyridyl rings were then treated as riding atoms, with  $C-H = 0.95 \text{ \AA}$  and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . The remaining H atoms were all allowed to ride at the locations deduced from difference maps, with distances  $C-H = 0.94\text{--}0.97 \text{ \AA}$ ,  $N-H = 0.86\text{--}0.87 \text{ \AA}$  and  $O-H = 0.85\text{--}0.86 \text{ \AA}$ , and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,N,O})$ .

For all compounds, 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).

The 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: SK1873). Services for accessing these data are described at the back of the journal.

**References**

- Atovmyan, E. G., Nikonova, L. A., Filipenko, O. S., Fedotova, T. N. & Aldoshin, S. M. (2002). *Russ. Chem. Bull.* **51**, 99–104.
- Batten, S. R. & Robson, R. (1998). *Angew. Chem. Int. Ed.* **37**, 1460–1494.
- Bernstein, J., Davis, R. E., Shimon, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Chuev, I. I., Aldoshin, S. M., Atovmyan, E. G., Frolov, D. B. & Utenyshev, A. N. (1996). *Russ. Chem. Bull.* **45**, 851–855.
- Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.
- Fun, H.-K., Lu, Z.-L., Duan, C.-Y., Tian, Y.-P., You, X.-Z., Guo, Y.-M. & Gong, X.-Y. (1997). *Acta Cryst.* **C53**, 1452–1454.
- Liu, S.-H., Chen, X.-F., Xu, Y.-H., You, X.-Z., Chen, W. & Arifin, Z. (1998). *Acta Cryst.* **C54**, 1919–1921.
- 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.