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Supramolecular structures of three isomeric 2-chloro-*N*-(nitrophenyl)-nicotinamides

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Molecules of 2-chloro-*N*-(2-nitrophenyl)nicotinamide, $C_{12}H_8ClN_3O_3$, are linked by two C—H···O hydrogen bonds into a chain of edge-fused $R_2^2(14)$ and $R_4^4(24)$ rings. In 2-chloro-*N*-(3-nitrophenyl)nicotinamide monohydrate, $C_{12}H_8ClN_3O_3 \cdot H_2O$, the molecules are linked by a combination of N—H···O, O—H···O and O—H···N hydrogen bonds into a chain of edge-fused rings containing two distinct types of $R_4^4(16)$ ring. In 2-chloro-*N*-(4-nitrophenyl)nicotinamide, $C_{12}H_8ClN_3O_3$, which crystallizes with $Z' = 2$ in space group $P2_1/n$, the molecules are linked by two N—H···N hydrogen bonds into simple $C_2^2(12)$ chains.

Comment

We report here the molecular and supramolecular structures of three isomeric 2-chloro-*N*-(nitrophenyl)nicotinamides (Figs. 1–3). Of these isomers, the 3-nitrophenyl isomer, (II), crystallizes from acetone as a monohydrate, whereas the 2-nitrophenyl isomer, (I), crystallizes from the same solvent in the unsolvated form. The 4-nitrophenyl isomer, (III), crystallizes from ethanol with $Z' = 2$ (Fig. 3).

In compounds (I) and (II), and in each of the independent molecules of (III), the central amide spacer unit is essentially planar, as demonstrated by the C—C—N—C torsion angles (Tables 1, 3 and 5). However, the torsion angles describing the conformations of the two rings relative to the spacer unit show some variations, particularly for the heteroaryl rings. The nitroaryl rings do not deviate significantly from the plane of the amide spacer unit, and in each molecule there is a short intramolecular C—H···O contact involving atom C26 in the aryl ring [atom C46 in molecule 2 of compound (III)] and the amide O atom (Tables 2, 4 and 6); this interaction may have

some influence on the conformation. The planes of the nitro groups are all close to the planes of the adjacent aryl rings. The two independent molecules in (III) adopt very similar conformations so that for the selected asymmetric unit the two molecules are nearly enantiomeric (Table 5 and Fig. 3).
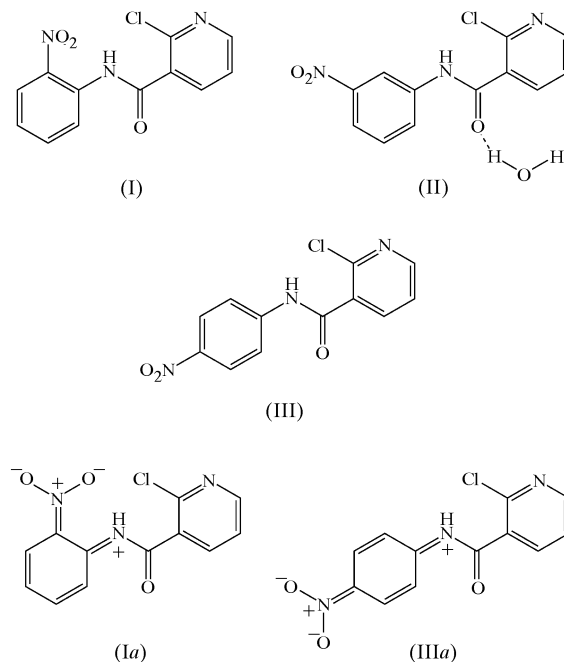
Within the spacer units, the backbone C—C—N angles are consistently significantly less than 120°, while the C—N—C angles are significantly greater than 120°. There is no evidence from the bond length in the nitroaniline fragments in compounds (I) and (III) of any bond fixation, such as is typically found in simple 2-nitro- and 4-nitroanilines. Thus, polarization of types (I*a*) and (III*a*) cannot effectively compete with the normal polarization of the amide units in these compounds.

The molecules of (I) are linked into a chain of edge-fused rings by two C—H···O hydrogen bonds, involving both the carbonyl O and one of the nitro O atoms (Table 2). Atom C14 of the heteroaryl ring in the molecule at (x, y, z) acts as a hydrogen-bond donor to nitro atom O2 in the molecule at
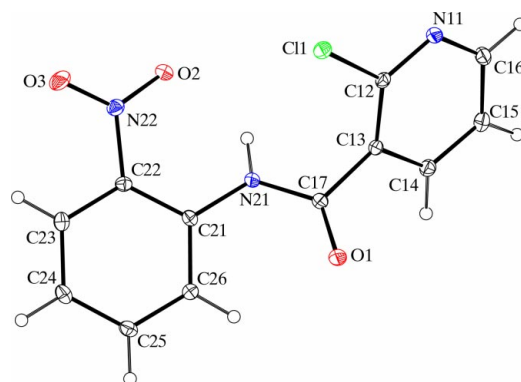

Figure 1
The molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

$(-1 + x, y, z)$, so generating by translation a $C(9)$ chain (Bernstein *et al.*, 1995) running parallel to the [100] direction. At the same time, aryl atom C25 in the molecule at (x, y, z) acts as a donor to carbonyl atom O1 in the molecule at $(-x, 1 - y, 1 - z)$, so forming a centrosymmetric $R_2^2(14)$ ring centred at $(0, \frac{1}{2}, \frac{1}{2})$. The combination of these two motifs then generates a chain of centrosymmetric edge-fused rings along [100], with $R_2^2(14)$ rings centred at $(n, \frac{1}{2}, \frac{1}{2})$ (n = zero or integer) and $R_4^4(24)$ rings centred at $(n + \frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (n = zero or integer)
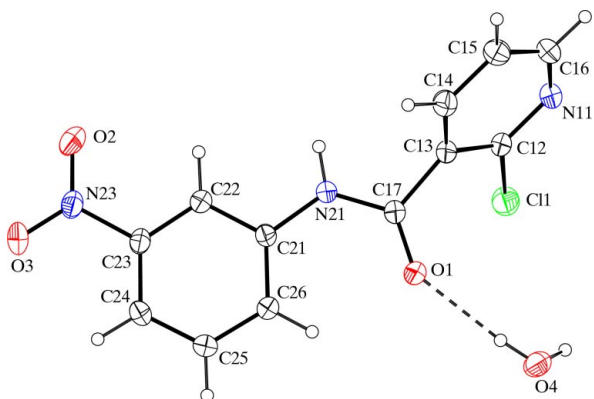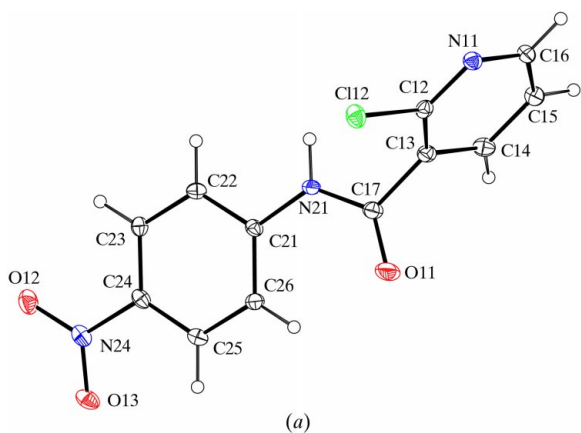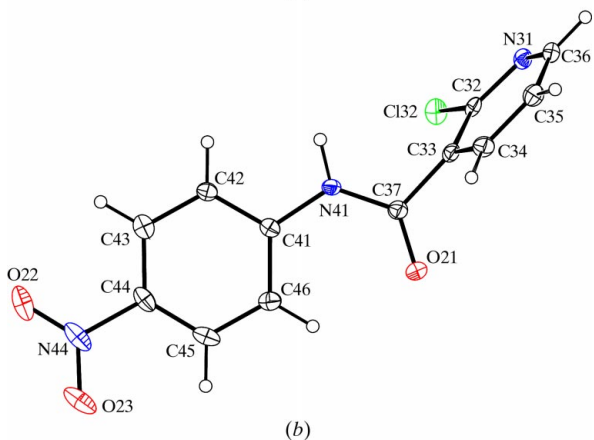

Figure 2
The molecular components of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

(a)

(b)

Figure 3
The two independent molecules of (III), showing the atom-labelling schemes for (a) molecule 1 and (b) molecule 2. Displacement ellipsoids are drawn at the 30% probability level.

(Fig. 4). Two chains of this type pass through each unit cell, along the lines $(x, 0, 0)$ and $(x, \frac{1}{2}, \frac{1}{2})$, but there are no direction-specific interactions between adjacent chains.

The independent components in (II) are linked by a combination of O—H⋯O, O—H⋯N and N—H⋯O hydrogen bonds (Table 4) into a chain of edge-fused rings. Water atom O41 acts as a hydrogen-bond donor, *via* H41, to carbonyl atom O1 within the asymmetric unit. In addition, amine atom N21 at (x, y, z) acts as a hydrogen-bond donor to water atom O4 at $(x, -1 + y, z)$, so generating by translation a $C_2^2(6)$ chain running parallel to the [010] direction, in which O—H⋯O hydrogen bonds alternate with N—H⋯O hydrogen bonds (Fig. 5). Two chains of this type, antiparallel to one another, pass through each unit cell, and these are linked by the O—H⋯N hydrogen bonds. Water atom O41 at (x, y, z) also acts as a hydrogen-bond donor, this time *via* H42, to ring atom N11 at $(1 - x, 1 - y, -z)$, so generating a centrosymmetric $R_4^4(16)$ ring, centred at $(\frac{1}{2}, \frac{1}{2}, 0)$ (Fig. 5). The combination of these two motifs then generates a chain of centrosymmetric edge-fused rings along the line $(\frac{1}{2}, y, 0)$, in which $R_4^4(16)$ rings containing O—H⋯O and O—H⋯N hydrogen bonds and centred at $(\frac{1}{2}, n + \frac{1}{2}, 0)$ (n = zero or integer) alternate with $R_4^4(16)$ rings containing N—H⋯O and

Figure 4
A stereoview of part of the crystal structure of (I), showing the formation of a chain of edge-fused rings along [100]. For clarity, H atoms not involved in the motifs shown have been omitted.

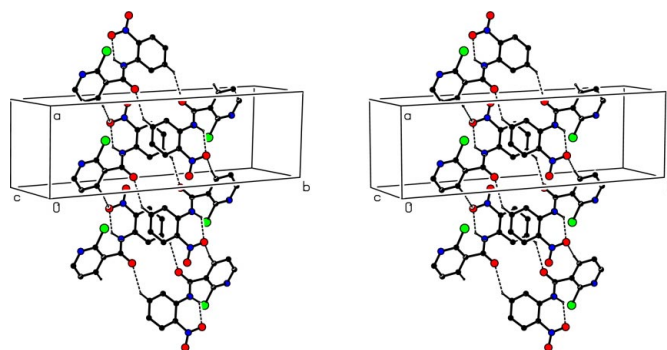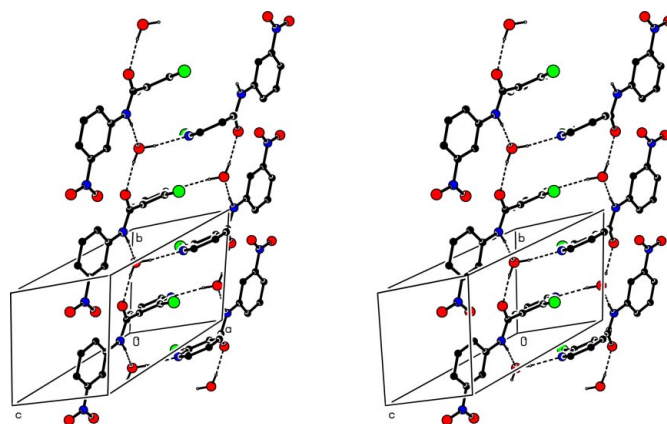**Figure 5**
A stereoview of part of the crystal structure of (II), showing the formation of a chain of edge-fused rings along [010]. For clarity, H atoms bonded to C atoms have been omitted.

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O—H···N hydrogen bonds and centred at $(\frac{1}{2}, n, 0)$ (n = zero or integer) (Fig. 5).

The hydrogen-bonded chains in compound (II) are linked by three distinct aromatic π–π stacking interactions, all of them centrosymmetric but some of them fairly weak, into a continuous three-dimensional array. The heteroaryl ring in the molecule at (x, y, z) is parallel to the corresponding ring in the molecule at ($-x$, $1 - y$, $-z$), which itself forms part of the hydrogen-bonded chain along ($-\frac{1}{2}$, y, 0); the interplanar spacing is 3.546 (2) Å, with a ring-centroid separation of 3.795 (2) Å, corresponding to a ring offset of 1.352 (2) Å. This interaction thus links the [010] chains into (001) sheets. In a similar fashion, the aryl rings of the molecules at (x, y, z) and ($1 - x$, $-y$, $1 - z$), where the latter forms part of the hydrogen-bonded chain along ($\frac{1}{2}$, y, 1), are also parallel, with an interplanar spacing of 3.707 (2) Å, a ring-centroid separation of 3.917 (2) Å and a ring offset of 1.264 (2) Å. Finally, the aryl rings of the molecules at (x, y, z) and ($-x$, $-y$, $1 - z$), which forms part of the hydrogen-bonded chain along ($-\frac{1}{2}$, y, 1), are also parallel, with an interplanar spacing of 3.384 (2) Å, a ring-centroid separation of 3.793 (2) Å and a ring offset of 1.715 (2) Å. These latter interactions connect the (001) sheets, so linking all of the hydrogen-bonded chains into a continuous framework.

The two independent molecules in (III) are linked into simple chains by two N—H···N hydrogen bonds (Table 6). Amide atom N21 acts as a hydrogen-bond donor to ring atom N31 within the asymmetric unit; similarly, amide atom N41 at (x, y, z) acts as a donor to ring atom N11 at ($-1 + x$, y, z), so generating by translation a $C_2^2(12)$ chain running parallel to the [100] direction (Fig. 6). There are number of short C—H···O contacts within this chain (Table 6), although it is doubtful if any of them could be regarded as a hydrogen bond; it is likely that these contacts are simply adventitious consequences of the N—H···N hydrogen bonds. Two $C_2^2(12)$ chains, antiparallel to one another, pass through each unit cell, but there are no direction-specific interactions between adjacent chains.

It is thus striking that modest changes in the geometric position of a single substituent are associated with significant changes in crystallization characteristics, in the direction-specific intermolecular interactions manifested and hence in the overall supramolecular structures; none of these changes is readily predictable.
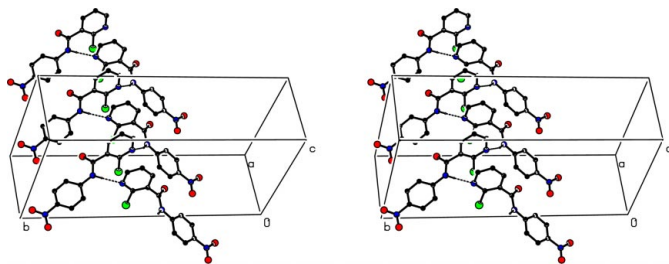

Figure 6
A stereoview of part of the crystal structure of (III), showing the formation of a $C_2^2(12)$ chain along [100]. For clarity, H atoms bonded to C atoms have been omitted.

Compound (I)

Crystal data

C$_{12}$H$_8$ClN$_3$O$_3$	D_x = 1.633 Mg m^{-3}
M_r = 277.66	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 2580
a = 6.9964 (1) Å	reflections
b = 22.4244 (4) Å	θ = 3.4–27.5°
c = 7.2085 (1) Å	μ = 0.35 mm^{-1}
β = 93.0910 (11)°	T = 120 (2) K
V = 1129.30 (3) Å^3	Block, colourless
Z = 4	0.54 × 0.44 × 0.36 mm

Data collection

Nonius KappaCCD diffractometer	2355 reflections with $I > 2\sigma(I)$
φ and ω scans	R_{int} = 0.029
Absorption correction: multi-scan	θ_{max} = 27.5°
($SADABS$; Sheldrick, 2003)	$h = -9 \rightarrow 9$
T_{min} = 0.835, T_{max} = 0.886	$k = -29 \rightarrow 28$
13 129 measured reflections	$l = -9 \rightarrow 9$
2580 independent reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0562P)^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.038	$+ 0.4042P]$
$wR(F^2)$ = 0.104	where $P = (F_o^2 + 2F_c^2)/3$
S = 1.19	$(\Delta/\sigma)_{max}$ = 0.001
2580 reflections	$\Delta\rho_{max}$ = 0.57 e Å^{-3}
174 parameters	$\Delta\rho_{min}$ = -0.47 e Å^{-3}
H-atom parameters constrained	Extinction correction: $SHELXL97$
	Extinction coefficient: 0.078 (6)

Table 1
Selected geometric parameters (Å, °) for (I).

N21—C21	1.4052 (17)	C22—N22	1.4618 (18)
N21—C17—C13	114.40 (12)	C17—N21—C21	127.03 (12)
C12—C13—C17—N21	-62.93 (18)	C17—N21—C21—C22	-157.61 (14)
C13—C17—N21—C21	178.88 (13)	C21—C22—N22—O2	-15.1 (2)

Table 2
Hydrogen-bond parameters and short intramolecular contacts (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
N21—H21···O2	0.88	2.01	2.6416 (16)	128
C14—H14···O2^i	0.95	2.49	3.4084 (17)	162
C25—H25···O1^{ii}	0.95	2.53	3.2921 (18)	137
C26—H26···O1	0.95	2.30	2.8771 (18)	119

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

Table 3
Selected geometric parameters (Å, °) for (II).

N21—C21	1.4122 (18)	C23—N23	1.465 (2)
N21—C17—C13	114.31 (13)	C17—N21—C21	127.89 (13)
C12—C13—C17—N21	−123.99 (17)	C17—N21—C21—C22	−178.35 (16)
C13—C17—N21—C21	−174.38 (15)	C22—C23—N23—O2	3.2 (2)

Table 4
Hydrogen-bond parameters and short intramolecular contacts (Å, °) for (II).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N21—H21$\cdots$O4^{iii}	0.88	2.03	2.907 (2)	173
O4—H41$\cdots$O1^{iv}	0.85	2.07	2.916 (2)	173
O4—H42$\cdots$N11^{iv}	0.88	2.06	2.935 (2)	170
C26—H26$\cdots$O1	0.95	2.25	2.864 (2)	121

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

Compound (II)

Crystal data

$C_{12}H_8ClN_3O_3\cdot H_2O$	$Z = 2$
$M_r = 295.68$	$D_x = 1.547$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 7.5607$ (4) Å	Cell parameters from 2891
$b = 7.6518$ (3) Å	reflections
$c = 12.6775$ (5) Å	$\theta = 3.3$–$27.6°$
$\alpha = 81.177$ (3)°	$\mu = 0.32$ mm^{-1}
$\beta = 84.367$ (2)°	$T = 120$ (2) K
$\gamma = 61.172$ (2)°	Block, colourless
$V = 634.69$ (5) Å^3	$0.2 \times 0.2 \times 0.2$ mm

Data collection

Nonius KappaCCD diffractometer	2318 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.028$
Absorption correction: multi-scan	$\theta_{max} = 27.6°$
(SADABS; Sheldrick, 2003)	$h = -9 \rightarrow 9$
$T_{min} = 0.926$, $T_{max} = 0.938$	$k = -9 \rightarrow 9$
12 769 measured reflections	$l = -16 \rightarrow 16$
2891 independent reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.074P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.044$	$+ 0.1161P]$
$wR(F^2) = 0.129$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.08$	$(\Delta/\sigma)_{max} < 0.001$
2891 reflections	$\Delta\rho_{max} = 0.27$ e Å^{-3}
183 parameters	$\Delta\rho_{min} = -0.43$ e Å^{-3}
H-atom parameters constrained	

Compound (III)

Crystal data

$C_{12}H_8ClN_3O_3$	Mo $K\alpha$ radiation
$M_r = 277.66$	Cell parameters from 5494
Monoclinic, $P2_1/n$	reflections
$a = 7.2385$ (2) Å	$\theta = 2.9$–$27.6°$
$b = 24.5094$ (6) Å	$\mu = 0.33$ mm^{-1}
$c = 13.5018$ (4) Å	$T = 120$ (2) K
$\beta = 92.834$ (2)°	Block, colourless
$V = 2392.44$ (11) Å^3	$0.2 \times 0.1 \times 0.1$ mm
$Z = 8$	
$D_x = 1.542$ Mg m^{-3}	

Table 5
Selected geometric parameters (Å, °) for (III).

N21—C21	1.410 (3)	N41—C41	1.412 (3)
C24—N24	1.467 (3)	C44—N44	1.471 (3)
N21—C17—C13	114.8 (2)	N41—C37—C33	114.6 (2)
C17—N21—C21	127.75 (19)	C37—N41—C41	127.63 (19)
C12—C13—C17—N21	78.1 (3)	C32—C33—C37—N41	−71.5 (3)
C13—C17—N21—C21	173.29 (19)	C33—C37—N41—C41	−173.4 (2)
C17—N21—C21—C22	−179.8 (2)	C37—N41—C41—C42	173.6 (2)
C25—C24—N24—O13	−8.1 (3)	C43—C44—N44—O22	5.2 (3)

Table 6
Hydrogen-bond parameters and short intramolecular contacts (Å, °) for (III).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N21—H21$\cdots$N31	0.92	2.08	2.999 (3)	178
N41—H41$\cdots$N11^i	0.95	2.14	3.067 (3)	164
C22—H22$\cdots$O11^i	0.95	2.58	3.117 (3)	116
C23—H23$\cdots$O11^i	0.95	2.37	3.011 (3)	124
C26—H26$\cdots$O11	0.95	2.25	2.861 (3)	121
C43—H43$\cdots$O21^i	0.95	2.57	3.166 (3)	121
C46—H46$\cdots$O21	0.95	2.27	2.874 (3)	121

Symmetry code: (i) $x - 1, y, z$.

Data collection

Nonius KappaCCD diffractometer	3366 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.079$
Absorption correction: multi-scan	$\theta_{max} = 27.6°$
(SADABS; Sheldrick, 2003)	$h = -9 \rightarrow 9$
$T_{min} = 0.945$, $T_{max} = 0.968$	$k = -31 \rightarrow 30$
5494 measured reflections	$l = -17 \rightarrow 17$
5494 independent reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.073P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.051$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.143$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.00$	$\Delta\rho_{max} = 0.29$ e Å^{-3}
5494 reflections	$\Delta\rho_{min} = -0.44$ e Å^{-3}
343 parameters	
H-atom parameters constrained	

For isomers (I) and (III), the space groups $P2_1/c$ and $P2_1/n$ were uniquely assigned from the systematic absences. Crystals of compound (II) are triclinic; space group $P\bar{1}$ was selected and confirmed by the successful structure analysis. All H atoms were located from difference maps. H atoms bonded to C atoms were treated as riding atoms, with C—H distances of 0.95 Å and U_{iso}(H) values of $1.2U_{eq}$(C). H atoms bonded to N atoms were allowed to ride at the positions located from the difference maps, with N—H distances of 0.88–0.95 Å and U_{iso}(H) values of $1.2U_{eq}$(N). H atoms bonded to atom O4 in (II) were allowed to ride at the positions located from the difference maps, with O—H distances of 0.85 and 0.88 Å and individual isotropic displacement parameters.

For all compounds, data collection: COLLECT (Hooft, 1999); cell refinement: DENZO (Otwinowski & Minor, 1997) and COLLECT; data reduction: DENZO and COLLECT; structure solution: OSCAIL (McArdle, 2003) and SHELXS97 (Sheldrick, 1997); structure refinement: OSCAIL and SHELXL97 (Sheldrick, 1997); mol-

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ecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

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