

***N*-Amidino-4-hydroxy-L-proline  
monohydrate and *N*-amidino-  
L-methionine monohydrate**

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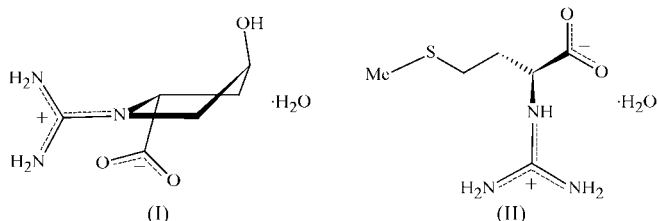
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The title amidino-amino acids (*a*-Hpro),  $C_6H_{11}N_3O_3 \cdot H_2O$ , (I), and *a*-Met,  $C_6H_{13}N_3O_2S \cdot H_2O$ , (II), respectively, exist in the form of zwitterions. The five-membered pyrrolidine ring in (I) adopts an envelope conformation, with the  $C_\gamma$  atom out of the plane defined by the rest of the ring atoms, and with the hydroxyl and carboxylate groups in a *trans* configuration relative to the ring plane. The two crystallographically independent zwitterions in (II) reveal quite different conformations of their side chains and a slightly different orientation of the guanidine moiety with respect to the carboxylate group. The crystal structures of both (I) and (II) are stabilized by extensive networks of  $O-H \cdots O$ ,  $N-H \cdots O$  and  $C-H \cdots O$  hydrogen bonds, the network being three-dimensional in (I) and two-dimensional in (II).

**Comment**

The title compounds, both  $\alpha$ -guanidino acids derived from 4-hydroxyproline and methionine, namely amidino-4-hydroxy-L-proline (*a*-Hpro), (I), and amidino-L-methionine (*a*-Met), (II), have been crystallized and structurally analysed by X-ray crystallography as a completion of broader studies on the chiro-optical properties of the guanidine chromophore (Siemion *et al.*, 2005). We present here the complete geometric characterization of (I) and (II) in the solid state, together with a comparison of their molecular structures with related compounds and an analysis of their intermolecular interactions in the crystal network.

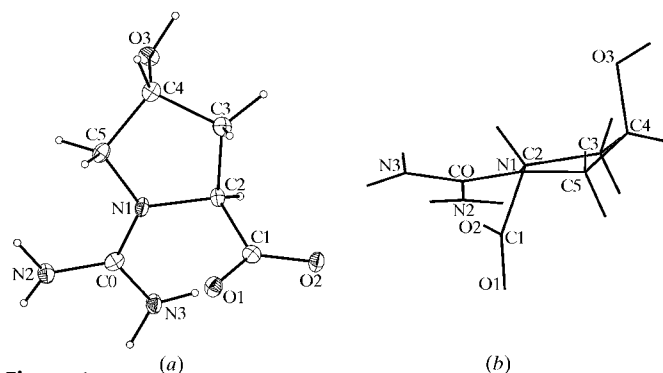


Both (I) and (II) crystallize as hydrated zwitterions, with one zwitterion in the asymmetric unit of (I) and two crystallographically independent zwitterions (denoted 1 and 2) in

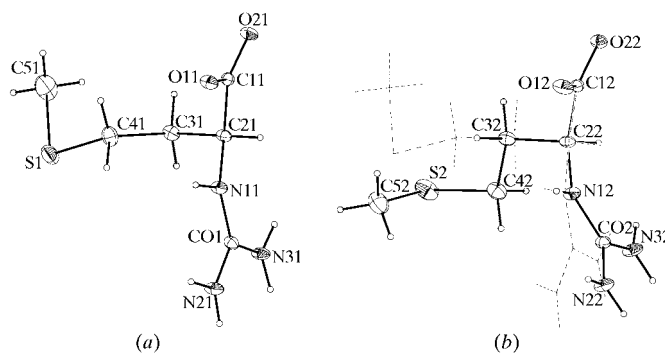
(II). All the zwitterions in both (I) and (II) exist with the carboxyl groups deprotonated and the amidine moieties protonated. The positive charge is delocalized into the whole amidine group; the  $\pi$ -electron pair is equally distributed between the three C–N bonds, which makes C0–N1, C0–N2 and C0–N3 equal in length (about 1.33 Å; Tables 1 and 3) and the whole guanidine group planar [atoms C0, N1, N2 and N3 lie in one plane to within 0.003 or 0.005 Å in (I) and (II), respectively].

A very interesting structural feature of  $\alpha$ -guanidino acids, of relevance to studies of the chiro-optical properties of the guanidine chromophore, is the orientation of amidine atom C0 relative to carboxylate atom C1, and the mutual orientation of the planar guanidine and carboxylate moieties. In (I), the amidine group is in a *gauche* (*–sc*) orientation with respect to the carboxylate substituent, whereas in the two crystallographically independent zwitterions of (II), the respective C0–N1–C2–C1 torsion angles reveal *ap* and *–ac* conformations for zwitterions 1 and 2, respectively. The dihedral angles between the planes of the guanidine and carboxylate groups are 79.9 (2)° in (I) and 21.1 (1)/44.3 (1)° in (II).

The  $\Psi^1$  (O1–C1–C2–N1) and  $\Psi^2$  (O2–C1–C2–N1) torsion angles are –24.9 (3) and 158.0 (2)°, respectively, for



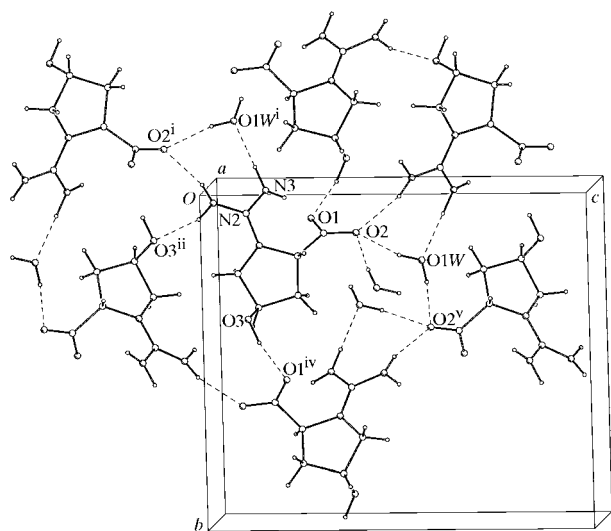
**Figure 1**  
(a) The molecular structure of the zwitterion in (I), showing the atom numbering scheme. Displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as small spheres of arbitrary radii. (b) The conformation of the pyrrolidine ring in (I).



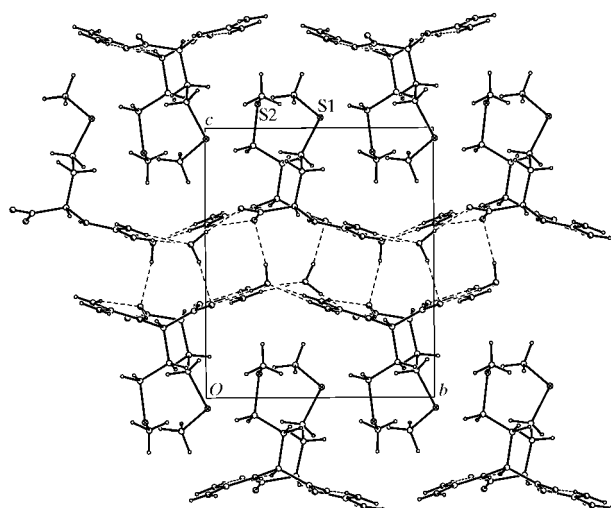
**Figure 2**  
The molecular structure of the two crystallographically independent zwitterions in (II), *viz.* (a) 1 and (b) 2. Displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as small spheres of arbitrary radii. The dashed lines in (b) indicate the superimposed structure of zwitterion 1, allowing a comparison of zwitterions 1 and 2. The common reference points are atoms C1, O1 and O2.

(I), and  $-20.2$  (2) and  $159.6$  (1) $^\circ$  and  $-29.4$  (2) and  $151.4$  (1) $^\circ$  for zwitterions 1 and 2, respectively, in (II). Thus, atom N1 is displaced from the plane of the carboxylate group by about  $0.43$  Å in (I), and by  $0.49$  and  $-0.64$  Å in zwitterions 1 and 2 of (II), respectively.

The molecular structure of (I) and the conformation of the pyrrolidine ring are shown in Fig. 1. The five-membered pyrrolidine ring adopts an envelope conformation, with the C $\gamma$  atom (C4) lying out of the ring plane [the dihedral angle between the N1/C2/C3/C5 and C3/C4/C5 planes is  $35.2$  (2) $^\circ$ ], and with the hydroxyl and carboxylate groups in a *trans* configuration relative to the plane of the pyrrolidine ring. A similar conformation of the ring and orientation of the OH and COOH substituents were found previously in 4-hydroxy-L-proline (Donohue & Trueblood, 1952; Koetzle *et al.*, 1973) and its palladium complex (Patel *et al.*, 1986). It is



**Figure 3**  
A view of part of the three-dimensional network of O–H...O and N–H...O hydrogen bonds linking adjacent zwitterions and water molecules in the crystal structure of (I). Symmetry codes are as given in Table 2.



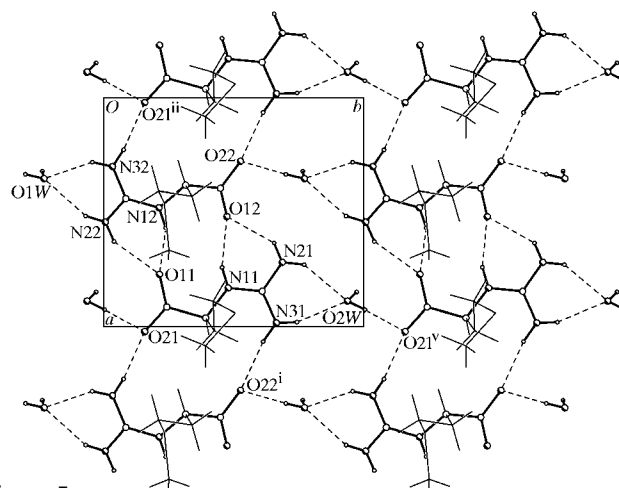
**Figure 4**  
A crystal packing diagram of (II), viewed down the *a* axis, showing the layer architecture.

interesting to note that a different puckering of the pyrrolidine ring has sometimes been observed in hydroxyproline derivatives and analogues, such as *allo*-4-hydroxy-L-proline dihydrate (Shamala *et al.*, 1976) and *2,3-cis-3,4-trans-3,4-dihydroxy-L-proline* (Karle, 1970) (envelope with C $\beta$  atom puckered), or *N*-methylated 4-hydroxyproline derivatives (Jones *et al.*, 1988) (envelope with N atom puckered).

The ring substituents in (I), *i.e.* amidine, carboxylate and hydroxyl groups, are in equatorial, bisecting and axial positions, respectively. The guanidine group is nearly coplanar with the four plane-defining pyrrolidine ring atoms; the dihedral angle between the respective planes is  $10.3$  (2) $^\circ$ .

The molecular structures of the two crystallographically independent zwitterions in (II) are shown in Fig. 2. Zwitterions 1 and 2 reveal quite different conformations of their side chains and, as described above, slightly different orientations of the guanidine moiety with respect to the rest of the molecule, especially to the carboxylate group, and this is readily observed in the superimposition of the two zwitterions shown in Fig. 2. The values of the  $\chi^1$  (N1–C2–C3–C4),  $\chi^2$  (C2–C3–C4–S) and  $\chi^3$  (C3–C4–S–C5) torsion angles (Table 3) indicate the *+gauche*, *trans*, *–gauche* and *–gauche*, *trans*, *–gauche* conformations of the side-chains in zwitterions 1 and 2, respectively.

Similar *gauche*, *trans*, *gauche* side-chain conformations are quite commonly present in methionine residues and have been observed previously, for example, in the methioninium cations in crystalline L-methioninium nitrate (Pandiarajan *et al.*, 2002) and DL-methioninium trichloroacetate (Rajagopal *et al.*, 2003), or in the methionine zwitterions in L-methionine L-methioninium perchlorate monohydrate (Sridhar *et al.*, 2002), and even in one of the methionine moieties in the L-methionyl-L-methionine dipeptide (Stenkamp & Jensen, 1975). However, in the crystal structure of L-methionine, two different conformations of the side chain were observed, neither of them being as described above (Torii & Iitaka, 1973).



**Figure 5**  
A packing diagram for (II), showing the arrangement of the zwitterions and water molecules within the layer formed by O–H...O and N–H...O hydrogen bonds, viewed down the *c* axis. The *a*-Met side chains are shown as thin lines. Symmetry codes are as given in Table 4.

The main difference in the side-chain conformations of zwitterions 1 and 2 is the orientation of their C $\gamma$  atom (C4) relative to carboxylate atom C1, which is *sc* in 1 and *ap* in 2. Three of the four side-chain atoms in 2, namely C32, C42 and S2, together with atoms C12 and C22 from the main chain, lie in one plane (to within 0.04 Å), from which methyl atom C52 deviates by about 1.67 Å. This is reflected in the C12–C22–C32–C42 and C22–C32–C42–S2 torsion angles, which are both close to 180° (Table 3).

The crystal structure of (I) is stabilized by a network of O–H···O and N–H···O hydrogen bonds, in which hydroxyl, amidine and carboxylate groups, as well as the solvent water molecules, are involved (Fig. 3 and Table 2). Additionally, there are also close C–H···O contacts. The strongest O–H···O interaction is formed between the hydroxyl and carboxylate groups of adjacent a-Hpro zwitterions. The water molecules act as donors of medium-strength O–H···O hydrogen bonds to the carboxylate O atoms of two different zwitterions. Simultaneously, a water O atom is an acceptor of one N–H···O contact from the amidine group, which also acts as a donor of three additional N–H···O hydrogen bonds to the hydroxyl and carboxylate groups from three different adjacent zwitterions. The carboxylate moiety is involved as acceptor in five different hydrogen-bond interactions, hence three- or four-centred contacts are formed. Thus, the hydrogen-bond network linking adjacent zwitterions and water molecules in the crystal structure of (I) is three-dimensional (Fig. 3).

The packing of (II) is quite different from that observed in (I) (Figs. 4 and 5; Table 4). As can be seen in Fig. 4, the crystal has a layer architecture. The two crystallographically independent zwitterions have almost identical hydrogen-bonding features. Zwitterions 1 and 2 are linked to each other by two three-centred N–H···O contacts formed by their guanidine and carboxylate groups. This results in 1–2 dimers, in which guanidine NH and one of the NH<sub>2</sub> groups are involved. The other NH<sub>2</sub> group acts as a linker to the adjacent 1–2 dimer by acting in an N–H···O hydrogen bond to the carboxylate O atom from an adjacent dimer, forming infinite ribbons along the *a* axis. Pairs of adjacent ribbons are linked by water molecules to form layers parallel to the (001) plane, in which the a-Met side chains of zwitterions 1 and 2 are located on one side of the plane defined by the two-dimensional O–H···O and N–H···O hydrogen-bond network. The arrangement of the zwitterions and water molecules within the layer is shown in Fig. 5. Both water molecules are involved in additional O–H···O interactions with the adjacent head-to-head layer and act as the linkers between each such pair of adjacent layers. This assembly of a-Met zwitterions and water molecules leads to the double-layer architecture of the crystal structure of (II). The result of this arrangement of the individual zwitterions in the crystal network is the aggregation of the hydrophilic and hydrophobic groups into two distinct regions in the crystal, which is very often observed in crystals containing the methionine moiety (Mathieson, 1952; Torii & Iitaka, 1973; Alagar *et al.*, 2002; Pandiarajan *et al.*, 2002; Sridhar *et al.*, 2002; Rajagopal *et al.*, 2003).

## Experimental

The synthesis of guanidino acids (amidino-amino acids) and their purification and characterization by high-pressure liquid chromatography and ESI-MS, along with their CD and UV spectroscopic characteristics, are described in detail by Siemion *et al.* (2004). Long thin colourless plates of (I) and very fragile colourless parallelepipeds of (II), with a tendency to twin, were obtained by slow evaporation of aqueous solutions at 277 K.

## Compound (I)

### Crystal data

C<sub>6</sub>H<sub>11</sub>N<sub>3</sub>O<sub>3</sub>·H<sub>2</sub>O  
*M<sub>r</sub>* = 191.19  
 Orthorhombic, *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>  
*a* = 4.604 (2) Å  
*b* = 12.514 (4) Å  
*c* = 14.422 (4) Å  
*V* = 830.9 (5) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.528 Mg m<sup>-3</sup>

Mo *K*α radiation  
 Cell parameters from 6400 reflections  
 $\theta$  = 3.3–28.3°  
 $\mu$  = 0.13 mm<sup>-1</sup>  
*T* = 100 (2) K  
 Plate, colourless  
 0.50 × 0.10 × 0.03 mm

### Data collection

Kuma KM-4 CCD diffractometer  
 $\omega$  scans  
 5278 measured reflections  
 1066 independent reflections  
 923 reflections with *I* > 2σ(*I*)

*R*<sub>int</sub> = 0.077  
 $\theta$ <sub>max</sub> = 27.0°  
*h* = –5 → 5  
*k* = –15 → 7  
*l* = –18 → 18

### Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.039  
*wR* (*F*<sup>2</sup>) = 0.081  
*S* = 1.03  
 1066 reflections  
 170 parameters

All H-atom parameters refined  
 $w = 1/[\sigma^2(F_o^2) + (0.0469P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 ( $\Delta/\sigma$ )<sub>max</sub> < 0.001  
 $\Delta\rho_{max} = 0.20 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{min} = -0.21 \text{ e } \text{Å}^{-3}$

**Table 1**

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

C0–N1	1.335 (3)	C0–N3	1.324 (3)
C0–N2	1.332 (3)		
N1–C0–N2	119.4 (2)	N2–C0–N3	119.5 (2)
N1–C0–N3	121.0 (2)		
N1–C2–C3–C4	–17.0 (3)	N3–C0–N1–C5	172.1 (2)
C1–C2–C3–C4	–138.6 (2)	C1–C2–N1–C0	–63.2 (3)
C2–C3–C4–C5	33.1 (3)	C3–C2–N1–C0	178.4 (2)
C3–C4–C5–N1	–36.0 (3)	C1–C2–N1–C5	112.2 (2)
N2–C0–N1–C2	166.9 (2)	C3–C2–N1–C5	–6.1 (3)
N3–C0–N1–C2	–12.9 (4)	C4–C5–N1–C0	–157.7 (2)
N2–C0–N1–C5	–8.0 (4)	C4–C5–N1–C2	26.9 (3)

**Table 2**

Geometry of hydrogen bonds and close C–H···O contacts (Å, °) for (I).

<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>
N2–H21···O2 <sup>i</sup>	0.84 (3)	2.15 (3)	2.957 (3)	161 (3)
N2–H22···O3 <sup>ii</sup>	0.92 (4)	2.01 (4)	2.885 (3)	159 (3)
N3–H31···O1W <sup>t</sup>	0.96 (3)	1.89 (3)	2.850 (3)	180 (3)
N3–H32···O1 <sup>iii</sup>	0.82 (3)	2.08 (3)	2.882 (3)	163 (3)
O3–H3···O1 <sup>iv</sup>	0.95 (3)	1.70 (3)	2.642 (3)	169 (3)
O1W–H1W···O2 <sup>v</sup>	0.92 (4)	1.91 (5)	2.823 (3)	173 (4)
O1W–H2W···O2	0.86 (4)	2.00 (4)	2.800 (3)	154 (4)
C2–H2···O1 <sup>iii</sup>	1.01 (3)	2.71 (3)	3.515 (3)	138 (2)
C3–H3A···O1W <sup>v</sup>	0.93 (3)	2.67 (3)	3.531 (4)	154 (2)
C4–H4···O3 <sup>vi</sup>	0.96 (3)	2.72 (3)	3.533 (4)	143 (2)
C5–H5B···O3 <sup>ii</sup>	0.96 (3)	2.72 (3)	3.402 (3)	129 (2)

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

Compound (II)

Crystal data

$C_6H_{13}N_3O_2S \cdot H_2O$	$D_x = 1.353 \text{ Mg m}^{-3}$
$M_r = 209.27$	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 18 427 reflections
$a = 8.982 \text{ (3) \AA}$	$\theta = 3.1\text{--}36.6^\circ$
$b = 9.844 \text{ (3) \AA}$	$\mu = 0.30 \text{ mm}^{-1}$
$c = 12.066 \text{ (4) \AA}$	$T = 100 \text{ (2) K}$
$\beta = 105.64 \text{ (3)^\circ}$	Parallelepiped, colourless
$V = 1027.4 \text{ (6) \AA}^3$	$0.30 \times 0.10 \times 0.10 \text{ mm}$
$Z = 4$	

Data collection

Kuma KM-4 CCD diffractometer	$R_{\text{int}} = 0.036$
$\omega$ scans	$\theta_{\text{max}} = 36.0^\circ$
21 484 measured reflections	$h = -14 \rightarrow 14$
8879 independent reflections	$k = -15 \rightarrow 16$
7275 reflections with $I > 2\sigma(I)$	$l = -19 \rightarrow 17$

Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0399P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.039$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.078$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 0.98$	$\Delta\rho_{\text{max}} = 0.35 \text{ e \AA}^{-3}$
8879 reflections	$\Delta\rho_{\text{min}} = -0.23 \text{ e \AA}^{-3}$
354 parameters	Known absolute configuration
H atoms treated by a mixture of independent and constrained refinement	confirmed by anomalous dispersion effects (Flack, 1983), with 3832 Friedel pairs
	Flack parameter = $-0.02 \text{ (4)}$

Table 3

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for (II).

C01—N11	1.333 (2)	C02—N12	1.333 (2)
C01—N21	1.335 (2)	C02—N22	1.328 (2)
C01—N31	1.331 (2)	C02—N32	1.336 (2)
C51—S1—C41	100.79 (8)	C52—S2—C42	100.06 (8)
N31—C01—N11	121.71 (11)	N12—C02—N22	118.69 (11)
N31—C01—N21	119.34 (11)	N12—C02—N32	122.48 (11)
N11—C01—N21	118.94 (11)	N22—C02—N32	118.82 (11)
C51—S1—C41—C31	$-70.0 \text{ (2)}$	C52—S2—C42—C32	$-69.0 \text{ (1)}$
S1—C41—C31—C21	$-163.1 \text{ (1)}$	S2—C42—C32—C22	$-179.4 \text{ (1)}$
N11—C21—C31—C41	$53.6 \text{ (2)}$	N12—C22—C32—C42	$-63.3 \text{ (2)}$
C11—C21—C31—C41	$-69.1 \text{ (2)}$	C12—C22—C32—C42	$176.0 \text{ (1)}$
C11—C21—N11—C01	$-160.8 \text{ (1)}$	C12—C22—N12—C02	$-132.2 \text{ (2)}$
C31—C21—N11—C01	$75.1 \text{ (2)}$	C32—C22—N12—C02	$106.9 \text{ (2)}$
N21—C01—N11—C21	$-166.3 \text{ (1)}$	N22—C02—N12—C22	$177.7 \text{ (1)}$
N31—C01—N11—C21	$14.4 \text{ (2)}$	N32—C02—N12—C22	$-3.3 \text{ (2)}$

All H atoms were found in a difference map and were refined isotropically, except for atom H22 in (II), which was refined with  $U_{\text{iso}}(\text{H}) = U_{\text{eq}}(\text{C22})$ . Friedel opposites for (I) were merged and the absolute configuration was established on the basis of the known stereochemistry.

For both compounds, data collection: *CrysAlis CCD* (Oxford Diffraction, 2003); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2003); data reduction: *CrysAlis RED*; program(s) used to solve

Table 4

Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ ) for (II).

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
N11—H11 $\cdots$ O12	0.86 (2)	1.99 (2)	2.805 (2)	158 (2)
N21—H211 $\cdots$ O12	0.85 (2)	2.22 (2)	2.950 (2)	145 (2)
N21—H212 $\cdots$ O2W	0.84 (2)	2.22 (2)	2.960 (2)	147 (2)
N31—H311 $\cdots$ O22 <sup>i</sup>	0.87 (2)	2.08 (2)	2.922 (2)	165 (2)
N31—H312 $\cdots$ O2W	0.83 (2)	2.08 (2)	2.855 (2)	156 (2)
N12—H12 $\cdots$ O11	0.84 (2)	2.05 (1)	2.826 (2)	154 (2)
N22—H221 $\cdots$ O11	0.85 (2)	2.12 (1)	2.874 (2)	147 (2)
N22—H222 $\cdots$ O1W	0.80 (2)	2.12 (2)	2.854 (2)	154 (2)
N32—H321 $\cdots$ O21 <sup>ii</sup>	0.83 (2)	2.08 (2)	2.907 (2)	170 (2)
N32—H322 $\cdots$ O1W	0.83 (2)	2.18 (2)	2.921 (2)	150 (2)
O1W—H1W $\cdots$ O22 <sup>iii</sup>	0.81 (2)	1.94 (2)	2.744 (2)	176 (2)
O1W—H2W $\cdots$ O11 <sup>iv</sup>	0.82 (2)	2.00 (2)	2.809 (2)	169 (2)
O2W—H3W $\cdots$ O21 <sup>v</sup>	0.87 (2)	1.90 (2)	2.771 (2)	173 (2)
O2W—H3W $\cdots$ O11 <sup>v</sup>	0.87 (2)	2.62 (2)	3.220 (2)	126 (2)
O2W—H4W $\cdots$ O22 <sup>vi</sup>	0.83 (2)	2.04 (2)	2.858 (2)	168 (2)
C21—H21 $\cdots$ O22 <sup>i</sup>	0.96 (2)	2.47 (2)	3.364 (2)	155 (2)
C22—H22 $\cdots$ O21 <sup>ii</sup>	0.98 (2)	2.57 (2)	3.514 (2)	162 (2)

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

structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1216). Services for accessing these data are described at the back of the journal.

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