# organic compounds

# rac-N-[Hydroxy(4-pyridyl)methyl]-picolinamide: a hemiamidal

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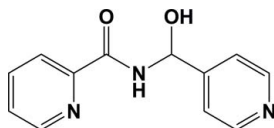Correspondence e-mail: muhammad.altaf@unine.ch

The title compound, $C_{12}H_{11}N_3O_2$, a hemiamidal, was synthesized by solvent-free aldol condensation at room temperature by grinding picolinamide with isonicotinaldehyde in a 1:1 molar ratio. In the molecule, the two pyridine rings are inclined to one another by 58.75 (6)°. They are linked, at positions 2 and 4, by the hemiamidal bridge (–CO—NH—CHOH–). The NH-group H atom forms an intramolecular hydrogen bond with the N atom of the picolinamide pyridine ring. In the crystal, symmetry-related molecules are linked *via* N—H⋯O hydrogen bonds, involving the NH group H atom of the hemiamidal bridge and the hydroxy O atom, forming inversion-related dimers, with graph-set $R_2^2(8)$. Adjacent molecules are also linked *via* O—H⋯N hydrogen bonds, involving the hydroxy substituent and the 4-pyridine N atom. Together these interactions lead to the formation of double-stranded ribbon-like hydrogen-bonded polymers propagating in [010]. The latter are further connected *via* C—H⋯O hydrogen bonds involving the carbonyl O atom, so forming a two-dimensional network in (011).

## Related literature

For background to green synthesis, see: Raston & Scott (2000). For solid-state reactions and solvent-free syntheses, see: Kaupp (2003, 2005). For the structure of a similar non-cyclic hemiamidal, see: Kawahara *et al.* (1992). For details of the Cambridge Structural Database, see: Allen (2002). For standard bond lengths, see: Allen *et al.* (1987). For details of hydrogen-bonding graph-set analysis, see: Bernstein *et al.* (1995). For the illustration and analysis of hydrogen bonding, see: Macrae *et al.* (2006).



## Experimental

### Crystal data

| | |
|---|---|
| $C_{12}H_{11}N_3O_2$ | $V = 1039.26$ (18) Å$^3$ |
| $M_r = 229.24$ | $Z = 4$ |
| Monoclinic, $P2_1/c$ | Mo $K\alpha$ radiation |
| $a = 12.1450$ (13) Å | $\mu = 0.10$ mm$^{-1}$ |
| $b = 5.6044$ (4) Å | $T = 173$ K |
| $c = 16.3940$ (19) Å | $0.50 \times 0.41 \times 0.10$ mm |
| $\beta = 111.354$ (9)° | |

### Data collection

| | |
|---|---|
| Stoe IPDS-2 diffractometer | 2196 reflections with $I > 2\sigma(I)$ |
| 14414 measured reflections | $R_{int} = 0.079$ |
| 2823 independent reflections | |

### Refinement

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)] = 0.042$ | H atoms treated by a mixture of |
| $wR(F^2) = 0.111$ | independent and constrained |
| $S = 1.04$ | refinement |
| 2823 reflections | $\Delta\rho_{max} = 0.37$ e Å$^{-3}$ |
| 163 parameters | $\Delta\rho_{min} = -0.22$ e Å$^{-3}$ |

**Table 1**
Hydrogen-bond geometry (Å, °).

| $D$—H⋯$A$ | $D$—H | H⋯$A$ | $D$⋯$A$ | $D$—H⋯$A$ |
|---|---|---|---|---|
| N2—H2$N$⋯N1 | 0.875 (17) | 2.468 (18) | 2.7769 (16) | 101.4 (13) |
| N2—H2$N$⋯O2$^i$ | 0.875 (17) | 2.091 (17) | 2.9304 (15) | 160.7 (16) |
| O2—H2$O$⋯N1$^{ii}$ | 0.905 (19) | 1.92 (2) | 2.8056 (16) | 167.6 (17) |
| C7—H7⋯O1$^{iii}$ | 1.00 | 2.43 | 3.3694 (15) | 157 |
| C12—H12⋯O1$^{iv}$ | 0.95 | 2.43 | 3.3517 (17) | 163 |

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

Data collection: *X-AREA* (Stoe & Cie, 2004); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97* and *PLATON*.

## References

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**supplementary materials**

## *rac-N*-[Hydroxy(4-pyridyl)methyl]picolinamide: a hemiamidal

## M. Altaf and H. Stoeckli-Evans

### Comment

Green chemistry is a well established field of research, enhanced by its numerous applications in high technology industries and because of the need for environmentally friendly syntheses. The perfect *green reaction* has been described as one which: proceeds at room temperature, requires no organic solvent, is highly selective and exhibits high atom efficiency, yet produces no waste products (Raston & Scott, 2000). In recent decades, numerous reactions using mechanical activation have been reported to give 100% yield (Kaupp, 2005). This procedure has a number of advantages, such as rapid and qualitatively solvent free synthesis and no necessary work up procedure (Kaupp, 2003). On the other hand, there are some disadvantages, such as the use of harmful sodium hydroxide, or other sodium salts, as intermediates in the reaction work up. The title compound was synthesized by grinding picolinamide with isonicotinaldehyde in a molar ratio of 1:1 giving a brown gelatinous material. On drying in air a brown microcrystalline powder was obtained, which proved to be the title compound. The compound is a result of the combination of green chemistry and mechanical activation.

The molecule structure of the title molecule is illustrated in Fig. 1. The bond distances are normal (Allen *et al.*, 1987) and the bond angles in the hemiamidal bridge (–CO—NH-CHOH–) are similar to those observed in (1-hydroxybut-2-yl)ammonium *N*-benzoyl-α-hydroxyglycine (Kawahara *et al.*, 1992). Interestingly, here the authors showed that Peptidylglycine-hydroxylating monooxygenase (PHM), converted *N*-benzoylglycine stereoselectively to *S-N*-benzoyl-hydroxyglycine. The latter is the only non-cyclic example of such a (–CO—NH-CHOH–) unit that was found during a search of the Cambridge Crystal Structure Database (CSD, V5.31, last update May 2010; Allen *et al.*, 2002).

In the title molecule the two pyridine rings are inclined to one another by 58.75 (6) °, and the NH H-atom (H2N) forms an intramolecular hydrogen bond with the picolinamide N-atom (N1) (Fig. 1 and Table 1).

In the crystal molecules are linked *via* N—H⋯O and O—H⋯O hydrogen bonds (Table 1). The N—H⋯O hydrogen bonds, involving the hemiamidal NH group and the hydroxyl O-atom, lead to the formation of inversion dimers, graph-set $R^2_2(8)$ (Fig. 2) (Bernstein *et al.*, 1995). Adjacent molecules are linked *via* O—H⋯N hydrogen bonds involving the hydroxyl H-atom (H2O) and the adjacent pyridine N-atom, N2 (Table 1). Together with molecules related by an inversion center these interactions lead to a graph-set of $R^4_4(14)$ (Fig. 3). Finally these hydrogen bonding interactions lead to the formation of double-stranded ribbon-like polymers propagating in [010]. They are further linked *via* C—H⋯O interactions, involving the C=O O-atom, leading to the formation of two dimensional networks stacking along [100] (Fig. 4 and Table 1).

### Experimental

The synthesis of the title compound was carried out by mixing by hand in a mortar a 1:1 molar ratio of picolinamide with isonicotinaldehyde. A viscous brown mixture was obtained which on drying in air gave a brown micro-crystalline powder (Yield 98.78%). Elemental analysis (%) for $C_{12}H_{11}N_3O_2$: C, 62.88; H, 4.80; N, 18.34. Found: C, 62.75; H, 4.91; N, 18.54. IR (cm$^{-1}$): 3471.51, 3288.31, 3025.77, 1676.26, 1616.03, 1590.90, 1569.42, 1412.63, 1156.79, 922.55, 747.07, 581.52.

# supplementary materials

Crystals suitable for X-ray analysis were obtained during a failed attempt of complex formation with MnCl$_2$.6H$_2$O in a methanol/water solution. The colourless reaction solution obtained was filtered and the filtrate left undisturbed at RT for slow evaporation. After five days colourless plate-like crystals, suitable for X-ray diffraction analysis, were obtained.

## Refinement

The NH and OH H-atoms were located in a difference electron-density map and were freely refined: O—H = 0.905 (19) Å, N—H = 0.875 (17) Å. The C-bound H-atoms were included in calculated positions and treated as riding atoms: C—H = 0.95 Å for H-aromatic, and 1.00 Å for H-methine, with $U_{iso}(H) = 1.2U_{eq}(C)$.

## Figures



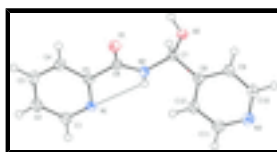Fig. 1. A view of the molecular structure of the title molecule, with dispacement ellipsoids drawn at the 50% probability level [The intramolecular N—H···N hydrogen bond is shown as a dashed line].
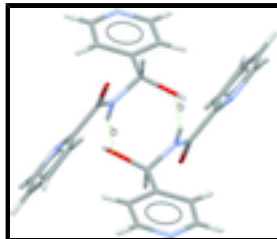


Fig. 2. A view of the hydrogen bonded inversion dimers in the crystal of the title compound; graph-set $R^2_2(8)$>b>b (Mercury: Macrae *et al.*, 2006).
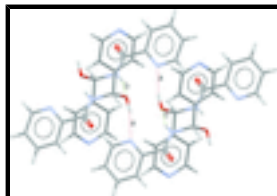


Fig. 3. A view of the hydrogen bonded $R^4_4(14)$a>b>a>b graph-set, involving adjacent molecules and those related by an inversion center, in the crystal structure of the title compound (Mercury: Macrae *et al.*, 2006).



Fig. 4. A view along the *b*-axis of the crystal packing of the title compound, with the N—H···O, O—H···N and C—H···O hydrogen bonds shown as dashed lines (see Table 1 for details).

### *rac-N*-[Hydroxy(4-pyridyl)methyl]picolinamide

*Crystal data*

| | |
|---|---|
| C$_{12}$H$_{11}$N$_3$O$_2$ | $F(000) = 480$ |
| $M_r = 229.24$ | $D_x = 1.465$ Mg m$^{-3}$ |

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 12.1450 (13)$ Å

$b = 5.6044 (4)$ Å

$c = 16.3940 (19)$ Å

$\beta = 111.354 (9)°$

$V = 1039.26 (18)$ Å$^3$

$Z = 4$

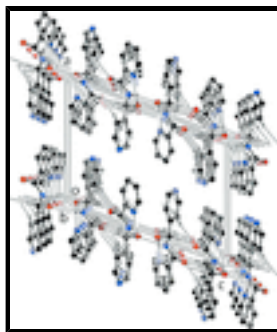Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 10944 reflections

$\theta = 1.8–29.6°$

$\mu = 0.10$ mm$^{-1}$

$T = 173$ K

Plate, colourless

$0.50 \times 0.41 \times 0.10$ mm

*Data collection*

Stoe IPDS-2 diffractometer

Radiation source: fine-focus sealed tube

graphite

phi + ω rotation scans

14414 measured reflections

2823 independent reflections

2196 reflections with $I > 2\sigma(I)$

$R_{int} = 0.079$

$\theta_{max} = 29.3°$, $\theta_{min} = 1.8°$

$h = -16 \rightarrow 16$

$k = -7 \rightarrow 7$

$l = -22 \rightarrow 22$

*Refinement*

Refinement on $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.042$

$wR(F^2) = 0.111$

$S = 1.04$

2823 reflections

163 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0672P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.37$ e Å$^{-3}$

$\Delta\rho_{min} = -0.22$ e Å$^{-3}$

Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.020 (4)

*Special details*

**Geometry**. Bond distances, angles *etc*. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

**Refinement**. Refinement of $F^2$ against ALL reflections. The weighted $R$-factor $wR$ and goodness of fit $S$ are based on $F^2$, conventional $R$-factors $R$ are based on $F$, with $F$ set to zero for negative $F^2$. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating $R$-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. $R$-factors based on $F^2$ are statistically about twice as large as those based on $F$, and $R$- factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)*

|  | *x* | *y* | *z* | $U_{iso}*/U_{eq}$ |
|---|---|---|---|---|
| O1 | −0.08117 (8) | 1.01540 (16) | 0.21882 (6) | 0.0269 (3) |
| O2 | 0.03250 (8) | 1.27719 (16) | 0.06003 (6) | 0.0233 (2) |
| N1 | −0.15978 (9) | 0.51231 (18) | 0.08046 (7) | 0.0216 (3) |
| N2 | −0.01442 (9) | 0.91083 (19) | 0.11117 (7) | 0.0206 (3) |
| N3 | 0.42324 (10) | 0.8732 (2) | 0.16564 (8) | 0.0328 (3) |
| C1 | −0.24525 (11) | 0.3491 (2) | 0.05116 (9) | 0.0253 (3) |
| C2 | −0.35054 (11) | 0.3619 (3) | 0.06494 (9) | 0.0293 (4) |
| C3 | −0.36862 (11) | 0.5519 (3) | 0.11228 (10) | 0.0299 (4) |
| C4 | −0.28077 (11) | 0.7220 (2) | 0.14387 (9) | 0.0254 (3) |
| C5 | −0.17819 (10) | 0.6966 (2) | 0.12589 (8) | 0.0206 (3) |
| C6 | −0.08534 (10) | 0.8875 (2) | 0.15735 (8) | 0.0204 (3) |
| C7 | 0.06900 (10) | 1.1054 (2) | 0.12781 (8) | 0.0195 (3) |
| C8 | 0.19102 (10) | 1.0180 (2) | 0.13730 (7) | 0.0202 (3) |
| C9 | 0.26572 (11) | 1.1592 (2) | 0.11155 (9) | 0.0256 (3) |
| C10 | 0.37952 (12) | 1.0795 (3) | 0.12702 (10) | 0.0318 (4) |
| C11 | 0.34982 (12) | 0.7394 (2) | 0.19001 (9) | 0.0298 (4) |
| C12 | 0.23415 (11) | 0.8019 (2) | 0.17731 (9) | 0.0258 (3) |
| H1 | −0.23290 | 0.21720 | 0.01910 | 0.0300* |
| H2 | −0.40940 | 0.24250 | 0.04240 | 0.0350* |
| H2N | −0.0255 (14) | 0.824 (3) | 0.0645 (11) | 0.026 (4)* |
| H2O | −0.0220 (16) | 1.371 (3) | 0.0699 (12) | 0.038 (5)* |
| H3 | −0.44020 | 0.56550 | 0.12300 | 0.0360* |
| H4 | −0.29040 | 0.85360 | 0.17720 | 0.0310* |
| H7 | 0.07430 | 1.18470 | 0.18380 | 0.0230* |
| H9 | 0.23950 | 1.30840 | 0.08370 | 0.0310* |
| H10 | 0.42980 | 1.17870 | 0.10890 | 0.0380* |
| H11 | 0.37860 | 0.59140 | 0.21790 | 0.0360* |
| H12 | 0.18560 | 0.69880 | 0.19570 | 0.0310* |

*Atomic displacement parameters (Å²)*

|  | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| O1 | 0.0345 (5) | 0.0250 (5) | 0.0274 (5) | −0.0026 (4) | 0.0186 (4) | −0.0048 (4) |
| O2 | 0.0272 (4) | 0.0201 (4) | 0.0265 (4) | 0.0048 (3) | 0.0145 (4) | 0.0036 (3) |
| N1 | 0.0231 (5) | 0.0199 (5) | 0.0238 (5) | 0.0013 (4) | 0.0108 (4) | 0.0005 (4) |
| N2 | 0.0236 (5) | 0.0197 (5) | 0.0209 (5) | −0.0023 (4) | 0.0110 (4) | −0.0025 (4) |
| N3 | 0.0246 (5) | 0.0305 (6) | 0.0421 (7) | −0.0003 (4) | 0.0107 (5) | −0.0041 (5) |
| C1 | 0.0276 (6) | 0.0210 (6) | 0.0275 (6) | −0.0008 (5) | 0.0104 (5) | −0.0002 (5) |
| C2 | 0.0250 (6) | 0.0279 (7) | 0.0342 (7) | −0.0042 (5) | 0.0100 (5) | 0.0012 (5) |
| C3 | 0.0235 (6) | 0.0322 (7) | 0.0377 (7) | 0.0003 (5) | 0.0156 (5) | 0.0025 (6) |
| C4 | 0.0255 (6) | 0.0253 (6) | 0.0290 (6) | 0.0022 (5) | 0.0141 (5) | 0.0002 (5) |
| C5 | 0.0236 (5) | 0.0197 (5) | 0.0205 (5) | 0.0026 (4) | 0.0104 (4) | 0.0036 (4) |
| C6 | 0.0231 (5) | 0.0187 (5) | 0.0213 (5) | 0.0028 (4) | 0.0103 (4) | 0.0019 (4) |
| C7 | 0.0236 (5) | 0.0167 (5) | 0.0208 (5) | −0.0007 (4) | 0.0111 (4) | −0.0009 (4) |

| | | | | | |
|---|---|---|---|---|---|
| C8 | 0.0220 (5) | 0.0203 (6) | 0.0191 (5) | −0.0025 (4) | 0.0086 (4) | −0.0029 (4) |
| C9 | 0.0270 (6) | 0.0222 (6) | 0.0293 (6) | −0.0034 (5) | 0.0124 (5) | 0.0002 (5) |
| C10 | 0.0257 (6) | 0.0312 (7) | 0.0418 (8) | −0.0051 (5) | 0.0162 (6) | −0.0008 (6) |
| C11 | 0.0270 (6) | 0.0249 (6) | 0.0339 (7) | 0.0029 (5) | 0.0069 (5) | −0.0007 (5) |
| C12 | 0.0264 (6) | 0.0231 (6) | 0.0279 (6) | −0.0005 (5) | 0.0099 (5) | 0.0017 (5) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| O1—C6 | 1.2226 (15) | C7—C8 | 1.5141 (18) |
| O2—C7 | 1.4140 (15) | C8—C9 | 1.3807 (18) |
| O2—H2O | 0.905 (19) | C8—C12 | 1.3861 (16) |
| N1—C1 | 1.3348 (17) | C9—C10 | 1.385 (2) |
| N1—C5 | 1.3389 (16) | C11—C12 | 1.388 (2) |
| N2—C7 | 1.4452 (16) | C1—H1 | 0.9500 |
| N2—C6 | 1.3443 (17) | C2—H2 | 0.9500 |
| N3—C10 | 1.332 (2) | C3—H3 | 0.9500 |
| N3—C11 | 1.3328 (19) | C4—H4 | 0.9500 |
| N2—H2N | 0.875 (17) | C7—H7 | 1.0000 |
| C1—C2 | 1.379 (2) | C9—H9 | 0.9500 |
| C2—C3 | 1.382 (2) | C10—H10 | 0.9500 |
| C3—C4 | 1.383 (2) | C11—H11 | 0.9500 |
| C4—C5 | 1.3881 (19) | C12—H12 | 0.9500 |
| C5—C6 | 1.5029 (17) | | |
| C7—O2—H2O | 107.2 (11) | N3—C10—C9 | 124.42 (14) |
| C1—N1—C5 | 117.60 (12) | N3—C11—C12 | 124.34 (11) |
| C6—N2—C7 | 121.06 (10) | C8—C12—C11 | 118.62 (12) |
| C10—N3—C11 | 115.87 (13) | N1—C1—H1 | 118.00 |
| C7—N2—H2N | 117.3 (12) | C2—C1—H1 | 118.00 |
| C6—N2—H2N | 120.8 (12) | C1—C2—H2 | 121.00 |
| N1—C1—C2 | 123.46 (12) | C3—C2—H2 | 121.00 |
| C1—C2—C3 | 118.60 (14) | C2—C3—H3 | 121.00 |
| C2—C3—C4 | 118.87 (13) | C4—C3—H3 | 121.00 |
| C3—C4—C5 | 118.65 (12) | C3—C4—H4 | 121.00 |
| N1—C5—C4 | 122.81 (11) | C5—C4—H4 | 121.00 |
| C4—C5—C6 | 118.26 (11) | O2—C7—H7 | 108.00 |
| N1—C5—C6 | 118.92 (11) | N2—C7—H7 | 108.00 |
| N2—C6—C5 | 115.50 (11) | C8—C7—H7 | 108.00 |
| O1—C6—C5 | 120.06 (12) | C8—C9—H9 | 121.00 |
| O1—C6—N2 | 124.37 (12) | C10—C9—H9 | 121.00 |
| O2—C7—N2 | 111.58 (10) | N3—C10—H10 | 118.00 |
| O2—C7—C8 | 108.43 (10) | C9—C10—H10 | 118.00 |
| N2—C7—C8 | 111.59 (10) | N3—C11—H11 | 118.00 |
| C9—C8—C12 | 117.93 (12) | C12—C11—H11 | 118.00 |
| C7—C8—C9 | 120.71 (10) | C8—C12—H12 | 121.00 |
| C7—C8—C12 | 121.23 (11) | C11—C12—H12 | 121.00 |
| C8—C9—C10 | 118.82 (12) | | |
| C5—N1—C1—C2 | 0.34 (19) | N1—C5—C6—O1 | −158.19 (12) |
| C1—N1—C5—C4 | 0.59 (18) | N1—C5—C6—N2 | 24.74 (16) |
| C1—N1—C5—C6 | −178.08 (11) | C4—C5—C6—O1 | 23.08 (17) |

| | | | |
|---|---|---|---|
| C7—N2—C6—O1 | −4.40 (19) | C4—C5—C6—N2 | −153.99 (12) |
| C7—N2—C6—C5 | 172.53 (10) | O2—C7—C8—C9 | 25.04 (15) |
| C6—N2—C7—O2 | −107.33 (13) | O2—C7—C8—C12 | −159.37 (11) |
| C6—N2—C7—C8 | 131.21 (12) | N2—C7—C8—C9 | 148.32 (11) |
| C11—N3—C10—C9 | 0.1 (2) | N2—C7—C8—C12 | −36.09 (15) |
| C10—N3—C11—C12 | 0.2 (2) | C7—C8—C9—C10 | 175.51 (12) |
| N1—C1—C2—C3 | −0.7 (2) | C12—C8—C9—C10 | −0.22 (19) |
| C1—C2—C3—C4 | 0.1 (2) | C7—C8—C12—C11 | −175.24 (11) |
| C2—C3—C4—C5 | 0.7 (2) | C9—C8—C12—C11 | 0.47 (18) |
| C3—C4—C5—N1 | −1.1 (2) | C8—C9—C10—N3 | −0.1 (2) |
| C3—C4—C5—C6 | 177.56 (12) | N3—C11—C12—C8 | −0.5 (2) |

*Hydrogen-bond geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N2—H2N···N1 | 0.875 (17) | 2.468 (18) | 2.7769 (16) | 101.4 (13) |
| N2—H2N···O2[i] | 0.875 (17) | 2.091 (17) | 2.9304 (15) | 160.7 (16) |
| O2—H2O···N1[ii] | 0.905 (19) | 1.92 (2) | 2.8056 (16) | 167.6 (17) |
| C7—H7···O1[iii] | 1.00 | 2.43 | 3.3694 (15) | 157 |
| C12—H12···O1[iv] | 0.95 | 2.43 | 3.3517 (17) | 163 |

Symmetry codes: (i) −*x*, −*y*+2, −*z*; (ii) *x*, *y*+1, *z*; (iii) −*x*, *y*+1/2, −*z*+1/2; (iv) −*x*, *y*−1/2, −*z*+1/2.

**Fig. 1**

**Fig. 2**

Fig. 3

**Fig. 4**