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ISSN 2414-3146

2-Amino-4-methylpyridin-1-ium 2-(4-nitrophenyl)-acetate

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Received 25 August 2016
Accepted 9 September 2016

Edited by R. F. Baggio, Comisión Nacional de Energía Atómica, Argentina

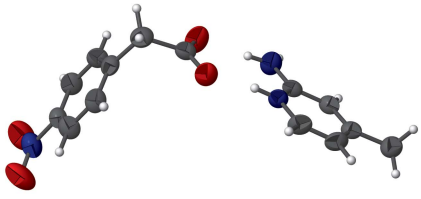
Keywords: molecular salt; crystal structure; hydrogen bonding.

CCDC reference: 1503502

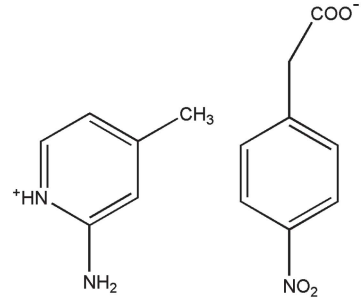
Structural data: full structural data are available from iucrdata.iucr.org

In the title molecular salt, $C_6H_9N_2^+\cdot C_8H_6NO_4^-$, the cation is protonated at its pyridine N atom. In the crystal, the anion and cation are connected by weak N—H···O hydrogen bonds, generating an $R_2^2(8)$ ring motif. A pair of N—H···O hydrogen bonds and a C—H···O contact generate an $R_2^3(19)$ ring motif. In the crystal, adjacent anions and cations are linked by N—H···O hydrogen bonds into infinite chains along [001]. The components are further linked by weak C—H···O contacts and C—H···π interactions, forming a three-dimensional network.

3D view



Chemical scheme



Structure description

Pyridine derivatives show a wide range of biological activities such as anti-inflammatory (Rupert *et al.*, 2003), antiviral (Hamdouchi *et al.*, 1999) and antibacterial (Rival *et al.*, 1992). We herein report the synthesis and crystal structure of the title molecular salt (Fig. 1). The geometric parameters are agree well with those for similar reported structures (Sivakumar *et al.*, 2016*a*,*b*).

The asymmetric unit (Fig. 1) comprises a 2-amino-4-methylpyridin-1-ium cation and 2-(4-nitrophenyl)acetate anion. The cation is protonated at the N1 atom and the anion is deprotonated at the hydroxyl O3 atom. In the crystal, the anion and cation are connected by weak N1—H1*A*···O3 and N2—H2*B*···O4 hydrogen bonds, by generating an $R_2^2(8)$ ring-motif (Fig. 2). The N2—H2*B*···O4 and N2—H2*A*···O3^{i} hydrogen bonds and C12—H12···O1^{i} contact generate an $R_2^3(19)$ ring motif (Fig. 2).

In the crystal, adjacent anions and cations are linked by N2—H2*A*···O3^{i} hydrogen bonds (Table 1) into infinite chains along [00] . The components are further linked by

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

*Cg*2 is the centroid of the N1/C1–C5 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O3	0.86 (1)	1.79 (2)	2.643 (5)	169 (5)
N2—H2*B*···O4	0.86 (1)	1.97 (2)	2.822 (6)	173 (4)
N2—H2*A*···O3^{i}	0.86 (1)	2.03 (2)	2.885 (5)	174 (4)
C2—H2···O2^{ii}	0.93	2.57	3.420 (6)	152
C6—H6*C*···O1^{iii}	0.96	2.44	3.371 (6)	163
C9—H9···O4^{iv}	0.93	2.50	3.328 (5)	149
C12—H12···O1^{i}	0.93	2.59	3.249 (6)	128
C6—H6*C*···*Cg*2^{v}	0.96	2.71	3.448 (4)	134

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

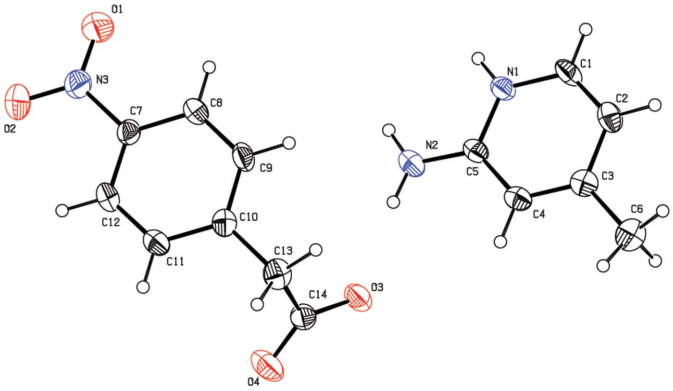


Figure 1
The molecular structure of the title molecular salt, with atom labelling and 30% probability displacement ellipsoids.

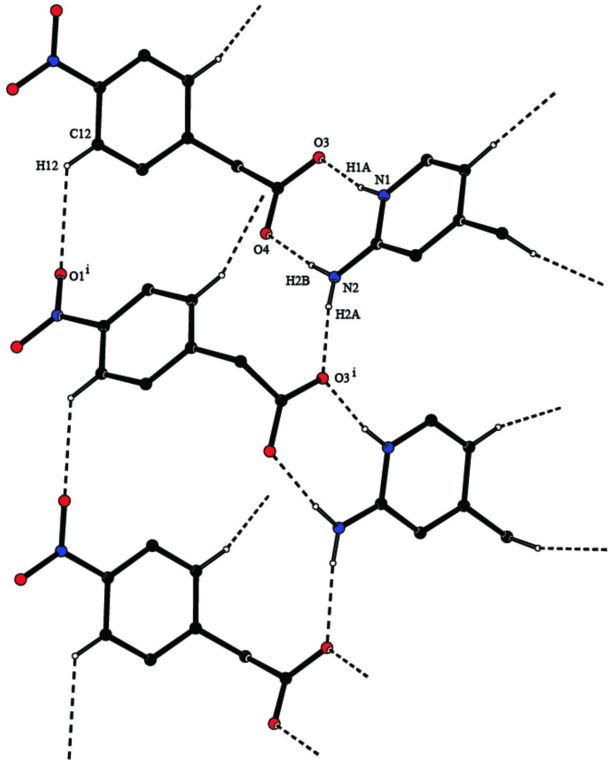


Figure 2
A partial view of the crystal packing of the title molecular salt, showing the ring motifs. Symmetry code: (i) $x, 1-y, -\frac{1}{2}+z$.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_6H_9N_2^+\cdot C_8H_6NO_4^-$
M_r	289.29
Crystal system, space group	Monoclinic, *Pc*
Temperature (K)	295
a, *b*, *c* (Å)	13.856 (2), 4.5401 (7), 11.926 (2)
β (°)	111.173 (5)
V (Å^3)	699.6 (2)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.10
Crystal size (mm)	0.30 × 0.25 × 0.20
Data collection	
Diffractometer	Bruker Kappa APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2004)
T_{min}, T_{max}	0.604, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8319, 2718, 1886
R_{int}	0.025
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.644
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.046, 0.101, 1.03
No. of reflections	2718
No. of parameters	203
No. of restraints	5
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.22, −0.20

Computer programs: *APEX2* and *SAINT* (Bruker, 2004), *SHELXS97* (Sheldrick, 2008), *SHELXL2016* (Sheldrick, 2015) and *PLATON* (Spek, 2009).

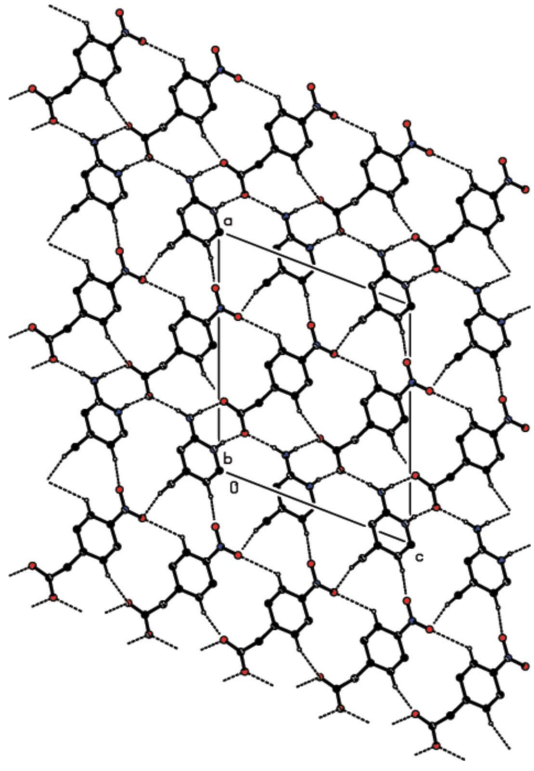


Figure 3
The crystal packing of the title molecular salt viewed along *b* axis. The hydrogen bonds are shown as dashed lines. H atoms not involved in hydrogen bonds have been omitted for clarity.

weak C—H···O and C—H···π interactions (Table 1), forming a three-dimensional network (Fig. 3).

Synthesis and crystallization

The title compound was synthesized by mixing 4-methylpyridine (0.93 g) and 4-nitrophenylacetic acid (1.81 g) in (1:1) ratio in 10 ml acetone. This saturated solution was allowed to evaporate slowly at room temperature, yielding single crystals suitable for X-ray diffraction.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The reflections ($\bar{1}$00) and (100) were omitted during refinement due to probable shadowing by the beam stop.

Acknowledgements

The authors acknowledge the SAIF, IIT, Madras for the data collection.

References

Bruker (2004). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Hamdouchi, C., de Blas, J., del Prado, M., Gruber, J., Heinz, B. A. & Vance, L. (1999). *J. Med. Chem.* **42**, 50–59.
Rival, Y., Grassy, G. & Michel, G. (1992). *Chem. Pharm. Bull.* **40**, 1170–1176.
Rupert, K. C., Henry, J. R., Dodd, J. H., Wadsworth, S. A., Cavender, D. E., Olini, G. C., Fahmy, B. & Siekierka, J. J. (2003). *Bioorg. Med. Chem. Lett.* **13**, 347–350.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Sheldrick, G. M. (2015). *Acta Cryst.* A**71**, 3–8.
Sivakumar, P., Sudhahar, S., Gunasekaran, B., Israel, S. & Chakkaravarthi, G. (2016*b*). *IUCrData*, **1**, x160817.
Sivakumar, P., Sudhahar, S., Israel, S. & Chakkaravarthi, G. (2016*a*). *IUCrData*, **1**, x160747.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

full crystallographic data

IUCrData (2016). **1**, x161433 [doi:10.1107/S2414314616014334]

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Crystal data

$C_6H_9N_2^+·C_8H_6NO_4^-$
M_r = 289.29
Monoclinic, *Pc*
a = 13.856 (2) Å
b = 4.5401 (7) Å
c = 11.926 (2) Å
β = 111.173 (5)°
V = 699.6 (2) Å^3
Z = 2
F(000) = 304
D_x = 1.373 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 3185 reflections
θ = 3.2–27.2°
μ = 0.10 mm^{-1}
T = 295 K
Block, colourless
0.30 × 0.25 × 0.20 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
ω and *φ* scan
Absorption correction: multi-scan (SADABS; Bruker, 2004)
T_{min} = 0.604, T_{max} = 0.746
8319 measured reflections
2718 independent reflections
1886 reflections with $I > 2\sigma(I)$
R_{int} = 0.025
θ_{max} = 27.2°, θ_{min} = 3.2°
h = −17→16
k = −5→5
l = −15→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.101
S = 1.03
2718 reflections
203 parameters
5 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0206P)^2 + 0.4424P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	−0.0033 (4)	0.6796 (10)	0.5037 (4)	0.0498 (12)

H1	−0.011296	0.607231	0.572757	0.060*
C2	−0.0719 (4)	0.8768 (10)	0.4360 (4)	0.0506 (12)
H2	−0.125667	0.944028	0.458519	0.061*
C3	−0.0605 (3)	0.9792 (9)	0.3303 (4)	0.0437 (10)
C4	0.0203 (3)	0.8827 (10)	0.3020 (4)	0.0425 (10)
H4	0.028963	0.953470	0.233113	0.051*
C5	0.0910 (3)	0.6783 (9)	0.3748 (3)	0.0383 (10)
C6	−0.1387 (4)	1.1939 (11)	0.2509 (5)	0.0598 (14)
H6A	−0.106304	1.314928	0.208587	0.090*
H6B	−0.164471	1.316119	0.299533	0.090*
H6C	−0.195057	1.087173	0.194049	0.090*
C7	0.5945 (3)	0.4240 (11)	0.9353 (4)	0.0405 (10)
C8	0.5118 (3)	0.3703 (11)	0.9693 (4)	0.0501 (12)
H8	0.509297	0.451168	1.039877	0.060*
C9	0.4324 (3)	0.1949 (11)	0.8978 (4)	0.0479 (11)
H9	0.376499	0.154529	0.920964	0.057*
C10	0.4348 (3)	0.0787 (10)	0.7924 (3)	0.0408 (10)
C11	0.5190 (3)	0.1367 (11)	0.7598 (4)	0.0482 (12)
H11	0.521242	0.058504	0.688750	0.058*
C12	0.5998 (4)	0.3095 (11)	0.8314 (4)	0.0512 (12)
H12	0.656653	0.347214	0.809596	0.061*
C13	0.3445 (4)	−0.0941 (10)	0.7099 (4)	0.0518 (12)
H13A	0.307906	−0.186722	0.756152	0.062*
H13B	0.369170	−0.247746	0.670433	0.062*
C14	0.2711 (3)	0.1111 (10)	0.6155 (4)	0.0444 (10)
N1	0.0765 (3)	0.5834 (9)	0.4748 (3)	0.0404 (8)
N2	0.1693 (3)	0.5673 (10)	0.3502 (4)	0.0552 (10)
N3	0.6791 (3)	0.6122 (10)	1.0109 (4)	0.0572 (11)
O1	0.6716 (3)	0.7190 (10)	1.1007 (3)	0.0894 (14)
O2	0.7543 (3)	0.6494 (10)	0.9824 (3)	0.0849 (12)
O3	0.1947 (2)	0.2097 (8)	0.6360 (3)	0.0552 (9)
O4	0.2937 (3)	0.1761 (9)	0.5275 (3)	0.0723 (11)
H1A	0.119 (3)	0.455 (8)	0.520 (3)	0.060 (16)*
H2A	0.181 (3)	0.635 (9)	0.289 (2)	0.048 (12)*
H2B	0.211 (3)	0.452 (8)	0.403 (3)	0.046 (13)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.061 (3)	0.057 (3)	0.046 (3)	0.004 (2)	0.036 (2)	−0.003 (2)
C2	0.051 (3)	0.051 (3)	0.058 (3)	0.004 (2)	0.031 (2)	−0.009 (2)
C3	0.050 (3)	0.036 (2)	0.045 (3)	−0.006 (2)	0.017 (2)	−0.0051 (19)
C4	0.050 (3)	0.042 (2)	0.038 (2)	−0.006 (2)	0.020 (2)	0.000 (2)
C5	0.044 (3)	0.041 (3)	0.035 (2)	−0.007 (2)	0.0198 (19)	−0.0056 (19)
C6	0.058 (3)	0.052 (3)	0.066 (3)	0.001 (3)	0.018 (3)	−0.003 (3)
C7	0.036 (2)	0.045 (3)	0.040 (2)	−0.004 (2)	0.0129 (19)	0.005 (2)
C8	0.049 (3)	0.064 (3)	0.044 (3)	−0.007 (3)	0.025 (2)	0.002 (2)
C9	0.040 (2)	0.061 (3)	0.051 (3)	−0.002 (2)	0.026 (2)	0.010 (2)

C10	0.039 (2)	0.037 (2)	0.046 (3)	0.003 (2)	0.016 (2)	0.0096 (19)
C11	0.052 (3)	0.055 (3)	0.045 (3)	0.001 (2)	0.026 (2)	−0.003 (2)
C12	0.044 (3)	0.065 (3)	0.054 (3)	−0.003 (2)	0.030 (2)	0.001 (3)
C13	0.056 (3)	0.040 (3)	0.062 (3)	−0.004 (2)	0.025 (2)	0.001 (2)
C14	0.045 (3)	0.044 (2)	0.047 (3)	−0.005 (2)	0.019 (2)	−0.008 (2)
N1	0.045 (2)	0.045 (2)	0.036 (2)	0.0017 (18)	0.0202 (18)	−0.0008 (17)
N2	0.055 (3)	0.071 (3)	0.049 (2)	0.007 (2)	0.031 (2)	0.008 (2)
N3	0.050 (3)	0.071 (3)	0.050 (2)	−0.013 (2)	0.017 (2)	0.007 (2)
O1	0.079 (3)	0.125 (4)	0.071 (3)	−0.036 (3)	0.035 (2)	−0.037 (3)
O2	0.058 (2)	0.118 (3)	0.087 (3)	−0.034 (2)	0.035 (2)	−0.012 (2)
O3	0.053 (2)	0.072 (2)	0.0488 (18)	0.0082 (17)	0.0286 (16)	0.0008 (16)
O4	0.074 (3)	0.099 (3)	0.058 (2)	0.030 (2)	0.041 (2)	0.016 (2)

Geometric parameters (Å, º)

C1—C2	1.342 (6)	C8—H8	0.9300
C1—N1	1.345 (5)	C9—C10	1.375 (6)
C1—H1	0.9300	C9—H9	0.9300
C2—C3	1.405 (6)	C10—C11	1.381 (5)
C2—H2	0.9300	C10—C13	1.503 (6)
C3—C4	1.353 (6)	C11—C12	1.382 (6)
C3—C6	1.510 (6)	C11—H11	0.9300
C4—C5	1.400 (6)	C12—H12	0.9300
C4—H4	0.9300	C13—C14	1.531 (6)
C5—N2	1.321 (6)	C13—H13A	0.9700
C5—N1	1.350 (5)	C13—H13B	0.9700
C6—H6A	0.9600	C14—O4	1.234 (5)
C6—H6B	0.9600	C14—O3	1.253 (5)
C6—H6C	0.9600	N1—H1A	0.862 (14)
C7—C8	1.368 (6)	N2—H2A	0.858 (13)
C7—C12	1.371 (6)	N2—H2B	0.860 (14)
C7—N3	1.467 (6)	N3—O1	1.214 (5)
C8—C9	1.377 (6)	N3—O2	1.219 (5)
C2—C1—N1	122.1 (4)	C8—C9—H9	119.6
C2—C1—H1	118.9	C9—C10—C11	119.1 (4)
N1—C1—H1	118.9	C9—C10—C13	120.6 (4)
C1—C2—C3	118.4 (4)	C11—C10—C13	120.2 (4)
C1—C2—H2	120.8	C10—C11—C12	120.9 (4)
C3—C2—H2	120.8	C10—C11—H11	119.6
C4—C3—C2	119.2 (4)	C12—C11—H11	119.6
C4—C3—C6	121.6 (4)	C7—C12—C11	118.5 (4)
C2—C3—C6	119.3 (4)	C7—C12—H12	120.7
C3—C4—C5	121.2 (4)	C11—C12—H12	120.7
C3—C4—H4	119.4	C10—C13—C14	109.8 (4)
C5—C4—H4	119.4	C10—C13—H13A	109.7
N2—C5—N1	118.1 (4)	C14—C13—H13A	109.7
N2—C5—C4	124.2 (4)	C10—C13—H13B	109.7

N1—C5—C4	117.7 (4)	C14—C13—H13B	109.7
C3—C6—H6A	109.5	H13A—C13—H13B	108.2
C3—C6—H6B	109.5	O4—C14—O3	124.9 (4)
H6A—C6—H6B	109.5	O4—C14—C13	117.8 (4)
C3—C6—H6C	109.5	O3—C14—C13	117.2 (4)
H6A—C6—H6C	109.5	C1—N1—C5	121.4 (4)
H6B—C6—H6C	109.5	C1—N1—H1A	119 (3)
C8—C7—C12	121.7 (4)	C5—N1—H1A	119 (3)
C8—C7—N3	119.4 (4)	C5—N2—H2A	118 (3)
C12—C7—N3	118.9 (4)	C5—N2—H2B	118 (3)
C7—C8—C9	119.1 (4)	H2A—N2—H2B	123 (4)
C7—C8—H8	120.4	O1—N3—O2	122.9 (5)
C9—C8—H8	120.4	O1—N3—C7	118.1 (4)
C10—C9—C8	120.7 (4)	O2—N3—C7	119.0 (4)
C10—C9—H9	119.6		

N1—C1—C2—C3	1.5 (7)	C8—C7—C12—C11	0.3 (7)
C1—C2—C3—C4	−1.8 (6)	N3—C7—C12—C11	−178.9 (4)
C1—C2—C3—C6	178.1 (4)	C10—C11—C12—C7	−0.4 (7)
C2—C3—C4—C5	1.5 (6)	C9—C10—C13—C14	92.7 (5)
C6—C3—C4—C5	−178.5 (4)	C11—C10—C13—C14	−83.7 (5)
C3—C4—C5—N2	177.5 (4)	C10—C13—C14—O4	80.8 (5)
C3—C4—C5—N1	−0.8 (6)	C10—C13—C14—O3	−96.4 (5)
C12—C7—C8—C9	0.5 (7)	C2—C1—N1—C5	−0.8 (7)
N3—C7—C8—C9	179.6 (4)	N2—C5—N1—C1	−178.0 (4)
C7—C8—C9—C10	−1.1 (7)	C4—C5—N1—C1	0.4 (6)
C8—C9—C10—C11	0.9 (7)	C8—C7—N3—O1	−1.3 (7)
C8—C9—C10—C13	−175.5 (4)	C12—C7—N3—O1	177.8 (5)
C9—C10—C11—C12	−0.2 (7)	C8—C7—N3—O2	177.1 (5)
C13—C10—C11—C12	176.3 (4)	C12—C7—N3—O2	−3.7 (7)

Hydrogen-bond geometry (Å, º)

Cg2 is the centroid of the N1/C1–C5 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O3	0.86 (1)	1.79 (2)	2.643 (5)	169 (5)
N2—H2*B*···O4	0.86 (1)	1.97 (2)	2.822 (6)	173 (4)
N2—H2*A*···O3^{i}	0.86 (1)	2.03 (2)	2.885 (5)	174 (4)
C2—H2···O2^{ii}	0.93	2.57	3.420 (6)	152
C6—H6*C*···O1^{iii}	0.96	2.44	3.371 (6)	163
C9—H9···O4^{iv}	0.93	2.50	3.328 (5)	149
C12—H12···O1^{i}	0.93	2.59	3.249 (6)	128
C6—H6*C*···*Cg*2^{v}	0.96	2.71	3.448 (4)	134

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