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2-Amino-4-methylpyridinium 2-(4-nitrophenyl)-acetate

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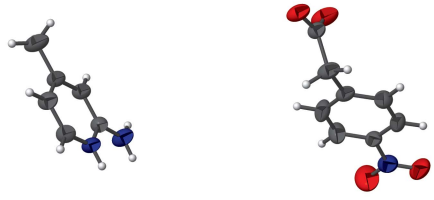
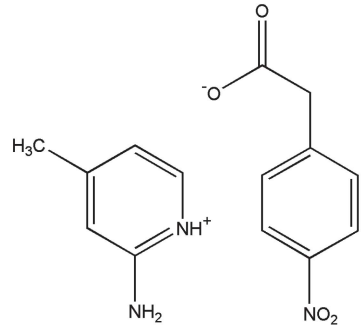
In the title molecular salt, $C_6H_9N_2^+\cdot C_8H_6NO_4^-$, the cation is protonated at its pyridine N atom. In the crystal, the anions are connected by a pair of C—H···O contacts into [100] chains, which generate $R_2^2(11)$ loops and these chains are linked *via* another C—H···O contact which encloses an $R_2^4(10)$ loop. Adjacent anions and cations are connected through N—H··· O hydrogen bonds, generating an $R_2^2(8)$ loop. Two pairs of anions and cations are linked by N—H···O hydrogen bonds, forming a tetramer with an $R_2^2(8)$ loop motif. The packing also features weak C—H···π and π–π [centroid-to-centroid distances = 3.8972 (11) and 3.9549 (10) Å] interactions, which result in a three-dimensional network.

3D view



Chemical scheme



Structure description

The asymmetric unit of of the title salt consists of a 2-amino-4-methylpyridinium cation (protonated at the pyridine N atom) and a 2-(4-nitrophenyl)acetate anion (Fig. 1). The bond lengths are comparable with reported similar structures (Babu *et al.*, 2014; Rajkumar *et al.*, 2014).

The anions are connected by C—H···O [C3—H3···O2^{iii} and C6—H6···O3^{vi}] contacts into [100] chains, generating an $R_2^2(11)$ loop; these chains are further linked *via* C5—H5···O3^{iv} [symmetry codes: (iii) $1+x, y, z$; (iv) $-x, 1-y, -z$; (vi) $x-1, y, z$] contacts, enclosing $R_2^4(10)$ loops (Table 1 and Fig. 2).

In the extended structure, the anions and cations are connected by N—H··· O [N2—H2···O3^{i} and N3—H3*A*···O4^{i}] hydrogen bonds, generating an $R_2^2(8)$ loop, and two pairs of anions and cations are linked by N—H···O [N3—H3*A*···O4^{i} and N3—H3*B*···O4^{ii}; symmetry codes: (i) $x, y, 1+z$; (ii) $-x, 2-y, 1-z$] hydrogen bonds to form a tetramer

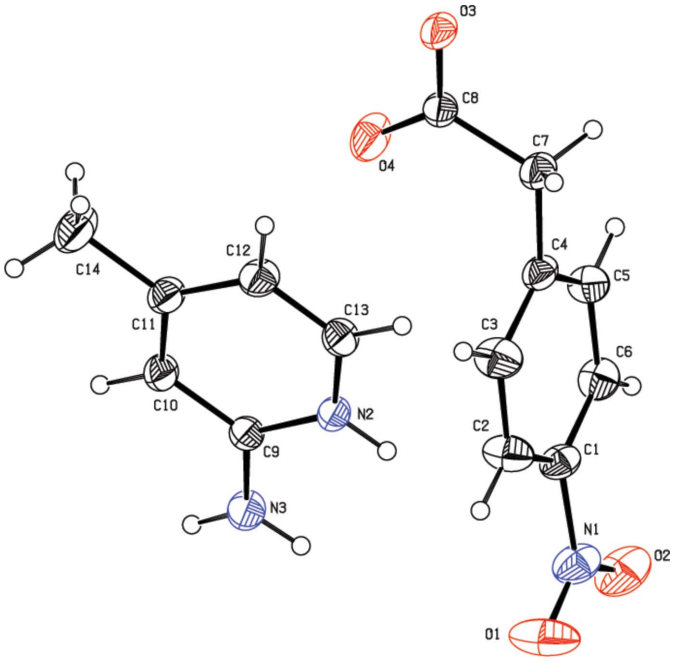


Figure 1
The molecular structure of the title molecular salt, shown with 30% probability displacement ellipsoids.

with an $R_2^2(8)$ ring-motif (Table 1 and Fig. 3). The packing is consolidated by weak C—H$\cdots\pi$ (Table 1) and π–π [$Cg1\cdots Cg1^{vii}$ = 3.8972 (11) Å; $Cg2\cdots Cg2^{viii}$ = 3.9549 (10) Å; symmetry codes: (vii) $-1-x, 1-y, 1-z$; (viii) $1-x, 2-y, 2-z$; $Cg1$ and $Cg2$ are the centroids of the C1–C6 and N2/C9–C13 rings, respectively] interactions, forming a three-dimensional network (Fig. 4).

Synthesis and crystallization

4-Nitrophenylacetic acid (1.811 g) and 2-amino-4-methylpyridine (1.081 g) in an equimolar ratio were dissolved in 15 ml methanol, and a white solid precipitate formed from the mixture. The precipitate was dissolved in water and kept at room temperature for crystallization. After a span of 12 days, colourless blocks of the title salt were formed.

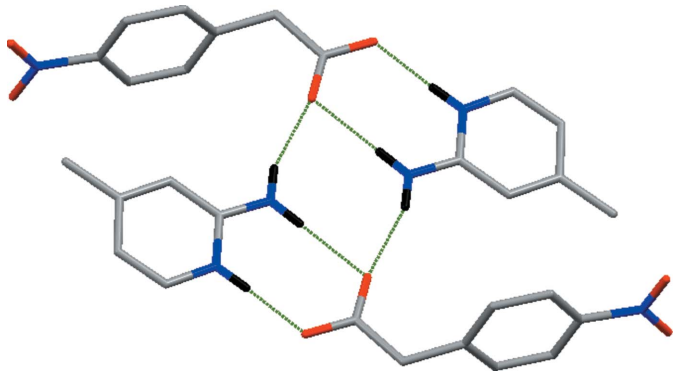


Figure 3
A partial view of the crystal packing of the title salt, showing the hydrogen-bonded tetramer connected by hydrogen bonds.

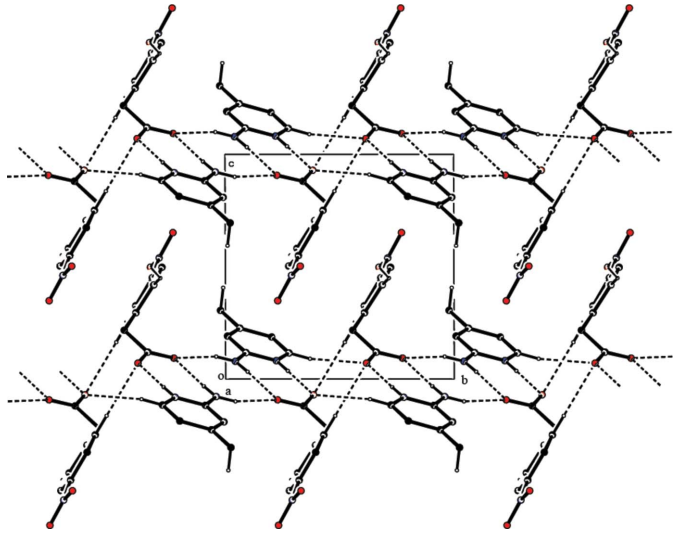


Figure 4
The crystal packing of the title compound viewed along *a* axis. The hydrogen bonds are shown as dashed lines (see Table 1) and C-bound H atoms have been omitted for clarity.

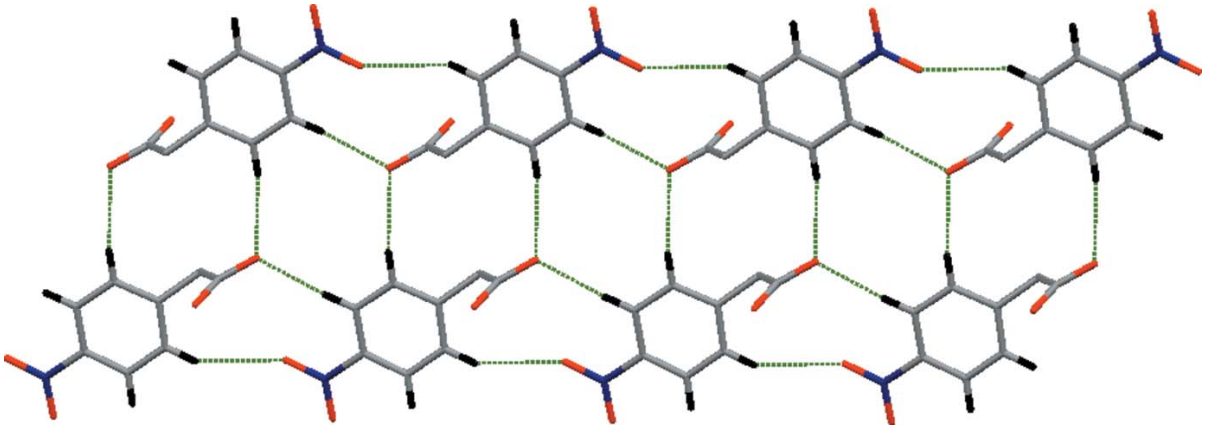


Figure 2
A partial view of the crystal packing of the title salt, showing the the anions which are connected *via* C—H$\cdots$O contacts.

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

*Cg*2 is the centroid of the N2/C9–C13 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···O3^{i}	0.86	1.77	2.6263 (19)	173
N3—H3*A*···O4^{i}	0.86	2.04	2.900 (2)	174
N3—H3*B*···O4^{ii}	0.86	2.02	2.847 (2)	160
C3—H3···O2^{iii}	0.93	2.57	3.419 (2)	152
C5—H5···O3^{iv}	0.93	2.56	3.478 (2)	170
C13—H13···O3^{v}	0.93	2.48	3.396 (2)	168
C6—H6···O3^{vi}	0.93	2.70	3.475 (2)	142
C2—H2*A*···*Cg*2^{vi}	0.93	2.79	3.668 (2)	158

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

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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Table 2
Experimental details.

Crystal data	
Chemical formula	$C_6H_9N_2^+·C_8H_6NO_4^-$
M_r	289.29
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	295
a, b, c (Å)	7.9359 (3), 9.6283 (4), 9.6807 (5)
α, β, γ (°)	88.010 (3), 74.936 (2), 81.561 (2)
V (Å^3)	706.54 (5)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.10
Crystal size (mm)	0.24 × 0.22 × 0.18
Data collection	
Diffractometer	Bruker Kappa APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2004)
T_{min}, T_{max}	0.976, 0.982
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	17186, 3659, 2306
R_{int}	0.028
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.686
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.052, 0.144, 1.03
No. of reflections	3659
No. of parameters	191
No. of restraints	1
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.30, −0.30

Computer programs: *APEX2* and *SAINT* (Bruker, 2004), *SHELXS97* and *SHELXL97* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

full crystallographic data

IUCrData (2016). **1**, x161203 [doi:10.1107/S2414314616012037]

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Crystal data

$C_6H_9N_2^+·C_8H_6NO_4^-$
M_r = 289.29
Triclinic, $P\overline{1}$
Hall symbol: -P 1
a = 7.9359 (3) Å
b = 9.6283 (4) Å
c = 9.6807 (5) Å
α = 88.010 (3)°
β = 74.936 (2)°
γ = 81.561 (2)°
V = 706.54 (5) Å^3
Z = 2
F(000) = 304
D_x = 1.360 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 5711 reflections
θ = 2.2–28.8°
μ = 0.10 mm^{-1}
T = 295 K
Block, colourless
0.24 × 0.22 × 0.18 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω and φ scan
Absorption correction: multi-scan (SADABS; Bruker, 2004)
T_{min} = 0.976, T_{max} = 0.982
17186 measured reflections
3659 independent reflections
2306 reflections with $I > 2\sigma(I)$
R_{int} = 0.028
θ_{max} = 29.2°, θ_{min} = 2.1°
h = −10→10
k = −13→13
l = −12→13

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.144
S = 1.03
3659 reflections
191 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0524P)^2 + 0.3009P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 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.

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 $F^2 > 2\text{sigma}(F^2)$ 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}
C1	−0.5718 (2)	0.6802 (2)	0.45065 (19)	0.0412 (4)
C2	−0.4397 (2)	0.7227 (2)	0.4973 (2)	0.0550 (5)
H2A	−0.4650	0.7753	0.5808	0.066*
C3	−0.2682 (2)	0.6864 (2)	0.4186 (2)	0.0551 (5)
H3	−0.1770	0.7151	0.4494	0.066*
C4	−0.2294 (2)	0.60809 (18)	0.2948 (2)	0.0404 (4)
C5	−0.3670 (2)	0.5717 (2)	0.2490 (2)	0.0471 (5)
H5	−0.3431	0.5217	0.1640	0.057*
C6	−0.5397 (2)	0.6075 (2)	0.3262 (2)	0.0472 (5)
H6	−0.6319	0.5826	0.2940	0.057*
C7	−0.0415 (2)	0.55678 (19)	0.2171 (2)	0.0484 (5)
H7A	−0.0412	0.4757	0.1603	0.058*
H7B	0.0221	0.5248	0.2881	0.058*
C8	0.0605 (2)	0.65936 (17)	0.11973 (19)	0.0379 (4)
C9	0.3858 (2)	0.91090 (17)	0.88276 (18)	0.0372 (4)
C10	0.5138 (2)	0.99143 (18)	0.80895 (19)	0.0417 (4)
H10	0.4794	1.0832	0.7835	0.050*
C11	0.6879 (2)	0.93718 (19)	0.7739 (2)	0.0429 (4)
C12	0.7369 (2)	0.7985 (2)	0.8130 (2)	0.0467 (5)
H12	0.8549	0.7591	0.7901	0.056*
C13	0.6117 (2)	0.72288 (18)	0.8841 (2)	0.0436 (4)
H13	0.6442	0.6309	0.9100	0.052*
C14	0.8268 (3)	1.0217 (2)	0.6948 (3)	0.0682 (7)
H14A	0.8447	1.0099	0.5937	0.102*
H14B	0.9351	0.9902	0.7205	0.102*
H14C	0.7895	1.1190	0.7196	0.102*
N1	−0.7538 (2)	0.7107 (2)	0.5390 (2)	0.0562 (5)
N2	0.43950 (18)	0.77853 (14)	0.91833 (16)	0.0391 (3)
H2	0.3622	0.7281	0.9640	0.047*
N3	0.21474 (19)	0.95774 (17)	0.92141 (19)	0.0522 (4)
H3A	0.1419	0.9040	0.9677	0.063*
H3B	0.1765	1.0419	0.9002	0.063*
O1	−0.7802 (2)	0.7713 (2)	0.6516 (2)	0.0950 (7)
O2	−0.87043 (18)	0.6723 (2)	0.4977 (2)	0.0765 (5)
O3	0.22208 (15)	0.61628 (13)	0.07048 (15)	0.0491 (4)
O4	−0.01532 (18)	0.77352 (15)	0.09299 (19)	0.0689 (5)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0272 (8)	0.0506 (10)	0.0424 (10)	−0.0018 (7)	−0.0058 (7)	0.0070 (8)
C2	0.0401 (10)	0.0739 (14)	0.0494 (12)	−0.0005 (9)	−0.0104 (9)	−0.0172 (10)
C3	0.0323 (9)	0.0708 (14)	0.0643 (13)	−0.0084 (9)	−0.0140 (9)	−0.0137 (11)
C4	0.0304 (8)	0.0388 (9)	0.0466 (10)	−0.0031 (7)	−0.0023 (7)	0.0079 (8)
C5	0.0443 (10)	0.0527 (11)	0.0427 (10)	−0.0067 (8)	−0.0082 (8)	−0.0023 (8)
C6	0.0350 (9)	0.0546 (11)	0.0559 (12)	−0.0095 (8)	−0.0170 (8)	0.0018 (9)
C7	0.0354 (9)	0.0402 (9)	0.0595 (12)	−0.0009 (7)	0.0023 (8)	0.0085 (8)
C8	0.0309 (8)	0.0349 (8)	0.0446 (10)	−0.0029 (7)	−0.0054 (7)	0.0017 (7)
C9	0.0340 (8)	0.0333 (8)	0.0407 (9)	−0.0001 (7)	−0.0060 (7)	0.0016 (7)
C10	0.0391 (9)	0.0338 (9)	0.0475 (10)	−0.0011 (7)	−0.0063 (8)	0.0066 (7)
C11	0.0366 (9)	0.0431 (10)	0.0454 (10)	−0.0058 (7)	−0.0048 (8)	0.0058 (8)
C12	0.0307 (8)	0.0465 (10)	0.0563 (12)	0.0029 (7)	−0.0050 (8)	0.0063 (9)
C13	0.0392 (9)	0.0349 (9)	0.0519 (11)	0.0035 (7)	−0.0089 (8)	0.0058 (8)
C14	0.0468 (12)	0.0644 (14)	0.0838 (17)	−0.0124 (10)	−0.0001 (11)	0.0242 (12)
N1	0.0339 (8)	0.0682 (12)	0.0592 (11)	0.0022 (8)	−0.0060 (8)	0.0128 (9)
N2	0.0336 (7)	0.0326 (7)	0.0456 (8)	−0.0032 (6)	−0.0020 (6)	0.0056 (6)
N3	0.0333 (8)	0.0400 (8)	0.0729 (12)	0.0029 (6)	−0.0007 (7)	0.0078 (8)
O1	0.0544 (10)	0.1393 (18)	0.0742 (12)	0.0096 (10)	0.0054 (9)	−0.0338 (12)
O2	0.0312 (7)	0.1038 (13)	0.0919 (13)	−0.0129 (8)	−0.0119 (8)	0.0181 (10)
O3	0.0323 (6)	0.0398 (7)	0.0637 (9)	−0.0007 (5)	0.0045 (6)	0.0091 (6)
O4	0.0401 (7)	0.0479 (8)	0.1027 (13)	0.0041 (6)	0.0005 (8)	0.0292 (8)

Geometric parameters (Å, º)

C1—C2	1.362 (3)	C9—N2	1.346 (2)
C1—C6	1.362 (3)	C9—C10	1.399 (2)
C1—N1	1.468 (2)	C10—C11	1.362 (2)
C2—C3	1.377 (3)	C10—H10	0.9300
C2—H2A	0.9300	C11—C12	1.402 (2)
C3—C4	1.379 (3)	C11—C14	1.498 (3)
C3—H3	0.9300	C12—C13	1.346 (3)
C4—C5	1.373 (3)	C12—H12	0.9300
C4—C7	1.503 (2)	C13—N2	1.351 (2)
C5—C6	1.380 (3)	C13—H13	0.9300
C5—H5	0.9300	C14—H14A	0.9600
C6—H6	0.9300	C14—H14B	0.9600
C7—C8	1.514 (2)	C14—H14C	0.9600
C7—H7A	0.9700	N1—O2	1.207 (2)
C7—H7B	0.9700	N1—O1	1.210 (2)
C8—O4	1.227 (2)	N2—H2	0.8600
C8—O3	1.2583 (19)	N3—H3A	0.8600
C9—N3	1.325 (2)	N3—H3B	0.8600
C2—C1—C6	122.03 (16)	N2—C9—C10	118.22 (14)
C2—C1—N1	119.00 (18)	C11—C10—C9	120.88 (16)

C6—C1—N1	118.95 (17)	C11—C10—H10	119.6
C1—C2—C3	118.81 (19)	C9—C10—H10	119.6
C1—C2—H2A	120.6	C10—C11—C12	118.63 (16)
C3—C2—H2A	120.6	C10—C11—C14	121.66 (17)
C2—C3—C4	121.02 (18)	C12—C11—C14	119.70 (17)
C2—C3—H3	119.5	C13—C12—C11	119.53 (16)
C4—C3—H3	119.5	C13—C12—H12	120.2
C5—C4—C3	118.20 (16)	C11—C12—H12	120.2
C5—C4—C7	120.93 (18)	C12—C13—N2	121.03 (16)
C3—C4—C7	120.76 (17)	C12—C13—H13	119.5
C4—C5—C6	121.57 (18)	N2—C13—H13	119.5
C4—C5—H5	119.2	C11—C14—H14A	109.5
C6—C5—H5	119.2	C11—C14—H14B	109.5
C1—C6—C5	118.28 (17)	H14A—C14—H14B	109.5
C1—C6—H6	120.9	C11—C14—H14C	109.5
C5—C6—H6	120.9	H14A—C14—H14C	109.5
C4—C7—C8	117.54 (14)	H14B—C14—H14C	109.5
C4—C7—H7A	107.9	O2—N1—O1	122.69 (19)
C8—C7—H7A	107.9	O2—N1—C1	118.86 (19)
C4—C7—H7B	107.9	O1—N1—C1	118.44 (19)
C8—C7—H7B	107.9	C9—N2—C13	121.70 (15)
H7A—C7—H7B	107.2	C9—N2—H2	119.2
O4—C8—O3	125.07 (16)	C13—N2—H2	119.2
O4—C8—C7	120.19 (15)	C9—N3—H3A	120.0
O3—C8—C7	114.73 (14)	C9—N3—H3B	120.0
N3—C9—N2	117.87 (15)	H3A—N3—H3B	120.0
N3—C9—C10	123.90 (15)		

C6—C1—C2—C3	−2.4 (3)	N3—C9—C10—C11	179.25 (18)
N1—C1—C2—C3	176.04 (19)	N2—C9—C10—C11	0.1 (3)
C1—C2—C3—C4	−0.2 (3)	C9—C10—C11—C12	0.1 (3)
C2—C3—C4—C5	2.4 (3)	C9—C10—C11—C14	180.0 (2)
C2—C3—C4—C7	−173.96 (19)	C10—C11—C12—C13	−0.1 (3)
C3—C4—C5—C6	−2.2 (3)	C14—C11—C12—C13	−180.0 (2)
C7—C4—C5—C6	174.15 (17)	C11—C12—C13—N2	−0.1 (3)
C2—C1—C6—C5	2.6 (3)	C2—C1—N1—O2	−179.68 (19)
N1—C1—C6—C5	−175.85 (17)	C6—C1—N1—O2	−1.2 (3)
C4—C5—C6—C1	−0.2 (3)	C2—C1—N1—O1	−0.9 (3)
C5—C4—C7—C8	102.7 (2)	C6—C1—N1—O1	177.6 (2)
C3—C4—C7—C8	−81.0 (2)	N3—C9—N2—C13	−179.47 (17)
C4—C7—C8—O4	−8.6 (3)	C10—C9—N2—C13	−0.3 (3)
C4—C7—C8—O3	172.25 (17)	C12—C13—N2—C9	0.3 (3)

Hydrogen-bond geometry (Å, º)

*Cg*2 is the centroid of the N2/C9–C13 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···O3^{i}	0.86	1.77	2.6263 (19)	173

N3—H3*A*···O4^{i}	0.86	2.04	2.900 (2)	174
N3—H3*B*···O4^{ii}	0.86	2.02	2.847 (2)	160
C3—H3···O2^{iii}	0.93	2.57	3.419 (2)	152
C5—H5···O3^{iv}	0.93	2.56	3.478 (2)	170
C13—H13···O3^{v}	0.93	2.48	3.396 (2)	168
C6—H6···O3^{vi}	0.93	2.70	3.475 (2)	142
C2—H2*A*···*Cg*2^{vi}	0.93	2.79	3.668 (2)	158

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