

Anilinium-3-carboxylate 3-carboxy-anilinium nitrate

Saeed Ahmad,^{a*} Sajjad Hussain,^b Shahzad Sharif,^b
Islam Ullah Khan^b and Muhammad Nawaz Tahir^c

^aDepartment of Chemistry, University of Engineering and Technology, Lahore 54890, Pakistan, ^bDepartment of Chemistry, Government College University, Lahore, Pakistan, and ^cDepartment of Physics, University of Sargodha, Sargodha, Pakistan
Correspondence e-mail: saeed_a786@hotmail.com

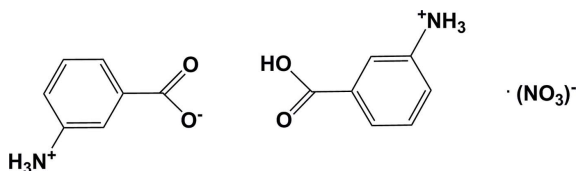
Received 1 November 2012; accepted 1 December 2012

Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.037; wR factor = 0.101; data-to-parameter ratio = 14.0.

The title compound, $\text{C}_7\text{H}_8\text{NO}_2^+ \cdot \text{NO}_3^- \cdot \text{C}_7\text{H}_7\text{NO}_2$, exists in the form of a protonated dimer of two anilinium-3-carboxylate molecules related by an inversion center, and a nitrate anion located on a twofold rotation axis. The bridging H atom occupies, with equal probability, the two sites associated with the carboxyl atoms. In addition to the strong $\text{O}-\text{H} \cdots \text{O}$ hydrogen bond, in the crystal, the various units are linked via $\text{N}-\text{H} \cdots \text{O}$ and $\text{C}-\text{H} \cdots \text{O}$ hydrogen bonds forming a three-dimensional structure.

Related literature

For applications of aminobenzoic acids, see: Congiu *et al.* (2005); Swislocka *et al.* (2005). For related structures and details of their hydrogen-bonding motifs, see: Arora *et al.* (1973); Bahadur *et al.* (2007); Hansen *et al.* (2007); Lai & Marsh (1967); Lu *et al.* (2001); Smith *et al.* (1995); Zaidi *et al.* (2008).



Experimental

Crystal data

$\text{C}_7\text{H}_8\text{NO}_2^+ \cdot \text{NO}_3^- \cdot \text{C}_7\text{H}_7\text{NO}_2$
 $M_r = 337.29$
Monoclinic, $C2/c$
 $a = 16.0451$ (3) Å
 $b = 4.7575$ (1) Å
 $c = 19.7143$ (4) Å
 $\beta = 107.660$ (1)°

$V = 1433.96$ (5) Å³
 $Z = 4$
Mo $K\alpha$ radiation
 $\mu = 0.13$ mm⁻¹
 $T = 296$ K
 $0.23 \times 0.16 \times 0.07$ mm

Data collection

Bruker Kappa APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.525$, $T_{\max} = 0.806$
6955 measured reflections
1777 independent reflections
1604 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.017$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.101$
 $S = 1.07$
1777 reflections
127 parameters
H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.29$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.20$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
$\text{O1}-\text{H1O} \cdots \text{O1}^{\text{i}}$	0.88 (4)	1.61 (4)	2.4868 (13)	171 (4)
$\text{O1}-\text{H1O} \cdots \text{O2}^{\text{i}}$	0.88 (4)	2.55 (3)	3.0686 (14)	118 (3)
$\text{N1}-\text{H1N} \cdots \text{O2}^{\text{ii}}$	0.913 (18)	2.027 (19)	2.9157 (13)	164.2 (17)
$\text{N1}-\text{H2N} \cdots \text{O2}^{\text{iii}}$	0.944 (18)	1.918 (18)	2.8609 (13)	177.0 (16)
$\text{N1}-\text{H3N} \cdots \text{O3}^{\text{iv}}$	0.939 (19)	2.498 (15)	2.9220 (14)	107.6 (11)
$\text{N1}-\text{H3N} \cdots \text{O3}$	0.939 (19)	2.526 (15)	2.9582 (14)	108.3 (11)
$\text{N1}-\text{H3N} \cdots \text{O4}$	0.939 (19)	1.920 (19)	2.8345 (11)	163.9 (13)
$\text{C3}-\text{H3} \cdots \text{O2}^{\text{ii}}$	0.93	2.41	3.1189 (15)	132
$\text{C5}-\text{H5} \cdots \text{O3}^{\text{iv}}$	0.93	2.58	3.3058 (18)	135

Symmetry codes: (i) $-x, -y + 2, -z$; (ii) $-x + \frac{1}{2}, -y + \frac{3}{2}, -z$; (iii) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z$; (iv) $x, y - 1, z$.

Data collection: APEX2 (Bruker, 2007); cell refinement: SAINT (Bruker, 2007); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: PLATON (Spek, 2009); software used to prepare material for publication: SHELXL97, PLATON and publCIF (Westrip, 2010).

The authors are grateful to Government College University Lahore for providing the X-ray diffraction facility, and to Professor Helen Stoeckli-Evans for valuable discussions.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: KJ2215).

References

- Arora, S. K., Sundaralingam, M., Dancz, J. S., Stanford, R. H. & Marsh, R. E. (1973). *Acta Cryst.* **B29**, 1849–1855.
Bahadur, S. A., Kannan, R. S. & Sridhar, B. (2007). *Acta Cryst.* **E63**, o2722–o2723.
Bruker (2007). APEX2 and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA.
Congiu, C., Cocco, M. T., Lilliu, V. & Onnis, V. (2005). *J. Med. Chem.* **48**, 8245–8252.
Hansen, L. K., Perlovich, G. L. & Bauer-Brandl, A. (2007). *Acta Cryst.* **E63**, o2361.
Lai, T. F. & Marsh, R. E. (1967). *Acta Cryst.* **22**, 885–893.
Lu, T. H., Chattopadhyay, P., Liao, F. L. & Lo, J.-M. (2001). *Anal. Sci.* **17**, 905–906.
Sheldrick, G. M. (1996). SADABS. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
Smith, G., Lynch, D. E., Byriel, K. A. & Kennard, C. H. L. (1995). *Aust. J. Chem.* **48**, 1133–1149.
Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
Swislocka, R., Regulska, E., Samsonowicz, M., Hrynaskiewicz, T. & Lewandowski, W. (2005). *Spectrochim. Acta Part A*, **61**, 2966–2973.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
Zaidi, S. A. R. A., Tahir, M. N., Iqbal, J. & Chaudhary, M. A. (2008). *Acta Cryst.* **E64**, o1957.

supporting information

Acta Cryst. (2013). E69, o29 [https://doi.org/10.1107/S1600536812049392]

Anilinium-3-carboxylate 3-carboxyanilinium nitrate

Saeed Ahmad, Sajjad Hussain, Shahzad Sharif, Islam Ullah Khan and Muhammad Nawaz Tahir

S1. Comment

Amino derivatives of benzoic acid are of considerable importance because of their use as anti-inflammatory and anticancer agents (Congiu *et al.*, 2005). Benzoic acid, its derivatives and their complexes are also used as food preservatives and as antiseptic agents applied in various industrial branches: pharmaceuticals, textile and cosmetics (Swislocka *et al.*, 2005). In view of this interest, the crystal structures of various amino derivatives of benzoic acid (Hansen *et al.*, 2007; Lai *et al.*, 1967; Lu *et al.*, 2001; Smith *et al.*, 1995), and their ammonium salts (Arora *et al.*, 1973; Bahadur *et al.*, 2007; Zaidi *et al.*, 2008), have been reported in the literature. The crystal structures of these compounds are characterized by strong hydrogen bonding.

The ammonium salts of 2-aminobenzoic acid are monomers (Bahadur *et al.*, 2007; Zaidi *et al.*, 2008), whereas the chloride salt of the anilinium-3-carboxylate ion (Arora *et al.*, 1973) exists in the form of hydrogen-bonded dimers formed through the carboxylic acid groups of inversion related molecules. In the present study, we attempted to prepare a cerium(III) complex of 3-aminobenzoic acid but the resulting product was a simple nitrate salt of the acid. Herein, we present the crystal structure of this salt.

In the title compound two anilinium-3-carboxylate molecules related by an inversion center are bound to a proton to form a protonated dimer through strong O—H \cdots O hydrogen bonds (Fig. 1 and Table 1). A nitrate anion located on a 2-fold rotation axis is present as counter ion. The bridging H atom (H1O) occupies, with equal probability, the two sites associated with the carboxyl atoms, O1 and O1a [symmetry code: (*a*) = -*x*, -*y* + 2, -*z*]. The ammonium groups are involved in strong hydrogen bonds to the carbonyl as well as to the nitrate O atoms (Table 1).

In the crystal, (Fig. 2 and Table 1) molecules are linked *via* N—H \cdots O and C—H \cdots O hydrogen bonds forming a three-dimensional structure.

S2. Experimental

The title compound was prepared by adding one equivalent of 3-aminobenzoic acid (0.07 g) in 15 ml methanol to a solution of cerium nitrate (0.22 g, 0.5 mmol) in 15 ml methanol. The brown solution was stirred for one hour, after which it was filtered and the filtrate was kept for crystallization at room temperature. The solution was covered with aluminium foil. After 3 days large orange-brown crystals were obtained (*M.p.* = 492 (1) K). A plate-shaped fragment cut from a large crystal was used for data collection.

S3. Refinement

The OH H atom was located in a difference Fourier map and refined freely with a fixed occupancy of 0.5. The NH₃ atoms were located from a difference Fourier map and refined freely. The C—H atoms were placed in calculated positions and treated as riding atoms: C—H = 0.93 Å with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

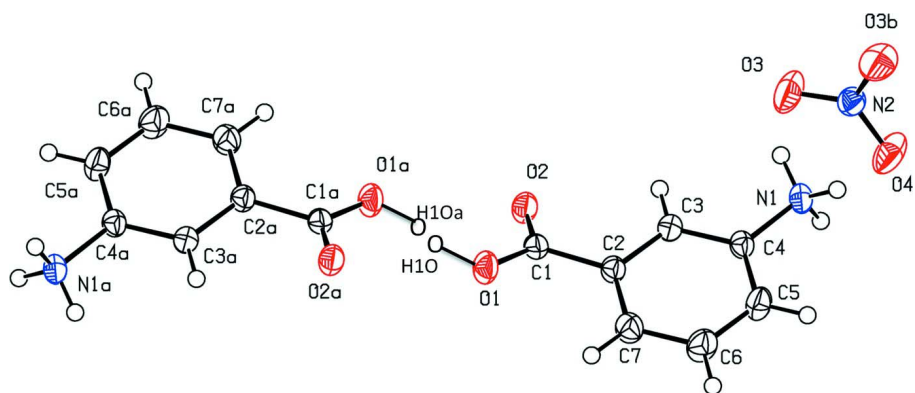


Figure 1

A view of the molecular structure of the title compound, with the atom numbering. Displacement ellipsoids are drawn at the 50% probability level. Atom H1O has an occupancy of 0.5 [symmetry codes: (a) = -x, -y + 2, -z; (b) -x + 1, y, -z + 1/2].

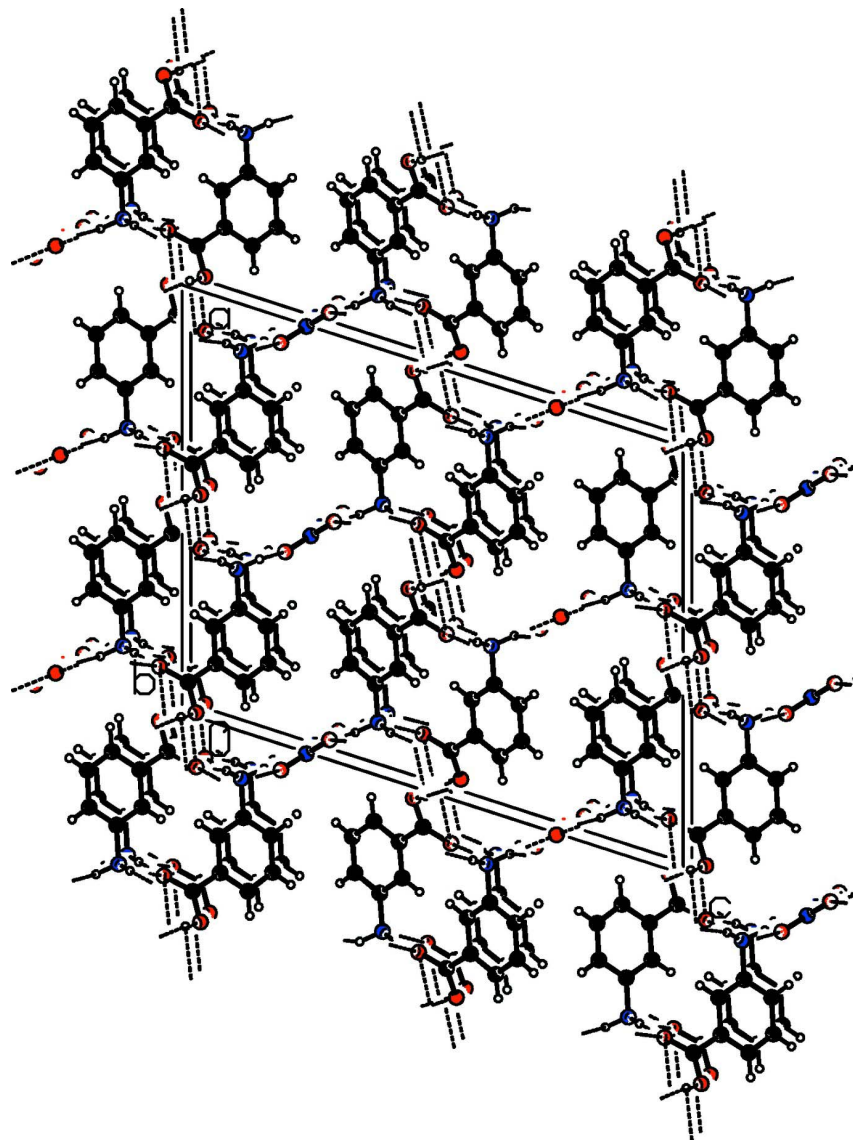


Figure 2

A view along the *b* axis of the crystal packing of the title compound. Hydrogen bonds are shown as dashed lines - see Table 1 for details [C-bound H atoms have been omitted for clarity].

Anilinium-3-carboxylate 3-carboxyanilinium nitrate

Crystal data

$C_7H_8NO_2^+ \cdot NO_3^- \cdot C_7H_7NO_2$

$M_r = 337.29$

Monoclinic, $C2/c$

Hall symbol: $-C 2yc$

$a = 16.0451 (3) \text{ \AA}$

$b = 4.7575 (1) \text{ \AA}$

$c = 19.7143 (4) \text{ \AA}$

$\beta = 107.660 (1)^\circ$

$V = 1433.96 (5) \text{ \AA}^3$

$Z = 4$

$F(000) = 704$

$D_x = 1.562 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 1777 reflections

$\theta = 2.9\text{--}28.3^\circ$

$\mu = 0.13 \text{ mm}^{-1}$

$T = 296 \text{ K}$

Plate, pale orange

$0.23 \times 0.16 \times 0.07 \text{ mm}$

Data collection

Bruker Kappa APEXII CCD area-detector
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

ω scans

Absorption correction: multi-scan
(*SADABS*; Sheldrick, 1996)

$T_{\min} = 0.525$, $T_{\max} = 0.806$

6955 measured reflections

1777 independent reflections

1604 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.017$

$\theta_{\max} = 28.3^\circ$, $\theta_{\min} = 3.9^\circ$

$h = -20 \rightarrow 21$

$k = -6 \rightarrow 6$

$l = -26 \rightarrow 24$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.037$

$wR(F^2) = 0.101$

$S = 1.07$

1777 reflections

127 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

$w = 1/[\sigma^2(F_o^2) + (0.0497P)^2 + 1.028P]$

where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{\max} = 0.29 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.20 \text{ e } \text{\AA}^{-3}$

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

Extinction coefficient: 0.0050 (11)

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
O1	0.03166 (6)	0.8054 (2)	0.04202 (5)	0.0316 (3)	
O2	0.11051 (6)	0.75160 (18)	-0.03226 (4)	0.0292 (3)	
N1	0.38230 (6)	0.2414 (2)	0.11339 (6)	0.0256 (3)	
C1	0.09454 (7)	0.6963 (2)	0.02418 (6)	0.0232 (3)	
C2	0.15270 (7)	0.4950 (2)	0.07568 (6)	0.0234 (3)	
C3	0.23625 (7)	0.4507 (2)	0.07021 (6)	0.0241 (3)	
C4	0.29346 (7)	0.2769 (2)	0.11825 (6)	0.0232 (3)	
C5	0.26851 (8)	0.1375 (3)	0.17048 (6)	0.0316 (3)	
C6	0.18493 (9)	0.1785 (3)	0.17490 (7)	0.0355 (4)	
C7	0.12742 (8)	0.3602 (3)	0.12863 (7)	0.0308 (3)	
O3	0.44638 (8)	0.7461 (2)	0.20141 (6)	0.0512 (4)	
O4	0.50000	0.3567 (3)	0.25000	0.0540 (5)	
N2	0.50000	0.6216 (3)	0.25000	0.0283 (4)	
H1N	0.3935 (11)	0.384 (4)	0.0864 (9)	0.045 (4)*	
H1O	0.014 (2)	0.953 (8)	0.0144 (17)	0.032 (8)*	0.500

H2N	0.3850 (11)	0.075 (4)	0.0881 (9)	0.044 (4)*
H3	0.25330	0.53810	0.03430	0.0290*
H3N	0.4235 (12)	0.243 (3)	0.1589 (10)	0.043 (4)*
H5	0.30730	0.01800	0.20220	0.0380*
H6	0.16720	0.08300	0.20930	0.0430*
H7	0.07210	0.39160	0.13310	0.0370*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0287 (4)	0.0321 (5)	0.0368 (5)	0.0116 (4)	0.0142 (4)	0.0065 (4)
O2	0.0284 (4)	0.0300 (5)	0.0308 (4)	0.0075 (3)	0.0113 (3)	0.0065 (3)
N1	0.0214 (5)	0.0265 (5)	0.0268 (5)	0.0049 (4)	0.0040 (4)	0.0010 (4)
C1	0.0201 (5)	0.0209 (5)	0.0281 (5)	0.0006 (4)	0.0064 (4)	-0.0005 (4)
C2	0.0222 (5)	0.0215 (5)	0.0257 (5)	0.0022 (4)	0.0059 (4)	-0.0005 (4)
C3	0.0232 (5)	0.0232 (5)	0.0254 (5)	0.0021 (4)	0.0068 (4)	0.0023 (4)
C4	0.0214 (5)	0.0223 (5)	0.0247 (5)	0.0023 (4)	0.0050 (4)	-0.0022 (4)
C5	0.0334 (6)	0.0322 (6)	0.0281 (6)	0.0089 (5)	0.0078 (5)	0.0077 (5)
C6	0.0390 (7)	0.0392 (7)	0.0321 (6)	0.0062 (6)	0.0164 (5)	0.0117 (5)
C7	0.0275 (6)	0.0335 (6)	0.0340 (6)	0.0044 (5)	0.0132 (5)	0.0038 (5)
O3	0.0579 (7)	0.0333 (6)	0.0462 (6)	0.0102 (5)	-0.0086 (5)	0.0069 (5)
O4	0.0663 (10)	0.0240 (7)	0.0470 (9)	0.0000	-0.0196 (7)	0.0000
N2	0.0291 (7)	0.0251 (7)	0.0286 (7)	0.0000	0.0056 (6)	0.0000

Geometric parameters (Å, °)

O1—C1	1.2753 (15)	C2—C3	1.3932 (17)
O2—C1	1.2434 (14)	C2—C7	1.3865 (17)
O1—H1O	0.88 (4)	C3—C4	1.3769 (15)
O3—N2	1.2283 (13)	C4—C5	1.3822 (17)
O4—N2	1.260 (2)	C5—C6	1.384 (2)
N1—C4	1.4671 (16)	C6—C7	1.386 (2)
N1—H2N	0.944 (18)	C3—H3	0.9300
N1—H3N	0.939 (19)	C5—H5	0.9300
N1—H1N	0.913 (18)	C6—H6	0.9300
C1—C2	1.4980 (15)	C7—H7	0.9300
C1—O1—H1O	107 (2)	C2—C3—C4	119.60 (10)
C4—N1—H3N	110.7 (12)	C3—C4—C5	121.15 (11)
H1N—N1—H2N	105.5 (16)	N1—C4—C3	118.84 (10)
C4—N1—H2N	109.4 (11)	N1—C4—C5	120.01 (10)
H2N—N1—H3N	112.3 (14)	C4—C5—C6	118.98 (12)
H1N—N1—H3N	110.2 (15)	C5—C6—C7	120.73 (13)
C4—N1—H1N	108.6 (12)	C2—C7—C6	119.71 (12)
O3 ⁱ —N2—O4	118.83 (8)	C2—C3—H3	120.00
O3—N2—O4	118.83 (8)	C4—C3—H3	120.00
O3—N2—O3 ⁱ	122.34 (13)	C6—C5—H5	120.00
O2—C1—C2	119.12 (10)	C4—C5—H5	121.00

O1—C1—C2	117.10 (10)	C5—C6—H6	120.00
O1—C1—O2	123.76 (10)	C7—C6—H6	120.00
C3—C2—C7	119.77 (10)	C2—C7—H7	120.00
C1—C2—C3	117.42 (10)	C6—C7—H7	120.00
C1—C2—C7	122.79 (11)		
O1—C1—C2—C3	-158.16 (10)	C3—C2—C7—C6	-1.16 (18)
O1—C1—C2—C7	20.10 (16)	C2—C3—C4—N1	-177.64 (9)
O2—C1—C2—C3	20.63 (15)	C2—C3—C4—C5	2.25 (16)
O2—C1—C2—C7	-161.12 (11)	N1—C4—C5—C6	178.75 (11)
C1—C2—C3—C4	177.24 (9)	C3—C4—C5—C6	-1.13 (18)
C7—C2—C3—C4	-1.08 (16)	C4—C5—C6—C7	-1.2 (2)
C1—C2—C7—C6	-179.38 (11)	C5—C6—C7—C2	2.3 (2)

Symmetry code: (i) $-x+1, y, -z+1/2$.

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1O \cdots O1 ⁱⁱ	0.88 (4)	1.61 (4)	2.4868 (13)	171 (4)
O1—H1O \cdots O2 ⁱⁱ	0.88 (4)	2.55 (3)	3.0686 (14)	118 (3)
N1—H1N \cdots O2 ⁱⁱⁱ	0.913 (18)	2.027 (19)	2.9157 (13)	164.2 (17)
N1—H2N \cdots O2 ^{iv}	0.944 (18)	1.918 (18)	2.8609 (13)	177.0 (16)
N1—H3N \cdots O3 ^v	0.939 (19)	2.498 (15)	2.9220 (14)	107.6 (11)
N1—H3N \cdots O3	0.939 (19)	2.526 (15)	2.9582 (14)	108.3 (11)
N1—H3N \cdots O4	0.939 (19)	1.920 (19)	2.8345 (11)	163.9 (13)
C3—H3 \cdots O2 ⁱⁱⁱ	0.93	2.41	3.1189 (15)	132
C5—H5 \cdots O3 ^v	0.93	2.58	3.3058 (18)	135

Symmetry codes: (ii) $-x, -y+2, -z$; (iii) $-x+1/2, -y+3/2, -z$; (iv) $-x+1/2, -y+1/2, -z$; (v) $x, y-1, z$.