Acta Cryst E CRYSTALLOGRAPHIC COMMUNICATIONS

ISSN 2056-9890

Crystal structure and Hirshfeld surface analysis of 4-bromoanilinium nitrate

Radhakrishnan Anbarasan,[a] Palaniyasan Eniya,[a] Jeyaperumal Kalyana Sundar[a] and Menberu Mengesha Woldemariam[b]*

[a]Materials Science Laboratory, Department of Physics, Periyar University, Salem, India, and [b]Department of Physics, Jimma University, Jimma, Ethiopia. *Correspondence e-mail: menberu.mengesha@ju.edu.et

Received 19 February 2020
Accepted 22 May 2020

Edited by J. T. Mague, Tulane University, USA

Keywords: crystal structure; Hirshfeld surface; hydrogen bonds; aniline.

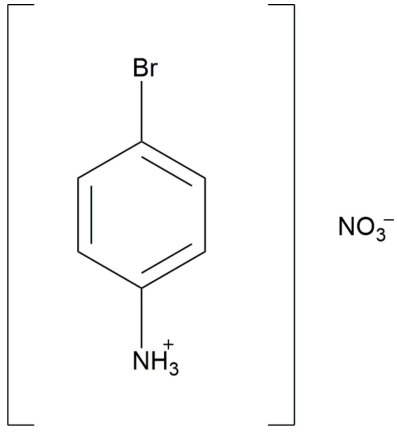
CCDC reference: 1909800

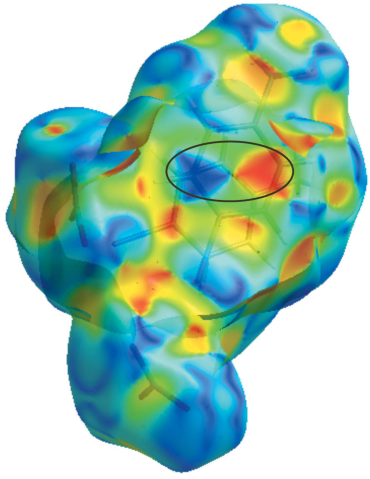
Supporting information: this article has supporting information at journals.iucr.org/e

The title compound $C_4H_7BrN^+\cdot NO_3^-$ crystallizes in the monoclinic crystal system with space group $P2_1/c$. In the crystal, π-π stacking interactions and strong N—H···O and C—H···O hydrogen bonds link the cations and anions into layers parallel to the *bc* plane. The O···H/H···O interactions between the cation and anion are the major factor determining the crystal packing.

1. Chemical context

In recent years, halogenated anilines and their derivatives have been studied extensively for applications as anti-corrosives, antibacterials and in non-linear optical systems (Glidewell *et al.*, 2005; Vivek *et al.*, 2014). The simplest halogenated aniline readily forms metal/non-metal complexes (Hartmann *et al.*, 1990). Strong hydrogen bonding, non-covalent bonding and π–π stacking interactions are prominent in the supramolecular arrangements of this molecule. Here, we report the crystal structure of 4-bromoanilinium nitrate, a salt complex whose structure is closely related to its 4-iodo analogue regarding the hydrogen-bond networks and π–π interactions (Fu *et al.*, 2010) although having significantly different unit-cell parameters.





2. Structural commentary

The asymmetric unit consists of two 4-bromoanilinium cations and two nitrate anions which are associated through N1—H10···O4^{ii}, N2—H13···O3^{iv} and a bifurcated N1—H9···O2^{i}/N1—H9···O3^{i} hydrogen bonds (Fig. 1). This motif generates a van der Waals contact (O3···O6) of 2.980 (4) Å between the

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H9···O2^{i}	0.89	2.19	2.930 (5)	140
N1—H9···O3^{i}	0.89	2.15	3.002 (5)	160
N1—H10···O4^{i}	0.89	2.08	2.957 (4)	167
N1—H11···O2^{ii}	0.89	1.91	2.773 (4)	162
N2—H12···O1^{i}	0.89	2.59	3.356 (6)	145
N2—H12···O6^{i}	0.89	2.11	2.827 (5)	137
N2—H12···O1^{iii}	0.89	2.59	3.158 (5)	122
N2—H13···O3^{iv}	0.89	2.12	2.774 (5)	130
N2—H13···O6^{iv}	0.89	2.55	3.345 (5)	149
N2—H14···O4^{iii}	0.89	2.19	2.831 (5)	129
C4—H3···O1^{iii}	0.93	2.41	3.129 (5)	134
C12—H8···O3^{i}	0.93	2.59	3.410 (5)	147
C12—H8···O6^{i}	0.93	2.58	3.1943 (3)	124

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

two nitrate ions. The phenyl rings in the independent cations extend in the same direction from the pair of anions with a dihedral angle of only 4.8 (2)° between their mean planes and participate in a π–π stacking interaction with a centroid···centroid distance of 3.932 (2) Å. Meanwhile, one cation is rotated with respect to the other so that the Br1—C2···C10—Br2 torsion angle is 50.4 **(su?)**°.

3. Supramolecular features

In the crystal, the anions are arranged in coarsely corrugated layers parallel to the *bc* plane with the hydrogen-bonded cations protruding from each face in an alternating fashion (Fig. 2). The cations containing Br1 are perpendicular to the layers and make close Br1···O5 contacts of 3.229 (5) Å (0.14 Å less than the sum of the van der Waals radii) with nitrate ions in adjacent layers (Fig. 2, Table 1).

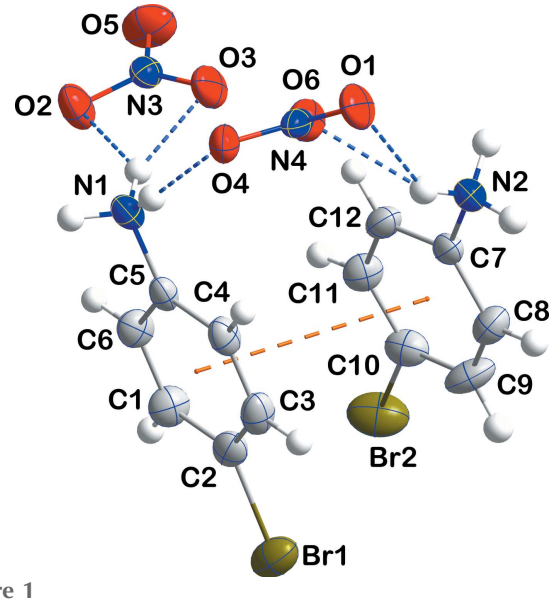


Figure 1
The asymmetric unit with labelling scheme and 50% probability ellipsoids. N—H···O hydrogen bonds and π-stacking interactions are shown, respectively, by blue and orange dashed lines.

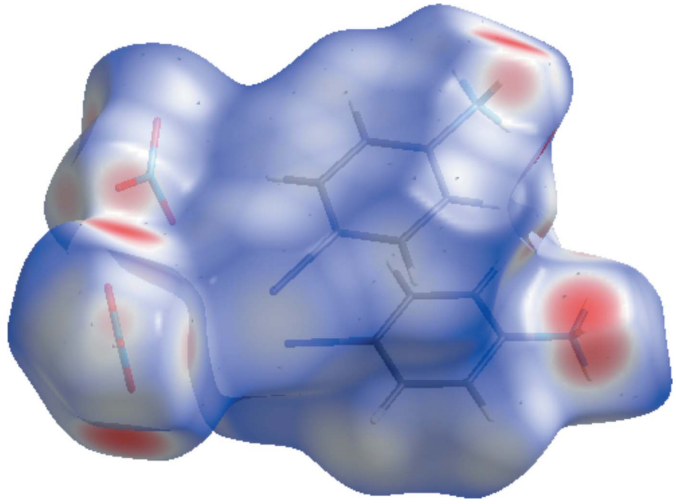


Figure 3
Hirshfeld surface plotted over d_{norm}.

4. Hirshfeld surface analysis

The intermolecular interactions were investigated quantitatively and visualized with *Crystal Explorer 3.1* (Wolff *et al.*, 2012; Spackman *et al.*, 2009). The d_{norm}, curvedness and 2D fingerprint plots are depicted in Figs. 3–5, respectively. The red spots on the Hirshfeld surface represent N—H···O contacts (Br···O contacts are not visible as red spots) while the blue regions correspond to weak interactions such as C—H···O

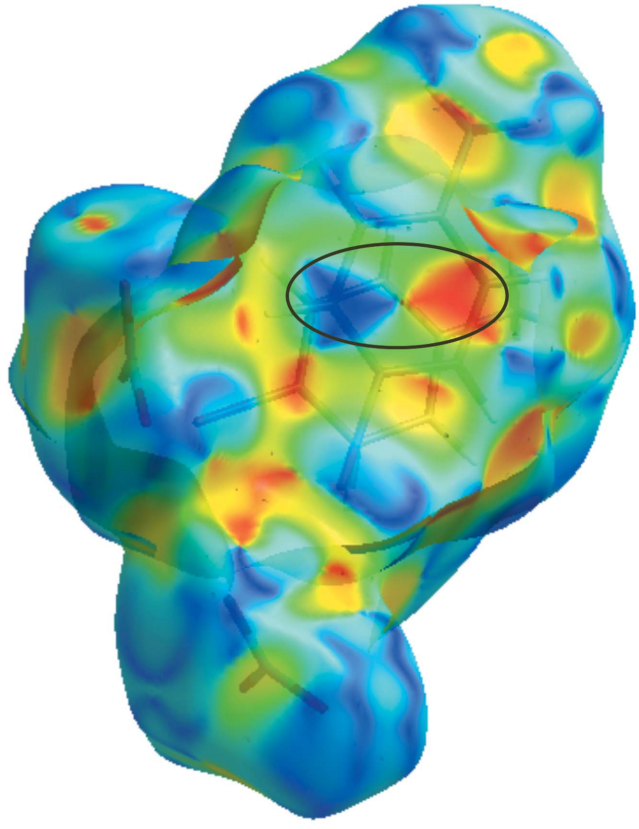


Figure 4
Curvedness surface of the title compound showing the π–π stacking.

contacts. The two triangles in the curvedness surface clearly illustrate the π–π stacking interactions. The O···H/H···O (51.4%) interactions are the major factor in the crystal packing with H···H (15.5%) interactions representing the next highest contribution. The percentage contributions of other weak interactions are: H···Br/Br···H (10.3%), C···H/H···C (9.2%), O···Br/Br···O (4.1%), Br···Br (2.7%), N···H/H···N (1.7%), O···O (1.6%), C···C (1.5%), C···O/O···C (0.8%), N···Br/Br···N (0.4), C···Br/Br···C (0.4%), N···O/O···N (0.3%) and N···C/C···N (0.1%).

4.1. Database survey

A search of the Cambridge Structural Database (CSD version 5.41, last update April 2020; Groom *et al.*, 2016) for the 4-bromoanilinium cation gave 22 hits excluding metal complexes. Among these, 13 structures have this cation combined with various acid anions including $[PO_2(OH)_2]^-$ (EBEFAV; Yoshii *et al.*, 2015; UGISEI; Zhang *et al.*, 2001; UGISEI01; Yoshii *et al.*, 2015), $[HC_2O_4]^-$ (ROBXOY; Radhakrishnan & Jeyaperumal, 2019), $[C_4H_5O_6]^-$ (ROPTEX; Yoshii *et al.*, 2014) and $[p\text{-}CH_3C_6H_4SO_3]^-$ (VUCBAY; Sivakumar *et al.*, 2015). Two more have amide anions $[N(SO_2R)_2]^-$ [R = Me (TAJWOT; Jones *et al.*, 2016), 4-BrC_6H_4 (DOHSOJ; Lozano *et al.*, 2008)]. The remainder have inorganic anions such as $[SiF_6]^{2-}$ (PBANIL; Denne *et al.*, 1971), $[PF_6]^-$ (TUPWUX; Yang & Fu, 2010) and chloride (TAWRAL; Portalone, 2005). Additionally, there is an unpublished structure of the title compound (ROCNOP; Anbarasan & Sundar, 2019) of comparable quality to the present study but without the additional investigations presented here.

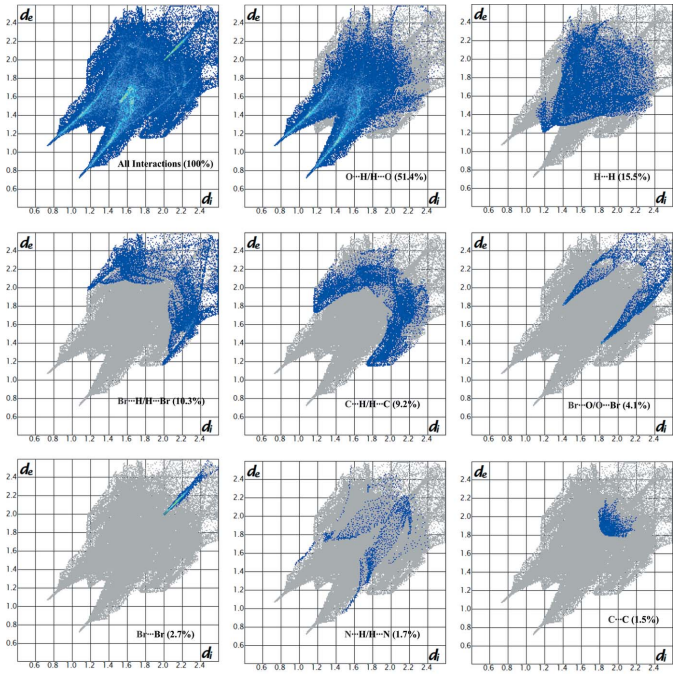


Figure 5
Fingerprint plots for the title compound

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_6H_7BrN^+\cdot NO_3^-$
M_r	235.04
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	293
a, b, c (Å)	9.7123 (8), 23.4964 (19), 7.6264 (6)
β (°)	97.052 (4)
V (Å^3)	1727.2 (2)
Z	8
Radiation type	Mo $K\alpha$
μ (mm^{-1})	4.73
Crystal size (mm)	0.42 × 0.18 × 0.12
Data collection	
Diffractometer	Bruker *SMART* APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Sheldrick, 1996)
T_{min}, T_{max}	0.374, 0.567
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	16821, 4609, 2355
R_{int}	0.058
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.684
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.059, 0.183, 1.02
No. of reflections	4609
No. of parameters	218
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.68, −0.84

Computer programs: *APEX2* and *SAINT* (Bruker, 2004), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2017* (Sheldrick, 2015*b*), *ORTEP-3 for Windows* and *WinGX* (Farrugia, 2012), *PLATON* (Spek, 2020), *Mercury* (Macrae *et al.*, 2020) and *publCIF* (Westrip, 2010).

5. Synthesis and crystallization

The title salt was synthesized by dissolving analytical grade 4-bromoaniline and nitric acid in a 1:1 stoichiometric ratio in methanol. The solution was stirred continuously for 2 h. Slow evaporation of this solution at room temperature yielded transparent colourless single crystals of the product.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The H atoms were positioned geometrically and refined using a riding model: C—H = 0.93 Å with U_{iso}(H) = 1.2U_{eq}(C) and N—H = 0.86 Å with U_{iso}(H) = 1.2U_{eq}(N). Reflection (100) was obscured by the beam stop and was omitted during the final refinement cycle.

Funding information

RA gratefully acknowledges Periyar University for providing financial support under the University Research Fellowship (URF) scheme.

References

Anbarasan, R. & Sundar, J. K. (2019). CSD Communication (refcode ROCNOP). CCDC, Cambridge, England.
Bruker (2004). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Denne, W. A., Mathieson, A. & Mackay, M. F. (1971). *J. Cryst. Mol. Struct.* **1**, 55–62.
Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.

Fu, X. (2010). *Acta Cryst.* E**66**, o1326.
Glidewell, C., Low, J. N., Skakle, J. M. S. & Wardell, J. L. (2005). *Acta Cryst.* C**61**, o276–o280.
Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.
Hartmann, J., Dou, S.-Q. & Weiss, A. (1990). *Berichte der Bunsengesellschaft für physikalische Chemie*, **94**, 1110–1121.
Jones, P. G., Blaschette, A. & Moers, O. (2016). CSD Communication (refcode TAJWOT). CCDC, Cambridge, England.
Lozano, V., Freytag, M., Jones, P. G. & Blaschette, A. (2008). *Z. Naturforsch. B*, **63**, 954–962.
Macrae, C. F., Sovago, I., Cottrell, S. J., Galek, P. T. A., McCabe, P., Pidcock, E., Platings, M., Shields, G. P., Stevens, J. S., Towler, M. & Wood, P. A. (2020). *J. Appl. Cryst.* **53**, 226–235.
Portalone, G. (2005). *Acta Cryst.* E**61**, o3083–o3085.
Radhakrishnan, A. & Jeyaperumal, K. S. (2019). CSD Communication (refcode ROBXOY). CCDC, Cambridge, England.
Sheldrick, G. M. (1996). *SADABS*.
Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.
Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.
Sivakumar, P. K., Kumar, M. K., Kumar, R. M., Chakkaravarthi, G. & Kanagadurai, R. (2015). *Acta Cryst.* E**71**, o163–o164.
Spackman, M. A. & Jayatilaka, D. (2009). *CrystEngComm*, **11**, 19–32.
Spek, A. L. (2020). *Acta Cryst.* E**76**, 1–11.
Vivek, P. & Murugakoothan, P. (2014). *Appl. Phys. A*, **115**, 1139–1146.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
Wolff, S. K., Grimwood, D. J., McKinnon, J. J., Turner, M. J., Jayatilaka, D. & Spackman, M. A. (2012). *Crystal Explorer*. University of Western Australia.
Yang, Y. & Fu, X. (2010). *Acta Cryst.* E**66**, o1430.
Yoshii, Y., Hoshino, N., Takeda, T. & Akutagawa, T. (2015). *J. Phys. Chem. C*, **119**, 20845–20854.
Yoshii, Y., Hoshino, N., Takeda, T., Moritomo, H., Kawamata, J., Nakamura, T. & Akutagawa, T. (2014). *Chem. Eur. J.* **20**, 16279–16285.
Zhang, B.-G., Gou, S.-H., Duan, C.-Y. & You, X.-Z. (2001). *Wuhan Dax. Xuebao, Zir. Kex.* **47**, 425–427.

supporting information

Acta Cryst. (2020). E**76**, 973-976 [https://doi.org/10.1107/S2056989020006945]

Crystal structure and Hirshfeld surface analysis of 4-bromoanilinium nitrate

Radhakrishnan Anbarasan, Palaniyasan Eniya, Jeyaperumal Kalyana Sundar and Menberu Mengesha Woldemariam

Computing details

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT* (Bruker, 2004); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2017* (Sheldrick, 2015b); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *WinGX* (Farrugia, 2012), *PLATON* (Spek, 2020), *Mercury* (Macrae *et al.*, 2020) and *publCIF* (Westrip, 2010).

p-Bromoanilinium nitrate

Crystal data

$C_6H_7BrN^+·NO_3^-$
M_r = 235.04
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 9.7123 (8) Å
b = 23.4964 (19) Å
c = 7.6264 (6) Å
β = 97.052 (4)°
V = 1727.2 (2) Å^3
Z = 8
$F(000)$ = 928
D_x = 1.808 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 4609 reflections
θ = 2.6–29.1°
μ = 4.73 mm^{-1}
T = 293 K
Needle, colorless
0.42 × 0.18 × 0.12 mm

Data collection

Bruker SMART APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
ω and φ scan
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
T_{min} = 0.374, T_{max} = 0.567
16821 measured reflections
4609 independent reflections
2355 reflections with $I > 2\sigma(I)$
R_{int} = 0.058
θ_{max} = 29.1°, θ_{min} = 2.1°
h = −13→11
k = −29→32
l = −8→10

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.059
$wR(F^2)$ = 0.183
S = 1.02
4609 reflections
218 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0927P)^2 + 0.2455P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.68 e Å^{-3}
$\Delta\rho_{min}$ = −0.84 e Å^{-3}

Extinction correction: SHELXL2018/3 (Sheldrick 2015b)

Extinction coefficient: 0.0181 (17)

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}
N1	1.0463 (4)	0.32338 (12)	0.2075 (4)	0.0513 (8)
H10	1.083534	0.351431	0.150589	0.077*
H9	1.063697	0.329131	0.323465	0.077*
H11	1.082988	0.290327	0.180092	0.077*
N2	0.8383 (4)	0.52952 (13)	0.2737 (5)	0.0571 (9)
H14	0.798745	0.556374	0.202137	0.086*
H13	0.880154	0.545557	0.371772	0.086*
H12	0.900523	0.510739	0.219564	0.086*
N3	0.0880 (3)	0.32409 (14)	0.6621 (5)	0.0481 (8)
N4	0.1286 (3)	0.46630 (13)	0.1594 (5)	0.0531 (9)
O2	0.1085 (4)	0.28155 (12)	0.5705 (5)	0.0762 (10)
O3	0.0604 (4)	0.36877 (12)	0.5772 (5)	0.0891 (12)
O4	0.1736 (3)	0.42637 (11)	0.0733 (4)	0.0613 (8)
O5	0.0995 (5)	0.32142 (18)	0.8212 (5)	0.0941 (12)
O6	0.0681 (3)	0.45499 (12)	0.2920 (4)	0.0656 (8)
O1	0.1429 (4)	0.51579 (11)	0.1125 (5)	0.0766 (10)
C1	0.6768 (5)	0.28047 (18)	0.1770 (6)	0.0632 (12)
H1	0.622297	0.253605	0.225586	0.076*
C2	0.6166 (5)	0.31894 (18)	0.0536 (5)	0.0549 (11)
C3	0.6968 (5)	0.35869 (17)	−0.0173 (6)	0.0611 (12)
H2	0.655897	0.384689	−0.099684	0.073*
C4	0.8371 (5)	0.36032 (15)	0.0328 (5)	0.0539 (11)
H3	0.891543	0.387124	−0.016287	0.065*
C5	0.8970 (4)	0.32216 (14)	0.1558 (5)	0.0449 (9)
C6	0.8179 (5)	0.28202 (17)	0.2278 (6)	0.0576 (11)
H4	0.859217	0.256095	0.310167	0.069*
C7	0.7319 (4)	0.48981 (15)	0.3193 (5)	0.0466 (9)
C8	0.5964 (5)	0.49725 (19)	0.2493 (6)	0.0638 (12)
H5	0.571499	0.527478	0.173184	0.077*
C9	0.4971 (5)	0.4596 (2)	0.2925 (7)	0.0779 (14)
H6	0.40465	0.463954	0.245794	0.094*
C10	0.5363 (5)	0.4159 (2)	0.4046 (6)	0.0640 (12)
C11	0.6718 (5)	0.40804 (19)	0.4725 (6)	0.0607 (11)
H7	0.696645	0.377689	0.548105	0.073*
C12	0.7710 (4)	0.44517 (19)	0.4285 (5)	0.0562 (11)
H8	0.863752	0.439985	0.472598	0.067*

Br1	0.42315 (6)	0.31590 (3)	−0.02005 (7)	0.0826 (3)
Br2	0.40126 (7)	0.36433 (3)	0.47100 (8)	0.1017 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.070 (2)	0.0398 (16)	0.0435 (19)	−0.0049 (16)	0.0034 (17)	−0.0031 (14)
N2	0.056 (2)	0.0473 (19)	0.065 (2)	0.0020 (16)	−0.0038 (17)	−0.0121 (17)
N3	0.0476 (19)	0.0412 (18)	0.054 (2)	−0.0059 (14)	0.0019 (16)	0.0022 (17)
N4	0.0414 (19)	0.0379 (18)	0.075 (3)	−0.0029 (15)	−0.0123 (17)	0.0051 (18)
O2	0.113 (3)	0.0430 (17)	0.072 (2)	−0.0017 (16)	0.010 (2)	−0.0044 (15)
O3	0.119 (3)	0.0353 (16)	0.103 (3)	0.0007 (17)	−0.026 (2)	0.0073 (17)
O4	0.0609 (19)	0.0433 (15)	0.079 (2)	0.0103 (14)	0.0043 (15)	−0.0019 (14)
O5	0.095 (3)	0.140 (3)	0.047 (2)	0.007 (2)	0.0077 (19)	−0.007 (2)
O6	0.067 (2)	0.0597 (18)	0.072 (2)	−0.0003 (15)	0.0160 (17)	0.0087 (16)
O1	0.097 (3)	0.0328 (15)	0.099 (3)	−0.0081 (15)	0.007 (2)	0.0106 (16)
C1	0.068 (3)	0.065 (3)	0.058 (3)	−0.006 (2)	0.012 (2)	0.015 (2)
C2	0.063 (3)	0.060 (3)	0.042 (2)	0.008 (2)	0.0049 (19)	−0.007 (2)
C3	0.084 (4)	0.051 (2)	0.048 (3)	0.013 (2)	0.006 (2)	0.010 (2)
C4	0.073 (3)	0.036 (2)	0.053 (3)	−0.0020 (19)	0.007 (2)	0.0068 (18)
C5	0.062 (3)	0.0344 (18)	0.038 (2)	0.0014 (17)	0.0056 (18)	−0.0034 (16)
C6	0.070 (3)	0.052 (2)	0.050 (2)	−0.002 (2)	0.004 (2)	0.0139 (19)
C7	0.047 (2)	0.047 (2)	0.044 (2)	0.0037 (18)	0.0029 (17)	−0.0105 (18)
C8	0.054 (3)	0.070 (3)	0.066 (3)	0.013 (2)	0.002 (2)	0.007 (2)
C9	0.042 (3)	0.118 (4)	0.071 (3)	0.004 (3)	−0.005 (2)	0.013 (3)
C10	0.060 (3)	0.078 (3)	0.056 (3)	−0.013 (2)	0.014 (2)	−0.007 (2)
C11	0.063 (3)	0.066 (3)	0.054 (3)	−0.002 (2)	0.008 (2)	0.007 (2)
C12	0.048 (2)	0.065 (3)	0.053 (3)	0.009 (2)	−0.005 (2)	−0.001 (2)
Br1	0.0635 (4)	0.1164 (5)	0.0676 (4)	0.0127 (3)	0.0060 (3)	−0.0013 (3)
Br2	0.0876 (5)	0.1390 (6)	0.0825 (5)	−0.0422 (4)	0.0262 (3)	0.0036 (3)

Geometric parameters (Å, º)

N1—C5	1.456 (5)	C2—Br1	1.895 (5)
N1—H10	0.89	C3—C4	1.369 (6)
N1—H9	0.89	C3—H2	0.93
N1—H11	0.89	C4—C5	1.375 (5)
N2—C7	1.465 (5)	C4—H3	0.93
N2—H14	0.89	C5—C6	1.373 (6)
N2—H13	0.89	C6—H4	0.93
N2—H12	0.89	C7—C12	1.364 (6)
N3—O5	1.207 (5)	C7—C8	1.370 (6)
N3—O3	1.245 (4)	C8—C9	1.379 (7)
N3—O2	1.249 (4)	C8—H5	0.93
N4—O1	1.229 (4)	C9—C10	1.360 (7)
N4—O4	1.254 (4)	C9—H6	0.93
N4—O6	1.258 (4)	C10—C11	1.366 (6)
C1—C6	1.378 (7)	C10—Br2	1.900 (4)

C1—C2	1.382 (6)	C11—C12	1.372 (6)
C1—H1	0.93	C11—H7	0.93
C2—C3	1.369 (6)	C12—H8	0.93

C5—N1—H10	109.5	C3—C4—C5	119.7 (4)
C5—N1—H9	109.5	C3—C4—H3	120.2
H10—N1—H9	109.5	C5—C4—H3	120.2
C5—N1—H11	109.5	C6—C5—C4	120.7 (4)
H10—N1—H11	109.5	C6—C5—N1	119.5 (3)
H9—N1—H11	109.5	C4—C5—N1	119.8 (4)
C7—N2—H14	109.5	C5—C6—C1	119.4 (4)
C7—N2—H13	109.5	C5—C6—H4	120.3
H14—N2—H13	109.5	C1—C6—H4	120.3
C7—N2—H12	109.5	C12—C7—C8	121.2 (4)
H14—N2—H12	109.5	C12—C7—N2	118.9 (4)
H13—N2—H12	109.5	C8—C7—N2	119.9 (4)
O5—N3—O3	123.7 (4)	C7—C8—C9	119.5 (4)
O5—N3—O2	121.3 (4)	C7—C8—H5	120.3
O3—N3—O2	115.0 (4)	C9—C8—H5	120.3
O1—N4—O4	119.8 (4)	C10—C9—C8	119.0 (4)
O1—N4—O6	120.9 (4)	C10—C9—H6	120.5
O4—N4—O6	119.3 (3)	C8—C9—H6	120.5
C6—C1—C2	119.8 (4)	C9—C10—C11	121.5 (4)
C6—C1—H1	120.1	C9—C10—Br2	120.0 (4)
C2—C1—H1	120.1	C11—C10—Br2	118.5 (4)
C3—C2—C1	120.1 (5)	C10—C11—C12	119.6 (4)
C3—C2—Br1	120.0 (3)	C10—C11—H7	120.2
C1—C2—Br1	119.9 (4)	C12—C11—H7	120.2
C2—C3—C4	120.3 (4)	C7—C12—C11	119.2 (4)
C2—C3—H2	119.9	C7—C12—H8	120.4
C4—C3—H2	119.9	C11—C12—H8	120.4

C6—C1—C2—C3	−0.4 (7)	C12—C7—C8—C9	1.2 (7)
C6—C1—C2—Br1	178.7 (3)	N2—C7—C8—C9	179.8 (4)
C1—C2—C3—C4	0.4 (6)	C7—C8—C9—C10	0.2 (7)
Br1—C2—C3—C4	−178.7 (3)	C8—C9—C10—C11	−1.1 (8)
C2—C3—C4—C5	−0.6 (6)	C8—C9—C10—Br2	178.5 (4)
C3—C4—C5—C6	0.7 (6)	C9—C10—C11—C12	0.6 (7)
C3—C4—C5—N1	179.2 (3)	Br2—C10—C11—C12	−179.1 (3)
C4—C5—C6—C1	−0.6 (6)	C8—C7—C12—C11	−1.8 (6)
N1—C5—C6—C1	−179.2 (4)	N2—C7—C12—C11	179.6 (4)
C2—C1—C6—C5	0.4 (7)	C10—C11—C12—C7	0.9 (6)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H9···O2^{i}	0.89	2.19	2.930 (5)	140
N1—H9···O3^{i}	0.89	2.15	3.002 (5)	160

N1—H10···O4^{i}	0.89	2.08	2.957 (4)	167
N1—H11···O2^{ii}	0.89	1.91	2.773 (4)	162
N2—H12···O1^{i}	0.89	2.59	3.356 (6)	145
N2—H12···O6^{i}	0.89	2.11	2.827 (5)	137
N2—H12···O1^{iii}	0.89	2.59	3.158 (5)	122
N2—H13···O3^{iv}	0.89	2.12	2.774 (5)	130
N2—H13···O6^{iv}	0.89	2.55	3.345 (5)	149
N2—H14···O4^{iii}	0.89	2.19	2.831 (5)	129
C4—H3···O1^{iii}	0.93	2.41	3.129 (5)	134
C12—H8···O3^{i}	0.93	2.59	3.410 (5)	147
C12—H8···O6^{i}	0.93	2.58	3.1943 (3)	124

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