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Bis(2-hydroxyethyl)ammonium 2-bromophenolate

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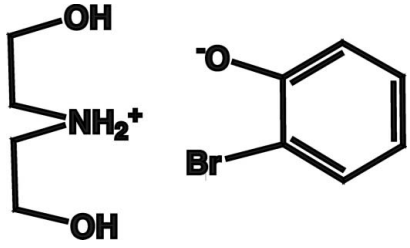
Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.002 Å; R factor = 0.018; wR factor = 0.042; data-to-parameter ratio = 18.7.

In the crystal structure of the 1:1 title salt, $C_4H_{12}NO_2^+\cdot C_6H_4BrO^-$, hydrogen-bonding interactions originate from the ammonium cation, which adopts a *syn* conformation. A *gauche* relationship between the C—O and C—N bonds of the 2-hydroxyethyl fragments also facilitates O—H···O interactions of bis(2-hydroxyethyl)ammonium cation chains to phenolate O atoms. The resulting double-ion chains along [100] are further linked by N—H···O interactions, forming chains parallel to [110].

Related literature

For structures of related 2-haloethylammonium salts and properties of these salts, see: Cody (1981); Cody & Strong (1980); Prout *et al.* (1988); Castellari & Ottani (1995); de Sousa *et al.* (2010*a*,*b*); Larsen *et al.* (2005); Mootz *et al.* (1989). For graph-set motifs, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$C_4H_{12}NO_2^+\cdot C_6H_4BrO^-$
M_r = 278.15
Monoclinic, $P2_1$
a = 8.0592 (1) Å
b = 7.6653 (1) Å
c = 9.7659 (2) Å
β = 107.250 (1)°
V = 576.16 (2) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 3.56 mm^{-1}
T = 173 K
0.48 × 0.21 × 0.20 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: gaussian (*XPREP*; Bruker, 2005)
T_{min} = 0.280, T_{max} = 0.537
11689 measured reflections
2784 independent reflections
2638 reflections with $I > 2\sigma(I)$
R_{int} = 0.033

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.018
$wR(F^2)$ = 0.042
S = 1.05
2784 reflections
149 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.17 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}
Absolute structure: Flack (1983), 1290 Friedel pairs
Flack parameter: −0.012 (5)

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2···O1	0.83 (2)	1.83 (2)	2.6393 (16)	165 (2)
O3—H3···O2^{i}	0.84	1.87	2.7010 (18)	171
N1—H1A···O1^{ii}	0.969 (18)	1.789 (19)	2.738 (2)	165.7 (16)
N1—H1B···O1	0.93 (2)	1.91 (2)	2.8259 (19)	169 (2)

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

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT-NT* (Bruker, 2005); data reduction: *SAINT-NT*; 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: *WinGX* (Farrugia, 1999) and *PLATON*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BH2446).

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supplementary materials

Acta Cryst. (2012). E**68**, o2610 [doi:10.1107/S1600536812033752]

Bis(2-hydroxyethyl)ammonium 2-bromophenolate

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Comment

The molecular structure (Fig. 1) of the 1:1 salt of 2-bromophenol with diethanolamine (DEA) is reported. Our interest in studying DEA is aimed at developing amino alcohols as supramolecules in a crystal engineering strategy, for template self-assembly of these compounds in supramolecular structures. Directional hydrogen-bonding patterns associated with DEA have labeled this compound a potential supramolecule. It is known to aggregate into tubular columns (Mootz *et al.*, 1989); the behaviour is emulated by C— and N—alkylated derivatives (de Sousa *et al.*, 2010*a*,*b*). Specific O—H···O interactions of the 2-hydroxyalkyl groups contribute significantly towards tubular aggregation in alkylated derivatives of this compound. These hydrogen bonds also feature prominently in salts of DEA elucidating binding modes of thyroid hormones to transport proteins (Cody, 1981; Cody & Strong, 1980; Prout *et al.*, 1988); the template synthesis of heterometallic wheels (Larsen *et al.*, 2005); and in studies aimed at correlating structural and pharmacological properties of anti-inflammatory drugs (Castellari & Ottani, 1995).

O—H···O hydrogen bonds are highly influential in the molecular structure reported here for the 2-bromophenol (1:1) salt with DEA. The unitary level *C*(8) chain (Bernstein *et al.*, 1995), described by O3—H3···O2 hydrogen bonds along [100], defines the backbone of the crystal structure (Fig. 2 and Table 1). In these chains *syn* conformations of the bis(2-hydroxyethyl) ammonium cations enjoy *gauche* relationships between C—O and C—N bonds, enabling further O—H···O and N—H···O hydrogen bonds of this supramolecular synthon. Hydroxyethyl O atom O2 acts as a weakly bifurcated H-donor, *via* H2, to phenolate O1 and Br1 atoms (Table 1). The hydrogen bonding array of the double-ion pair is completed by the N1—H1B···O1 interaction involving the ammonium N1 atom acting as a hydrogen donor, *via* H1B, to the phenolate oxygen atom O1. The combined O2—H2···O1 and N1—H1B···O1 interactions describe a $R_2^1(7)$ ring motif (Fig. 2) at the binary level (Bernstein *et al.*, 1995). Chains of double-ion pairs along [100] are linked by N1—H1A···O1 interactions (Table 1) to form layers parallel to the *ab* plane (Fig. 3). Within these layers N—H···O interactions define $C_2^1(4)$ and $C_2^1(7)$ motifs along [010] (Fig. 4) when combined with interactions N1—H1B···O1 and O2—H2···O1, respectively.

Experimental

Diethanolamine (0.501 g, 4.8 mmol) was stirred in 20 ml of dimethylformamide. To this solution, sodium carbonate (0.504 g, 4.75 mmol) and 2-bromophenol (0.823 g, 4.76 mmol) was added with continuous stirring. The reaction mixture was allowed to stir for an additional 24 hours under ambient conditions. The mixture was filtered and the solvent removed under reduced pressure, to yield a clear viscous oil that crystallized upon standing.

Refinement

Hydrogen atoms were visible in the difference maps, but those bonded to C atoms were positioned geometrically and refined as riding atoms, with C—H = 0.99 Å (CH_2) or 0.95 Å (aromatic CH), as well as H3, bonded to O3, with O3—H3 bond length fixed to 0.84 Å. Isotropic displacement parameters for these H atoms were defined as U_{iso}(H) = 1.2U_{eq}(parent C atom) and U_{iso}(H3) = 1.5U_{eq}(O3). Other H atoms (H1A, H1B and H2), which are involved in hydrogen bonds, were refined freely.

Computing details

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT-NT* (Bruker, 2005); data reduction: *SAINT-NT* (Bruker, 2005); 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: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2009).

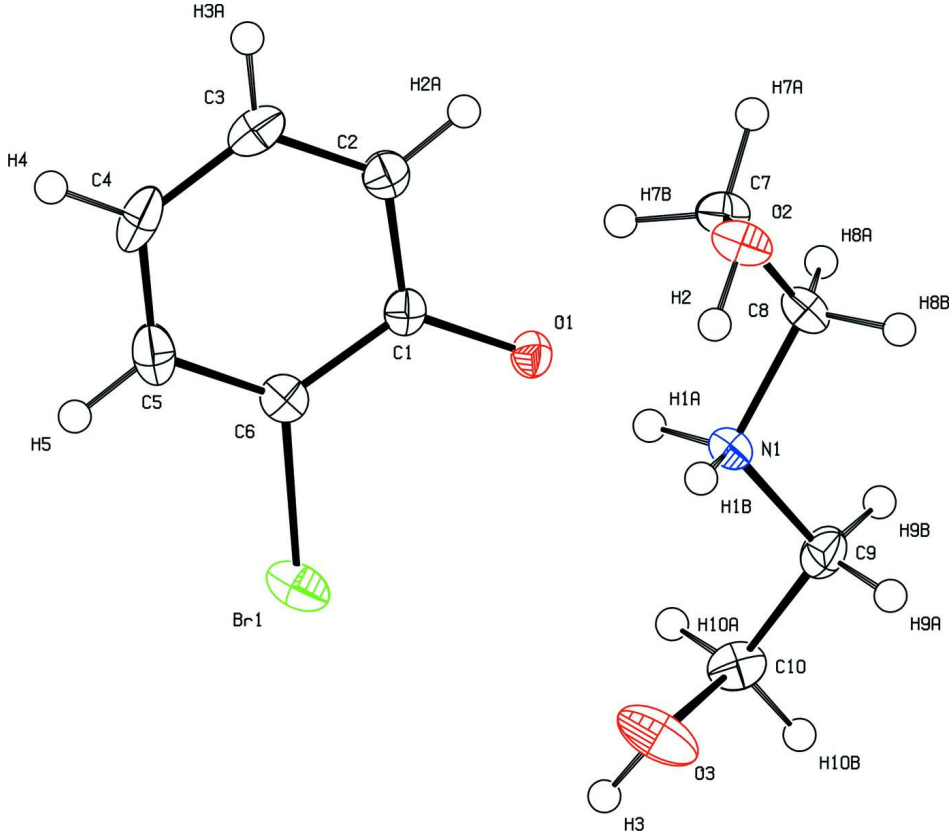

Figure 1

Molecular structure of the title compound, showing displacement ellipsoids at the 50% probability level.

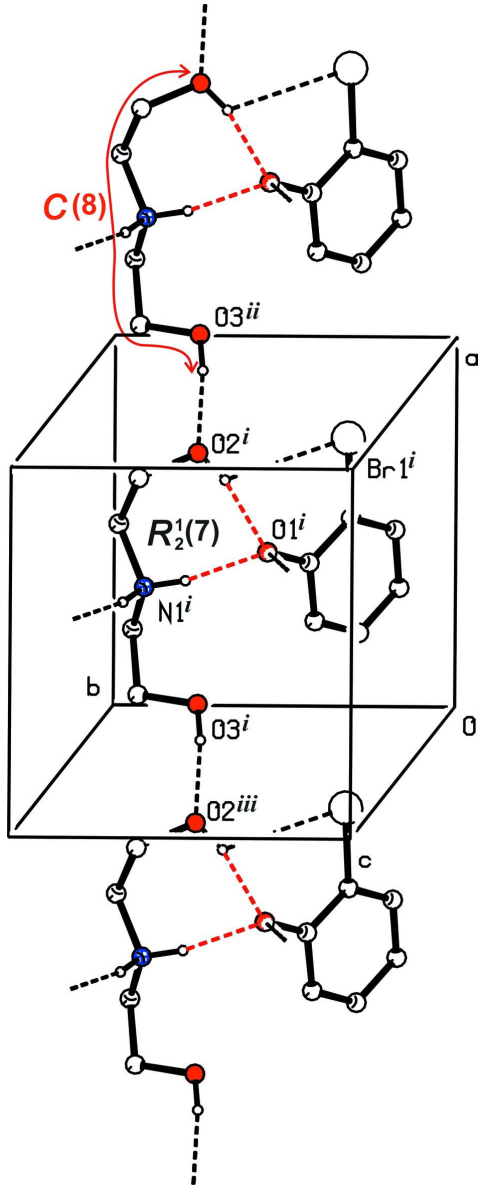

Figure 2

Chains along [100] defined by intermolecular O—H···O hydrogen bonds. Symmetry codes: (*i*) *x*, *y*, *z*; (*ii*) 1+*x*, *y*, *z*; (*iii*) -1+*x*, *y*, *z*.

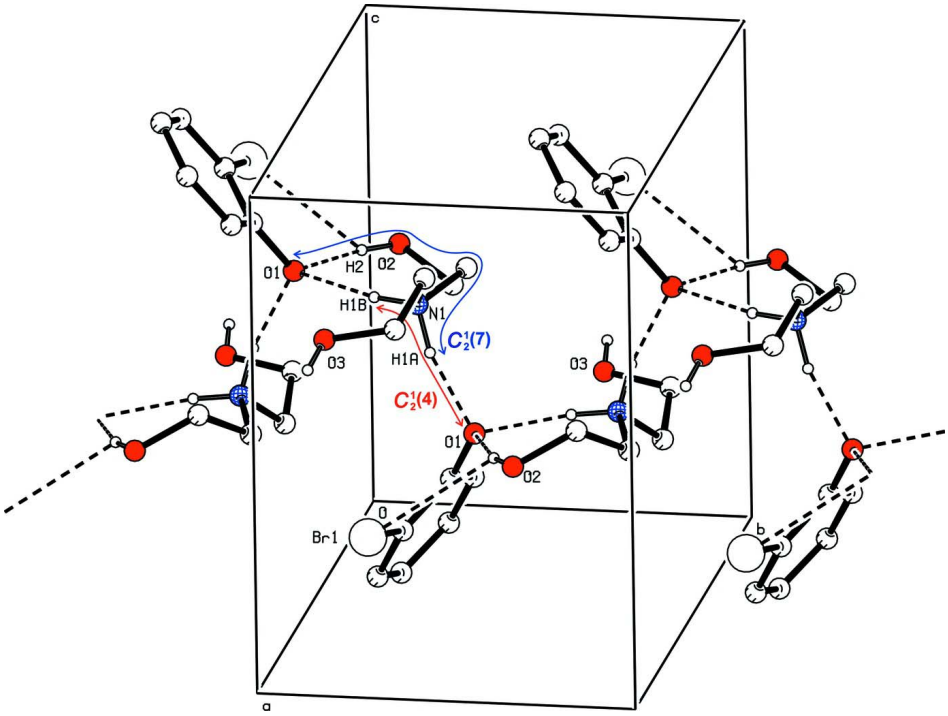

Figure 3

Layers parallel to (110) formed by hydrogen bonding double-ion chains along [100].

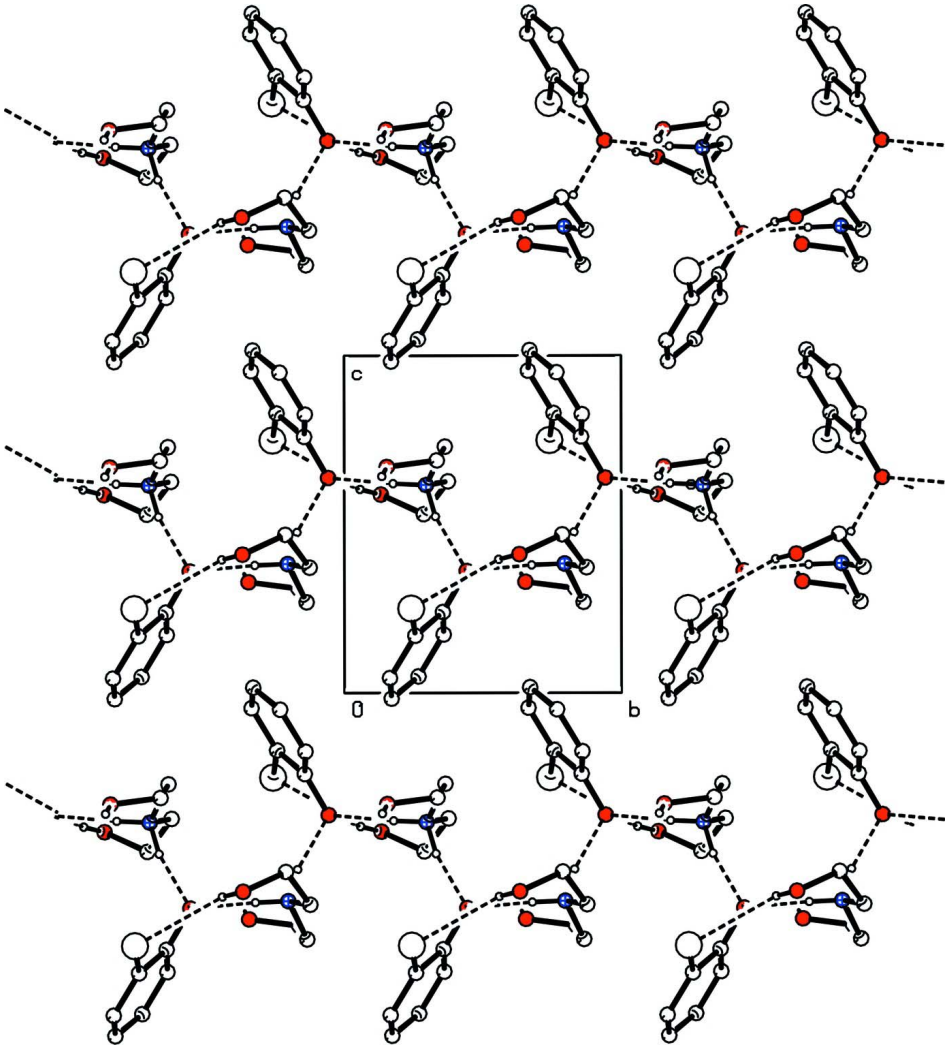

Figure 4

Binary $C_2^1(4)$ and $C_2^1(7)$ motifs along [010] described by N—H···O and O—H···O interactions originating at the bis(2-hydroxyethyl)ammonium cation.

bis(2-hydroxyethyl)ammonium 2-bromophenolate

Crystal data

$C_4H_{12}NO_2^+ \cdot C_6H_4BrO^-$
M_r = 278.15
Monoclinic, $P2_1$
Hall symbol: P 2yb
a = 8.0592 (1) Å
b = 7.6653 (1) Å
c = 9.7659 (2) Å
β = 107.250 (1)°
V = 576.16 (2) Å^3
Z = 2
F(000) = 284
D_x = 1.603 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 8333 reflections
θ = 2.2–28.2°
μ = 3.56 mm^{-1}
T = 173 K
Needle, colourless
0.48 × 0.21 × 0.20 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: gaussian (*XPREP*; Bruker, 2005)
T_{min} = 0.280, T_{max} = 0.537
11689 measured reflections
2784 independent reflections
2638 reflections with $I > 2\sigma(I)$
R_{int} = 0.033
θ_{max} = 28.0°, θ_{min} = 2.2°
$h = -10 \rightarrow 10$
$k = -10 \rightarrow 10$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.018
$wR(F^2)$ = 0.042
S = 1.05
2784 reflections
149 parameters
1 restraint
0 constraints
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
$w = 1/[\sigma^2(F_o^2) + (0.025P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.17 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}
Absolute structure: Flack (1983), 1290 Friedel pairs
Flack parameter: −0.012 (5)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
C1	0.4737 (2)	0.35547 (19)	0.23985 (15)	0.0163 (3)
C2	0.2924 (2)	0.3582 (2)	0.17355 (16)	0.0204 (3)
H2A	0.2208	0.4246	0.2157	0.025*
C3	0.2168 (2)	0.2669 (3)	0.04897 (18)	0.0278 (4)
H3A	0.0942	0.2709	0.0076	0.033*
C4	0.3155 (3)	0.1699 (2)	−0.01670 (18)	0.0299 (4)
H4	0.2619	0.1080	−0.1028	0.036*
C5	0.4937 (3)	0.1639 (2)	0.04447 (18)	0.0263 (4)
H5	0.5637	0.0972	0.0009	0.032*
C6	0.56985 (19)	0.2557 (3)	0.16984 (15)	0.0191 (3)
O1	0.54554 (14)	0.44173 (13)	0.36173 (11)	0.0181 (2)
Br1	0.815421 (18)	0.24105 (3)	0.250455 (16)	0.02891 (5)
C7	0.7822 (2)	0.7869 (2)	0.46980 (18)	0.0222 (4)
H7A	0.8807	0.8699	0.4908	0.027*
H7B	0.7600	0.7583	0.5617	0.027*
C8	0.6234 (2)	0.8745 (2)	0.37228 (18)	0.0210 (3)
H8A	0.6257	0.9999	0.3971	0.025*
H8B	0.6266	0.8654	0.2720	0.025*
C9	0.3024 (2)	0.8634 (2)	0.26948 (17)	0.0235 (4)
H9A	0.3174	0.9897	0.2557	0.028*
H9B	0.2930	0.8035	0.1777	0.028*
C10	0.1394 (3)	0.8345 (3)	0.3100 (2)	0.0235 (4)
H10A	0.1458	0.8977	0.3998	0.028*
H10B	0.0379	0.8786	0.2334	0.028*

N1	0.4570 (2)	0.7953 (2)	0.38319 (17)	0.0168 (3)
O2	0.83024 (16)	0.63195 (16)	0.41133 (14)	0.0241 (3)
O3	0.1216 (2)	0.65362 (19)	0.3294 (2)	0.0379 (4)
H3	0.0341	0.6357	0.3575	0.057*
H1A	0.449 (2)	0.829 (2)	0.4768 (19)	0.017 (4)*
H2	0.752 (3)	0.557 (3)	0.396 (2)	0.038 (6)*
H1B	0.473 (3)	0.676 (3)	0.3791 (19)	0.012 (5)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0227 (8)	0.0118 (7)	0.0152 (7)	−0.0009 (6)	0.0069 (6)	0.0028 (5)
C2	0.0243 (9)	0.0182 (7)	0.0196 (8)	0.0012 (6)	0.0077 (6)	0.0030 (6)
C3	0.0265 (8)	0.0303 (12)	0.0213 (7)	0.0000 (8)	−0.0008 (6)	0.0043 (7)
C4	0.0424 (11)	0.0284 (8)	0.0144 (8)	−0.0062 (8)	0.0016 (8)	−0.0026 (7)
C5	0.0398 (11)	0.0213 (8)	0.0217 (9)	0.0017 (7)	0.0150 (8)	−0.0010 (7)
C6	0.0211 (6)	0.0157 (8)	0.0219 (7)	−0.0016 (8)	0.0087 (5)	0.0026 (8)
O1	0.0192 (6)	0.0182 (5)	0.0170 (5)	−0.0016 (4)	0.0055 (4)	−0.0027 (4)
Br1	0.02163 (8)	0.02397 (8)	0.04356 (10)	0.00235 (9)	0.01340 (6)	−0.00094 (11)
C7	0.0176 (8)	0.0238 (10)	0.0252 (8)	−0.0027 (6)	0.0063 (6)	−0.0042 (6)
C8	0.0210 (8)	0.0180 (7)	0.0267 (8)	−0.0036 (6)	0.0111 (7)	0.0011 (6)
C9	0.0244 (9)	0.0243 (8)	0.0191 (8)	0.0031 (7)	0.0022 (7)	0.0042 (6)
C10	0.0195 (10)	0.0225 (9)	0.0273 (10)	0.0044 (7)	0.0050 (8)	−0.0048 (8)
N1	0.0162 (7)	0.0151 (6)	0.0201 (7)	−0.0009 (4)	0.0070 (5)	0.0006 (4)
O2	0.0187 (6)	0.0195 (6)	0.0356 (7)	−0.0023 (5)	0.0104 (5)	−0.0033 (5)
O3	0.0285 (9)	0.0231 (8)	0.0722 (12)	−0.0009 (6)	0.0306 (8)	−0.0068 (7)

Geometric parameters (Å, º)

C1—O1	1.3344 (18)	C7—H7B	0.9900
C1—C6	1.403 (2)	C8—N1	1.505 (2)
C1—C2	1.411 (2)	C8—H8A	0.9900
C2—C3	1.379 (2)	C8—H8B	0.9900
C2—H2A	0.9500	C9—C10	1.496 (3)
C3—C4	1.378 (3)	C9—N1	1.496 (2)
C3—H3A	0.9500	C9—H9A	0.9900
C4—C5	1.383 (3)	C9—H9B	0.9900
C4—H4	0.9500	C10—O3	1.412 (2)
C5—C6	1.388 (2)	C10—H10A	0.9900
C5—H5	0.9500	C10—H10B	0.9900
C6—Br1	1.9041 (15)	N1—H1A	0.969 (18)
C7—O2	1.4204 (19)	N1—H1B	0.93 (2)
C7—C8	1.508 (2)	O2—H2	0.83 (2)
C7—H7A	0.9900	O3—H3	0.8400
O1—C1—C6	123.26 (14)	N1—C8—H8A	109.1
O1—C1—C2	121.22 (14)	C7—C8—H8A	109.1
C6—C1—C2	115.53 (14)	N1—C8—H8B	109.1
C3—C2—C1	121.58 (16)	C7—C8—H8B	109.1
C3—C2—H2A	119.2	H8A—C8—H8B	107.8

C1—C2—H2A	119.2	C10—C9—N1	110.82 (14)
C4—C3—C2	121.27 (17)	C10—C9—H9A	109.5
C4—C3—H3A	119.4	N1—C9—H9A	109.5
C2—C3—H3A	119.4	C10—C9—H9B	109.5
C3—C4—C5	119.06 (16)	N1—C9—H9B	109.5
C3—C4—H4	120.5	H9A—C9—H9B	108.1
C5—C4—H4	120.5	O3—C10—C9	108.25 (17)
C4—C5—C6	119.67 (16)	O3—C10—H10A	110.0
C4—C5—H5	120.2	C9—C10—H10A	110.0
C6—C5—H5	120.2	O3—C10—H10B	110.0
C5—C6—C1	122.89 (15)	C9—C10—H10B	110.0
C5—C6—Br1	117.92 (13)	H10A—C10—H10B	108.4
C1—C6—Br1	119.19 (12)	C9—N1—C8	111.74 (13)
O2—C7—C8	113.57 (13)	C9—N1—H1A	109.6 (10)
O2—C7—H7A	108.9	C8—N1—H1A	105.5 (10)
C8—C7—H7A	108.9	C9—N1—H1B	114.2 (12)
O2—C7—H7B	108.9	C8—N1—H1B	104.8 (14)
C8—C7—H7B	108.9	H1A—N1—H1B	110.6 (16)
H7A—C7—H7B	107.7	C7—O2—H2	111.9 (16)
N1—C8—C7	112.52 (13)	C10—O3—H3	109.5

O1—C1—C2—C3	−178.80 (15)	C2—C1—C6—C5	−0.6 (2)
C6—C1—C2—C3	0.6 (2)	O1—C1—C6—Br1	−0.1 (2)
C1—C2—C3—C4	−0.5 (3)	C2—C1—C6—Br1	−179.51 (11)
C2—C3—C4—C5	0.3 (3)	O2—C7—C8—N1	82.70 (18)
C3—C4—C5—C6	−0.3 (3)	N1—C9—C10—O3	−59.0 (2)
C4—C5—C6—C1	0.4 (3)	C10—C9—N1—C8	−160.34 (16)
C4—C5—C6—Br1	179.38 (13)	C7—C8—N1—C9	−170.68 (14)
O1—C1—C6—C5	178.81 (15)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O1	0.83 (2)	1.83 (2)	2.6393 (16)	165 (2)
O3—H3···O2^{i}	0.84	1.87	2.7010 (18)	171
N1—H1*A*···O1^{ii}	0.969 (18)	1.789 (19)	2.738 (2)	165.7 (16)
N1—H1*B*···O1	0.93 (2)	1.91 (2)	2.8259 (19)	169 (2)
O2—H2···Br1	0.83 (2)	2.92 (2)	3.3690 (13)	115.6 (18)

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