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Crystal structure and Hirshfeld surface analysis of 1-carboxy-2-(3,4-dihydroxyphenyl)ethan-1-aminium bromide 2-ammonio-3-(3,4-dihydroxyphenyl)propanoate

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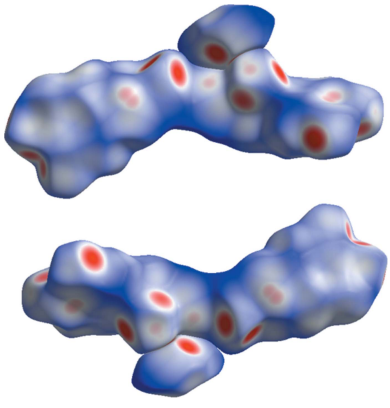
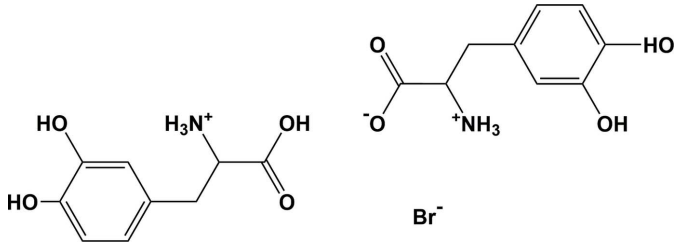
In the title molecular salt, $C_9H_{12}NO_4^+\cdot Br^-\cdot C_9H_{11}NO_4$, one of the dopa molecules is in the cationic form in which the α-amino group is protonated and the α-carboxylic acid group is uncharged, while the second dopa molecule is in the zwitterion form. The Br^- anion occupies a special position and is located on a twofold rotation axis. The two dopa molecules are interconnected by short O—H···O hydrogen bonds. In the crystal, the various units are linked by O—H···O, N—H···Br and N—H···O hydrogen bonds, forming a three-dimensional framework. The title compound was refined as an inversion twin with an absolute structure parameter of 0.023 (8).

1. Chemical context

An aromatic amino acid enzyme hydroxylase converts L-tyrosine into L-dopa (L-3,4-dihydroxyphenylalanine). After conversion, L-dopa acts as a precursor for the neurotransmitters dopamine, norepinephrine and epinephrine. The L-dopa molecule is also effectively used in the symptomatic treatment of Parkinson's disease (Chan *et al.*, 2012). In view of this interest, we have crystallized the title salt and report herein on its crystal structure. The hydrogen-bonding pattern and the relative contributions of various intermolecular interactions present are compared with the closely related chloride counterpart reported on earlier (Jandacek & Earle, 1971; Mostad & Rømming, 1974).





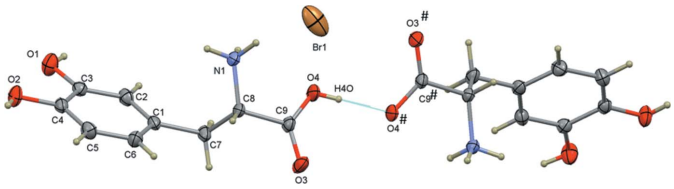


Figure 1
The molecular structure of the title molecular salt, showing the atom labelling [symmetry code: (#) $-x+3, y, -z+1$]. Displacement ellipsoids are drawn at the 50% probability level.

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1O···O3^{i}	0.82	1.98	2.782 (2)	166
O2—H2O···O1^{ii}	0.82	2.32	3.004 (2)	142
O2—H2O···O2^{ii}	0.82	2.26	2.9557 (8)	144
O4—H4O···O4^{iii}	0.85 (4)	1.61 (4)	2.449 (2)	169 (6)
N1—H1A···Br1^{iv}	0.95 (3)	2.41 (3)	3.359 (3)	179 (3)
N1—H1B···Br1	0.91 (3)	2.41 (3)	3.295 (3)	164 (2)
N1—H1C···O3^{v}	0.89 (3)	1.95 (3)	2.821 (2)	164 (3)

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

2. Structural commentary

The asymmetric unit of the title salt, Fig. 1, is composed of a Br^- anion located on a twofold rotation axis, a dopa molecule in the zwitterionic form and a cationic dopa molecule. In the latter, the α-amino group is protonated and carries a positive charge and the hydrogen atom (H4O) of the α-carboxylic acid group is located on a general position and was refined with 50% occupancy.

The crystal structures of L-dopa (Mostad *et al.*, 1971) and its hydrochloride form (Jandacek & Earle, 1971; Mostad & Rømming, 1974) have been reported. Both of these compounds crystallized in the monoclinic space group $P2_1$. In the crystal structure of L-dopa HCl, the α-amino group is protonated and the α-carboxylic acid is neutral. The stoichiometry between the cation and the Cl^- anion is 1:1. The authors of these structures concluded that L-dopa exists as the *S* enantiomer, based on the *R* factor and the effects of anomalous scattering. However, the deposited coordinates for these structures belong to the *R* configuration. Therefore, the L-dopa HCl structure was inverted and used for superposition with one of the dopa molecules of the title compound. These structures superimpose well, with an r.m.s. deviation of 0.045 Å (Fig. 2).

3. Supramolecular features

The structure of the title compound features a network of intermolecular N—H···Br, N—H···O and O—H···O hydrogen bonds (Table 1), forming a three-dimensional framework. The cationic dopa molecules form dimers in which the carboxylic acid groups (O4) of the dopa molecules are interconnected *via* a short O—H···O hydrogen bond and the dimers are arranged as ribbons propagating along the *b* axis (Fig. 3). The protonated amino group forms three hydrogen bonds; two of them with the Br^- anions and one with the carbonyl oxygen atom, O3, of the carboxylic acid group. The dopa molecules aggregate in a head-to-tail sequence of the type $\cdots NH_3^+—CHR—COO^-\cdots NH_3^+—CHR—COO^-\cdots$, in which the α-amino atom, N1, and the α-carboxylate atom O3 form a hydrogen-bonded peptide-like arrangement (layers), as observed in many amino acid–carboxylic acid complexes (Sharma *et al.*, 2006; Selvaraj *et al.*, 2007). Adjacent layers are interconnected by short O—H···O hydrogen bonds. These two interactions combine to form an $R_4^4(18)$ ring motif (Fig. 4). Similar interactions are observed in dopa and its HCl form (Mostad *et al.*, 1971; Jandacek & Earle, 1971; Mostad & Rømming, 1974).

The amino group (*via* H1A and H1B) of the cationic dopa molecule participates in intermolecular N—H···Br interactions with two different Br^- anions (Table 1). These interactions interconnect the cations and anions into a cyclic motif

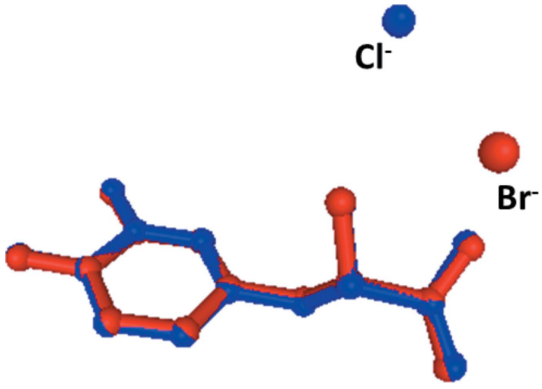


Figure 2
Superposition of the cationic dopa molecule in the title compound (red) and in L-dopa·HCl (blue).

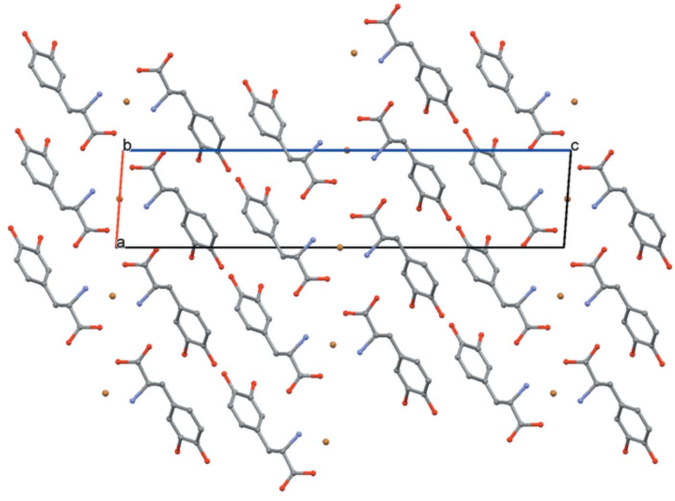


Figure 3
The crystal packing of the title molecular salt, viewed along the *b* axis. H atoms have been omitted for clarity.

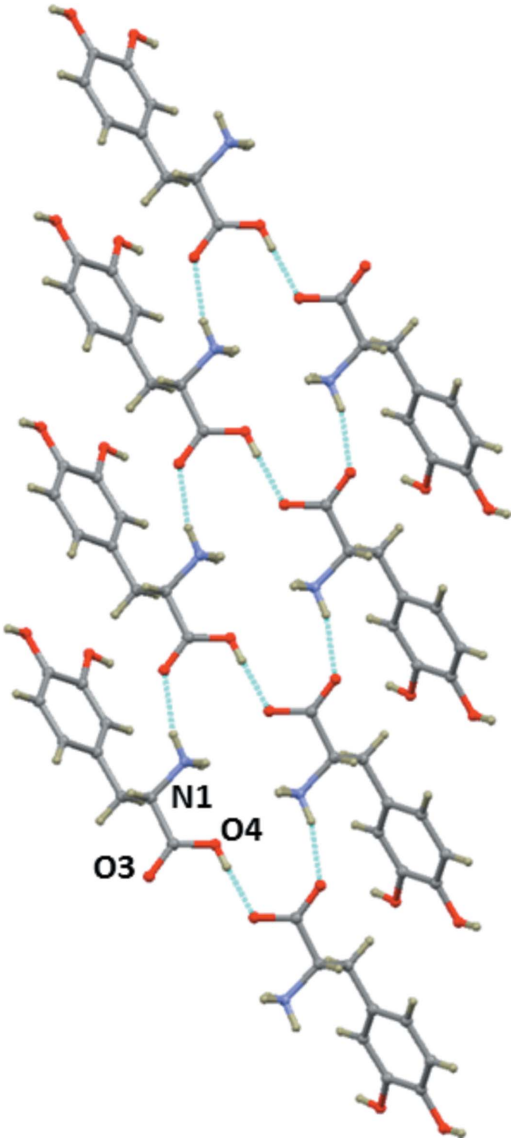


Figure 4
Part of the crystal structure of the title molecular salt, showing the $R_4^4(18)$ ring motifs formed by N—H···O and O—H···O hydrogen bonds.

that can be described as an $R_2^4(8)$ ring and it runs parallel to the *b* axis (Fig. 5). This pattern is also observed in the crystal structure of L-dopa·HCl, where two intermolecular N—H···Cl hydrogen bonds link the cations and anions into a chain. There, adjacent chains are interconnected through O—H···Cl hydrogen bonds (carboxylic acid···Cl).

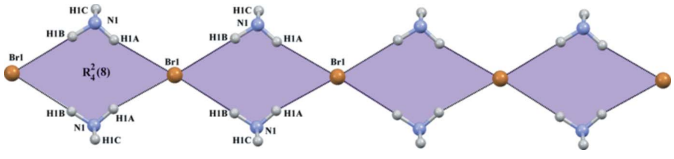


Figure 5
Part of the crystal structure of the title molecular salt, showing the $R_2^4(8)$ ring motifs formed by N—H···Br hydrogen bonds.

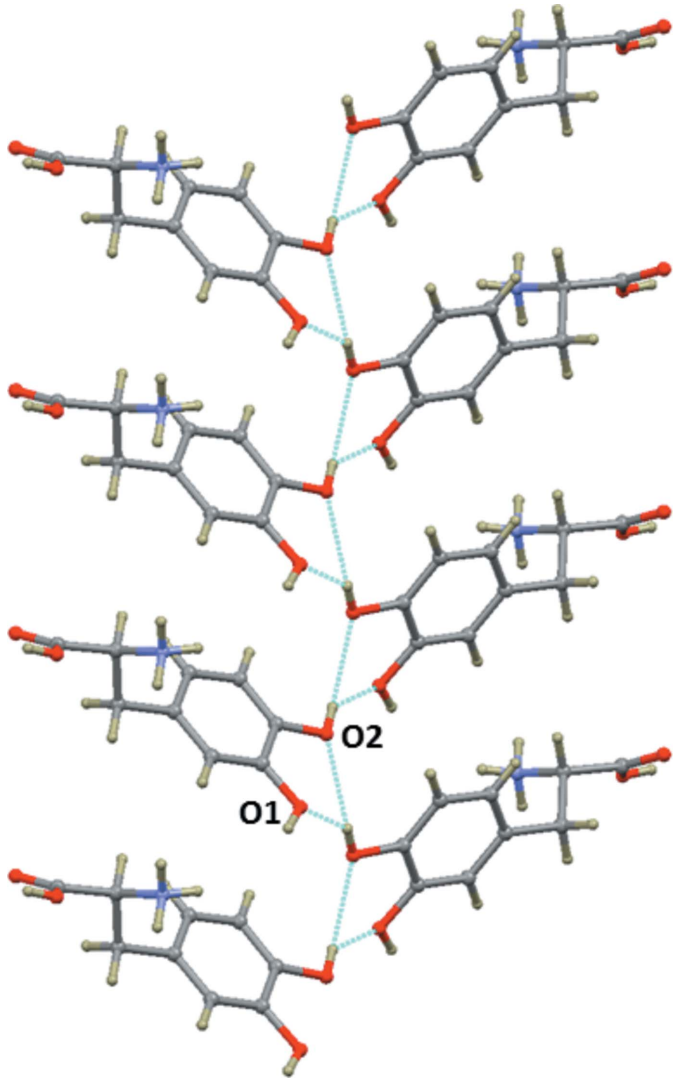


Figure 6
The side chain···side chain interactions of the dopa molecules in the title molecular salt, through intermolecular O—H···O hydrogen bonds.

One of the hydroxy groups (O1—H1*O*) is involved in an intermolecular O—H···O hydrogen bond with the carbonyl oxygen (O3) of the dopa molecule. This interaction links the dopa molecules into a *C*(9) chain. The other hydroxy (O2—H2*O*) group participates in bifurcated hydrogen bonds with two different hydroxy O atoms (O1 and O2) of adjacent dopa layers. The side chain of the dopa molecules in one layer is interconnected by the side chain of the dopa molecules in the adjacent layer through these interactions (Fig. 6). These interactions are also observed in the dopa hydrochloride structure.

4. Hirshfeld surface analysis

The Hirshfeld surfaces (HS) mapped with d_{norm} and 2D fingerprint plots were generated using the program *Crystal-Explorer* (Wolff *et al.*, 2012). The two different orientations of the HS diagram for complete dopa molecules along with Br^-

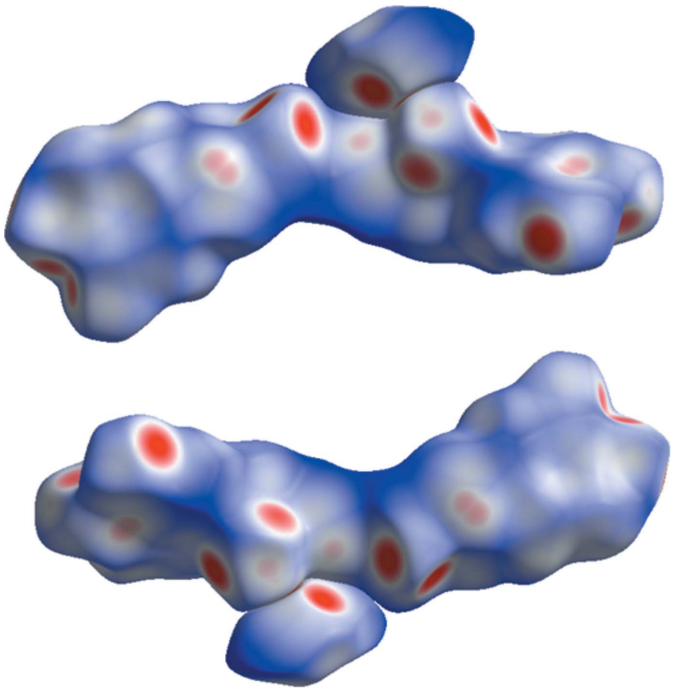


Figure 7
Two different views of the Hirshfeld surfaces of the dimeric dopa molecules along with a Br^- anion.

anion are shown in Fig. 7. The two-dimensional fingerprint plots are illustrated in Fig. 8. The HS analysis suggests that the intermolecular O···H contacts contribute most (41.4%) to the crystal packing compared to other contacts. For example, the relative contributions of H···H, C···H and H···Br contacts are 29, 18.6 and 6.1%, respectively, with regard to the complete unit of the dopa molecule. Concerning the Br^- anion, the relative contributions of H···Br and O···Br contacts are 64.1 and 10.2%, respectively.

In the dopa HCl structure, the relative contributions of O···H, H···H, C···H and H···Cl contacts are 40.5, 25.2, 17.1 and 14.1%, respectively, with respect to the cationic dopa molecule. It is of interest to note that O···H and H···H contacts are reduced by 1.1 and 3.8%, respectively, when compared to the title salt. Concerning the Cl^- anion, the relative contribution of H···Cl contacts is 90.4%. This is approximately 26% higher compared to the relative contributions of H···Br contacts in the title salt.

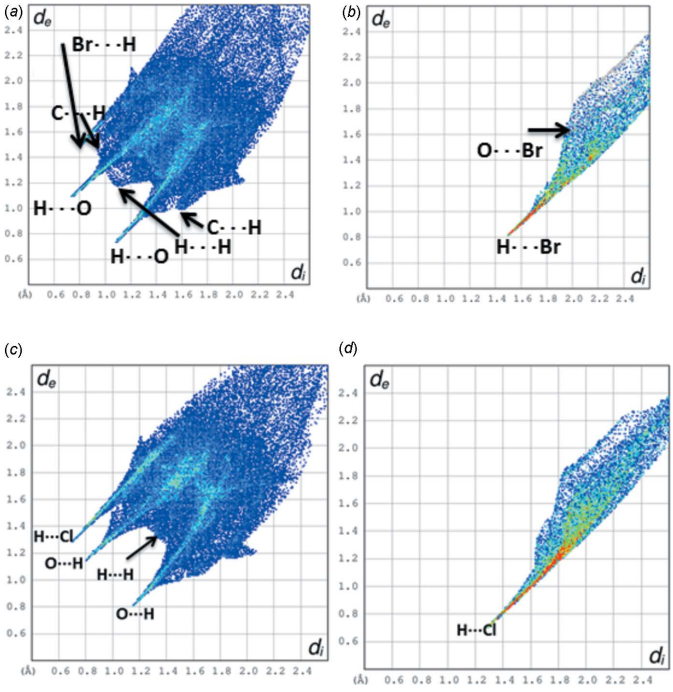


Figure 8
Two-dimensional fingerprint plots: (*a*) complete unit of dopa and (*b*) anionic Br^- in the title salt, and (*c*) cationic dopa and (*d*) anionic Cl^- in L-dopa hydrochloride. The various types of contacts are indicated.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_9H_{12}NO_4^+\cdot Br^-\cdot C_9H_{11}NO_4$
M_r	475.29
Crystal system, space group	Monoclinic, *I*2
Temperature (K)	293
a, *b*, *c* (Å)	6.1456 (3), 5.6385 (2), 28.2561 (10)
β (°)	94.147 (2)
V (Å^3)	976.57 (7)
Z	2
Radiation type	Mo *K*α
μ (mm^{-1})	2.16
Crystal size (mm)	0.30 × 0.25 × 0.25
Data collection	
Diffractometer	Bruker Kappa APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2004)
T_{min}, T_{max}	0.562, 0.619
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8138, 2827, 2421
R_{int}	0.024
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.833
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.026, 0.056, 0.97
No. of reflections	2827
No. of parameters	151
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.37, −0.31
Absolute structure	Refined as an inversion twin
Absolute structure parameter	0.023 (8)

Computer programs: *APEX2*, *SAINT* and *XPREP* (Bruker, 2004), *SIR92* (Altomare *et al.*, 1994), *Mercury* (Macrae *et al.*, 2006), *SHELXL2014* (Sheldrick, 2015) and *publCIF* (Westrip, 2010).

5. Synthesis and crystallization

L-dopa and HBr (1:1 molar ratio) were dissolved in double-distilled water and stirred well for 4 h. The homogeneous solution was filtered and the filtrate allowed to evaporate slowly. Colourless block-like crystals were harvested after a growth period of two weeks.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The amino and carboxylic acid H atoms were located in a difference Fourier map and freely refined. The OH and C-bound H atoms were included in calculated positions and treated as riding atoms: C—H = 0.93–0.98 Å, O—H = 0.82 Å with U_{iso}(H) = 1.2U_{eq}(C) and U_{iso}(H) = 1.5U_{eq}(O). The title compound was refined as an inversion twin; absolute structure parameter = 0.023 (8).

Acknowledgements

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supporting information

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Perumal Kathiravan, Thangavelu Balakrishnan, Perumal Venkatesan, Kandasamy Ramamurthi, María Judith Percino and Subbiah Thamotharan

Computing details

Data collection: *APEX2* (Bruker, 2004); cell refinement: *APEX2* (Bruker, 2004) and *SAINT* (Bruker, 2004); data reduction: *SAINT* (Bruker, 2004) and *XPREP* (Bruker, 2004); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015) and *publCIF* (Westrip, 2010).

1-Carboxy-2-(3,4-dihydroxyphenyl)ethan-1-aminium bromide 2-ammonio-3-(3,4-dihydroxyphenyl)propanoate

Crystal data

$C_9H_{12}NO_4^+·Br^-·C_9H_{11}NO_4$
M_r = 475.29
Monoclinic, $I2$
a = 6.1456 (3) Å
b = 5.6385 (2) Å
c = 28.2561 (10) Å
β = 94.147 (2)°
V = 976.57 (7) Å^3
Z = 2
$F(000)$ = 488
D_x = 1.616 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 4553 reflections
θ = 2.4–32.1°
μ = 2.16 mm^{-1}
T = 293 K
Block, colourless
0.30 × 0.25 × 0.25 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
ω and φ scan
Absorption correction: multi-scan (SADABS; Bruker, 2004)
T_{min} = 0.562, T_{max} = 0.619
8138 measured reflections
2827 independent reflections
2421 reflections with $I > 2\sigma(I)$
R_{int} = 0.024
θ_{max} = 36.3°, θ_{min} = 2.9°
h = −8→8
k = −7→9
l = −37→37

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.026
$wR(F^2)$ = 0.056
S = 0.97
2827 reflections
151 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0178P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.37$ e Å^{-3}
$\Delta\rho_{min} = -0.31$ e Å^{-3}
Absolute structure: Refined as an inversion twin
Absolute structure parameter: 0.023 (8)

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. Refined as a 2-component inversion twin.

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
O1	0.4002 (2)	1.2639 (3)	0.32975 (6)	0.0314 (3)	
H1O	0.4444	1.3490	0.3519	0.047*	
O2	0.3013 (2)	0.9618 (3)	0.26190 (5)	0.0296 (3)	
H2O	0.2781	0.8520	0.2432	0.044*	
O3	1.4783 (2)	0.5473 (3)	0.40977 (5)	0.0317 (4)	
O4	1.3241 (2)	0.6326 (4)	0.47670 (4)	0.0279 (3)	
H4O	1.446 (6)	0.614 (10)	0.4922 (15)	0.021 (11)*	0.5
N1	0.9218 (2)	0.6239 (5)	0.43861 (5)	0.0198 (3)	
H1A	0.943 (4)	0.765 (6)	0.4564 (11)	0.033 (8)*	
H1B	0.927 (4)	0.503 (5)	0.4600 (9)	0.020 (6)*	
H1C	0.788 (4)	0.613 (7)	0.4245 (8)	0.042 (6)*	
C1	0.8776 (3)	0.8691 (4)	0.34526 (6)	0.0209 (4)	
C2	0.7366 (3)	1.0550 (4)	0.35295 (7)	0.0227 (4)	
H2	0.7713	1.1616	0.3775	0.027*	
C3	0.5451 (3)	1.0840 (3)	0.32468 (6)	0.0198 (4)	
C4	0.4911 (3)	0.9215 (4)	0.28859 (6)	0.0205 (4)	
C5	0.6293 (3)	0.7354 (4)	0.28093 (7)	0.0248 (4)	
H5	0.5935	0.6270	0.2568	0.030*	
C6	0.8220 (3)	0.7097 (4)	0.30924 (7)	0.0245 (4)	
H6	0.9148	0.5838	0.3039	0.029*	
C7	1.0906 (3)	0.8400 (4)	0.37490 (7)	0.0230 (4)	
H7A	1.1131	0.9771	0.3954	0.028*	
H7B	1.2091	0.8349	0.3540	0.028*	
C8	1.0982 (2)	0.6168 (5)	0.40531 (6)	0.0183 (3)	
H8	1.0753	0.4786	0.3845	0.022*	
C9	1.3203 (3)	0.5942 (4)	0.43256 (6)	0.0195 (4)	
Br1	1.0000	0.13069 (5)	0.5000	0.05492 (14)	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0287 (8)	0.0279 (8)	0.0363 (9)	0.0055 (7)	−0.0067 (7)	−0.0073 (7)
O2	0.0219 (7)	0.0347 (9)	0.0306 (8)	−0.0001 (6)	−0.0101 (6)	−0.0027 (7)

O3	0.0150 (6)	0.0536 (11)	0.0260 (7)	0.0049 (6)	−0.0012 (5)	−0.0099 (7)
O4	0.0154 (6)	0.0493 (8)	0.0180 (6)	0.0013 (9)	−0.0051 (5)	−0.0025 (10)
N1	0.0134 (7)	0.0274 (7)	0.0183 (7)	−0.0010 (9)	−0.0006 (5)	0.0023 (10)
C1	0.0184 (9)	0.0280 (10)	0.0159 (9)	−0.0020 (8)	−0.0010 (7)	0.0059 (7)
C2	0.0241 (10)	0.0240 (9)	0.0193 (9)	−0.0038 (8)	−0.0029 (7)	−0.0005 (7)
C3	0.0199 (9)	0.0199 (13)	0.0195 (8)	−0.0005 (7)	0.0011 (7)	0.0028 (7)
C4	0.0172 (9)	0.0260 (10)	0.0180 (9)	−0.0024 (8)	−0.0017 (7)	0.0046 (8)
C5	0.0265 (10)	0.0280 (10)	0.0193 (9)	−0.0016 (9)	−0.0018 (8)	−0.0040 (8)
C6	0.0217 (10)	0.0292 (10)	0.0225 (10)	0.0054 (8)	0.0001 (8)	0.0005 (8)
C7	0.0169 (9)	0.0307 (11)	0.0207 (9)	−0.0045 (8)	−0.0035 (7)	0.0072 (8)
C8	0.0128 (7)	0.0256 (9)	0.0163 (7)	0.0001 (9)	−0.0011 (6)	0.0009 (10)
C9	0.0149 (8)	0.0232 (13)	0.0197 (8)	0.0002 (8)	−0.0032 (6)	−0.0022 (8)
Br1	0.1055 (3)	0.01895 (14)	0.03896 (18)	0.000	−0.00415 (18)	0.000

Geometric parameters (Å, º)

O1—C3	1.364 (2)	C1—C7	1.511 (3)
O1—H1O	0.8200	C2—C3	1.384 (3)
O2—C4	1.362 (2)	C2—H2	0.9300
O2—H2O	0.8200	C3—C4	1.393 (3)
O3—C9	1.232 (2)	C4—C5	1.377 (3)
O4—C9	1.265 (2)	C5—C6	1.388 (3)
O4—H4O	0.85 (4)	C5—H5	0.9300
N1—C8	1.486 (2)	C6—H6	0.9300
N1—H1A	0.95 (3)	C7—C8	1.523 (3)
N1—H1B	0.91 (3)	C7—H7A	0.9700
N1—H1C	0.89 (3)	C7—H7B	0.9700
C1—C6	1.382 (3)	C8—C9	1.523 (2)
C1—C2	1.387 (3)	C8—H8	0.9800
C3—O1—H1O	109.5	C4—C5—C6	119.94 (19)
C4—O2—H2O	109.5	C4—C5—H5	120.0
C9—O4—H4O	116 (3)	C6—C5—H5	120.0
C8—N1—H1A	106.1 (17)	C1—C6—C5	120.78 (19)
C8—N1—H1B	114.1 (15)	C1—C6—H6	119.6
H1A—N1—H1B	106.3 (17)	C5—C6—H6	119.6
C8—N1—H1C	114.1 (14)	C1—C7—C8	113.12 (16)
H1A—N1—H1C	113 (3)	C1—C7—H7A	109.0
H1B—N1—H1C	103 (3)	C8—C7—H7A	109.0
C6—C1—C2	118.87 (18)	C1—C7—H7B	109.0
C6—C1—C7	119.72 (18)	C8—C7—H7B	109.0
C2—C1—C7	121.41 (18)	H7A—C7—H7B	107.8
C3—C2—C1	120.92 (18)	N1—C8—C7	109.9 (2)
C3—C2—H2	119.5	N1—C8—C9	110.50 (14)
C1—C2—H2	119.5	C7—C8—C9	110.12 (18)
O1—C3—C2	124.17 (17)	N1—C8—H8	108.8
O1—C3—C4	116.33 (17)	C7—C8—H8	108.8
C2—C3—C4	119.50 (17)	C9—C8—H8	108.8

O2—C4—C5	123.61 (18)	O3—C9—O4	126.40 (17)
O2—C4—C3	116.40 (17)	O3—C9—C8	117.71 (15)
C5—C4—C3	119.98 (18)	O4—C9—C8	115.85 (15)
C6—C1—C2—C3	−1.1 (3)	C7—C1—C6—C5	−178.73 (18)
C7—C1—C2—C3	178.05 (17)	C4—C5—C6—C1	0.1 (3)
C1—C2—C3—O1	−179.13 (18)	C6—C1—C7—C8	−66.3 (2)
C1—C2—C3—C4	1.3 (3)	C2—C1—C7—C8	114.5 (2)
O1—C3—C4—O2	0.9 (2)	C1—C7—C8—N1	−60.3 (2)
C2—C3—C4—O2	−179.49 (16)	C1—C7—C8—C9	177.70 (16)
O1—C3—C4—C5	179.62 (17)	N1—C8—C9—O3	168.4 (2)
C2—C3—C4—C5	−0.7 (3)	C7—C8—C9—O3	−70.0 (3)
O2—C4—C5—C6	178.75 (18)	N1—C8—C9—O4	−13.5 (3)
C3—C4—C5—C6	0.1 (3)	C7—C8—C9—O4	108.1 (2)
C2—C1—C6—C5	0.4 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*O*···O3^{i}	0.82	1.98	2.782 (2)	166
O2—H2*O*···O1^{ii}	0.82	2.32	3.004 (2)	142
O2—H2*O*···O2^{ii}	0.82	2.26	2.9557 (8)	144
O4—H4*O*···O4^{iii}	0.85 (4)	1.61 (4)	2.449 (2)	169 (6)
N1—H1*A*···Br1^{iv}	0.95 (3)	2.41 (3)	3.359 (3)	179 (3)
N1—H1*B*···Br1	0.91 (3)	2.41 (3)	3.295 (3)	164 (2)
N1—H1*C*···O3^{v}	0.89 (3)	1.95 (3)	2.821 (2)	164 (3)

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