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(*S*)-(−)-6-(4-Bromophenyl)-2,3,5,6-tetrahydrothiazolo[2,3-*b*]imidazolium hydrogen oxalate

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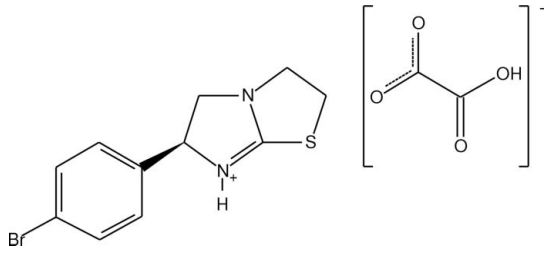
Key indicators: single-crystal X-ray study; T = 89 K; mean σ(C–C) = 0.004 Å; R factor = 0.032; wR factor = 0.074; data-to-parameter ratio = 17.7.

The structure of the title compound, $C_{11}H_{12}BrN_2S^+\cdot C_2HO_4^-$ (common name 6-bromolevamisole hydrogen oxalate), is stabilized mainly by hydrogen bonds. Hydrogen oxalate anions form parallel coplanar chains *via* O—H···O hydrogen bonds, while there are N—H···O hydrogen-bonding interactions between the 6-bromolevamisole cations and oxalate anions. Both five-membered rings from the 6-bromolevamisole molecule have a twist conformation. The molecule has an extended conformation, with the 4-bromophenyl substituent positioned equatorially with N—C—C—C and C—C—C—C torsion angles of 39.8 (3) and 100.4 (3)°, respectively.

Related literature

For background information, see: Denier *et al.* (2002); Lee *et al.* (1975); Luo *et al.* (2000).



Experimental

Crystal data

$C_{11}H_{12}BrN_2S^+\cdot C_2HO_4^-$
M_r = 373.22
Orthorhombic, $P2_12_12_1$
a = 5.615 (1) Å
b = 8.256 (1) Å
c = 32.539 (1) Å
V = 1508.4 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 2.88 mm^{-1}
T = 89 (2) K
0.50 × 0.03 × 0.03 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Absorption correction: multi-scan (Otwinowski *et al.*, 2003)
T_{min} = 0.90, T_{max} = 0.92
39658 measured reflections
4061 independent reflections
3438 reflections with $I > 2\sigma(I)$
R_{int} = 0.081

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.074
S = 1.10
4061 reflections
230 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.67 e Å^{-3}
$\Delta\rho_{min}$ = −0.51 e Å^{-3}
Absolute structure: Flack (1983), 1863 Friedel pairs
Flack parameter: −0.018 (7)

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1*O*···O3^{i}	1.03 (5)	1.48 (5)	2.483 (2)	164 (4)
N2—H1*N*···O4	0.83 (4)	1.95 (4)	2.753 (3)	163 (4)
N2—H1*N*···O1	0.83 (4)	2.37 (4)	2.879 (3)	120 (3)

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

Data collection: *HKL-2000* (Otwinowski & Minor, 1997); cell refinement: *HKL-2000*; data reduction: *HKL-2000*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008) and *HKL-3000SM* (Minor *et al.*, 2006); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008) and *HKL-3000SM*; molecular graphics: *HKL-3000SM*, *Mercury* (Macrae *et al.*, 2006), *ORTEPIII* (Burnett & Johnson, 1996) and *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *HKL-3000SM*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FL2215).

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supporting information

Acta Cryst. (2008). E**64**, o1954 [doi:10.1107/S1600536808029085]

(*S*)-(−)-6-(4-Bromophenyl)-2,3,5,6-tetrahydrothiazolo[2,3-*b*]imidazolium hydrogen oxalate

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S1. Comment

6-Bromolevamisole (Fig. 1) is a salt of a strong activator of cystic fibrosis conductance regulator (CTFR) chloride channels, including those in human airway epithelial cells. It shows a strong reduction in activity of Protein Phosphatases 2C and 2A, two of the most likely candidates for being a CTFR phosphatase (Luo *et al.*, 2000). It has also been shown to inhibit alkaline phosphatases, including being an uncompetitive inhibitor of an alkaline phosphatase involved in sarcoma (Lee *et al.*, 1975). Furthermore, since inhibitors affect alkaline phosphatase from the white blood cells of mothers of fetuses with Down's syndrome differently, the cation could be involved in screening for it (Denier *et al.*, 2002).

Packing (Fig. 2) is stabilized by hydrogen bonds (Table 1). The oxalate ions form parallel, coplanar, one-dimensional chains *via* O—H···O hydrogen bonds, with each link in the chain having an N—H···O hydrogen bond from the deprotonated oxygen to the protonated nitrogen (N2) of the 6-bromolevamisole. The bromine also forms a short contact (3.111 Å) with the O3 (-1/2 + *x*, 1/2 - *y*, 2 - *z*) atom.

S2. Experimental

6-Bromolevamisole oxalate was purchased from Sigma, and dissolved in a mixture of 1-butanol and DMSO in a 1:1 ratio. A single crystal suitable for X-ray diffraction study was obtained by slow evaporation at room temperature.

S3. Refinement

Hydrogen atoms attached to C7, C8, and C9 were placed in ideal positions, and refined using a riding-model approximation with C—H bond lengths of 0.98 Å in the case of C7 and 0.97 Å in the cases of C8 and C9. All other hydrogen atoms were located in a difference density Fourier map and refined with isotropic displacement parameters.

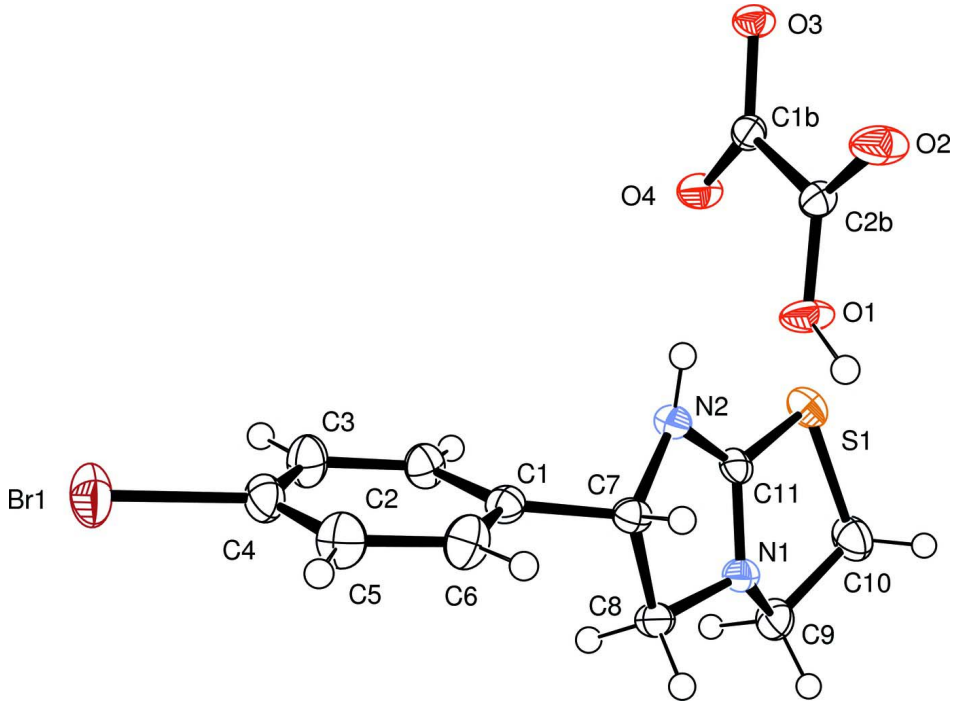

Figure 1

An asymmetric unit of the title compound. Displacement ellipsoids are drawn at the 50% probability level, while hydrogen atoms are drawn as spheres of an arbitrary radius.

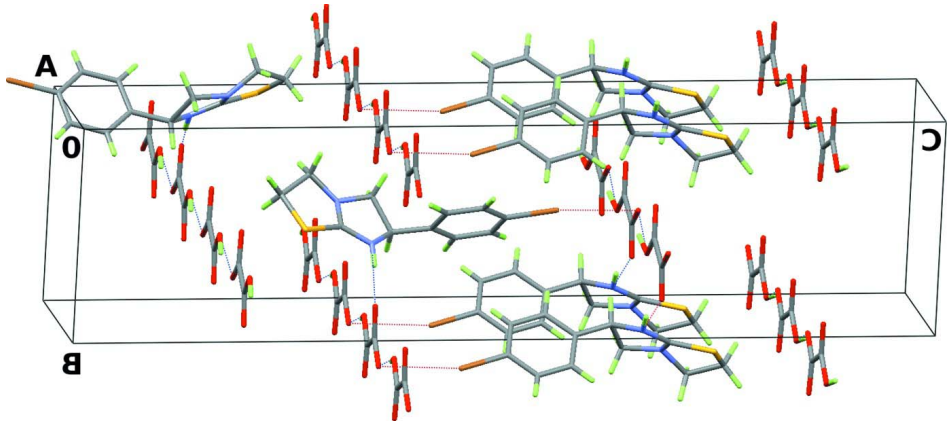

Figure 2

A packing diagram with hydrogen bonds marked with blue, dashed lines. Short contacts between Br···O3 (-1/2 + *x*, 1/2 - *y*, 2 - *z*) are marked with red, dashed lines.

(*S*)-(-)-6-(4-Bromophenyl)-2,3,5,6-tetrahydrothiazolo[2,3- *b*]imidazolium hydrogen oxalate

Crystal data

$C_{11}H_{12}BrN_2S^+·C_2HO_4^-$
M_r = 373.22
Orthorhombic, $P2_12_12_1$
Hall symbol: P 2ac 2ab
a = 5.615 (1) Å
b = 8.256 (1) Å
c = 32.539 (1) Å
V = 1508.4 (3) Å^3
Z = 4
F(000) = 752

D_x = 1.643 Mg m^{-3}
Melting point: 465 K
Mo $K\alpha$ radiation, λ = 0.71074 Å
Cell parameters from 39658 reflections
θ = 2.6–29.1°

μ = 2.88 mm^{-1}
T = 89 K
Needle, colourless
0.50 × 0.03 × 0.03 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 10 pixels mm^{-1}
ω scans with χ offset
Absorption correction: multi-scan (Otwinowski *et al.*, 2003)
T_{min} = 0.90, T_{max} = 0.92

39658 measured reflections
4061 independent reflections
3438 reflections with $I > 2\sigma(I)$
R_{int} = 0.081
θ_{max} = 29.1°, θ_{min} = 2.6°
h = −7→7
k = −11→11
l = −44→44

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.074
S = 1.10
4061 reflections
230 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
$w = 1/[\sigma^2(F_o^2) + (0.0326P)^2 + 0.8007P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.67 e Å^{-3}
$\Delta\rho_{min}$ = −0.51 e Å^{-3}
Absolute structure: Flack (1983), 1686 Friedel pairs?
Absolute structure parameter: −0.018 (7)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

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

	x	y	z	U_{iso}*/U_{eq}
Br1	0.32101 (6)	0.56744 (4)	1.059826 (8)	0.03817 (9)
S1	0.35196 (13)	0.49266 (9)	0.76858 (2)	0.02854 (14)
N2	0.2692 (4)	0.4064 (3)	0.84952 (6)	0.0204 (4)
C11	0.2064 (4)	0.4764 (3)	0.81524 (7)	0.0196 (5)
C7	0.0668 (4)	0.4192 (3)	0.87900 (7)	0.0198 (5)
H7	−0.0267	0.3190	0.8781	0.024*
N1	−0.0024 (4)	0.5521 (3)	0.81664 (6)	0.0201 (4)
C8	−0.0808 (4)	0.5585 (3)	0.85977 (7)	0.0211 (5)
H8A	−0.2505	0.5387	0.8622	0.025*
H8B	−0.0427	0.6620	0.8723	0.025*
C9	−0.0363 (6)	0.6744 (4)	0.78469 (8)	0.0261 (6)
C1	0.1407 (4)	0.4519 (3)	0.92285 (7)	0.0208 (5)
C2	0.3255 (5)	0.5587 (3)	0.93230 (7)	0.0247 (5)

C10	0.0970 (6)	0.6059 (4)	0.74766 (9)	0.0329 (7)
C3	0.3820 (5)	0.5913 (4)	0.97307 (9)	0.0307 (6)
C5	0.0649 (5)	0.4154 (4)	0.99535 (9)	0.0313 (6)
C6	0.0123 (6)	0.3807 (4)	0.95449 (9)	0.0288 (6)
C4	0.2489 (5)	0.5198 (3)	1.00383 (8)	0.0272 (6)
O3	0.8027 (3)	−0.0585 (2)	0.84464 (5)	0.0197 (3)
O4	0.6388 (3)	0.1887 (2)	0.84329 (6)	0.0238 (4)
C1B	0.6295 (4)	0.0378 (3)	0.84479 (7)	0.0172 (5)
C2B	0.3822 (4)	−0.0442 (3)	0.84594 (7)	0.0186 (5)
O1	0.2089 (3)	0.0602 (2)	0.84707 (6)	0.0279 (4)
O2	0.3598 (3)	−0.1898 (2)	0.84549 (7)	0.0320 (5)
H2	0.405 (6)	0.611 (4)	0.9106 (11)	0.040 (10)*
H5	−0.032 (7)	0.372 (5)	1.0134 (12)	0.051 (11)*
H10B	0.158 (8)	0.694 (5)	0.7302 (12)	0.058 (11)*
H9A	−0.201 (7)	0.684 (4)	0.7791 (9)	0.027 (8)*
H3	0.500 (7)	0.655 (4)	0.9791 (10)	0.037 (9)*
H9B	0.031 (6)	0.780 (4)	0.7948 (9)	0.027 (8)*
H10A	0.009 (7)	0.530 (5)	0.7315 (12)	0.052 (11)*
H6	−0.104 (7)	0.305 (5)	0.9487 (10)	0.045 (10)*
H1O	0.042 (9)	0.012 (5)	0.8512 (14)	0.076 (15)*
H1N	0.361 (7)	0.327 (4)	0.8501 (11)	0.044 (10)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0587 (2)	0.03403 (15)	0.02182 (11)	0.00178 (15)	−0.00718 (13)	−0.00204 (11)
S1	0.0306 (3)	0.0314 (3)	0.0237 (3)	0.0028 (3)	0.0062 (3)	−0.0047 (2)
N2	0.0192 (10)	0.0191 (11)	0.0230 (9)	0.0027 (8)	−0.0002 (8)	−0.0023 (8)
C11	0.0207 (11)	0.0133 (12)	0.0248 (11)	−0.0011 (9)	−0.0004 (9)	−0.0053 (8)
C7	0.0188 (11)	0.0176 (12)	0.0230 (11)	0.0011 (10)	0.0009 (9)	−0.0003 (9)
N1	0.0192 (9)	0.0205 (11)	0.0206 (9)	0.0028 (9)	−0.0001 (7)	−0.0001 (8)
C8	0.0186 (11)	0.0235 (12)	0.0212 (10)	0.0031 (11)	0.0009 (8)	0.0011 (10)
C9	0.0315 (16)	0.0259 (14)	0.0209 (12)	0.0032 (12)	−0.0035 (11)	0.0018 (10)
C1	0.0212 (12)	0.0186 (12)	0.0225 (10)	0.0015 (10)	−0.0018 (9)	0.0009 (9)
C2	0.0248 (12)	0.0240 (12)	0.0254 (11)	−0.0056 (12)	0.0014 (10)	−0.0017 (9)
C10	0.0430 (18)	0.0332 (16)	0.0225 (12)	0.0072 (13)	−0.0009 (12)	−0.0022 (11)
C3	0.0328 (16)	0.0310 (16)	0.0282 (13)	−0.0079 (12)	−0.0028 (11)	−0.0046 (11)
C5	0.0358 (15)	0.0316 (16)	0.0263 (12)	−0.0052 (13)	0.0022 (11)	0.0044 (12)
C6	0.0315 (15)	0.0262 (14)	0.0285 (13)	−0.0081 (12)	−0.0030 (11)	0.0025 (11)
C4	0.0369 (14)	0.0251 (13)	0.0195 (11)	0.0047 (11)	−0.0038 (10)	0.0006 (9)
O3	0.0130 (7)	0.0178 (7)	0.0285 (8)	0.0007 (7)	0.0008 (6)	−0.0009 (7)
O4	0.0174 (9)	0.0172 (8)	0.0368 (9)	−0.0001 (7)	−0.0003 (8)	−0.0004 (7)
C1B	0.0153 (10)	0.0211 (13)	0.0153 (9)	0.0003 (9)	0.0006 (8)	−0.0010 (8)
C2B	0.0153 (11)	0.0214 (13)	0.0191 (10)	0.0004 (9)	−0.0011 (8)	−0.0012 (9)
O1	0.0113 (8)	0.0192 (8)	0.0532 (11)	0.0004 (7)	0.0000 (7)	−0.0015 (9)
O2	0.0170 (9)	0.0183 (9)	0.0606 (13)	−0.0004 (7)	0.0001 (9)	−0.0025 (9)

Geometric parameters (Å, º)

Br1—C4	1.908 (3)	C1—C2	1.396 (4)
S1—C11	1.729 (2)	C2—C3	1.390 (3)
S1—C10	1.840 (3)	C2—H2	0.94 (4)
N2—C11	1.305 (3)	C10—H10B	0.98 (4)
N2—C7	1.491 (3)	C10—H10A	0.96 (4)
N2—H1N	0.83 (4)	C3—C4	1.382 (4)
C11—N1	1.329 (3)	C3—H3	0.87 (4)
C7—C1	1.510 (3)	C5—C4	1.373 (4)
C7—C8	1.549 (3)	C5—C6	1.392 (4)
C7—H7	0.9800	C5—H5	0.88 (4)
N1—C9	1.461 (3)	C6—H6	0.92 (4)
N1—C8	1.472 (3)	O3—C1B	1.257 (3)
C8—H8A	0.9700	O4—C1B	1.248 (3)
C8—H8B	0.9700	C1B—C2B	1.546 (3)
C9—C10	1.527 (4)	C2B—O2	1.208 (3)
C9—H9A	0.95 (4)	C2B—O1	1.300 (3)
C9—H9B	1.00 (3)	O1—H1O	1.03 (5)
C1—C6	1.387 (4)		
C11—S1—C10	89.80 (13)	C2—C1—C7	121.7 (2)
C11—N2—C7	108.2 (2)	C3—C2—C1	120.2 (2)
C11—N2—H1N	122 (2)	C3—C2—H2	121 (2)
C7—N2—H1N	121 (3)	C1—C2—H2	118 (2)
N2—C11—N1	114.6 (2)	C9—C10—S1	106.10 (19)
N2—C11—S1	131.1 (2)	C9—C10—H10B	111 (2)
N1—C11—S1	114.23 (18)	S1—C10—H10B	109 (3)
N2—C7—C1	114.3 (2)	C9—C10—H10A	115 (2)
N2—C7—C8	101.55 (19)	S1—C10—H10A	106 (2)
C1—C7—C8	113.3 (2)	H10B—C10—H10A	110 (3)
N2—C7—H7	109.1	C4—C3—C2	119.0 (3)
C1—C7—H7	109.1	C4—C3—H3	121 (2)
C8—C7—H7	109.1	C2—C3—H3	120 (2)
C11—N1—C9	114.5 (2)	C4—C5—C6	118.7 (3)
C11—N1—C8	108.2 (2)	C4—C5—H5	126 (3)
C9—N1—C8	127.9 (2)	C6—C5—H5	115 (3)
N1—C8—C7	101.46 (19)	C1—C6—C5	120.8 (3)
N1—C8—H8A	111.5	C1—C6—H6	120 (2)
C7—C8—H8A	111.5	C5—C6—H6	119 (2)
N1—C8—H8B	111.5	C5—C4—C3	122.0 (3)
C7—C8—H8B	111.5	C5—C4—Br1	118.7 (2)
H8A—C8—H8B	109.3	C3—C4—Br1	119.3 (2)
N1—C9—C10	104.0 (2)	O4—C1B—O3	126.8 (2)
N1—C9—H9A	108.6 (19)	O4—C1B—C2B	118.5 (2)
C10—C9—H9A	110.9 (18)	O3—C1B—C2B	114.69 (19)
N1—C9—H9B	108.4 (17)	O2—C2B—O1	125.6 (2)
C10—C9—H9B	113.1 (18)	O2—C2B—C1B	121.9 (2)

H9A—C9—H9B	111 (3)	O1—C2B—C1B	112.4 (2)
C6—C1—C2	119.3 (2)	C2B—O1—H1O	115 (3)
C6—C1—C7	118.9 (2)		
C7—N2—C11—N1	6.2 (3)	N2—C7—C1—C2	39.8 (3)
C7—N2—C11—S1	−175.80 (19)	C8—C7—C1—C2	−75.9 (3)
C10—S1—C11—N2	179.2 (3)	C6—C1—C2—C3	0.9 (4)
C10—S1—C11—N1	−2.8 (2)	C7—C1—C2—C3	177.2 (2)
C11—N2—C7—C1	−141.1 (2)	N1—C9—C10—S1	−32.9 (3)
C11—N2—C7—C8	−18.8 (2)	C11—S1—C10—C9	21.4 (2)
N2—C11—N1—C9	159.8 (2)	C1—C2—C3—C4	−1.6 (4)
S1—C11—N1—C9	−18.5 (3)	C2—C1—C6—C5	0.4 (4)
N2—C11—N1—C8	10.3 (3)	C7—C1—C6—C5	−176.0 (3)
S1—C11—N1—C8	−168.00 (17)	C4—C5—C6—C1	−0.9 (5)
C11—N1—C8—C7	−21.0 (3)	C6—C5—C4—C3	0.2 (4)
C9—N1—C8—C7	−165.2 (2)	C6—C5—C4—Br1	180.0 (2)
N2—C7—C8—N1	23.0 (2)	C2—C3—C4—C5	1.1 (4)
C1—C7—C8—N1	146.1 (2)	C2—C3—C4—Br1	−178.7 (2)
C11—N1—C9—C10	33.8 (3)	O4—C1B—C2B—O2	176.5 (2)
C8—N1—C9—C10	176.1 (2)	O3—C1B—C2B—O2	−2.1 (3)
N2—C7—C1—C6	−143.9 (3)	O4—C1B—C2B—O1	−3.0 (3)
C8—C7—C1—C6	100.4 (3)	O3—C1B—C2B—O1	178.4 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*O*···O3^{i}	1.03 (5)	1.48 (5)	2.483 (2)	164 (4)
N2—H1*N*···O4	0.83 (4)	1.95 (4)	2.753 (3)	163 (4)
N2—H1*N*···O1	0.83 (4)	2.37 (4)	2.879 (3)	120 (3)

Symmetry code: (i) *x*−1, *y*, *z*.