organic compounds

L-Histidinium p-toluenesulfonate

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In the title salt, $C_6H_{10}N_3O_2{}^+{\cdot}C_7H_7O_3S^-$, the imidazole ring makes a dihedral angle of 70.93 (12)° with the plane of the toluene ring. In the crystal, the ions are linked via N—H⋯O and weak C—H⋯O hydrogen bonds forming two-dimensional networks lying parallel to (001). These networks are linked via C—H⋯π interactions, forming a three-dimensional structure.

Related literature

For related structures of 4-toluenesulfonate salts, see: Koshima et al. (2004); Biradha & Mahata (2005); Sivakumar et al. (2012). For the structure of L-histidine, see: Madden et al. (1972); Andra et al. (2010).
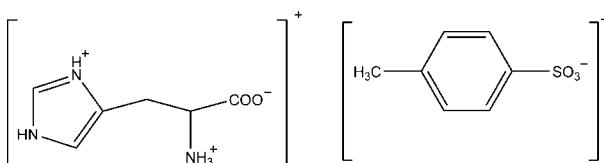
Experimental

Crystal data

$C_6H_{10}N_3O_2{}^+{\cdot}C_7H_7O_3S^-$
$M_r = 327.36$
Orthorhombic, $P2_12_12_1$
$a = 5.2700 (2)$ Å
$b = 7.3691 (3)$ Å
$c = 38.2042 (14)$ Å

$V = 1483.67 (10)$ Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.25$ mm^{-1}
$T = 293$ K
$0.30 \times 0.25 \times 0.20$ mm

Data collection

Bruker SMART APEXII area-detector diffractometer
Absorption correction: multi-scan (SADABS; Bruker, 2008)
$T_{min} = 0.930$, $T_{max} = 0.952$

8400 measured reflections
3638 independent reflections
3533 reflections with $I > 2\sigma(I)$
$R_{int} = 0.022$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.094$
$S = 1.20$
3638 reflections
212 parameters
H atoms treated by a mixture of independent and constrained refinement

$\Delta\rho_{max} = 0.22$ e Å^{-3}
$\Delta\rho_{min} = -0.29$ e Å^{-3}
Absolute structure: Flack (1983), 1479 Friedel pairs
Flack parameter: 0.07 (7)

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

$Cg1$ and $Cg2$ are the centroids the C1–C6 and N1/N2/C8–C10 rings, respectively.

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1⋯O2[i]	0.86	2.00	2.828 (2)	160
N2—H2A⋯O3[ii]	0.86	1.89	2.746 (2)	175
N3—H3B⋯O4[iii]	0.96 (3)	1.80 (3)	2.755 (2)	176 (2)
N3—H3C⋯O4[iv]	0.83 (3)	2.10 (3)	2.896 (2)	161 (2)
N3—H3D⋯O3[i]	0.92 (2)	2.15 (2)	3.000 (2)	153.4 (19)
C8—H8⋯O1[v]	0.93	2.41	2.967 (3)	118
C9—H9⋯O5[vi]	0.93	2.47	3.062 (3)	122
C6—H6⋯$Cg2$	0.93	2.73	3.515 (2)	143
C8—H8⋯$Cg1$[ii]	0.93	2.71	3.394 (2)	131

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

Data collection: APEX2 (Bruker, 2008); cell refinement: SAINT (Bruker, 2008); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 for Windows (Farrugia, 2012); software used to prepare material for publication: SHELXL97 and PLATON (Spek, 2009).

References

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supporting information

ʟ-Histidinium *p*-toluenesulfonate

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S1. Comment

The asymmetric unit of the title compound, Fig. 1, contains an L-histidinium cation and a 4-toluenesulfonate anion. The histidine molecule exists as an histidinium ion due to the protonation at the N atom of the imidazole ring. The 4-toluenesulfonic acid exists as a 4-toluenesulfonate since the proton is transferred to the amino acid.

In the crystal, the imidazole ring (N1/N2/C8-C10) makes a dihedral angle of 70.93 (12)° with the toluene ring (C1-C6).

In the crystal, the ions are linked via N-H⋯O and weak C-H⋯O hydrogen bonds forming two-dimensional networks lying parallel to (001); see Table 1 and Fig. 2. These networks are linked via C-H⋯π interactions forming a three-dimensional structure.

S2. Experimental

L-histidine and 4-toluenesulfonic acid were mixed in an equimolar (1:1) ratio using distilled water as solvent and stirred for 1 h, giving a clear solution. The solution was filtered into a clean beaker and optimally closed and kept at room temperature for slow evaporation. After a period of 10 days, block-like colourless crystals suitable for X-ray diffraction analysis were obtained.

S3. Refinement

The NH_3 H atoms were located in a difference Fourier map and refined freely. The NH H atoms and the C-bound H atoms were positioned geometrically and refined using a riding model: N—H = 0.86 Å, C—H = 0.93 and 0.98 Å for CH(aromatic) and CH(methine) H atoms, respectively, and 0.96 Å for CH_2 and CH_3 H atoms, with $U_{iso}(H) = 1.5U_{eq}(C$-methyl) and $= 1.2U_{eq}(N,C)$ for other H atoms.
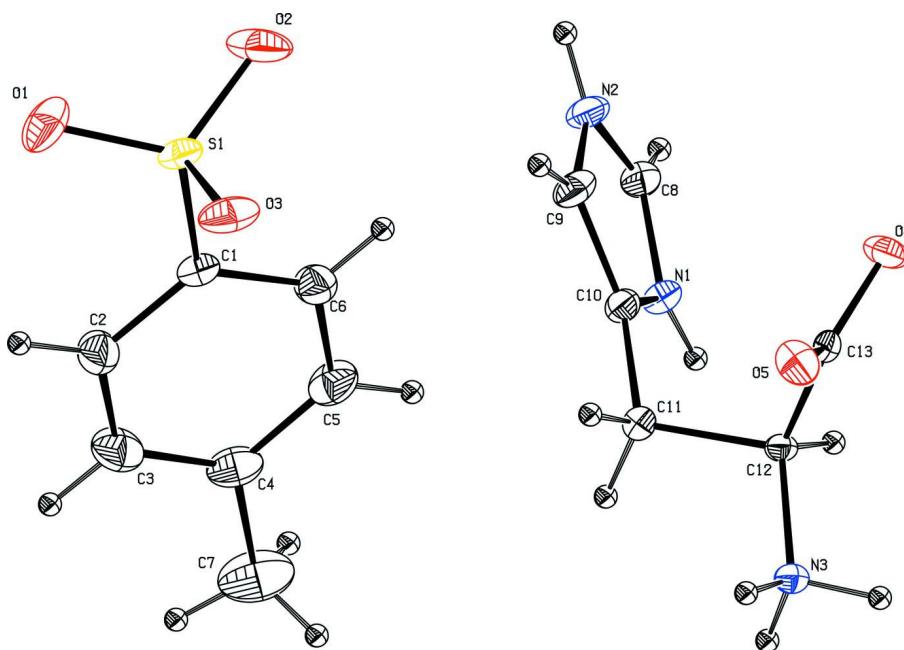
Figure 1

The molecular structure of the title salt, with atom labelling. Displacement ellipsoids are drawn at the 30% probability level.
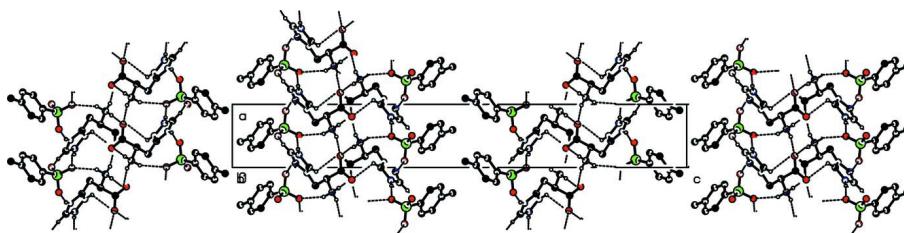
Figure 2

The crystal packing of the title compound viewed along the *b* axis. The hydrogen bonds are shown as dashed lines (see Table 1 for details; H-atoms not involved in hydrogen bonds have been omitted for clarity).

L-**Histidinium** *p*-**toluenesulfonate**

Crystal data
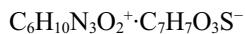
$C_6H_{10}N_3O_2{}^+ \cdot C_7H_7O_3S^-$	$F(000) = 688$
$M_r = 327.36$	$D_x = 1.466$ Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: P 2ac 2ab	Cell parameters from 3638 reflections
$a = 5.2700$ (2) Å	$\theta = 2.1$–$28.3°$
$b = 7.3691$ (3) Å	$\mu = 0.25$ mm^{-1}
$c = 38.2042$ (14) Å	$T = 293$ K
$V = 1483.67$ (10) Å^3	Block, colourless
$Z = 4$	$0.30 \times 0.25 \times 0.20$ mm

Data collection

Bruker SMART APEXII area-detector diffractometer	8400 measured reflections
Radiation source: fine-focus sealed tube	3638 independent reflections
Graphite monochromator	3533 reflections with $I > 2\sigma(I)$
ω and φ scans	$R_{int} = 0.022$
Absorption correction: multi-scan ($SADABS$; Bruker, 2008)	$\theta_{max} = 28.3°$, $\theta_{min} = 2.1°$
	$h = -6 \rightarrow 6$
	$k = -9 \rightarrow 6$
$T_{min} = 0.930$, $T_{max} = 0.952$	$l = -41 \rightarrow 50$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.038$	
$wR(F^2) = 0.094$	$w = 1/[\sigma^2(F_o^2) + (0.0378P)^2 + 0.5138P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.20$	
3638 reflections	$(\Delta/\sigma)_{max} = 0.014$
212 parameters	$\Delta\rho_{max} = 0.22$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.29$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack (1983), 1479 Friedel pairs
Secondary atom site location: difference Fourier map	Absolute structure parameter: 0.07 (7)

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. 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 > 2sigma(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 (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$
C1	0.5686 (4)	0.8856 (3)	0.08354 (5)	0.0267 (4)
C2	0.3546 (5)	0.8904 (3)	0.06249 (6)	0.0378 (5)
H2	0.2447	0.9891	0.0633	0.045*
C3	0.3067 (5)	0.7455 (4)	0.04012 (6)	0.0445 (6)
H3	0.1645	0.7493	0.0257	0.053*
C4	0.4653 (5)	0.5955 (3)	0.03871 (6)	0.0410 (5)
C5	0.6786 (5)	0.5940 (3)	0.05970 (6)	0.0413 (5)
H5	0.7888	0.4956	0.0588	0.050*
C6	0.7307 (4)	0.7383 (3)	0.08214 (6)	0.0352 (5)
H6	0.8747	0.7355	0.0962	0.042*
C7	0.4046 (8)	0.4355 (4)	0.01540 (8)	0.0698 (9)
H7A	0.2604	0.4640	0.0010	0.105*
H7B	0.3667	0.3315	0.0296	0.105*
H7C	0.5479	0.4093	0.0007	0.105*
C8	1.2390 (4)	0.5424 (3)	0.13142 (5)	0.0305 (4)

H8	1.3637	0.5258	0.1145	0.037*
C9	1.0008 (4)	0.6656 (3)	0.17226 (5)	0.0312 (4)
H9	0.9349	0.7496	0.1880	0.037*
C10	0.9162 (4)	0.4935 (2)	0.16686 (5)	0.0240 (4)
C11	0.7122 (4)	0.3892 (2)	0.18479 (5)	0.0242 (4)
H11A	0.6039	0.3330	0.1673	0.029*
H11B	0.6089	0.4719	0.1985	0.029*
C12	0.8209 (3)	0.2411 (2)	0.20905 (4)	0.0190 (3)
H12	0.9473	0.1693	0.1963	0.023*
C13	0.9463 (3)	0.3308 (2)	0.24112 (5)	0.0217 (4)
N1	1.0671 (3)	0.4207 (2)	0.14111 (4)	0.0261 (3)
H1	1.0525	0.3132	0.1326	0.031*
N2	1.2021 (4)	0.6914 (2)	0.15002 (5)	0.0325 (4)
H2A	1.2904	0.7892	0.1484	0.039*
N3	0.6079 (3)	0.1216 (2)	0.22022 (4)	0.0227 (3)
O1	0.4968 (4)	1.2199 (2)	0.10150 (5)	0.0513 (5)
O2	0.8939 (3)	1.0777 (2)	0.11806 (5)	0.0564 (5)
O3	0.5067 (4)	0.9933 (2)	0.14701 (4)	0.0448 (4)
O4	1.1834 (3)	0.3507 (2)	0.23929 (4)	0.0344 (4)
O5	0.8051 (3)	0.3822 (2)	0.26480 (4)	0.0340 (3)
S1	0.62131 (10)	1.05973 (6)	0.114496 (13)	0.02896 (12)
H3D	0.534 (4)	0.064 (3)	0.2015 (6)	0.027 (5)*
H3B	0.673 (5)	0.024 (4)	0.2341 (7)	0.037 (7)*
H3C	0.487 (5)	0.173 (4)	0.2300 (6)	0.036 (7)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0301 (10)	0.0217 (8)	0.0283 (8)	−0.0061 (8)	0.0041 (8)	−0.0026 (7)
C2	0.0372 (12)	0.0342 (10)	0.0421 (11)	0.0033 (9)	−0.0061 (10)	−0.0038 (9)
C3	0.0450 (14)	0.0514 (14)	0.0372 (11)	−0.0084 (12)	−0.0092 (10)	−0.0068 (10)
C4	0.0515 (14)	0.0352 (12)	0.0363 (11)	−0.0120 (10)	0.0078 (10)	−0.0102 (9)
C5	0.0457 (13)	0.0272 (10)	0.0509 (13)	0.0019 (9)	0.0099 (11)	−0.0077 (9)
C6	0.0312 (11)	0.0306 (10)	0.0437 (11)	−0.0002 (9)	−0.0012 (9)	−0.0043 (9)
C7	0.095 (3)	0.0578 (17)	0.0570 (16)	−0.0227 (19)	0.0094 (17)	−0.0293 (14)
C8	0.0280 (10)	0.0273 (9)	0.0361 (10)	−0.0045 (9)	0.0013 (8)	0.0055 (8)
C9	0.0449 (12)	0.0186 (8)	0.0302 (10)	−0.0051 (8)	−0.0014 (9)	−0.0016 (7)
C10	0.0275 (9)	0.0202 (8)	0.0244 (8)	−0.0024 (7)	−0.0016 (8)	0.0021 (6)
C11	0.0245 (9)	0.0210 (8)	0.0273 (8)	−0.0011 (7)	−0.0025 (7)	0.0032 (7)
C12	0.0161 (8)	0.0176 (7)	0.0234 (8)	−0.0030 (6)	0.0006 (6)	0.0000 (6)
C13	0.0214 (9)	0.0139 (7)	0.0300 (9)	0.0024 (6)	−0.0055 (7)	0.0004 (6)
N1	0.0307 (9)	0.0176 (7)	0.0301 (7)	−0.0037 (6)	0.0013 (6)	0.0002 (6)
N2	0.0392 (10)	0.0221 (8)	0.0362 (9)	−0.0119 (7)	−0.0043 (8)	0.0049 (7)
N3	0.0188 (7)	0.0202 (7)	0.0290 (8)	−0.0031 (7)	−0.0001 (7)	0.0008 (6)
O1	0.0761 (14)	0.0229 (7)	0.0550 (10)	0.0084 (8)	−0.0015 (10)	−0.0024 (7)
O2	0.0336 (9)	0.0439 (9)	0.0917 (14)	−0.0153 (8)	0.0063 (9)	−0.0324 (10)
O3	0.0614 (11)	0.0379 (8)	0.0350 (8)	−0.0244 (8)	0.0022 (8)	−0.0085 (6)
O4	0.0192 (7)	0.0312 (7)	0.0529 (9)	−0.0031 (6)	−0.0052 (6)	−0.0140 (6)

O5	0.0322 (8)	0.0386 (8)	0.0312 (7)	0.0045 (6)	−0.0018 (6)	−0.0095 (6)
S1	0.0314 (3)	0.0191 (2)	0.0364 (2)	−0.00777 (18)	0.0038 (2)	−0.00459 (18)

Geometric parameters (Å, º)

C1—C6	1.382 (3)	C9—H9	0.9300
C1—C2	1.386 (3)	C10—N1	1.374 (2)
C1—S1	1.7671 (19)	C10—C11	1.488 (3)
C2—C3	1.391 (3)	C11—C12	1.542 (2)
C2—H2	0.9300	C11—H11A	0.9700
C3—C4	1.387 (4)	C11—H11B	0.9700
C3—H3	0.9300	C12—N3	1.490 (2)
C4—C5	1.381 (4)	C12—C13	1.541 (2)
C4—C7	1.512 (3)	C12—H12	0.9800
C5—C6	1.393 (3)	C13—O5	1.231 (2)
C5—H5	0.9300	C13—O4	1.260 (2)
C6—H6	0.9300	N1—H1	0.8600
C7—H7A	0.9600	N2—H2A	0.8600
C7—H7B	0.9600	N3—H3D	0.92 (2)
C7—H7C	0.9600	N3—H3B	0.96 (3)
C8—N2	1.322 (3)	N3—H3C	0.83 (3)
C8—N1	1.327 (2)	O1—S1	1.4391 (17)
C8—H8	0.9300	O2—S1	1.4490 (18)
C9—C10	1.360 (3)	O3—S1	1.4652 (17)
C9—N2	1.372 (3)		
C6—C1—C2	120.04 (18)	C10—C11—C12	111.95 (15)
C6—C1—S1	119.94 (16)	C10—C11—H11A	109.2
C2—C1—S1	119.85 (16)	C12—C11—H11A	109.2
C1—C2—C3	119.0 (2)	C10—C11—H11B	109.2
C1—C2—H2	120.5	C12—C11—H11B	109.2
C3—C2—H2	120.5	H11A—C11—H11B	107.9
C4—C3—C2	121.8 (2)	N3—C12—C13	110.43 (14)
C4—C3—H3	119.1	N3—C12—C11	108.10 (14)
C2—C3—H3	119.1	C13—C12—C11	109.47 (14)
C5—C4—C3	118.3 (2)	N3—C12—H12	109.6
C5—C4—C7	120.5 (2)	C13—C12—H12	109.6
C3—C4—C7	121.1 (3)	C11—C12—H12	109.6
C4—C5—C6	120.8 (2)	O5—C13—O4	127.17 (18)
C4—C5—H5	119.6	O5—C13—C12	117.22 (16)
C6—C5—H5	119.6	O4—C13—C12	115.52 (17)
C1—C6—C5	120.1 (2)	C8—N1—C10	109.33 (16)
C1—C6—H6	119.9	C8—N1—H1	125.3
C5—C6—H6	119.9	C10—N1—H1	125.3
C4—C7—H7A	109.5	C8—N2—C9	109.36 (17)
C4—C7—H7B	109.5	C8—N2—H2A	125.3
H7A—C7—H7B	109.5	C9—N2—H2A	125.3
C4—C7—H7C	109.5	C12—N3—H3D	111.8 (14)

H7A—C7—H7C	109.5	C12—N3—H3B	109.6 (15)
H7B—C7—H7C	109.5	H3D—N3—H3B	104 (2)
N2—C8—N1	108.10 (18)	C12—N3—H3C	115.8 (18)
N2—C8—H8	125.9	H3D—N3—H3C	104 (2)
N1—C8—H8	125.9	H3B—N3—H3C	112 (2)
C10—C9—N2	106.77 (19)	O1—S1—O2	114.19 (12)
C10—C9—H9	126.6	O1—S1—O3	112.24 (12)
N2—C9—H9	126.6	O2—S1—O3	111.07 (12)
C9—C10—N1	106.42 (17)	O1—S1—C1	107.04 (10)
C9—C10—C11	130.43 (19)	O2—S1—C1	106.56 (10)
N1—C10—C11	123.10 (16)	O3—S1—C1	105.06 (9)
C6—C1—C2—C3	0.0 (3)	N3—C12—C13—O5	−39.4 (2)
S1—C1—C2—C3	−175.30 (18)	C11—C12—C13—O5	79.5 (2)
C1—C2—C3—C4	0.9 (4)	N3—C12—C13—O4	143.72 (16)
C2—C3—C4—C5	−1.4 (4)	C11—C12—C13—O4	−97.38 (19)
C2—C3—C4—C7	177.3 (2)	N2—C8—N1—C10	−0.4 (2)
C3—C4—C5—C6	1.0 (4)	C9—C10—N1—C8	0.7 (2)
C7—C4—C5—C6	−177.7 (2)	C11—C10—N1—C8	−176.84 (17)
C2—C1—C6—C5	−0.3 (3)	N1—C8—N2—C9	−0.1 (2)
S1—C1—C6—C5	174.95 (17)	C10—C9—N2—C8	0.6 (2)
C4—C5—C6—C1	−0.2 (3)	C6—C1—S1—O1	157.65 (17)
N2—C9—C10—N1	−0.8 (2)	C2—C1—S1—O1	−27.0 (2)
N2—C9—C10—C11	176.54 (19)	C6—C1—S1—O2	35.1 (2)
C9—C10—C11—C12	−106.9 (2)	C2—C1—S1—O2	−149.61 (18)
N1—C10—C11—C12	70.1 (2)	C6—C1—S1—O3	−82.85 (19)
C10—C11—C12—N3	−169.02 (15)	C2—C1—S1—O3	92.46 (19)
C10—C11—C12—C13	70.64 (19)		

Hydrogen-bond geometry (Å, º)

Cg1 and Cg2 are the centroids the C1–C6 and N1/N2/C8–C10 rings, respectively.

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O2[i]	0.86	2.00	2.828 (2)	160
N2—H2A···O3[ii]	0.86	1.89	2.746 (2)	175
N3—H3B···O4[iii]	0.96 (3)	1.80 (3)	2.755 (2)	176 (2)
N3—H3C···O4[iv]	0.83 (3)	2.10 (3)	2.896 (2)	161 (2)
N3—H3D···O3[i]	0.92 (2)	2.15 (2)	3.000 (2)	153.4 (19)
C8—H8···O1[v]	0.93	2.41	2.967 (3)	118
C9—H9···O5[vi]	0.93	2.47	3.062 (3)	122
C6—H6···Cg2	0.93	2.73	3.515 (2)	143
C8—H8···Cg1[ii]	0.93	2.71	3.394 (2)	131

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