organic compounds

Bis(2-aminothiazolium) succinate succinic acid

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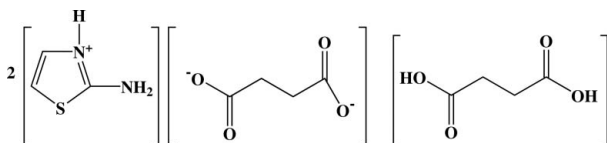Correspondence e-mail: hkfun@usm.my

In the title compound, $2C_3H_5N_2S^+ \cdot C_4H_4O_4^{2-} \cdot C_4H_6O_4$, the thiazolium ring is almost planar, with the maximum deviation from planarity being 0.0056 (8) Å for the C atom carrying the amine substituent. The N atom of the 2-aminothiazole molecule is protonated. Both the anion and the acid lie across inversion centres. The crystal packing is consolidated by intermolecular O—H···O, N—H···O and C—H···O hydrogen bonds. Molecules are stacked down the b axis.

Related literature

For the structure of 2-aminothiazole, see: Caranoni & Reboul (1982). For applications of 2-aminothiazole, see: Saarnivaara & Matilla (1974); Windholz (2001). For the structure of succinic acid, see: Gopalan *et al.* (2000); Leviel *et al.* (1981). For applications of succinic acid, see: Sauer *et al.* (2008); Song & Lee (2006); Zeikus *et al.* (1999). For the stability of the temperature controller used in the data collection, see: Cosier & Glazer (1986).

Experimental

Crystal data

$2C_3H_5N_2S^+ \cdot C_4H_4O_4^{2-} \cdot C_4H_6O_4$
M_r = 436.46
Monoclinic, $P2_1/n$
a = 10.1680 (2) Å
b = 5.1012 (1) Å
c = 18.3850 (4) Å
β = 105.961 (1)°
V = 916.85 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.34 mm^{-1}
T = 100 K
$0.58 \times 0.42 \times 0.32$ mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.826, T_{max} = 0.897
16689 measured reflections
3691 independent reflections
3442 reflections with $I > 2\sigma(I)$
R_{int} = 0.022

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.027
$wR(F^2)$ = 0.077
S = 1.04
3691 reflections
167 parameters
All H-atom parameters refined
$\Delta\rho_{max}$ = 0.45 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H1N2···O1[i]	0.868 (15)	1.974 (15)	2.8156 (9)	163.0 (14)
N2—H2N2···O1[ii]	0.889 (13)	1.959 (13)	2.8297 (9)	165.7 (13)
N1—H1N1···O2[i]	0.865 (14)	1.823 (14)	2.6868 (8)	176.2 (15)
O3—H1O3···O2[ii]	0.888 (19)	1.696 (19)	2.5820 (8)	176.5 (19)
C1—H1···O4[iii]	0.985 (13)	2.431 (14)	3.3086 (10)	148.2 (12)

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

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ2582).

References

Bruker (2005). *APEX2, SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Caranoni, C. & Reboul, J. P. (1982). *Acta Cryst.* B**38**, 1255–1259.
Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* **19**, 105–107.
Gopalan, R. S., Kumaradhas, P., Kulkarani, G. U. & Rao, C. N. R. (2000). *J. Mol. Struct.* **521**, 97–106.
Leviel, J.-L., Auvert, G. & Savariault, J.-M. (1981). *Acta Cryst.* B**37**, 2185–2189.
Saarnivaara, L. & Matilla, K. J. (1974). *Psychopharmacology (Berl)*, **35**, 221–236.
Sauer, M., Porro, D., Mattanovich, D. & Branduaradi, P. (2008). *Trends Biotechnol.* **26**, 100–108.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Song, H. & Lee, S. Y. (2006). *Enzyme Microb. Technol.* **39**, 352–361.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Windholz, M. (2001). *The Merck Index*, 13th ed. Boca Raton, USA: Merck & Co. Inc.
Zeikus, J. G., Jain, M. K. & Elankovan, P. (1999). *Appl. Microbiol. Biotechnol.* **51**, 545–552.

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supporting information

Bis(2-aminothiazolium) succinate succinic acid

Hoong-Kun Fun, Jain John, Samuel Robinson Jebas and T. Balasubramanian

S1. Comment

2-Aminothiazole derivatives have shown heribicidal, anti-inflammatory, anti-microbial and antiparasitic activities (Saarnivaara & Matilla, 1974). 2-Aminothiazole is listed as a thyroid inhibitor (Windholz, 2001). The orthorhombic form of 2-amino-1,3-thiazole has been reported (Caranoni & Reboul, 1982). Succinic acid is a dicarboxylic acid and is a precursor for many chemicals of industrial importance (Zeikus *et al.*, 1999; Song & Lee, 2006). Succinic acid derivatives are mostly used in chemicals, food and pharmaceuticals (Sauer *et al.*, 2008). The crystal structure of succinic acid has been reported (Gopalan *et al.*, 2000; Leviel *et al.* 1981). Due to all these important properties, the title compound (I) has been synthesized and is reported here.

The asymmetric unit of (I) (Fig. 1) contains one molecule of protonated 2-aminothiazole, a half molecule of succinate and a half molecule of succinic acid. The anion and the acid lie across different inversion centres [symmetry codes (i) -x + 1, -y + 2, -z and (ii) -x + 2, -y + 2, -z respectively]. The thiazolium ring is planar with the maximum deviation from planarity being 0.0056 (8)Å for atom C3. The ring nitrogen of the 2-aminothiazole molecule is protonated thereby leading to a widening of the corresponding internal angle (C2–N1–C3) of the thiazolium ring to 113.99 (6)° [which is 109.4 (5)° in the unprotonated form of 2-aminothiazole] and an increase in the bond lengths of N1–C3 to 1.334 (9)Å and N1–C2 to 1.387 (9)Å [which are 1.298 (6)Å and 1.375 (6)Å respectively in its uncomplexed form] (Caranoni & Reboul, 1982). An increase in the C1–S1–C3 bond angle to 90.47 (3)° [which is 88.6 (3)° in the unprotonated form] and a decrease in the S1–C3–N1 bond angle to 111.38 (5)° [which is 114.9 (5)° in the uncomplexed form of 2-aminothiazole] (Caranoni & Reboul, 1982) are also observed.

The bond lengths and bond angles of the succinate and succinic acid are found to have normal values (Gopalan *et al.*, 2000; Leviel & Auvert, 1981). The crystal packing is consolidated by O—H⋯O, N—H⋯O and C—H⋯O intermolecular hydrogen bonds (Table 1) together with intermolecular [O—O^i = 2.5820 (8) Å; O—N^{ii-iii} = 2.6868 (8) to 2.8297 (9) Å, short contacts [symmetry code: (i) x,-1 + y,z; (ii) 3/2 - x,1/2 + y,1/2 - z; (iii) x,1 + y,z]. Molecules are stacked down the *b* axis(Fig.2).

S2. Experimental

2- Aminothiazole (0.100 g, 1 mmol) and succinic acid (0.118 g, 1 mmol) were dissolved in ethanol (25 ml) in a 1:1 molar ratio. The clear brown solution obtained was refluxed for 6 h at a temperature of 323 K. Brown coloured crystals were harvested after two weeks on slow evaporation of the solvent.

S3. Refinement

All the hydrogen atoms were located from the Fourier map and were allowed to refine freely with isotropic displacement parameters.
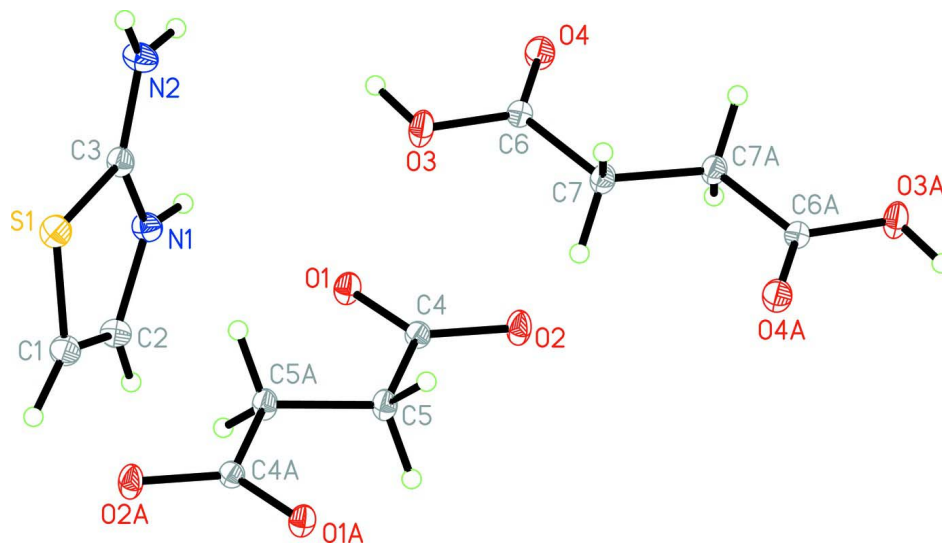
Figure 1

The molecular structure of the title compound, showing 50% probability displacement ellipsoids and the atom numbering scheme. [symmetry operators used to generate equivalent atoms are (i) -*x* + 1, -*y* + 2, -*z* and (ii) -*x* + 2, -*y* + 2, -*z* for the anion and acid respectively].
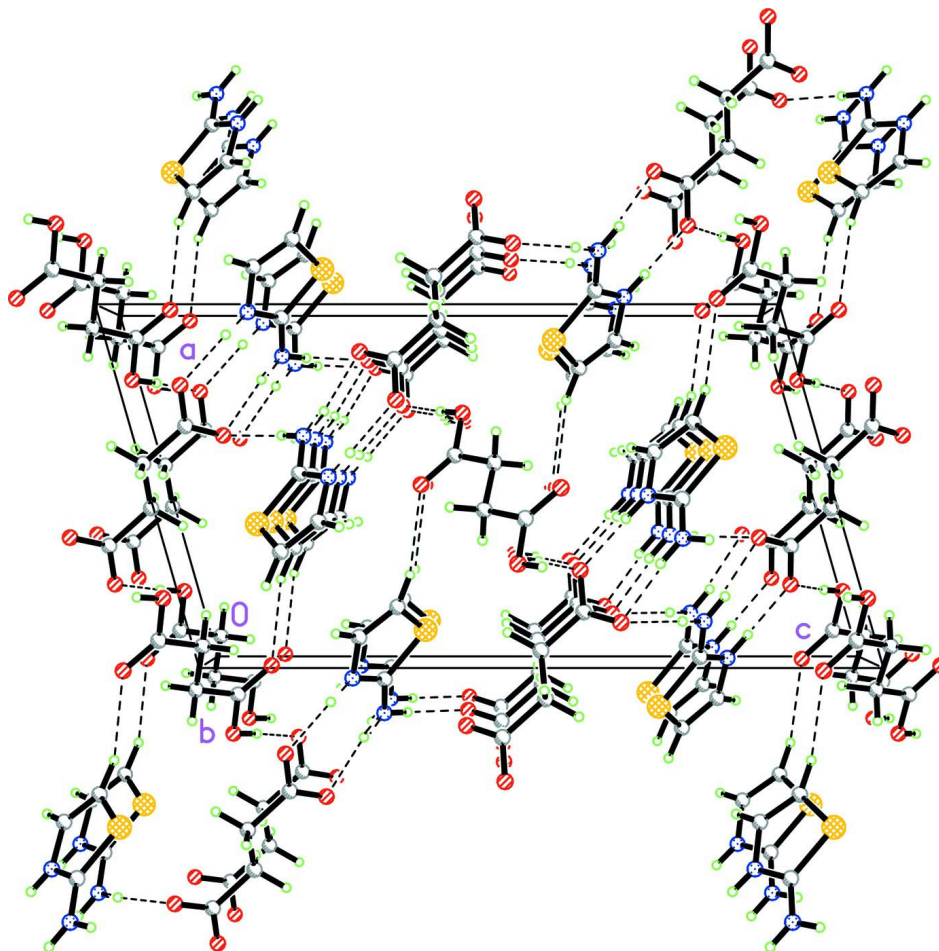
Figure 2
The crystal packing of the title compound, viewed along the *b* axis. Dashed lines indicate the hydrogen bonding.

Bis(2-aminothiazolium) succinate succinic acid solvate

Crystal data

$2C_3H_5N_2S^+ \cdot C_4H_4O_4{}^{2-} \cdot C_4H_6O_4$	$F(000) = 456$
$M_r = 436.46$	$D_x = 1.581$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 9994 reflections
$a = 10.1680$ (2) Å	$\theta = 2.3–40.1°$
$b = 5.1012$ (1) Å	$\mu = 0.34$ mm^{-1}
$c = 18.3850$ (4) Å	$T = 100$ K
$\beta = 105.961$ (1)°	Block, yellow
$V = 916.85$ (3) Å^3	$0.58 \times 0.42 \times 0.32$ mm
$Z = 2$	

Data collection

Bruker SMART APEXII CCD area-detector diffractometer	Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
Radiation source: fine-focus sealed tube	$T_{min} = 0.826$, $T_{max} = 0.897$
Graphite monochromator	16689 measured reflections
φ and ω scans	3691 independent reflections

3442 reflections with $I > 2\sigma(I)$

$R_{int} = 0.022$

$\theta_{max} = 34.0°$, $\theta_{min} = 2.1°$

$h = -16\rightarrow16$

$k = -7\rightarrow7$

$l = -28\rightarrow24$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.027$

$wR(F^2) = 0.077$

$S = 1.04$

3691 reflections

167 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: difference Fourier map

All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0423P)^2 + 0.2556P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.45$ e Å^{-3}

$\Delta\rho_{min} = -0.35$ e Å^{-3}

Special details

Experimental. The crystal was placed in the cold stream of an Oxford Cyrosystems Cobra open-flow nitrogen cryostat (Cosier & Glazer, 1986) operating at 100.0 (1) K.

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.

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 $F^2 > \sigma(F^2)$ 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}
S1	0.398521 (18)	0.38496 (4)	0.154349 (10)	0.01603 (6)
O1	0.64045 (5)	0.89655 (11)	0.12963 (3)	0.01367 (10)
O2	0.77343 (5)	1.19344 (12)	0.09559 (3)	0.01562 (10)
O3	0.80012 (6)	0.57645 (12)	0.00894 (3)	0.01703 (11)
O4	0.99583 (6)	0.66022 (12)	0.09808 (3)	0.01646 (11)
N1	0.52407 (6)	0.60443 (12)	0.27794 (3)	0.01361 (11)
N2	0.63526 (6)	0.22575 (14)	0.25269 (4)	0.01565 (12)
C1	0.32820 (7)	0.66562 (16)	0.18253 (4)	0.01749 (13)
C2	0.40776 (7)	0.75502 (15)	0.24905 (4)	0.01599 (13)
C3	0.53433 (7)	0.39842 (14)	0.23509 (4)	0.01261 (12)
C4	0.66461 (6)	1.05440 (14)	0.08264 (4)	0.01101 (11)
C5	0.56100 (7)	1.09079 (14)	0.00653 (4)	0.01307 (12)
C6	0.91584 (7)	0.70771 (13)	0.03682 (4)	0.01173 (11)
C7	0.93722 (7)	0.91684 (14)	−0.01673 (4)	0.01291 (12)
H1	0.2400 (13)	0.731 (3)	0.1506 (7)	0.027 (3)*
H2	0.3948 (13)	0.900 (2)	0.2779 (7)	0.023 (3)*
H7A	0.8557 (13)	1.025 (3)	−0.0314 (7)	0.023 (3)*
H7B	0.9449 (13)	0.826 (3)	−0.0630 (7)	0.025 (3)*
H1N2	0.7022 (15)	0.248 (3)	0.2933 (8)	0.035 (4)*
H2N2	0.6384 (13)	0.100 (3)	0.2197 (7)	0.025 (3)*

H1C5	0.6093 (14)	1.070 (3)	−0.0333 (8)	0.030 (3)*
H2C5	0.5330 (13)	1.280 (3)	0.0047 (8)	0.030 (3)*
H1N1	0.5877 (14)	0.640 (3)	0.3188 (8)	0.031 (3)*
H1O3	0.7940 (17)	0.447 (4)	0.0401 (9)	0.052 (5)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.01505 (8)	0.01672 (9)	0.01227 (8)	−0.00239 (5)	−0.00303 (6)	0.00025 (5)
O1	0.0141 (2)	0.0152 (2)	0.0103 (2)	−0.00308 (17)	0.00095 (16)	0.00264 (16)
O2	0.0127 (2)	0.0175 (2)	0.0136 (2)	−0.00582 (18)	−0.00159 (17)	0.00353 (18)
O3	0.0150 (2)	0.0181 (3)	0.0151 (2)	−0.00693 (18)	−0.00061 (18)	0.00485 (19)
O4	0.0145 (2)	0.0178 (2)	0.0146 (2)	−0.00236 (18)	−0.00011 (18)	0.00380 (19)
N1	0.0128 (2)	0.0147 (3)	0.0116 (2)	0.00017 (19)	0.00047 (19)	−0.00062 (19)
N2	0.0141 (2)	0.0176 (3)	0.0128 (2)	0.0022 (2)	−0.0003 (2)	−0.0030 (2)
C1	0.0137 (3)	0.0171 (3)	0.0189 (3)	−0.0001 (2)	−0.0001 (2)	0.0044 (3)
C2	0.0141 (3)	0.0152 (3)	0.0179 (3)	0.0014 (2)	0.0031 (2)	0.0022 (2)
C3	0.0119 (3)	0.0143 (3)	0.0102 (2)	−0.0016 (2)	0.0008 (2)	0.0004 (2)
C4	0.0106 (2)	0.0116 (3)	0.0097 (2)	−0.0009 (2)	0.00098 (19)	0.0002 (2)
C5	0.0115 (2)	0.0153 (3)	0.0101 (2)	−0.0035 (2)	−0.0009 (2)	0.0027 (2)
C6	0.0113 (2)	0.0111 (3)	0.0127 (3)	−0.0006 (2)	0.0032 (2)	0.0002 (2)
C7	0.0129 (3)	0.0129 (3)	0.0122 (3)	−0.0022 (2)	0.0023 (2)	0.0018 (2)

Geometric parameters (Å, º)

S1—C3	1.7285 (7)	N2—H2N2	0.888 (13)
S1—C1	1.7416 (9)	C1—C2	1.3468 (11)
O1—C4	1.2538 (8)	C1—H1	0.986 (13)
O2—C4	1.2802 (8)	C2—H2	0.941 (13)
O3—C6	1.3281 (8)	C4—C5	1.5139 (9)
O3—H1O3	0.887 (18)	C5—C5^i	1.5135 (14)
O4—C6	1.2185 (8)	C5—H1C5	0.993 (14)
N1—C3	1.3346 (9)	C5—H2C5	1.003 (14)
N1—C2	1.3877 (9)	C6—C7	1.5075 (10)
N1—H1N1	0.864 (14)	C7—C7^{ii}	1.5153 (14)
N2—C3	1.3233 (9)	C7—H7A	0.970 (13)
N2—H1N2	0.868 (15)	C7—H7B	0.989 (13)
C3—S1—C1	90.47 (3)	O1—C4—C5	119.82 (6)
C6—O3—H1O3	109.7 (10)	O2—C4—C5	116.75 (6)
C3—N1—C2	113.99 (6)	C5^i—C5—C4	113.78 (7)
C3—N1—H1N1	121.0 (9)	C5^i—C5—H1C5	111.6 (8)
C2—N1—H1N1	125.0 (9)	C4—C5—H1C5	108.0 (8)
C3—N2—H1N2	119.6 (10)	C5^i—C5—H2C5	111.7 (8)
C3—N2—H2N2	118.9 (8)	C4—C5—H2C5	105.5 (8)
H1N2—N2—H2N2	121.0 (13)	H1C5—C5—H2C5	105.7 (11)
C2—C1—S1	110.81 (6)	O4—C6—O3	123.50 (6)
C2—C1—H1	130.3 (8)	O4—C6—C7	124.39 (6)

S1—C1—H1	118.9 (8)	O3—C6—C7	112.10 (6)
C1—C2—N1	113.33 (7)	C6—C7—C7ⁱⁱ	112.82 (7)
C1—C2—H2	129.5 (8)	C6—C7—H7A	108.6 (7)
N1—C2—H2	117.2 (8)	C7ⁱⁱ—C7—H7A	110.8 (8)
N2—C3—N1	124.12 (6)	C6—C7—H7B	106.9 (8)
N2—C3—S1	124.49 (5)	C7ⁱⁱ—C7—H7B	110.7 (7)
N1—C3—S1	111.38 (5)	H7A—C7—H7B	106.8 (10)
O1—C4—O2	123.42 (6)		
C3—S1—C1—C2	0.33 (6)	C1—S1—C3—N1	−0.78 (6)
S1—C1—C2—N1	0.18 (9)	O1—C4—C5—C5ⁱ	−4.29 (11)
C3—N1—C2—C1	−0.80 (9)	O2—C4—C5—C5ⁱ	176.67 (8)
C2—N1—C3—N2	−178.46 (7)	O4—C6—C7—C7ⁱⁱ	−5.84 (12)
C2—N1—C3—S1	1.04 (8)	O3—C6—C7—C7ⁱⁱ	175.31 (7)
C1—S1—C3—N2	178.72 (7)		

Symmetry codes: (i) −*x*+1, −*y*+2, −*z*; (ii) −*x*+2, −*y*+2, −*z*.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H1*N*2···O1ⁱⁱⁱ	0.868 (15)	1.974 (15)	2.8156 (9)	163.0 (14)
N2—H2*N*2···O1ⁱᵛ	0.889 (14)	1.959 (13)	2.8297 (9)	165.7 (13)
N1—H1*N*1···O2ⁱⁱⁱ	0.865 (14)	1.823 (14)	2.6868 (8)	176.2 (15)
O3—H1*O*3···O2ⁱᵛ	0.888 (19)	1.696 (19)	2.5820 (8)	176.5 (19)
C1—H1···O4ᵛ	0.985 (13)	2.431 (14)	3.3086 (10)	148.2 (12)

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