Crystal structure of 2-amino-4,6-dimethoxypyrimidinium thiophene-2-carboxylate

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In the title salt, $C_6H_{10}N_3O_2^+ \cdot C_5H_3O_2S^-$, the 2-amino-4,6-dimethoxypyrimidinium cation interacts with the carboxylate group of the thiophene-2-carboxylate anion through a pair of N—H···O hydrogen bonds, forming an $R_2^2(8)$ ring motif. These motifs are centrosymmetrically paired via N—H···O hydrogen bonds, forming a complementary DDAA array. The separate DDAA arrays are linked by π–π stacking interactions between the pyrimidine rings, as well as by a number of weak C—H···O and N—H···O interactions. In the anion, the dihedral angle between the ring plane and the CO_2 group is 11.60 (3)°. In the cation, the C atoms of methoxy groups deviate from the ring plane by 0.433 (10) Å.

1. Related literature

For the role played by non-covalent interactions in molecular recognition porcesses, see: Desiraju (1989). For amino-pryimidine–carboxylate interactions in protein–nucleic acid recognition and protein–drug binding inteactions, see: Hunt et al. (1980); Alkorta & Elguero (2003). For 1:1 salts between 2-aminopyrimidine and mono- and dicarboxylic acids, see: Etter & Adsmond (1990). For self-assembly of 2-aminopyrimidine compounds, see: Scheinbeim & Schempp (1976). For carboxylic acid and 2-amino heterocyclic ring system synthons, see: Lynch & Jones (2004). For crystal structures of related salts, see: Ebenezer et al. (2012); Jennifer & Muthiah (2014). DDAA

arrays have been observed in trimethoprim hydrogen glutarate (Robert et al., 2001), trimethoprim formate (Umadevi et al., 2002), trimethoprim-m-chlorobenzoate (Raj et al., 2003), pyrimethaminium 3,5-dinitrobenzoate (Subashini et al., 2007) and 2-amino-4,6-dimethoxypyrimidinum-salicylate (Thanigaimani et al., 2007).
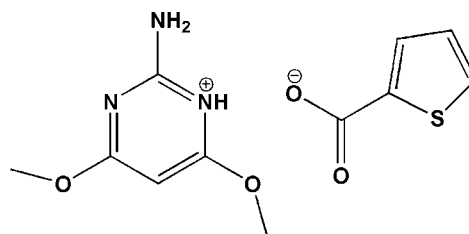
2. Experimental

2.1. Crystal data

$C_6H_{10}N_3O_2^+ \cdot C_5H_3O_2S^-$
$M_r = 283.30$
Monoclinic, $P2_1/n$
$a = 6.7335 (3)$ Å
$b = 7.6307 (4)$ Å
$c = 25.0638 (10)$ Å
$\beta = 93.928 (4)°$

$V = 1284.78 (10)$ Å^3
$Z = 4$
Mo Kα radiation
$\mu = 0.27$ mm^{-1}
$T = 173$ K
$0.32 \times 0.28 \times 0.14$ mm

2.2. Data collection

Agilent Eos Gemini diffractometer
Absorption correction: multi-scan (CrysAlis RED; Agilent, 2012)
$T_{min} = 0.789$, $T_{max} = 1.000$

8844 measured reflections
4245 independent reflections
3071 reflections with $I > 2\sigma(I)$
$R_{int} = 0.028$

2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.062$
$wR(F^2) = 0.186$
$S = 1.05$
4245 reflections

174 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.79$ e Å^{-3}
$\Delta\rho_{min} = -0.55$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O2A[i]	0.88	1.76	2.637 (2)	175
N3—H3A···O1A[ii]	0.88	2.04	2.826 (2)	148
N3—H3B···O1A[i]	0.88	1.92	2.798 (2)	173
C6—H6B···O1[iii]	0.98	2.52	3.434 (3)	155
C1A—H1A···O1[iv]	0.95	2.60	3.365 (3)	138
C1A—H1A···O2A[v]	0.95	2.60	3.383 (3)	140

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

Data collection: CrysAlis PRO (Agilent, 2012); cell refinement: CrysAlis PRO; data reduction: CrysAlis RED (Agilent, 2012); program(s) used to solve structure: SUPERFLIP (Palatinus & Chapuis, 2007; Palatinus & van der Lee, 2008; Palatinus et al., 2012); program(s) used to refine structure: SHELXL2014 (Sheldrick, 2015); molecular graphics: OLEX2 (Dolomanov et al., 2009); software used to prepare material for publication: OLEX2.

data reports

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supporting information

Crystal structure of 2-amino-4,6-dimethoxypyrimidinium thiophene-2-carboxylate

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S1. Structural commentary

The asymmetric unit of $C_6H_{10}N_3O_2^+$ $C_5H_3O_2S^-$, (I), contains one 2-amino-4,6-dimethoxypyrimidinium cation and one thiophene-2-carboxylate anion (Fig 1). Protonation of the cation occurs at N1, providing a C1/N1/C2 angle of 119.39 (16)° compared to the C1/N2/C4 angle (115.99 (16)°) of the unprotonated N2 atom. The carboxylate group of the thiophene-2-carboxylate anion interacts with the protonated atom N1 and the 2-amino group of the pyrimidine moiety through a pair of N—H⋯O hydrogen bonds, forming an eight membered $R_2^2(8)$ ring motif. These motifs are centrosymmetrically paired via N—H⋯O hydrogen bonds to produce a DDAA (D = donor in hydrogen bonds, A = acceptor in hydrogen bonds) array of quadruple hydrogen bonds represented by the graph-set notation $R_2^2(8)$, $R_2^4(8)$ and $R_2^2(8)$ (Fig. 2). This type of array has also been identified in trimethoprim hydrogen glutarate (Robert *et al.*, 2001), trimethoprim formate (Umadevi *et al.*, 2002), trimethoprim- m-chlorobenzoate (Raj *et al.*, 2003), pyrimethaminium 3,5-dinitrobenzoate (Subashini *et al.*, 2007) and 2-amino-4,6-dimethoxypyrimidinum-salicylate (Thanigaimani *et al.*, 2007). An infinite number of several such quadruple arrays are interconnected and stabilized by π—π stacking interactions between the pyrimidine ring of one array with a neighbouring array, with an observed interplanar distance of 3.356 Å, a centroid (Cg1)-to-centroid (Cg1) distance of 3.4689 (12) Å (where Cg1 equals the centroid of the ring N1/C1/N2/C2/C3/C4, Fig 3) and slip angle (the angle between the centroid vector and the normal to the plane) of 14.68°, which are typical aromatic stacking values (Hunter, 1994). In addition, a number of weak C—H⋯O and N—H⋯O intermolecular interactions are also observed which contribute to crystal packing stability (Table 2).

S2. Synthesis and crystallization

A hot methanolic solution of 2-amino-4,6-dimethoxy pyrimidine (38 mg, Aldrich) and thiophene-2-carboxylic acid (32 mg, Aldrich) was warmed for half an hour over a water bath. The mixture was cooled slowly and kept at room temperature. After a few days colourless crystals were obtained.

S3. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. All of the H atoms were placed in their calculated positions andthen refined using the riding model with atom—H lengths of 0.95Å (CH), 0.98Å (CH_3)or 0.88Å (NH, NH_2). Isotropic displacement parameters for these atoms were set to 1.2 (CH, NH, NH_2) or 1.5 (CH_3) times Ueq of the parent atom. Idealised Me refined as rotating groups.
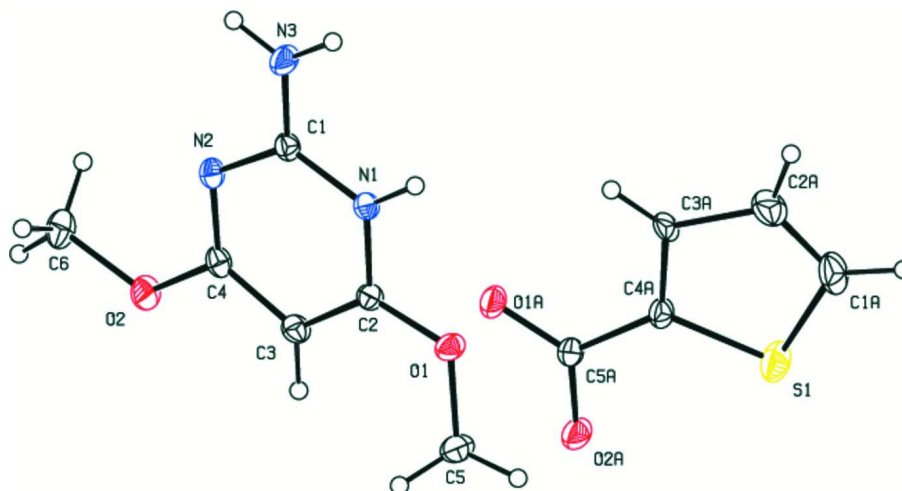
Figure 1

The asymmetric unit of the title compound, showing 30% probability displacement ellipsoids.
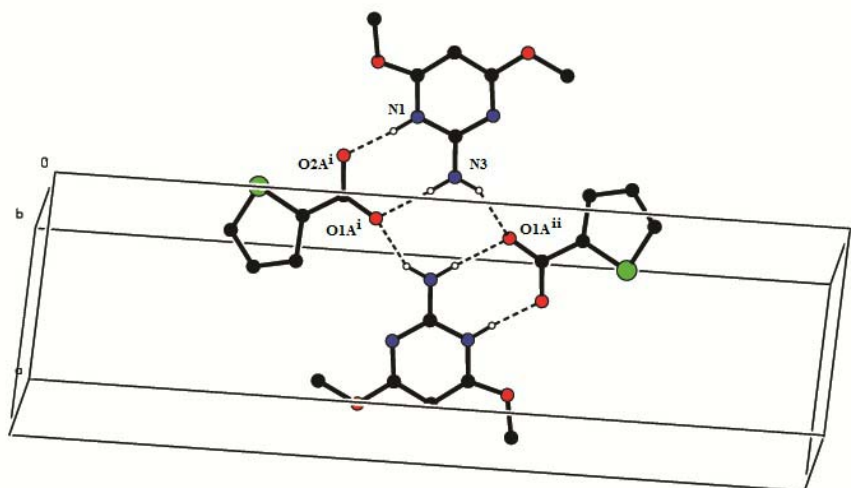
Figure 2

A view of DDAA array along the *b* axis formed by independent N—H⋯O hydrogen bonds. Symmetry codes are given in Table 1. Dashed lines represent hydrogen bonds.
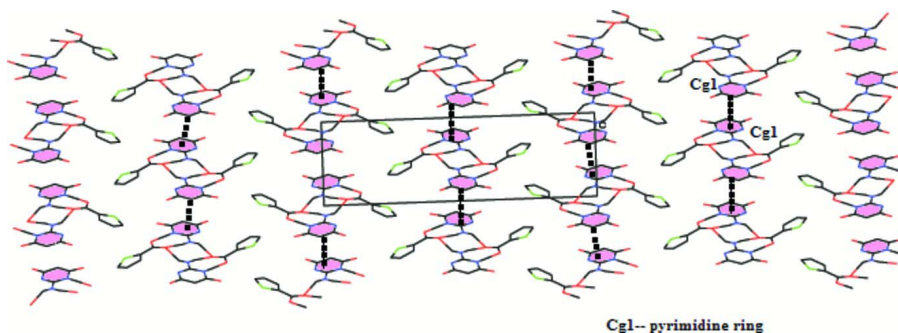
Figure 3

A view of infinite number of DDAA arrays interconnected by π–π stacking interactions indicated by dotted lines. $Cg1 \cdots Cg1 = 3.4689\ (12)$ Å, where $Cg1$ represents the centroid of the ring N1/C1/N2/C2/C3/C4.

2-Amino-4,6-dimethoxypyrimidinium thiophene-2-carboxylate

Crystal data

$C_6H_{10}N_3O_2{}^+ \cdot C_5H_3O_2S^-$	$F(000) = 592$
$M_r = 283.30$	$D_x = 1.465$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 6.7335\ (3)$ Å	Cell parameters from 2092 reflections
$b = 7.6307\ (4)$ Å	$\theta = 4.0$–$32.4°$
$c = 25.0638\ (10)$ Å	$\mu = 0.27$ mm^{-1}
$\beta = 93.928\ (4)°$	$T = 173$ K
$V = 1284.78\ (10)$ Å^3	Irregular, colourless
$Z = 4$	$0.32 \times 0.28 \times 0.14$ mm

Data collection

Agilent Eos Gemini diffractometer	8844 measured reflections
Radiation source: Enhance (Mo) X-ray Source	4245 independent reflections
Detector resolution: 16.0416 pixels mm^{-1}	3071 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.028$
Absorption correction: multi-scan (*CrysAlis RED*; Agilent, 2012)	$\theta_{max} = 32.7°$, $\theta_{min} = 3.3°$
	$h = -7 \rightarrow 9$
	$k = -11 \rightarrow 10$
$T_{min} = 0.789$, $T_{max} = 1.000$	$l = -36 \rightarrow 33$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.062$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.186$	
$S = 1.05$	H-atom parameters constrained
4245 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0861P)^2 + 0.9218P]$ where $P = (F_o^2 + 2F_c^2)/3$
174 parameters	
0 restraints	$(\Delta/\sigma)_{max} < 0.001$
	$\Delta\rho_{max} = 0.79$ e Å^{-3}
	$\Delta\rho_{min} = -0.55$ e Å^{-3}

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}
O1	0.3208 (2)	0.1426 (2)	0.38775 (6)	0.0280 (3)
O2	0.2312 (2)	0.1346 (2)	0.57319 (6)	0.0324 (4)
N1	0.5394 (2)	0.2619 (2)	0.44749 (6)	0.0228 (3)
H1	0.6074	0.2925	0.4202	0.027*
N2	0.5086 (2)	0.2608 (2)	0.54146 (6)	0.0240 (3)
N3	0.7832 (3)	0.3787 (3)	0.50524 (7)	0.0329 (4)
H3A	0.8323	0.4043	0.5377	0.039*
H3B	0.8504	0.4053	0.4775	0.039*
C1	0.6093 (3)	0.3005 (3)	0.49820 (8)	0.0230 (4)
C2	0.3645 (3)	0.1761 (3)	0.43926 (8)	0.0223 (4)
C3	0.2549 (3)	0.1307 (3)	0.48120 (8)	0.0257 (4)
H3	0.1315	0.0706	0.4763	0.031*
C4	0.3372 (3)	0.1789 (3)	0.53174 (8)	0.0242 (4)
C5	0.1469 (3)	0.0367 (3)	0.37450 (9)	0.0333 (5)
H5A	0.1320	0.0186	0.3357	0.050*
H5B	0.0286	0.0966	0.3862	0.050*
H5C	0.1617	−0.0769	0.3926	0.050*
C6	0.3184 (4)	0.1689 (4)	0.62628 (9)	0.0352 (5)
H6A	0.3659	0.2903	0.6284	0.053*
H6B	0.4305	0.0890	0.6342	0.053*
H6C	0.2182	0.1507	0.6523	0.053*
S1	−0.15194 (10)	0.54563 (10)	0.26469 (2)	0.0427 (2)
O1A	−0.0066 (2)	0.4332 (2)	0.41417 (6)	0.0326 (4)
O2A	−0.2775 (2)	0.3607 (3)	0.36279 (6)	0.0361 (4)
C1A	0.0377 (5)	0.6516 (4)	0.23842 (10)	0.0434 (6)
H1A	0.0295	0.7014	0.2036	0.052*
C2A	0.2037 (4)	0.6582 (4)	0.27227 (11)	0.0431 (6)
H2A	0.3227	0.7142	0.2631	0.052*
C3A	0.1860 (3)	0.5737 (3)	0.32322 (8)	0.0268 (4)
H3AA	0.2874	0.5637	0.3513	0.032*
C4A	−0.0153 (3)	0.5071 (3)	0.32345 (8)	0.0253 (4)
C5A	−0.1048 (3)	0.4276 (3)	0.37009 (8)	0.0250 (4)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0286 (7)	0.0348 (8)	0.0209 (7)	−0.0082 (6)	0.0042 (5)	−0.0050 (6)
O2	0.0321 (8)	0.0437 (10)	0.0228 (7)	−0.0045 (7)	0.0110 (6)	0.0022 (6)
N1	0.0241 (7)	0.0250 (8)	0.0196 (7)	−0.0027 (6)	0.0044 (6)	0.0006 (6)

N2	0.0269 (8)	0.0271 (8)	0.0185 (7)	0.0015 (6)	0.0054 (6)	0.0015 (6)
N3	0.0316 (9)	0.0479 (12)	0.0193 (8)	−0.0135 (8)	0.0023 (7)	−0.0005 (8)
C1	0.0267 (9)	0.0229 (9)	0.0198 (8)	0.0003 (7)	0.0039 (7)	0.0016 (7)
C2	0.0241 (9)	0.0214 (9)	0.0217 (8)	−0.0009 (7)	0.0032 (7)	−0.0006 (7)
C3	0.0241 (9)	0.0279 (10)	0.0256 (9)	−0.0034 (7)	0.0062 (7)	0.0015 (8)
C4	0.0275 (9)	0.0243 (9)	0.0217 (9)	0.0032 (7)	0.0079 (7)	0.0029 (7)
C5	0.0321 (10)	0.0379 (12)	0.0296 (11)	−0.0087 (9)	0.0009 (8)	−0.0066 (9)
C6	0.0372 (11)	0.0494 (14)	0.0202 (9)	0.0037 (10)	0.0101 (8)	−0.0003 (9)
S1	0.0476 (4)	0.0578 (5)	0.0226 (3)	0.0000 (3)	0.0015 (2)	0.0018 (3)
O1A	0.0325 (8)	0.0457 (10)	0.0194 (7)	−0.0082 (7)	−0.0006 (6)	0.0043 (6)
O2A	0.0340 (8)	0.0530 (11)	0.0213 (7)	−0.0147 (7)	0.0015 (6)	0.0006 (7)
C1A	0.0661 (17)	0.0416 (14)	0.0241 (11)	0.0038 (12)	0.0141 (11)	0.0050 (10)
C2A	0.0517 (15)	0.0439 (15)	0.0354 (13)	−0.0110 (11)	0.0155 (11)	0.0029 (11)
C3A	0.0409 (11)	0.0239 (9)	0.0170 (8)	−0.0072 (8)	0.0112 (7)	0.0013 (7)
C4A	0.0311 (10)	0.0277 (10)	0.0171 (8)	0.0014 (8)	0.0026 (7)	0.0002 (7)
C5A	0.0291 (9)	0.0277 (10)	0.0186 (8)	−0.0026 (7)	0.0034 (7)	−0.0002 (7)

Geometric parameters (Å, º)

O1—C2	1.329 (2)	C5—H5B	0.9800
O1—C5	1.443 (3)	C5—H5C	0.9800
O2—C4	1.343 (2)	C6—H6A	0.9800
O2—C6	1.441 (3)	C6—H6B	0.9800
N1—H1	0.8800	C6—H6C	0.9800
N1—C1	1.357 (2)	S1—C1A	1.683 (3)
N1—C2	1.351 (3)	S1—C4A	1.708 (2)
N2—C1	1.352 (2)	O1A—C5A	1.249 (2)
N2—C4	1.321 (3)	O2A—C5A	1.272 (3)
N3—H3A	0.8800	C1A—H1A	0.9500
N3—H3B	0.8800	C1A—C2A	1.357 (4)
N3—C1	1.315 (3)	C2A—H2A	0.9500
C2—C3	1.370 (3)	C2A—C3A	1.443 (3)
C3—H3	0.9500	C3A—H3AA	0.9500
C3—C4	1.396 (3)	C3A—C4A	1.448 (3)
C5—H5A	0.9800	C4A—C5A	1.481 (3)
C2—O1—C5	116.97 (16)	H5A—C5—H5C	109.5
C4—O2—C6	117.66 (17)	H5B—C5—H5C	109.5
C1—N1—H1	120.3	O2—C6—H6A	109.5
C2—N1—H1	120.3	O2—C6—H6B	109.5
C2—N1—C1	119.40 (16)	O2—C6—H6C	109.5
C4—N2—C1	115.98 (17)	H6A—C6—H6B	109.5
H3A—N3—H3B	120.0	H6A—C6—H6C	109.5
C1—N3—H3A	120.0	H6B—C6—H6C	109.5
C1—N3—H3B	120.0	C1A—S1—C4A	92.37 (12)
N2—C1—N1	122.80 (18)	S1—C1A—H1A	123.6
N3—C1—N1	118.20 (17)	C2A—C1A—S1	112.83 (19)
N3—C1—N2	119.00 (18)	C2A—C1A—H1A	123.6

O1—C2—N1	111.98 (16)	C1A—C2A—H2A	122.5
O1—C2—C3	126.99 (18)	C1A—C2A—C3A	115.0 (2)
N1—C2—C3	121.02 (18)	C3A—C2A—H2A	122.5
C2—C3—H3	122.3	C2A—C3A—H3AA	126.4
C2—C3—C4	115.38 (18)	C2A—C3A—C4A	107.1 (2)
C4—C3—H3	122.3	C4A—C3A—H3AA	126.4
O2—C4—C3	115.91 (18)	C3A—C4A—S1	112.68 (14)
N2—C4—O2	118.68 (18)	C3A—C4A—C5A	125.34 (18)
N2—C4—C3	125.40 (17)	C5A—C4A—S1	121.78 (16)
O1—C5—H5A	109.5	O1A—C5A—O2A	124.37 (18)
O1—C5—H5B	109.5	O1A—C5A—C4A	117.69 (18)
O1—C5—H5C	109.5	O2A—C5A—C4A	117.92 (18)
H5A—C5—H5B	109.5		
O1—C2—C3—C4	178.67 (19)	C6—O2—C4—N2	−4.2 (3)
N1—C2—C3—C4	−0.2 (3)	C6—O2—C4—C3	174.98 (19)
C1—N1—C2—O1	−177.64 (17)	S1—C1A—C2A—C3A	0.3 (3)
C1—N1—C2—C3	1.3 (3)	S1—C4A—C5A—O1A	−167.06 (17)
C1—N2—C4—O2	179.44 (18)	S1—C4A—C5A—O2A	11.8 (3)
C1—N2—C4—C3	0.4 (3)	C1A—S1—C4A—C3A	−1.39 (18)
C2—N1—C1—N2	−1.8 (3)	C1A—S1—C4A—C5A	173.67 (19)
C2—N1—C1—N3	177.7 (2)	C1A—C2A—C3A—C4A	−1.3 (3)
C2—C3—C4—O2	−179.84 (19)	C2A—C3A—C4A—S1	1.7 (2)
C2—C3—C4—N2	−0.7 (3)	C2A—C3A—C4A—C5A	−173.1 (2)
C4—N2—C1—N1	0.9 (3)	C3A—C4A—C5A—O1A	7.3 (3)
C4—N2—C1—N3	−178.5 (2)	C3A—C4A—C5A—O2A	−173.8 (2)
C5—O1—C2—N1	174.26 (18)	C4A—S1—C1A—C2A	0.6 (2)
C5—O1—C2—C3	−4.7 (3)		

Hydrogen-bond geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1A[i]	0.88	2.83	3.479 (2)	132
N1—H1···O2A[i]	0.88	1.76	2.637 (2)	175
N3—H3A···O1A[ii]	0.88	2.04	2.826 (2)	148
N3—H3B···O1A[i]	0.88	1.92	2.798 (2)	173
C5—H5B···O1A	0.98	2.68	3.369 (3)	128
C6—H6B···O1[iii]	0.98	2.52	3.434 (3)	155
C1A—H1A···O1[iv]	0.95	2.60	3.365 (3)	138
C1A—H1A···O2A[v]	0.95	2.60	3.383 (3)	140

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