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2-Amino-1-methyl-4-oxo-4,5-dihydro-1*H*-imidazol-3-ium 4-methylbenzenesulfonate

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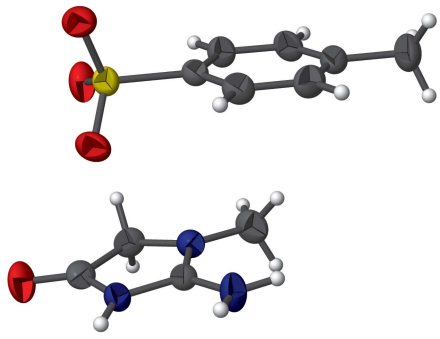
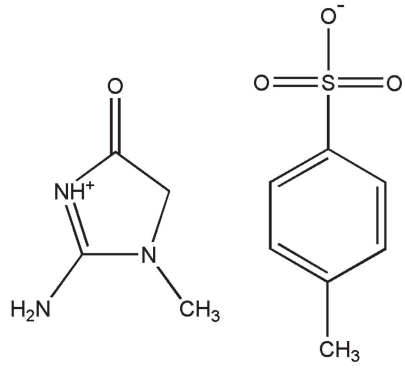
The title molecular salt, $C_4H_8N_3O^+\cdot C_7H_7O_3S^-$, is composed of a 2-amino-1-methyl-4-oxo-4,5-dihydro-1*H*-imidazol-3-ium cation and a 4-methylbenzenesulfonate anion. The cation is protonated at its N atom and the anion is deprotonated at its hydroxy O atom. The imidazole ring is planar (r.m.s. deviation = 0.033 Å) and makes a dihedral angle of 7.87 (10)° with the benzene ring of the anion. In the crystal, the anions and cations are connected by two N—H···O hydrogen bonds, generating an $R_2^2(8)$ ring motif. These units are linked by further N—H···O hydrogen bonds and C—H···O and C—H···π contacts to form chains propagating along the *a*-axis direction.

3D view



Chemical scheme



Structure description

Creatinine is found in the muscle tissue of vertebrates, mainly in the form of phosphocreatine, and supplies energy for muscle contraction. It has been proven that determination of creatinine is more valuable for the detection of renal dysfunction than that of urea (Sharma *et al.*, 2004). Abnormal levels of creatinine in biological fluids is an indicator of various disease states (Narayanan & Appleton, 1980). Benzenesulfonic acid is a particularly strong organic acid which is capable of protonating N-containing heterocycles and other Lewis bases (Wang & Wei, 2007). We report herein on the synthesis and crystal structure of the title molecular salt. The geometric parameters are comparable with those of similar structures (Moghimi *et al.*, 2004; Hemamalini *et al.*, 2005)

The title molecular salt, Fig. 1, contains a 2-amino-1-methyl-5*H*-imidazolium-4-one cation (protonated at the N atom, N1, in the imidazole unit) and a 4-methylbenzenesulfonate anion (deprotonated at the hydroxyl O atom, O1). The imidazole ring is almost planar (r.m.s. deviation = 0.033 Å) and makes a dihedral angle of 7.87 (10)° with the benzene ring (C1–C6) of the anion.

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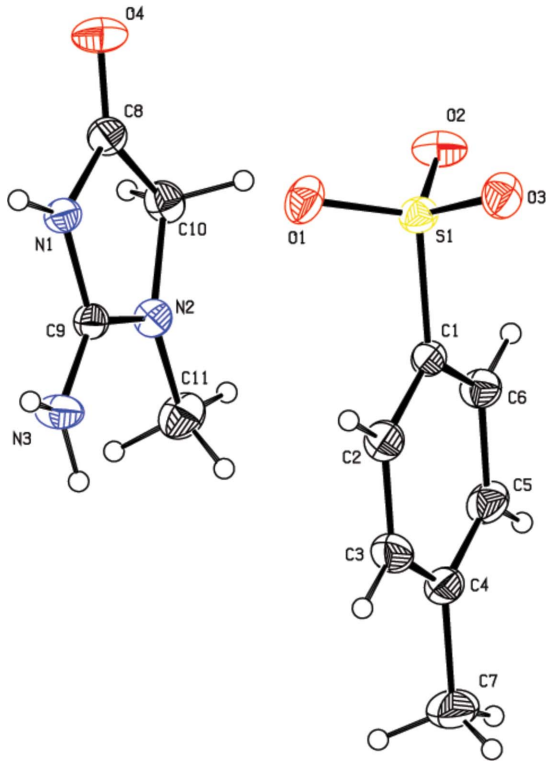

Figure 1
The molecular structure of the title molecular salt, showing the atom labelling and 30% probability displacement ellipsoids.

In the crystal, the anions and cations are connected by two N—H···O hydrogen bonds, generating an $R_2^2(8)$ ring motif (Table 1 and Fig. 2). These units are linked by further N—H···O hydrogen bonds and C—H···O and C—H···π contacts to form chains propagating along the *a*-axis direction (Table 1 and Figs. 2 and 3).

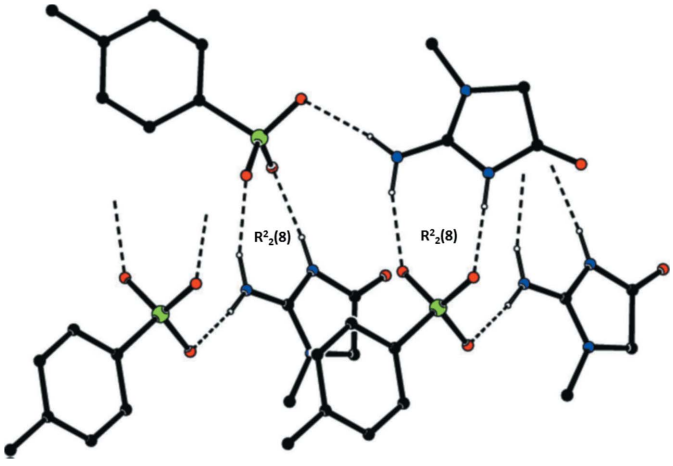

Figure 2
A partial view of the crystal packing of the title salt, showing the formation of the $R_2^2(8)$ ring motifs. Hydrogen bonds (see Table 1) are shown as dashed lines and C-bound H atoms have been omitted for clarity.

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

*Cg*1 is the centroid of the C1–C6 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3*A*···O2^{i}	0.89 (1)	2.09 (1)	2.967 (2)	171 (2)
N1—H1···O3^{ii}	0.87 (1)	1.94 (1)	2.811 (2)	173 (2)
N3—H3*B*···O1^{ii}	0.88 (1)	1.96 (1)	2.813 (2)	163 (2)
C10—H10*B*···O2	0.97	2.59	3.463 (3)	150
C11—H11*C*···*Cg*1	0.96	2.78	3.537 (2)	136

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

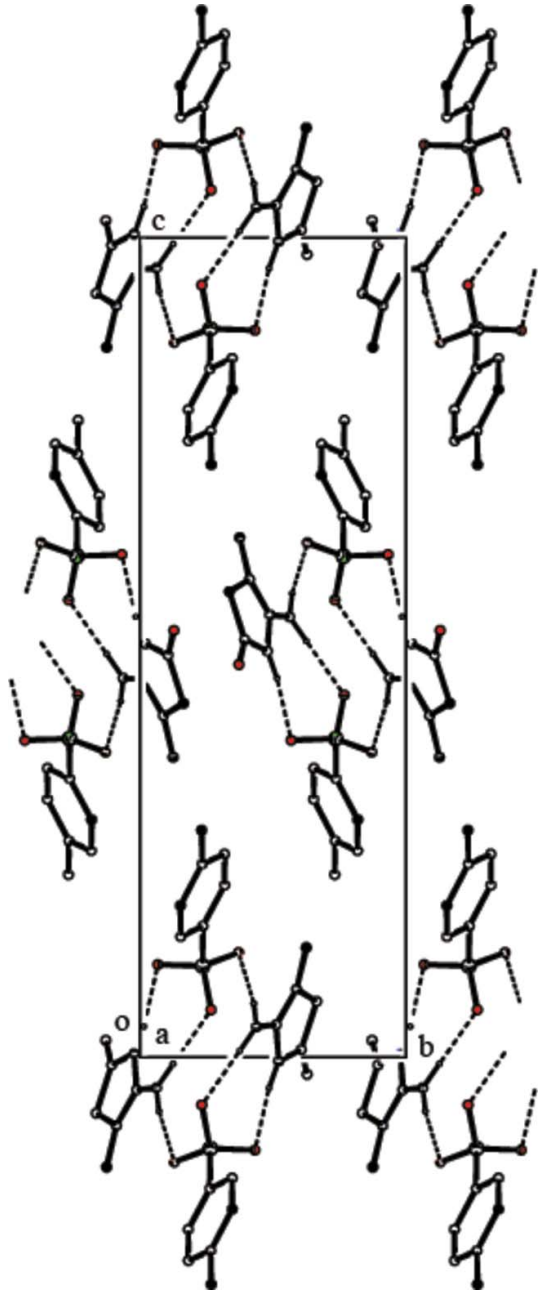

Figure 3
The crystal packing of the title compound, viewed along the *a* axis. The hydrogen bonds (see Table 1) are shown as dashed lines and C-bound H atoms have been omitted for clarity.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_4H_8N_3O^+\cdot C_7H_7O_3S^-$
M_r	285.32
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	295
a, b, c (Å)	7.0564 (4), 7.8593 (5), 24.1907 (18)
V (Å^3)	1341.58 (15)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.26
Crystal size (mm)	0.28 × 0.24 × 0.20
Data collection	
Diffractometer	Bruker Kappa APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2004)
T_{min}, T_{max}	0.932, 0.951
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	19256, 4179, 3607
R_{int}	0.026
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.743
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.041, 0.110, 1.05
No. of reflections	4179
No. of parameters	185
No. of restraints	3
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.23, −0.35
Absolute structure	Flack (1983), 1712 Friedal pairs
Absolute structure parameter	0.04 (8)

Computer programs: *APEX2* and *SAINT* (Bruker, 2004), *SHELXS97* and *SHELXL97* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

Synthesis and crystallization

Creatinine (2-amino-1-methyl-5*H*-imidazol-4-one) (1.13 g, 0.01 mol) and 4-methylbenzenesulfonic acid monohydrate (1.90 g, 0.01 mol) were dissolved in deionized water. The solution was stirred well for 3 h, filtered and kept in a dust-free environment for evaporation. Crystals were obtained over a period of five days by slow evaporation of the solvent, and subjected to single-crystal X-ray diffraction analysis.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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full crystallographic data

IUCrData (2016). **1**, x161125 [https://doi.org/10.1107/S2414314616011251]

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2-Amino-1-methyl-4-oxo-4,5-dihydro-1*H*-imidazol-3-ium 4-methylbenzenesulfonate

Crystal data

$C_4H_8N_3O^+·C_7H_7O_3S^-$
M_r = 285.32
Orthorhombic, $P2_12_12_1$
Hall symbol: P 2ac 2ab
a = 7.0564 (4) Å
b = 7.8593 (5) Å
c = 24.1907 (18) Å
V = 1341.58 (15) Å^3
Z = 4
$F(000)$ = 600
D_x = 1.413 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 8207 reflections
θ = 2.2–27.9°
μ = 0.26 mm^{-1}
T = 295 K
Block, colourless
0.28 × 0.24 × 0.20 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω and φ scan
Absorption correction: multi-scan (SADABS; Bruker, 2004)
T_{min} = 0.932, T_{max} = 0.951
19256 measured reflections
4179 independent reflections
3607 reflections with $I > 2\sigma(I)$
R_{int} = 0.026
θ_{max} = 31.9°, θ_{min} = 2.7°
h = −10→10
k = −10→11
l = −33→35

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.110
S = 1.05
4179 reflections
185 parameters
3 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
$w = 1/[\sigma^2(F_o^2) + (0.0598P)^2 + 0.2554P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e Å^{-3}
Absolute structure: Flack (1983), 1712 Friedal pairs
Absolute structure parameter: 0.04 (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. 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 $F^2 > 2\text{sigma}(F^2)$ 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.5492 (2)	0.7635 (2)	0.66004 (6)	0.0310 (3)
C2	0.3811 (3)	0.8465 (2)	0.64735 (8)	0.0393 (4)
H2	0.3669	0.9012	0.6135	0.047*
C3	0.2352 (3)	0.8472 (3)	0.68525 (9)	0.0466 (5)
H3	0.1229	0.9033	0.6767	0.056*
C4	0.2524 (3)	0.7658 (3)	0.73601 (8)	0.0448 (4)
C5	0.4206 (3)	0.6824 (3)	0.74788 (8)	0.0447 (4)
H5	0.4342	0.6262	0.7815	0.054*
C6	0.5697 (3)	0.6816 (3)	0.71009 (7)	0.0386 (4)
H6	0.6824	0.6261	0.7186	0.046*
C7	0.0916 (4)	0.7681 (4)	0.77703 (11)	0.0697 (8)
H7A	0.0593	0.8838	0.7857	0.105*
H7B	0.1297	0.7102	0.8102	0.105*
H7C	−0.0165	0.7118	0.7614	0.105*
C8	0.5860 (3)	0.3940 (2)	0.50931 (8)	0.0369 (4)
C9	0.3041 (2)	0.4880 (2)	0.53959 (7)	0.0306 (3)
C10	0.5602 (3)	0.3361 (2)	0.56814 (8)	0.0394 (4)
H10A	0.5554	0.2129	0.5705	0.047*
H10B	0.6614	0.3778	0.5916	0.047*
C11	0.2787 (4)	0.3750 (3)	0.63391 (8)	0.0493 (5)
H11A	0.3625	0.3192	0.6593	0.074*
H11B	0.1728	0.3022	0.6261	0.074*
H11C	0.2341	0.4793	0.6500	0.074*
N1	0.4224 (2)	0.47883 (19)	0.49552 (6)	0.0322 (3)
N2	0.3792 (2)	0.41182 (19)	0.58312 (6)	0.0340 (3)
N3	0.1389 (2)	0.5624 (2)	0.53732 (7)	0.0436 (4)
O1	0.6482 (2)	0.73257 (19)	0.55797 (5)	0.0480 (3)
O2	0.8645 (2)	0.6292 (2)	0.62769 (6)	0.0511 (4)
O3	0.8221 (2)	0.93207 (17)	0.61315 (6)	0.0462 (3)
O4	0.7202 (2)	0.3721 (2)	0.47927 (7)	0.0546 (4)
S1	0.73557 (6)	0.76400 (5)	0.611355 (17)	0.03468 (11)
H1	0.395 (3)	0.515 (3)	0.4624 (5)	0.038 (5)*
H3A	0.061 (3)	0.572 (3)	0.5658 (7)	0.045 (6)*
H3B	0.116 (4)	0.625 (3)	0.5079 (7)	0.053 (7)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0325 (7)	0.0309 (8)	0.0295 (7)	−0.0004 (7)	0.0009 (6)	−0.0016 (6)
C2	0.0398 (9)	0.0396 (9)	0.0384 (9)	0.0066 (8)	−0.0043 (8)	−0.0004 (7)
C3	0.0336 (9)	0.0477 (10)	0.0586 (12)	0.0060 (9)	−0.0010 (9)	−0.0108 (8)
C4	0.0412 (9)	0.0459 (9)	0.0472 (10)	−0.0100 (10)	0.0114 (8)	−0.0155 (8)
C5	0.0532 (11)	0.0513 (11)	0.0297 (8)	−0.0059 (9)	0.0067 (8)	−0.0004 (8)
C6	0.0389 (9)	0.0438 (9)	0.0332 (8)	0.0034 (8)	0.0009 (7)	0.0036 (7)
C7	0.0570 (13)	0.0796 (17)	0.0726 (16)	−0.0192 (15)	0.0322 (12)	−0.0239 (15)
C8	0.0359 (9)	0.0302 (8)	0.0445 (9)	0.0041 (7)	0.0001 (7)	−0.0047 (7)
C9	0.0309 (8)	0.0293 (7)	0.0316 (7)	−0.0009 (6)	0.0008 (6)	−0.0014 (6)
C10	0.0363 (9)	0.0351 (8)	0.0467 (10)	0.0047 (7)	−0.0060 (8)	0.0020 (7)
C11	0.0627 (13)	0.0521 (11)	0.0332 (9)	−0.0030 (11)	0.0058 (9)	0.0066 (8)
N1	0.0319 (7)	0.0340 (7)	0.0308 (7)	0.0033 (6)	0.0019 (6)	−0.0013 (5)
N2	0.0363 (7)	0.0334 (7)	0.0324 (7)	0.0006 (6)	0.0000 (6)	0.0017 (6)
N3	0.0337 (8)	0.0569 (11)	0.0403 (8)	0.0115 (8)	0.0074 (7)	0.0066 (8)
O1	0.0643 (9)	0.0496 (8)	0.0302 (6)	−0.0154 (7)	0.0044 (6)	−0.0034 (6)
O2	0.0428 (8)	0.0538 (8)	0.0566 (9)	0.0138 (7)	0.0147 (7)	0.0062 (7)
O3	0.0536 (8)	0.0428 (7)	0.0423 (7)	−0.0149 (6)	0.0040 (6)	−0.0015 (6)
O4	0.0444 (8)	0.0545 (8)	0.0649 (10)	0.0167 (7)	0.0172 (7)	−0.0022 (7)
S1	0.0365 (2)	0.0351 (2)	0.03242 (18)	−0.00248 (17)	0.00560 (16)	0.00011 (15)

Geometric parameters (Å, º)

C1—C6	1.379 (2)	C8—C10	1.505 (3)
C1—C2	1.388 (3)	C9—N3	1.305 (2)
C1—S1	1.7655 (16)	C9—N2	1.322 (2)
C2—C3	1.378 (3)	C9—N1	1.356 (2)
C2—H2	0.9300	C10—N2	1.455 (2)
C3—C4	1.390 (3)	C10—H10A	0.9700
C3—H3	0.9300	C10—H10B	0.9700
C4—C5	1.386 (3)	C11—N2	1.448 (2)
C4—C7	1.508 (3)	C11—H11A	0.9600
C5—C6	1.394 (3)	C11—H11B	0.9600
C5—H5	0.9300	C11—H11C	0.9600
C6—H6	0.9300	N1—H1	0.872 (9)
C7—H7A	0.9600	N3—H3A	0.885 (9)
C7—H7B	0.9600	N3—H3B	0.882 (10)
C7—H7C	0.9600	O1—S1	1.4523 (14)
C8—O4	1.206 (2)	O2—S1	1.4510 (15)
C8—N1	1.374 (2)	O3—S1	1.4559 (13)
C6—C1—C2	120.22 (16)	N2—C9—N1	110.85 (15)
C6—C1—S1	120.55 (13)	N2—C10—C8	102.59 (14)
C2—C1—S1	119.22 (13)	N2—C10—H10A	111.2
C3—C2—C1	119.54 (18)	C8—C10—H10A	111.2
C3—C2—H2	120.2	N2—C10—H10B	111.2

C1—C2—H2	120.2	C8—C10—H10B	111.2
C2—C3—C4	121.36 (19)	H10A—C10—H10B	109.2
C2—C3—H3	119.3	N2—C11—H11A	109.5
C4—C3—H3	119.3	N2—C11—H11B	109.5
C5—C4—C3	118.41 (17)	H11A—C11—H11B	109.5
C5—C4—C7	120.9 (2)	N2—C11—H11C	109.5
C3—C4—C7	120.7 (2)	H11A—C11—H11C	109.5
C4—C5—C6	120.83 (18)	H11B—C11—H11C	109.5
C4—C5—H5	119.6	C9—N1—C8	110.61 (15)
C6—C5—H5	119.6	C9—N1—H1	124.5 (15)
C1—C6—C5	119.63 (18)	C8—N1—H1	124.7 (15)
C1—C6—H6	120.2	C9—N2—C11	124.78 (17)
C5—C6—H6	120.2	C9—N2—C10	109.78 (14)
C4—C7—H7A	109.5	C11—N2—C10	124.02 (16)
C4—C7—H7B	109.5	C9—N3—H3A	124.1 (15)
H7A—C7—H7B	109.5	C9—N3—H3B	116.8 (18)
C4—C7—H7C	109.5	H3A—N3—H3B	118 (2)
H7A—C7—H7C	109.5	O2—S1—O1	112.60 (10)
H7B—C7—H7C	109.5	O2—S1—O3	113.02 (10)
O4—C8—N1	125.64 (19)	O1—S1—O3	111.04 (9)
O4—C8—C10	128.43 (18)	O2—S1—C1	106.48 (8)
N1—C8—C10	105.93 (16)	O1—S1—C1	106.04 (9)
N3—C9—N2	126.45 (16)	O3—S1—C1	107.14 (8)
N3—C9—N1	122.70 (16)		

C6—C1—C2—C3	0.3 (3)	O4—C8—N1—C9	−176.92 (19)
S1—C1—C2—C3	−179.74 (15)	C10—C8—N1—C9	3.4 (2)
C1—C2—C3—C4	−0.3 (3)	N3—C9—N2—C11	9.9 (3)
C2—C3—C4—C5	−0.3 (3)	N1—C9—N2—C11	−169.69 (16)
C2—C3—C4—C7	179.9 (2)	N3—C9—N2—C10	176.69 (18)
C3—C4—C5—C6	0.7 (3)	N1—C9—N2—C10	−2.86 (19)
C7—C4—C5—C6	−179.5 (2)	C8—C10—N2—C9	4.62 (19)
C2—C1—C6—C5	0.1 (3)	C8—C10—N2—C11	171.58 (17)
S1—C1—C6—C5	−179.85 (15)	C6—C1—S1—O2	16.90 (18)
C4—C5—C6—C1	−0.6 (3)	C2—C1—S1—O2	−163.02 (15)
O4—C8—C10—N2	175.6 (2)	C6—C1—S1—O1	137.03 (16)
N1—C8—C10—N2	−4.70 (19)	C2—C1—S1—O1	−42.88 (17)
N3—C9—N1—C8	179.99 (17)	C6—C1—S1—O3	−104.31 (16)
N2—C9—N1—C8	−0.4 (2)	C2—C1—S1—O3	75.78 (16)

Hydrogen-bond geometry (Å, º)

Cg1 is the centroid of the C1–C6 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3*A*···O2^{i}	0.89 (1)	2.09 (1)	2.967 (2)	171 (2)
N1—H1···O3^{ii}	0.87 (1)	1.94 (1)	2.811 (2)	173 (2)
N3—H3*B*···O1^{ii}	0.88 (1)	1.96 (1)	2.813 (2)	163 (2)

C10—H10*B*···O2	0.97	2.59	3.463 (3)	150
C11—H11*C*···*Cg*1	0.96	2.78	3.537 (2)	136

Symmetry codes: (i) $x-1, y, z$; (ii) $x-1/2, -y+3/2, -z+1$.