

Crystal structure of 4,4'-bipyridine-1,1'-dium naphthalene-2,6-disulfonate dihydrate

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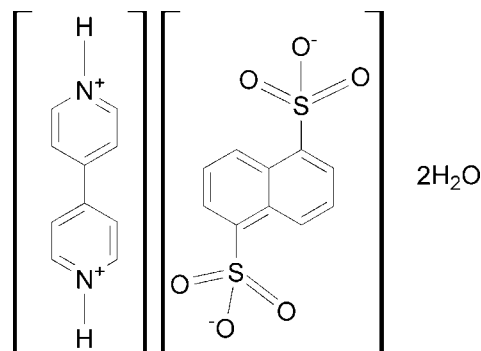
The title hydrated molecular organic salt, $C_{10}H_{10}N_2^{2+} \cdot C_{10}H_6O_6S_2^{2-} \cdot 2H_2O$, crystallized with half a bipyridinium cation, half a naphthalene-2,6-disulfonate anion and a water molecule in the asymmetric unit. The whole cation and anion are generated by inversion symmetry, the inversion centers being at the center of the bridging C—C bond of the cation, and at the center of the fused C—C bond of the naphthalene group of the anion. In the crystal, the anions and cations stack alternately along the *a* axis with π – π interactions [intercentroid distance = 3.491 (1) Å]. The anions are linked *via* O—H...O(sulfonate) hydrogen bonds involving two inversion-related water molecules, forming chains along [10 $\bar{1}$]. These chains are bridged by bifurcated N—H...O(O) hydrogen bonds, forming a three-dimensional framework structure. There are also C—H...O hydrogen bonds present, reinforcing the framework structure.

Keywords: crystal structure; molecular salt; bipyridine; naphthalenedisulfonate; dihydrate.

CCDC reference: 1006095

1. Related literature

For the use of 4,4'-bipyridine in the construction of metal-organic frameworks, see: Batten *et al.* (2012); Burd *et al.* (2012); Jeazet & Janiak (2012). For the use of naphthalene-2,6-disulfonate in the preparation of metal-organic frameworks, exploiting its different coordination modes, see: Zhao *et al.* (2013); Borodkin *et al.* (2013); Chen *et al.* (2001); Song *et al.* (2010); Pereira Silva *et al.* (2006).



2. Experimental

2.1. Crystal data

$C_{10}H_{10}N_2^{2+} \cdot C_{10}H_6O_6S_2^{2-} \cdot 2H_2O$
 $M_r = 480.50$
 Monoclinic, $P2_1/n$
 $a = 7.4022$ (2) Å
 $b = 10.9390$ (3) Å
 $c = 12.6500$ (4) Å
 $\beta = 99.908$ (1)°

$V = 1009.03$ (5) Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 0.32$ mm⁻¹
 $T = 296$ K
 $0.35 \times 0.24 \times 0.15$ mm

2.2. Data collection

Bruker SMART BREEZE CCD diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2012)
 $T_{min} = 0.912$, $T_{max} = 0.953$

39553 measured reflections
 2551 independent reflections
 2340 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.033$

2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.103$
 $S = 1.04$
 2551 reflections
 153 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{max} = 0.41$ e Å⁻³
 $\Delta\rho_{min} = -0.23$ e Å⁻³

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1W—H1A...O1 ⁱ	0.82 (3)	2.01 (3)	2.8293 (18)	176 (2)
O1W—H1B...O3 ⁱⁱ	0.82 (3)	2.04 (3)	2.8484 (18)	172 (2)
N1—H3...O2 ⁱⁱⁱ	0.86	2.55	3.0212 (18)	116
N1—H3...O1W ^{iv}	0.86	1.98	2.7948 (19)	157
C1—H1...O1 ^v	0.93	2.51	3.1946 (17)	130
C10—H10...O1 ^{vi}	0.93	2.60	3.294 (2)	132
C11—H11...O2 ^{vii}	0.93	2.47	3.2036 (19)	136

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

Data collection: APEX2 (Bruker, 2012); cell refinement: APEX2 and SAINT (Bruker, 2012); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL2013 (Sheldrick, 2008); molecular graphics: ORTEP-3 for Windows (Farrugia, 2012) and PLATON (Spek, 2009); software used to prepare material for publication: SHELXL2013 and PLATON (Spek, 2009).

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: SU2764).

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supporting information

Acta Cryst. (2014). E70, o989–o990 [doi:10.1107/S160053681401784X]

Crystal structure of 4,4'-bipyridine-1,1'-dium naphthalene-2,6-disulfonate dihydrate

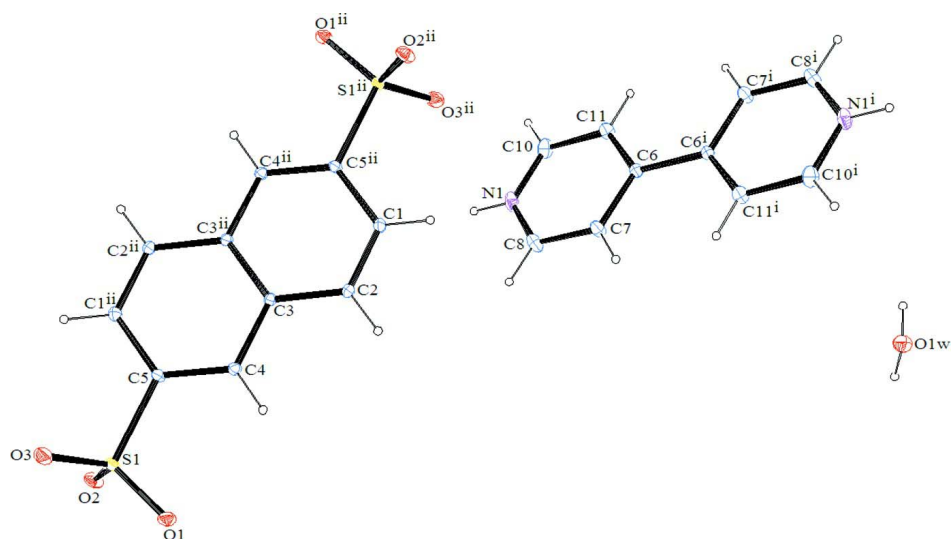
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S1. Synthesis and crystallization

The title compound was prepared by a hydrothermal reaction using a 23 ml Parr Teflon-lined acid digestion bomb, heated in a Nuve brand FN300 model programmable electric oven. A mixture of $\text{VOSO}_4 \cdot x\text{H}_2\text{O}$, naphthalene-2,6-dicarboxylic acid, 4,4'-bipyridine and water (in molar ratio 1:1:1:55.6 mmol) was placed in a 23 ml Parr Teflon-lined autoclave which was subsequently heated for 90 h inside the oven at 473 K. After, the acid digestion bomb was cooled to room temperature over a period of 4 h. Very-light-yellow–green prismatic single crystals of the title compound and a dark-green unidentified vanadium oxide powder were filtered from the light-blue–green mother liquor. The crystals were separated from the powder under an optical microscope. Analysis calculated for $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_8\text{V}_2$: C 49.991, H 4.195, N 5.831, S 13.346%; found: C 48.670, H 3.929, N 5.857, S 13.670%. Selected FT–IR peaks between 1650 and 400 cm^{-1} : 1635 (*m*), 1624 (*m*), 1591 (*m*), 1591 (*w*), 1502 (*w*), 1487 (*m*), 1372 (*m*), 1333 (*w*), 1314 (*w*), 1276 (*w*), 1244 (*m*), 1210 (*s, sh*), 1200 (*s*), 1194 (*s, sh*), 1183 (*m, sh*), 1144 (*m*), 1092 (*s*), 1029 (*s*), 1005 (*m*), 979 (*m*), 914 (*m*), 832 (*m*), 791 (*m*), 706 (*w*), 665 (*s*), 656 (*s*), 618 (*s*), 554 (*m*), 546 (*m*), 507 (*w*), 440 (*m*), 411 (*m*) cm^{-1} . Thermogravimetric analysis results supported the X-ray single-crystal structure analysis by giving a 7.5% weight loss in the range 393–413 K, corresponding to two water molecules per molecular formula.

S2. Refinement

The water molecule H atoms were located in a difference Fourier map and freely refined. The N- and C-bound H atoms were placed geometrically and refined using a riding model, with N—H = 0.86 and C—H = 0.93 Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N,C})$.

**Figure 1**

A view of the molecular structure of the title hydrated molecular salt, with the atom labelling. Displacement ellipsoids are drawn at the 40% probability level. [Symmetry codes: (i) $-x+1, -y+1, -z+2$; (ii) $-x+1, -y, -z+1$.] The inversion related water molecule is not shown.

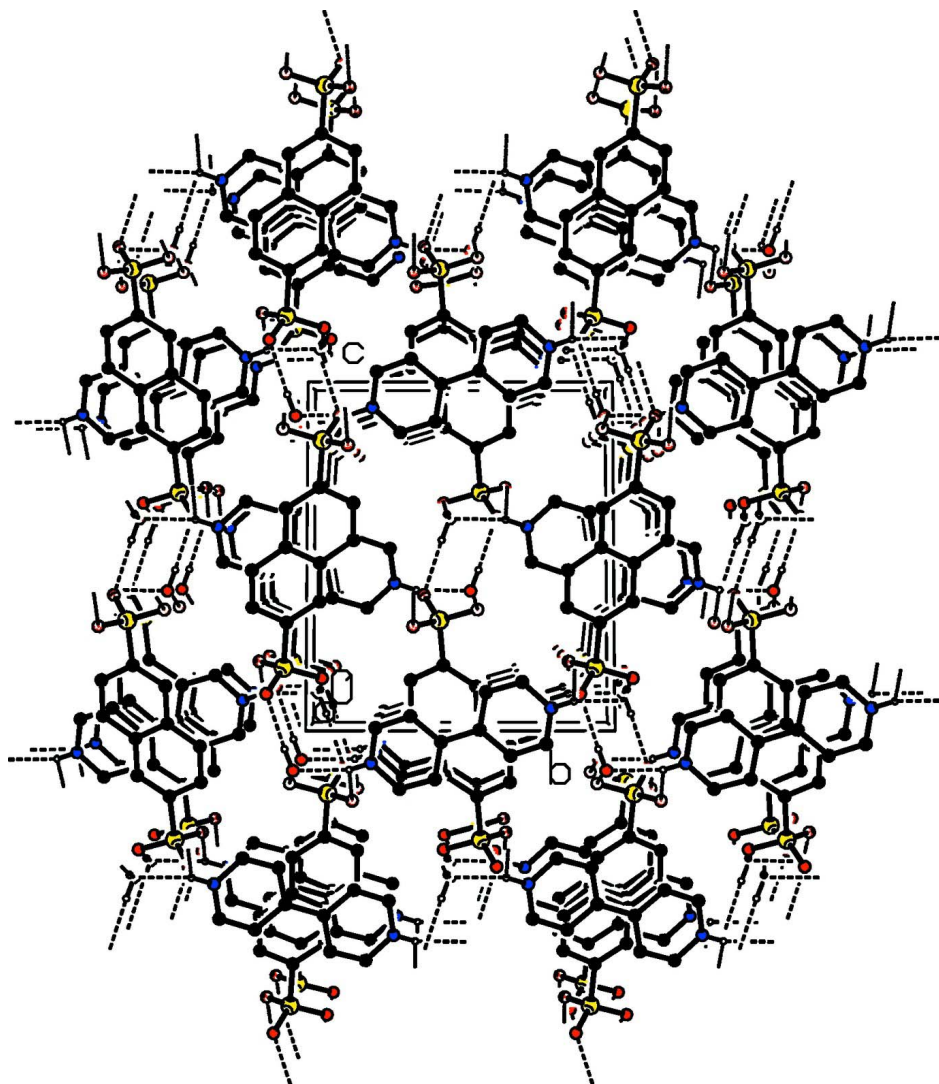


Figure 2

A view along the *a* axis of the crystal packing of the title compound, showing the hydrogen bonds as dashed lines (see Table 1 for details; H atoms not involved in hydrogen bonds have been omitted for clarity).

4,4'-Bipyridine-1,1'-diium naphthalene-2,6-disulfonate dihydrate

Crystal data

$C_{10}H_{10}N_2^{2+} \cdot C_{10}H_6O_6S_2^{2-} \cdot 2H_2O$

$M_r = 480.50$

Monoclinic, $P2_1/n$

$a = 7.4022$ (2) Å

$b = 10.9390$ (3) Å

$c = 12.6500$ (4) Å

$\beta = 99.908$ (1)°

$V = 1009.03$ (5) Å³

$Z = 2$

$F(000) = 500$

$D_x = 1.581$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 39513 reflections

$\theta = 2.5$ – 28.5 °

$\mu = 0.32$ mm⁻¹

$T = 296$ K

Plate, colourless

$0.35 \times 0.24 \times 0.15$ mm

Data collection

Bruker SMART BREEZE CCD
diffractometer

Radiation source: fine-focus sealed X-ray tube

Mirror monochromator

ω -scans

Absorption correction: multi-scan
(*SADABS*; Bruker, 2012)

$T_{\min} = 0.912$, $T_{\max} = 0.953$

39553 measured reflections

2551 independent reflections

2340 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.033$

$\theta_{\max} = 28.5^\circ$, $\theta_{\min} = 2.5^\circ$

$h = -9 \rightarrow 9$

$k = -14 \rightarrow 14$

$l = -16 \rightarrow 16$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.035$

$wR(F^2) = 0.103$

$S = 1.04$

2551 reflections

153 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0614P)^2 + 0.3867P]$

where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{\max} = 0.41 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.23 \text{ e } \text{\AA}^{-3}$

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.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.21510 (4)	-0.06706 (3)	0.18311 (2)	0.02743 (12)
O1	0.14850 (17)	0.05494 (9)	0.15242 (9)	0.0398 (3)
O2	0.06807 (15)	-0.14963 (10)	0.19836 (9)	0.0421 (3)
O3	0.33036 (17)	-0.11776 (14)	0.11235 (9)	0.0513 (3)
C1	0.55029 (19)	0.16047 (12)	0.64530 (11)	0.0305 (3)
H1	0.5516	0.2306	0.6870	0.037*
C2	0.45657 (18)	0.15973 (11)	0.54200 (10)	0.0291 (3)
H2	0.3943	0.2295	0.5138	0.035*
C3	0.45389 (16)	0.05348 (10)	0.47790 (10)	0.0230 (2)
C4	0.35783 (17)	0.05061 (11)	0.37022 (10)	0.0254 (2)
H4	0.2972	0.1200	0.3400	0.030*
C5	0.35503 (17)	-0.05470 (11)	0.31137 (10)	0.0254 (3)
N1	0.30960 (19)	0.21624 (13)	0.91922 (12)	0.0454 (3)
H3	0.2627	0.1463	0.8994	0.054*
C6	0.46027 (17)	0.43924 (12)	0.98236 (11)	0.0282 (3)
C7	0.3717 (2)	0.41942 (15)	0.87696 (13)	0.0412 (3)
H7	0.3633	0.4821	0.8267	0.049*
C8	0.2972 (2)	0.30668 (18)	0.84798 (14)	0.0493 (4)
H8	0.2375	0.2935	0.7780	0.059*
C10	0.3922 (3)	0.23110 (15)	1.01926 (15)	0.0479 (4)

H10	0.3989	0.1662	1.0673	0.057*
C11	0.4686 (2)	0.34212 (14)	1.05306 (12)	0.0398 (3)
H11	0.5261	0.3519	1.1239	0.048*
O1W	0.23786 (19)	0.96590 (12)	0.89658 (11)	0.0447 (3)
H1A	0.126 (4)	0.958 (2)	0.8846 (19)	0.058 (7)*
H1B	0.275 (3)	0.940 (2)	0.957 (2)	0.061 (7)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.03049 (19)	0.02730 (19)	0.02227 (18)	−0.00197 (11)	−0.00176 (12)	−0.00094 (10)
O1	0.0471 (6)	0.0292 (5)	0.0372 (6)	−0.0022 (4)	−0.0096 (5)	0.0062 (4)
O2	0.0435 (6)	0.0385 (6)	0.0391 (6)	−0.0158 (4)	−0.0076 (4)	0.0034 (4)
O3	0.0470 (7)	0.0765 (9)	0.0290 (5)	0.0134 (6)	0.0025 (5)	−0.0100 (5)
C1	0.0381 (7)	0.0221 (6)	0.0293 (6)	0.0007 (5)	0.0005 (5)	−0.0037 (5)
C2	0.0352 (6)	0.0200 (5)	0.0301 (6)	0.0036 (5)	−0.0003 (5)	0.0002 (5)
C3	0.0241 (5)	0.0198 (5)	0.0246 (6)	−0.0009 (4)	0.0024 (4)	0.0014 (4)
C4	0.0269 (6)	0.0217 (5)	0.0259 (6)	−0.0003 (4)	0.0002 (4)	0.0024 (4)
C5	0.0270 (6)	0.0258 (6)	0.0219 (6)	−0.0028 (4)	0.0001 (4)	0.0006 (4)
N1	0.0439 (7)	0.0390 (7)	0.0573 (8)	−0.0149 (6)	0.0200 (6)	−0.0172 (6)
C6	0.0250 (6)	0.0320 (7)	0.0291 (6)	−0.0030 (5)	0.0085 (5)	−0.0050 (5)
C7	0.0474 (9)	0.0421 (8)	0.0324 (7)	−0.0079 (6)	0.0019 (6)	−0.0050 (6)
C8	0.0510 (9)	0.0537 (10)	0.0417 (8)	−0.0144 (8)	0.0037 (7)	−0.0167 (7)
C10	0.0582 (10)	0.0366 (8)	0.0531 (10)	−0.0097 (7)	0.0217 (8)	0.0011 (7)
C11	0.0468 (8)	0.0393 (8)	0.0336 (7)	−0.0079 (6)	0.0081 (6)	0.0003 (6)
O1W	0.0425 (7)	0.0486 (7)	0.0417 (7)	−0.0014 (5)	0.0037 (5)	0.0042 (5)

Geometric parameters (Å, °)

S1—O3	1.4489 (12)	N1—C10	1.317 (2)
S1—O1	1.4523 (11)	N1—C8	1.331 (3)
S1—O2	1.4525 (11)	N1—H3	0.8595
S1—C5	1.7735 (12)	C6—C11	1.383 (2)
C1—C2	1.3700 (18)	C6—C7	1.398 (2)
C1—C5 ⁱ	1.4136 (17)	C6—C6 ⁱⁱ	1.491 (2)
C1—H1	0.9300	C7—C8	1.375 (2)
C2—C3	1.4154 (17)	C7—H7	0.9300
C2—H2	0.9300	C8—H8	0.9300
C3—C3 ⁱ	1.420 (2)	C10—C11	1.376 (2)
C3—C4	1.4244 (17)	C10—H10	0.9300
C4—C5	1.3698 (17)	C11—H11	0.9300
C4—H4	0.9300	O1W—H1A	0.82 (3)
C5—C1 ⁱ	1.4135 (17)	O1W—H1B	0.82 (3)
O3—S1—O1	113.29 (8)	C1 ⁱ —C5—S1	117.70 (9)
O3—S1—O2	112.23 (8)	C10—N1—C8	121.70 (14)
O1—S1—O2	112.29 (7)	C10—N1—H3	119.2
O3—S1—C5	106.32 (7)	C8—N1—H3	119.1

O1—S1—C5	107.01 (6)	C11—C6—C7	117.33 (13)
O2—S1—C5	105.01 (6)	C11—C6—C6 ⁱⁱ	121.33 (16)
C2—C1—C5 ⁱ	120.06 (11)	C7—C6—C6 ⁱⁱ	121.33 (16)
C2—C1—H1	120.0	C8—C7—C6	119.63 (15)
C5 ⁱ —C1—H1	120.0	C8—C7—H7	120.2
C1—C2—C3	120.41 (11)	C6—C7—H7	120.2
C1—C2—H2	119.8	N1—C8—C7	120.56 (15)
C3—C2—H2	119.8	N1—C8—H8	119.7
C2—C3—C3 ⁱ	119.52 (14)	C7—C8—H8	119.7
C2—C3—C4	121.43 (11)	N1—C10—C11	120.35 (16)
C3 ⁱ —C3—C4	119.05 (13)	N1—C10—H10	119.8
C5—C4—C3	119.78 (11)	C11—C10—H10	119.8
C5—C4—H4	120.1	C10—C11—C6	120.44 (15)
C3—C4—H4	120.1	C10—C11—H11	119.8
C4—C5—C1 ⁱ	121.17 (11)	C6—C11—H11	119.8
C4—C5—S1	120.87 (9)	H1A—O1W—H1B	107 (2)
C5 ⁱ —C1—C2—C3	-0.1 (2)	O1—S1—C5—C1 ⁱ	-174.50 (11)
C1—C2—C3—C3 ⁱ	1.3 (2)	O2—S1—C5—C1 ⁱ	65.99 (12)
C1—C2—C3—C4	-179.84 (12)	C11—C6—C7—C8	0.2 (2)
C2—C3—C4—C5	-178.61 (12)	C6 ⁱⁱ —C6—C7—C8	-178.78 (17)
C3 ⁱ —C3—C4—C5	0.3 (2)	C10—N1—C8—C7	0.3 (3)
C3—C4—C5—C1 ⁱ	-1.51 (19)	C6—C7—C8—N1	-0.4 (3)
C3—C4—C5—S1	172.51 (9)	C8—N1—C10—C11	0.1 (3)
O3—S1—C5—C4	132.64 (12)	N1—C10—C11—C6	-0.3 (3)
O1—S1—C5—C4	11.27 (13)	C7—C6—C11—C10	0.1 (2)
O2—S1—C5—C4	-108.24 (12)	C6 ⁱⁱ —C6—C11—C10	179.13 (16)
O3—S1—C5—C1 ⁱ	-53.13 (13)		

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

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
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N1—H3 \cdots O1W ^{vi}	0.86	1.98	2.7948 (19)	157
C1—H1 \cdots O1 ^{vii}	0.93	2.51	3.1946 (17)	130
C10—H10 \cdots O1 ^{viii}	0.93	2.60	3.294 (2)	132
C11—H11 \cdots O2 ^{ix}	0.93	2.47	3.2036 (19)	136

Symmetry codes: (iii) $-x, -y+1, -z+1$; (iv) $x, y+1, z+1$; (v) $-x, -y, -z+1$; (vi) $x, y-1, z$; (vii) $x+1/2, -y+1/2, z+1/2$; (viii) $x, y, z+1$; (ix) $-x+1/2, y+1/2, -z+3/2$.