



Crystal structure of dilithium biphenyl-4,4'-disulfonate dihydrate

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Received 31 October 2023

Accepted 4 December 2023

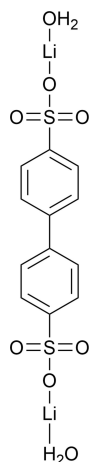
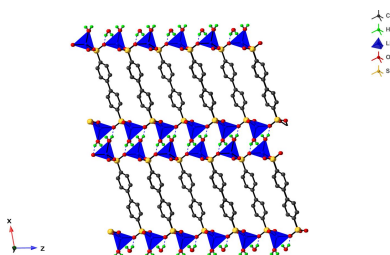
Edited by T. Akitsu, Tokyo University of Science, Japan

Keywords: crystal structure; hydrogen bonding; Li ion.**CCDC reference:** 2295223**Supporting information:** this article has supporting information at journals.iucr.org/e

The asymmetric unit of the title compound, μ -biphenyl-4,4'-disulfonato-bis(aqualithium), $[\text{Li}_2(\text{C}_{12}\text{H}_8\text{O}_6\text{S}_2)(\text{H}_2\text{O})_2]$ or $\text{Li}_2[\text{Bph}(\text{SO}_3)_2](\text{H}_2\text{O})_2$, consists of an Li ion, half of the diphenyl-4,4'-disulfonate $[\text{Bph}(\text{SO}_3^-)_2]$ ligand, and a water molecule. The Li ion exhibits a four-coordinate tetrahedral geometry with three oxygen atoms of the $\text{Bph}(\text{SO}_3^-)_2$ ligands and a water molecule. The tetrahedral LiO_4 units, which are interconnected by biphenyl moieties, form a layer structure parallel to (100). These layers are further connected by hydrogen-bonding interactions to yield a three-dimensional network.

1. Chemical context

Coordination networks (CNs) are crystalline materials composed of infinite arrays of *s*-block metal ions, connected by organic linkers, forming chain, layer or 3-D networks. These materials offer several advantages such as being non-toxic, abundant on the planet, and cheap and provide good results when gravimetric methods are used (Banerjee & Parise 2011). Li-dicarboxylates may be good candidates as electrode materials for eco-friendly alternatives to other inorganic materials, and have been reported for use in battery applications (Armand *et al.*, 2009; Ogihara *et al.*, 2014, 2023; Yasuda & Ogihara, 2014; Mikita *et al.*, 2020). To improve our chemistry and electrode applications, we investigated CNs using disulfonate ligands. While the structures of dicarboxylate salts of alkali metals have been reported (Banerjee & Parise, 2011), the CNs of the disulfonates of alkali metals are still scarcely reported. Our present investigation focuses on the use of diphenyl-4,4'-disulfonic acid $[\text{Bph}(\text{SO}_3\text{H})_2]$ as a structural building block in the synthesis of CNs. Here, we report a rare example of a crystal structure of a Li-disulfonate CN material.



2. Structural commentary

The title compound $[\text{Li}_2(\text{Bph}(\text{SO}_3^-)_2)(\text{H}_2\text{O})_2]$ (Fig. 1) consists of two Li cations, two water molecules, and a diphenyl-4,4'-disulfonate $[\text{Bph}(\text{SO}_3^-)_2]$ ligand. Its asymmetric unit consists of an Li ion, half of the $\text{Bph}(\text{SO}_3^-)_2$ ligand, and a water molecule. The key feature of the structure is a di-periodic layer structure in which the layers are built up by LiO_4 units bridged by $\text{Bph}(\text{SO}_3^-)_2$ ligands (Fig. 2). The biphenyl groups of the ligands exhibit a planar and herringbone-type arrangement in the layer (Fig. 3). Two parallel biphenyl groups are stacked not in a face-to-face but rather in a parallel-displaced fashion. The slippage of the layers is 4.43 Å and the nearest intermolecular centroid-to-centroid distance between adjacent parallel phenyl groups is 5.47 Å. The angle formed by the two centroids of the phenyl rings and the ring plane is 34.5°. Intermolecular distances between the carbon atoms of the planar biphenyl moieties of 3.66 Å are indicative of some degree of π - π stacking interaction along the crystallographic b -axis direction. Similar herringbone-type stacking of aromatic organic moieties are found in Li-dicarboxylate CN materials in which herringbone-type stacking structures play an important role in electron mobilities and electrode performance (Ogihara *et al.*, 2017; Ozawa *et al.*, 2018). The Li cation exhibits a four-coordinate tetrahedral geometry formed by an oxygen atom of a coordinated water molecule and three oxygen atoms coming from three different $\text{Bph}(\text{SO}_3^-)_2$ ligands. The tetrahedrons are connected to one another by O–S–O bridges of the disulfonate group, and the shortest Li···Li distance is 4.80 Å. All the oxygen atoms of a sulfonate group coordinate to different Li cations. Thus, each sulfonate group

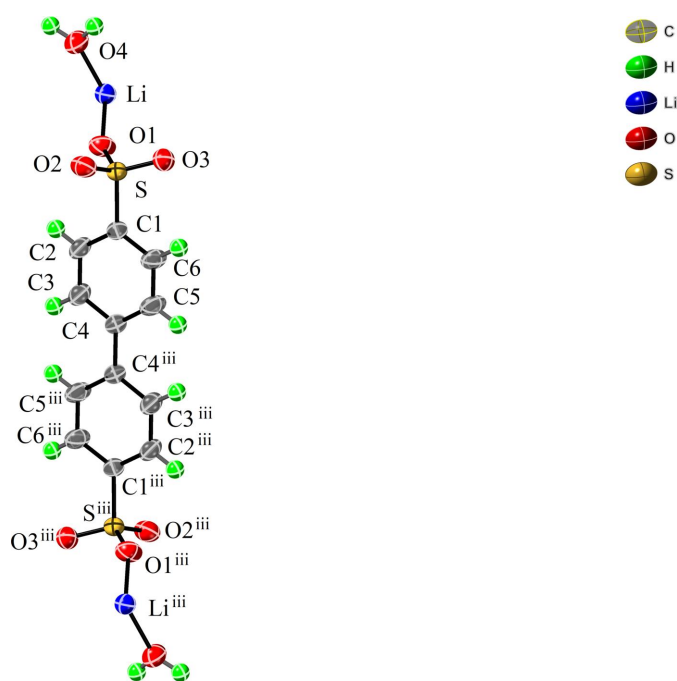


Figure 1
Part of the crystal structure of the title compound with labeling scheme and 50% probability displacement ellipsoids. [Symmetry code: (iii) $-x + 2, -y + 1, -z + 1$.]

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O4}-\text{H4}\cdots\text{O2}^{\text{i}}$	0.89 (5)	2.17 (5)	3.016 (3)	157 (5)
$\text{O4}-\text{H1}\cdots\text{O3}^{\text{ii}}$	2.41 (5)	3.21 (1)	0.89 (5)	149 (4)
$\text{O4}-\text{H1}\cdots\text{O4}^{\text{iii}}$	2.50 (5)	3.14 (1)	0.89 (5)	129 (4)

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

coordinates to three Li cations to obtain a di-periodic layer. The bond distances between the Li cation and the oxygen atoms lie in the range 1.901 (5)–1.944 (5) Å at angles of 103.7 (2)–114.8 (2)°, which are shorter than those of reported Na_2 -disulfonate [2.313 (3)–2.560 (3) Å] and K_2 -disulfonate [2.657 (3)–3.079 (4) Å] complexes (Albat & Stock 2016; Smith *et al.*, 2007). Similar trends of bond distances are observed in alkali metal-carboxylate network materials (Banerjee & Parise, 2011).

3. Supramolecular features

The hydrogen atoms of the coordinated water molecules are oriented in such a direction exiting the di-periodic layers to form hydrogen-bonding interactions (Table 1). A hydrogen atom of the water molecule (H4) and an oxygen atom of the $\text{Bph}(\text{SO}_3^-)_2$ ligand acts as a hydrogen-bond donor and a hydrogen-bond acceptor, respectively, resulting in a three-dimensional hydrogen-bonding network (Fig. 2). Because of the hydrogen-bonding interaction, another hydrogen atom of the coordinated water molecule (H1) is directed towards the oxygen atom of the $\text{Bph}(\text{SO}_3^-)_2$ ligand, where the distance between the oxygen atoms of 3.204 (3) Å is indicative of some degree of interaction. Li_2 -dicarboxylates where the dicarboxylate is terephthalate, biphenyl dicarboxylate or naphthalene dicarboxylate, also consist of LiO_4 layers (Banerjee & Parise 2011; Kaduk *et al.*, 2000; Armand *et al.*, 2009; Banerjee

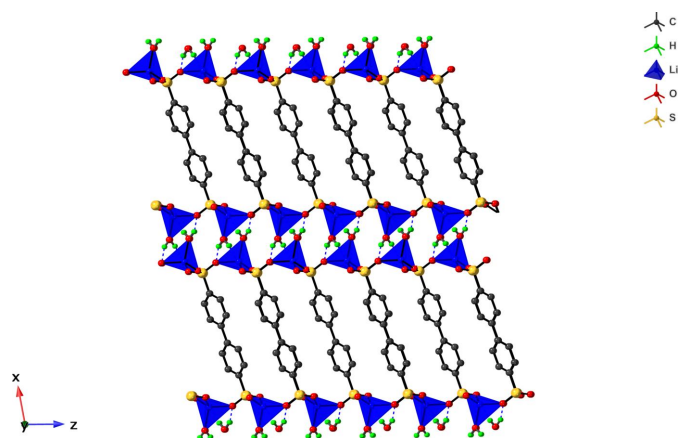


Figure 2
View of the layer structure of the title compound along the crystallographic b -axis. The layer is built up by LiO_4 tetrahedra connected by the organic ligands. The dashed lines represent hydrogen bonds between the oxygen atoms of the $\text{Bph}(\text{SO}_3^-)_2$ ligands and the coordinated water molecules.

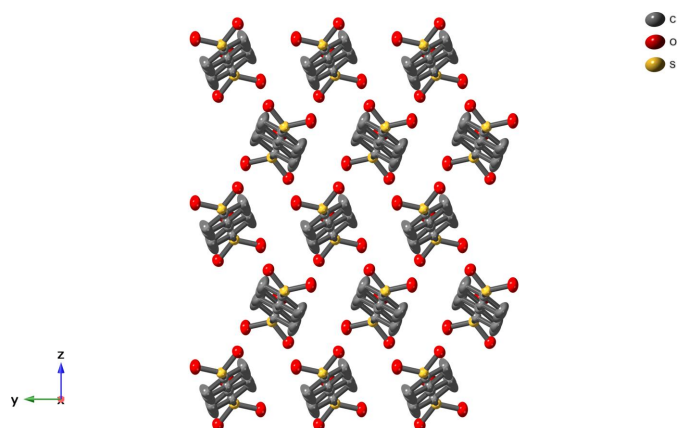


Figure 3
View of the herringbone-type stacking structure in the layer along the crystallographic *a*-axis.

et al., 2009*a,b*; Ogiyama *et al.*, 2014). In contrast to the sulfonate compound, four oxygen atoms come from the carboxylate group and LiO_4 units share the edges and corners of the tetrahedrons, forming a coordination-bonded three-dimensional structure in these Li_2 -dicarboxylates.

4. Database survey

A survey of the Cambridge Structural Database (CSD, v5.44, April 2023; Groom *et al.*, 2016) for structures with biphenyl and sulfonate and alkali metals resulted in seven hits. Of these, the alkali metal-coordinated compounds are a potassium complex (HIQKEY; Smith *et al.*, 2007), which is related to this work, and a sodium complex (SIWVUP; Anderson *et al.*, 1998). No coordination bonds are found in other alkali-metal salts. Our structure is a rare example of the crystal structure of an Li-disulfonate CN material.

5. Synthesis and crystallization

An aqueous solution (5 mL) of LiOH (0.28 g, 1 mmol L^{-1}) was added to an aqueous solution of Bph(SO_3H)₂ (1.8 g, 2 mmol L^{-1}). Colorless crystals began to form at ambient temperature in one month. One of these crystals was used for X-ray crystallography.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Hydrogen-atom parameters were fully refined. The final cycle of the full-matrix least-squares refinement on F^2 was based on 1666 observed reflections and 133 variable parameters.

Acknowledgements

We would like to thank Dr Mitsutaro Umehara for the help with the database survey.

Table 2
Experimental details.

Crystal data	
Chemical formula	$[\text{Li}_2(\text{C}_{12}\text{H}_8\text{O}_6\text{S}_2)(\text{H}_2\text{O})_2]$
M_r	362.22
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	286
a, b, c (Å)	15.8584 (11), 5.3693 (4), 8.8636 (6)
β (°)	99.994 (7)
V (Å ³)	743.27 (9)
Z	2
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	0.40
Crystal size (mm)	0.50 × 0.40 × 0.20
Data collection	
Diffractometer	Rigaku R-AXIS RAPID
Absorption correction	Multi-scan (ABSCOR; Rigaku, 1995)
T_{\min}, T_{\max}	0.213, 0.924
No. of measured, independent and observed [$F^2 > 2.0\sigma(F^2)$] reflections	9858, 1666, 1490
R_{int}	0.067
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.649
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.061, 0.159, 1.12
No. of reflections	1666
No. of parameters	133
No. of restraints	3
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.74, -0.28

Computer programs: RAPID-AUTO (Rigaku, 1995), SHELXT2014/5 (Sheldrick, 2015*a*), SHELXL2018/3 (Sheldrick, 2015*b*) and CrystalStructure (Rigaku, 2019).

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supporting information

Acta Cryst. (2024). E80, 22-24 [https://doi.org/10.1107/S2056989023010411]

Crystal structure of dilithium biphenyl-4,4'-disulfonate dihydrate

Hitoshi Kumagai, Satoshi Kawata and Nobuhiro Ogihara

Computing details

 μ -Biphenyl-4,4'-disulfonato-bis(aqualithium)

Crystal data

[Li₂(C₁₂H₈O₆S₂)(H₂O)₂]

$M_r = 362.22$

Monoclinic, $P2_1/c$

$a = 15.8584$ (11) Å

$b = 5.3693$ (4) Å

$c = 8.8636$ (6) Å

$\beta = 99.994$ (7)°

$V = 743.27$ (9) Å³

$Z = 2$

$F(000) = 372.00$

$D_x = 1.618$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71075$ Å

Cell parameters from 17604 reflections

$\theta = 3.2$ – 27.6 °

$\mu = 0.40$ mm⁻¹

$T = 286$ K

Block, colorless

$0.50 \times 0.40 \times 0.20$ mm

Data collection

Rigaku R-AXIS RAPID

diffractometer

Detector resolution: 10.000 pixels mm⁻¹

ω scans

Absorption correction: multi-scan

(ABSCOR; Rigaku, 1995)

$T_{\min} = 0.213$, $T_{\max} = 0.924$

9858 measured reflections

1666 independent reflections

1490 reflections with $F^2 > 2.0\sigma(F^2)$

$R_{\text{int}} = 0.067$

$\theta_{\max} = 27.5$ °, $\theta_{\min} = 3.9$ °

$h = -20 \rightarrow 20$

$k = -6 \rightarrow 6$

$l = -11 \rightarrow 11$

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.061$

$wR(F^2) = 0.159$

$S = 1.12$

1666 reflections

133 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

All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0948P)^2 + 0.3642P]$

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

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

$\Delta\rho_{\max} = 0.74$ e Å⁻³

$\Delta\rho_{\min} = -0.28$ e Å⁻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.

Refinement. Refinement was performed using all reflections. The weighted R-factor (wR) and goodness of fit (S) are based on F^2 . R-factor (gt) are based on F. The threshold expression of $F^2 > 2.0 \text{ sigma}(F^2)$ is used only for calculating R-factor (gt).

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	0.67846 (4)	0.56370 (10)	0.59448 (6)	0.0341 (3)
O1	0.66681 (15)	0.8238 (3)	0.6295 (3)	0.0550 (6)
O2	0.62416 (15)	0.4887 (5)	0.4532 (2)	0.0566 (6)
O3	0.67041 (13)	0.4012 (4)	0.7215 (2)	0.0451 (5)
O4	0.49748 (14)	1.0921 (5)	0.6579 (3)	0.0587 (6)
C1	0.78551 (17)	0.5384 (4)	0.5648 (3)	0.0346 (5)
C2	0.81715 (19)	0.7143 (6)	0.4756 (4)	0.0566 (8)
C3	0.90075 (19)	0.6964 (6)	0.4499 (4)	0.0588 (9)
C4	0.95484 (15)	0.5075 (4)	0.5137 (3)	0.0354 (5)
C5	0.9221 (2)	0.3349 (6)	0.6046 (5)	0.0628 (9)
C6	0.8381 (2)	0.3489 (6)	0.6297 (5)	0.0608 (9)
Li1	0.6195 (3)	1.0777 (8)	0.7388 (5)	0.0413 (9)
H1	0.464 (3)	0.986 (9)	0.696 (7)	0.13 (2)*
H2	0.778 (3)	0.874 (10)	0.441 (5)	0.083 (13)*
H3	0.916 (3)	0.789 (10)	0.375 (6)	0.099 (16)*
H4	0.462 (3)	1.197 (9)	0.600 (6)	0.12 (2)*
H5	0.954 (3)	0.196 (9)	0.644 (5)	0.078 (13)*
H6	0.823 (3)	0.262 (9)	0.695 (6)	0.096 (16)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0333 (4)	0.0345 (4)	0.0359 (4)	0.0043 (2)	0.0093 (2)	−0.0016 (2)
O1	0.0641 (13)	0.0359 (11)	0.0724 (13)	0.0116 (9)	0.0324 (11)	0.0000 (9)
O2	0.0377 (11)	0.0905 (17)	0.0413 (10)	0.0008 (10)	0.0057 (9)	−0.0115 (10)
O3	0.0481 (11)	0.0404 (9)	0.0485 (10)	−0.0001 (8)	0.0131 (8)	0.0050 (8)
O4	0.0396 (12)	0.0691 (14)	0.0666 (14)	0.0048 (10)	0.0073 (10)	0.0160 (11)
C1	0.0334 (12)	0.0316 (11)	0.0386 (11)	0.0022 (8)	0.0060 (9)	−0.0036 (8)
C2	0.0352 (13)	0.0581 (17)	0.077 (2)	0.0112 (12)	0.0120 (13)	0.0322 (15)
C3	0.0356 (14)	0.0630 (19)	0.079 (2)	0.0077 (12)	0.0137 (14)	0.0355 (16)
C4	0.0302 (13)	0.0337 (11)	0.0414 (12)	0.0007 (8)	0.0042 (10)	−0.0033 (9)
C5	0.0479 (17)	0.0465 (15)	0.100 (3)	0.0186 (13)	0.0298 (17)	0.0301 (17)
C6	0.0489 (16)	0.0460 (15)	0.095 (2)	0.0149 (13)	0.0333 (17)	0.0300 (17)
Li1	0.041 (2)	0.041 (2)	0.043 (2)	0.0029 (17)	0.0106 (18)	0.0036 (16)

Geometric parameters (\AA , $^\circ$)

S1—O3	1.4472 (19)	C1—C2	1.381 (4)
S1—O2	1.448 (2)	C2—C3	1.387 (4)
S1—O1	1.4492 (19)	C2—H2	1.07 (5)
S1—C1	1.768 (3)	C3—C4	1.384 (4)

O1—Li1	1.901 (5)	C3—H3	0.90 (5)
O2—Li1 ⁱ	1.922 (5)	C4—C5	1.387 (4)
O3—Li1 ⁱⁱ	1.933 (5)	C4—C4 ⁱⁱⁱ	1.496 (5)
O4—Li1	1.944 (5)	C5—C6	1.390 (4)
O4—H1	0.88 (2)	C5—H5	0.94 (5)
O4—H4	0.89 (2)	C6—H6	0.81 (5)
C1—C6	1.377 (4)		
O3—S1—O2	112.66 (14)	C4—C3—C2	121.8 (3)
O3—S1—O1	112.48 (12)	C4—C3—H3	119 (3)
O2—S1—O1	112.00 (15)	C2—C3—H3	118 (3)
O3—S1—C1	106.61 (11)	C3—C4—C5	117.3 (2)
O2—S1—C1	107.01 (12)	C3—C4—C4 ⁱⁱⁱ	121.1 (3)
O1—S1—C1	105.51 (12)	C5—C4—C4 ⁱⁱⁱ	121.6 (3)
S1—O1—Li1	151.24 (19)	C4—C5—C6	121.5 (3)
S1—O2—Li1 ⁱ	145.2 (2)	C4—C5—H5	121 (3)
S1—O3—Li1 ⁱⁱ	134.28 (19)	C6—C5—H5	118 (3)
Li1—O4—H1	117 (4)	C1—C6—C5	120.1 (3)
Li1—O4—H4	136 (4)	C1—C6—H6	119 (4)
H1—O4—H4	106 (4)	C5—C6—H6	120 (4)
C6—C1—C2	119.4 (3)	O1—Li1—O2 ^{iv}	114.8 (2)
C6—C1—S1	121.5 (2)	O1—Li1—O3 ^v	113.3 (2)
C2—C1—S1	119.09 (19)	O2 ^{iv} —Li1—O3 ^v	107.5 (2)
C1—C2—C3	119.9 (3)	O1—Li1—O4	107.2 (3)
C1—C2—H2	117 (2)	O2 ^{iv} —Li1—O4	103.7 (2)
C3—C2—H2	122 (2)	O3 ^v —Li1—O4	109.8 (2)
O3—S1—O1—Li1	-27.3 (5)	O2—S1—C1—C2	74.3 (3)
O2—S1—O1—Li1	100.8 (5)	O1—S1—C1—C2	-45.2 (3)
C1—S1—O1—Li1	-143.1 (4)	C6—C1—C2—C3	1.1 (5)
O3—S1—O2—Li1 ⁱ	-131.3 (4)	S1—C1—C2—C3	-179.5 (3)
O1—S1—O2—Li1 ⁱ	100.7 (4)	C1—C2—C3—C4	-1.1 (6)
C1—S1—O2—Li1 ⁱ	-14.4 (4)	C2—C3—C4—C5	0.2 (5)
O2—S1—O3—Li1 ⁱⁱ	12.8 (3)	C2—C3—C4—C4 ⁱⁱⁱ	-179.3 (3)
O1—S1—O3—Li1 ⁱⁱ	140.6 (3)	C3—C4—C5—C6	0.6 (6)
C1—S1—O3—Li1 ⁱⁱ	-104.2 (3)	C4 ⁱⁱⁱ —C4—C5—C6	-179.8 (4)
O3—S1—C1—C6	14.5 (3)	C2—C1—C6—C5	-0.3 (6)
O2—S1—C1—C6	-106.3 (3)	S1—C1—C6—C5	-179.7 (3)
O1—S1—C1—C6	134.3 (3)	C4—C5—C6—C1	-0.6 (6)
O3—S1—C1—C2	-165.0 (2)		

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O4—H4 \cdots O2 ^{vi}	0.89 (5)	2.17 (5)	3.016 (3)	157 (5)

O4—H1...O3 ^{vii}	2.41 (5)	3.21 (1)	0.89 (5)	149 (4)
O4—H1...O4 ^{viii}	2.50 (5)	3.14 (1)	0.89 (5)	129 (4)

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