

Acta Crystallographica Section E

## Structure Reports

Online

ISSN 1600-5368

## Methyl 2-(5-bromo-3-methylsulfinyl-1-benzofuran-2-yl)acetate

 Hong Dae Choi,<sup>a</sup> Pil Ja Seo,<sup>a</sup> Byung Wha Son<sup>b</sup> and Uk Lee<sup>b\*</sup>
<sup>a</sup>Department of Chemistry, Donggeui University, San 24 Kaya-dong, Busanjin-gu, Busan 614-714, Republic of Korea, and <sup>b</sup>Department of Chemistry, Pukyong National University, 599-1 Daeyeon 3-dong, Nam-gu, Busan 608-737, Republic of Korea

Correspondence e-mail: uklee@pknu.ac.kr

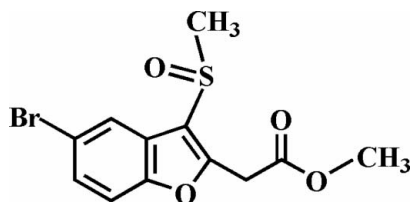
Received 30 October 2008; accepted 14 November 2008

 Key indicators: single-crystal X-ray study;  $T = 298$  K; mean  $\sigma(\text{C}-\text{C}) = 0.005$  Å;  $R$  factor = 0.035;  $wR$  factor = 0.099; data-to-parameter ratio = 15.6.

The title compound,  $\text{C}_{12}\text{H}_{11}\text{BrO}_4\text{S}$ , was synthesized by the oxidation of methyl 2-(5-bromo-3-methylsulfinyl-1-benzofuran-2-yl)acetate with 3-chloroperoxybenzoic acid. The O atom and the methyl group of the methylsulfinyl substituent lie on opposite sides of the plane of the benzofuran ring system. The crystal structure is stabilized by  $\text{C}-\text{H}\cdots\pi$  interactions, involving a methyl H atom and the benzene ring of a neighbouring molecule, and by weak intermolecular  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonds.

## Related literature

For the crystal structures of similar methyl 2-(3-methylsulfinyl-1-benzofuran-2-yl)acetate derivatives, see: Choi *et al.* (2008*a,b*).



## Experimental

## Crystal data

$\text{C}_{12}\text{H}_{11}\text{BrO}_4\text{S}$	$\gamma = 69.082$ (1) $^\circ$
$M_r = 331.18$	$V = 664.17$ (8) Å <sup>3</sup>
Triclinic, $P\bar{1}$	$Z = 2$
$a = 7.9696$ (5) Å	Mo $K\alpha$ radiation
$b = 9.1146$ (6) Å	$\mu = 3.25$ mm <sup>-1</sup>
$c = 10.3100$ (7) Å	$T = 298$ (2) K
$\alpha = 72.587$ (1) $^\circ$	$0.40 \times 0.30 \times 0.20$ mm
$\beta = 78.716$ (1) $^\circ$	

## Data collection

Bruker SMART CCD diffractometer	3786 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1999)	2560 independent reflections
$T_{\min} = 0.327$ , $T_{\max} = 0.530$	2084 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.015$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$	164 parameters
$wR(F^2) = 0.099$	H-atom parameters constrained
$S = 0.98$	$\Delta\rho_{\text{max}} = 0.35$ e Å <sup>-3</sup>
2560 reflections	$\Delta\rho_{\text{min}} = -0.80$ e Å <sup>-3</sup>

Table 1

 Hydrogen-bond geometry (Å,  $^\circ$ ).

 C<sub>g</sub> is the centroid of the benzene ring C2–C7.

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{C3}-\text{H3}\cdots\text{O2}^i$	0.93	2.43	3.334 (4)	163
$\text{C9}-\text{H9B}\cdots\text{O1}^{ii}$	0.97	2.59	3.555 (3)	171
$\text{C9}-\text{H9A}\cdots\text{O2}^{iii}$	0.97	2.22	3.177 (4)	169
$\text{C12}-\text{H12B}\cdots\text{Cg}^{iv}$	0.96	2.99	3.903 (4)	159

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

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 (Farrugia, 1997) and DIAMOND (Brandenburg, 1998); software used to prepare material for publication: SHELXL97.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SU2077).

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## supporting information

*Acta Cryst.* (2008). E64, o2397 [doi:10.1107/S1600536808037768]

## Methyl 2-(5-bromo-3-methylsulfinyl-1-benzofuran-2-yl)acetate

Hong Dae Choi, Pil Ja Seo, Byeng Wha Son and Uk Lee

### S1. Comment

As a part of our ongoing research on the synthesis and structure of methyl 2-(3-methylsulfinyl-1-benzofuran-2-yl)acetate analogues, the crystal structure of methyl 2-(5-methyl-3-methylsulfinyl-1-benzofuran-2-yl)acetate (Choi *et al.*, 2008a) and methyl 2-(5-chloro-3-methylsulfinyl-1-benzofuran-2-yl) acetate (Choi *et al.*, 2008b) have been reported. Here we describe the crystal structure of the title compound (I), synthesized by the oxidation of methyl 2-(5-bromo-3-methylsulfinyl-1-benzofuran-2-yl)acetate with 3-chloroperoxybenzoic acid.

The molecular structure of compound (I) is illustrated in Fig. 1. The benzofuran unit is essentially planar, with a mean deviation of 0.013 (2) Å from the least-squares plane defined by the nine constituent atoms.

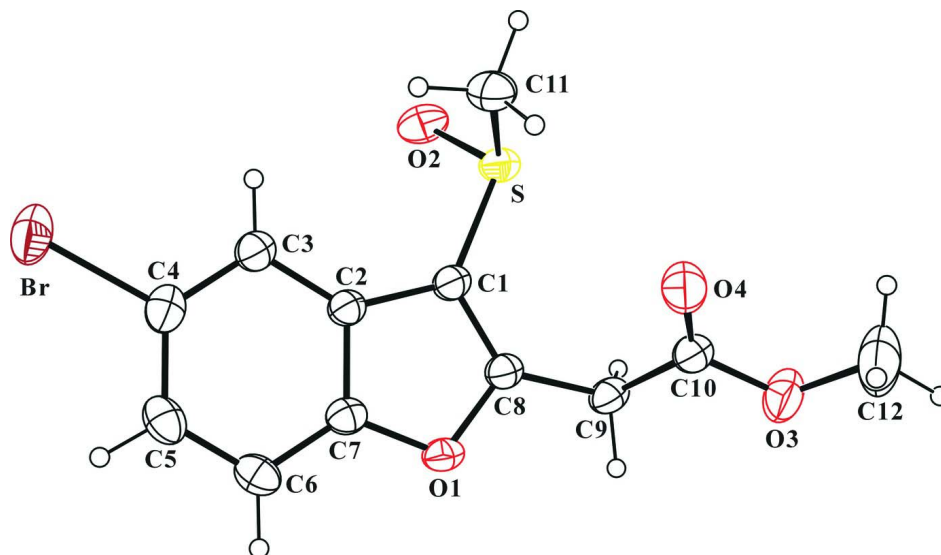
The crystal packing of compound (I) (see Fig. 2) is stabilized by intermolecular C—H $\cdots$  $\pi$  interactions between an H-atom of the C12-methyl group and the benzene ring of the benzofuran fragment, with a C12—H12B $\cdots$ Cg<sup>iv</sup> separation of 3.903 (4) Å (Fig. 2 and Table 1; Cg is the centroid of benzene ring C2–C7, symmetry codes as in Fig. 2). In addition, the molecular packing exhibits three intermolecular C—H $\cdots$ O hydrogen bonds (Fig. 2 & Table 1).

### S2. Experimental

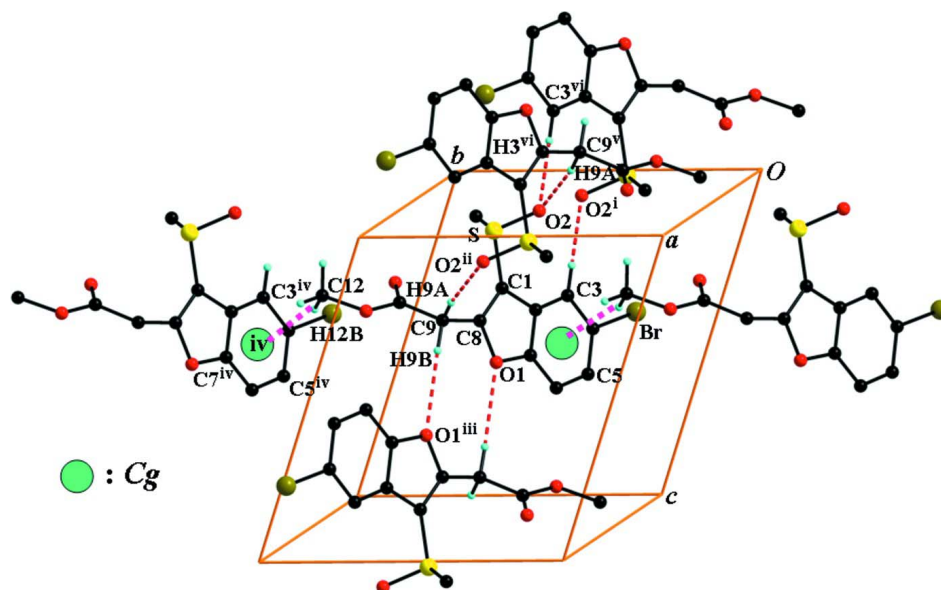
77% 3-Chloroperoxybenzoic acid (190 mg, 0.85 mmol) was added in small portions to a stirred solution of methyl 2-(5-bromo-3-methylsulfinyl-1-benzofuran-2-yl)acetate (252 mg, 0.8 mmol) in dichloromethane (30 ml) at 273 K. After stirring for 3 h at rt, the mixture was washed with a saturated sodium bicarbonate solution and the organic layer was separated, dried over magnesium sulfate, filtered and concentrated under vacuum. The residue was purified by column chromatography (hexane-ethyl acetate 1:2, v/v) to afford compound (I) as a colorless solid [yield 86%, m.p. 405–406 K;  $R_f$  = 0.45 (hexane-ethyl acetate, 1:2, v/v)]. Single crystals, suitable for X-ray analysis, were prepared by evaporation of a solution of compound (I) in benzene at rt. Spectroscopic analysis: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  3.06 (s, 3H), 3.75 (s, 3H), 4.04 (s, 2H), 7.34–7.53 (m, 2H), 7.44 (d, J = 8.80 Hz, 1H), 8.07 (d, J = 1.84 Hz, 1H); EI—MS 332 [ $M+2$ ], 330 [ $M^+$ ].

### S3. Refinement

All the H-atoms were geometrically positioned and refined using a riding model: C—H = 0.93 (aromatic), 0.97 (methylene), and 0.96 Å (methyl) H atoms, with  $U_{iso}(H) = 1.2U_{eq}(C)$  (aromatic & methylene), and  $1.5U_{eq}(C)$  (methyl) H atoms.


**Figure 1**

The molecular structure of compound (I), showing the atom numbering scheme and displacement ellipsoids drawn at the 30% probability level.


**Figure 2**

A view of the crystal packing of compound (I), showing the C—H $\cdots$  $\pi$  and C—H $\cdots$ O interactions as dotted lines. *Cg* denotes the ring centroid. [Symmetry codes: (i)  $-x + 1, -y + 1, -z$ ; (ii)  $-x + 2, -y + 1, -z + 1$ ; (iii)  $-x + 2, -y + 1, -z$ ; (iv)  $x, y + 1, z$ ; (v)  $-x + 2, -y + 1, -z$ ; (vi)  $-x + 1, -y + 1, -z$ .]

### Methyl 2-(5-bromo-3-methylsulfinyl-1-benzofuran-2-yl)acetate

#### Crystal data

$C_{12}H_{11}BrO_4S$

$M_r = 331.18$

Triclinic,  $P\bar{1}$

Hall symbol:  $-P\ 1$

$a = 7.9696(5)\ \text{\AA}$

$b = 9.1146(6)\ \text{\AA}$

$c = 10.3100$  (7) Å  
 $\alpha = 72.587$  (1)°  
 $\beta = 78.716$  (1)°  
 $\gamma = 69.082$  (1)°  
 $V = 664.17$  (8) Å<sup>3</sup>  
 $Z = 2$   
 $F(000) = 332$   
 $D_x = 1.656$  Mg m<sup>-3</sup>

Melting point = 405–406 K  
 Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å  
 Cell parameters from 1892 reflections  
 $\theta = 2.1$ – $27.8$ °  
 $\mu = 3.25$  mm<sup>-1</sup>  
 $T = 298$  K  
 Block, colourless  
 $0.40 \times 0.30 \times 0.20$  mm

*Data collection*

Bruker SMART CCD  
 diffractometer  
 Radiation source: fine-focus sealed tube  
 Graphite monochromator  
 Detector resolution: 10.0 pixels mm<sup>-1</sup>  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan  
 (SADABS; Sheldrick, 1999)  
 $T_{\min} = 0.327$ ,  $T_{\max} = 0.530$

3786 measured reflections  
 2560 independent reflections  
 2084 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.015$   
 $\theta_{\max} = 26.0$ °,  $\theta_{\min} = 2.5$ °  
 $h = -9 \rightarrow 5$   
 $k = -11 \rightarrow 11$   
 $l = -12 \rightarrow 12$

*Refinement*

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.035$   
 $wR(F^2) = 0.099$   
 $S = 0.98$   
 2560 reflections  
 164 parameters  
 0 restraints  
 Primary atom site location: structure-invariant  
 direct methods

Secondary atom site location: difference Fourier  
 map  
 Hydrogen site location: inferred from  
 neighbouring sites  
 H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0506P)^2 + 0.5362P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.35$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.80$  e Å<sup>-3</sup>

*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.

**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<sup>2</sup>)*

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
Br	0.26775 (5)	0.20066 (4)	0.38327 (5)	0.07396 (18)
S	0.73771 (11)	0.63026 (10)	0.03527 (7)	0.0505 (2)
O1	0.8367 (3)	0.4636 (2)	0.42105 (19)	0.0450 (5)
O2	0.7437 (4)	0.4993 (3)	-0.0262 (2)	0.0668 (7)
O3	1.0188 (3)	0.8974 (3)	0.2240 (3)	0.0718 (7)
O4	0.7513 (3)	0.8989 (3)	0.1905 (3)	0.0724 (7)
C1	0.7429 (4)	0.5435 (3)	0.2117 (3)	0.0422 (6)
C2	0.6455 (4)	0.4363 (3)	0.2987 (3)	0.0408 (6)

C3	0.5121 (4)	0.3798 (3)	0.2824 (3)	0.0466 (7)
H3	0.4651	0.4089	0.1993	0.056*
C4	0.4537 (4)	0.2784 (4)	0.3965 (4)	0.0510 (7)
C5	0.5227 (5)	0.2305 (4)	0.5228 (4)	0.0550 (8)
H5	0.4796	0.1604	0.5964	0.066*
C6	0.6542 (4)	0.2870 (4)	0.5381 (3)	0.0526 (8)
H6	0.7023	0.2566	0.6210	0.063*
C7	0.7117 (4)	0.3904 (3)	0.4254 (3)	0.0419 (6)
C8	0.8535 (4)	0.5552 (3)	0.2893 (3)	0.0413 (6)
C9	0.9848 (4)	0.6447 (4)	0.2609 (3)	0.0473 (7)
H9A	1.0742	0.6117	0.1877	0.057*
H9B	1.0470	0.6145	0.3416	0.057*
C10	0.9012 (4)	0.8259 (4)	0.2215 (3)	0.0483 (7)
C11	0.5088 (5)	0.7628 (4)	0.0366 (4)	0.0637 (9)
H11A	0.4834	0.8234	-0.0551	0.096*
H11B	0.4918	0.8363	0.0916	0.096*
H11C	0.4285	0.6997	0.0740	0.096*
C12	0.9545 (7)	1.0738 (5)	0.1880 (7)	0.1065 (18)
H12A	1.0493	1.1133	0.1927	0.160*
H12B	0.8527	1.1114	0.2506	0.160*
H12C	0.9191	1.1131	0.0968	0.160*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Br	0.0572 (2)	0.0513 (2)	0.1163 (4)	-0.02436 (17)	-0.0138 (2)	-0.0133 (2)
S	0.0535 (5)	0.0626 (5)	0.0392 (4)	-0.0239 (4)	-0.0121 (3)	-0.0067 (3)
O1	0.0450 (11)	0.0494 (11)	0.0411 (10)	-0.0113 (9)	-0.0157 (9)	-0.0094 (9)
O2	0.0746 (17)	0.0842 (17)	0.0506 (13)	-0.0229 (14)	-0.0132 (12)	-0.0286 (12)
O3	0.0615 (15)	0.0579 (14)	0.108 (2)	-0.0253 (12)	-0.0235 (14)	-0.0201 (14)
O4	0.0561 (15)	0.0537 (14)	0.103 (2)	-0.0180 (12)	-0.0308 (14)	0.0016 (13)
C1	0.0433 (15)	0.0454 (15)	0.0412 (14)	-0.0144 (13)	-0.0090 (12)	-0.0122 (12)
C2	0.0431 (15)	0.0361 (14)	0.0437 (15)	-0.0096 (12)	-0.0107 (12)	-0.0105 (12)
C3	0.0475 (17)	0.0398 (15)	0.0533 (17)	-0.0105 (13)	-0.0115 (13)	-0.0131 (13)
C4	0.0404 (16)	0.0385 (15)	0.073 (2)	-0.0091 (13)	-0.0074 (15)	-0.0153 (15)
C5	0.0507 (18)	0.0400 (16)	0.0600 (19)	-0.0085 (14)	-0.0028 (15)	-0.0010 (14)
C6	0.0524 (18)	0.0459 (17)	0.0472 (17)	-0.0063 (14)	-0.0094 (14)	-0.0025 (13)
C7	0.0393 (15)	0.0379 (14)	0.0455 (15)	-0.0044 (12)	-0.0102 (12)	-0.0117 (12)
C8	0.0424 (16)	0.0395 (14)	0.0429 (15)	-0.0099 (12)	-0.0103 (12)	-0.0116 (12)
C9	0.0423 (16)	0.0534 (17)	0.0510 (16)	-0.0155 (13)	-0.0136 (13)	-0.0142 (14)
C10	0.0496 (18)	0.0541 (17)	0.0458 (16)	-0.0208 (15)	-0.0087 (13)	-0.0116 (14)
C11	0.063 (2)	0.059 (2)	0.066 (2)	-0.0120 (17)	-0.0275 (17)	-0.0062 (17)
C12	0.100 (4)	0.057 (2)	0.175 (5)	-0.034 (2)	-0.038 (4)	-0.019 (3)

*Geometric parameters (Å, °)*

Br—C4	1.898 (3)	C4—C5	1.400 (5)
S—O2	1.493 (3)	C5—C6	1.374 (5)

S—C1	1.755 (3)	C5—H5	0.9300
S—C11	1.793 (4)	C6—C7	1.376 (4)
O1—C7	1.370 (3)	C6—H6	0.9300
O1—C8	1.375 (3)	C8—C9	1.481 (4)
O3—C10	1.327 (4)	C9—C10	1.501 (4)
O3—C12	1.454 (5)	C9—H9A	0.9700
O4—C10	1.195 (4)	C9—H9B	0.9700
C1—C8	1.350 (4)	C11—H11A	0.9600
C1—C2	1.451 (4)	C11—H11B	0.9600
C2—C3	1.391 (4)	C11—H11C	0.9600
C2—C7	1.395 (4)	C12—H12A	0.9600
C3—C4	1.377 (4)	C12—H12B	0.9600
C3—H3	0.9300	C12—H12C	0.9600
O2—S—C1	106.07 (14)	C6—C7—C2	123.2 (3)
O2—S—C11	106.21 (17)	C1—C8—O1	111.1 (2)
C1—S—C11	98.55 (16)	C1—C8—C9	133.3 (3)
C7—O1—C8	106.4 (2)	O1—C8—C9	115.6 (2)
C10—O3—C12	116.0 (3)	C8—C9—C10	114.0 (2)
C8—C1—C2	107.2 (3)	C8—C9—H9A	108.8
C8—C1—S	124.7 (2)	C10—C9—H9A	108.8
C2—C1—S	127.9 (2)	C8—C9—H9B	108.8
C3—C2—C7	120.0 (3)	C10—C9—H9B	108.8
C3—C2—C1	135.6 (3)	H9A—C9—H9B	107.7
C7—C2—C1	104.4 (2)	O4—C10—O3	123.4 (3)
C4—C3—C2	116.2 (3)	O4—C10—C9	126.2 (3)
C4—C3—H3	121.9	O3—C10—C9	110.4 (3)
C2—C3—H3	121.9	S—C11—H11A	109.5
C3—C4—C5	123.5 (3)	S—C11—H11B	109.5
C3—C4—Br	118.6 (3)	H11A—C11—H11B	109.5
C5—C4—Br	117.9 (2)	S—C11—H11C	109.5
C6—C5—C4	119.9 (3)	H11A—C11—H11C	109.5
C6—C5—H5	120.0	H11B—C11—H11C	109.5
C4—C5—H5	120.0	O3—C12—H12A	109.5
C5—C6—C7	117.1 (3)	O3—C12—H12B	109.5
C5—C6—H6	121.5	H12A—C12—H12B	109.5
C7—C6—H6	121.5	O3—C12—H12C	109.5
O1—C7—C6	125.9 (3)	H12A—C12—H12C	109.5
O1—C7—C2	110.9 (2)	H12B—C12—H12C	109.5
O2—S—C1—C8	131.5 (3)	C5—C6—C7—C2	-1.3 (5)
C11—S—C1—C8	-118.8 (3)	C3—C2—C7—O1	-177.8 (2)
O2—S—C1—C2	-42.4 (3)	C1—C2—C7—O1	1.1 (3)
C11—S—C1—C2	67.3 (3)	C3—C2—C7—C6	1.4 (4)
C8—C1—C2—C3	177.9 (3)	C1—C2—C7—C6	-179.7 (3)
S—C1—C2—C3	-7.3 (5)	C2—C1—C8—O1	0.1 (3)
C8—C1—C2—C7	-0.7 (3)	S—C1—C8—O1	-174.9 (2)
S—C1—C2—C7	174.1 (2)	C2—C1—C8—C9	-179.8 (3)

C7—C2—C3—C4	-0.3 (4)	S—C1—C8—C9	5.1 (5)
C1—C2—C3—C4	-178.8 (3)	C7—O1—C8—C1	0.6 (3)
C2—C3—C4—C5	-0.8 (4)	C7—O1—C8—C9	-179.5 (2)
C2—C3—C4—Br	178.5 (2)	C1—C8—C9—C10	63.6 (4)
C3—C4—C5—C6	0.9 (5)	O1—C8—C9—C10	-116.3 (3)
Br—C4—C5—C6	-178.4 (2)	C12—O3—C10—O4	0.8 (5)
C4—C5—C6—C7	0.1 (5)	C12—O3—C10—C9	-179.9 (4)
C8—O1—C7—C6	179.7 (3)	C8—C9—C10—O4	-12.9 (5)
C8—O1—C7—C2	-1.1 (3)	C8—C9—C10—O3	167.7 (3)
C5—C6—C7—O1	177.8 (3)		

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>
C3—H3...O2 <sup>i</sup>	0.93	2.43	3.334 (4)	163
C9—H9B...O1 <sup>ii</sup>	0.97	2.59	3.555 (3)	171
C9—H9A...O2 <sup>iii</sup>	0.97	2.22	3.177 (4)	169
C12—H12B...Cg <sup>iv</sup>	0.96	2.99	3.903 (4)	159

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