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3-(4-Bromophenylsulfinyl)-5-chloro-2-methyl-1-benzofuran

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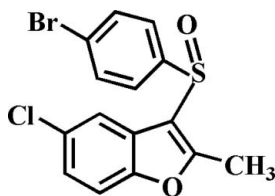
Received 15 May 2012; accepted 7 June 2012

Key indicators: single-crystal X-ray study; $T = 173$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.031; wR factor = 0.081; data-to-parameter ratio = 19.4.

In the title compound, $\text{C}_{15}\text{H}_{10}\text{BrClO}_2\text{S}$, the 4-bromophenyl ring makes a dihedral angle of $86.85(6)^\circ$ with the mean plane [mean deviation = $0.009(2)$ Å] of the benzofuran fragment. In the crystal, molecules are linked by slipped π - π interactions between the benzene and the furan rings of adjacent molecules [centroid-centroid distance = $3.884(2)$, interplanar distance = $3.369(2)$ and slippage = $1.945(2)$ Å], and between the 4-bromophenyl rings of adjacent molecules [centroid-centroid distance = $3.882(2)$, interplanar distance = $3.552(2)$ and slippage = $1.566(2)$ Å]. A $\text{Br} \cdots \text{Br}$ [$3.6446(4)$ Å] halogen interaction is also observed.

Related literature

For background information and the crystal structures of related compounds, see: Choi *et al.* (2008, 2010).



Experimental

Crystal data

$\text{C}_{15}\text{H}_{10}\text{BrClO}_2\text{S}$
 $M_r = 369.65$
 Triclinic, $P\bar{1}$
 $a = 6.4192(1)$ Å
 $b = 9.9185(2)$ Å
 $c = 11.7755(2)$ Å
 $\alpha = 100.681(1)^\circ$
 $\beta = 92.113(1)^\circ$

$\gamma = 104.168(1)^\circ$
 $V = 711.67(2)$ Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 3.22$ mm⁻¹
 $T = 173$ K
 $0.38 \times 0.31 \times 0.27$ mm

Data collection

Bruker SMART APEXII CCD diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2009)
 $T_{\min} = 0.374$, $T_{\max} = 0.475$

13131 measured reflections
 3529 independent reflections
 3236 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.034$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.031$
 $wR(F^2) = 0.081$
 $S = 1.12$
 3529 reflections

182 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.55$ e Å⁻³
 $\Delta\rho_{\min} = -0.76$ e Å⁻³

Data collection: APEX2 (Bruker, 2009); cell refinement: SAINT (Bruker, 2009); 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: DS2198).

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supporting information

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3-(4-Bromophenylsulfonyl)-5-chloro-2-methyl-1-benzofuran

Hong Dae Choi, Pil Ja Seo and Uk Lee

S1. Comment

As a part of our ongoing study of 5-chloro-2-methyl-1-benzofuran derivatives containing 3-phenylsulfonyl (Choi *et al.*, 2008) and 3-(4-fluorophenylsulfonyl) (Choi *et al.*, 2010) substituents, we report herein the crystal structure of the title compound.

In the title molecule (Fig. 1), the benzofuran unit is essentially planar, with a mean deviation of 0.009 (2) Å from the least-squares plane defined by the nine constituent atoms. The dihedral angle between the 4-bromophenyl ring and the mean plane of the benzofuran fragment is 86.85 (6)°. In the crystal structure (Fig. 2), molecules are connected by slipped $\pi\cdots\pi$ interactions; the first one between the benzene and the furan rings of adjacent molecules, with a Cg1 \cdots Cg2ⁱ distance of 3.884 (2) Å and an interplanar distance of 3.369 (2) Å resulting in a slippage of 1.945 (2) Å (Cg1 and Cg2 are the centroids of the C2–C7 benzene ring and the C1/C2/C7/O1/C8 furan ring, respectively), and the second one between the 4-bromophenyl rings of adjacent molecules, with a Cg3 \cdots Cg3ⁱⁱ distance of 3.882 (2) Å and an interplanar distance of 3.552 (2) Å resulting in a slippage of 1.566 (2) Å (Cg3 is the centroid of the C10–C15 benzene ring). The crystal packing (Fig. 2) also exhibits a Br \cdots Br contact at [3.6446 (4) Å].

S2. Experimental

3-Chloroperoxybenzoic acid (77%, 202 mg, 0.9 mmol) was added in small portions to a stirred solution of 3-(4-bromophenylsulfonyl)-5-chloro-2-methyl-1-benzofuran (283 mg, 0.8 mmol) in dichloromethane (30 mL) at 273 K. After being stirred at room temperature for 5h, the mixture was washed with saturated sodium bicarbonate solution and the organic layer was separated, dried over magnesium sulfate, filtered and concentrated at reduced pressure. The residue was purified by column chromatography (hexane/ethyl acetate, 2:1 v/v) to afford the title compound as a colorless solid [yield 73%, m.p. 395–396 K; R_f = 0.44 (hexane/ethyl acetate, 2:1 v/v)]. Single crystals suitable for X-ray diffraction were prepared by slow evaporation of a solution of the title compound in ethyl acetate at room temperature.

S3. Refinement

All H atoms were positioned geometrically and refined using a riding model, with C—H = 0.95 Å for aryl and 0.98 Å for methyl H atoms. $U_{iso}(H) = 1.2U_{eq}(C)$ for aryl and $1.5U_{eq}(C)$ for methyl H atoms. The positions of methyl hydrogens were optimized rotationally.

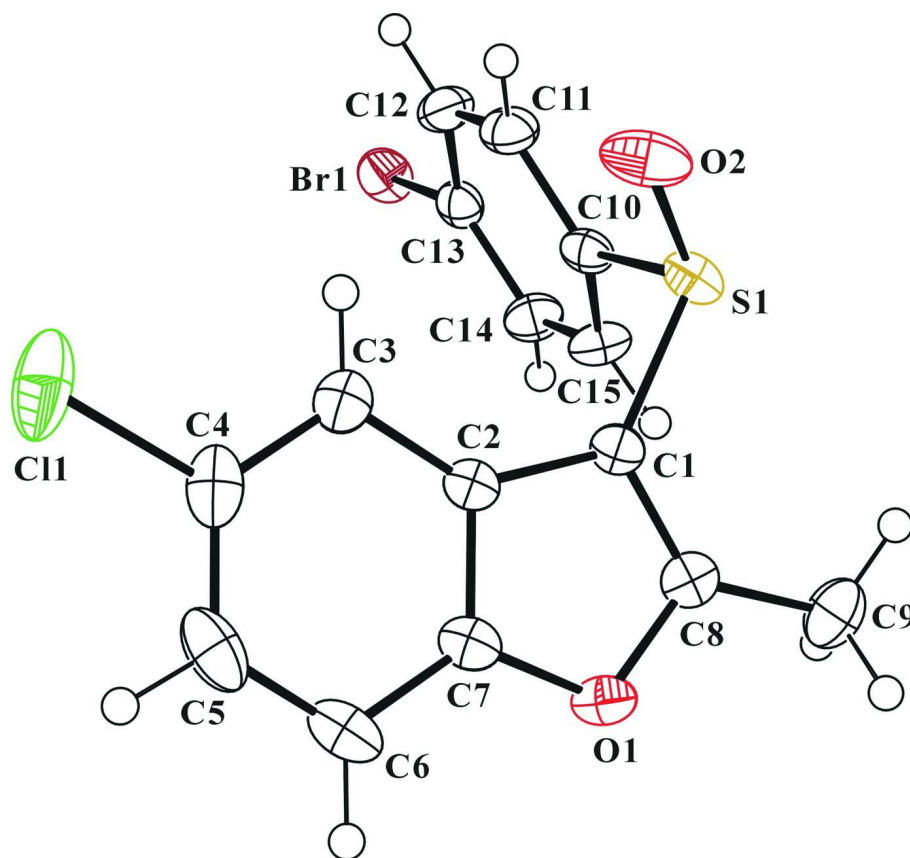


Figure 1

The molecular structure of the title compound with the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are presented as small spheres of arbitrary radius.

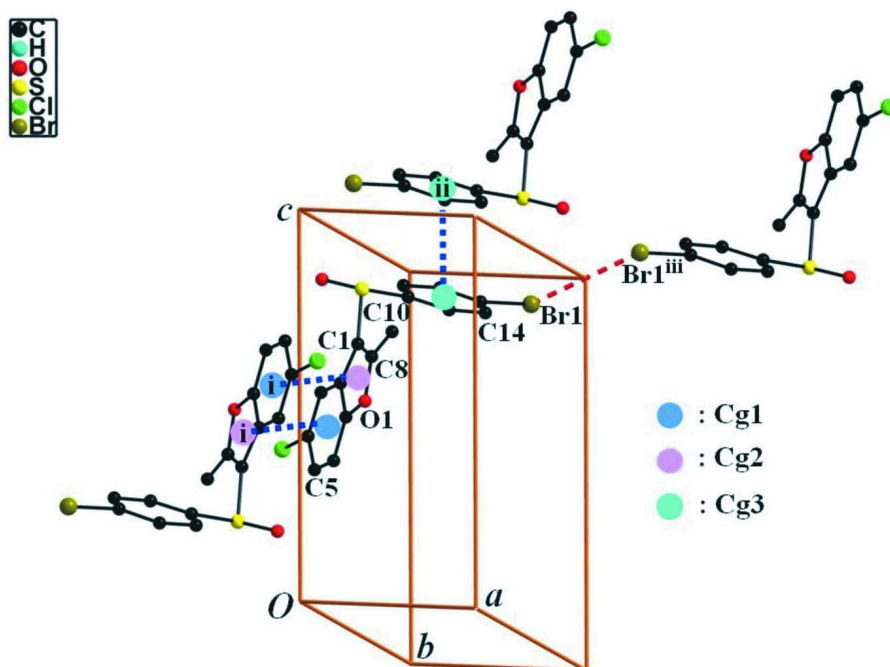


Figure 2

A view of the $\pi\cdots\pi$ and Br \cdots Br interactions (dotted lines) in the crystal structure of the title compound. H atoms were omitted for clarity. [Symmetry codes: (i) $-x, -y, -z + 1$; (ii) $-x + 1, -y + 1, -z + 2$; (iii) $-x + 2, -y + 2, -z + 2$.]

3-(4-Bromophenylsulfinyl)-5-chloro-2-methyl-1-benzofuran

Crystal data

$C_{15}H_{10}BrClO_2S$
 $M_r = 369.65$
 Triclinic, $P\bar{1}$
 Hall symbol: $-P\ 1$
 $a = 6.4192$ (1) Å
 $b = 9.9185$ (2) Å
 $c = 11.7755$ (2) Å
 $\alpha = 100.681$ (1)°
 $\beta = 92.113$ (1)°
 $\gamma = 104.168$ (1)°
 $V = 711.67$ (2) Å³

$Z = 2$
 $F(000) = 368$
 $D_x = 1.725$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 7922 reflections
 $\theta = 2.5$ – 28.3 °
 $\mu = 3.22$ mm⁻¹
 $T = 173$ K
 Block, colourless
 $0.38 \times 0.31 \times 0.27$ mm

Data collection

Bruker SMART APEXII CCD
 diffractometer
 Radiation source: rotating anode
 Graphite multilayer monochromator
 Detector resolution: 10.0 pixels mm⁻¹
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Bruker, 2009)
 $T_{\min} = 0.374$, $T_{\max} = 0.475$

13131 measured reflections
 3529 independent reflections
 3236 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.034$
 $\theta_{\text{max}} = 28.3$ °, $\theta_{\text{min}} = 1.8$ °
 $h = -8 \rightarrow 8$
 $k = -13 \rightarrow 13$
 $l = -15 \rightarrow 15$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.031$
 $wR(F^2) = 0.081$
 $S = 1.12$
 3529 reflections
 182 parameters
 0 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 Hydrogen site location: difference Fourier map
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0418P)^2 + 0.3308P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.55 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.76 \text{ e } \text{\AA}^{-3}$

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.

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 $F^2 > 2\sigma(F^2)$ 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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	0.73945 (4)	0.92053 (2)	0.917091 (18)	0.03412 (8)
Cl1	-0.34796 (9)	0.39254 (7)	0.44410 (7)	0.05267 (19)
S1	0.18432 (8)	0.27154 (5)	0.84285 (4)	0.02666 (11)
O1	0.3068 (2)	0.10245 (15)	0.53223 (12)	0.0280 (3)
O2	-0.0436 (3)	0.27377 (19)	0.86385 (15)	0.0408 (4)
C1	0.1970 (3)	0.21347 (19)	0.69398 (16)	0.0221 (3)
C2	0.0811 (3)	0.23994 (19)	0.59651 (16)	0.0218 (3)
C3	-0.0758 (3)	0.3123 (2)	0.58146 (19)	0.0273 (4)
H3	-0.1307	0.3616	0.6456	0.033*
C4	-0.1474 (3)	0.3084 (2)	0.4682 (2)	0.0329 (5)
C5	-0.0676 (4)	0.2384 (3)	0.3725 (2)	0.0381 (5)
H5	-0.1203	0.2402	0.2965	0.046*
C6	0.0869 (4)	0.1664 (3)	0.38686 (19)	0.0353 (5)
H6	0.1427	0.1179	0.3225	0.042*
C7	0.1560 (3)	0.1686 (2)	0.49963 (17)	0.0254 (4)
C8	0.3276 (3)	0.1306 (2)	0.65100 (18)	0.0253 (4)
C9	0.4833 (4)	0.0697 (2)	0.7071 (2)	0.0357 (5)
H9A	0.6304	0.1255	0.7026	0.054*
H9B	0.4668	-0.0287	0.6672	0.054*
H9C	0.4555	0.0720	0.7886	0.054*
C10	0.3331 (3)	0.4532 (2)	0.85442 (15)	0.0222 (3)
C11	0.2396 (3)	0.5607 (2)	0.89910 (18)	0.0283 (4)
H11	0.0936	0.5387	0.9172	0.034*
C12	0.3588 (3)	0.7010 (2)	0.91761 (18)	0.0296 (4)
H12	0.2961	0.7758	0.9486	0.036*

C13	0.5709 (3)	0.7301 (2)	0.89001 (16)	0.0247 (4)
C14	0.6662 (3)	0.6227 (2)	0.84636 (19)	0.0294 (4)
H14	0.8119	0.6448	0.8279	0.035*
C15	0.5474 (3)	0.4829 (2)	0.82977 (19)	0.0292 (4)
H15	0.6119	0.4080	0.8018	0.035*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.04322 (14)	0.02544 (12)	0.02911 (12)	0.00304 (9)	0.00126 (9)	0.00208 (8)
Cl1	0.0273 (3)	0.0545 (4)	0.0839 (5)	0.0083 (2)	−0.0072 (3)	0.0384 (4)
S1	0.0281 (2)	0.0293 (2)	0.0188 (2)	0.00123 (18)	0.00349 (17)	0.00343 (18)
O1	0.0258 (7)	0.0302 (7)	0.0268 (7)	0.0092 (6)	0.0044 (5)	−0.0010 (6)
O2	0.0277 (8)	0.0484 (9)	0.0358 (8)	−0.0032 (7)	0.0136 (6)	−0.0022 (7)
C1	0.0210 (8)	0.0223 (8)	0.0210 (8)	0.0032 (7)	0.0012 (7)	0.0024 (7)
C2	0.0194 (8)	0.0224 (8)	0.0214 (8)	0.0020 (7)	0.0022 (7)	0.0032 (7)
C3	0.0207 (9)	0.0270 (9)	0.0344 (10)	0.0038 (7)	0.0034 (7)	0.0090 (8)
C4	0.0203 (9)	0.0330 (10)	0.0460 (12)	0.0002 (8)	−0.0024 (8)	0.0195 (9)
C5	0.0302 (11)	0.0500 (13)	0.0286 (10)	−0.0052 (9)	−0.0063 (8)	0.0165 (10)
C6	0.0338 (11)	0.0448 (12)	0.0215 (9)	0.0014 (9)	0.0033 (8)	0.0035 (9)
C7	0.0208 (8)	0.0290 (9)	0.0233 (9)	0.0024 (7)	0.0026 (7)	0.0025 (7)
C8	0.0220 (9)	0.0233 (8)	0.0283 (9)	0.0030 (7)	0.0014 (7)	0.0032 (7)
C9	0.0286 (10)	0.0325 (11)	0.0471 (13)	0.0110 (8)	−0.0020 (9)	0.0075 (10)
C10	0.0216 (8)	0.0264 (9)	0.0160 (8)	0.0043 (7)	0.0001 (6)	0.0002 (7)
C11	0.0218 (9)	0.0363 (10)	0.0279 (10)	0.0105 (8)	0.0053 (7)	0.0042 (8)
C12	0.0308 (10)	0.0311 (10)	0.0290 (10)	0.0150 (8)	0.0053 (8)	0.0014 (8)
C13	0.0287 (9)	0.0246 (9)	0.0189 (8)	0.0057 (7)	−0.0013 (7)	0.0022 (7)
C14	0.0215 (9)	0.0316 (10)	0.0337 (10)	0.0067 (8)	0.0054 (8)	0.0026 (8)
C15	0.0251 (9)	0.0290 (10)	0.0323 (10)	0.0090 (8)	0.0087 (8)	−0.0005 (8)

Geometric parameters (Å, °)

Br1—C13	1.895 (2)	C5—H5	0.9500
Br1—Br1 ⁱ	3.6446 (4)	C6—C7	1.379 (3)
Cl1—C4	1.738 (2)	C6—H6	0.9500
Cl1—Cl1 ⁱⁱ	3.3576 (15)	C8—C9	1.482 (3)
S1—O2	1.4973 (16)	C9—H9A	0.9800
S1—C1	1.7522 (19)	C9—H9B	0.9800
S1—C10	1.798 (2)	C9—H9C	0.9800
O1—C8	1.369 (2)	C10—C11	1.380 (3)
O1—C7	1.375 (2)	C10—C15	1.388 (3)
C1—C8	1.360 (3)	C11—C12	1.387 (3)
C1—C2	1.444 (3)	C11—H11	0.9500
C2—C7	1.393 (3)	C12—C13	1.385 (3)
C2—C3	1.396 (3)	C12—H12	0.9500
C3—C4	1.386 (3)	C13—C14	1.383 (3)
C3—H3	0.9500	C14—C15	1.383 (3)
C4—C5	1.392 (3)	C14—H14	0.9500

C5—C6	1.378 (4)	C15—H15	0.9500
C13—Br1—Br1 ⁱ	129.17 (6)	C1—C8—O1	110.68 (17)
C4—C11—C11 ⁱⁱ	147.84 (10)	C1—C8—C9	132.7 (2)
O2—S1—C1	108.52 (9)	O1—C8—C9	116.58 (17)
O2—S1—C10	106.57 (9)	C8—C9—H9A	109.5
C1—S1—C10	98.01 (9)	C8—C9—H9B	109.5
C8—O1—C7	106.55 (14)	H9A—C9—H9B	109.5
C8—C1—C2	107.50 (16)	C8—C9—H9C	109.5
C8—C1—S1	123.01 (15)	H9A—C9—H9C	109.5
C2—C1—S1	129.49 (14)	H9B—C9—H9C	109.5
C7—C2—C3	119.56 (18)	C11—C10—C15	120.93 (18)
C7—C2—C1	104.41 (16)	C11—C10—S1	119.38 (15)
C3—C2—C1	136.02 (18)	C15—C10—S1	119.34 (15)
C4—C3—C2	116.62 (19)	C10—C11—C12	119.95 (18)
C4—C3—H3	121.7	C10—C11—H11	120.0
C2—C3—H3	121.7	C12—C11—H11	120.0
C3—C4—C5	122.8 (2)	C13—C12—C11	118.80 (18)
C3—C4—C11	118.67 (18)	C13—C12—H12	120.6
C5—C4—C11	118.47 (17)	C11—C12—H12	120.6
C6—C5—C4	120.8 (2)	C14—C13—C12	121.50 (19)
C6—C5—H5	119.6	C14—C13—Br1	118.71 (15)
C4—C5—H5	119.6	C12—C13—Br1	119.75 (15)
C5—C6—C7	116.4 (2)	C13—C14—C15	119.41 (18)
C5—C6—H6	121.8	C13—C14—H14	120.3
C7—C6—H6	121.8	C15—C14—H14	120.3
O1—C7—C6	125.35 (18)	C14—C15—C10	119.37 (18)
O1—C7—C2	110.85 (17)	C14—C15—H15	120.3
C6—C7—C2	123.8 (2)	C10—C15—H15	120.3
O2—S1—C1—C8	-144.10 (17)	C1—C2—C7—C6	-179.82 (19)
C10—S1—C1—C8	105.36 (17)	C2—C1—C8—O1	0.7 (2)
O2—S1—C1—C2	35.8 (2)	S1—C1—C8—O1	-179.37 (13)
C10—S1—C1—C2	-74.70 (18)	C2—C1—C8—C9	179.8 (2)
C8—C1—C2—C7	-0.4 (2)	S1—C1—C8—C9	-0.3 (3)
S1—C1—C2—C7	179.69 (15)	C7—O1—C8—C1	-0.7 (2)
C8—C1—C2—C3	178.4 (2)	C7—O1—C8—C9	-179.98 (17)
S1—C1—C2—C3	-1.6 (3)	O2—S1—C10—C11	11.79 (19)
C7—C2—C3—C4	-0.2 (3)	C1—S1—C10—C11	123.91 (16)
C1—C2—C3—C4	-178.8 (2)	O2—S1—C10—C15	-174.93 (16)
C2—C3—C4—C5	-0.9 (3)	C1—S1—C10—C15	-62.81 (18)
C2—C3—C4—C11	178.31 (14)	C15—C10—C11—C12	1.4 (3)
C11 ⁱⁱ —C11—C4—C3	8.9 (3)	S1—C10—C11—C12	174.58 (16)
C11 ⁱⁱ —C11—C4—C5	-171.87 (13)	C10—C11—C12—C13	0.3 (3)
C3—C4—C5—C6	1.1 (3)	C11—C12—C13—C14	-1.0 (3)
C11—C4—C5—C6	-178.09 (17)	C11—C12—C13—Br1	-178.79 (15)
C4—C5—C6—C7	-0.2 (3)	Br1 ⁱ —Br1—C13—C14	-52.56 (18)
C8—O1—C7—C6	-179.8 (2)	Br1 ⁱ —Br1—C13—C12	125.32 (15)

C8—O1—C7—C2	0.5 (2)	C12—C13—C14—C15	0.0 (3)
C5—C6—C7—O1	179.31 (19)	Br1—C13—C14—C15	177.84 (16)
C5—C6—C7—C2	-1.0 (3)	C13—C14—C15—C10	1.7 (3)
C3—C2—C7—O1	-179.05 (16)	C11—C10—C15—C14	-2.4 (3)
C1—C2—C7—O1	-0.1 (2)	S1—C10—C15—C14	-175.55 (16)
C3—C2—C7—C6	1.2 (3)		

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