

Crystal structure of 5-chloro-2-(3-fluorophenyl)-3-methylsulfinyl-1-benzofuran

Hong Dae Choi^a and Uk Lee^{b*}^aDepartment of Chemistry, Dongeui University, San 24 Kaya-dong, Busanjin-gu, Busan 614-714, Republic of Korea, and ^bDepartment of Chemistry, Pukyong National University, 599-1 Daeyon 3-dong, Nam-gu, Busan 608-737, Republic of Korea. *Correspondence e-mail: uklee@pknu.ac.kr

Received 24 July 2014; accepted 5 August 2014

Edited by O. Blacque, University of Zürich, Switzerland

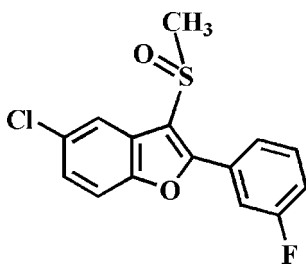
In the title compound, C₁₅H₁₀ClFO₂S, the dihedral angle between the plane of the benzofuran ring system [r.m.s. deviation = 0.013 (1) Å] and that of the 3-fluorophenyl ring [r.m.s. deviation = 0.005 (1) Å] is 31.36 (5)°. In the crystal, molecules are linked by two different pairs of C—H···O hydrogen bonds, forming inversion dimers.

Keywords: crystal structure; benzofuran; 3-fluorophenyl; C—H···O hydrogen bonds.

CCDC reference: 1017893

1. Related literature

For the pharmaceutical properties of compounds containing the benzofuran moiety, see: Aslam *et al.* (2009); Choi *et al.* (2003); Galal *et al.* (2009); Khan *et al.* (2005); Ono *et al.* (2002). For natural products with a benzofuran ring, see: Akgul & Anil (2003); Soekamto *et al.* (2003). For the synthesis of the starting material 5-chloro-2-(3-fluorophenyl)-3-methylsulfonyl-1-benzofuran, see: Choi *et al.* (1999). For a related structure, see: Choi *et al.* (2009).



2. Experimental

2.1. Crystal data

C₁₅H₁₀ClFO₂SM_r = 308.74

Triclinic, $P\bar{1}$
 $a = 8.0038$ (1) Å
 $b = 8.4322$ (1) Å
 $c = 10.6782$ (2) Å
 $\alpha = 88.933$ (1)°
 $\beta = 81.008$ (1)°
 $\gamma = 66.859$ (1)°

$V = 653.81$ (2) Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 0.46$ mm⁻¹
 $T = 173$ K
 $0.47 \times 0.34 \times 0.33$ mm

2.2. Data collection

Bruker SMART APEXII CCD diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2009)
 $T_{\min} = 0.813$, $T_{\max} = 0.863$

11737 measured reflections
 3124 independent reflections
 2887 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.022$

2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.086$
 $S = 1.07$
 3124 reflections

182 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.30$ e Å⁻³
 $\Delta\rho_{\min} = -0.44$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C11—H11···O2 ⁱ	0.95	2.57	3.3470 (18)	139
C14—H14···O2 ⁱⁱ	0.95	2.59	3.4884 (17)	157

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

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 for Windows (Farrugia, 2012) and DIAMOND (Brandenburg, 1998); software used to prepare material for publication: SHELXL97.

Acknowledgements

The X-ray centre of the Gyeongsang National University is acknowledged for providing access to the single-crystal diffractometer.

Supporting information for this paper is available from the IUCr electronic archives (Reference: ZQ2226).

References

- Akgul, Y. Y. & Anil, H. (2003). *Phytochemistry*, **63**, 939–943.
 Aslam, S. N., Stevenson, P. C., Kokubun, T. & Hall, D. R. (2009). *Microbiol. Res.* **164**, 191–195.
 Brandenburg, K. (1998). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
 Bruker (2009). *APEX2*, *SADABS* and *S SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
 Choi, H. D., Seo, P. J. & Son, B. W. (1999). *J. Korean Chem. Soc.* **43**, 606–608.
 Choi, H. D., Seo, P. J., Son, B. W. & Kang, B. W. (2003). *Arch. Pharm. Res.* **26**, 985–989.
 Choi, H. D., Seo, P. J., Son, B. W. & Lee, U. (2009). *Acta Cryst.* **E65**, o2649.
 Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
 Galal, S. A., Abd El-All, A. S., Abdallah, M. M. & El-Diwani, H. I. (2009). *Bioorg. Med. Chem. Lett.* **19**, 2420–2428.
 Khan, M. W., Alam, M. J., Rashid, M. A. & Chowdhury, R. (2005). *Bioorg. Med. Chem.* **13**, 4796–4805.

Ono, M., Kung, M. P., Hou, C. & Kung, H. F. (2002). *Nucl. Med. Biol.* **29**, 633–642.
Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.

Soekamto, N. H., Achmad, S. A., Ghisalberti, E. L., Hakim, E. H. & Syah, Y. M. (2003). *Phytochemistry*, **64**, 831–834.

supporting information

Acta Cryst. (2014). E70, o991–o992 [doi:10.1107/S1600536814017966]

Crystal structure of 5-chloro-2-(3-fluorophenyl)-3-methylsulfinyl-1-benzofuran

Hong Dae Choi and Uk Lee

S1. Comment

Recently, a number of benzofuran compounds have drawn much attention owing to their interesting pharmaceutical properties such as antibacterial and antifungal, antitumor and antiviral, antimicrobial activities (Aslam *et al.* 2009; Galal *et al.*, 2009; Khan *et al.*, 2005), and potential inhibitors of β -amyloid formation (Choi *et al.*, 2003, Ono *et al.*, 2002). These benzofuran derivatives occur in a wide range of natural products (Akgul & Anil, 2003; Soekamto *et al.*, 2003). As a part of our ongoing project of 2-aryl-5-chloro-3-methylsulfinyl-1-benzofuran derivatives containing 4-fluorophenyl substituent in 2-position (Choi *et al.*, 2009), we report herein on the crystal structure of the title compound.

In the title molecule (Fig. 1), the benzofuran unit is essentially planar, with a mean deviation of 0.013 (1) Å from the least-squares plane defined by the nine constituent atoms. The 3-fluorophenyl ring is essentially planar, with a mean deviation of 0.005 (1) Å from the least-squares plane defined by the six constituent atoms. The dihedral angle formed by the benzofuran ring system and the 3-fluorophenyl ring is 31.36 (5)°. In the crystal structure (Fig. 2), molecules are linked by two different pairs of C—H···O hydrogen bonds (Table 1), forming inversion dimers.

S2. Experimental

The starting material 5-chloro-2-(3-fluorophenyl)-3-methylsulfonyl-1-benzofuran was prepared by literature method (Choi *et al.* 1999). 3-Chloroperoxybenzoic acid (77%, 269 mg, 1.2 mmol) was added in small portions to a stirred solution of the starting material (322 mg, 1.1 mmol) in dichloromethane (30 mL) at 273 K. After being stirred at room temperature for 6h, the mixture was washed with saturated sodium bicarbonate solution (2 X 20 mL) 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, 1:1 v/v) to afford the title compound as a colorless solid [yield 73% (248 mg); m.p. 483–484 K; R_f = 0.48 (hexane-ethyl acetate, 1:1 v/v)]. Single crystals suitable for X-ray diffraction were prepared by slow evaporation of a solution of the title compound (120 mg) in acetone (20 mL) 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, $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for aryl and $1.5U_{\text{eq}}(\text{C})$ for methyl H atoms. The positions of methyl hydrogens were optimized using the SHELXL-97's command AFIX 137 (Sheldrick, 2008).

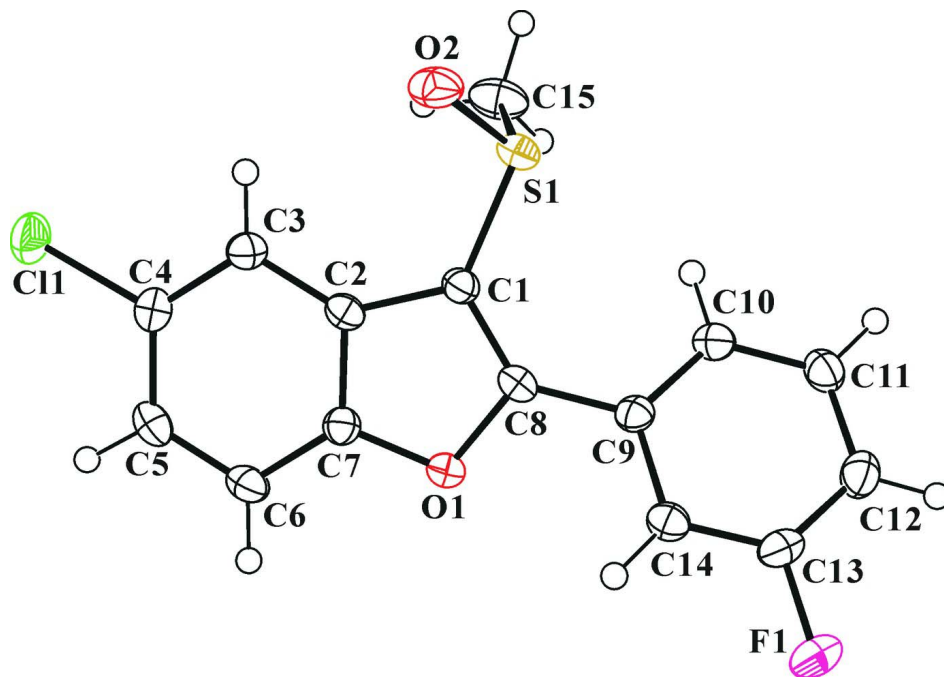


Figure 1

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

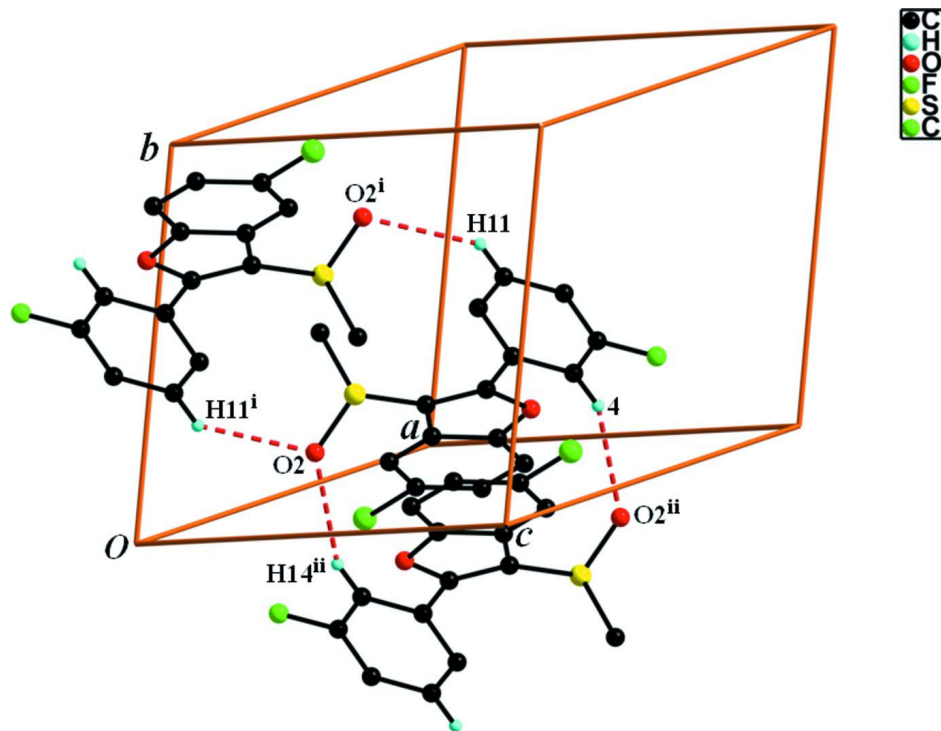


Figure 2

A view of the C—H···O hydrogen bonds (dotted lines) in the crystal structure of the title compound. H atoms non-participating in hydrogen-bonding were omitted for clarity [symmetry codes: (i) $-x, -y + 1, -z + 1$; (ii) $-x + 1, -y, -z + 1$].

5-Chloro-2-(3-fluorophenyl)-3-methylsulfinyl-1-benzofuran

Crystal data

$C_{15}H_{10}ClFO_2S$

$M_r = 308.74$

Triclinic, $P\bar{1}$

Hall symbol: $-P\ 1$

$a = 8.0038$ (1) Å

$b = 8.4322$ (1) Å

$c = 10.6782$ (2) Å

$\alpha = 88.933$ (1)°

$\beta = 81.008$ (1)°

$\gamma = 66.859$ (1)°

$V = 653.81$ (2) Å³

$Z = 2$

$F(000) = 316$

$D_x = 1.568$ Mg m⁻³

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

Cell parameters from 6836 reflections

$\theta = 2.6$ – 28.5 °

$\mu = 0.46$ mm⁻¹

$T = 173$ K

Block, colourless

$0.47 \times 0.34 \times 0.33$ 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)

$T_{\min} = 0.813$, $T_{\max} = 0.863$

11737 measured reflections

3124 independent reflections

2887 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.022$

$\theta_{\text{max}} = 28.0$ °, $\theta_{\text{min}} = 1.9$ °

$h = -10 \rightarrow 10$

$k = -11 \rightarrow 11$

$l = -14 \rightarrow 13$

*Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.032$ $wR(F^2) = 0.086$ $S = 1.07$

3124 reflections

182 parameters

0 restraints

Primary atom site location: structure-invariant
direct methodsSecondary atom site location: difference Fourier
map

Hydrogen site location: difference Fourier map

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0458P)^2 + 0.2424P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 0.30 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\min} = -0.44 \text{ e } \text{\AA}^{-3}$ *Special details***Experimental.** ^1H NMR (δ p.p.m., CDCl_3 , 400 Hz): 8.23 (d, $J = 2.04$ Hz, 1H), 7.62 (d, $J = 7.88$ Hz, 1H), 7.54-7.58 (m, 1H), 7.45-7.52 (m, 2H), 7.38 (dd, $J = 8.88$ and 2.04 Hz, 1H), 7.16-7.22 (m, 1H), 3.11 (s, 3H).**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>	$U_{\text{iso}}^*/U_{\text{eq}}$
C11	0.82187 (5)	-0.13963 (5)	-0.02027 (3)	0.03515 (11)
S1	0.21038 (4)	0.30346 (4)	0.39543 (3)	0.02300 (10)
F1	0.53226 (14)	0.29209 (13)	0.95736 (8)	0.0395 (2)
O1	0.70635 (13)	0.13881 (12)	0.49383 (9)	0.0234 (2)
O2	0.17787 (15)	0.16956 (13)	0.32625 (11)	0.0325 (2)
C1	0.44633 (17)	0.21871 (16)	0.40865 (12)	0.0210 (3)
C2	0.59652 (17)	0.10631 (16)	0.31628 (12)	0.0210 (3)
C3	0.61509 (18)	0.04393 (17)	0.19238 (13)	0.0231 (3)
H3	0.5120	0.0719	0.1499	0.028*
C4	0.79058 (19)	-0.06027 (18)	0.13484 (13)	0.0252 (3)
C5	0.94567 (19)	-0.10505 (18)	0.19490 (14)	0.0275 (3)
H5	1.0635	-0.1775	0.1510	0.033*
C6	0.92781 (19)	-0.04413 (18)	0.31773 (14)	0.0265 (3)
H6	1.0308	-0.0728	0.3605	0.032*
C7	0.75209 (18)	0.06058 (16)	0.37470 (13)	0.0221 (3)
C8	0.51944 (17)	0.23358 (16)	0.51261 (13)	0.0214 (3)
C9	0.44315 (18)	0.32961 (17)	0.63441 (12)	0.0216 (3)
C10	0.29269 (19)	0.48798 (18)	0.64645 (13)	0.0256 (3)
H10	0.2383	0.5349	0.5740	0.031*
C11	0.2218 (2)	0.57761 (18)	0.76298 (14)	0.0281 (3)
H11	0.1182	0.6846	0.7703	0.034*
C12	0.3016 (2)	0.51149 (19)	0.86908 (14)	0.0296 (3)
H12	0.2542	0.5717	0.9495	0.036*

C13	0.4517 (2)	0.35607 (19)	0.85427 (13)	0.0270 (3)
C14	0.52576 (18)	0.26207 (17)	0.74107 (13)	0.0235 (3)
H14	0.6293	0.1551	0.7350	0.028*
C15	0.2148 (2)	0.4624 (2)	0.28245 (17)	0.0365 (4)
H15A	0.3053	0.4062	0.2070	0.055*
H15B	0.2488	0.5481	0.3205	0.055*
H15C	0.0927	0.5199	0.2581	0.055*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0340 (2)	0.0413 (2)	0.02564 (19)	-0.01237 (16)	0.00258 (14)	-0.00911 (14)
S1	0.01657 (16)	0.02380 (17)	0.02762 (18)	-0.00635 (12)	-0.00525 (12)	0.00218 (12)
F1	0.0448 (6)	0.0467 (5)	0.0251 (4)	-0.0123 (4)	-0.0156 (4)	0.0027 (4)
O1	0.0190 (4)	0.0254 (5)	0.0236 (5)	-0.0056 (4)	-0.0057 (4)	-0.0006 (4)
O2	0.0296 (5)	0.0282 (5)	0.0451 (6)	-0.0133 (4)	-0.0166 (5)	0.0030 (4)
C1	0.0169 (6)	0.0214 (6)	0.0233 (6)	-0.0058 (5)	-0.0038 (5)	0.0009 (5)
C2	0.0181 (6)	0.0204 (6)	0.0238 (6)	-0.0069 (5)	-0.0034 (5)	0.0025 (5)
C3	0.0220 (6)	0.0244 (6)	0.0232 (6)	-0.0091 (5)	-0.0048 (5)	0.0016 (5)
C4	0.0268 (7)	0.0245 (6)	0.0236 (6)	-0.0104 (5)	-0.0008 (5)	-0.0017 (5)
C5	0.0206 (6)	0.0255 (6)	0.0316 (7)	-0.0058 (5)	0.0007 (5)	-0.0016 (5)
C6	0.0189 (6)	0.0257 (6)	0.0326 (7)	-0.0058 (5)	-0.0057 (5)	0.0008 (5)
C7	0.0213 (6)	0.0213 (6)	0.0233 (6)	-0.0077 (5)	-0.0045 (5)	0.0009 (5)
C8	0.0178 (6)	0.0201 (6)	0.0248 (6)	-0.0058 (5)	-0.0039 (5)	0.0021 (5)
C9	0.0205 (6)	0.0231 (6)	0.0226 (6)	-0.0099 (5)	-0.0044 (5)	0.0005 (5)
C10	0.0248 (7)	0.0250 (6)	0.0265 (7)	-0.0082 (5)	-0.0067 (5)	0.0018 (5)
C11	0.0252 (7)	0.0249 (6)	0.0306 (7)	-0.0065 (5)	-0.0026 (5)	-0.0036 (5)
C12	0.0303 (7)	0.0326 (7)	0.0259 (7)	-0.0132 (6)	-0.0019 (6)	-0.0052 (5)
C13	0.0296 (7)	0.0330 (7)	0.0231 (7)	-0.0155 (6)	-0.0095 (5)	0.0040 (5)
C14	0.0214 (6)	0.0246 (6)	0.0258 (7)	-0.0096 (5)	-0.0055 (5)	0.0017 (5)
C15	0.0326 (8)	0.0312 (7)	0.0499 (10)	-0.0138 (6)	-0.0176 (7)	0.0173 (7)

Geometric parameters (Å, °)

Cl1—C4	1.7418 (14)	C6—C7	1.3800 (19)
S1—O2	1.4866 (11)	C6—H6	0.9500
S1—C1	1.7652 (13)	C8—C9	1.4568 (18)
S1—C15	1.7937 (15)	C9—C10	1.3943 (18)
F1—C13	1.3584 (16)	C9—C14	1.4049 (18)
O1—C7	1.3724 (16)	C10—C11	1.385 (2)
O1—C8	1.3745 (15)	C10—H10	0.9500
C1—C8	1.3625 (18)	C11—C12	1.388 (2)
C1—C2	1.4439 (17)	C11—H11	0.9500
C2—C7	1.3945 (18)	C12—C13	1.377 (2)
C2—C3	1.3972 (18)	C12—H12	0.9500
C3—C4	1.3794 (19)	C13—C14	1.372 (2)
C3—H3	0.9500	C14—H14	0.9500
C4—C5	1.402 (2)	C15—H15A	0.9800

C5—C6	1.383 (2)	C15—H15B	0.9800
C5—H5	0.9500	C15—H15C	0.9800
O2—S1—C1	107.08 (6)	C1—C8—C9	133.92 (12)
O2—S1—C15	105.95 (7)	O1—C8—C9	115.20 (11)
C1—S1—C15	97.48 (7)	C10—C9—C14	119.61 (12)
C7—O1—C8	106.62 (10)	C10—C9—C8	121.37 (12)
C8—C1—C2	106.92 (11)	C14—C9—C8	119.01 (12)
C8—C1—S1	126.40 (10)	C11—C10—C9	120.64 (13)
C2—C1—S1	126.42 (10)	C11—C10—H10	119.7
C7—C2—C3	119.41 (12)	C9—C10—H10	119.7
C7—C2—C1	105.03 (11)	C10—C11—C12	120.19 (13)
C3—C2—C1	135.54 (12)	C10—C11—H11	119.9
C4—C3—C2	116.67 (12)	C12—C11—H11	119.9
C4—C3—H3	121.7	C13—C12—C11	118.02 (13)
C2—C3—H3	121.7	C13—C12—H12	121.0
C3—C4—C5	123.22 (13)	C11—C12—H12	121.0
C3—C4—C11	118.56 (11)	F1—C13—C14	117.86 (13)
C5—C4—C11	118.22 (11)	F1—C13—C12	118.28 (13)
C6—C5—C4	120.30 (13)	C14—C13—C12	123.86 (13)
C6—C5—H5	119.8	C13—C14—C9	117.67 (12)
C4—C5—H5	119.8	C13—C14—H14	121.2
C7—C6—C5	116.25 (12)	C9—C14—H14	121.2
C7—C6—H6	121.9	S1—C15—H15A	109.5
C5—C6—H6	121.9	S1—C15—H15B	109.5
O1—C7—C6	125.27 (12)	H15A—C15—H15B	109.5
O1—C7—C2	110.56 (11)	S1—C15—H15C	109.5
C6—C7—C2	124.14 (13)	H15A—C15—H15C	109.5
C1—C8—O1	110.86 (11)	H15B—C15—H15C	109.5
O2—S1—C1—C8	-138.71 (12)	C1—C2—C7—C6	-178.69 (13)
C15—S1—C1—C8	112.01 (13)	C2—C1—C8—O1	0.06 (15)
O2—S1—C1—C2	34.63 (13)	S1—C1—C8—O1	174.46 (9)
C15—S1—C1—C2	-74.66 (13)	C2—C1—C8—C9	178.33 (14)
C8—C1—C2—C7	0.43 (14)	S1—C1—C8—C9	-7.3 (2)
S1—C1—C2—C7	-173.96 (10)	C7—O1—C8—C1	-0.54 (14)
C8—C1—C2—C3	-178.15 (15)	C7—O1—C8—C9	-179.16 (11)
S1—C1—C2—C3	7.5 (2)	C1—C8—C9—C10	-30.9 (2)
C7—C2—C3—C4	-0.39 (19)	O1—C8—C9—C10	147.27 (12)
C1—C2—C3—C4	178.04 (14)	C1—C8—C9—C14	150.28 (15)
C2—C3—C4—C5	0.4 (2)	O1—C8—C9—C14	-31.51 (17)
C2—C3—C4—C11	-179.30 (10)	C14—C9—C10—C11	-1.3 (2)
C3—C4—C5—C6	-0.2 (2)	C8—C9—C10—C11	179.97 (13)
C11—C4—C5—C6	179.54 (11)	C9—C10—C11—C12	0.9 (2)
C4—C5—C6—C7	-0.1 (2)	C10—C11—C12—C13	0.1 (2)
C8—O1—C7—C6	178.70 (13)	C11—C12—C13—F1	178.95 (13)
C8—O1—C7—C2	0.83 (14)	C11—C12—C13—C14	-0.6 (2)
C5—C6—C7—O1	-177.52 (12)	F1—C13—C14—C9	-179.35 (12)

C5—C6—C7—C2	0.1 (2)	C12—C13—C14—C9	0.2 (2)
C3—C2—C7—O1	178.08 (11)	C10—C9—C14—C13	0.7 (2)
C1—C2—C7—O1	-0.78 (15)	C8—C9—C14—C13	179.52 (12)
C3—C2—C7—C6	0.2 (2)		

Hydrogen-bond geometry (Å, °)

<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>
C11—H11 \cdots O2 ⁱ	0.95	2.57	3.3470 (18)	139
C14—H14 \cdots O2 ⁱⁱ	0.95	2.59	3.4884 (17)	157

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