

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

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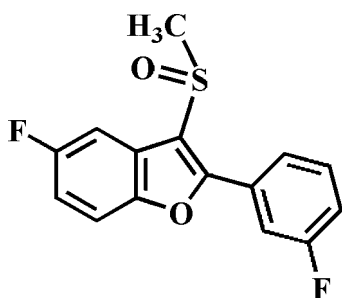
In the title compound, C₁₅H₁₀F₂O₂S, the dihedral angle between the planes of the benzofuran ring system [r.m.s. deviation = 0.015 (1) Å] and the 3-fluorophenyl ring is 26.60 (5)°. In the crystal, molecules are linked by C—H...O and C—H...F hydrogen bonds, and by π – π interactions between the benzofuran rings of inversion-related molecules [centroid(benzene)–centroid(furan) distance = 3.819 (2) Å], forming a three-dimensional network.

Keywords: crystal structure; benzofuran; 3-fluorophenyl; π – π interactions.

CCDC reference: 1029041

1. Related literature

For a related structure and background to benzofuran derivatives, see: Choi & Lee (2014). For further synthetic details, see: Choi *et al.* (1999).



2. Experimental

2.1. Crystal data

C ₁₅ H ₁₀ F ₂ O ₂ S	V = 1258.81 (5) Å ³
M _r = 292.29	Z = 4
Monoclinic, P2 ₁ /c	Mo K α radiation
a = 8.4826 (2) Å	μ = 0.28 mm ⁻¹
b = 16.6307 (4) Å	T = 173 K
c = 9.7493 (2) Å	0.62 × 0.55 × 0.42 mm
β = 113.756 (1)°	

2.2. Data collection

Bruker SMART APEXII CCD diffractometer	12021 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2009)	3111 independent reflections
T _{min} = 0.846, T _{max} = 0.892	2736 reflections with I > 2 σ (I)
	R _{int} = 0.027

2.3. Refinement

R[F ² > 2 σ (F ²)] = 0.036	182 parameters
wR(F ²) = 0.098	H-atom parameters constrained
S = 1.03	$\Delta\rho_{\max}$ = 0.41 e Å ⁻³
3111 reflections	$\Delta\rho_{\min}$ = -0.35 e Å ⁻³

Table 1

Hydrogen-bond geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
C5—H5...O2 ⁱ	0.95	2.45	3.2612 (18)	143
C12—H12...O2 ⁱⁱ	0.95	2.42	3.3361 (19)	161
C15—H15A...F1 ⁱⁱⁱ	0.98	2.54	3.409 (2)	147
C15—H15B...F2 ^{iv}	0.98	2.55	3.163 (2)	121

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

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

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Supporting information for this paper is available from the IUCr electronic archives (Reference: FY2119).

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supporting information

Acta Cryst. (2014). E70, o1168 [doi:10.1107/S160053681402251X]

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

Hong Dae Choi and Uk Lee

S1. Comment

As a part of our continuing program for benzofuran derivatives (Choi & Lee, 2014), 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 0.015 (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 0.009 (1) Å from the least-squares plane defined by the six constituent atoms. The dihedral angle formed by the benzofuran ring and the 3-fluorophenyl ring is 26.60 (5)°. In the crystal structure (Fig. 2), molecules are linked by C—H⋯O and C—H⋯F hydrogen bonds (Table 1), and by π – π interactions between the benzene and furan rings of neighbouring molecules, with a $Cg1\cdots Cg2^v$ distance of 3.819 (2) Å and an interplanar distance of 3.283 (2) Å resulting in a slippage of 1.951 (2) Å ($Cg1$ and $Cg2$ are the centroids of the C2–C7 benzene ring and C1/C2/C7/O1/C8 furan ring, respectively), forming a three-dimensional network.

S2. Experimental

The starting material 5-fluoro-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 5-fluoro-2-(3-fluorophenyl)-3-methylsulfonyl-1-benzofuran (304 mg, 1.1 mmol) in dichloromethane (30 ml) at 273 K. After being stirred at room temperature for 8h, the mixture was washed with saturated sodium bicarbonate solution (2 × 10 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, 1:2 *v/v*) to afford the title compound as a colorless solid [yield 71% (207 mg); m.p. 459–460 K; R_f = 0.48 (hexane–ethyl acetate, 1:2 *v/v*)]. Single crystals suitable for X-ray diffraction were prepared by slow evaporation of a solution of the title compound (24 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, respectively. U_{iso} (H) = 1.2 U_{eq} (C) for aryl and 1.5 U_{eq} (C) for methyl H atoms. The rotations of methyl groups were optimized using the SHELXL-97 command AFIX 137 (Sheldrick, 2008).

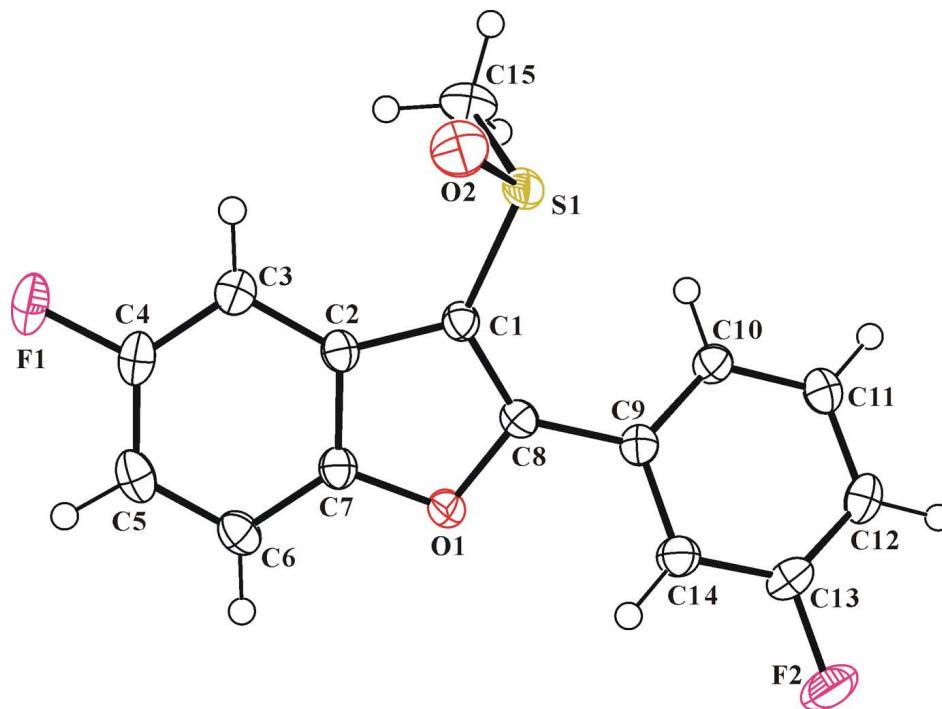


Figure 1

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.

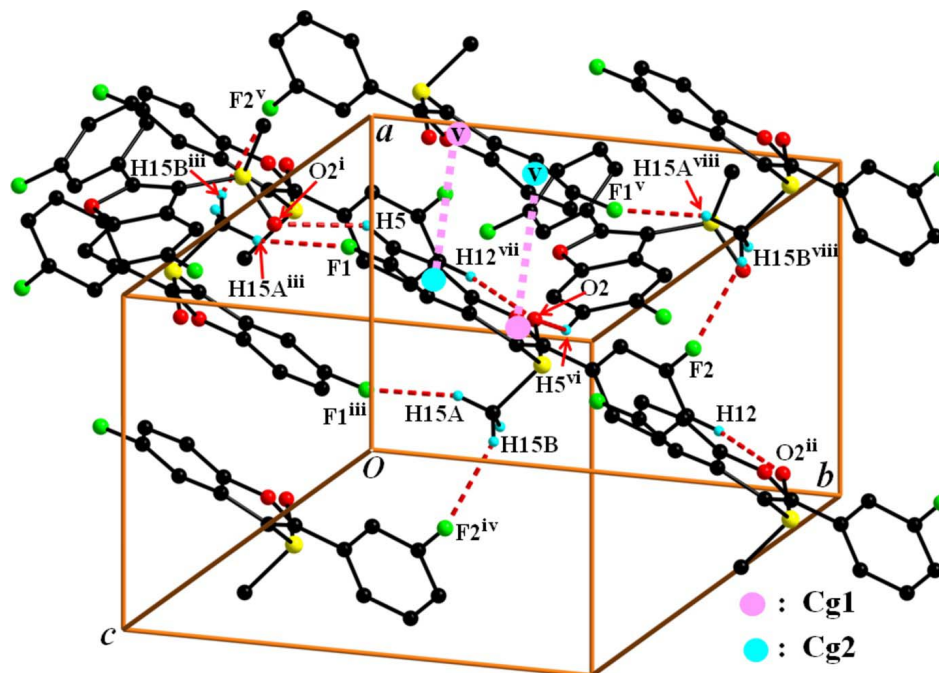


Figure 2

A view of the C—H···O, C—H···F and π — π interactions (dotted lines) in the crystal structure of the title compound. H atoms not participating in hydrogen-bonding were omitted for clarity. [Symmetry codes: (i) $-x + 2, y - 1/2, -z + 3/2$; (ii) $x - 1, y, z - 1$; (iii) $-x + 2, -y + 1, -z + 2$; (iv) $x, y, z + 1$; (v) $-x + 2, -y + 1, -z + 1$; (vi) $-x + 2, y + 1/2, -z + 3/2$; (vii) $x + 1, y, z + 1$; (viii) $-x + 2, y + 1/2, -z + 3/2$.]

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

Crystal data

$C_{15}H_{10}F_2O_2S$

$M_r = 292.29$

Monoclinic, $P2_1/c$

Hall symbol: $-P 2_1 ybc$

$a = 8.4826 (2) \text{ \AA}$

$b = 16.6307 (4) \text{ \AA}$

$c = 9.7493 (2) \text{ \AA}$

$\beta = 113.756 (1)^\circ$

$V = 1258.81 (5) \text{ \AA}^3$

$Z = 4$

$F(000) = 600$

$D_x = 1.542 \text{ Mg m}^{-3}$

Melting point = 460–459 K

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 5007 reflections

$\theta = 2.5\text{--}28.3^\circ$

$\mu = 0.28 \text{ mm}^{-1}$

$T = 173 \text{ K}$

Block, colourless

$0.62 \times 0.55 \times 0.42 \text{ mm}$

Data collection

Bruker SMART APEXII CCD
diffractometer

Radiation source: rotating anode

Graphite multilayer monochromator

Detector resolution: $10.0 \text{ pixels mm}^{-1}$

φ and ω scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2009)

$T_{\min} = 0.846, T_{\max} = 0.892$

12021 measured reflections

3111 independent reflections

2736 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.027$

$\theta_{\max} = 28.3^\circ, \theta_{\min} = 2.5^\circ$

$h = -11 \rightarrow 11$

$k = -18 \rightarrow 22$

$l = -12 \rightarrow 12$

*Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.036$ $wR(F^2) = 0.098$ $S = 1.03$

3111 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

 $w = 1/[\sigma^2(F_o^2) + (0.0527P)^2 + 0.4861P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = 0.001$ $\Delta\rho_{\max} = 0.41 \text{ e } \text{\AA}^{-3}$ $\Delta\rho_{\min} = -0.35 \text{ e } \text{\AA}^{-3}$ *Special details***Experimental.** ^1H NMR (δ p.p.m., CDCl_3 , 400 Hz): 7.91 (dd, $J = 8.56$ and 2.40 Hz, 1H), 7.47-7.64 (m, 4H), 7.13-7.22 (m, 2H), 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>	$U_{\text{iso}}^*/U_{\text{eq}}$
S1	0.68157 (5)	0.69175 (2)	0.61814 (4)	0.02500 (11)
F1	1.15704 (13)	0.43458 (6)	0.91143 (11)	0.0407 (3)
F2	0.31417 (14)	0.61447 (8)	-0.13611 (11)	0.0455 (3)
O1	0.66160 (13)	0.50305 (6)	0.36646 (11)	0.0228 (2)
O2	0.86399 (15)	0.71766 (7)	0.69804 (14)	0.0380 (3)
C1	0.68851 (17)	0.59646 (8)	0.54180 (15)	0.0206 (3)
C2	0.81117 (17)	0.53330 (8)	0.61313 (16)	0.0213 (3)
C3	0.93765 (18)	0.51943 (9)	0.75628 (16)	0.0257 (3)
H3	0.9568	0.5554	0.8371	0.031*
C4	1.03265 (19)	0.45056 (9)	0.77310 (17)	0.0284 (3)
C5	1.0128 (2)	0.39587 (9)	0.65947 (19)	0.0288 (3)
H5	1.0839	0.3494	0.6794	0.035*
C6	0.88870 (19)	0.40976 (8)	0.51726 (18)	0.0263 (3)
H6	0.8720	0.3742	0.4364	0.032*
C7	0.79001 (17)	0.47831 (8)	0.49901 (16)	0.0220 (3)
C8	0.60314 (17)	0.57525 (8)	0.39537 (15)	0.0207 (3)
C9	0.46688 (17)	0.61298 (8)	0.26667 (15)	0.0211 (3)
C10	0.34606 (18)	0.66392 (8)	0.28439 (16)	0.0231 (3)
H10	0.3529	0.6755	0.3821	0.028*
C11	0.21572 (19)	0.69790 (9)	0.16032 (17)	0.0263 (3)
H11	0.1338	0.7324	0.1737	0.032*
C12	0.20422 (19)	0.68181 (9)	0.01715 (17)	0.0280 (3)
H12	0.1159	0.7049	-0.0685	0.034*

C13	0.3254 (2)	0.63115 (10)	0.00347 (16)	0.0287 (3)
C14	0.45608 (19)	0.59613 (9)	0.12251 (17)	0.0262 (3)
H14	0.5368	0.5615	0.1076	0.031*
C15	0.6103 (2)	0.66132 (11)	0.7597 (2)	0.0377 (4)
H15A	0.6903	0.6213	0.8250	0.057*
H15B	0.4949	0.6378	0.7123	0.057*
H15C	0.6068	0.7082	0.8193	0.057*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0261 (2)	0.01759 (17)	0.02614 (19)	−0.00056 (12)	0.00519 (15)	−0.00347 (13)
F1	0.0340 (5)	0.0452 (6)	0.0317 (5)	0.0116 (4)	0.0017 (4)	0.0127 (4)
F2	0.0443 (6)	0.0705 (8)	0.0194 (5)	0.0076 (5)	0.0105 (4)	−0.0019 (4)
O1	0.0240 (5)	0.0197 (5)	0.0223 (5)	0.0023 (4)	0.0069 (4)	−0.0015 (4)
O2	0.0311 (6)	0.0311 (6)	0.0427 (7)	−0.0107 (5)	0.0055 (5)	−0.0085 (5)
C1	0.0204 (6)	0.0183 (6)	0.0215 (6)	0.0002 (5)	0.0068 (5)	0.0003 (5)
C2	0.0202 (6)	0.0192 (6)	0.0240 (7)	−0.0003 (5)	0.0086 (5)	0.0019 (5)
C3	0.0245 (7)	0.0262 (7)	0.0244 (7)	−0.0006 (6)	0.0077 (6)	0.0020 (5)
C4	0.0225 (7)	0.0312 (8)	0.0276 (7)	0.0027 (6)	0.0061 (6)	0.0099 (6)
C5	0.0258 (7)	0.0230 (7)	0.0395 (9)	0.0049 (5)	0.0152 (7)	0.0085 (6)
C6	0.0291 (7)	0.0198 (6)	0.0328 (8)	0.0017 (5)	0.0153 (6)	0.0017 (5)
C7	0.0221 (6)	0.0197 (6)	0.0238 (7)	−0.0004 (5)	0.0087 (6)	0.0021 (5)
C8	0.0207 (6)	0.0187 (6)	0.0229 (7)	0.0001 (5)	0.0090 (5)	−0.0007 (5)
C9	0.0188 (6)	0.0200 (6)	0.0224 (7)	−0.0024 (5)	0.0061 (5)	−0.0002 (5)
C10	0.0222 (6)	0.0252 (7)	0.0214 (6)	−0.0003 (5)	0.0081 (5)	−0.0001 (5)
C11	0.0228 (7)	0.0245 (7)	0.0303 (7)	0.0021 (5)	0.0092 (6)	0.0023 (6)
C12	0.0227 (7)	0.0314 (8)	0.0238 (7)	−0.0003 (6)	0.0030 (6)	0.0062 (6)
C13	0.0285 (7)	0.0371 (8)	0.0190 (7)	−0.0035 (6)	0.0081 (6)	−0.0009 (6)
C14	0.0243 (7)	0.0301 (7)	0.0240 (7)	0.0014 (5)	0.0095 (6)	−0.0021 (6)
C15	0.0439 (10)	0.0383 (9)	0.0378 (9)	0.0002 (7)	0.0237 (8)	−0.0091 (7)

Geometric parameters (Å, °)

S1—O2	1.4885 (12)	C6—C7	1.3828 (19)
S1—C1	1.7619 (14)	C6—H6	0.9500
S1—C15	1.7880 (17)	C8—C9	1.4614 (19)
F1—C4	1.3624 (17)	C9—C10	1.3930 (19)
F2—C13	1.3540 (17)	C9—C14	1.399 (2)
O1—C8	1.3710 (16)	C10—C11	1.388 (2)
O1—C7	1.3754 (17)	C10—H10	0.9500
C1—C8	1.3616 (19)	C11—C12	1.385 (2)
C1—C2	1.4444 (19)	C11—H11	0.9500
C2—C7	1.3949 (19)	C12—C13	1.377 (2)
C2—C3	1.395 (2)	C12—H12	0.9500
C3—C4	1.372 (2)	C13—C14	1.370 (2)
C3—H3	0.9500	C14—H14	0.9500
C4—C5	1.390 (2)	C15—H15A	0.9800

C5—C6	1.381 (2)	C15—H15B	0.9800
C5—H5	0.9500	C15—H15C	0.9800
O2—S1—C1	106.07 (7)	C1—C8—C9	133.75 (12)
O2—S1—C15	106.34 (8)	O1—C8—C9	115.22 (11)
C1—S1—C15	98.65 (7)	C10—C9—C14	119.50 (13)
C8—O1—C7	106.50 (10)	C10—C9—C8	121.44 (12)
C8—C1—C2	106.99 (12)	C14—C9—C8	119.04 (12)
C8—C1—S1	125.57 (11)	C11—C10—C9	120.46 (13)
C2—C1—S1	126.22 (11)	C11—C10—H10	119.8
C7—C2—C3	119.31 (13)	C9—C10—H10	119.8
C7—C2—C1	104.86 (12)	C12—C11—C10	120.49 (13)
C3—C2—C1	135.77 (13)	C12—C11—H11	119.8
C4—C3—C2	115.84 (14)	C10—C11—H11	119.8
C4—C3—H3	122.1	C13—C12—C11	117.62 (13)
C2—C3—H3	122.1	C13—C12—H12	121.2
F1—C4—C3	117.68 (14)	C11—C12—H12	121.2
F1—C4—C5	117.26 (13)	F2—C13—C14	118.00 (14)
C3—C4—C5	125.05 (14)	F2—C13—C12	118.02 (14)
C6—C5—C4	119.27 (13)	C14—C13—C12	123.98 (14)
C6—C5—H5	120.4	C13—C14—C9	117.95 (13)
C4—C5—H5	120.4	C13—C14—H14	121.0
C5—C6—C7	116.38 (14)	C9—C14—H14	121.0
C5—C6—H6	121.8	S1—C15—H15A	109.5
C7—C6—H6	121.8	S1—C15—H15B	109.5
O1—C7—C6	125.23 (13)	H15A—C15—H15B	109.5
O1—C7—C2	110.61 (11)	S1—C15—H15C	109.5
C6—C7—C2	124.14 (14)	H15A—C15—H15C	109.5
C1—C8—O1	111.03 (12)	H15B—C15—H15C	109.5
O2—S1—C1—C8	-126.44 (13)	C1—C2—C7—C6	176.94 (13)
C15—S1—C1—C8	123.68 (13)	C2—C1—C8—O1	-0.09 (15)
O2—S1—C1—C2	39.24 (14)	S1—C1—C8—O1	167.87 (9)
C15—S1—C1—C2	-70.64 (14)	C2—C1—C8—C9	-179.62 (14)
C8—C1—C2—C7	0.90 (15)	S1—C1—C8—C9	-11.7 (2)
S1—C1—C2—C7	-166.96 (10)	C7—O1—C8—C1	-0.78 (15)
C8—C1—C2—C3	177.95 (15)	C7—O1—C8—C9	178.85 (11)
S1—C1—C2—C3	10.1 (2)	C1—C8—C9—C10	-28.6 (2)
C7—C2—C3—C4	-0.32 (19)	O1—C8—C9—C10	151.91 (12)
C1—C2—C3—C4	-177.04 (15)	C1—C8—C9—C14	152.70 (16)
C2—C3—C4—F1	-179.70 (12)	O1—C8—C9—C14	-26.82 (18)
C2—C3—C4—C5	0.8 (2)	C14—C9—C10—C11	0.0 (2)
F1—C4—C5—C6	-179.77 (13)	C8—C9—C10—C11	-178.75 (13)
C3—C4—C5—C6	-0.3 (2)	C9—C10—C11—C12	-0.2 (2)
C4—C5—C6—C7	-0.7 (2)	C10—C11—C12—C13	0.3 (2)
C8—O1—C7—C6	-176.95 (13)	C11—C12—C13—F2	179.38 (13)
C8—O1—C7—C2	1.38 (14)	C11—C12—C13—C14	-0.2 (2)
C5—C6—C7—O1	179.33 (13)	F2—C13—C14—C9	-179.58 (13)

C5—C6—C7—C2	1.2 (2)	C12—C13—C14—C9	0.0 (2)
C3—C2—C7—O1	-179.05 (11)	C10—C9—C14—C13	0.1 (2)
C1—C2—C7—O1	-1.41 (15)	C8—C9—C14—C13	178.89 (13)
C3—C2—C7—C6	-0.7 (2)		

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>
C5—H5...O2 ⁱ	0.95	2.45	3.2612 (18)	143
C12—H12...O2 ⁱⁱ	0.95	2.42	3.3361 (19)	161
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C15—H15 <i>B</i> ...F2 ^{iv}	0.98	2.55	3.163 (2)	121

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