

5-Bromo-3-ethylsulfinyl-2-(4-fluorophenyl)-1-benzofuran

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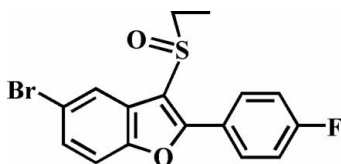
Received 4 January 2010; accepted 6 January 2010

Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.024; wR factor = 0.068; data-to-parameter ratio = 16.9.

In the title compound, $\text{C}_{16}\text{H}_{12}\text{BrFO}_2\text{S}$, the 4-fluorophenyl ring is rotated out of the benzofuran plane, as indicated by the dihedral angle of $5.94(5)^\circ$. The crystal structure exhibits aromatic π - π interactions between the benzene ring and the 4-fluorophenyl ring of an adjacent molecule [centroid-centroid distance = $3.632(2)$ Å], and a $\text{Br}\cdots\text{O}$ halogen bond with a $\text{Br}\cdots\text{O}$ distance of $3.101(1)$ Å.

Related literature

For the crystal structures of similar 2-(4-fluorophenyl)-5-halo-3-methylsulfinyl-1-benzofuran derivatives, see: Choi *et al.* (2009, 2010*a,b*). For the biological activity of benzofuran compounds, see: Aslam *et al.* (2006); Galal *et al.* (2009); Howlett *et al.* (1999). For natural products with benzofuran rings, see: Akgul & Anil (2003); Soekamto *et al.* (2003). For a review of halogen bonding, see: Politzer *et al.* (2007).



Experimental

Crystal data

$\text{C}_{16}\text{H}_{12}\text{BrFO}_2\text{S}$	$\gamma = 104.771(3)^\circ$
$M_r = 367.23$	$V = 693.87(8)$ Å ³
Triclinic, $P\bar{1}$	$Z = 2$
$a = 7.2806(5)$ Å	Mo $K\alpha$ radiation
$b = 9.4999(6)$ Å	$\mu = 3.12$ mm ⁻¹
$c = 10.8334(6)$ Å	$T = 100$ K
$\alpha = 101.360(3)^\circ$	$0.30 \times 0.26 \times 0.18$ mm
$\beta = 98.783(3)^\circ$	

Data collection

Bruker SMART APEXII CCD diffractometer	12298 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2009)	3202 independent reflections
$T_{\min} = 0.457$, $T_{\max} = 0.606$	3040 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.033$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.024$	190 parameters
$wR(F^2) = 0.068$	H-atom parameters constrained
$S = 1.01$	$\Delta\rho_{\text{max}} = 0.48$ e Å ⁻³
3202 reflections	$\Delta\rho_{\text{min}} = -0.47$ 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: SI2236).

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supplementary materials

Acta Cryst. (2010). E66, o323 [doi:10.1107/S1600536810000590]

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Comment

Benzofuran ring systems have drawn considerable attention due to their diverse biological activities (Aslam *et al.*, 2006; Galal *et al.*, 2009; Howlett *et al.* 1999) and these compounds are occurring in natural products (Akgul & Anil, 2003; Soekamto *et al.*, 2003). As a part of our continuing studies of the effect of side chain substituents on the solid state structures of 2-(4-fluorophenyl)-5-halo-3-methylsulfinyl-1-benzofuran analogues (Choi *et al.*, 2009, 2010*a,b*), we report the crystal structure of the title compound (Fig. 1).

The benzofuran unit is essentially planar, with a mean deviation of 0.007 (1) Å from the least-squares plane defined by the nine constituent atoms. The dihedral angle formed by the plane of the benzofuran and the 4-fluorophenyl ring is 5.94 (5)°. The crystal packing (Fig. 2) is stabilized by aromatic π - π interactions between the benzene ring and the 4-fluorophenyl ring of an adjacent molecule. The Cg1-Cg2ⁱ distance is 3.632 (2) Å (Cg1 and Cg2 are the centroids of the C2-C7 benzene ring and the C9-C14 4-fluorophenyl ring, respectively). The crystal packing (Fig. 2) is further stabilized by a Br \cdots O halogen bond between the bromine and the oxygen of the S=O unit [Br \cdots O2ⁱⁱ = 3.101 (1) Å; C-Br \cdots O2 = 168.51 (6)°] (Poltzer *et al.*, 2007).

Experimental

77% 3-Chloroperoxybenzoic acid (208 mg, 0.93 mmol) was added in small portions to a stirred solution of 5-bromo-3-ethylsulfonyl-2-(4-fluorophenyl)-1-benzofuran (298 mg, 0.85 mmol) in dichloromethane (30 mL) at 273 K. After being stirred at room temperature for 3h, the mixture was washed with saturated sodium bicarbonate solution and the organic layer was separated, dried over magnesium sulfate, filtered and concentrated in vacuum. The residue was purified by column chromatography (hexane-ethyl acetate, 2:1 v/v) to afford the title compound as a colorless solid [yield 83%, m.p. 428-429 K; R_f = 0.58 (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 tetrahydrofuran at room temperature.

Refinement

All H atoms were positioned geometrically and refined using a riding model, with C-H = 0.93 Å for aryl, 0.97 Å for methylene, and 0.96 Å for methyl H atoms. $U_{iso}(H) = 1.2U_{eq}(C)$ for all H atoms.

Figures

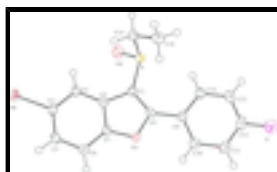


Fig. 1. The molecular structure of the title compound with the atom numbering scheme. Displacement ellipsoids are drawn at the 50 % probability level. H atoms are presented as small spheres of arbitrary radius.

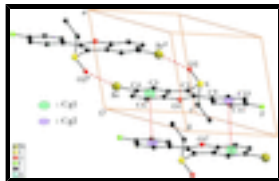


Fig. 2. π - π and C-Br \cdots O interactions (dotted lines) in the crystal structure of the title compound. [Symmetry codes: (i) $-x, -y + 1, -z + 1$; (ii) $-x + 1, -y + 1, -z$.]

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Crystal data

$C_{16}H_{12}BrFO_2S$	$Z = 2$
$M_r = 367.23$	$F(000) = 368$
Triclinic, $P\bar{1}$	$D_x = 1.758 \text{ Mg m}^{-3}$
Hall symbol: $-P 1$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$a = 7.2806 (5) \text{ \AA}$	Cell parameters from 8968 reflections
$b = 9.4999 (6) \text{ \AA}$	$\theta = 2.3\text{--}27.5^\circ$
$c = 10.8334 (6) \text{ \AA}$	$\mu = 3.12 \text{ mm}^{-1}$
$\alpha = 101.360 (3)^\circ$	$T = 100 \text{ K}$
$\beta = 98.783 (3)^\circ$	Block, colourless
$\gamma = 104.771 (3)^\circ$	$0.30 \times 0.26 \times 0.18 \text{ mm}$
$V = 693.87 (8) \text{ \AA}^3$	

Data collection

Bruker SMART APEXII CCD diffractometer	3202 independent reflections
Radiation source: Rotating Anode HELIOS	3040 reflections with $I > 2\sigma(I)$
Detector resolution: $10.0 \text{ pixels mm}^{-1}$	$R_{\text{int}} = 0.033$
ϕ and ω scans	$\theta_{\text{max}} = 27.5^\circ$, $\theta_{\text{min}} = 2.0^\circ$
Absorption correction: multi-scan (SADABS; Bruker, 2009)	$h = -9 \rightarrow 9$
$T_{\text{min}} = 0.457$, $T_{\text{max}} = 0.606$	$k = -12 \rightarrow 12$
12298 measured reflections	$l = -14 \rightarrow 14$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.024$	Hydrogen site location: difference Fourier map
$wR(F^2) = 0.068$	H-atom parameters constrained
$S = 1.01$	$w = 1/[\sigma^2(F_o^2) + (0.0419P)^2 + 0.3178P]$
3202 reflections	where $P = (F_o^2 + 2F_c^2)/3$
190 parameters	$(\Delta/\sigma)_{\text{max}} < 0.001$
	$\Delta\rho_{\text{max}} = 0.48 \text{ e \AA}^{-3}$

0 restraints

$$\Delta\rho_{\min} = -0.47 \text{ e } \text{\AA}^{-3}$$

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 $F^2 > 2\text{sigma}(F^2)$ 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)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Br	0.27979 (3)	0.266152 (19)	-0.060167 (15)	0.02863 (7)
S	0.45510 (6)	0.80533 (4)	0.40790 (4)	0.02178 (10)
O1	0.20904 (16)	0.41876 (12)	0.48809 (11)	0.0196 (2)
O2	0.59525 (19)	0.79599 (16)	0.32187 (14)	0.0323 (3)
F	0.25971 (19)	0.84421 (15)	1.01927 (11)	0.0399 (3)
C1	0.3410 (2)	0.62021 (18)	0.41607 (15)	0.0189 (3)
C2	0.2982 (2)	0.48799 (18)	0.31181 (15)	0.0186 (3)
C3	0.3185 (2)	0.45934 (19)	0.18372 (15)	0.0207 (3)
H3	0.3712	0.5366	0.1468	0.025*
C4	0.2567 (2)	0.31116 (19)	0.11464 (16)	0.0222 (3)
C5	0.1791 (2)	0.19150 (19)	0.16709 (17)	0.0246 (3)
H5	0.1407	0.0933	0.1168	0.030*
C6	0.1596 (2)	0.21979 (19)	0.29435 (17)	0.0233 (3)
H6	0.1091	0.1425	0.3319	0.028*
C7	0.2188 (2)	0.36812 (18)	0.36236 (15)	0.0191 (3)
C8	0.2848 (2)	0.57296 (17)	0.51972 (16)	0.0186 (3)
C9	0.2833 (2)	0.64583 (19)	0.65130 (15)	0.0193 (3)
C10	0.2268 (2)	0.5583 (2)	0.73659 (17)	0.0238 (3)
H10	0.1946	0.4542	0.7098	0.029*
C11	0.2185 (3)	0.6250 (2)	0.86028 (17)	0.0272 (4)
H11	0.1786	0.5668	0.9165	0.033*
C12	0.2703 (3)	0.7792 (2)	0.89850 (17)	0.0277 (4)
C13	0.3302 (3)	0.8695 (2)	0.81914 (18)	0.0283 (4)
H13	0.3672	0.9736	0.8483	0.034*
C14	0.3342 (2)	0.8021 (2)	0.69475 (17)	0.0243 (3)
H14	0.3715	0.8617	0.6390	0.029*
C15	0.2449 (3)	0.8353 (2)	0.31525 (17)	0.0256 (3)
H15A	0.2868	0.9230	0.2818	0.031*
H15B	0.1836	0.7493	0.2425	0.031*
C16	0.0982 (3)	0.8580 (2)	0.39692 (19)	0.0278 (4)
H16A	0.1582	0.9436	0.4686	0.033*

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H16B	0.0539	0.7702	0.4282	0.033*
H16C	-0.0104	0.8745	0.3457	0.033*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br	0.03874 (12)	0.02938 (11)	0.01775 (10)	0.01314 (8)	0.00627 (7)	0.00147 (7)
S	0.02209 (19)	0.01876 (19)	0.0229 (2)	0.00193 (15)	0.00670 (15)	0.00547 (15)
O1	0.0233 (5)	0.0168 (5)	0.0184 (5)	0.0045 (4)	0.0059 (4)	0.0045 (4)
O2	0.0298 (6)	0.0334 (7)	0.0362 (7)	0.0059 (5)	0.0179 (6)	0.0107 (6)
F	0.0514 (7)	0.0480 (7)	0.0191 (5)	0.0180 (6)	0.0106 (5)	-0.0016 (5)
C1	0.0184 (7)	0.0182 (7)	0.0198 (7)	0.0051 (6)	0.0045 (6)	0.0044 (6)
C2	0.0170 (7)	0.0189 (7)	0.0203 (8)	0.0060 (6)	0.0039 (6)	0.0047 (6)
C3	0.0214 (7)	0.0227 (8)	0.0191 (8)	0.0073 (6)	0.0055 (6)	0.0057 (6)
C4	0.0234 (7)	0.0261 (8)	0.0181 (8)	0.0107 (6)	0.0043 (6)	0.0033 (6)
C5	0.0276 (8)	0.0205 (8)	0.0246 (8)	0.0094 (7)	0.0034 (6)	0.0019 (6)
C6	0.0254 (8)	0.0188 (8)	0.0260 (8)	0.0066 (6)	0.0054 (6)	0.0061 (6)
C7	0.0195 (7)	0.0212 (8)	0.0186 (7)	0.0080 (6)	0.0052 (6)	0.0059 (6)
C8	0.0174 (7)	0.0167 (7)	0.0213 (8)	0.0052 (6)	0.0036 (6)	0.0045 (6)
C9	0.0171 (7)	0.0233 (8)	0.0174 (7)	0.0064 (6)	0.0033 (5)	0.0044 (6)
C10	0.0268 (8)	0.0239 (8)	0.0212 (8)	0.0076 (7)	0.0054 (6)	0.0060 (6)
C11	0.0310 (9)	0.0351 (10)	0.0189 (8)	0.0117 (7)	0.0073 (7)	0.0097 (7)
C12	0.0273 (8)	0.0383 (10)	0.0167 (8)	0.0132 (7)	0.0043 (6)	0.0006 (7)
C13	0.0307 (9)	0.0253 (9)	0.0249 (9)	0.0078 (7)	0.0050 (7)	-0.0014 (7)
C14	0.0261 (8)	0.0239 (8)	0.0218 (8)	0.0059 (6)	0.0066 (6)	0.0043 (6)
C15	0.0303 (8)	0.0237 (8)	0.0241 (8)	0.0082 (7)	0.0052 (7)	0.0094 (7)
C16	0.0247 (8)	0.0258 (9)	0.0323 (10)	0.0070 (7)	0.0045 (7)	0.0078 (7)

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

Br—O2 ⁱ	3.101 (1)	C6—H6	0.9300
Br—C4	1.901 (2)	C8—C9	1.460 (2)
S—O2	1.491 (1)	C9—C10	1.399 (2)
S—C1	1.769 (2)	C9—C14	1.398 (2)
S—C15	1.816 (2)	C10—C11	1.382 (2)
O1—C7	1.372 (2)	C10—H10	0.9300
O1—C8	1.378 (2)	C11—C12	1.375 (3)
F—C12	1.355 (2)	C11—H11	0.9300
C1—C8	1.369 (2)	C12—C13	1.371 (3)
C1—C2	1.444 (2)	C13—C14	1.381 (2)
C2—C7	1.392 (2)	C13—H13	0.9300
C2—C3	1.398 (2)	C14—H14	0.9300
C3—C4	1.380 (2)	C15—C16	1.517 (3)
C3—H3	0.9300	C15—H15A	0.9700
C4—C5	1.400 (2)	C15—H15B	0.9700
C5—C6	1.388 (2)	C16—H16A	0.9600
C5—H5	0.9300	C16—H16B	0.9600
C6—C7	1.378 (2)	C16—H16C	0.9600

C4—Br—O2 ⁱ	168.51 (6)	C10—C9—C8	119.77 (15)
O2—S—C1	107.40 (8)	C14—C9—C8	121.70 (15)
O2—S—C15	106.91 (8)	C11—C10—C9	120.65 (16)
C1—S—C15	97.23 (8)	C11—C10—H10	119.7
C7—O1—C8	107.06 (12)	C9—C10—H10	119.7
C8—C1—C2	107.15 (14)	C12—C11—C10	118.61 (16)
C8—C1—S	128.11 (13)	C12—C11—H11	120.7
C2—C1—S	124.69 (12)	C10—C11—H11	120.7
C7—C2—C3	119.18 (15)	F—C12—C13	118.78 (17)
C7—C2—C1	105.14 (14)	F—C12—C11	118.47 (17)
C3—C2—C1	135.68 (15)	C13—C12—C11	122.75 (17)
C4—C3—C2	116.93 (15)	C12—C13—C14	118.37 (17)
C4—C3—H3	121.5	C12—C13—H13	120.8
C2—C3—H3	121.5	C14—C13—H13	120.8
C3—C4—C5	123.31 (15)	C13—C14—C9	121.07 (16)
C3—C4—Br	118.62 (13)	C13—C14—H14	119.5
C5—C4—Br	118.07 (13)	C9—C14—H14	119.5
C6—C5—C4	119.80 (16)	C16—C15—S	111.41 (12)
C6—C5—H5	120.1	C16—C15—H15A	109.3
C4—C5—H5	120.1	S—C15—H15A	109.3
C7—C6—C5	116.67 (15)	C16—C15—H15B	109.3
C7—C6—H6	121.7	S—C15—H15B	109.3
C5—C6—H6	121.7	H15A—C15—H15B	108.0
O1—C7—C6	125.37 (14)	C15—C16—H16A	109.5
O1—C7—C2	110.52 (14)	C15—C16—H16B	109.5
C6—C7—C2	124.10 (15)	H16A—C16—H16B	109.5
C1—C8—O1	110.12 (14)	C15—C16—H16C	109.5
C1—C8—C9	135.64 (15)	H16A—C16—H16C	109.5
O1—C8—C9	114.23 (13)	H16B—C16—H16C	109.5
C10—C9—C14	118.52 (15)		
O2—S—C1—C8	143.78 (15)	C2—C1—C8—O1	0.09 (17)
C15—S—C1—C8	-105.92 (15)	S—C1—C8—O1	-177.28 (11)
O2—S—C1—C2	-33.17 (15)	C2—C1—C8—C9	-178.63 (16)
C15—S—C1—C2	77.13 (14)	S—C1—C8—C9	4.0 (3)
C8—C1—C2—C7	-0.47 (17)	C7—O1—C8—C1	0.32 (17)
S—C1—C2—C7	177.02 (12)	C7—O1—C8—C9	179.35 (12)
C8—C1—C2—C3	179.55 (17)	C1—C8—C9—C10	-175.02 (17)
S—C1—C2—C3	-3.0 (3)	O1—C8—C9—C10	6.3 (2)
C7—C2—C3—C4	0.2 (2)	C1—C8—C9—C14	6.0 (3)
C1—C2—C3—C4	-179.86 (17)	O1—C8—C9—C14	-172.71 (14)
C2—C3—C4—C5	-0.9 (2)	C14—C9—C10—C11	1.1 (2)
C2—C3—C4—Br	179.69 (11)	C8—C9—C10—C11	-177.92 (15)
C3—C4—C5—C6	0.7 (3)	C9—C10—C11—C12	-1.2 (3)
Br—C4—C5—C6	-179.91 (13)	C10—C11—C12—F	179.22 (16)
C4—C5—C6—C7	0.3 (2)	C10—C11—C12—C13	-0.1 (3)
C8—O1—C7—C6	179.18 (15)	F—C12—C13—C14	-177.84 (16)
C8—O1—C7—C2	-0.64 (16)	C11—C12—C13—C14	1.5 (3)
C5—C6—C7—O1	179.14 (15)	C12—C13—C14—C9	-1.6 (3)

supplementary materials

C5—C6—C7—C2	-1.1 (2)	C10—C9—C14—C13	0.3 (2)
C3—C2—C7—O1	-179.33 (13)	C8—C9—C14—C13	179.32 (15)
C1—C2—C7—O1	0.68 (17)	O2—S—C15—C16	-175.84 (12)
C3—C2—C7—C6	0.9 (2)	C1—S—C15—C16	73.45 (14)
C1—C2—C7—C6	-179.14 (15)		

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

Fig. 1

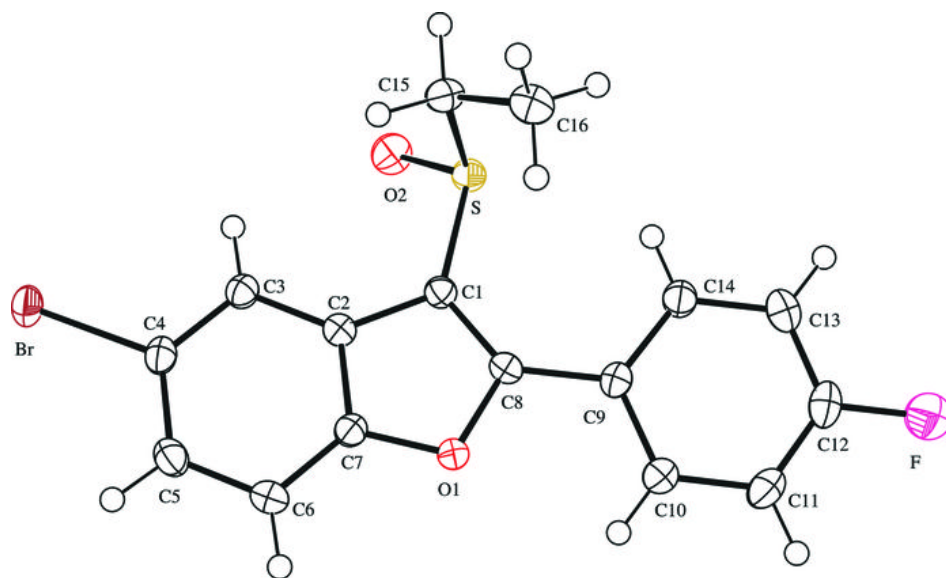


Fig. 2

