

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

5-Bromo-2-(4-fluorophenyl)-7-methyl-3-methylsulfinyl-1-benzofuran

Hong Dae Choi,^a Pil Ja Seo,^a Byeng Wha Son^b and Uk Lee^{b*}^aDepartment of Chemistry, Donggeui University, San 24 Kaya-dong Busanjin-gu, Busan 614-714, Republic of Korea, and ^bDepartment 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

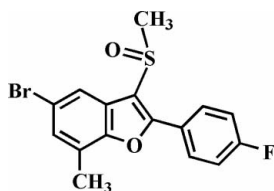
Received 15 December 2009; accepted 16 December 2009

Key indicators: single-crystal X-ray study; $T = 173$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.023; wR factor = 0.060; data-to-parameter ratio = 16.1.

In the title compound, $\text{C}_{16}\text{H}_{12}\text{BrFO}_2\text{S}$, the O atom and the methyl group of the methylsulfinyl substituent are located on opposite sides of the plane through the benzofuran fragment. The 4-fluorophenyl ring is rotated out of the benzofuran plane, as indicated by the dihedral angle of $16.17(5)^\circ$. The crystal structure exhibits an intermolecular $\text{C}-\text{H}\cdots\text{O}$ hydrogen bond and a $\text{Br}\cdots\text{O}$ halogen interaction [$3.112(2)$ Å].

Related literature

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



Experimental

Crystal data

 $\text{C}_{16}\text{H}_{12}\text{BrFO}_2\text{S}$ $M_r = 367.23$

Triclinic, $P\bar{1}$
 $a = 7.5313(6)$ Å
 $b = 9.8089(7)$ Å
 $c = 10.9117(8)$ Å
 $\alpha = 106.567(1)^\circ$
 $\beta = 92.634(1)^\circ$
 $\gamma = 109.526(1)^\circ$

$V = 719.23(9)$ Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 3.01$ mm⁻¹
 $T = 173$ K
 $0.60 \times 0.40 \times 0.20$ mm

Data collection

Bruker SMART APEXII CCD diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 2009)
 $T_{\min} = 0.586$, $T_{\max} = 0.746$

6248 measured reflections
 3083 independent reflections
 2802 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.016$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.023$
 $wR(F^2) = 0.060$
 $S = 1.05$
 3083 reflections

192 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.34$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.39$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{C}15-\text{H}15\text{C}\cdots\text{O}2^i$	0.96	2.58	3.294 (2)	131

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

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: KP2245).

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supplementary materials

Acta Cryst. (2010). E66, o215 [doi:10.1107/S160053680905418X]

5-Bromo-2-(4-fluorophenyl)-7-methyl-3-methylsulfinyl-1-benzofuran

H. D. Choi, P. J. Seo, B. W. Son and U. Lee

Comment

Molecules of benzofuran ring skeleton have attracted considerable interest, on account of their pharmacological activity (Howlett *et al.*, 1999; Twyman & Allsop, 1999) and their occurrence as natural products (Akgul & Anil, 2003; Soekamto *et al.*, 2003). As a part of our continuing studies on 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*a, b*, 2010), we report the crystal structure of the title compound (Fig. 1).

The benzofuran unit is essentially planar, with a mean deviation of 0.014 (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 16.17 (5)°. The crystal packing (Fig. 2) is stabilized by an intermolecular C—H...O hydrogen bond between the methyl H atom and the oxygen of the S=O unit, with a C15—H15C...O2ⁱ (Table 1 and Fig. 2). The contact C—Br...O involving the the oxygen atom of the S=O unit [Br...O2ⁱⁱ = 3.112 (1) Å; C—Br...O2ⁱⁱ = 173.44 (7)°] is significantly shorter than the sum of van der Waals radii (3.40 Å) (Poltzer *et al.*, 2007).

Experimental

77% 3-Chloroperoxybenzoic acid (247 mg, 1.1 mmol) was added in small portions to a stirred solution of 5-bromo-2-(4-fluorophenyl)-7-methyl-3-methylsulfonyl-1-benzofuran (351 mg, 1.0 mmol) in dichloromethane (30 mL) at 273 K. After being stirred at room temperature for 3 h, 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, 1:1 v/v) to afford the title compound as a colourless solid [yield 85%, m.p. 477–478 K; R_f = 0.71 (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 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 aromatic H atoms and 0.96 Å for methyl H atoms, and with $U_{iso}(H) = 1.2U_{eq}(C)$ for aromatic H atoms and $1.5U_{eq}(C)$ for methyl H atoms.

Figures

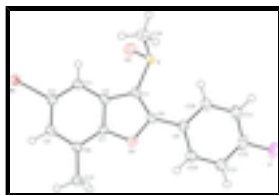


Fig. 1. The molecular structure of the title compound with the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are presented as a small spheres of arbitrary radius.

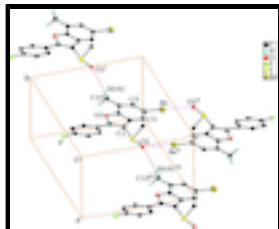


Fig. 2. C—H...O and C—Br...O interactions (dotted lines) in the crystal structure of the title compound. [Symmetry codes: (i) $x, y + 1, z$; (ii) $-x + 1, -y + 1, -z + 2$; (iii) $x, y - 1, z$.]

5-Bromo-2-(4-fluorophenyl)-7-methyl-3-methylsulfinyl-1-benzofuran

Crystal data

$C_{16}H_{12}BrFO_2S$

$M_r = 367.23$

Triclinic, $P\bar{1}$

Hall symbol: $-P\ 1$

$a = 7.5313\ (6)\ \text{\AA}$

$b = 9.8089\ (7)\ \text{\AA}$

$c = 10.9117\ (8)\ \text{\AA}$

$\alpha = 106.567\ (1)^\circ$

$\beta = 92.634\ (1)^\circ$

$\gamma = 109.526\ (1)^\circ$

$V = 719.23\ (9)\ \text{\AA}^3$

$Z = 2$

$F(000) = 368$

$D_x = 1.696\ \text{Mg m}^{-3}$

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

Cell parameters from 4231 reflections

$\theta = 2.3\text{--}27.4^\circ$

$\mu = 3.01\ \text{mm}^{-1}$

$T = 173\ \text{K}$

Block, colourless

$0.60 \times 0.40 \times 0.20\ \text{mm}$

Data collection

Bruker SMART APEXII CCD
diffractometer

Radiation source: Rotating Anode
HELIOS

Detector resolution: $10.0\ \text{pixels mm}^{-1}$
 ϕ and ω scans

Absorption correction: multi-scan
(*SADABS*; Bruker, 2009)

$T_{\min} = 0.586$, $T_{\max} = 0.746$

6248 measured reflections

3083 independent reflections

2802 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.016$

$\theta_{\max} = 27.0^\circ$, $\theta_{\min} = 2.0^\circ$

$h = -9 \rightarrow 9$

$k = -12 \rightarrow 12$

$l = -13 \rightarrow 13$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.023$

$wR(F^2) = 0.060$

$S = 1.05$

3083 reflections

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

$w = 1/[\sigma^2(F_o^2) + (0.0302P)^2 + 0.3573P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

192 parameters

$$\Delta\rho_{\max} = 0.34 \text{ e } \text{\AA}^{-3}$$

0 restraints

$$\Delta\rho_{\min} = -0.39 \text{ e } \text{\AA}^{-3}$$

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)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Br	0.56892 (3)	0.75819 (2)	1.066631 (17)	0.02668 (7)
S	0.18420 (7)	0.22498 (5)	0.55788 (4)	0.02381 (11)
O1	0.31077 (18)	0.62985 (14)	0.50645 (12)	0.0214 (3)
O2	0.3359 (2)	0.21723 (16)	0.64548 (14)	0.0320 (3)
F	-0.0757 (2)	0.21942 (17)	-0.05951 (11)	0.0476 (4)
C1	0.2455 (3)	0.4180 (2)	0.56565 (17)	0.0207 (4)
C2	0.3406 (3)	0.5483 (2)	0.67945 (17)	0.0197 (3)
C3	0.3970 (3)	0.5713 (2)	0.81000 (17)	0.0217 (4)
H3	0.3726	0.4901	0.8427	0.026*
C4	0.4906 (3)	0.7202 (2)	0.88760 (17)	0.0216 (4)
C5	0.5318 (3)	0.8455 (2)	0.84171 (18)	0.0217 (4)
H5	0.5973	0.9434	0.8985	0.026*
C6	0.4760 (3)	0.8255 (2)	0.71248 (18)	0.0207 (4)
C7	0.3798 (2)	0.6748 (2)	0.63653 (17)	0.0193 (3)
C8	0.2316 (2)	0.4724 (2)	0.46474 (18)	0.0203 (4)
C9	0.1517 (3)	0.4038 (2)	0.32705 (17)	0.0215 (4)
C10	0.0209 (3)	0.2541 (2)	0.27673 (19)	0.0283 (4)
H10	-0.0167	0.1961	0.3316	0.034*
C11	-0.0534 (3)	0.1909 (3)	0.1460 (2)	0.0332 (5)
H11	-0.1376	0.0903	0.1121	0.040*
C12	0.0004 (3)	0.2802 (3)	0.06824 (19)	0.0318 (5)
C13	0.1276 (3)	0.4285 (3)	0.11316 (19)	0.0298 (4)
H13	0.1607	0.4860	0.0575	0.036*
C14	0.2051 (3)	0.4901 (2)	0.24326 (19)	0.0252 (4)
H14	0.2933	0.5895	0.2752	0.030*
C15	0.5111 (3)	0.9548 (2)	0.65832 (19)	0.0268 (4)
H15A	0.5531	0.9286	0.5760	0.040*
H15B	0.6076	1.0448	0.7168	0.040*
H15C	0.3952	0.9737	0.6475	0.040*
C16	-0.0164 (3)	0.2099 (3)	0.6426 (2)	0.0351 (5)

supplementary materials

H16A	-0.0639	0.1111	0.6538	0.053*
H16B	-0.1150	0.2230	0.5936	0.053*
H16C	0.0222	0.2874	0.7258	0.053*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br	0.03804 (12)	0.02214 (11)	0.01767 (10)	0.01046 (8)	-0.00056 (7)	0.00439 (7)
S	0.0331 (3)	0.0152 (2)	0.0220 (2)	0.00897 (19)	0.00200 (19)	0.00445 (17)
O1	0.0269 (7)	0.0172 (6)	0.0193 (6)	0.0071 (5)	0.0009 (5)	0.0062 (5)
O2	0.0397 (8)	0.0274 (8)	0.0342 (8)	0.0167 (7)	0.0012 (6)	0.0128 (6)
F	0.0504 (8)	0.0559 (9)	0.0194 (6)	0.0055 (7)	-0.0086 (6)	0.0053 (6)
C1	0.0239 (9)	0.0164 (8)	0.0205 (9)	0.0066 (7)	0.0025 (7)	0.0052 (7)
C2	0.0223 (8)	0.0170 (8)	0.0208 (9)	0.0087 (7)	0.0039 (7)	0.0055 (7)
C3	0.0282 (9)	0.0175 (9)	0.0211 (9)	0.0095 (7)	0.0039 (7)	0.0075 (7)
C4	0.0260 (9)	0.0226 (9)	0.0174 (8)	0.0112 (7)	0.0019 (7)	0.0058 (7)
C5	0.0232 (9)	0.0159 (9)	0.0232 (9)	0.0071 (7)	0.0020 (7)	0.0026 (7)
C6	0.0222 (9)	0.0170 (9)	0.0239 (9)	0.0083 (7)	0.0051 (7)	0.0065 (7)
C7	0.0211 (8)	0.0186 (9)	0.0186 (8)	0.0076 (7)	0.0015 (7)	0.0062 (7)
C8	0.0200 (8)	0.0173 (9)	0.0221 (9)	0.0063 (7)	0.0034 (7)	0.0046 (7)
C9	0.0203 (8)	0.0242 (9)	0.0202 (9)	0.0095 (7)	0.0020 (7)	0.0059 (7)
C10	0.0276 (10)	0.0276 (10)	0.0253 (10)	0.0051 (8)	0.0010 (8)	0.0083 (8)
C11	0.0282 (10)	0.0311 (11)	0.0287 (11)	0.0026 (9)	-0.0032 (8)	0.0033 (9)
C12	0.0290 (10)	0.0415 (12)	0.0187 (9)	0.0108 (9)	-0.0018 (8)	0.0037 (9)
C13	0.0310 (10)	0.0368 (12)	0.0233 (10)	0.0117 (9)	0.0031 (8)	0.0130 (9)
C14	0.0259 (9)	0.0247 (10)	0.0242 (9)	0.0093 (8)	0.0022 (8)	0.0070 (8)
C15	0.0364 (11)	0.0192 (9)	0.0261 (10)	0.0102 (8)	0.0063 (8)	0.0087 (8)
C16	0.0333 (11)	0.0280 (11)	0.0443 (13)	0.0068 (9)	0.0101 (10)	0.0164 (10)

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

Br—C4	1.907 (2)	C6—C15	1.497 (3)
Br—O2 ⁱ	3.112 (2)	C8—C9	1.463 (2)
S—O2	1.491 (2)	C9—C10	1.397 (3)
S—C1	1.768 (2)	C9—C14	1.401 (3)
S—C16	1.794 (2)	C10—C11	1.386 (3)
O1—C7	1.379 (2)	C10—H10	0.9300
O1—C8	1.381 (2)	C11—C12	1.368 (3)
F—C12	1.360 (2)	C11—H11	0.9300
C1—C8	1.368 (3)	C12—C13	1.375 (3)
C1—C2	1.445 (2)	C13—C14	1.386 (3)
C2—C7	1.394 (2)	C13—H13	0.9300
C2—C3	1.399 (2)	C14—H14	0.9300
C3—C4	1.378 (3)	C15—H15A	0.9600
C3—H3	0.9300	C15—H15B	0.9600
C4—C5	1.403 (3)	C15—H15C	0.9600
C5—C6	1.391 (3)	C16—H16A	0.9600
C5—H5	0.9300	C16—H16B	0.9600

C6—C7	1.389 (2)	C16—H16C	0.9600
C4—Br—O2 ⁱ	173.44 (7)	C10—C9—C8	121.62 (17)
O2—S—C1	107.33 (9)	C14—C9—C8	119.58 (17)
O2—S—C16	105.95 (10)	C11—C10—C9	120.85 (19)
C1—S—C16	97.80 (9)	C11—C10—H10	119.6
C7—O1—C8	106.74 (13)	C9—C10—H10	119.6
C8—C1—C2	107.32 (16)	C12—C11—C10	118.3 (2)
C8—C1—S	127.08 (14)	C12—C11—H11	120.8
C2—C1—S	125.27 (14)	C10—C11—H11	120.8
C7—C2—C3	118.96 (16)	F—C12—C11	118.39 (19)
C7—C2—C1	105.04 (15)	F—C12—C13	118.55 (19)
C3—C2—C1	136.00 (17)	C11—C12—C13	123.06 (19)
C4—C3—C2	116.62 (16)	C12—C13—C14	118.48 (19)
C4—C3—H3	121.7	C12—C13—H13	120.8
C2—C3—H3	121.7	C14—C13—H13	120.8
C3—C4—C5	123.42 (17)	C13—C14—C9	120.46 (18)
C3—C4—Br	118.40 (14)	C13—C14—H14	119.8
C5—C4—Br	118.17 (14)	C9—C14—H14	119.8
C6—C5—C4	120.97 (17)	C6—C15—H15A	109.5
C6—C5—H5	119.5	C6—C15—H15B	109.5
C4—C5—H5	119.5	H15A—C15—H15B	109.5
C7—C6—C5	114.57 (16)	C6—C15—H15C	109.5
C7—C6—C15	121.86 (17)	H15A—C15—H15C	109.5
C5—C6—C15	123.54 (17)	H15B—C15—H15C	109.5
O1—C7—C6	124.01 (16)	S—C16—H16A	109.5
O1—C7—C2	110.54 (15)	S—C16—H16B	109.5
C6—C7—C2	125.44 (17)	H16A—C16—H16B	109.5
C1—C8—O1	110.33 (16)	S—C16—H16C	109.5
C1—C8—C9	135.27 (17)	H16A—C16—H16C	109.5
O1—C8—C9	114.40 (15)	H16B—C16—H16C	109.5
C10—C9—C14	118.79 (17)		
O2—S—C1—C8	138.31 (17)	C1—C2—C7—O1	1.57 (19)
C16—S—C1—C8	-112.23 (18)	C3—C2—C7—C6	1.6 (3)
O2—S—C1—C2	-34.18 (18)	C1—C2—C7—C6	-177.92 (17)
C16—S—C1—C2	75.29 (18)	C2—C1—C8—O1	-0.4 (2)
C8—C1—C2—C7	-0.7 (2)	S—C1—C8—O1	-173.93 (13)
S—C1—C2—C7	172.99 (14)	C2—C1—C8—C9	-179.25 (19)
C8—C1—C2—C3	179.9 (2)	S—C1—C8—C9	7.2 (3)
S—C1—C2—C3	-6.4 (3)	C7—O1—C8—C1	1.32 (19)
C7—C2—C3—C4	-0.6 (3)	C7—O1—C8—C9	-179.53 (14)
C1—C2—C3—C4	178.7 (2)	C1—C8—C9—C10	17.4 (3)
C2—C3—C4—C5	-0.7 (3)	O1—C8—C9—C10	-161.47 (17)
C2—C3—C4—Br	179.49 (13)	C1—C8—C9—C14	-163.3 (2)
C3—C4—C5—C6	1.1 (3)	O1—C8—C9—C14	17.8 (2)
Br—C4—C5—C6	-179.08 (14)	C14—C9—C10—C11	0.7 (3)
C4—C5—C6—C7	-0.2 (3)	C8—C9—C10—C11	180.00 (18)
C4—C5—C6—C15	178.35 (17)	C9—C10—C11—C12	-1.8 (3)
C8—O1—C7—C6	177.69 (17)	C10—C11—C12—F	-178.57 (19)

supplementary materials

C8—O1—C7—C2	-1.81 (19)	C10—C11—C12—C13	1.4 (3)
C5—C6—C7—O1	179.43 (16)	F—C12—C13—C14	-179.89 (18)
C15—C6—C7—O1	0.9 (3)	C11—C12—C13—C14	0.1 (3)
C5—C6—C7—C2	-1.1 (3)	C12—C13—C14—C9	-1.3 (3)
C15—C6—C7—C2	-179.68 (17)	C10—C9—C14—C13	0.8 (3)
C3—C2—C7—O1	-178.94 (15)	C8—C9—C14—C13	-178.44 (17)

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

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C15—H15C \cdots O2 ⁱⁱ	0.96	2.58	3.294 (2)	131

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

Fig. 1

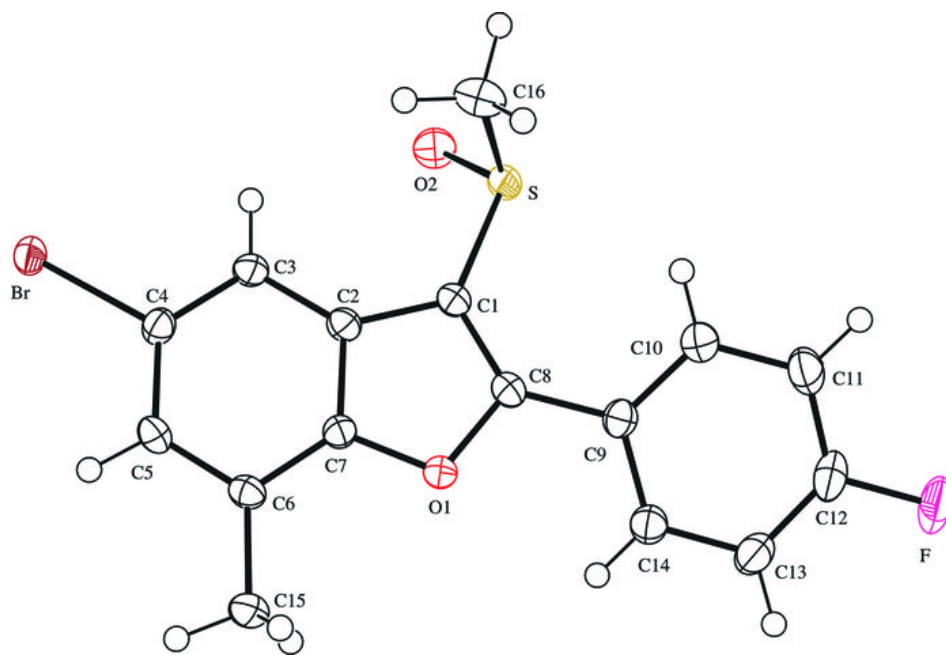


Fig. 2

