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2-(4-Bromophenyl)-5-fluoro-3-methylsulfanyl-1-benzofuran

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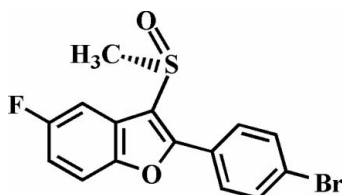
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.024; wR factor = 0.062; data-to-parameter ratio = 15.7.

In the title compound, $\text{C}_{15}\text{H}_{10}\text{BrFO}_2\text{S}$, the O atom and the methyl group of the methylsulfanyl substituent lie on opposite sides of the plane through the benzofuran fragment. The 4-bromophenyl ring is rotated out of the benzofuran plane [dihedral angle = $38.98(8)^\circ$], while the structure is stabilized by an intermolecular $\text{C}-\text{H}\cdots\text{O}$ hydrogen bond and a $\text{Br}\cdots\text{O}$ halogen bond [$3.036(2)$ Å] and has an intermolecular $\text{C}-\text{H}\cdots\pi$ interaction between the 4-bromophenyl H atom and the benzene ring of an adjacent benzofuran molecule, as well as aromatic $\pi-\pi$ interactions between the benzene rings of the benzofuran systems [centroid-centroid distance = $3.482(3)$ Å].

Related literature

For the crystal structures of similar 2-(4-bromophenyl)-3-methylsulfanyl-1-benzofuran derivatives, see: Choi *et al.* (2007*a,b*). For the pharmacological activity of benzofuran compounds, see: Howlett *et al.* (1999); Twyman & Allsop (1999). For a review of halogen bonding, see: Politzer *et al.* (2007).



Experimental

Crystal data

$\text{C}_{15}\text{H}_{10}\text{BrFO}_2\text{S}$
 $M_r = 353.20$
 Triclinic, $P\bar{1}$
 $a = 8.6909(7)$ Å
 $b = 9.1765(7)$ Å
 $c = 10.1308(8)$ Å
 $\alpha = 105.989(1)^\circ$
 $\beta = 114.811(1)^\circ$
 $\gamma = 99.423(1)^\circ$
 $V = 667.91(9)$ Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 3.24$ mm⁻¹
 $T = 293$ K
 $0.40 \times 0.20 \times 0.10$ mm

Data collection

Bruker SMART CCD-detector diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.461$, $T_{\max} = 0.720$
 5792 measured reflections
 2861 independent reflections
 2589 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.016$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.024$
 $wR(F^2) = 0.062$
 $S = 1.05$
 2861 reflections
 182 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.56$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.52$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{C15}-\text{H15C}\cdots\text{O2}^{\text{i}}$	0.96	2.36	3.251 (3)	155
$\text{C13}-\text{H13}\cdots\text{C8}^{\text{ii}}$	0.93	2.74	3.366 (3)	125

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

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); 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: ZS2004).

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supplementary materials

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2-(4-Bromophenyl)-5-fluoro-3-methylsulfinyl-1-benzofuran

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Comment

Benzofuran derivatives are of considerable interest because of their pharmacological properties (Howlett et al., 1999; Twyman & Allsop, 1999). This present work is related to our communications on the synthesis and structures of 2-(4-bromophenyl)-3-methylsulfinyl-1-benzofuran analogues, viz. 2-(4-bromophenyl)-5-methyl-3-methylsulfinyl-1-benzofuran (Choi et al., 2007a) and 2-(4-bromophenyl)-5,7-dimethyl-3-methylsulfinyl-1-benzofuran (Choi et al., 2007b). Here we report the crystal structure of the title compound (I) (Fig. 1). The benzofuran unit in (I) is essentially planar, with a mean deviation of 0.006 (2) Å from the least-squares plane defined by the nine constituent atoms. The dihedral angle formed by the planes of the benzofuran and the 4-bromophenyl rings is 38.98 (8) °. The crystal packing (Fig. 2) is stabilized by an intermolecular C–H···O hydrogen bond between the methyl H atom and the S=O unit (Table 1) and a Br···O halogen bond [Br···O2ⁱⁱⁱ, 3.036 (2) Å; C–Br···O, 165.46 (7) °] (symmetry code : (iii) x, y-1, z-1) (Politzer et al., 2007). The crystal packing also has an intermolecular C–H···π interaction between a 4-bromophenyl H atom (C13) and the benzene ring of an adjacent molecule [C–H···Cgⁱⁱ] (Table 1), (where Cg is the centroid of the C2-C7 benzene ring). Further stability comes from aromatic π–π interactions between the benzene rings of the adjacent molecules, with a Cg···Cg^{iv} distance of 3.482 (3) Å [symmetry code: (iv) -x + 1, -y + 1, -z + 1].

Experimental

3-Chloroperoxybenzoic acid (77%) (291 mg, 1.3 mmol) was added in small portions to a stirred solution of 2-(4-bromophenyl)-5-fluoro-3-methylsulfonyl-1-benzofuran (310 mg, 1.2 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, 1 : 2 (v/v)] to afford the title compound as a colorless solid [yield 81%, m.p. 442-443 K; R_f = 0.68 (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 in tetrahydrofuran at room temperature.

Refinement

All H atoms were positioned geometrically and refined using a riding model, with C–H(aromatic) = 0.93 Å C–H (aliphatic) = 0.96 Å. and with $U_{iso}(H) = 1.2U_{eq}(C)$ (aromatic) H atoms and $1.5 U_{eq}(C)$ (aliphatic).

Figures

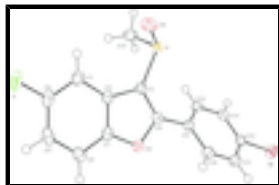


Fig. 1. The molecular structure of the title compound with the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

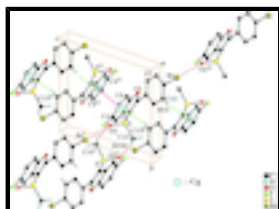


Fig. 2. C–H...O, C–Br...O, C–H... π , and π – π interactions (dotted lines) in the crystal structure of title compound. Cg denotes the ring centroid. [Symmetry codes: (i) $-x + 2, -y + 2, -z + 1$; (ii) $-x + 1, -y + 1, -z$; (iii) $x, y - 1, z - 1$; (iv) $-x + 1, -y + 1, -z + 1$ (v) $x, y + 1, z + 1$]. For other codes, see Table 1.

2-(4-Bromophenyl)-5-fluoro-3-methylsulfinyl-1-benzofuran

Crystal data

$C_{15}H_{10}BrFO_2S$

$M_r = 353.20$

Triclinic, $P\bar{1}$

Hall symbol: $-P\ 1$

$a = 8.6909\ (7)\ \text{\AA}$

$b = 9.1765\ (7)\ \text{\AA}$

$c = 10.1308\ (8)\ \text{\AA}$

$\alpha = 105.989\ (1)^\circ$

$\beta = 114.811\ (1)^\circ$

$\gamma = 99.423\ (1)^\circ$

$V = 667.91\ (9)\ \text{\AA}^3$

$Z = 2$

$F_{000} = 352$

$D_x = 1.756\ \text{Mg m}^{-3}$

Melting point = 442–443 K

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

Cell parameters from 4045 reflections

$\theta = 2.4\text{--}27.5^\circ$

$\mu = 3.24\ \text{mm}^{-1}$

$T = 293\ \text{K}$

Block, colorless

$0.40 \times 0.20 \times 0.10\ \text{mm}$

Data collection

Bruker SMART CCD-detector
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

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

$T = 293\ \text{K}$

φ and ω scans

Absorption correction: multi-scan
(SADABS; Sheldrick, 1996)

$T_{\min} = 0.461, T_{\max} = 0.720$

5792 measured reflections

2861 independent reflections

2589 reflections with $I > 2\sigma(I)$

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

$\theta_{\max} = 27.0^\circ$

$\theta_{\min} = 2.4^\circ$

$h = -11 \rightarrow 11$

$k = -11 \rightarrow 11$

$l = -12 \rightarrow 12$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.024$	H-atom parameters constrained
$wR(F^2) = 0.062$	$w = 1/[\sigma^2(F_o^2) + (0.0263P)^2 + 0.5235P]$
$S = 1.05$	where $P = (F_o^2 + 2F_c^2)/3$
2861 reflections	$(\Delta/\sigma)_{\max} = 0.001$
182 parameters	$\Delta\rho_{\max} = 0.56 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{\min} = -0.52 \text{ e } \text{\AA}^{-3}$
	Extinction correction: none

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>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br	0.87777 (3)	0.07461 (3)	-0.19442 (3)	0.03165 (8)
S	0.83195 (6)	0.75073 (6)	0.37122 (6)	0.02170 (11)
F	0.27524 (19)	0.78610 (17)	0.54077 (16)	0.0402 (3)
O1	0.44103 (18)	0.34213 (15)	0.19174 (16)	0.0212 (3)
O2	0.8984 (2)	0.83704 (18)	0.54254 (17)	0.0315 (3)
C1	0.6353 (2)	0.5929 (2)	0.3021 (2)	0.0194 (4)
C2	0.4984 (3)	0.5994 (2)	0.3476 (2)	0.0200 (4)
C3	0.4642 (3)	0.7204 (3)	0.4402 (2)	0.0249 (4)
H3	0.5391	0.8260	0.4910	0.030*
C4	0.3134 (3)	0.6731 (3)	0.4513 (2)	0.0278 (4)
C5	0.1973 (3)	0.5170 (3)	0.3795 (3)	0.0285 (5)
H5	0.0969	0.4935	0.3914	0.034*
C6	0.2324 (3)	0.3962 (3)	0.2896 (2)	0.0262 (4)
H6	0.1586	0.2903	0.2410	0.031*
C7	0.3836 (3)	0.4430 (2)	0.2768 (2)	0.0210 (4)
C8	0.5949 (3)	0.4379 (2)	0.2100 (2)	0.0196 (4)
C9	0.6748 (2)	0.3554 (2)	0.1231 (2)	0.0194 (4)
C10	0.6747 (3)	0.1994 (2)	0.1089 (2)	0.0236 (4)
H10	0.6313	0.1507	0.1612	0.028*

supplementary materials

C11	0.7387 (3)	0.1167 (2)	0.0176 (2)	0.0254 (4)
H11	0.7386	0.0130	0.0083	0.031*
C12	0.8029 (3)	0.1910 (2)	-0.0596 (2)	0.0219 (4)
C13	0.8077 (3)	0.3461 (2)	-0.0451 (2)	0.0217 (4)
H13	0.8534	0.3948	-0.0961	0.026*
C14	0.7437 (3)	0.4286 (2)	0.0465 (2)	0.0212 (4)
H14	0.7466	0.5330	0.0570	0.025*
C15	0.7267 (3)	0.8706 (3)	0.2720 (3)	0.0310 (5)
H15A	0.6331	0.8880	0.2950	0.047*
H15B	0.6768	0.8163	0.1604	0.047*
H15C	0.8138	0.9718	0.3075	0.047*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br	0.04037 (14)	0.03169 (13)	0.03461 (13)	0.01806 (10)	0.02714 (11)	0.01103 (10)
S	0.0186 (2)	0.0212 (2)	0.0202 (2)	0.00384 (18)	0.00880 (19)	0.00360 (19)
F	0.0428 (8)	0.0511 (9)	0.0360 (7)	0.0286 (7)	0.0263 (7)	0.0104 (6)
O1	0.0217 (7)	0.0186 (6)	0.0234 (7)	0.0064 (5)	0.0122 (6)	0.0062 (5)
O2	0.0288 (8)	0.0312 (8)	0.0212 (7)	-0.0001 (6)	0.0108 (6)	-0.0005 (6)
C1	0.0179 (9)	0.0206 (9)	0.0180 (9)	0.0065 (7)	0.0077 (7)	0.0065 (7)
C2	0.0199 (9)	0.0245 (10)	0.0172 (9)	0.0102 (8)	0.0086 (7)	0.0093 (8)
C3	0.0252 (10)	0.0266 (10)	0.0199 (10)	0.0111 (8)	0.0098 (8)	0.0053 (8)
C4	0.0306 (11)	0.0392 (12)	0.0200 (10)	0.0220 (10)	0.0137 (9)	0.0119 (9)
C5	0.0233 (10)	0.0449 (13)	0.0281 (11)	0.0186 (9)	0.0150 (9)	0.0206 (10)
C6	0.0221 (10)	0.0327 (11)	0.0276 (10)	0.0097 (8)	0.0123 (9)	0.0160 (9)
C7	0.0220 (10)	0.0253 (10)	0.0183 (9)	0.0119 (8)	0.0096 (8)	0.0098 (8)
C8	0.0192 (9)	0.0215 (9)	0.0185 (9)	0.0068 (7)	0.0088 (7)	0.0087 (7)
C9	0.0186 (9)	0.0206 (9)	0.0165 (9)	0.0070 (7)	0.0075 (7)	0.0053 (7)
C10	0.0266 (10)	0.0231 (10)	0.0253 (10)	0.0082 (8)	0.0153 (9)	0.0106 (8)
C11	0.0298 (11)	0.0204 (9)	0.0299 (11)	0.0106 (8)	0.0170 (9)	0.0095 (8)
C12	0.0208 (9)	0.0246 (10)	0.0199 (9)	0.0096 (8)	0.0112 (8)	0.0050 (8)
C13	0.0210 (9)	0.0238 (10)	0.0183 (9)	0.0046 (8)	0.0095 (8)	0.0072 (8)
C14	0.0229 (10)	0.0175 (9)	0.0196 (9)	0.0060 (7)	0.0084 (8)	0.0057 (7)
C15	0.0287 (11)	0.0232 (10)	0.0358 (12)	0.0059 (9)	0.0115 (10)	0.0121 (9)

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

Br—C12	1.897 (2)	C6—C7	1.384 (3)
Br—O2 ⁱ	3.036 (2)	C6—H6	0.9300
S—C1	1.771 (2)	C8—C9	1.466 (3)
S—C15	1.796 (2)	C9—C14	1.398 (3)
F—C4	1.361 (2)	C9—C10	1.398 (3)
O1—C8	1.383 (2)	C10—C11	1.388 (3)
O1—C7	1.386 (2)	C10—H10	0.9300
C1—C8	1.359 (3)	C11—C12	1.387 (3)
C1—C2	1.449 (3)	C11—H11	0.9300
C2—C7	1.391 (3)	C12—C13	1.382 (3)

C2—C3	1.404 (3)	C13—C14	1.388 (3)
C3—C4	1.373 (3)	C13—H13	0.9300
C3—H3	0.9300	C14—H14	0.9300
C4—C5	1.391 (3)	C15—H15A	0.9600
C5—C6	1.392 (3)	C15—H15B	0.9600
C5—H5	0.9300	C15—H15C	0.9600
C12—Br—O2 ⁱ	165.46 (7)	C1—C8—C9	133.66 (18)
O2—S—C1	106.07 (9)	O1—C8—C9	115.03 (16)
O2—S—C15	107.01 (10)	C14—C9—C10	119.19 (18)
C1—S—C15	97.48 (10)	C14—C9—C8	120.39 (17)
C8—O1—C7	105.92 (14)	C10—C9—C8	120.34 (17)
C8—C1—C2	106.94 (17)	C11—C10—C9	120.58 (18)
C8—C1—S	125.96 (15)	C11—C10—H10	119.7
C2—C1—S	126.73 (15)	C9—C10—H10	119.7
C7—C2—C3	119.59 (18)	C12—C11—C10	119.00 (18)
C7—C2—C1	105.25 (16)	C12—C11—H11	120.5
C3—C2—C1	135.15 (19)	C10—C11—H11	120.5
C4—C3—C2	115.79 (19)	C13—C12—C11	121.53 (18)
C4—C3—H3	122.1	C13—C12—Br	119.15 (15)
C2—C3—H3	122.1	C11—C12—Br	119.28 (15)
F—C4—C3	117.9 (2)	C12—C13—C14	119.28 (18)
F—C4—C5	117.34 (19)	C12—C13—H13	120.4
C3—C4—C5	124.73 (19)	C14—C13—H13	120.4
C4—C5—C6	119.66 (19)	C13—C14—C9	120.40 (18)
C4—C5—H5	120.2	C13—C14—H14	119.8
C6—C5—H5	120.2	C9—C14—H14	119.8
C7—C6—C5	116.0 (2)	S—C15—H15A	109.5
C7—C6—H6	122.0	S—C15—H15B	109.5
C5—C6—H6	122.0	H15A—C15—H15B	109.5
C6—C7—O1	125.17 (18)	S—C15—H15C	109.5
C6—C7—C2	124.19 (18)	H15A—C15—H15C	109.5
O1—C7—C2	110.64 (16)	H15B—C15—H15C	109.5
C1—C8—O1	111.24 (16)		
O2—S—C1—C8	-132.93 (17)	C1—C2—C7—O1	0.0 (2)
C15—S—C1—C8	116.90 (18)	C2—C1—C8—O1	0.0 (2)
O2—S—C1—C2	39.08 (19)	S—C1—C8—O1	173.31 (13)
C15—S—C1—C2	-71.09 (18)	C2—C1—C8—C9	176.90 (19)
C8—C1—C2—C7	0.0 (2)	S—C1—C8—C9	-9.8 (3)
S—C1—C2—C7	-173.23 (15)	C7—O1—C8—C1	0.0 (2)
C8—C1—C2—C3	179.5 (2)	C7—O1—C8—C9	-177.54 (15)
S—C1—C2—C3	6.3 (3)	C1—C8—C9—C14	-37.8 (3)
C7—C2—C3—C4	-1.2 (3)	O1—C8—C9—C14	139.07 (18)
C1—C2—C3—C4	179.4 (2)	C1—C8—C9—C10	145.6 (2)
C2—C3—C4—F	179.60 (17)	O1—C8—C9—C10	-37.6 (2)
C2—C3—C4—C5	0.6 (3)	C14—C9—C10—C11	-1.3 (3)
F—C4—C5—C6	-178.56 (18)	C8—C9—C10—C11	175.46 (18)
C3—C4—C5—C6	0.4 (3)	C9—C10—C11—C12	0.0 (3)
C4—C5—C6—C7	-0.8 (3)	C10—C11—C12—C13	1.3 (3)

supplementary materials

C5—C6—C7—O1	-179.26 (17)	C10—C11—C12—Br	-176.36 (15)
C5—C6—C7—C2	0.2 (3)	C11—C12—C13—C14	-1.3 (3)
C8—O1—C7—C6	179.56 (19)	Br—C12—C13—C14	176.41 (14)
C8—O1—C7—C2	0.0 (2)	C12—C13—C14—C9	-0.1 (3)
C3—C2—C7—C6	0.8 (3)	C10—C9—C14—C13	1.3 (3)
C1—C2—C7—C6	-179.57 (18)	C8—C9—C14—C13	-175.41 (17)
C3—C2—C7—O1	-179.62 (16)		

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

Hydrogen-bond geometry (\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	2.36	3.251 (3)	155
C13—H13 \cdots Cg ⁱⁱⁱ	0.93	2.74	3.366 (3)	125

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

Fig. 1

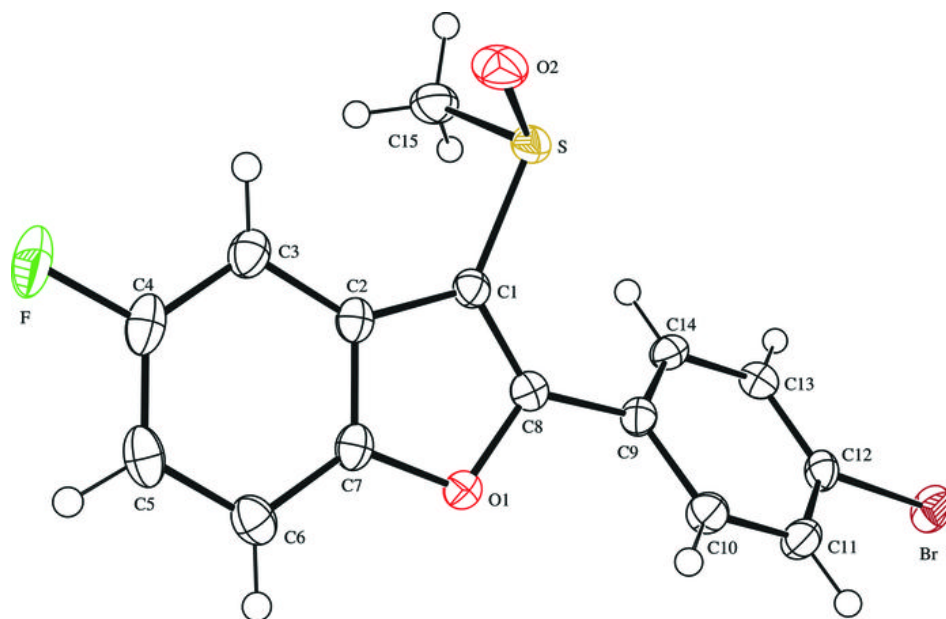


Fig. 2

