

Methyl 2-(5-bromo-3-methylsulfinyl-1-benzofuran-2-yl)acetate

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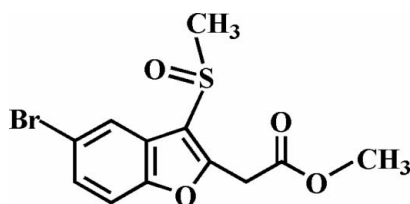
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Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.035; wR factor = 0.099; data-to-parameter ratio = 15.6.

The title compound, $\text{C}_{12}\text{H}_{11}\text{BrO}_4\text{S}$, was synthesized by the oxidation of methyl 2-(5-bromo-3-methylsulfinyl-1-benzofuran-2-yl)acetate with 3-chloroperoxybenzoic acid. The O atom and the methyl group of the methylsulfinyl substituent lie on opposite sides of the plane of the benzofuran ring system. The crystal structure is stabilized by $\text{C}-\text{H}\cdots\pi$ interactions, involving a methyl H atom and the benzene ring of a neighbouring molecule, and by weak intermolecular $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds.

Related literature

For the crystal structures of similar methyl 2-(3-methylsulfinyl-1-benzofuran-2-yl)acetate derivatives, see: Choi *et al.* (2008*a,b*).



Experimental

Crystal data

$\text{C}_{12}\text{H}_{11}\text{BrO}_4\text{S}$	$\gamma = 69.082 (1)^\circ$
$M_r = 331.18$	$V = 664.17 (8) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 7.9696 (5) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 9.1146 (6) \text{ \AA}$	$\mu = 3.25 \text{ mm}^{-1}$
$c = 10.3100 (7) \text{ \AA}$	$T = 298 (2) \text{ K}$
$\alpha = 72.587 (1)^\circ$	$0.40 \times 0.30 \times 0.20 \text{ mm}$
$\beta = 78.716 (1)^\circ$	

Data collection

Bruker SMART CCD diffractometer	3786 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1999)	2560 independent reflections
$T_{\min} = 0.327$, $T_{\max} = 0.530$	2084 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.015$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$	164 parameters
$wR(F^2) = 0.099$	H-atom parameters constrained
$S = 0.98$	$\Delta\rho_{\text{max}} = 0.35 \text{ e \AA}^{-3}$
2560 reflections	$\Delta\rho_{\text{min}} = -0.80 \text{ e \AA}^{-3}$

Table 1

Hydrogen-bond geometry (Å, °).

C_g is the centroid of the benzene ring $\text{C}2-\text{C}7$.

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{C}3-\text{H}3\cdots\text{O}2^i$	0.93	2.43	3.334 (4)	163
$\text{C}9-\text{H}9\text{B}\cdots\text{O}1^{\text{ii}}$	0.97	2.59	3.555 (3)	171
$\text{C}9-\text{H}9\text{A}\cdots\text{O}2^{\text{iii}}$	0.97	2.22	3.177 (4)	169
$\text{C}12-\text{H}12\text{B}\cdots\text{C}_g^{\text{iv}}$	0.96	2.99	3.903 (4)	159

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

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: SU2077).

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supplementary materials

Acta Cryst. (2008). E64, o2397 [doi:10.1107/S1600536808037768]

Methyl 2-(5-bromo-3-methylsulfinyl-1-benzofuran-2-yl)acetate

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

Comment

As a part of our ongoing research on the synthesis and structure of methyl 2-(3-methylsulfinyl-1-benzofuran-2-yl)acetate analogues, the crystal structure of methyl 2-(5-methyl-3-methylsulfinyl-1-benzofuran-2-yl)acetate (Choi *et al.*, 2008*a*) and methyl 2-(5-chloro-3-methylsulfinyl-1-benzofuran-2-yl) acetate (Choi *et al.*, 2008*b*) have been reported. Here we describe the crystal structure of the title compound (I), synthesized by the oxidation of methyl 2-(5-bromo-3-methylsulfonyl-1-benzofuran-2-yl)acetate with 3-chloroperoxybenzoic acid.

The molecular structure of compound (I) is illustrated in Fig. 1. The benzofuran unit is essentially planar, with a mean deviation of 0.013 (2) Å from the least-squares plane defined by the nine constituent atoms.

The crystal packing of compound (I) (see Fig. 2) is stabilized by intermolecular C—H \cdots π interactions between an H-atom of the C12-methyl group and the benzene ring of the benzofuran fragment, with a C12—H12B \cdots Cg^{iv} separation of 3.903 (4) Å (Fig. 2 and Table 1; Cg is the centroid of benzene ring C2–C7, symmetry codes as in Fig. 2). In addition, the molecular packing exhibits three intermolecular C—H \cdots O hydrogen bonds (Fig. 2 & Table 1).

Experimental

77% 3-Chloroperoxybenzoic acid (190 mg, 0.85 mmol) was added in small portions to a stirred solution of methyl 2-(5-bromo-3-methylsulfonyl-1-benzofuran-2-yl)acetate (252 mg, 0.8 mmol) in dichloromethane (30 ml) at 273 K. After stirring for 3 h at rt, the mixture was washed with a saturated sodium bicarbonate solution and the organic layer was separated, dried over magnesium sulfate, filtered and concentrated under vacuum. The residue was purified by column chromatography (hexane-ethyl acetate 1:2, *v/v*) to afford compound (I) as a colorless solid [yield 86%, m.p. 405–406 K; *R*_f = 0.45 (hexane-ethyl acetate, 1:2, *v/v*)]. Single crystals, suitable for X-ray analysis, were prepared by evaporation of a solution of compound (I) in benzene at rt. Spectroscopic analysis: ¹H NMR (CDCl₃, 400 MHz) δ 3.06 (s, 3H), 3.75 (s, 3H), 4.04 (s, 2H), 7.34–7.53 (m, 2H), 7.44 (d, *J* = 8.80 Hz, 1H), 8.07 (d, *J* = 1.84 Hz, 1H); EI—MS 332 [*M*+2], 330 [*M*⁺].

Refinement

All the H-atoms were geometrically positioned and refined using a riding model: C—H = 0.93 (aromatic), 0.97 (methylene), and 0.96 Å (methyl) H atoms, with *U*_{iso}(H) = 1.2U_{eq}(C) (aromatic & methylene), and 1.5U_{eq}(C) (methyl) H atoms.

Figures

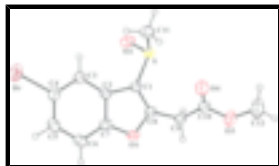


Fig. 1. The molecular structure of compound (I), showing the atom numbering scheme and displacement ellipsoids drawn at the 30% probability level.

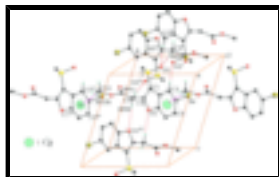


Fig. 2. A view of the crystal packing of compound (I), showing the C—H... π and C—H...O interactions as dotted lines. Cg denotes the ring centroid. [Symmetry codes: (i) $-x + 1, -y + 1, -z$; (ii) $-x + 2, -y + 1, -z + 1$; (iii) $-x + 2, -y + 1, -z$; (iv) $x, y + 1, z$; (v) $-x + 2, -y + 1, -z$; (vi) $-x + 1, -y + 1, -z$.]

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$M_r = 331.18$	$F_{000} = 332$
Triclinic, $P\bar{1}$	$D_x = 1.656 \text{ Mg m}^{-3}$
Hall symbol: $-P\ 1$	Melting point = 405–406 K
$a = 7.9696 (5) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 9.1146 (6) \text{ \AA}$	$\lambda = 0.71073 \text{ \AA}$
$c = 10.3100 (7) \text{ \AA}$	Cell parameters from 1892 reflections
$\alpha = 72.587 (1)^\circ$	$\theta = 2.1\text{--}27.8^\circ$
$\beta = 78.716 (1)^\circ$	$\mu = 3.25 \text{ mm}^{-1}$
$\gamma = 69.082 (1)^\circ$	$T = 298 (2) \text{ K}$
$V = 664.17 (8) \text{ \AA}^3$	Block, colourless
	$0.40 \times 0.30 \times 0.20 \text{ mm}$

Data collection

Bruker SMART CCD diffractometer	2560 independent reflections
Radiation source: fine-focus sealed tube	2084 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.015$
Detector resolution: $10.0 \text{ pixels mm}^{-1}$	$\theta_{\text{max}} = 26.0^\circ$
$T = 298(2) \text{ K}$	$\theta_{\text{min}} = 2.5^\circ$
φ and ω scans	$h = -9 \rightarrow 5$
Absorption correction: multi-scan (SADABS; Sheldrick, 1999)	$k = -11 \rightarrow 11$
$T_{\text{min}} = 0.327, T_{\text{max}} = 0.530$	$l = -12 \rightarrow 12$
3786 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
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Least-squares matrix: full

$$R[F^2 > 2\sigma(F^2)] = 0.035$$

$$wR(F^2) = 0.099$$

$$S = 0.98$$

2560 reflections

164 parameters

Primary atom site location: structure-invariant direct methods

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0506P)^2 + 0.5362P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

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

$$\Delta\rho_{\max} = 0.35 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.80 \text{ e } \text{\AA}^{-3}$$

Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s 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 $F^2 > \sigma(F^2)$ 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	0.26775 (5)	0.20066 (4)	0.38327 (5)	0.07396 (18)
S	0.73771 (11)	0.63026 (10)	0.03527 (7)	0.0505 (2)
O1	0.8367 (3)	0.4636 (2)	0.42105 (19)	0.0450 (5)
O2	0.7437 (4)	0.4993 (3)	-0.0262 (2)	0.0668 (7)
O3	1.0188 (3)	0.8974 (3)	0.2240 (3)	0.0718 (7)
O4	0.7513 (3)	0.8989 (3)	0.1905 (3)	0.0724 (7)
C1	0.7429 (4)	0.5435 (3)	0.2117 (3)	0.0422 (6)
C2	0.6455 (4)	0.4363 (3)	0.2987 (3)	0.0408 (6)
C3	0.5121 (4)	0.3798 (3)	0.2824 (3)	0.0466 (7)
H3	0.4651	0.4089	0.1993	0.056*
C4	0.4537 (4)	0.2784 (4)	0.3965 (4)	0.0510 (7)
C5	0.5227 (5)	0.2305 (4)	0.5228 (4)	0.0550 (8)
H5	0.4796	0.1604	0.5964	0.066*
C6	0.6542 (4)	0.2870 (4)	0.5381 (3)	0.0526 (8)
H6	0.7023	0.2566	0.6210	0.063*
C7	0.7117 (4)	0.3904 (3)	0.4254 (3)	0.0419 (6)
C8	0.8535 (4)	0.5552 (3)	0.2893 (3)	0.0413 (6)
C9	0.9848 (4)	0.6447 (4)	0.2609 (3)	0.0473 (7)
H9A	1.0742	0.6117	0.1877	0.057*
H9B	1.0470	0.6145	0.3416	0.057*
C10	0.9012 (4)	0.8259 (4)	0.2215 (3)	0.0483 (7)
C11	0.5088 (5)	0.7628 (4)	0.0366 (4)	0.0637 (9)

supplementary materials

H11A	0.4834	0.8234	-0.0551	0.096*
H11B	0.4918	0.8363	0.0916	0.096*
H11C	0.4285	0.6997	0.0740	0.096*
C12	0.9545 (7)	1.0738 (5)	0.1880 (7)	0.1065 (18)
H12A	1.0493	1.1133	0.1927	0.160*
H12B	0.8527	1.1114	0.2506	0.160*
H12C	0.9191	1.1131	0.0968	0.160*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br	0.0572 (2)	0.0513 (2)	0.1163 (4)	-0.02436 (17)	-0.0138 (2)	-0.0133 (2)
S	0.0535 (5)	0.0626 (5)	0.0392 (4)	-0.0239 (4)	-0.0121 (3)	-0.0067 (3)
O1	0.0450 (11)	0.0494 (11)	0.0411 (10)	-0.0113 (9)	-0.0157 (9)	-0.0094 (9)
O2	0.0746 (17)	0.0842 (17)	0.0506 (13)	-0.0229 (14)	-0.0132 (12)	-0.0286 (12)
O3	0.0615 (15)	0.0579 (14)	0.108 (2)	-0.0253 (12)	-0.0235 (14)	-0.0201 (14)
O4	0.0561 (15)	0.0537 (14)	0.103 (2)	-0.0180 (12)	-0.0308 (14)	0.0016 (13)
C1	0.0433 (15)	0.0454 (15)	0.0412 (14)	-0.0144 (13)	-0.0090 (12)	-0.0122 (12)
C2	0.0431 (15)	0.0361 (14)	0.0437 (15)	-0.0096 (12)	-0.0107 (12)	-0.0105 (12)
C3	0.0475 (17)	0.0398 (15)	0.0533 (17)	-0.0105 (13)	-0.0115 (13)	-0.0131 (13)
C4	0.0404 (16)	0.0385 (15)	0.073 (2)	-0.0091 (13)	-0.0074 (15)	-0.0153 (15)
C5	0.0507 (18)	0.0400 (16)	0.0600 (19)	-0.0085 (14)	-0.0028 (15)	-0.0010 (14)
C6	0.0524 (18)	0.0459 (17)	0.0472 (17)	-0.0063 (14)	-0.0094 (14)	-0.0025 (13)
C7	0.0393 (15)	0.0379 (14)	0.0455 (15)	-0.0044 (12)	-0.0102 (12)	-0.0117 (12)
C8	0.0424 (16)	0.0395 (14)	0.0429 (15)	-0.0099 (12)	-0.0103 (12)	-0.0116 (12)
C9	0.0423 (16)	0.0534 (17)	0.0510 (16)	-0.0155 (13)	-0.0136 (13)	-0.0142 (14)
C10	0.0496 (18)	0.0541 (17)	0.0458 (16)	-0.0208 (15)	-0.0087 (13)	-0.0116 (14)
C11	0.063 (2)	0.059 (2)	0.066 (2)	-0.0120 (17)	-0.0275 (17)	-0.0062 (17)
C12	0.100 (4)	0.057 (2)	0.175 (5)	-0.034 (2)	-0.038 (4)	-0.019 (3)

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

Br—C4	1.898 (3)	C4—C5	1.400 (5)
S—O2	1.493 (3)	C5—C6	1.374 (5)
S—C1	1.755 (3)	C5—H5	0.9300
S—C11	1.793 (4)	C6—C7	1.376 (4)
O1—C7	1.370 (3)	C6—H6	0.9300
O1—C8	1.375 (3)	C8—C9	1.481 (4)
O3—C10	1.327 (4)	C9—C10	1.501 (4)
O3—C12	1.454 (5)	C9—H9A	0.9700
O4—C10	1.195 (4)	C9—H9B	0.9700
C1—C8	1.350 (4)	C11—H11A	0.9600
C1—C2	1.451 (4)	C11—H11B	0.9600
C2—C3	1.391 (4)	C11—H11C	0.9600
C2—C7	1.395 (4)	C12—H12A	0.9600
C3—C4	1.377 (4)	C12—H12B	0.9600
C3—H3	0.9300	C12—H12C	0.9600
O2—S—C1	106.07 (14)	C6—C7—C2	123.2 (3)

O2—S—C11	106.21 (17)	C1—C8—O1	111.1 (2)
C1—S—C11	98.55 (16)	C1—C8—C9	133.3 (3)
C7—O1—C8	106.4 (2)	O1—C8—C9	115.6 (2)
C10—O3—C12	116.0 (3)	C8—C9—C10	114.0 (2)
C8—C1—C2	107.2 (3)	C8—C9—H9A	108.8
C8—C1—S	124.7 (2)	C10—C9—H9A	108.8
C2—C1—S	127.9 (2)	C8—C9—H9B	108.8
C3—C2—C7	120.0 (3)	C10—C9—H9B	108.8
C3—C2—C1	135.6 (3)	H9A—C9—H9B	107.7
C7—C2—C1	104.4 (2)	O4—C10—O3	123.4 (3)
C4—C3—C2	116.2 (3)	O4—C10—C9	126.2 (3)
C4—C3—H3	121.9	O3—C10—C9	110.4 (3)
C2—C3—H3	121.9	S—C11—H11A	109.5
C3—C4—C5	123.5 (3)	S—C11—H11B	109.5
C3—C4—Br	118.6 (3)	H11A—C11—H11B	109.5
C5—C4—Br	117.9 (2)	S—C11—H11C	109.5
C6—C5—C4	119.9 (3)	H11A—C11—H11C	109.5
C6—C5—H5	120.0	H11B—C11—H11C	109.5
C4—C5—H5	120.0	O3—C12—H12A	109.5
C5—C6—C7	117.1 (3)	O3—C12—H12B	109.5
C5—C6—H6	121.5	H12A—C12—H12B	109.5
C7—C6—H6	121.5	O3—C12—H12C	109.5
O1—C7—C6	125.9 (3)	H12A—C12—H12C	109.5
O1—C7—C2	110.9 (2)	H12B—C12—H12C	109.5
O2—S—C1—C8	131.5 (3)	C5—C6—C7—C2	-1.3 (5)
C11—S—C1—C8	-118.8 (3)	C3—C2—C7—O1	-177.8 (2)
O2—S—C1—C2	-42.4 (3)	C1—C2—C7—O1	1.1 (3)
C11—S—C1—C2	67.3 (3)	C3—C2—C7—C6	1.4 (4)
C8—C1—C2—C3	177.9 (3)	C1—C2—C7—C6	-179.7 (3)
S—C1—C2—C3	-7.3 (5)	C2—C1—C8—O1	0.1 (3)
C8—C1—C2—C7	-0.7 (3)	S—C1—C8—O1	-174.9 (2)
S—C1—C2—C7	174.1 (2)	C2—C1—C8—C9	-179.8 (3)
C7—C2—C3—C4	-0.3 (4)	S—C1—C8—C9	5.1 (5)
C1—C2—C3—C4	-178.8 (3)	C7—O1—C8—C1	0.6 (3)
C2—C3—C4—C5	-0.8 (4)	C7—O1—C8—C9	-179.5 (2)
C2—C3—C4—Br	178.5 (2)	C1—C8—C9—C10	63.6 (4)
C3—C4—C5—C6	0.9 (5)	O1—C8—C9—C10	-116.3 (3)
Br—C4—C5—C6	-178.4 (2)	C12—O3—C10—O4	0.8 (5)
C4—C5—C6—C7	0.1 (5)	C12—O3—C10—C9	-179.9 (4)
C8—O1—C7—C6	179.7 (3)	C8—C9—C10—O4	-12.9 (5)
C8—O1—C7—C2	-1.1 (3)	C8—C9—C10—O3	167.7 (3)
C5—C6—C7—O1	177.8 (3)		

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>
C3—H3 \cdots O2 ⁱ	0.93	2.43	3.334 (4)	163
C9—H9B \cdots O1 ⁱⁱ	0.97	2.59	3.555 (3)	171

supplementary materials

C9—H9A \cdots O2 ⁱⁱⁱ	0.97	2.22	3.177 (4)	169
C12—H12B \cdots Cg ^{iv}	0.96	2.99	3.903 (4)	159

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

Fig. 1

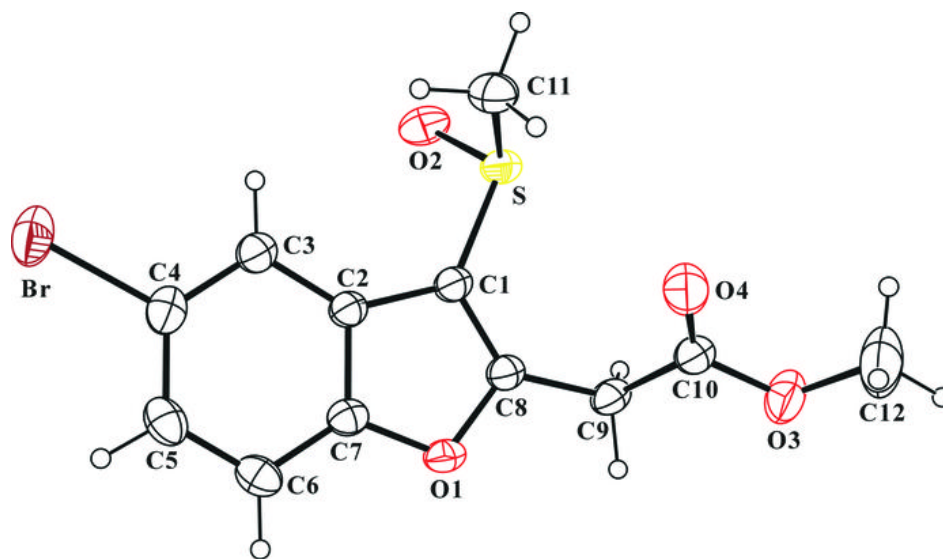


Fig. 2

