

Isopropyl 2-(5-methyl-3-methylsulfinyl-1-benzofuran-2-yl)acetate

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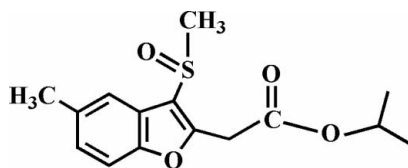
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Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.036; wR factor = 0.105; data-to-parameter ratio = 15.3.

The title compound, $\text{C}_{15}\text{H}_{18}\text{O}_4\text{S}$, was prepared by the oxidation of isopropyl 2-(5-methyl-3-methylsulfonyl-1-benzofuran-2-yl)acetate with 3-chloroperoxybenzoic acid. The crystal structure is stabilized by intermolecular $\pi-\pi$ interactions between the benzene rings; the centroid-centroid distance between the adjacent benzene rings (symmetry code: $1-x, 1-y, 1-z$) is 3.713 (2) Å. In addition, $\text{C}-\text{H}\cdots\pi$ and weak intermolecular $\text{C}-\text{H}\cdots\text{O}$ interactions are present in the structure.

Related literature

For the crystal structures of similar 2-(5-methyl-3-methylsulfinyl-1-benzofuran-2-yl)acetic acid derivatives, see: Choi *et al.* (2007, 2008).



Experimental

Crystal data

$\text{C}_{15}\text{H}_{18}\text{O}_4\text{S}$	$\gamma = 66.421 (1)^\circ$
$M_r = 294.35$	$V = 736.76 (8) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 8.1829 (5) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 9.7027 (6) \text{ \AA}$	$\mu = 0.23 \text{ mm}^{-1}$
$c = 10.6545 (7) \text{ \AA}$	$T = 298 (2) \text{ K}$
$\alpha = 73.057 (1)^\circ$	$0.40 \times 0.30 \times 0.30 \text{ mm}$
$\beta = 77.463 (1)^\circ$	

Data collection

Bruker SMART CCD diffractometer	2838 independent reflections
Absorption correction: none	2479 reflections with $I > 2\sigma(I)$
5802 measured reflections	$R_{\text{int}} = 0.035$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$	185 parameters
$wR(F^2) = 0.105$	H-atom parameters constrained
$S = 1.07$	$\Delta\rho_{\text{max}} = 0.22 \text{ e \AA}^{-3}$
2838 reflections	$\Delta\rho_{\text{min}} = -0.24 \text{ e \AA}^{-3}$

Table 1

Hydrogen-bond geometry (Å, °).

C_{g1} and C_{g2} are the centroids of the $C2-C7$ and $C1/C2/C7/C8/O1$ rings, respectively.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C9-H9A\cdots O2^i$	0.97	2.38	3.249 (2)	149
$C13-H13\cdots C_{g1}^{ii}$	0.98	2.91	3.656 (2)	134
$C15-H15C\cdots C_{g2}^{ii}$	0.96	2.96	3.837 (2)	152

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

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: FB2111).

References

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supplementary materials

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Isopropyl 2-(5-methyl-3-methylsulfinyl-1-benzofuran-2-yl)acetate

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Comment

This work is related to our previous communications on the synthesis and structure of 2-(5-methyl-3-methylsulfinyl-1-benzofuran-2-yl)acetic acid analogues, viz. ethyl 2-(5-methyl-3-methylsulfinyl-1-benzofuran-2-yl)acetate (Choi *et al.*, 2007) and methyl 2-(5-methyl-3-methylsulfinyl-1-benzofuran-2-yl)acetate (Choi *et al.*, 2008). Here we report the crystal structure of the title compound, isopropyl 2-(5-methyl-3-methylsulfinyl-1-benzofuran-2-yl)acetate (Fig. 1).

The benzofuran unit is essentially planar, with a mean deviation of 0.004 (1) Å from the least-squares plane defined by the nine constituent atoms. The molecular packing (Fig. 2) is stabilized by π — π electron interactions between the benzofuran rings of the adjacent molecules. The distances between the centroids of the stacked benzene rings are 3.713 (2) Å (symmetry code: 1-x, 1-y, 1-z). The crystal packing is further stabilized by C—H \cdots π electron interactions (Tab. 1). Additionally, intermolecular C—H \cdots O interactions are present in the structure (Tab. 1).

Experimental

77% 3-chloroperoxybenzoic acid (471 mg, 2.1 mmol) was added in small portions to a stirred solution of isopropyl 2-(5-methyl-3-methylsulfinyl-1-benzofuran-2-yl)acetate (556 mg, 2.0 mmol) in dichloromethane (40 ml) at 273 K. After having been stirred for 3 h at room temperature, the mixture was washed with saturated sodium hydrogencarbonate solution and the organic layer was separated, dried over magnesium sulfate, filtered and concentrated under vacuum. The residue was purified by column chromatography (ethyl acetate) to afford the title compound as a colorless solid [yield 81%, m.p. 403–404 K; R_f = 0.74 (ethyl acetate)]. Single crystals suitable for X-ray diffraction were prepared by evaporation of a solution of the title compound in ethyl acetate at room temperature. The average crystal size was approximately 1.0 x 1.0 x 0.5 mm. The crystals are colourless and soluble in polar solvents. Spectroscopic analysis: ^1H NMR (CDCl_3 , 400 MHz) δ 1.25 (d, J = 6.20 Hz, 6H), 2.46 (s, 3H), 3.08 (s, 3H), 3.99 (s, 2H), 5.00–5.08 (m, 1H), 7.17 (d, J = 8.44 Hz, 1H), 7.39 (d, J = 8.44 Hz, 1H), 7.74 (s, 1H); EI—MS 294 [M^+].

Refinement

All the hydrogen atoms could have been distinguished in the difference electron density maps. However, all the H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93 Å for the aryl, 0.97 Å for the methylene, 0.98 Å for the methine and 0.96 Å for the methyl H atoms. $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for the aryl, methine and methylene H atoms, and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for the methyl H atoms.

Figures

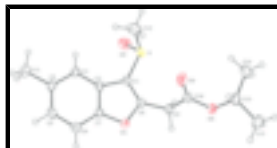


Fig. 1. The molecular structure of the title compound, showing the displacement ellipsoids drawn at the 30% probability level.

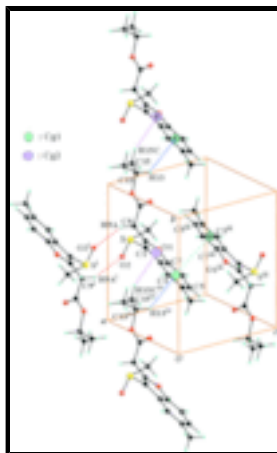


Fig. 2. π — π , C—H... π and C—H...O interactions (dotted lines) in the title compound. Cg denotes the ring centroid. [Symmetry codes: (i) $-x + 2, -y + 1, -z$; (ii) $x, y + 1, z$; (iii) $-x + 1, -y + 1, -z + 1$; (iv) $x, y - 1, z$.]

Isopropyl 2-(5-methyl-3-methylsulfinyl-1-benzofuran-2-yl)acetate

Crystal data

$C_{15}H_{18}O_4S$	$Z = 2$
$M_r = 294.35$	$F_{000} = 312$
Triclinic, $P\bar{1}$	$D_x = 1.327 \text{ Mg m}^{-3}$
Hall symbol: $-P_1$	Melting point = 403–404 K
$a = 8.1829 (5) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 9.7027 (6) \text{ \AA}$	$\lambda = 0.71073 \text{ \AA}$
$c = 10.6545 (7) \text{ \AA}$	Cell parameters from 4030 reflections
$\alpha = 73.057 (1)^\circ$	$\theta = 2.4\text{--}28.2^\circ$
$\beta = 77.463 (1)^\circ$	$\mu = 0.23 \text{ mm}^{-1}$
$\gamma = 66.421 (1)^\circ$	$T = 298 (2) \text{ K}$
$V = 736.76 (8) \text{ \AA}^3$	Block, colourless
	$0.40 \times 0.30 \times 0.30 \text{ mm}$

Data collection

Bruker SMART CCD diffractometer	2838 independent reflections
Radiation source: fine-focus sealed tube	2479 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.035$
Detector resolution: $10.0 \text{ pixels mm}^{-1}$	$\theta_{\text{max}} = 26.0^\circ$
$T = 298(2) \text{ K}$	$\theta_{\text{min}} = 2.7^\circ$
φ and ω scans	$h = -10 \rightarrow 10$
Absorption correction: none	$k = -11 \rightarrow 11$

5802 measured reflections

$l = -13 \rightarrow 13$

Refinement

Refinement on F^2

Secondary atom site location: difference Fourier map

Least-squares matrix: full

Hydrogen site location: difference Fourier map

$R[F^2 > 2\sigma(F^2)] = 0.036$

H-atom parameters constrained

$wR(F^2) = 0.105$

$$w = 1/[\sigma^2(F_o^2) + (0.0509P)^2 + 0.2101P]$$

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

$S = 1.07$

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

2838 reflections

$\Delta\rho_{\max} = 0.22 \text{ e } \text{\AA}^{-3}$

185 parameters

$\Delta\rho_{\min} = -0.24 \text{ e } \text{\AA}^{-3}$

68 constraints

Extinction correction: none

Primary atom site location: structure-invariant direct methods

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)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
S	0.74200 (6)	0.64759 (5)	0.04151 (4)	0.04706 (16)
O1	0.84827 (15)	0.47478 (12)	0.40980 (11)	0.0378 (3)
O2	0.7528 (2)	0.53592 (18)	-0.03283 (14)	0.0705 (4)
O3	0.73496 (17)	0.88857 (15)	0.23749 (16)	0.0603 (4)
O4	1.00780 (15)	0.88109 (12)	0.25158 (12)	0.0422 (3)
C1	0.7543 (2)	0.55223 (18)	0.20899 (15)	0.0356 (3)
C2	0.6619 (2)	0.45172 (16)	0.29204 (15)	0.0336 (3)
C3	0.5364 (2)	0.39518 (18)	0.27713 (16)	0.0380 (4)
H3	0.4913	0.4233	0.1967	0.046*
C4	0.4806 (2)	0.29641 (19)	0.38454 (17)	0.0405 (4)
C5	0.5499 (2)	0.25528 (19)	0.50517 (17)	0.0424 (4)
H5	0.5109	0.1888	0.5761	0.051*
C6	0.6736 (2)	0.30967 (18)	0.52246 (16)	0.0401 (4)
H6	0.7189	0.2818	0.6027	0.048*
C7	0.7260 (2)	0.40767 (17)	0.41396 (15)	0.0343 (3)
C8	0.8622 (2)	0.56095 (18)	0.28352 (15)	0.0361 (3)
C9	0.9868 (2)	0.64659 (18)	0.25585 (18)	0.0405 (4)

supplementary materials

H9A	1.0607	0.6321	0.1728	0.049*
H9B	1.0657	0.6029	0.3247	0.049*
C10	0.8915 (2)	0.81825 (18)	0.24831 (16)	0.0384 (4)
C11	0.3469 (3)	0.2312 (3)	0.3719 (2)	0.0598 (5)
H11A	0.2959	0.2846	0.2902	0.090*
H11B	0.2533	0.2443	0.4443	0.090*
H11C	0.4066	0.1232	0.3731	0.090*
C12	0.5114 (3)	0.7722 (3)	0.0561 (2)	0.0717 (6)
H12A	0.4814	0.8392	-0.0284	0.108*
H12B	0.4926	0.8332	0.1182	0.108*
H12C	0.4367	0.7112	0.0865	0.108*
C13	0.9392 (2)	1.04906 (18)	0.24297 (18)	0.0426 (4)
H13	0.8239	1.0791	0.2982	0.051*
C14	0.9158 (3)	1.1356 (2)	0.1023 (2)	0.0603 (5)
H14A	0.8323	1.1104	0.0707	0.090*
H14B	1.0294	1.1071	0.0488	0.090*
H14C	0.8708	1.2446	0.0974	0.090*
C15	1.0762 (3)	1.0762 (2)	0.2963 (3)	0.0692 (6)
H15A	1.1907	1.0407	0.2453	0.104*
H15B	1.0850	1.0206	0.3868	0.104*
H15C	1.0407	1.1846	0.2910	0.104*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S	0.0572 (3)	0.0469 (3)	0.0365 (2)	-0.0241 (2)	-0.00906 (19)	0.00182 (17)
O1	0.0416 (6)	0.0381 (6)	0.0392 (6)	-0.0204 (5)	-0.0113 (5)	-0.0035 (5)
O2	0.0994 (12)	0.0694 (9)	0.0444 (8)	-0.0262 (9)	-0.0159 (8)	-0.0158 (7)
O3	0.0408 (7)	0.0449 (7)	0.0966 (11)	-0.0190 (6)	-0.0103 (7)	-0.0113 (7)
O4	0.0420 (6)	0.0328 (6)	0.0568 (7)	-0.0177 (5)	-0.0114 (5)	-0.0075 (5)
C1	0.0406 (8)	0.0324 (7)	0.0355 (8)	-0.0163 (7)	-0.0064 (6)	-0.0040 (6)
C2	0.0373 (8)	0.0292 (7)	0.0352 (8)	-0.0128 (6)	-0.0055 (6)	-0.0067 (6)
C3	0.0411 (9)	0.0370 (8)	0.0415 (8)	-0.0167 (7)	-0.0096 (7)	-0.0098 (7)
C4	0.0394 (9)	0.0362 (8)	0.0512 (10)	-0.0175 (7)	-0.0047 (7)	-0.0124 (7)
C5	0.0458 (9)	0.0356 (8)	0.0454 (9)	-0.0205 (7)	-0.0016 (7)	-0.0031 (7)
C6	0.0449 (9)	0.0377 (8)	0.0375 (8)	-0.0165 (7)	-0.0095 (7)	-0.0024 (6)
C7	0.0357 (8)	0.0304 (7)	0.0394 (8)	-0.0140 (6)	-0.0076 (6)	-0.0063 (6)
C8	0.0395 (8)	0.0312 (7)	0.0386 (8)	-0.0159 (6)	-0.0057 (6)	-0.0040 (6)
C9	0.0396 (9)	0.0376 (8)	0.0490 (9)	-0.0200 (7)	-0.0070 (7)	-0.0068 (7)
C10	0.0394 (9)	0.0387 (8)	0.0397 (8)	-0.0206 (7)	-0.0038 (7)	-0.0038 (6)
C11	0.0605 (12)	0.0615 (12)	0.0731 (13)	-0.0393 (10)	-0.0128 (10)	-0.0095 (10)
C12	0.0665 (14)	0.0616 (13)	0.0692 (14)	-0.0084 (11)	-0.0246 (11)	0.0023 (11)
C13	0.0444 (9)	0.0327 (8)	0.0540 (10)	-0.0160 (7)	-0.0051 (8)	-0.0119 (7)
C14	0.0797 (15)	0.0395 (10)	0.0607 (12)	-0.0235 (10)	-0.0124 (10)	-0.0039 (8)
C15	0.0745 (15)	0.0483 (11)	0.1006 (18)	-0.0231 (11)	-0.0311 (13)	-0.0232 (11)

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

S—O2	1.4839 (15)	C8—C9	1.490 (2)
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S—C1	1.7583 (16)	C9—C10	1.516 (2)
S—C12	1.790 (2)	C9—H9A	0.9700
O1—C8	1.3698 (18)	C9—H9B	0.9700
O1—C7	1.3830 (18)	C11—H11A	0.9600
O3—C10	1.199 (2)	C11—H11B	0.9600
O4—C10	1.3305 (19)	C11—H11C	0.9600
O4—C13	1.4774 (19)	C12—H12A	0.9600
C1—C8	1.349 (2)	C12—H12B	0.9600
C1—C2	1.450 (2)	C12—H12C	0.9600
C2—C7	1.392 (2)	C13—C15	1.500 (3)
C2—C3	1.397 (2)	C13—C14	1.500 (3)
C3—C4	1.386 (2)	C13—H13	0.9800
C3—H3	0.9300	C14—H14A	0.9600
C4—C5	1.403 (2)	C14—H14B	0.9600
C4—C11	1.511 (2)	C14—H14C	0.9600
C5—C6	1.379 (2)	C15—H15A	0.9600
C5—H5	0.9300	C15—H15B	0.9600
C6—C7	1.376 (2)	C15—H15C	0.9600
C6—H6	0.9300		
O2—S—C1	108.11 (8)	H9A—C9—H9B	107.7
O2—S—C12	106.21 (11)	O3—C10—O4	124.63 (15)
C1—S—C12	97.74 (9)	O3—C10—C9	125.20 (14)
C8—O1—C7	106.03 (11)	O4—C10—C9	110.14 (13)
C10—O4—C13	117.80 (13)	C4—C11—H11A	109.5
C8—C1—C2	107.31 (13)	C4—C11—H11B	109.5
C8—C1—S	123.03 (12)	H11A—C11—H11B	109.5
C2—C1—S	129.65 (12)	C4—C11—H11C	109.5
C7—C2—C3	119.08 (14)	H11A—C11—H11C	109.5
C7—C2—C1	104.42 (13)	H11B—C11—H11C	109.5
C3—C2—C1	136.50 (15)	S—C12—H12A	109.5
C4—C3—C2	118.66 (15)	S—C12—H12B	109.5
C4—C3—H3	120.7	H12A—C12—H12B	109.5
C2—C3—H3	120.7	S—C12—H12C	109.5
C3—C4—C5	119.95 (15)	H12A—C12—H12C	109.5
C3—C4—C11	120.26 (16)	H12B—C12—H12C	109.5
C5—C4—C11	119.79 (16)	O4—C13—C15	105.45 (14)
C6—C5—C4	122.50 (15)	O4—C13—C14	109.85 (14)
C6—C5—H5	118.7	C15—C13—C14	112.29 (17)
C4—C5—H5	118.7	O4—C13—H13	109.7
C7—C6—C5	116.08 (15)	C15—C13—H13	109.7
C7—C6—H6	122.0	C14—C13—H13	109.7
C5—C6—H6	122.0	C13—C14—H14A	109.5
C6—C7—O1	125.47 (14)	C13—C14—H14B	109.5
C6—C7—C2	123.73 (14)	H14A—C14—H14B	109.5
O1—C7—C2	110.80 (13)	C13—C14—H14C	109.5
C1—C8—O1	111.44 (13)	H14A—C14—H14C	109.5
C1—C8—C9	132.89 (15)	H14B—C14—H14C	109.5
O1—C8—C9	115.66 (13)	C13—C15—H15A	109.5
C8—C9—C10	113.54 (14)	C13—C15—H15B	109.5

supplementary materials

C8—C9—H9A	108.9	H15A—C15—H15B	109.5
C10—C9—H9A	108.9	C13—C15—H15C	109.5
C8—C9—H9B	108.9	H15A—C15—H15C	109.5
C10—C9—H9B	108.9	H15B—C15—H15C	109.5
O2—S—C1—C8	133.07 (16)	C3—C2—C7—C6	0.4 (2)
C12—S—C1—C8	-117.00 (17)	C1—C2—C7—C6	-179.35 (15)
O2—S—C1—C2	-45.61 (17)	C3—C2—C7—O1	-179.98 (13)
C12—S—C1—C2	64.32 (17)	C1—C2—C7—O1	0.30 (17)
C8—C1—C2—C7	0.00 (18)	C2—C1—C8—O1	-0.30 (19)
S—C1—C2—C7	178.83 (13)	S—C1—C8—O1	-179.23 (11)
C8—C1—C2—C3	-179.65 (18)	C2—C1—C8—C9	-178.84 (17)
S—C1—C2—C3	-0.8 (3)	S—C1—C8—C9	2.2 (3)
C7—C2—C3—C4	-0.3 (2)	C7—O1—C8—C1	0.48 (18)
C1—C2—C3—C4	179.36 (17)	C7—O1—C8—C9	179.29 (13)
C2—C3—C4—C5	0.1 (2)	C1—C8—C9—C10	74.3 (2)
C2—C3—C4—C11	-179.20 (16)	O1—C8—C9—C10	-104.20 (16)
C3—C4—C5—C6	0.0 (3)	C13—O4—C10—O3	0.8 (2)
C11—C4—C5—C6	179.31 (17)	C13—O4—C10—C9	179.02 (13)
C4—C5—C6—C7	0.1 (3)	C8—C9—C10—O3	-14.9 (2)
C5—C6—C7—O1	-179.86 (15)	C8—C9—C10—O4	166.85 (14)
C5—C6—C7—C2	-0.3 (2)	C10—O4—C13—C15	160.41 (17)
C8—O1—C7—C6	179.16 (15)	C10—O4—C13—C14	-78.39 (19)
C8—O1—C7—C2	-0.48 (17)		

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C9—H9A \cdots O2 ⁱ	0.97	2.38	3.249 (2)	149
C13—H13 \cdots Cg1 ⁱⁱ	0.98	2.91	3.656 (2)	134
C15—H15C \cdots Cg2 ⁱⁱ	0.96	2.96	3.837 (2)	152

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

Fig. 1

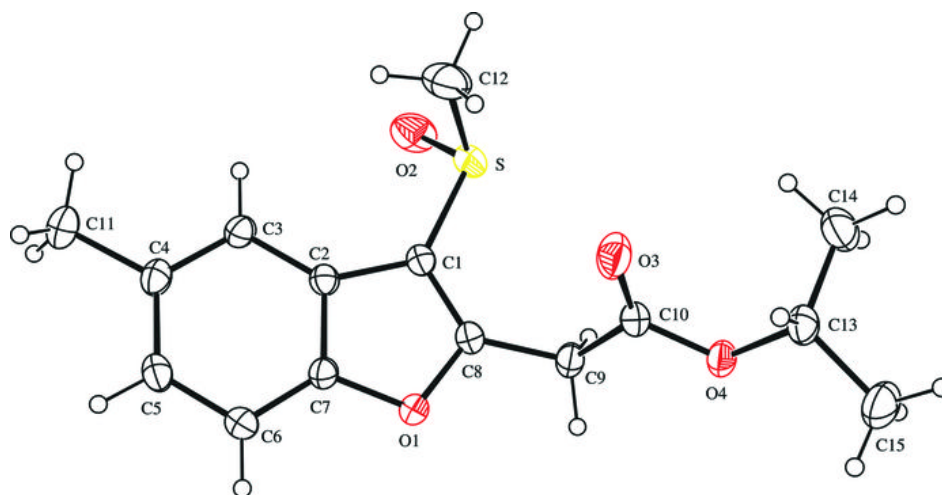


Fig. 2

