

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

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

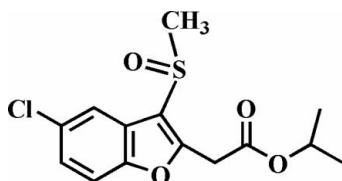
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Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.048; wR factor = 0.124; data-to-parameter ratio = 14.1.

In the title compound, $\text{C}_{14}\text{H}_{15}\text{ClO}_4\text{S}$, the S atom has a distorted trigonal-pyramidal coordination. The O atom and the methyl group of the methylsulfinyl substituent lie on opposite sides of the benzofuran ring system. The crystal structure is stabilized by intermolecular aromatic $\pi-\pi$ interactions between the benzene rings of neighbouring molecules [centroid-centroid distance = $4.057(3)$ Å], and by $\text{C}-\text{H}\cdots\pi$ interactions between a methyl H atom and the benzene ring of an adjacent molecule.

Related literature

For the crystal structures of similar compounds, see: Choi *et al.* (2008*a,b*).



Experimental

Crystal data

$\text{C}_{14}\text{H}_{15}\text{ClO}_4\text{S}$	$\gamma = 67.703(1)^\circ$
$M_r = 314.77$	$V = 745.98(10)$ Å ³
Triclinic, $P\bar{1}$	$Z = 2$
$a = 7.8824(6)$ Å	Mo $K\alpha$ radiation
$b = 10.0352(8)$ Å	$\mu = 0.41$ mm ⁻¹
$c = 10.9004(8)$ Å	$T = 298(2)$ K
$\alpha = 69.254(1)^\circ$	$0.50 \times 0.40 \times 0.15$ mm
$\beta = 81.662(1)^\circ$	

Data collection

Bruker SMART CCD diffractometer	5508 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1999)	2602 independent reflections
$T_{\min} = 0.816$, $T_{\max} = 0.939$	2354 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.017$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.048$	184 parameters
$wR(F^2) = 0.124$	H-atom parameters constrained
$S = 1.12$	$\Delta\rho_{\text{max}} = 0.49$ e Å ⁻³
2602 reflections	$\Delta\rho_{\text{min}} = -0.29$ e Å ⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{C13}-\text{H13B}\cdots\text{Cg}^i$	0.96	2.78	3.515(3)	134

Symmetry code: (i) $x, y + 1, z$. Cg is the centroid of the C2–C7 benzene ring.

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: NG2521).

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supplementary materials

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Isopropyl 2-(5-chloro-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 isopropyl 2-(5-halo-3-methylsulfinyl-1-benzofuran-2-yl)acetate analogues, we have recently described the crystal structures of isopropyl 2-(5-bromo-3-methylsulfinyl-1-benzofuran-2-yl)acetate (Choi *et al.*, 2008a) and isopropyl 2-(5-iodo-3-methylsulfinyl-1-benzofuran-2-yl)acetate (Choi *et al.*, 2008b). Here we report the crystal structure of the title compound, isopropyl 2-(5-chloro-3-methylsulfinyl-1-benzofuran-2-yl)acetate (Fig. 1).

The benzofuran unit is essentially planar, with a mean deviation of 0.012 (2) Å from the least-squares plane defined by the nine constituent atoms. The molecular packing is stabilized by aromatic π – π stacking interactions between the benzene rings of adjacent molecules. The Cg \cdots Cgⁱⁱ distance is 4.057 (3) Å (Fig. 2; Cg is the centroid of C2–C7 benzene ring; symmetry code as in Fig. 2). The molecular packing is further stabilized by C–H \cdots π interactions between a methyl H atom of isopropyl group and the benzene ring of the benzofuran unit, with a C13–H13B \cdots Cgⁱ separation of 2.78 Å (Fig. 2 and Table 1; Cg is the centroid of the C2–C7 benzene ring).

Experimental

77% 3-chloroperoxybenzoic acid (173 mg, 0.77 mmol) was added in small portions to a stirred solution of isopropyl 2-(5-chloro-3-methylsulfonyl-1-benzofuran-2-yl)acetate (209 mg, 0.7 mmol) in dichloromethane (30 ml) at 273 K. After being stirred for 3 h at room temperature, 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 83%, m.p. 422–423 K; R_f = 0.52 (hexane-ethyl acetate, 1;2 v/v)]. Single crystals suitable for X-ray diffraction were prepared by evaporation of a solution of the title compound in acetone at room temperature. Spectroscopic analysis: ¹H NMR (CDCl₃, 400 MHz) δ 1.28 (d, J = 6.20 Hz, 6H), 3.08 (s, 3H), 4.0 (s, 2H), 5.02–5.08 (m, 1H), 7.35 (dd, J = 8.76 Hz and J = 1.84 Hz, 1H), 7.45 (d, J = 8.76 Hz, 1H), 7.95 (d, J = 1.84 Hz, 1H); EI-MS 316 [M+2], 314 [M⁺].

Refinement

All H atoms were geometrically positioned 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. $U_{iso}(H) = 1.2U_{eq}(C)$ for the aryl, methine and methylene H atoms, and $1.5U_{eq}(C)$ for methyl H atoms.

Figures

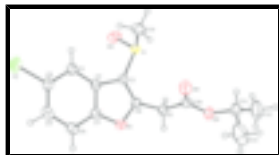


Fig. 1. The molecular structure of the title compound, showing displacement ellipsoids drawn at the 30% probability level.

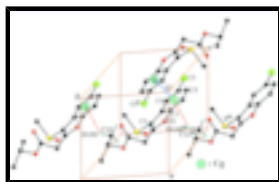


Fig. 2. π — π and C—H \cdots π interactions (dotted lines) in the title compound. Cg denotes ring centroid. [Symmetry code: (i) $x, y+1, z$; (ii) $-x+1, -y+1, -z+2$; (iii) $x, y-1, z$.]

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

Crystal data

$C_{14}H_{15}ClO_4S$	$Z = 2$
$M_r = 314.77$	$F_{000} = 328$
Triclinic, $P\bar{1}$	$D_x = 1.401 \text{ Mg m}^{-3}$
Hall symbol: -P 1	Melting point = 422–423 K
$a = 7.8824 (6) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 10.0352 (8) \text{ \AA}$	$\lambda = 0.71073 \text{ \AA}$
$c = 10.9004 (8) \text{ \AA}$	Cell parameters from 4167 reflections
$\alpha = 69.254 (1)^\circ$	$\theta = 2.5\text{--}28.3^\circ$
$\beta = 81.662 (1)^\circ$	$\mu = 0.41 \text{ mm}^{-1}$
$\gamma = 67.703 (1)^\circ$	$T = 298 (2) \text{ K}$
$V = 745.98 (10) \text{ \AA}^3$	Plate, colorless
	$0.50 \times 0.40 \times 0.15 \text{ mm}$

Data collection

Bruker SMART CCD diffractometer	2602 independent reflections
Radiation source: fine-focus sealed tube	2354 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.017$
Detector resolution: $10.0 \text{ pixels mm}^{-1}$	$\theta_{\text{max}} = 25.0^\circ$
$T = 298(2) \text{ K}$	$\theta_{\text{min}} = 2.5^\circ$
φ and ω scans	$h = -9 \rightarrow 9$
Absorption correction: multi-scan (SADABS; Sheldrick, 1999)	$k = -11 \rightarrow 11$
$T_{\text{min}} = 0.816, T_{\text{max}} = 0.939$	$l = -12 \rightarrow 12$
5508 measured reflections	

Refinement

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

$$R[F^2 > 2\sigma(F^2)] = 0.048$$

$$wR(F^2) = 0.125$$

$$S = 1.12$$

2602 reflections

184 parameters

Primary atom site location: structure-invariant direct methods

Hydrogen site location: difference Fourier map

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0534P)^2 + 0.4971P]$$

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

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

$$\Delta\rho_{\max} = 0.49 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.29 \text{ e } \text{\AA}^{-3}$$

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>	$U_{\text{iso}}^*/U_{\text{eq}}$
S	0.74726 (9)	0.60225 (8)	0.54010 (6)	0.0480 (2)
Cl	0.29574 (12)	0.21443 (10)	0.87346 (10)	0.0816 (3)
O1	0.8348 (2)	0.45903 (19)	0.91914 (16)	0.0435 (4)
O2	0.7488 (3)	0.4832 (3)	0.48756 (19)	0.0637 (6)
O3	1.0254 (3)	0.8446 (2)	0.7284 (2)	0.0582 (5)
O4	0.7414 (3)	0.8557 (2)	0.7070 (2)	0.0674 (6)
C1	0.7475 (3)	0.5246 (3)	0.7125 (2)	0.0393 (5)
C2	0.6447 (3)	0.4337 (3)	0.7973 (2)	0.0378 (5)
C3	0.5137 (3)	0.3799 (3)	0.7797 (3)	0.0462 (6)
H3	0.4686	0.4043	0.6972	0.055*
C4	0.4550 (4)	0.2888 (3)	0.8910 (3)	0.0510 (7)
C5	0.5171 (4)	0.2520 (3)	1.0159 (3)	0.0544 (7)
H5	0.4720	0.1905	1.0878	0.065*
C6	0.6450 (4)	0.3061 (3)	1.0341 (3)	0.0486 (6)
H6	0.6878	0.2832	1.1170	0.058*
C7	0.7062 (3)	0.3959 (3)	0.9229 (2)	0.0408 (5)
C8	0.8579 (3)	0.5352 (3)	0.7894 (2)	0.0409 (5)
C9	0.9910 (3)	0.6147 (3)	0.7601 (3)	0.0455 (6)
H9A	1.0667	0.5947	0.6856	0.055*
H9B	1.0708	0.5735	0.8347	0.055*
C10	0.9005 (4)	0.7845 (3)	0.7302 (2)	0.0437 (6)
C11	0.9615 (5)	1.0095 (3)	0.7059 (4)	0.0697 (9)
H11	0.8528	1.0642	0.6503	0.084*

supplementary materials

C12	1.1212 (8)	1.0569 (5)	0.6388 (5)	0.1199 (18)
H12A	1.0856	1.1656	0.6142	0.180*
H12B	1.1570	1.0267	0.5619	0.180*
H12C	1.2226	1.0085	0.6979	0.180*
C13	0.9213 (8)	1.0315 (4)	0.8347 (5)	0.1195 (19)
H13A	0.8255	0.9938	0.8777	0.179*
H13B	0.8825	1.1381	0.8233	0.179*
H13C	1.0296	0.9770	0.8872	0.179*
C14	0.5183 (4)	0.7385 (4)	0.5211 (3)	0.0671 (8)
H14A	0.4977	0.7998	0.4304	0.101*
H14B	0.5018	0.8027	0.5728	0.101*
H14C	0.4327	0.6861	0.5499	0.101*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S	0.0489 (4)	0.0589 (4)	0.0385 (4)	-0.0261 (3)	-0.0038 (3)	-0.0100 (3)
Cl	0.0694 (5)	0.0748 (6)	0.1092 (7)	-0.0480 (5)	-0.0073 (5)	-0.0132 (5)
O1	0.0486 (10)	0.0464 (9)	0.0398 (9)	-0.0184 (8)	-0.0057 (7)	-0.0154 (7)
O2	0.0685 (13)	0.0804 (14)	0.0515 (12)	-0.0250 (11)	-0.0047 (9)	-0.0322 (11)
O3	0.0622 (12)	0.0429 (10)	0.0740 (13)	-0.0240 (9)	-0.0176 (10)	-0.0120 (9)
O4	0.0501 (12)	0.0510 (11)	0.0946 (16)	-0.0161 (10)	-0.0120 (11)	-0.0139 (11)
C1	0.0427 (13)	0.0388 (12)	0.0383 (13)	-0.0157 (10)	-0.0035 (10)	-0.0124 (10)
C2	0.0390 (12)	0.0345 (12)	0.0401 (13)	-0.0113 (10)	-0.0023 (10)	-0.0134 (10)
C3	0.0438 (14)	0.0438 (14)	0.0532 (15)	-0.0174 (11)	-0.0051 (11)	-0.0146 (12)
C4	0.0428 (14)	0.0421 (14)	0.0682 (18)	-0.0179 (11)	-0.0002 (12)	-0.0153 (13)
C5	0.0541 (16)	0.0437 (14)	0.0553 (16)	-0.0172 (13)	0.0089 (13)	-0.0084 (12)
C6	0.0509 (15)	0.0428 (14)	0.0432 (14)	-0.0102 (12)	0.0007 (11)	-0.0111 (11)
C7	0.0404 (13)	0.0353 (12)	0.0457 (13)	-0.0099 (10)	-0.0016 (10)	-0.0155 (10)
C8	0.0430 (13)	0.0374 (12)	0.0434 (13)	-0.0130 (10)	-0.0041 (10)	-0.0145 (10)
C9	0.0443 (14)	0.0476 (14)	0.0509 (15)	-0.0201 (11)	-0.0050 (11)	-0.0176 (12)
C10	0.0484 (15)	0.0482 (14)	0.0384 (13)	-0.0223 (12)	-0.0030 (11)	-0.0121 (11)
C11	0.082 (2)	0.0406 (15)	0.085 (2)	-0.0242 (15)	-0.0304 (18)	-0.0055 (15)
C12	0.181 (5)	0.083 (3)	0.115 (4)	-0.086 (3)	0.035 (3)	-0.027 (3)
C13	0.159 (5)	0.056 (2)	0.121 (4)	-0.018 (3)	0.045 (3)	-0.042 (2)
C14	0.0657 (19)	0.0586 (18)	0.0640 (19)	-0.0112 (15)	-0.0194 (15)	-0.0095 (15)

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

S—O2	1.493 (2)	C6—C7	1.378 (4)
S—C1	1.761 (2)	C6—H6	0.9300
S—C14	1.790 (3)	C8—C9	1.482 (3)
Cl—C4	1.747 (3)	C9—C10	1.506 (4)
O1—C8	1.372 (3)	C9—H9A	0.9700
O1—C7	1.374 (3)	C9—H9B	0.9700
O3—C10	1.331 (3)	C11—C13	1.469 (6)
O3—C11	1.472 (3)	C11—C12	1.513 (6)
O4—C10	1.196 (3)	C11—H11	0.9800
C1—C8	1.348 (3)	C12—H12A	0.9600

C1—C2	1.445 (3)	C12—H12B	0.9600
C2—C7	1.392 (3)	C12—H12C	0.9600
C2—C3	1.396 (3)	C13—H13A	0.9600
C3—C4	1.376 (4)	C13—H13B	0.9600
C3—H3	0.9300	C13—H13C	0.9600
C4—C5	1.390 (4)	C14—H14A	0.9600
C5—C6	1.378 (4)	C14—H14B	0.9600
C5—H5	0.9300	C14—H14C	0.9600
O2—S—C1	107.34 (12)	C10—C9—H9A	109.0
O2—S—C14	106.36 (14)	C8—C9—H9B	109.0
C1—S—C14	98.16 (14)	C10—C9—H9B	109.0
C8—O1—C7	106.25 (18)	H9A—C9—H9B	107.8
C10—O3—C11	117.8 (2)	O4—C10—O3	124.9 (2)
C8—C1—C2	107.3 (2)	O4—C10—C9	125.3 (2)
C8—C1—S	123.59 (19)	O3—C10—C9	109.8 (2)
C2—C1—S	129.04 (18)	C13—C11—O3	107.5 (3)
C7—C2—C3	119.7 (2)	C13—C11—C12	111.2 (4)
C7—C2—C1	104.6 (2)	O3—C11—C12	104.8 (3)
C3—C2—C1	135.7 (2)	C13—C11—H11	111.0
C4—C3—C2	116.3 (2)	O3—C11—H11	111.0
C4—C3—H3	121.8	C12—C11—H11	111.0
C2—C3—H3	121.8	C11—C12—H12A	109.5
C3—C4—C5	123.4 (2)	C11—C12—H12B	109.5
C3—C4—C1	118.1 (2)	H12A—C12—H12B	109.5
C5—C4—C1	118.5 (2)	C11—C12—H12C	109.5
C6—C5—C4	120.5 (2)	H12A—C12—H12C	109.5
C6—C5—H5	119.8	H12B—C12—H12C	109.5
C4—C5—H5	119.8	C11—C13—H13A	109.5
C5—C6—C7	116.4 (2)	C11—C13—H13B	109.5
C5—C6—H6	121.8	H13A—C13—H13B	109.5
C7—C6—H6	121.8	C11—C13—H13C	109.5
O1—C7—C6	125.7 (2)	H13A—C13—H13C	109.5
O1—C7—C2	110.7 (2)	H13B—C13—H13C	109.5
C6—C7—C2	123.6 (2)	S—C14—H14A	109.5
C1—C8—O1	111.2 (2)	S—C14—H14B	109.5
C1—C8—C9	132.5 (2)	H14A—C14—H14B	109.5
O1—C8—C9	116.3 (2)	S—C14—H14C	109.5
C8—C9—C10	113.1 (2)	H14A—C14—H14C	109.5
C8—C9—H9A	109.0	H14B—C14—H14C	109.5
O2—S—C1—C8	133.8 (2)	C3—C2—C7—O1	179.7 (2)
C14—S—C1—C8	-116.2 (2)	C1—C2—C7—O1	0.9 (3)
O2—S—C1—C2	-42.4 (3)	C3—C2—C7—C6	0.1 (4)
C14—S—C1—C2	67.7 (3)	C1—C2—C7—C6	-178.6 (2)
C8—C1—C2—C7	-0.3 (3)	C2—C1—C8—O1	-0.5 (3)
S—C1—C2—C7	176.39 (19)	S—C1—C8—O1	-177.37 (16)
C8—C1—C2—C3	-178.7 (3)	C2—C1—C8—C9	-178.7 (2)
S—C1—C2—C3	-2.1 (4)	S—C1—C8—C9	4.4 (4)
C7—C2—C3—C4	-0.9 (4)	C7—O1—C8—C1	1.1 (3)

supplementary materials

C1—C2—C3—C4	177.4 (3)	C7—O1—C8—C9	179.6 (2)
C2—C3—C4—C5	1.1 (4)	C1—C8—C9—C10	75.3 (4)
C2—C3—C4—C1	-178.30 (19)	O1—C8—C9—C10	-102.9 (2)
C3—C4—C5—C6	-0.5 (4)	C11—O3—C10—O4	4.8 (4)
C1—C4—C5—C6	178.9 (2)	C11—O3—C10—C9	-177.6 (2)
C4—C5—C6—C7	-0.3 (4)	C8—C9—C10—O4	-13.6 (4)
C8—O1—C7—C6	178.3 (2)	C8—C9—C10—O3	168.8 (2)
C8—O1—C7—C2	-1.2 (3)	C10—O3—C11—C13	91.0 (4)
C5—C6—C7—O1	-179.0 (2)	C10—O3—C11—C12	-150.6 (3)
C5—C6—C7—C2	0.5 (4)		

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C13—H13B \cdots Cg ⁱ	0.96	2.78	3.515 (3)	134

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

Fig. 1

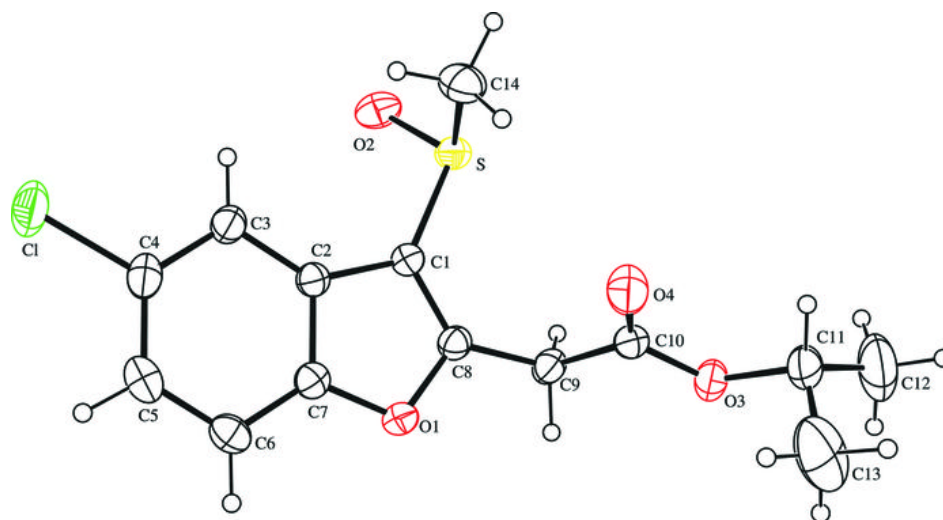


Fig. 2

