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

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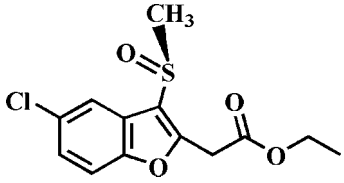
Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.003 Å; R factor = 0.033; wR factor = 0.082; data-to-parameter ratio = 16.9.

The title compound, $C_{13}H_{13}ClO_4S$, was prepared by the oxidation of ethyl 2-(5-chloro-3-methylsulfanyl-1-benzofuran-2-yl)acetate using 3-chloroperbenzoic acid. The O atom and the methyl group of the methylsulfinyl substituent lie on opposite sides of the plane of the benzofuran fragment. The crystal structure is stabilized by intermolecular aromatic π–π interactions, with a centroid–centroid distance of 3.609 (2) Å between the benzene rings of neighboring molecules, and by two intermolecular C—H···O hydrogen bonds.

Related literature

For crystal structures of isomers of the title compound, see: Choi *et al.* (2007); Seo *et al.* (2007).



Experimental

Crystal data

$C_{13}H_{13}ClO_4S$
M_r = 300.74
Triclinic, $P\overline{1}$
a = 8.2750 (4) Å
b = 9.3951 (4) Å
c = 10.0755 (5) Å
α = 72.883 (1)°
β = 78.837 (1)°
γ = 65.280 (1)°
V = 677.77 (6) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.44 mm^{-1}
T = 173 (2) K
0.60 × 0.35 × 0.10 mm

Data collection

Bruker SMART CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1999)
T_{min} = 0.840, T_{max} = 0.961
5881 measured reflections
2905 independent reflections
2576 reflections with $I > 2\sigma(I)$
R_{int} = 0.014

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.082
S = 1.11
2905 reflections
172 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.40 e Å^{-3}
$\Delta\rho_{min}$ = −0.31 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C3—H3···O2^{i}	0.95	2.40	3.334 (2)	166
C9—H9A···O2^{ii}	0.99	2.17	3.160 (2)	178

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

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); 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: AT2372).

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supplementary materials

Acta Cryst. (2007). E**63**, o3832 [**doi:10.1107/S160053680704007X**]

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

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

Comment

This work is related to preceding communications on the synthesis and structure of 2-benzofuranacetic acid derivatives, 2-(3-methylsulfanyl-5-phenyl-1-benzofuran-2-yl)acetic acid (Choi *et al.*, 2007) and 2-(5-ethyl-3-methylsulfanyl-1-benzofuran-2-yl)acetic acid (Seo *et al.*, 2007). Herein we report the molecular and crystal structures of the title compound, ethyl 2-(5-chloro-3-methylsulfinyl-1-benzofuran-2-yl)acetate (Fig. 1).

The benzofuran unit is essentially planar, with a mean deviation of 0.011 Å from the least-squares plane defined by the nine constituent atoms. The molecular packing (Fig. 2) is stabilized by π···π stacking interactions between adjacent benzene units. The *Cg*···*Cg*^{iii} distance is 3.609 (2) Å (*Cg* is the centroid of the C2—C7 benzene ring; symmetry code as in Fig. 2). The molecular packing is further stabilized by two kind of intermolecular C—H···O hydrogen bonds (Table 1 and Fig. 2); one between the hydrogen on benzene ring and the oxygen of the S═O unit with a C3—H3···O2^{i}, and a second between the hydrogen of methylene group and the oxygen of the S═O unit with a C9—H9A···O2^{ii}, respectively.

Experimental

3-Chloroperbenzoic acid (77%, 292 mg, 1.30 mmol) was added in small portions to a stirred solution of ethyl 2-(5-chloro-3-methylsulfanyl-1-benzofuran-2-yl)acetate (341 mg, 1.20 mmol) in dichloromethane (30 ml) at 273 K. After being stirred at room temperature for 2 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 (ethyl acetate) to afford the title compound as a colourless solid [yield 89%, m.p. 447–448 K; R_f = 0.70 (ethyl acetate)]. Single crystals suitable for X-ray diffraction were prepared by slow evaporation of a dilute solution of the title compound in chloroform at room temperature.

Refinement

All H atoms were positioned geometrically and refined using a riding model, with C—H = 0.95 Å for aromatic H atoms, 0.98 Å for methyl H atoms and 0.99 Å for methylene H atoms, respectively, and with U_{iso}(H) = 1.2U_{eq}(C) for aromatic and methylene H atoms and 1.5U_{eq}(C) for methyl H atoms. The highest peak in the difference map is 0.79 Å from Cl and the largest hole is 0.56 Å from S.

Figures

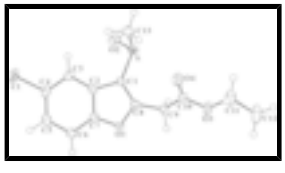


Fig. 1. The structure of the title molecule, showing displacement ellipsoids drawn at the 50% probability level.

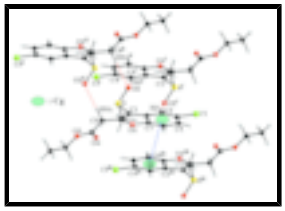


Fig. 2. π···π interactions and intermolecular C—H···O hydrogen bonds (dotted lines) in the title compound. *Cg* denotes the benzene ring centroid. [Symmetry codes: (i) −*x*, 1 − *y*, −*z*; (ii) 1 − *x*, 1 − *y*, −*z*; (iii) −*x*, 1 − *y*, 1 − *z*.]

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

Crystal data

$C_{13}H_{13}ClO_4S$	$Z = 2$
$M_r = 300.74$	$F_{000} = 312$
Triclinic, $P\overline{1}$	$D_x = 1.474$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 8.2750$ (4) Å	Cell parameters from 3909 reflections
$b = 9.3951$ (4) Å	$\theta = 2.5$–$28.3°$
$c = 10.0755$ (5) Å	$\mu = 0.44$ mm^{-1}
$\alpha = 72.883$ (1)°	$T = 173$ (2) K
$\beta = 78.837$ (1)°	Block, colourless
$\gamma = 65.280$ (1)°	0.60 × 0.35 × 0.10 mm
$V = 677.77$ (6) Å^3	

Data collection

Bruker SMART CCD diffractometer	2905 independent reflections
Radiation source: fine-focus sealed tube	2576 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.014$
Detector resolution: 10.00 pixels mm^{-1}	$\theta_{max} = 27.0°$
$T = 173(2)$ K	$\theta_{min} = 2.1°$
φ and ω scans	$h = -10 \rightarrow 10$
Absorption correction: multi-scan (SADABS; Sheldrick, 1999)	$k = -11 \rightarrow 11$
$T_{min} = 0.840$, $T_{max} = 0.961$	$l = -12 \rightarrow 12$
5881 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.033$	H-atom parameters constrained
$wR(F^2) = 0.082$	$w = 1/[\sigma^2(F_o^2) + (0.0312P)^2 + 0.3845P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.11$	$(\Delta/\sigma)_{max} < 0.001$

2905 reflections	$\Delta\rho_{max} = 0.40$ e Å^{-3}
172 parameters	$\Delta\rho_{min} = -0.30$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	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 $F^2 > 2\text{sigma}(F^2)$ 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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
S	0.22529 (6)	0.61850 (5)	0.03696 (4)	0.02606 (12)
Cl	−0.19460 (6)	0.21213 (6)	0.39767 (6)	0.03849 (14)
O1	0.33984 (14)	0.44917 (13)	0.42870 (11)	0.0215 (2)
O2	0.23374 (18)	0.48883 (17)	−0.02516 (13)	0.0361 (3)
O3	0.48845 (16)	0.87627 (14)	0.22936 (14)	0.0318 (3)
O4	0.23068 (17)	0.88156 (15)	0.18486 (15)	0.0375 (3)
C1	0.2349 (2)	0.53387 (18)	0.21755 (16)	0.0201 (3)
C2	0.1469 (2)	0.43132 (18)	0.30652 (16)	0.0199 (3)
C3	0.0171 (2)	0.37954 (19)	0.29186 (17)	0.0234 (3)
H3	−0.0354	0.4118	0.2065	0.028*
C4	−0.0307 (2)	0.27864 (19)	0.40868 (19)	0.0254 (3)
C5	0.0445 (2)	0.2272 (2)	0.53594 (18)	0.0270 (4)
H5	0.0082	0.1561	0.6122	0.032*
C6	0.1719 (2)	0.2801 (2)	0.55073 (17)	0.0249 (3)
H6	0.2242	0.2479	0.6362	0.030*
C7	0.2187 (2)	0.38205 (19)	0.43447 (17)	0.0208 (3)
C8	0.3477 (2)	0.54032 (18)	0.29495 (16)	0.0201 (3)
C9	0.4714 (2)	0.62598 (19)	0.26456 (17)	0.0223 (3)
H9A	0.5616	0.5891	0.1887	0.027*
H9B	0.5352	0.5962	0.3484	0.027*
C10	0.3791 (2)	0.8074 (2)	0.22247 (17)	0.0238 (3)
C11	0.4166 (3)	1.0527 (2)	0.1903 (3)	0.0416 (5)
H11A	0.3053	1.0965	0.2487	0.050*
H11B	0.3894	1.0926	0.0915	0.050*
C12	0.5542 (3)	1.1047 (3)	0.2121 (3)	0.0541 (6)
H12A	0.6640	1.0598	0.1545	0.065*
H12B	0.5788	1.0659	0.3105	0.065*
H12C	0.5104	1.2228	0.1857	0.065*

C13	−0.0024 (3)	0.7596 (2)	0.0363 (2)	0.0350 (4)
H13A	−0.0303	0.8187	−0.0597	0.052*
H13B	−0.0198	0.8359	0.0915	0.052*
H13C	−0.0816	0.7013	0.0769	0.052*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S	0.0269 (2)	0.0329 (2)	0.0187 (2)	−0.01322 (18)	−0.00490 (15)	−0.00219 (16)
Cl	0.0323 (2)	0.0335 (2)	0.0589 (3)	−0.0209 (2)	−0.0081 (2)	−0.0091 (2)
O1	0.0232 (6)	0.0228 (6)	0.0206 (5)	−0.0106 (5)	−0.0064 (4)	−0.0025 (4)
O2	0.0374 (7)	0.0467 (8)	0.0282 (7)	−0.0142 (6)	−0.0042 (5)	−0.0167 (6)
O3	0.0257 (6)	0.0204 (6)	0.0514 (8)	−0.0097 (5)	−0.0103 (6)	−0.0058 (5)
O4	0.0286 (7)	0.0264 (7)	0.0557 (9)	−0.0105 (5)	−0.0184 (6)	0.0022 (6)
C1	0.0211 (8)	0.0205 (8)	0.0187 (7)	−0.0076 (6)	−0.0036 (6)	−0.0040 (6)
C2	0.0201 (7)	0.0172 (7)	0.0220 (8)	−0.0053 (6)	−0.0032 (6)	−0.0061 (6)
C3	0.0224 (8)	0.0219 (8)	0.0280 (8)	−0.0071 (6)	−0.0052 (6)	−0.0089 (7)
C4	0.0212 (8)	0.0205 (8)	0.0388 (9)	−0.0097 (6)	−0.0022 (7)	−0.0108 (7)
C5	0.0265 (9)	0.0196 (8)	0.0318 (9)	−0.0089 (7)	0.0000 (7)	−0.0030 (7)
C6	0.0266 (8)	0.0224 (8)	0.0233 (8)	−0.0083 (7)	−0.0047 (6)	−0.0020 (6)
C7	0.0194 (7)	0.0191 (7)	0.0248 (8)	−0.0068 (6)	−0.0044 (6)	−0.0059 (6)
C8	0.0204 (8)	0.0181 (7)	0.0200 (7)	−0.0053 (6)	−0.0035 (6)	−0.0039 (6)
C9	0.0208 (8)	0.0227 (8)	0.0251 (8)	−0.0095 (6)	−0.0048 (6)	−0.0047 (6)
C10	0.0242 (8)	0.0250 (8)	0.0241 (8)	−0.0120 (7)	−0.0033 (6)	−0.0039 (6)
C11	0.0333 (10)	0.0201 (9)	0.0697 (15)	−0.0090 (8)	−0.0111 (10)	−0.0059 (9)
C12	0.0393 (12)	0.0249 (10)	0.101 (2)	−0.0145 (9)	−0.0108 (12)	−0.0126 (11)
C13	0.0330 (10)	0.0308 (10)	0.0361 (10)	−0.0059 (8)	−0.0155 (8)	−0.0023 (8)

Geometric parameters (Å, °)

S—O2	1.497 (1)	C5—H5	0.9500
S—C1	1.761 (2)	C6—C7	1.384 (2)
S—C13	1.794 (2)	C6—H6	0.9500
Cl—C4	1.747 (2)	C8—C9	1.488 (2)
O1—C8	1.374 (2)	C9—C10	1.510 (2)
O1—C7	1.375 (2)	C9—H9A	0.9900
O3—C10	1.335 (2)	C9—H9B	0.9900
O3—C11	1.462 (2)	C11—C12	1.486 (3)
O4—C10	1.203 (2)	C11—H11A	0.9900
C1—C8	1.356 (2)	C11—H11B	0.9900
C1—C2	1.445 (2)	C12—H12A	0.9800
C2—C7	1.394 (2)	C12—H12B	0.9800
C2—C3	1.397 (2)	C12—H12C	0.9800
C3—C4	1.385 (2)	C13—H13A	0.9800
C3—H3	0.9500	C13—H13B	0.9800
C4—C5	1.399 (2)	C13—H13C	0.9800
C5—C6	1.386 (2)		
O2—S—C1	105.84 (8)	O1—C8—C9	115.8 (1)

O2—S—C13	106.39 (9)	C8—C9—C10	113.6 (1)
C1—S—C13	99.06 (8)	C8—C9—H9A	108.8
C8—O1—C7	106.4 (1)	C10—C9—H9A	108.8
C10—O3—C11	116.0 (1)	C8—C9—H9B	108.8
C8—C1—C2	107.4 (1)	C10—C9—H9B	108.8
C8—C1—S	123.8 (1)	H9A—C9—H9B	107.7
C2—C1—S	128.4 (1)	O4—C10—O3	124.0 (2)
C7—C2—C3	119.7 (1)	O4—C10—C9	126.0 (2)
C7—C2—C1	104.5 (1)	O3—C10—C9	110.0 (1)
C3—C2—C1	135.8 (1)	O3—C11—C12	107.5 (2)
C4—C3—C2	116.3 (2)	O3—C11—H11A	110.2
C4—C3—H3	121.8	C12—C11—H11A	110.2
C2—C3—H3	121.8	O3—C11—H11B	110.2
C3—C4—C5	123.7 (2)	C12—C11—H11B	110.2
C3—C4—Cl	118.5 (1)	H11A—C11—H11B	108.5
C5—C4—Cl	117.9 (1)	C11—C12—H12A	109.5
C6—C5—C4	120.0 (2)	C11—C12—H12B	109.5
C6—C5—H5	120.0	H12A—C12—H12B	109.5
C4—C5—H5	120.0	C11—C12—H12C	109.5
C7—C6—C5	116.5 (2)	H12A—C12—H12C	109.5
C7—C6—H6	121.8	H12B—C12—H12C	109.5
C5—C6—H6	121.8	S—C13—H13A	109.5
O1—C7—C6	125.3 (1)	S—C13—H13B	109.5
O1—C7—C2	110.8 (1)	H13A—C13—H13B	109.5
C6—C7—C2	123.9 (2)	S—C13—H13C	109.5
C1—C8—O1	110.9 (1)	H13A—C13—H13C	109.5
C1—C8—C9	133.3 (2)	H13B—C13—H13C	109.5
O2—S—C1—C8	130.55 (14)	C5—C6—C7—C2	−0.6 (2)
C13—S—C1—C8	−119.43 (15)	C3—C2—C7—O1	−178.31 (13)
O2—S—C1—C2	−41.17 (16)	C1—C2—C7—O1	0.90 (17)
C13—S—C1—C2	68.84 (16)	C3—C2—C7—C6	1.3 (2)
C8—C1—C2—C7	−0.53 (17)	C1—C2—C7—C6	−179.46 (15)
S—C1—C2—C7	172.27 (12)	C2—C1—C8—O1	−0.02 (18)
C8—C1—C2—C3	178.49 (18)	S—C1—C8—O1	−173.23 (11)
S—C1—C2—C3	−8.7 (3)	C2—C1—C8—C9	−178.93 (16)
C7—C2—C3—C4	−0.7 (2)	S—C1—C8—C9	7.9 (3)
C1—C2—C3—C4	−179.58 (17)	C7—O1—C8—C1	0.58 (17)
C2—C3—C4—C5	−0.6 (2)	C7—O1—C8—C9	179.70 (13)
C2—C3—C4—Cl	179.09 (12)	C1—C8—C9—C10	60.8 (2)
C3—C4—C5—C6	1.3 (3)	O1—C8—C9—C10	−118.03 (15)
Cl—C4—C5—C6	−178.40 (13)	C11—O3—C10—O4	1.2 (3)
C4—C5—C6—C7	−0.6 (2)	C11—O3—C10—C9	179.60 (16)
C8—O1—C7—C6	179.43 (15)	C8—C9—C10—O4	−16.3 (3)
C8—O1—C7—C2	−0.93 (17)	C8—C9—C10—O3	165.26 (14)
C5—C6—C7—O1	178.95 (15)	C10—O3—C11—C12	177.06 (18)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*

C3—H3···O2^{i}	0.95	2.40	3.334 (2)	166
C9—H9A···O2^{ii}	0.99	2.17	3.160 (2)	178

Symmetry codes: (i) −*x*, −*y*+1, −*z*; (ii) −*x*+1, −*y*+1, −*z*.

Fig. 1

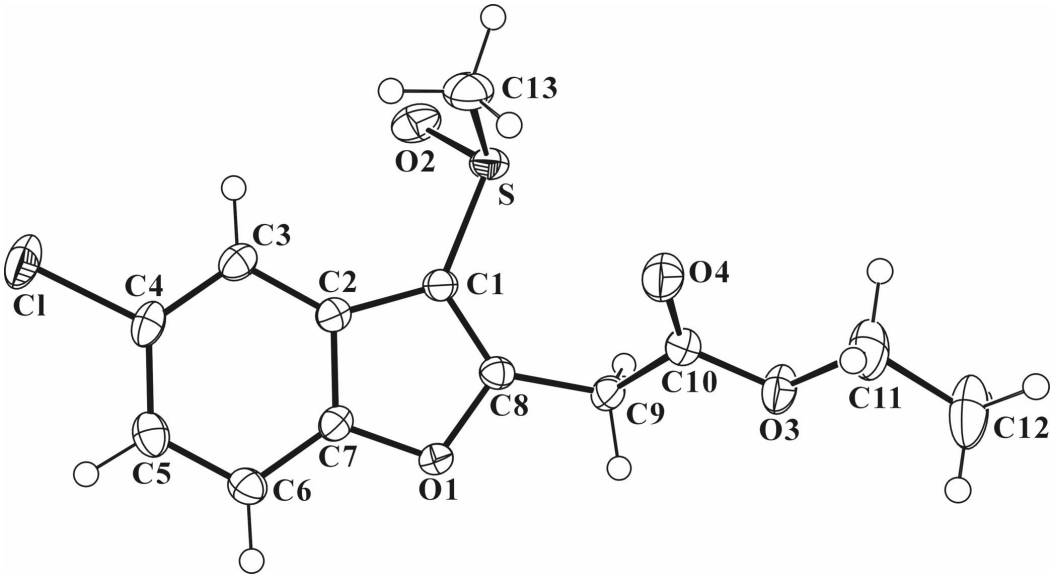
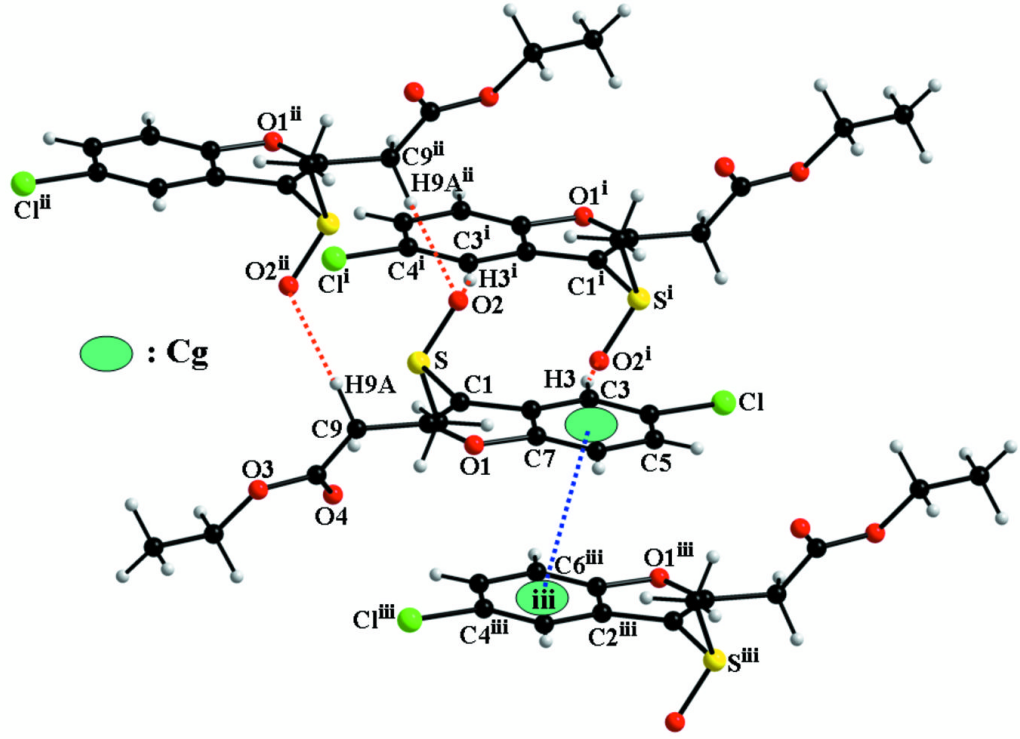


Fig. 2


O1ii
C9ii
H9Aii
Clii
O1i
C3i
O2ii
Cli
C4i
H3i
C1i
Si
O2
: Cg
S
O2i
H9A
C1
H3
C3
Cl
C9
O1
C7
C5
O3
O4
C6iii
O1iii
iii
Cliii
C4iii
C2iii
Siii