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

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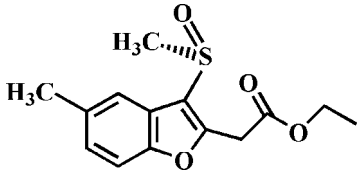
Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.004 Å; R factor = 0.048; wR factor = 0.110; data-to-parameter ratio = 14.0.

The title compound, $C_{14}H_{16}O_4S$, was prepared by the oxidation of ethyl 2-(5-methyl-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 3.641 (3) Å between benzene rings of neighboring molecules, and by two C—H···O hydrogen bonds.

Related literature

For crystal structures of isomers of the title compound, see: Choi *et al.* (2006); Seo *et al.* (2007).



Experimental

Crystal data

$C_{14}H_{16}O_4S$
M_r = 280.33
Triclinic, $P\overline{1}$
a = 8.1499 (8) Å
b = 9.4958 (9) Å
c = 10.283 (1) Å
α = 73.216 (2)°
β = 79.023 (2)°
γ = 65.188 (2)°
V = 689.37 (12) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.24 mm^{-1}
T = 173 (2) K
0.40 × 0.20 × 0.10 mm

Data collection

Bruker SMART CCD diffractometer
Absorption correction: none
3639 measured reflections
2416 independent reflections
2020 reflections with $I > 2\sigma(I)$
R_{int} = 0.044

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.110
S = 1.13
2416 reflections
173 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.37 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 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	2.48	3.407 (3)	164
C9—H9B···O2^{ii}	0.99	2.16	3.143 (3)	172

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

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: SJ2328).

References

Brandenburg, K. (1998). *DIAMOND*. Version 2.1. Crystal Impact GbR, Bonn, Germany.
Bruker (1997). *SMART* (Version 5.631) and *SAINT* (Version 6.12). Bruker AXS Inc., Madison, Wisconsin, USA.
Choi, H. D., Kang, B. W., Seo, P. J., Son, B. W. & Lee, U. (2006). *Acta Cryst.* E**62**, o5121–o5122.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Seo, P. J., Choi, H. D., Son, B. W. & Lee, U. (2007). *Acta Cryst.* E**63**, o2048–o2049.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

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supplementary materials

Acta Cryst. (2007). E**63**, o3839 [**doi:10.1107/S1600536807040263**]

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

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

Comment

As part of our ongoing work on the synthesis and structure of 2-benzofuranacetic acid derivatives, the crystal structures of ethyl [5-(4-hydroxyphenyl)-3-methylsulfanyl-1-benzofuran-2-yl]acetate (Choi *et al.*, 2006) and 2-(5-ethyl-3-methylsulfanyl-1-benzofuran-2-yl)acetic acid (Seo *et al.*, 2007) have been described previously. Herein we report the molecular and crystal structure of the title compound (Fig. 1).

The benzofuran unit is essentially planar, with a mean deviation of 0.007 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 $Cg\cdots Cg^{iii}$ distance is 3.641 (3) 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 kinds of C—H···O hydrogen bonds between the oxygen of the S═O group and hydrogen atoms on the benzene ring and of the benzylic methylene group respectively (Table 1 and Fig. 2).

Experimental

3-Chloroperbenzoic acid (77%, 336 mg, 1.50 mmol) was added in small portions to a stirred solution of ethyl 2-(5-methyl-3-methylsulfanyl-1-benzofuran-2-yl)acetate (370 mg, 1.40 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 colorless solid [yield 88%, m.p. 426–427 K; R_f = 0.56 (ethyl acetate)]. Single crystals suitable for X-ray diffraction were prepared by slow evaporation of a dilute 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 = 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) = 1.2Ueq(C) for aromatic and methylene H atoms and 1.5Ueq(C) for methyl H atoms. The highest peak in the difference map is 1.06 Å from S and the largest hole is 0.52 Å from S.

The crystals were small and weakly diffracting and some of the weak high angle intensities could not be detected. This resulted in a lower than normal data completeness.

Figures

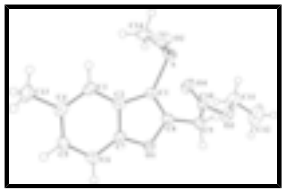


Fig. 1. The molecular structure of the title compound, showing displacement ellipsoids drawn at the 50% probability level.

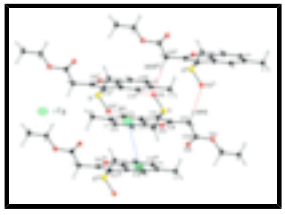


Fig. 2. π···π and C—H···O hydrogen bond interactions (dashed lines) in title compound. *Cg* denotes the ring centroid. [Symmetry codes: (i) 2 − *x*, 1 − *y*, 2 − *z*; (ii) 1 − *x*, 1 − *y*, 2 − *z*; (iii) 2 − *x*, 1 − *y*, 1 − *z*.]

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

Crystal data

$C_{14}H_{16}O_4S$	$Z = 2$
$M_r = 280.33$	$F_{000} = 296$
Triclinic, $P\overline{1}$	$D_x = 1.350$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation λ = 0.71073 Å
$a = 8.1499$ (8) Å	Cell parameters from 2164 reflections
$b = 9.4958$ (9) Å	θ = 2.8–28.2º
$c = 10.283$ (1) Å	μ = 0.24 mm^{-1}
α = 73.216 (2)º	$T = 173$ (2) K
β = 79.023 (2)º	Block, colorless
γ = 65.188 (2)º	0.40 × 0.20 × 0.10 mm
$V = 689.37$ (12) Å^3	

Data collection

Bruker SMART CCD diffractometer	2416 independent reflections
Radiation source: fine-focus sealed tube	2020 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.044$
Detector resolution: 10.00 pixels mm^{-1}	$\theta_{max} = 25.5$º
$T = 173(2)$ K	$\theta_{min} = 2.1$º
φ and ω scans	$h = -9\rightarrow9$
Absorption correction: none	$k = -11\rightarrow9$
3639 measured reflections	$l = -12\rightarrow12$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map

Least-squares matrix: full

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

$wR(F^2) = 0.110$

$S = 1.13$

2416 reflections

173 parameters

Primary atom site location: structure-invariant direct methods

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0258P)^2 + 0.6897P]$ where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{max} = 0.37$ e Å^{-3}

$\Delta\rho_{min} = -0.25$ e Å^{-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 $F^2 > 2$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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
S	0.77608 (9)	0.37116 (9)	0.95947 (6)	0.0313 (2)
O1	0.6542 (2)	0.54093 (19)	0.57810 (16)	0.0239 (4)
O2	0.7583 (3)	0.4964 (3)	1.0281 (2)	0.0471 (6)
O3	0.5072 (2)	0.1180 (2)	0.7741 (2)	0.0371 (5)
O4	0.7751 (3)	0.1114 (2)	0.8028 (2)	0.0426 (5)
C1	0.7611 (3)	0.4609 (3)	0.7840 (2)	0.0227 (5)
C2	0.8480 (3)	0.5637 (3)	0.6972 (2)	0.0223 (5)
C3	0.9769 (3)	0.6190 (3)	0.7105 (3)	0.0255 (6)
H3	1.0284	0.5886	0.7948	0.031*
C4	1.0282 (3)	0.7195 (3)	0.5981 (3)	0.0281 (6)
C5	0.9505 (3)	0.7637 (3)	0.4743 (3)	0.0293 (6)
H5	0.9867	0.8329	0.3987	0.035*
C6	0.8229 (3)	0.7102 (3)	0.4582 (3)	0.0280 (6)
H6	0.7711	0.7404	0.3741	0.034*
C7	0.7755 (3)	0.6100 (3)	0.5722 (2)	0.0233 (5)
C8	0.6482 (3)	0.4513 (3)	0.7094 (2)	0.0225 (5)
C9	0.5246 (3)	0.3651 (3)	0.7405 (3)	0.0258 (6)
H9A	0.4543	0.3977	0.6608	0.031*
H9B	0.4375	0.3979	0.8181	0.031*
C10	0.6202 (3)	0.1852 (3)	0.7753 (2)	0.0264 (6)
C11	0.5784 (4)	−0.0565 (3)	0.8073 (4)	0.0482 (8)
H11A	0.6075	−0.0994	0.9037	0.058*

H11B	0.6907	−0.0987	0.7490	0.058*
C12	0.4391 (5)	−0.1053 (4)	0.7841 (5)	0.0621 (11)
H12A	0.4842	−0.2221	0.8058	0.093*
H12B	0.4116	−0.0628	0.6883	0.093*
H12C	0.3288	−0.0635	0.8426	0.093*
C13	1.1675 (4)	0.7805 (4)	0.6083 (3)	0.0399 (7)
H13A	1.1795	0.7681	0.7045	0.060*
H13B	1.1290	0.8936	0.5614	0.060*
H13C	1.2846	0.7195	0.5658	0.060*
C14	1.0112 (4)	0.2413 (4)	0.9549 (3)	0.0397 (7)
H14A	1.0434	0.1802	1.0475	0.060*
H14B	1.0852	0.3049	0.9173	0.060*
H14C	1.0335	0.1677	0.8975	0.060*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S	0.0308 (4)	0.0403 (4)	0.0203 (3)	−0.0133 (3)	−0.0046 (3)	−0.0026 (3)
O1	0.0259 (9)	0.0238 (9)	0.0226 (8)	−0.0109 (8)	−0.0074 (7)	−0.0011 (7)
O2	0.0454 (12)	0.0636 (15)	0.0336 (11)	−0.0129 (11)	−0.0062 (9)	−0.0239 (10)
O3	0.0294 (10)	0.0217 (10)	0.0614 (13)	−0.0105 (8)	−0.0105 (9)	−0.0062 (9)
O4	0.0308 (11)	0.0278 (11)	0.0640 (14)	−0.0097 (9)	−0.0166 (10)	0.0028 (10)
C1	0.0242 (12)	0.0212 (13)	0.0210 (12)	−0.0063 (10)	−0.0033 (10)	−0.0053 (10)
C2	0.0226 (12)	0.0193 (13)	0.0236 (12)	−0.0041 (10)	−0.0034 (10)	−0.0079 (10)
C3	0.0246 (13)	0.0242 (14)	0.0302 (13)	−0.0079 (11)	−0.0054 (11)	−0.0103 (11)
C4	0.0235 (13)	0.0203 (14)	0.0421 (15)	−0.0054 (11)	−0.0039 (11)	−0.0138 (11)
C5	0.0291 (14)	0.0212 (14)	0.0347 (14)	−0.0097 (11)	−0.0001 (11)	−0.0038 (11)
C6	0.0292 (13)	0.0253 (14)	0.0258 (13)	−0.0074 (11)	−0.0058 (11)	−0.0033 (11)
C7	0.0216 (12)	0.0191 (13)	0.0286 (13)	−0.0059 (10)	−0.0048 (10)	−0.0061 (10)
C8	0.0233 (12)	0.0188 (13)	0.0219 (12)	−0.0053 (10)	−0.0019 (10)	−0.0041 (9)
C9	0.0236 (13)	0.0267 (14)	0.0270 (13)	−0.0103 (11)	−0.0028 (10)	−0.0047 (10)
C10	0.0272 (14)	0.0271 (14)	0.0249 (12)	−0.0121 (12)	−0.0036 (10)	−0.0028 (10)
C11	0.0380 (17)	0.0211 (16)	0.081 (2)	−0.0065 (13)	−0.0117 (16)	−0.0084 (15)
C12	0.046 (2)	0.0267 (18)	0.114 (3)	−0.0151 (15)	−0.010 (2)	−0.0145 (19)
C13	0.0368 (16)	0.0348 (17)	0.0541 (18)	−0.0197 (14)	−0.0066 (14)	−0.0082 (14)
C14	0.0374 (16)	0.0379 (17)	0.0356 (15)	−0.0065 (13)	−0.0157 (13)	−0.0009 (13)

Geometric parameters (Å, °)

S—O2	1.495 (2)	C6—C7	1.386 (4)
S—C1	1.763 (2)	C6—H6	0.9500
S—C14	1.792 (3)	C8—C9	1.485 (3)
O1—C8	1.377 (3)	C9—C10	1.513 (4)
O1—C7	1.382 (3)	C9—H9A	0.9900
O3—C10	1.326 (3)	C9—H9B	0.9900
O3—C11	1.463 (3)	C11—C12	1.473 (4)
O4—C10	1.202 (3)	C11—H11A	0.9900
C1—C8	1.350 (3)	C11—H11B	0.9900
C1—C2	1.444 (3)	C12—H12A	0.9800

C2—C7	1.393 (3)	C12—H12B	0.9800
C2—C3	1.399 (3)	C12—H12C	0.9800
C3—C4	1.391 (4)	C13—H13A	0.9800
C3—H3	0.9500	C13—H13B	0.9800
C4—C5	1.405 (4)	C13—H13C	0.9800
C4—C13	1.506 (4)	C14—H14A	0.9800
C5—C6	1.388 (4)	C14—H14B	0.9800
C5—H5	0.9500	C14—H14C	0.9800
O2—S—C1	106.9 (1)	C10—C9—H9A	108.7
O2—S—C14	106.4 (1)	C8—C9—H9B	108.7
C1—S—C14	98.7 (1)	C10—C9—H9B	108.7
C8—O1—C7	106.2 (2)	H9A—C9—H9B	107.6
C10—O3—C11	117.2 (2)	O4—C10—O3	123.9 (2)
C8—C1—C2	107.9 (2)	O4—C10—C9	125.8 (2)
C8—C1—S	122.7 (2)	O3—C10—C9	110.3 (2)
C2—C1—S	129.2 (2)	O3—C11—C12	108.2 (2)
C7—C2—C3	119.2 (2)	O3—C11—H11A	110.1
C7—C2—C1	104.3 (2)	C12—C11—H11A	110.1
C3—C2—C1	136.4 (2)	O3—C11—H11B	110.1
C4—C3—C2	118.8 (2)	C12—C11—H11B	110.1
C4—C3—H3	120.6	H11A—C11—H11B	108.4
C2—C3—H3	120.6	C11—C12—H12A	109.5
C3—C4—C5	119.9 (2)	C11—C12—H12B	109.5
C3—C4—C13	120.3 (2)	H12A—C12—H12B	109.5
C5—C4—C13	119.8 (2)	C11—C12—H12C	109.5
C6—C5—C4	122.5 (2)	H12A—C12—H12C	109.5
C6—C5—H5	118.8	H12B—C12—H12C	109.5
C4—C5—H5	118.8	C4—C13—H13A	109.5
C7—C6—C5	116.0 (2)	C4—C13—H13B	109.5
C7—C6—H6	122.0	H13A—C13—H13B	109.5
C5—C6—H6	122.0	C4—C13—H13C	109.5
O1—C7—C6	125.6 (2)	H13A—C13—H13C	109.5
O1—C7—C2	110.8 (2)	H13B—C13—H13C	109.5
C6—C7—C2	123.6 (2)	S—C14—H14A	109.5
C1—C8—O1	110.8 (2)	S—C14—H14B	109.5
C1—C8—C9	133.3 (2)	H14A—C14—H14B	109.5
O1—C8—C9	115.9 (2)	S—C14—H14C	109.5
C8—C9—C10	114.1 (2)	H14A—C14—H14C	109.5
C8—C9—H9A	108.7	H14B—C14—H14C	109.5
O2—S—C1—C8	−129.7 (2)	C5—C6—C7—C2	0.2 (4)
C14—S—C1—C8	120.2 (2)	C3—C2—C7—O1	178.7 (2)
O2—S—C1—C2	45.0 (3)	C1—C2—C7—O1	−0.7 (3)
C14—S—C1—C2	−65.1 (3)	C3—C2—C7—C6	−0.4 (4)
C8—C1—C2—C7	0.4 (3)	C1—C2—C7—C6	−179.8 (2)
S—C1—C2—C7	−174.91 (19)	C2—C1—C8—O1	0.1 (3)
C8—C1—C2—C3	−178.9 (3)	S—C1—C8—O1	175.77 (16)
S—C1—C2—C3	5.8 (4)	C2—C1—C8—C9	179.6 (3)
C7—C2—C3—C4	0.2 (4)	S—C1—C8—C9	−4.7 (4)

C1—C2—C3—C4	179.4 (3)	C7—O1—C8—C1	−0.6 (3)
C2—C3—C4—C5	0.1 (4)	C7—O1—C8—C9	179.8 (2)
C2—C3—C4—C13	−179.6 (2)	C1—C8—C9—C10	−64.4 (4)
C3—C4—C5—C6	−0.3 (4)	O1—C8—C9—C10	115.1 (2)
C13—C4—C5—C6	179.4 (2)	C11—O3—C10—O4	−0.6 (4)
C4—C5—C6—C7	0.1 (4)	C11—O3—C10—C9	−179.3 (2)
C8—O1—C7—C6	179.9 (2)	C8—C9—C10—O4	14.1 (4)
C8—O1—C7—C2	0.8 (3)	C8—C9—C10—O3	−167.2 (2)
C5—C6—C7—O1	−178.7 (2)	C10—O3—C11—C12	−173.3 (3)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3···O2^{i}	0.95	2.48	3.407 (3)	164
C9—H9B···O2^{ii}	0.99	2.16	3.143 (3)	172

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

Fig. 1

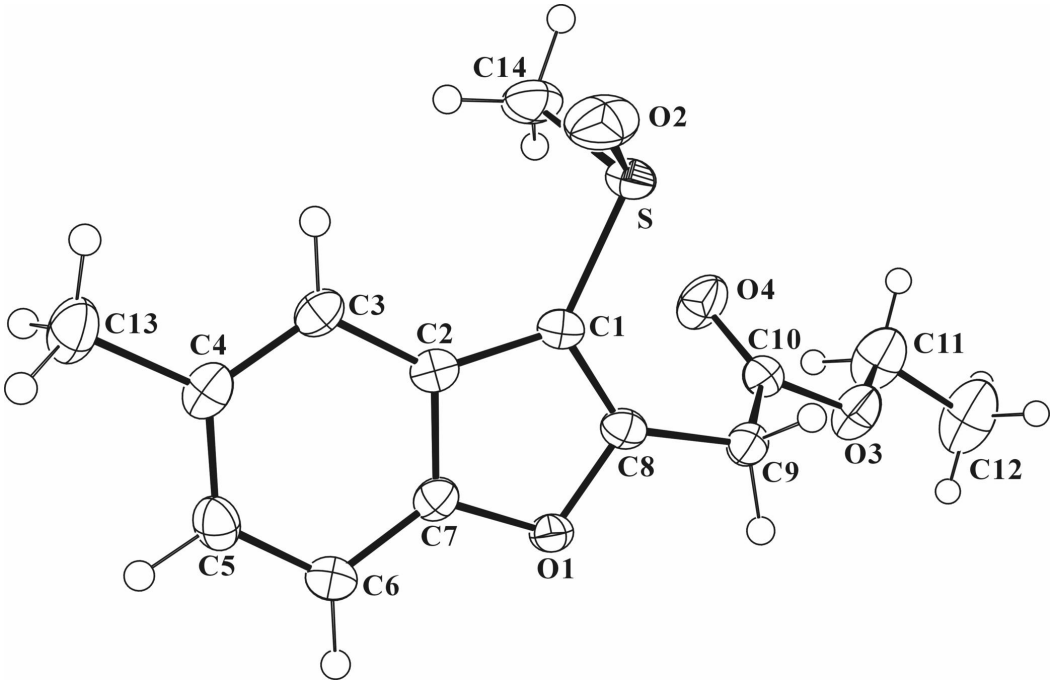
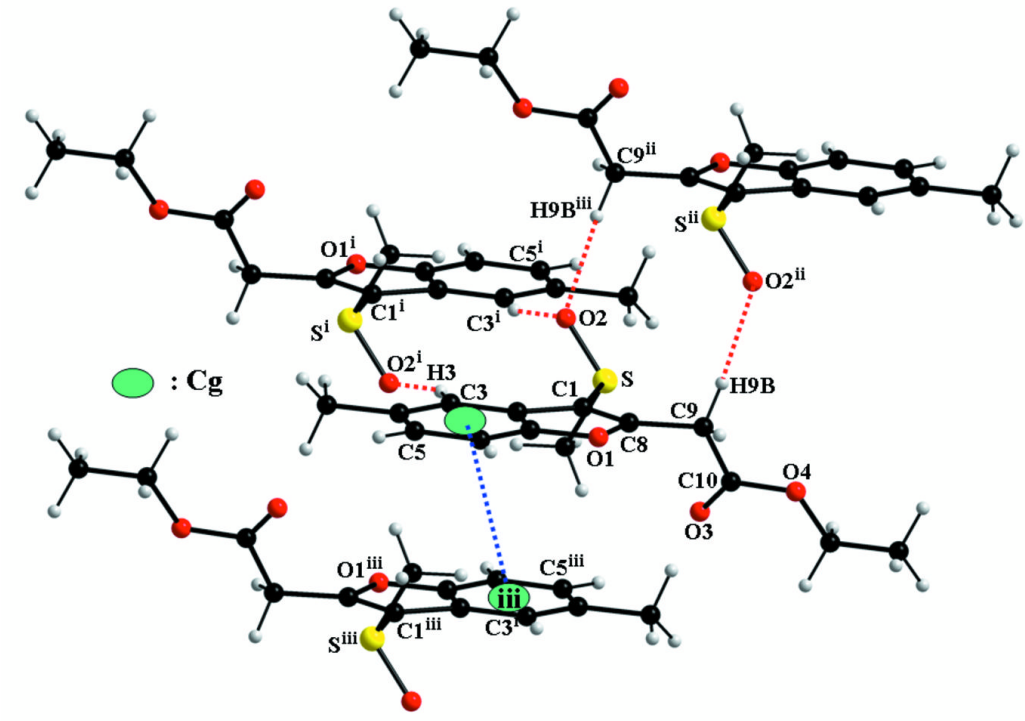


Fig. 2


C9ii
H9Biii
Sii
O2ii
O1i
C5i
C1i
C3i
O2
Si
O2i
H3
C3
C1
S
H9B
C9
C5
O1
C8
C10
O4
O3
: Cg
O1iii
C5iii
iii
C1iii
C3iii
Siii