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

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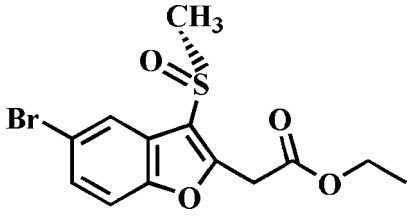
Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.003 Å; R factor = 0.022; wR factor = 0.059; data-to-parameter ratio = 17.2.

The title compound, $C_{13}H_{13}BrO_4S$, was prepared by the oxidation of ethyl 2-(5-bromo-3-methylsulfanyl-1-benzofuran-2-yl)acetate using 3-chloroperbenzoic acid. The O atom and methyl group of the methylsulfinyl substituent lie on opposite sides of the plane of the benzofuran moiety. The crystal structure is stabilized by intermolecular π–π interactions [centroid-to-centroid separation = 3.592 (2) Å], as well as by C—H···O hydrogen bonds.

Related literature

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



Experimental

Crystal data

$C_{13}H_{13}BrO_4S$
M_r = 345.20
Triclinic, $P\overline{1}$
a = 8.3557 (4) Å
b = 9.5625 (5) Å
c = 10.0192 (5) Å
α = 71.644 (1)°
β = 78.619 (1)°
γ = 65.304 (1)°
V = 688.31 (6) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 3.14 mm^{-1}
T = 173 (2) K
0.40 × 0.40 × 0.20 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1999)
T_{min} = 0.321, T_{max} = 0.541
5994 measured reflections
2961 independent reflections
2772 reflections with $I > 2\sigma(I)$
R_{int} = 0.016

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.022
$wR(F^2)$ = 0.059
S = 1.03
2961 reflections
172 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.41 e Å^{-3}
$\Delta\rho_{min}$ = −0.38 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	2.43	3.352 (2)	164
C9—H9B···O2^{ii}	0.99	2.17	3.161 (2)	176
C9—H9A···O1^{iii}	0.99	2.50	3.4816 (19)	173

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

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: TK2188).

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supplementary materials

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

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

Comment

As part of our on-going studies on the synthesis and structure of 2-benzofuranacetic acid derivatives, we have recently described the crystal structures of ethyl [5-(4-hydroxyphenyl)-3-methylsulfanyl-1-benzofuran-2-yl]acetate (Choi *et al.*, 2006) and 2-(3-methyllsulfanyl-5-phenyl-1-benzofuran-2-yl)acetic acid (Choi *et al.*, 2007). Herein, we report the molecular and crystal structure of the title compound, ethyl 2-(5-bromo-3-methylsulfinyl-1-benzofuran-2-yl)acetate (I, Fig. 1).

The benzofuran unit is essentially planar, with a mean deviation of 0.010 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*^{iv} distance is 3.592 (2) Å (*Cg* is the centroid of the C2–C7 ring; symmetry code as in Fig. 2). The molecular packing is further stabilized by C—H···O interactions (Table 1 and Fig. 2): one between a benzene-H and the S═O unit, *i.e.* C3—H3···O2^{i}, a second between a methylene-H and the S═O unit, *i.e.* C9—H9B···O2^{ii}, and a third between the second methylene-H the furan-O, *i.e.* C9—H9A···O1^{iii}.

Experimental

3-Chloroperbenzoic acid (77%, 359 mg, 1.60 mmol) was added in small portions to a stirred solution of ethyl 2-(5-bromo-3-methylsulfanyl-1-benzofuran-2-yl)acetate (494 mg, 1.50 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 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 (I) as a colorless solid [yield 86%, m.p. 453–454 K; R_f = 0.73 (ethyl acetate)]. Single crystals suitable for X-ray diffraction were prepared by slow evaporation of a dilute chloroform solution of (I) held at room temperature.

Refinement

All the H atoms were included in the riding-model approximation, with C—H = 0.95–0.99, and with U_{iso}(H) = 1.2 or 1.5U_{eq}(C).

Figures

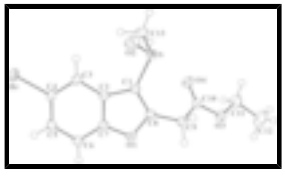


Fig. 1. The molecular structure of (I), showing displacement ellipsoides drawn at the 50% probability level.

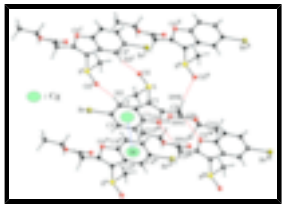


Fig. 2. π–π Interactions and C—H···O interactions (dotted lines) in (I). *Cg* denotes the ring centroid. [Symmetry codes: (i) 2 − *x*, −*y*, 1 − *z*; (ii) 1 − *x*, −*y*, 1 − *z*; (iii) 1 − *x*, −*y*, −*z*; (iv) 2 − *x*, −*y*, −*z*.]

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

Crystal data

$C_{13}H_{13}BrO_4S$	$Z = 2$
$M_r = 345.20$	$F_{000} = 348$
Triclinic, $P\overline{1}$	$D_x = 1.666$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 8.3557$ (4) Å	Cell parameters from 4506 reflections
$b = 9.5625$ (5) Å	$\theta = 2.2$–$28.3°$
$c = 10.0192$ (5) Å	$\mu = 3.14$ mm^{-1}
$\alpha = 71.644$ (1)°	$T = 173$ (2) K
$\beta = 78.619$ (1)°	Block, colourless
$\gamma = 65.304$ (1)°	0.40 × 0.40 × 0.20 mm
$V = 688.31$ (6) Å^3	

Data collection

Bruker SMART CCD area-detector diffractometer	2961 independent reflections
Radiation source: fine-focus sealed tube	2772 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.016$
Detector resolution: 10.0 pixels mm^{-1}	$\theta_{max} = 27.0°$
$T = 173$(2) K	$\theta_{min} = 2.2°$
φ and ω scans	$h = -10 \rightarrow 10$
Absorption correction: multi-scan (SADABS; Sheldrick, 1999)	$k = -12 \rightarrow 12$
$T_{min} = 0.321$, $T_{max} = 0.541$	$l = -12 \rightarrow 12$
5994 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
$R[F^2 > 2\sigma(F^2)] = 0.022$	H-atom parameters constrained
$wR(F^2) = 0.059$	$w = 1/[\sigma^2(F_o^2) + (0.031P)^2 + 0.3245P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{max} < 0.001$

2961 reflections	$\Delta\rho_{max} = 0.41$ e Å^{-3}
172 parameters	$\Delta\rho_{min} = -0.38$ 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}
Br	1.19929 (2)	0.29496 (2)	0.09731 (2)	0.03275 (7)
S	0.77219 (6)	−0.11607 (5)	0.46784 (4)	0.02467 (10)
O1	0.66177 (15)	0.04723 (13)	0.06926 (11)	0.0211 (2)
O2	0.76708 (18)	0.01229 (17)	0.52618 (13)	0.0339 (3)
O3	0.51765 (17)	−0.37582 (15)	0.27271 (15)	0.0303 (3)
O4	0.76958 (18)	−0.37966 (16)	0.32289 (16)	0.0359 (3)
C1	0.7622 (2)	−0.03343 (19)	0.28450 (16)	0.0198 (3)
C2	0.8492 (2)	0.06848 (19)	0.19260 (16)	0.0197 (3)
C3	0.9766 (2)	0.12143 (19)	0.20606 (17)	0.0219 (3)
H3	1.0273	0.0910	0.2928	0.026*
C4	1.0248 (2)	0.2206 (2)	0.08611 (18)	0.0231 (3)
C5	0.9530 (2)	0.2688 (2)	−0.04359 (18)	0.0246 (3)
H5	0.9900	0.3382	−0.1221	0.030*
C6	0.8282 (2)	0.2155 (2)	−0.05775 (17)	0.0236 (3)
H6	0.7778	0.2461	−0.1447	0.028*
C7	0.7807 (2)	0.11484 (19)	0.06213 (17)	0.0200 (3)
C8	0.6524 (2)	−0.04197 (19)	0.20650 (16)	0.0199 (3)
C9	0.5307 (2)	−0.1276 (2)	0.23858 (17)	0.0223 (3)
H9A	0.4667	−0.0971	0.1541	0.027*
H9B	0.4421	−0.0931	0.3154	0.027*
C10	0.6233 (2)	−0.3068 (2)	0.28198 (17)	0.0232 (3)
C11	0.5906 (3)	−0.5504 (2)	0.3129 (3)	0.0385 (5)
H11A	0.6164	−0.5916	0.4133	0.046*
H11B	0.7015	−0.5917	0.2548	0.046*
C12	0.4550 (3)	−0.6019 (3)	0.2887 (3)	0.0517 (6)
H12A	0.4308	−0.5606	0.1890	0.062*
H12B	0.3459	−0.5604	0.3468	0.062*
H12C	0.4993	−0.7187	0.3146	0.062*

C13	0.9969 (3)	−0.2565 (2)	0.4702 (2)	0.0339 (4)
H13A	1.0248	−0.3146	0.5679	0.051*
H13B	1.0760	−0.1996	0.4271	0.051*
H13C	1.0125	−0.3321	0.4169	0.051*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br	0.02947 (11)	0.02946 (11)	0.04696 (12)	−0.01799 (8)	−0.00698 (8)	−0.00823 (8)
S	0.0261 (2)	0.0304 (2)	0.01890 (18)	−0.01329 (17)	−0.00469 (15)	−0.00297 (16)
O1	0.0224 (6)	0.0224 (6)	0.0211 (5)	−0.0103 (5)	−0.0062 (4)	−0.0038 (4)
O2	0.0364 (7)	0.0424 (8)	0.0270 (6)	−0.0134 (6)	−0.0042 (5)	−0.0160 (6)
O3	0.0256 (6)	0.0204 (6)	0.0472 (8)	−0.0100 (5)	−0.0100 (5)	−0.0059 (5)
O4	0.0288 (7)	0.0269 (7)	0.0513 (8)	−0.0115 (6)	−0.0174 (6)	0.0009 (6)
C1	0.0208 (7)	0.0193 (8)	0.0194 (7)	−0.0071 (6)	−0.0039 (6)	−0.0043 (6)
C2	0.0201 (7)	0.0176 (7)	0.0217 (7)	−0.0059 (6)	−0.0032 (6)	−0.0065 (6)
C3	0.0220 (8)	0.0210 (8)	0.0256 (8)	−0.0076 (6)	−0.0051 (6)	−0.0086 (6)
C4	0.0193 (7)	0.0199 (8)	0.0337 (9)	−0.0087 (6)	−0.0027 (6)	−0.0099 (7)
C5	0.0248 (8)	0.0181 (8)	0.0278 (8)	−0.0071 (7)	−0.0015 (7)	−0.0036 (6)
C6	0.0247 (8)	0.0212 (8)	0.0232 (8)	−0.0073 (7)	−0.0057 (6)	−0.0032 (6)
C7	0.0187 (7)	0.0183 (7)	0.0240 (7)	−0.0059 (6)	−0.0049 (6)	−0.0066 (6)
C8	0.0201 (7)	0.0177 (7)	0.0209 (7)	−0.0056 (6)	−0.0039 (6)	−0.0046 (6)
C9	0.0210 (8)	0.0231 (8)	0.0253 (8)	−0.0101 (6)	−0.0051 (6)	−0.0051 (6)
C10	0.0234 (8)	0.0251 (8)	0.0232 (8)	−0.0114 (7)	−0.0038 (6)	−0.0049 (6)
C11	0.0330 (10)	0.0197 (9)	0.0622 (13)	−0.0098 (8)	−0.0116 (9)	−0.0055 (9)
C12	0.0407 (12)	0.0253 (10)	0.0935 (19)	−0.0149 (9)	−0.0159 (12)	−0.0114 (11)
C13	0.0318 (10)	0.0305 (10)	0.0346 (10)	−0.0057 (8)	−0.0145 (8)	−0.0034 (8)

Geometric parameters (Å, °)

Br—C4	1.904 (2)	C5—H5	0.9500
S—O2	1.500 (1)	C6—C7	1.389 (2)
S—C1	1.760 (2)	C6—H6	0.9500
S—C13	1.794 (2)	C8—C9	1.486 (2)
O1—C7	1.375 (2)	C9—C10	1.510 (2)
O1—C8	1.378 (2)	C9—H9A	0.9900
O3—C10	1.334 (2)	C9—H9B	0.9900
O3—C11	1.464 (2)	C11—C12	1.495 (3)
O4—C10	1.206 (2)	C11—H11A	0.9900
C1—C8	1.358 (2)	C11—H11B	0.9900
C1—C2	1.445 (2)	C12—H12A	0.9800
C2—C7	1.397 (2)	C12—H12B	0.9800
C2—C3	1.399 (2)	C12—H12C	0.9800
C3—C4	1.384 (2)	C13—H13A	0.9800
C3—H3	0.9500	C13—H13B	0.9800
C4—C5	1.400 (2)	C13—H13C	0.9800
C5—C6	1.383 (2)		
O2—S—C1	105.74 (8)	O1—C8—C9	115.7 (1)

O2—S—C13	106.19 (9)	C8—C9—C10	113.5 (1)
C1—S—C13	98.98 (8)	C8—C9—H9A	108.9
C7—O1—C8	106.3 (1)	C10—C9—H9A	108.9
C10—O3—C11	116.1 (1)	C8—C9—H9B	108.9
C8—C1—C2	107.4 (1)	C10—C9—H9B	108.9
C8—C1—S	124.3 (1)	H9A—C9—H9B	107.7
C2—C1—S	128.0 (1)	O4—C10—O3	123.8 (2)
C7—C2—C3	119.6 (2)	O4—C10—C9	125.9 (2)
C7—C2—C1	104.6 (1)	O3—C10—C9	110.2 (1)
C3—C2—C1	135.9 (2)	O3—C11—C12	107.2 (2)
C4—C3—C2	116.4 (2)	O3—C11—H11A	110.3
C4—C3—H3	121.8	C12—C11—H11A	110.3
C2—C3—H3	121.8	O3—C11—H11B	110.3
C3—C4—C5	123.6 (2)	C12—C11—H11B	110.3
C3—C4—Br	118.3 (1)	H11A—C11—H11B	108.5
C5—C4—Br	118.0 (1)	C11—C12—H12A	109.5
C6—C5—C4	120.2 (2)	C11—C12—H12B	109.5
C6—C5—H5	119.9	H12A—C12—H12B	109.5
C4—C5—H5	119.9	C11—C12—H12C	109.5
C5—C6—C7	116.3 (2)	H12A—C12—H12C	109.5
C5—C6—H6	121.8	H12B—C12—H12C	109.5
C7—C6—H6	121.8	S—C13—H13A	109.5
O1—C7—C6	125.3 (1)	S—C13—H13B	109.5
O1—C7—C2	110.9 (1)	H13A—C13—H13B	109.5
C6—C7—C2	123.9 (2)	S—C13—H13C	109.5
C1—C8—O1	110.8 (1)	H13A—C13—H13C	109.5
C1—C8—C9	133.5 (2)	H13B—C13—H13C	109.5
O2—S—C1—C8	−132.39 (15)	C5—C6—C7—C2	1.0 (2)
C13—S—C1—C8	117.86 (15)	C3—C2—C7—O1	178.24 (14)
O2—S—C1—C2	40.01 (17)	C1—C2—C7—O1	−0.64 (17)
C13—S—C1—C2	−69.74 (16)	C3—C2—C7—C6	−1.6 (2)
C8—C1—C2—C7	0.28 (18)	C1—C2—C7—C6	179.53 (15)
S—C1—C2—C7	−173.14 (12)	C2—C1—C8—O1	0.17 (18)
C8—C1—C2—C3	−178.31 (18)	S—C1—C8—O1	173.89 (11)
S—C1—C2—C3	8.3 (3)	C2—C1—C8—C9	179.06 (17)
C7—C2—C3—C4	0.9 (2)	S—C1—C8—C9	−7.2 (3)
C1—C2—C3—C4	179.38 (17)	C7—O1—C8—C1	−0.55 (17)
C2—C3—C4—C5	0.2 (2)	C7—O1—C8—C9	−179.66 (13)
C2—C3—C4—Br	−179.40 (12)	C1—C8—C9—C10	−62.5 (2)
C3—C4—C5—C6	−0.8 (3)	O1—C8—C9—C10	116.37 (15)
Br—C4—C5—C6	178.78 (13)	C11—O3—C10—O4	−1.3 (3)
C4—C5—C6—C7	0.2 (2)	C11—O3—C10—C9	−179.58 (16)
C8—O1—C7—C6	−179.42 (15)	C8—C9—C10—O4	18.2 (2)
C8—O1—C7—C2	0.74 (17)	C8—C9—C10—O3	−163.55 (14)
C5—C6—C7—O1	−178.85 (15)	C10—O3—C11—C12	−177.56 (18)

Hydrogen-bond geometry (Å, °)

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

C3—H3···O2^{i}	0.95	2.43	3.352 (2)	164
C9—H9B···O2^{ii}	0.99	2.17	3.161 (2)	176
C9—H9A···O1^{iii}	0.99	2.50	3.4816 (19)	173

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

Fig. 1

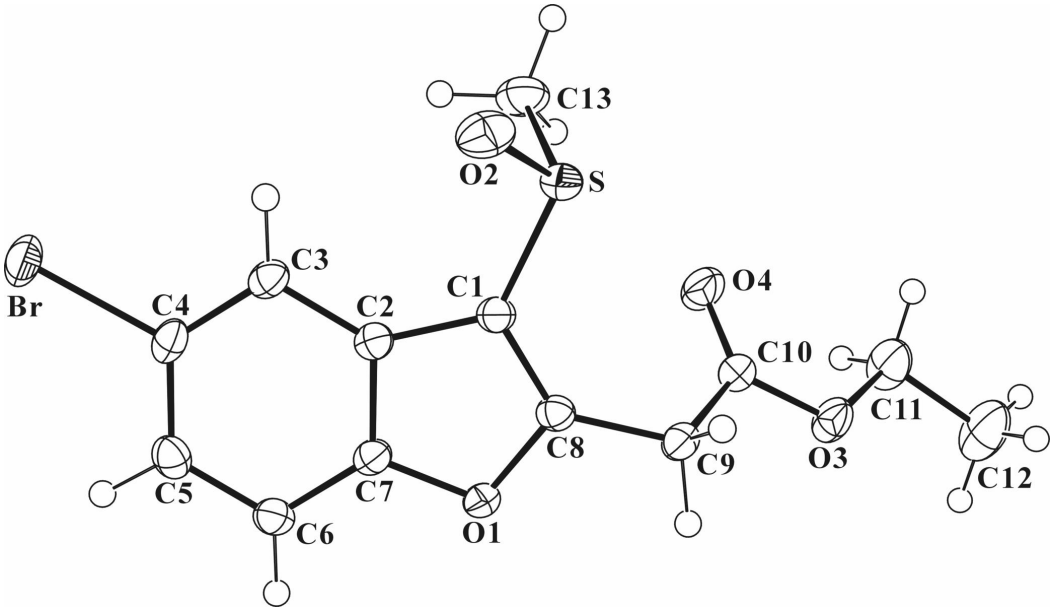
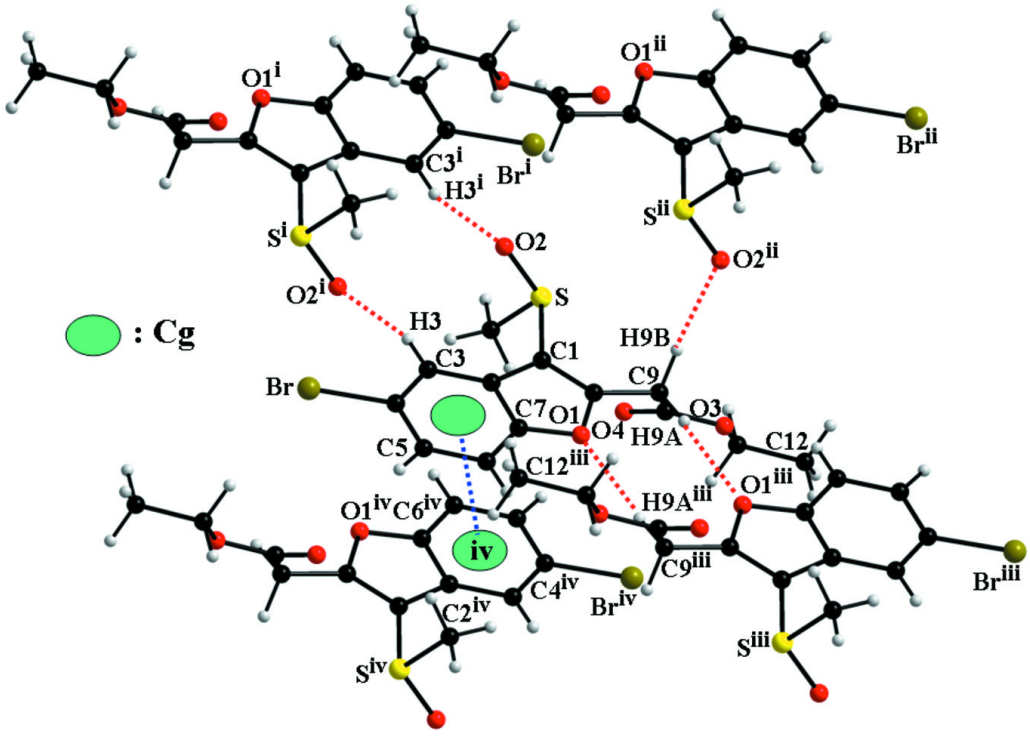


Fig. 2


O1i
O1ii
Brii
C3i
H3i
Bri
Sii
O2ii
O2
Si
O2i
S
: Cg
H3
C3
C1
H9B
C9
Br
C7
O1
O3
O4
H9A
C12
C5
C12iii
O1iii
H9Aiii
O1iv
C6iv
iv
C9iii
Briii
C4iv
Briv
C2iv
Siii
Siv