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2-[5-(4-Bromophenyl)-3-methylsulfanyl-1-benzofuran-2-yl]acetic acid

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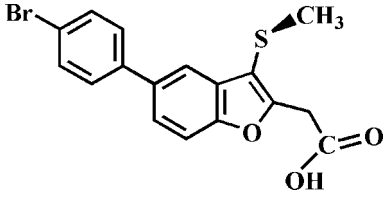
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.004 Å; R factor = 0.041; wR factor = 0.113; data-to-parameter ratio = 16.9.

The title compound, $C_{17}H_{13}BrO_3S$, was prepared by alkaline hydrolysis of ethyl 2-[5-(4-bromophenyl)-3-methylsulfanyl-1-benzofuran-2-yl]acetate. There are two symmetry-independent molecules in the asymmetric unit. The 4-bromophenyl rings are rotated out of the benzofuran planes, with dihedral angles for the two molecules of 50.22 (8) and 35.4 (1)°. The methyl groups of the methylsulfanyl substituent are almost perpendicular to the plane of the benzofuran fragment [99.5 (2) and 100.8 (2)°] and are slightly tilted towards it. The crystal structure is stabilized by a C—H···O hydrogen bond and a Br···O halogen bond [Br···O = 3.284 (2) Å], and by inversion-related intermolecular O—H···O hydrogen bonds between the carboxyl groups from two symmetry-independent molecules.

Related literature

For the crystal structures of similar benzofuran compounds, see: Choi *et al.* (2006, 2007). For a review of halogen bonding, see: Politzer *et al.* (2007).



Experimental

Crystal data

$C_{17}H_{13}BrO_3S$
M_r = 377.24
Triclinic, $P\overline{1}$
a = 7.7531 (1) Å
b = 10.8299 (1) Å
c = 19.5621 (2) Å
α = 104.131 (1)°
β = 93.631 (1)°
γ = 92.870 (1)°
V = 1585.99 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 2.73 mm^{-1}
T = 298 (2) K
0.40 × 0.22 × 0.17 mm

Data collection

Bruker SMART CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2000)
T_{min} = 0.482, T_{max} = 0.637
29666 measured reflections
6889 independent reflections
5128 reflections with $I > 2\sigma(I)$
R_{int} = 0.019

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.113
S = 1.02
6889 reflections
407 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.98 e Å^{-3}
$\Delta\rho_{min}$ = −0.82 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H35···O5^{i}	0.82 (6)	1.84 (6)	2.659 (3)	176 (6)
O6—H36···O2^{i}	0.73 (5)	1.93 (5)	2.655 (3)	172 (5)
C17—H17B···O2^{i}	0.96	2.60	3.374 (5)	138

Symmetry code: (i) $-x+3, -y, -z$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); 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: SJ2376).

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supplementary materials

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2-[5-(4-Bromophenyl)-3-methylsulfanyl-1-benzofuran-2-yl]acetic acid

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Comment

As part of our ongoing studies on the synthesis and structure of 2-(5-aryl-3-methylsulfanyl-1-benzofuran-2-yl)acetic acid derivatives, we have recently described ethyl 2-[5-(4-hydroxyphenyl)-3-methylsulfanyl-1-benzofuran-2-yl]acetate (Choi *et al.*, 2006) and 2-(3-methylsulfanyl-5-phenyl-1-benzofuran-2-yl)acetic acid (Choi *et al.*, 2007). Herein we report the molecular and crystal structure of the title compound, 2-[5-(4-bromophenyl)-3-methylsulfanyl-1-benzofuran-2-yl]acetic acid which crystallizes with two unique molecules, A & B, in the asymmetric unit (Fig. 1).

The benzofuran unit is essentially planar, with a mean deviation of 0.019 Å, for A, and 0.013 Å, for B, respectively, from the least-squares plane defined by the nine constituent atoms. In the title compound, the dihedral angles formed by the plane of the benzofuran and the plane of the 4-bromophenyl ring are 50.22 (8)° in A and 35.4 (1)° in B, respectively. The methyl groups (S1—CH_3 in A and S2—CH_3 in B) are tilted towards the plane of the benzofuran systems [99.5 (2)°, A and 100.8 (2)°, B]. The molecular packing (Fig. 2) is stabilized by a C—H···O hydrogen bond (Table 1 and Fig. 2), between a methyl H and the C═O unit, *i.e.* C17—H17B···O2^{i}. Further stability comes from a weak Br···O interaction (Fig. 2) (Politzer *et al.*, 2007) between the bromine atom and the oxygen of a neighbouring C═O unit, with a Br2···O6^{ii} distance of 3.284 (2) Å (Symmetry codes as in Fig. 2). Classical inversion-related O3—H35···O5^{i} and O6—H36···O2^{i} hydrogen bonds link the carboxyl groups from two symmetry-independent molecules (Table 1 and Fig. 2).

Experimental

Ethyl 2-[5-(4-bromophenyl)-3-methylsulfanyl-1-benzofuran-2-yl]acetate (729 mg, 1.8 mmol) was added to a solution of potassium hydroxide (561 mg, 10.0 mmol) in water (15 ml) and methanol (15 ml), and the mixture was heated at 343 K for 4 h, then cooled. Water was added, and the solution was washed with chloroform. The aqueous layer was acidified to pH 1 with concentrated hydrochloric acid and then extracted with chloroform, 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 87%, m.p. 476–477 K; R_f = 0.81 (ethyl acetate)]. Single crystals suitable for X-ray diffraction were prepared by slow evaporation of a dilute solution of the title compound in acetone at room temperature.

Refinement

H atoms of the carboxyl groups were found in a difference Fourier map and refined freely with isotropic displacement parameters. The other H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93 Å for aromatic H atoms, 0.96 Å for methyl H atoms and 0.97 Å for methylene H atoms, and with U_{iso}(H) = 1.2Ueq(C) for aromatic and methylene H atoms and U_{iso}(H) =1.5Ueq(C) for methyl H atoms.

Figures

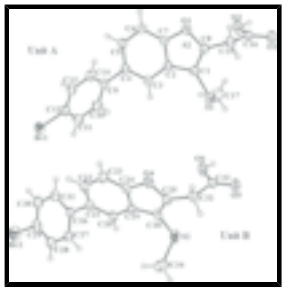


Fig. 1. The molecular structure of the title compound, showing displacement ellipsoids drawn at the 30% probability level.

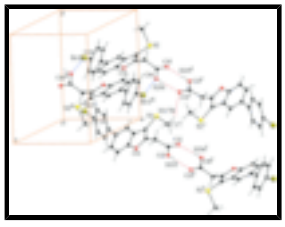


Fig. 2. The O—H···O and C—H···O hydrogen bonds, and Br···O halogen bond (dotted lines) in the title compound. [Symmetry codes: (i) 3 − *x*, −*y*, −*z*; (ii) 2 − *x*, 1 − *y*, 1 − *z*.]

2-[5-(4-Bromophenyl)-3-methylsulfanyl-1-benzofuran-2-yl]acetic acid

Crystal data

$C_{17}H_{13}BrO_3S$	$Z = 4$
$M_r = 377.24$	$F_{000} = 760$
Triclinic, $P\overline{1}$	$D_x = 1.580$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 7.7531$ (1) Å	Cell parameters from 6878 reflections
$b = 10.8299$ (1) Å	$\theta = 2.4$–$26.1°$
$c = 19.5621$ (2) Å	$\mu = 2.73$ mm^{-1}
$\alpha = 104.131$ (1)°	$T = 298$ (2) K
$\beta = 93.631$ (1)°	Block, colourless
$\gamma = 92.870$ (1)°	0.40 × 0.22 × 0.17 mm
$V = 1585.99$ (3) Å^3	

Data collection

Bruker SMART CCD diffractometer	6889 independent reflections
Radiation source: fine-focus sealed tube	5128 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.019$
Detector resolution: 10.0 pixels mm^{-1}	$\theta_{max} = 27.0°$
$T = 298(2)$ K	$\theta_{min} = 1.1°$
φ and ω scans	$h = -9 \rightarrow 7$
Absorption correction: multi-scan (SADABS; Sheldrick, 2000)	$k = -13 \rightarrow 13$
$T_{min} = 0.482$, $T_{max} = 0.637$	$l = -24 \rightarrow 24$
29666 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
$R[F^2 > 2\sigma(F^2)] = 0.042$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.113$	$w = 1/[\sigma^2(F_o^2) + (0.0468P)^2 + 1.5959P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} < 0.001$
6889 reflections	$\Delta\rho_{max} = 0.98$ e Å^{-3}
407 parameters	$\Delta\rho_{min} = -0.82$ 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 $F^2 > 2$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}
Br1	0.60522 (6)	0.18122 (4)	0.49776 (2)	0.07480 (15)
Br2	0.76860 (7)	0.72243 (5)	0.72068 (2)	0.08609 (17)
S1	1.25540 (10)	0.03549 (8)	0.06637 (5)	0.0514 (2)
S2	1.33833 (11)	0.73058 (10)	0.28286 (5)	0.0626 (2)
O1	0.9335 (3)	−0.27217 (19)	0.00294 (10)	0.0443 (5)
O2	1.3988 (3)	−0.2684 (2)	−0.12497 (12)	0.0577 (6)
O3	1.3216 (4)	−0.3477 (3)	−0.03577 (14)	0.0674 (7)
H35	1.406 (8)	−0.389 (5)	−0.045 (3)	0.13 (2)*
O4	0.9304 (3)	0.5069 (2)	0.18828 (11)	0.0527 (5)
O5	1.4056 (3)	0.4862 (2)	0.06232 (12)	0.0558 (6)
O6	1.3168 (4)	0.3951 (3)	0.14457 (13)	0.0630 (7)
H36	1.391 (6)	0.358 (4)	0.135 (2)	0.087 (16)*
C1	1.0950 (4)	−0.0895 (3)	0.05385 (15)	0.0388 (6)
C2	0.9754 (3)	−0.1131 (3)	0.10368 (15)	0.0378 (6)
C3	0.9381 (4)	−0.0489 (3)	0.17147 (14)	0.0394 (6)
H3	0.9978	0.0282	0.1945	0.047*
C4	0.8100 (4)	−0.1024 (3)	0.20400 (15)	0.0404 (6)

C5	0.7238 (4)	−0.2198 (3)	0.16914 (16)	0.0457 (7)
H5	0.6416	−0.2561	0.1923	0.055*
C6	0.7572 (4)	−0.2834 (3)	0.10136 (16)	0.0467 (7)
H6	0.6983	−0.3606	0.0781	0.056*
C7	0.8821 (4)	−0.2261 (3)	0.07034 (14)	0.0394 (6)
C8	1.0620 (4)	−0.1855 (3)	−0.00486 (15)	0.0413 (6)
C9	0.7624 (4)	−0.0338 (3)	0.27527 (15)	0.0430 (6)
C10	0.7279 (5)	0.0940 (3)	0.28954 (17)	0.0544 (8)
H10	0.7366	0.1374	0.2542	0.065*
C11	0.6808 (5)	0.1584 (3)	0.35513 (18)	0.0584 (8)
H11	0.6566	0.2439	0.3637	0.070*
C12	0.6703 (4)	0.0941 (3)	0.40722 (16)	0.0511 (8)
C13	0.7044 (4)	−0.0320 (3)	0.39538 (17)	0.0547 (8)
H13	0.6977	−0.0741	0.4314	0.066*
C14	0.7491 (4)	−0.0962 (3)	0.32900 (16)	0.0501 (7)
H14	0.7704	−0.1822	0.3205	0.060*
C15	1.1362 (4)	−0.2090 (3)	−0.07483 (16)	0.0470 (7)
H15A	1.1598	−0.1275	−0.0859	0.056*
H15B	1.0499	−0.2580	−0.1105	0.056*
C16	1.2989 (4)	−0.2782 (3)	−0.07950 (15)	0.0430 (6)
C17	1.4235 (5)	−0.0275 (5)	0.1136 (3)	0.0887 (14)
H17A	1.3829	−0.0393	0.1571	0.133*
H17B	1.5241	0.0313	0.1237	0.133*
H17C	1.4530	−0.1079	0.0851	0.133*
C18	1.1413 (4)	0.6404 (3)	0.25681 (16)	0.0467 (7)
C19	1.0116 (4)	0.6135 (3)	0.30190 (15)	0.0413 (6)
C20	0.9929 (4)	0.6474 (3)	0.37435 (15)	0.0428 (6)
H20	1.0772	0.7006	0.4051	0.051*
C21	0.8478 (4)	0.6011 (3)	0.39999 (15)	0.0455 (7)
C22	0.7219 (4)	0.5223 (3)	0.35249 (18)	0.0576 (8)
H22	0.6235	0.4931	0.3702	0.069*
C23	0.7373 (5)	0.4859 (4)	0.28023 (18)	0.0608 (9)
H23	0.6527	0.4335	0.2492	0.073*
C24	0.8854 (4)	0.5322 (3)	0.25728 (16)	0.0475 (7)
C25	1.0861 (4)	0.5761 (3)	0.19068 (16)	0.0467 (7)
C26	0.8272 (4)	0.6325 (3)	0.47745 (16)	0.0467 (7)
C27	0.8862 (4)	0.7505 (3)	0.52105 (16)	0.0520 (8)
H27	0.9382	0.8116	0.5015	0.062*
C28	0.8687 (5)	0.7789 (3)	0.59368 (18)	0.0584 (8)
H28	0.9078	0.8584	0.6224	0.070*
C29	0.7931 (5)	0.6879 (4)	0.62205 (17)	0.0578 (9)
C30	0.7355 (5)	0.5696 (4)	0.58056 (19)	0.0605 (9)
H30	0.6859	0.5083	0.6007	0.073*
C31	0.7523 (5)	0.5428 (3)	0.50844 (18)	0.0576 (8)
H31	0.7125	0.4630	0.4802	0.069*
C32	1.1614 (4)	0.5649 (3)	0.12150 (16)	0.0518 (8)
H32A	1.2035	0.6493	0.1188	0.062*
H32B	1.0700	0.5345	0.0841	0.062*
C33	1.3073 (4)	0.4775 (3)	0.10812 (14)	0.0415 (6)

C34	1.2640 (6)	0.8890 (4)	0.3101 (3)	0.0804 (12)
H34A	1.1966	0.9078	0.2715	0.121*
H34B	1.3620	0.9499	0.3241	0.121*
H34C	1.1939	0.8938	0.3493	0.121*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0754 (3)	0.0850 (3)	0.0525 (2)	−0.0104 (2)	0.02318 (18)	−0.00634 (18)
Br2	0.0983 (3)	0.1191 (4)	0.0429 (2)	0.0032 (3)	0.0189 (2)	0.0216 (2)
S1	0.0423 (4)	0.0513 (4)	0.0666 (5)	−0.0002 (3)	0.0061 (4)	0.0262 (4)
S2	0.0398 (4)	0.0817 (6)	0.0665 (5)	0.0022 (4)	0.0152 (4)	0.0164 (5)
O1	0.0474 (12)	0.0433 (11)	0.0421 (11)	0.0041 (9)	0.0105 (9)	0.0083 (8)
O2	0.0580 (14)	0.0611 (14)	0.0626 (14)	0.0147 (11)	0.0258 (11)	0.0244 (11)
O3	0.0770 (18)	0.0798 (18)	0.0624 (15)	0.0411 (15)	0.0278 (13)	0.0375 (13)
O4	0.0582 (14)	0.0560 (13)	0.0403 (11)	0.0047 (11)	0.0111 (10)	0.0031 (9)
O5	0.0593 (14)	0.0645 (14)	0.0569 (13)	0.0217 (11)	0.0290 (11)	0.0306 (11)
O6	0.0748 (18)	0.0715 (16)	0.0590 (15)	0.0333 (14)	0.0339 (13)	0.0346 (13)
C1	0.0353 (14)	0.0411 (15)	0.0443 (15)	0.0077 (11)	0.0068 (12)	0.0170 (12)
C2	0.0332 (14)	0.0406 (15)	0.0422 (14)	0.0043 (11)	0.0034 (11)	0.0148 (12)
C3	0.0388 (15)	0.0400 (15)	0.0401 (14)	0.0029 (12)	0.0010 (12)	0.0117 (12)
C4	0.0396 (15)	0.0446 (16)	0.0399 (14)	0.0094 (12)	0.0057 (12)	0.0139 (12)
C5	0.0409 (16)	0.0488 (17)	0.0508 (17)	0.0038 (13)	0.0128 (13)	0.0162 (14)
C6	0.0452 (17)	0.0413 (16)	0.0529 (17)	−0.0023 (13)	0.0079 (14)	0.0105 (13)
C7	0.0397 (15)	0.0419 (15)	0.0372 (14)	0.0073 (12)	0.0061 (11)	0.0093 (12)
C8	0.0413 (16)	0.0433 (15)	0.0453 (15)	0.0128 (12)	0.0112 (12)	0.0186 (13)
C9	0.0374 (15)	0.0530 (17)	0.0406 (15)	0.0062 (13)	0.0052 (12)	0.0140 (13)
C10	0.070 (2)	0.0508 (18)	0.0448 (17)	0.0076 (16)	0.0078 (15)	0.0150 (14)
C11	0.069 (2)	0.0480 (18)	0.0548 (19)	0.0068 (16)	0.0102 (17)	0.0042 (15)
C12	0.0441 (17)	0.063 (2)	0.0410 (16)	−0.0003 (14)	0.0096 (13)	0.0020 (14)
C13	0.0520 (19)	0.072 (2)	0.0450 (17)	0.0044 (16)	0.0122 (14)	0.0217 (16)
C14	0.0503 (18)	0.0548 (18)	0.0506 (17)	0.0131 (14)	0.0132 (14)	0.0190 (14)
C15	0.0512 (18)	0.0527 (17)	0.0426 (15)	0.0147 (14)	0.0102 (13)	0.0182 (13)
C16	0.0505 (17)	0.0404 (15)	0.0404 (15)	0.0080 (13)	0.0119 (13)	0.0114 (12)
C17	0.057 (2)	0.092 (3)	0.126 (4)	−0.009 (2)	−0.028 (2)	0.056 (3)
C18	0.0409 (16)	0.0550 (18)	0.0450 (16)	0.0101 (13)	0.0128 (13)	0.0100 (13)
C19	0.0365 (15)	0.0447 (15)	0.0432 (15)	0.0091 (12)	0.0116 (12)	0.0084 (12)
C20	0.0400 (15)	0.0469 (16)	0.0399 (15)	0.0054 (12)	0.0070 (12)	0.0065 (12)
C21	0.0444 (17)	0.0496 (17)	0.0429 (16)	0.0065 (13)	0.0110 (13)	0.0097 (13)
C22	0.0489 (19)	0.067 (2)	0.0546 (19)	−0.0065 (16)	0.0157 (15)	0.0094 (16)
C23	0.054 (2)	0.069 (2)	0.0516 (19)	−0.0123 (17)	0.0082 (15)	0.0011 (16)
C24	0.0515 (18)	0.0481 (17)	0.0407 (15)	0.0061 (14)	0.0102 (13)	0.0046 (13)
C25	0.0475 (17)	0.0493 (17)	0.0460 (16)	0.0162 (14)	0.0160 (13)	0.0112 (13)
C26	0.0427 (16)	0.0531 (18)	0.0464 (16)	0.0085 (13)	0.0137 (13)	0.0126 (14)
C27	0.0568 (19)	0.0534 (18)	0.0465 (17)	0.0010 (15)	0.0106 (14)	0.0128 (14)
C28	0.063 (2)	0.063 (2)	0.0476 (18)	0.0027 (17)	0.0095 (16)	0.0091 (16)
C29	0.057 (2)	0.080 (2)	0.0408 (17)	0.0138 (18)	0.0131 (15)	0.0187 (17)
C30	0.064 (2)	0.068 (2)	0.057 (2)	0.0071 (18)	0.0176 (17)	0.0276 (18)

C31	0.063 (2)	0.0557 (19)	0.0552 (19)	0.0024 (16)	0.0165 (16)	0.0135 (15)
C32	0.060 (2)	0.0585 (19)	0.0417 (16)	0.0217 (16)	0.0171 (14)	0.0144 (14)
C33	0.0471 (16)	0.0445 (16)	0.0335 (14)	0.0076 (13)	0.0082 (12)	0.0085 (12)
C34	0.065 (3)	0.069 (3)	0.105 (3)	−0.006 (2)	−0.009 (2)	0.024 (2)

Geometric parameters (Å, °)

Br1—C12	1.904 (3)	C13—H13	0.9300
Br2—C29	1.897 (3)	C14—H14	0.9300
Br2—O6^{i}	3.284 (2)	C15—C16	1.496 (4)
S1—C1	1.752 (3)	C15—H15A	0.9700
S1—C17	1.806 (4)	C15—H15B	0.9700
S2—C18	1.748 (3)	C17—H17A	0.9600
S2—C34	1.804 (4)	C17—H17B	0.9600
O1—C8	1.376 (3)	C17—H17C	0.9600
O1—C7	1.382 (3)	C18—C25	1.342 (4)
O2—C16	1.236 (3)	C18—C19	1.443 (4)
O3—C16	1.279 (4)	C19—C24	1.387 (4)
O3—H35	0.82 (6)	C19—C20	1.393 (4)
O4—C25	1.381 (4)	C20—C21	1.381 (4)
O4—C24	1.381 (3)	C20—H20	0.9300
O5—C33	1.230 (3)	C21—C22	1.399 (5)
O6—C33	1.273 (4)	C21—C26	1.490 (4)
O6—H36	0.73 (5)	C22—C23	1.386 (5)
C1—C8	1.348 (4)	C22—H22	0.9300
C1—C2	1.445 (4)	C23—C24	1.375 (5)
C2—C7	1.382 (4)	C23—H23	0.9300
C2—C3	1.394 (4)	C25—C32	1.488 (4)
C3—C4	1.388 (4)	C26—C31	1.387 (4)
C3—H3	0.9300	C26—C27	1.389 (4)
C4—C5	1.401 (4)	C27—C28	1.395 (4)
C4—C9	1.490 (4)	C27—H27	0.9300
C5—C6	1.384 (4)	C28—C29	1.368 (5)
C5—H5	0.9300	C28—H28	0.9300
C6—C7	1.374 (4)	C29—C30	1.374 (5)
C6—H6	0.9300	C30—C31	1.385 (5)
C8—C15	1.488 (4)	C30—H30	0.9300
C9—C10	1.386 (4)	C31—H31	0.9300
C9—C14	1.388 (4)	C32—C33	1.506 (4)
C10—C11	1.384 (4)	C32—H32A	0.9700
C10—H10	0.9300	C32—H32B	0.9700
C11—C12	1.372 (5)	C34—H34A	0.9600
C11—H11	0.9300	C34—H34B	0.9600
C12—C13	1.371 (5)	C34—H34C	0.9600
C13—C14	1.389 (4)		
C1—S1—C17	99.5 (2)	S1—C17—H17C	109.5
C18—S2—C34	100.8 (2)	H17A—C17—H17C	109.5
C8—O1—C7	105.4 (2)	H17B—C17—H17C	109.5
C16—O3—H35	109 (4)	C25—C18—C19	106.5 (3)

C25—O4—C24	105.5 (2)	C25—C18—S2	126.2 (2)
C33—O6—H36	110 (4)	C19—C18—S2	127.2 (2)
C8—C1—C2	106.2 (2)	C24—C19—C20	119.2 (3)
C8—C1—S1	126.0 (2)	C24—C19—C18	105.6 (3)
C2—C1—S1	127.8 (2)	C20—C19—C18	135.1 (3)
C7—C2—C3	119.3 (2)	C21—C20—C19	119.3 (3)
C7—C2—C1	105.6 (2)	C21—C20—H20	120.4
C3—C2—C1	135.0 (3)	C19—C20—H20	120.4
C4—C3—C2	118.7 (3)	C20—C21—C22	119.2 (3)
C4—C3—H3	120.7	C20—C21—C26	120.4 (3)
C2—C3—H3	120.7	C22—C21—C26	120.4 (3)
C3—C4—C5	119.9 (3)	C23—C22—C21	122.9 (3)
C3—C4—C9	120.0 (3)	C23—C22—H22	118.5
C5—C4—C9	120.1 (3)	C21—C22—H22	118.5
C6—C5—C4	122.1 (3)	C24—C23—C22	115.8 (3)
C6—C5—H5	119.0	C24—C23—H23	122.1
C4—C5—H5	119.0	C22—C23—H23	122.1
C7—C6—C5	116.3 (3)	C23—C24—O4	126.1 (3)
C7—C6—H6	121.8	C23—C24—C19	123.5 (3)
C5—C6—H6	121.8	O4—C24—C19	110.4 (3)
C6—C7—C2	123.7 (3)	C18—C25—O4	112.1 (2)
C6—C7—O1	125.8 (3)	C18—C25—C32	132.4 (3)
C2—C7—O1	110.6 (2)	O4—C25—C32	115.6 (3)
C1—C8—O1	112.1 (2)	C31—C26—C27	118.0 (3)
C1—C8—C15	131.0 (3)	C31—C26—C21	120.6 (3)
O1—C8—C15	116.9 (3)	C27—C26—C21	121.4 (3)
C10—C9—C14	118.1 (3)	C26—C27—C28	121.2 (3)
C10—C9—C4	120.9 (3)	C26—C27—H27	119.4
C14—C9—C4	121.0 (3)	C28—C27—H27	119.4
C11—C10—C9	121.5 (3)	C29—C28—C27	119.0 (3)
C11—C10—H10	119.2	C29—C28—H28	120.5
C9—C10—H10	119.2	C27—C28—H28	120.5
C12—C11—C10	118.8 (3)	C28—C29—C30	121.3 (3)
C12—C11—H11	120.6	C28—C29—Br2	120.2 (3)
C10—C11—H11	120.6	C30—C29—Br2	118.4 (3)
C13—C12—C11	121.4 (3)	C29—C30—C31	119.2 (3)
C13—C12—Br1	119.2 (2)	C29—C30—H30	120.4
C11—C12—Br1	119.4 (3)	C31—C30—H30	120.4
C12—C13—C14	119.2 (3)	C30—C31—C26	121.4 (3)
C12—C13—H13	120.4	C30—C31—H31	119.3
C14—C13—H13	120.4	C26—C31—H31	119.3
C9—C14—C13	120.9 (3)	C25—C32—C33	115.1 (3)
C9—C14—H14	119.6	C25—C32—H32A	108.5
C13—C14—H14	119.6	C33—C32—H32A	108.5
C8—C15—C16	114.9 (2)	C25—C32—H32B	108.5
C8—C15—H15A	108.6	C33—C32—H32B	108.5
C16—C15—H15A	108.6	H32A—C32—H32B	107.5
C8—C15—H15B	108.6	O5—C33—O6	124.0 (3)
C16—C15—H15B	108.6	O5—C33—C32	119.5 (3)

H15A—C15—H15B	107.5	O6—C33—C32	116.4 (3)
O2—C16—O3	124.4 (3)	S2—C34—H34A	109.5
O2—C16—C15	119.7 (3)	S2—C34—H34B	109.5
O3—C16—C15	115.9 (3)	H34A—C34—H34B	109.5
S1—C17—H17A	109.5	S2—C34—H34C	109.5
S1—C17—H17B	109.5	H34A—C34—H34C	109.5
H17A—C17—H17B	109.5	H34B—C34—H34C	109.5
C17—S1—C1—C8	−97.1 (3)	C34—S2—C18—C25	113.1 (3)
C17—S1—C1—C2	81.3 (3)	C34—S2—C18—C19	−71.2 (3)
C8—C1—C2—C7	1.8 (3)	C25—C18—C19—C24	0.1 (3)
S1—C1—C2—C7	−176.9 (2)	S2—C18—C19—C24	−176.3 (2)
C8—C1—C2—C3	−177.0 (3)	C25—C18—C19—C20	178.4 (3)
S1—C1—C2—C3	4.3 (5)	S2—C18—C19—C20	2.0 (5)
C7—C2—C3—C4	1.3 (4)	C24—C19—C20—C21	−1.0 (4)
C1—C2—C3—C4	180.0 (3)	C18—C19—C20—C21	−179.1 (3)
C2—C3—C4—C5	1.3 (4)	C19—C20—C21—C22	−0.7 (4)
C2—C3—C4—C9	−177.6 (2)	C19—C20—C21—C26	178.0 (3)
C3—C4—C5—C6	−2.5 (4)	C20—C21—C22—C23	1.3 (5)
C9—C4—C5—C6	176.4 (3)	C26—C21—C22—C23	−177.4 (3)
C4—C5—C6—C7	1.1 (4)	C21—C22—C23—C24	−0.1 (6)
C5—C6—C7—C2	1.6 (4)	C22—C23—C24—O4	178.6 (3)
C5—C6—C7—O1	−179.0 (3)	C22—C23—C24—C19	−1.8 (5)
C3—C2—C7—C6	−2.8 (4)	C25—O4—C24—C23	178.5 (3)
C1—C2—C7—C6	178.2 (3)	C25—O4—C24—C19	−1.1 (3)
C3—C2—C7—O1	177.7 (2)	C20—C19—C24—C23	2.4 (5)
C1—C2—C7—O1	−1.4 (3)	C18—C19—C24—C23	−179.0 (3)
C8—O1—C7—C6	−179.1 (3)	C20—C19—C24—O4	−178.0 (3)
C8—O1—C7—C2	0.4 (3)	C18—C19—C24—O4	0.6 (3)
C2—C1—C8—O1	−1.7 (3)	C19—C18—C25—O4	−0.8 (3)
S1—C1—C8—O1	177.03 (19)	S2—C18—C25—O4	175.7 (2)
C2—C1—C8—C15	176.2 (3)	C19—C18—C25—C32	−179.9 (3)
S1—C1—C8—C15	−5.1 (5)	S2—C18—C25—C32	−3.4 (5)
C7—O1—C8—C1	0.8 (3)	C24—O4—C25—C18	1.2 (3)
C7—O1—C8—C15	−177.4 (2)	C24—O4—C25—C32	−179.6 (3)
C3—C4—C9—C10	49.0 (4)	C20—C21—C26—C31	−143.1 (3)
C5—C4—C9—C10	−129.9 (3)	C22—C21—C26—C31	35.7 (5)
C3—C4—C9—C14	−131.8 (3)	C20—C21—C26—C27	35.2 (4)
C5—C4—C9—C14	49.3 (4)	C22—C21—C26—C27	−146.0 (3)
C14—C9—C10—C11	−0.3 (5)	C31—C26—C27—C28	−0.8 (5)
C4—C9—C10—C11	178.9 (3)	C21—C26—C27—C28	−179.2 (3)
C9—C10—C11—C12	0.8 (5)	C26—C27—C28—C29	0.5 (5)
C10—C11—C12—C13	−0.4 (5)	C27—C28—C29—C30	0.4 (5)
C10—C11—C12—Br1	−179.9 (3)	C27—C28—C29—Br2	179.5 (3)
C11—C12—C13—C14	−0.5 (5)	C28—C29—C30—C31	−0.9 (6)
Br1—C12—C13—C14	178.9 (2)	Br2—C29—C30—C31	180.0 (3)
C10—C9—C14—C13	−0.7 (5)	C29—C30—C31—C26	0.5 (5)
C4—C9—C14—C13	−179.9 (3)	C27—C26—C31—C30	0.3 (5)
C12—C13—C14—C9	1.1 (5)	C21—C26—C31—C30	178.7 (3)
C1—C8—C15—C16	86.6 (4)	C18—C25—C32—C33	77.1 (4)

O1—C8—C15—C16	−95.7 (3)	O4—C25—C32—C33	−102.0 (3)
C8—C15—C16—O2	−157.5 (3)	C25—C32—C33—O5	−161.6 (3)
C8—C15—C16—O3	24.2 (4)	C25—C32—C33—O6	20.5 (4)

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H35···O5^{ii}	0.82 (6)	1.84 (6)	2.659 (3)	176 (6)
O6—H36···O2^{ii}	0.73 (5)	1.93 (5)	2.655 (3)	172 (5)
C17—H17B···O2^{ii}	0.96	2.60	3.374 (5)	138

Symmetry codes: (ii) −*x*+3, −*y*, −*z*.

Fig. 1

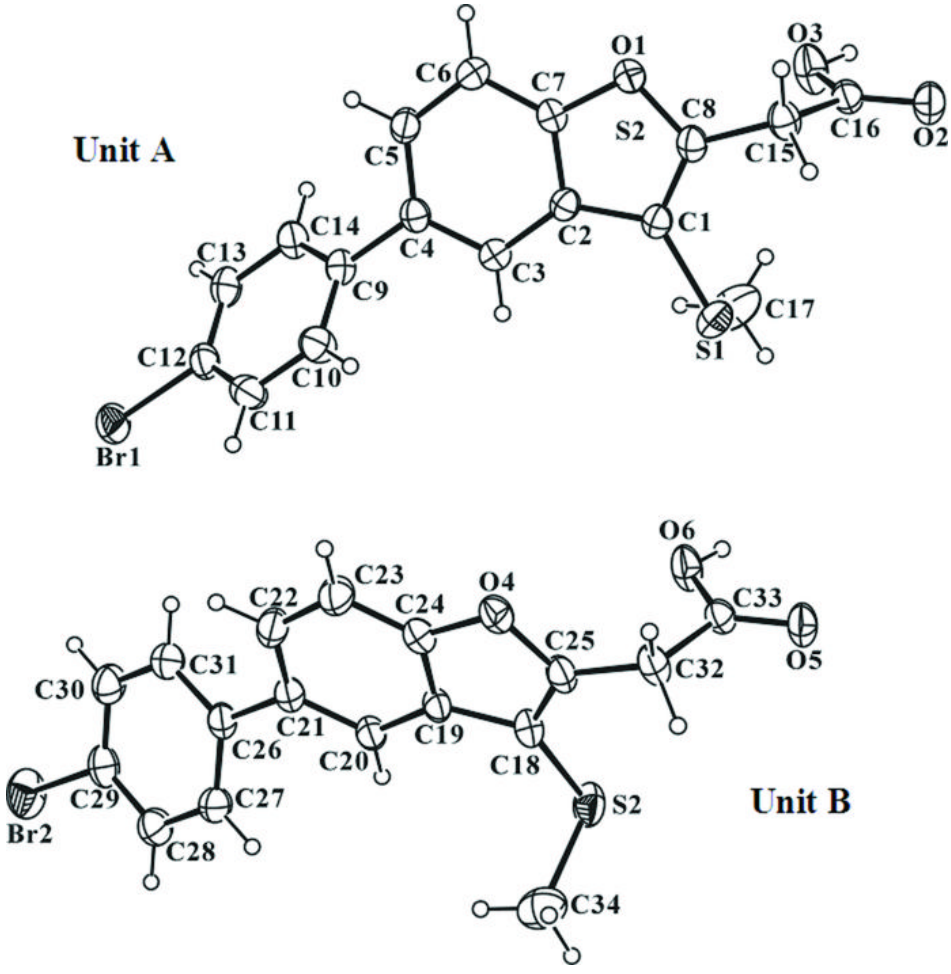
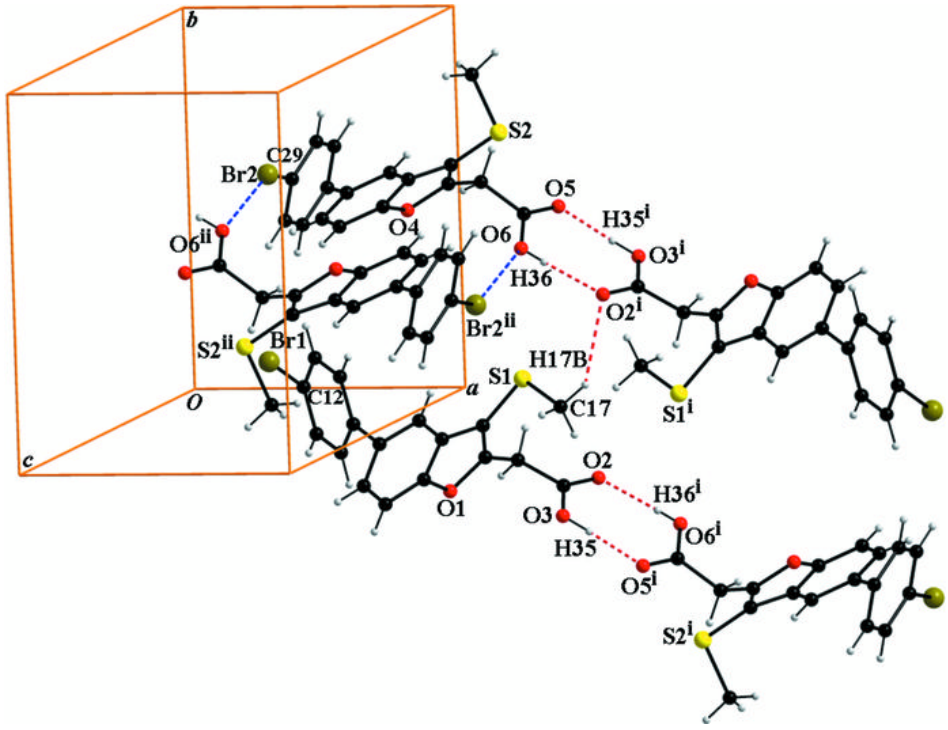

Unit A
O1
O3
C6
C7
C8
S2
C16
O2
C5
C15
C14
C4
C2
C1
C13
C3
C9
C17
S1
C12
C10
C11
Br1
O6
C23
O4
C22
C24
C33
C25
O5
C31
C32
C30
C21
C19
C26
C20
C18
C29
S2
Unit B
C27
Br2
C28
C34

Fig. 2


b
c
O
a
S2
C29
Br2
O5
H35i
O4
O6
O3i
O6ii
H36
O2i
Br2ii
S2ii
Br1
H17B
S1
C12
C17
S1i
O2
H36i
O1
O3
O6i
H35
O5i
S2i