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2-(5,7-Dimethyl-3-methylsulfanyl-1-benzofuran-2-yl)acetic acid

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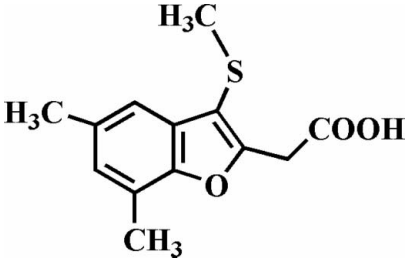
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.003 Å; R factor = 0.047; wR factor = 0.144; data-to-parameter ratio = 14.6.

The title compound, $C_{13}H_{14}O_3S$, was prepared by alkaline hydrolysis of ethyl 2-(5,7-dimethyl-3-methylsulfanyl-1-benzofuran-2-yl)acetate. In the crystal structure, the carboxyl groups are involved in intermolecular O—H···O hydrogen bonds, which link the molecules into centrosymmetric dimers. These dimers are further packed into stacks along the a axis by weak C—H···π interactions.

Related literature

For the crystal structures of similar 2-(3-methylsulfanyl-1-benzofuran-2-yl)acetic acid derivatives, see: Choi *et al.* (2007); Seo *et al.* (2007).



Experimental

Crystal data

$C_{13}H_{14}O_3S$
M_r = 250.30
Triclinic, $P\overline{1}$
a = 4.7225 (9) Å
b = 7.476 (2) Å
c = 17.687 (3) Å
α = 80.91 (3)°
β = 89.86 (3)°
γ = 80.67 (3)°
V = 608.3 (2) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.26 mm^{-1}
T = 293 (2) K
0.40 × 0.40 × 0.20 mm

Data collection

Bruker SMART CCD diffractometer
Absorption correction: none
4707 measured reflections
2344 independent reflections
2156 reflections with $I > 2\sigma(I)$
R_{int} = 0.059

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.144
S = 1.24
2344 reflections
161 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.38 e Å^{-3}
$\Delta\rho_{min}$ = −0.41 e Å^{-3}

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

Cg is the centroid of the C2–C7 ring.

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3O···O2^{i}	0.73 (4)	1.95 (4)	2.680 (3)	177 (4)
C9—H9A···Cg^{ii}	0.96	2.72	3.621 (4)	156

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

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: CV2433).

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Seo, P. J., Choi, H. D., Son, B. W. & Lee, U. (2007). *Acta Cryst.* E**63**, o2048–o2049.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

supporting information

Acta Cryst. (2008). E**64**, o1598 [doi:10.1107/S1600536808022988]

2-(5,7-Dimethyl-3-methylsulfanyl-1-benzofuran-2-yl)acetic acid

Hong Dae Choi, Pil Ja Seo, Byeng Wha Son and Uk Lee

S1. Comment

As a part of our ongoing studies on the synthesis and structures of 2-(3-methylsulfanyl-1-benzofuran-2-yl)acetic acid derivatives, we have described 2-(5-ethyl-3-methylsulfanyl-1-benzofuran-2-yl)acetic acid (Seo *et al.*, 2007) and 2-(3-methylsulfanyl-5-phenyl-1-benzofuran-2-yl)acetic acid (Choi *et al.*, 2007). Here we report the crystal structure of the title compound, (I) (Fig. 1).

In (I), the benzofuran unit is essentially planar, with a mean deviation of 0.004 (2) Å from the least-squares plane defined by the nine constituent atoms. The crystal packing (Fig. 2) is stabilized by classical inversion-related O—H···O hydrogen bonds (Table 1) and C—H···π interactions between a methyl H atom and the ring C2–C7 (Cg is its centroid) of a neighbouring molecule (Table 1).

S2. Experimental

Ethyl 2-(5,7-dimethyl-3-methylsulfanyl-1-benzofuran-2-yl)acetate (417 mg, 1.50 mmol) was added to a solution of potassium hydroxide (505 mg, 9.0 mmol) in water (25 ml) and methanol (25 ml), and the mixture was refluxed for 5 h, then cooled. Water was added, and the solution was extracted with dichloromethane. 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 82%, m.p. 420–421 K; R_f = 0.66 (ethyl acetate)]. Single crystals suitable for X-ray diffraction were prepared by evaporation of a solution of the title compound in benzene at room temperature. Spectroscopic analysis: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.32 (s, 3H), 2.43 (s, 3H), 2.45 (s, 3H), 4.03 (s, 2H), 6.93 (s, 1H), 7.25 (s, 1H), 10.10 (s, 1H); EI—MS 250 [M^+].

S3. Refinement

Atom H3O of the hydroxy group was found in a difference Fourier map and refined isotropically. The other H atoms were positioned geometrically and refined using a riding model, with C—H = 0.95 Å for aromatic H atoms, 0.97 Å for methylene H atoms and 0.96 Å for methyl 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.

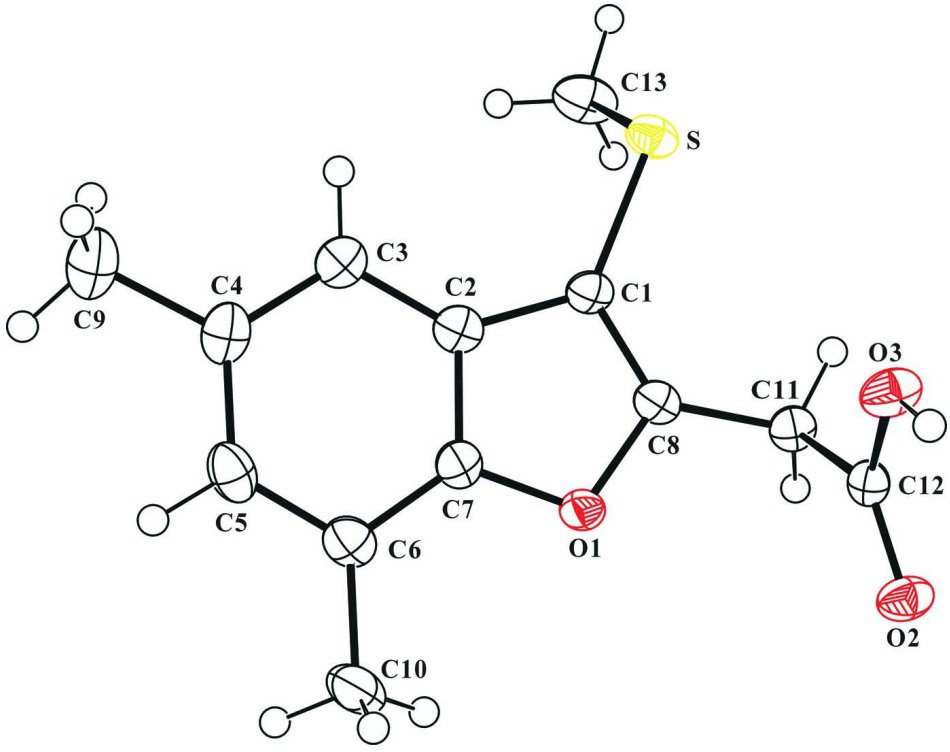

Figure 1

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

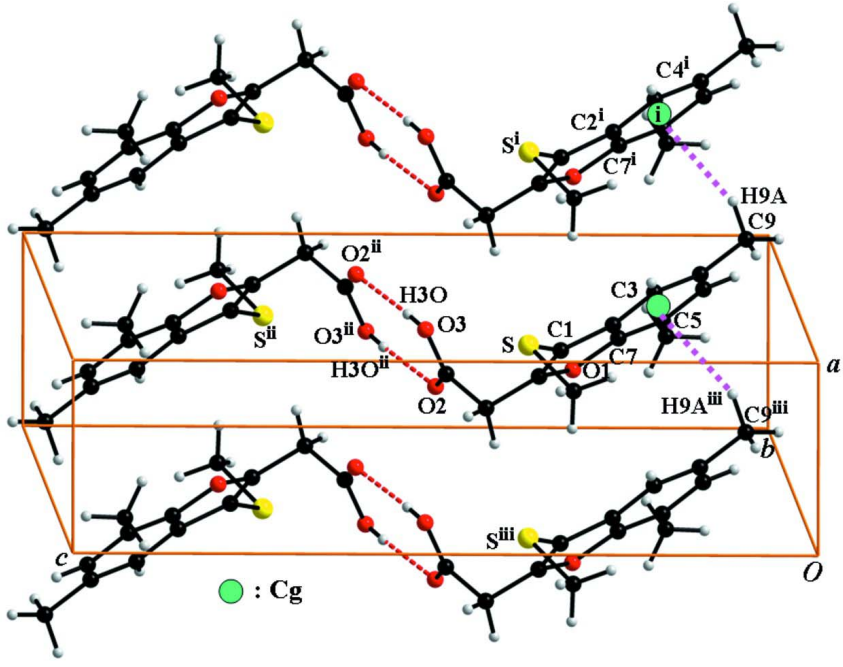

Figure 2

A portion of the crystal packing showing C—H···π interaction and hydrogen bonds (dotted lines). *Cg* denotes the C2–C7 ring centroid [symmetry codes: (i) $x + 1, y, z$; (ii) $-x + 1, -y + 2, -z + 1$; (iii) $x - 1, y, z$].

2-(5,7-Dimethyl-3-methylsulfanyl-1-benzofuran-2-yl)acetic acid

Crystal data

$C_{13}H_{14}O_3S$
$M_r = 250.30$
Triclinic, $P\overline{1}$
Hall symbol: -P_1
$a = 4.7225\ (9)$ Å
$b = 7.476\ (2)$ Å
$c = 17.687\ (3)$ Å
$\alpha = 80.91\ (3)°$
$\beta = 89.86\ (3)°$
$\gamma = 80.67\ (3)°$
$V = 608.3\ (2)$ Å^3
$Z = 2$
$F(000) = 264$
$D_x = 1.367$ Mg m^{-3}
Melting point = 420–421 K
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3835 reflections
$\theta = 2.3–28.3°$
$\mu = 0.26$ mm^{-1}
$T = 293$ K
Block, colourless
0.40 × 0.40 × 0.20 mm

Data collection

Bruker SMART CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 10.0 pixels mm^{-1}
φ and ω scans
4707 measured reflections
2344 independent reflections
2156 reflections with $I > 2\sigma(I)$
$R_{int} = 0.059$
$\theta_{max} = 26.0°$, $\theta_{min} = 1.2°$
$h = -5\rightarrow5$
$k = -9\rightarrow9$
$l = -21\rightarrow21$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.144$
$S = 1.24$
2344 reflections
161 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.063P)^2 + 0.3562P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.38$ e Å^{-3}
$\Delta\rho_{min} = -0.41$ e Å^{-3}

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 $F^2 > \sigma(F^2)$ 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	0.85977 (13)	0.34264 (8)	0.36615 (3)	0.0254 (2)
O1	0.4166 (3)	0.8236 (2)	0.27417 (9)	0.0223 (4)
O2	0.2357 (4)	0.9616 (2)	0.44893 (10)	0.0272 (4)

O3	0.6544 (4)	0.7728 (2)	0.47532 (11)	0.0282 (4)
H3O	0.685 (8)	0.848 (5)	0.494 (2)	0.049 (11)*
C1	0.6982 (5)	0.5473 (3)	0.30908 (14)	0.0214 (5)
C2	0.7803 (5)	0.6242 (3)	0.23378 (14)	0.0232 (5)
C3	0.9867 (5)	0.5690 (3)	0.18203 (15)	0.0268 (5)
H3	1.1098	0.4574	0.1936	0.032*
C4	1.0055 (6)	0.6834 (4)	0.11284 (15)	0.0293 (6)
C5	0.8179 (6)	0.8526 (3)	0.09713 (15)	0.0306 (6)
H5	0.8332	0.9275	0.0505	0.037*
C6	0.6115 (6)	0.9133 (3)	0.14758 (15)	0.0279 (5)
C7	0.6010 (5)	0.7931 (3)	0.21521 (14)	0.0231 (5)
C8	0.4821 (5)	0.6706 (3)	0.32972 (13)	0.0211 (5)
C9	1.2248 (6)	0.6283 (4)	0.05502 (17)	0.0400 (7)
H9A	1.4113	0.6436	0.0718	0.060*
H9B	1.1762	0.7043	0.0063	0.060*
H9C	1.2265	0.5021	0.0502	0.060*
C10	0.4134 (6)	1.0944 (3)	0.13076 (17)	0.0359 (6)
H10A	0.2325	1.0833	0.1544	0.054*
H10B	0.3842	1.1291	0.0764	0.054*
H10C	0.4972	1.1864	0.1508	0.054*
C11	0.3130 (5)	0.6760 (3)	0.40038 (13)	0.0225 (5)
H11A	0.3482	0.5562	0.4324	0.027*
H11B	0.1099	0.7050	0.3869	0.027*
C12	0.3944 (5)	0.8187 (3)	0.44444 (13)	0.0195 (5)
C13	0.7336 (6)	0.1752 (3)	0.31692 (18)	0.0360 (6)
H13A	0.5277	0.1920	0.3176	0.054*
H13B	0.8110	0.0538	0.3421	0.054*
H13C	0.7950	0.1908	0.2649	0.054*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S	0.0300 (3)	0.0185 (3)	0.0271 (3)	−0.0028 (2)	−0.0065 (2)	−0.0025 (2)
O1	0.0275 (8)	0.0163 (7)	0.0230 (9)	−0.0025 (6)	0.0001 (6)	−0.0039 (6)
O2	0.0275 (9)	0.0214 (8)	0.0334 (10)	−0.0003 (7)	−0.0053 (7)	−0.0105 (7)
O3	0.0251 (9)	0.0248 (9)	0.0370 (10)	−0.0017 (7)	−0.0069 (7)	−0.0140 (8)
C1	0.0254 (11)	0.0162 (10)	0.0241 (12)	−0.0044 (8)	−0.0027 (9)	−0.0063 (9)
C2	0.0256 (12)	0.0200 (11)	0.0263 (12)	−0.0079 (9)	−0.0025 (9)	−0.0066 (9)
C3	0.0267 (12)	0.0261 (12)	0.0297 (13)	−0.0068 (9)	0.0006 (10)	−0.0084 (10)
C4	0.0334 (13)	0.0314 (13)	0.0289 (13)	−0.0150 (10)	0.0057 (10)	−0.0125 (10)
C5	0.0418 (15)	0.0292 (13)	0.0235 (13)	−0.0155 (11)	0.0006 (10)	−0.0024 (10)
C6	0.0366 (13)	0.0209 (11)	0.0281 (13)	−0.0092 (10)	−0.0021 (10)	−0.0051 (10)
C7	0.0280 (12)	0.0209 (11)	0.0227 (12)	−0.0074 (9)	−0.0006 (9)	−0.0066 (9)
C8	0.0256 (11)	0.0170 (10)	0.0223 (11)	−0.0066 (8)	−0.0045 (9)	−0.0045 (9)
C9	0.0449 (16)	0.0437 (16)	0.0368 (15)	−0.0173 (13)	0.0140 (13)	−0.0125 (13)
C10	0.0480 (16)	0.0247 (13)	0.0318 (14)	−0.0035 (11)	−0.0049 (12)	0.0031 (11)
C11	0.0252 (11)	0.0191 (10)	0.0253 (12)	−0.0074 (9)	0.0000 (9)	−0.0059 (9)
C12	0.0218 (11)	0.0188 (10)	0.0193 (11)	−0.0071 (8)	0.0025 (8)	−0.0035 (8)

C13	0.0439 (15)	0.0200 (11)	0.0452 (16)	−0.0068 (11)	−0.0132 (12)	−0.0066 (11)

Geometric parameters (Å, º)

S—C1	1.755 (2)	C5—H5	0.9300
S—C13	1.808 (3)	C6—C7	1.384 (4)
O1—C8	1.379 (3)	C6—C10	1.503 (4)
O1—C7	1.380 (3)	C8—C11	1.484 (3)
O2—C12	1.215 (3)	C9—H9A	0.9600
O3—C12	1.316 (3)	C9—H9B	0.9600
O3—H3O	0.73 (4)	C9—H9C	0.9600
C1—C8	1.351 (3)	C10—H10A	0.9600
C1—C2	1.443 (3)	C10—H10B	0.9600
C2—C7	1.393 (3)	C10—H10C	0.9600
C2—C3	1.394 (3)	C11—C12	1.514 (3)
C3—C4	1.389 (4)	C11—H11A	0.9700
C3—H3	0.9300	C11—H11B	0.9700
C4—C5	1.410 (4)	C13—H13A	0.9600
C4—C9	1.509 (4)	C13—H13B	0.9600
C5—C6	1.390 (4)	C13—H13C	0.9600
C1—S—C13	100.58 (12)	C4—C9—H9A	109.5
C8—O1—C7	105.62 (18)	C4—C9—H9B	109.5
C12—O3—H3O	109 (3)	H9A—C9—H9B	109.5
C8—C1—C2	106.3 (2)	C4—C9—H9C	109.5
C8—C1—S	126.10 (19)	H9A—C9—H9C	109.5
C2—C1—S	127.50 (18)	H9B—C9—H9C	109.5
C7—C2—C3	119.3 (2)	C6—C10—H10A	109.5
C7—C2—C1	105.7 (2)	C6—C10—H10B	109.5
C3—C2—C1	135.1 (2)	H10A—C10—H10B	109.5
C4—C3—C2	118.9 (2)	C6—C10—H10C	109.5
C4—C3—H3	120.6	H10A—C10—H10C	109.5
C2—C3—H3	120.6	H10B—C10—H10C	109.5
C3—C4—C5	119.3 (2)	C8—C11—C12	110.56 (18)
C3—C4—C9	120.6 (3)	C8—C11—H11A	109.5
C5—C4—C9	120.1 (2)	C12—C11—H11A	109.5
C6—C5—C4	123.5 (2)	C8—C11—H11B	109.5
C6—C5—H5	118.3	C12—C11—H11B	109.5
C4—C5—H5	118.3	H11A—C11—H11B	108.1
C7—C6—C5	114.6 (2)	O2—C12—O3	124.3 (2)
C7—C6—C10	122.1 (2)	O2—C12—C11	122.7 (2)
C5—C6—C10	123.3 (2)	O3—C12—C11	112.94 (19)
O1—C7—C6	125.3 (2)	S—C13—H13A	109.5
O1—C7—C2	110.3 (2)	S—C13—H13B	109.5
C6—C7—C2	124.4 (2)	H13A—C13—H13B	109.5
C1—C8—O1	112.1 (2)	S—C13—H13C	109.5
C1—C8—C11	132.8 (2)	H13A—C13—H13C	109.5
O1—C8—C11	115.00 (19)	H13B—C13—H13C	109.5

C13—S—C1—C8	110.5 (2)	C10—C6—C7—O1	−0.8 (4)
C13—S—C1—C2	−74.3 (2)	C5—C6—C7—C2	0.5 (3)
C8—C1—C2—C7	0.2 (2)	C10—C6—C7—C2	−179.7 (2)
S—C1—C2—C7	−175.77 (17)	C3—C2—C7—O1	−178.87 (19)
C8—C1—C2—C3	179.0 (2)	C1—C2—C7—O1	0.2 (2)
S—C1—C2—C3	3.0 (4)	C3—C2—C7—C6	0.1 (3)
C7—C2—C3—C4	−0.7 (3)	C1—C2—C7—C6	179.1 (2)
C1—C2—C3—C4	−179.4 (2)	C2—C1—C8—O1	−0.5 (2)
C2—C3—C4—C5	0.6 (3)	S—C1—C8—O1	175.57 (15)
C2—C3—C4—C9	−179.7 (2)	C2—C1—C8—C11	−177.8 (2)
C3—C4—C5—C6	0.0 (4)	S—C1—C8—C11	−1.8 (4)
C9—C4—C5—C6	−179.6 (2)	C7—O1—C8—C1	0.5 (2)
C4—C5—C6—C7	−0.6 (4)	C7—O1—C8—C11	178.39 (17)
C4—C5—C6—C10	179.6 (2)	C1—C8—C11—C12	108.4 (3)
C8—O1—C7—C6	−179.4 (2)	O1—C8—C11—C12	−68.9 (2)
C8—O1—C7—C2	−0.4 (2)	C8—C11—C12—O2	109.1 (2)
C5—C6—C7—O1	179.4 (2)	C8—C11—C12—O3	−69.6 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3*O*···O2^{i}	0.73 (4)	1.95 (4)	2.680 (3)	177 (4)
C9—H9*A*···*Cg*^{ii}	0.96	2.72	3.621 (4)	156

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