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2-(3-Ethylsulfanyl-5-fluoro-1-benzofuran-2-yl)acetic acid

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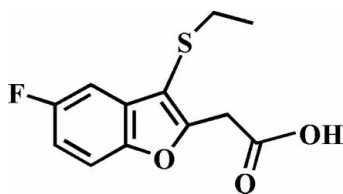
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Key indicators: single-crystal X-ray study; $T = 173$ K; mean $\sigma(\text{C}-\text{C}) = 0.005$ Å; R factor = 0.047; wR factor = 0.113; data-to-parameter ratio = 16.0.

The title compound, $\text{C}_{12}\text{H}_{11}\text{FO}_3\text{S}$, was prepared by alkaline hydrolysis of ethyl 2-(3-ethylsulfanyl-5-fluoro-1-benzofuran-2-yl) acetate. In the crystal structure, the carboxyl groups are involved in intermolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds, which link the molecules into centrosymmetric dimers. These dimers are further packed into stacks along the b axis by aromatic $\pi-\pi$ interactions between the furan ring and the benzene ring of neighbouring benzofuran ring systems [centroid-centroid distance = 3.684 (5) Å].

Related literature

For the crystal structures of similar 2-(5-halo-1-benzofuran-2-yl) acetic acid derivatives, see: Choi *et al.* (2009*a,b*). For the pharmacological properties of benzofuran compounds, see: Howlett *et al.* (1999); Twyman & Allsop (1999).



Experimental

Crystal data

$\text{C}_{12}\text{H}_{11}\text{FO}_3\text{S}$
 $M_r = 254.27$
 Monoclinic, $P2_1/n$
 $a = 10.6009$ (9) Å
 $b = 8.3319$ (7) Å
 $c = 13.395$ (1) Å
 $\beta = 96.138$ (1)°

$V = 1176.34$ (17) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.28$ mm⁻¹
 $T = 173$ K
 $0.25 \times 0.20 \times 0.16$ mm

Data collection

Bruker SMART CCD diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 2000)
 $T_{\min} = 0.931$, $T_{\max} = 0.958$

9646 measured reflections
 2543 independent reflections
 1541 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.072$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.047$
 $wR(F^2) = 0.113$
 $S = 1.16$
 2543 reflections
 159 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.28$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.33$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O2}-\text{H2}\cdots\text{O3}^i$	0.85 (5)	1.81 (5)	2.654 (3)	177 (5)

Symmetry code: (i) $-x + 2, -y, -z + 1$.

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: ZQ2007).

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supporting information

Acta Cryst. (2009). E65, o2482 [doi:10.1107/S160053680903671X]

2-(3-Ethylsulfanyl-5-fluoro-1-benzofuran-2-yl)acetic acid

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

S1. Comment

Molecules involving benzofuran moiety have attracted considerable interest in the view of their pharmacological properties (Howlett *et al.*, 1999; Twyman & Allsop, 1999). As a part of our ongoing studies on the synthesis and structures of 2-(5-halo-1-benzofuran-2-yl) acetic acid analogues, the crystal structures of 2-(5-bromo-3-methylsulfanyl-1-benzofuran-2-yl) acetic acid (Choi *et al.*, 2009a) and 2-(5-fluoro-3-methylsulfanyl-1-benzofuran-2-yl) acetic acid (Choi *et al.*, 2009b) have been described in the literature. Here we report the crystal structure of the title compound (Fig. 1).

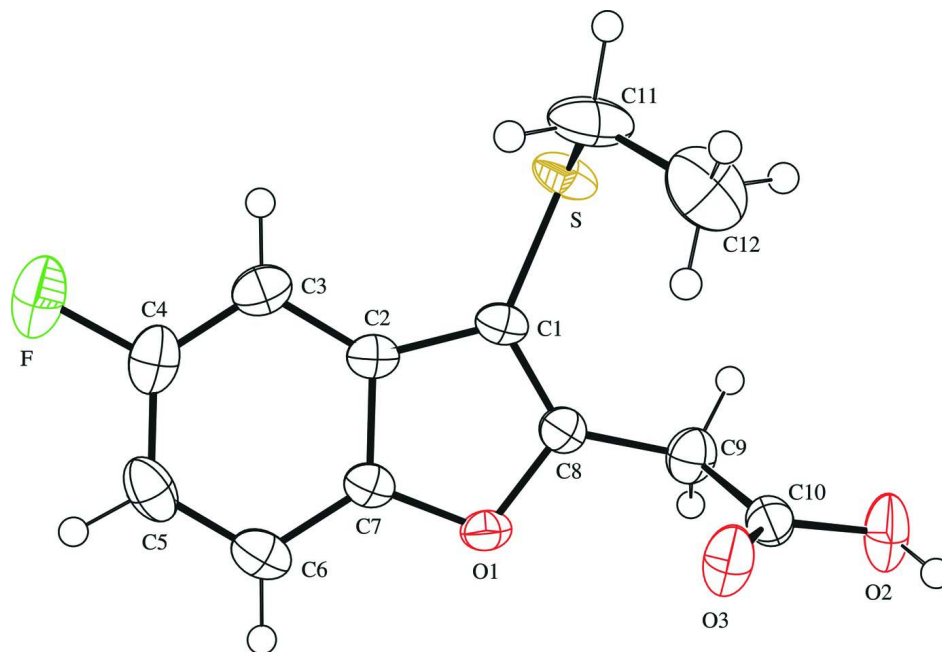
The benzofuran unit is essentially planar, with a mean deviation of 0.005 (2) Å from the least-squares plane defined by the nine constituent atoms. In the crystal structure, the carboxyl groups are involved in intermolecular O—H...O hydrogen bonds (Table 1 and Fig. 2), which link the molecules into centrosymmetric dimers. These dimers are further packed into stacks along the *b* axis by aromatic π ... π interactions between the furan ring and the benzene ring of adjacent benzofuran ring systems. The Cg1...Cg2ⁱⁱ distance is 3.684 (5) Å (Fig. 2; Cg1 and Cg2 is the centroids of the C1/C2/C7/O1/C8 furan ring and the C2–C7 benzene ring, respectively).

S2. Experimental

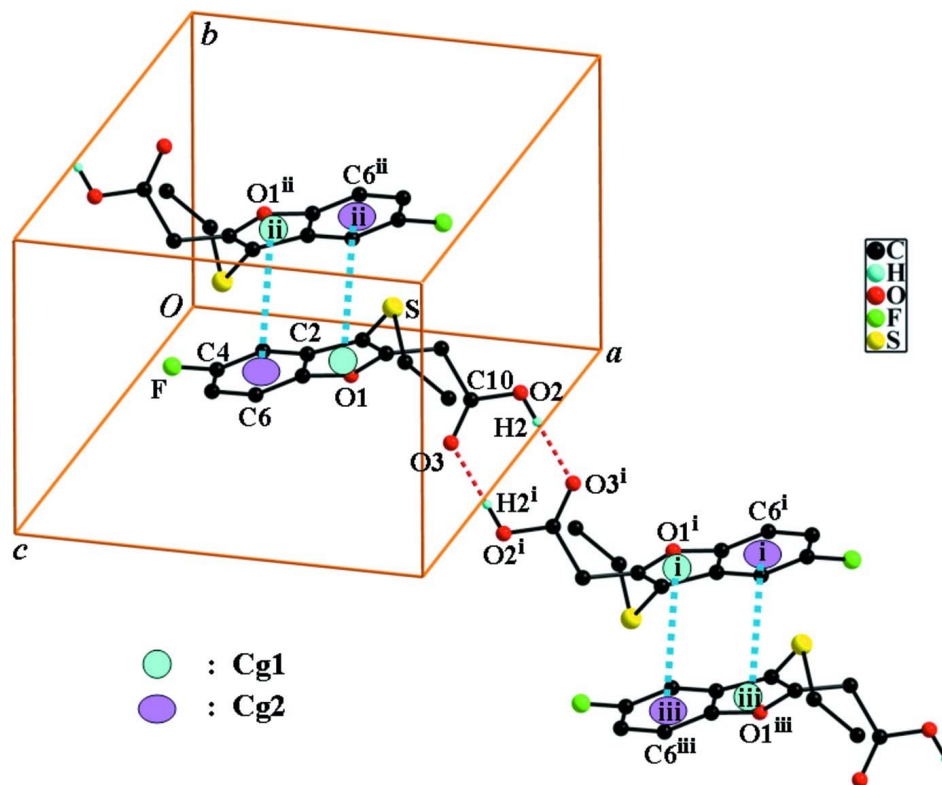
Ethyl 2-(3-ethylsulfanyl-5-fluoro-1-benzofuran-2-yl) acetate (254 mg, 1.0 mmol) was added to a solution of potassium hydroxide (348 mg, 6.0 mmol) in water (20 ml) and methanol (20 ml), and the mixture was refluxed for 6h, then cooled. Water was added, and the solution was extracted with dichloromethane. 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 87%, m.p. 401–402 K; R_f = 0.69 (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: EI-MS 254 [M⁺].

S3. Refinement

Atom H2 of the hydroxy group was found in a difference Fourier map and refined freely. The other H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93 Å for the aryl, 0.97 Å for the methylene, and 0.96 Å for the methyl H atoms with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for the aryl and methylene H atoms, and $1.5U_{\text{eq}}(\text{C})$ for the methyl H atoms.


Figure 1

The molecular structure of the title compound with the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are presented as small cycles of arbitrary radius.


Figure 2

O—H...O and π ... π interactions (dotted lines) in the title compound. Cg denotes the ring centroids. [Symmetry codes: (i) $-x + 2, -y, -z + 1$; (ii) $-x + 1, -y + 1, -z + 1$; (iii) $x + 1, y - 1, z$.]

2-(3-Ethylsulfanyl-5-fluoro-1-benzofuran-2-yl)acetic acid

Crystal data

C₁₂H₁₁FO₃S $M_r = 254.27$ Monoclinic, $P2_1/n$

Hall symbol: -P 2yn

 $a = 10.6009$ (9) Å $b = 8.3319$ (7) Å $c = 13.395$ (1) Å $\beta = 96.138$ (1)° $V = 1176.34$ (17) Å³ $Z = 4$ $F(000) = 528$ $D_x = 1.436$ Mg m⁻³Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 2478 reflections

 $\theta = 2.3$ – 27.4 ° $\mu = 0.28$ mm⁻¹ $T = 173$ K

Block, colorless

 $0.25 \times 0.20 \times 0.16$ 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

Absorption correction: multi-scan

(SADABS; Sheldrick, 2000)

 $T_{\min} = 0.931$, $T_{\max} = 0.958$

9646 measured reflections

2543 independent reflections

1541 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.072$ $\theta_{\max} = 27.0$ °, $\theta_{\min} = 2.3$ ° $h = -13$ → 13 $k = -10$ → 10 $l = -17$ → 17

Refinement

Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.047$ $wR(F^2) = 0.113$ $S = 1.16$

2543 reflections

159 parameters

0 restraints

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: difference Fourier map

H atoms treated by a mixture of independent and constrained refinement

 $w = 1/[\sigma^2(F_o^2) + (0.P)^2 + 1.581P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 0.28$ e Å⁻³ $\Delta\rho_{\min} = -0.33$ e Å⁻³

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
S	0.76702 (8)	0.59687 (10)	0.63171 (7)	0.0380 (2)
F	0.2776 (2)	0.4175 (3)	0.75176 (16)	0.0561 (6)
O1	0.5990 (2)	0.2294 (2)	0.48565 (15)	0.0279 (5)
O2	0.9881 (2)	0.1796 (3)	0.4247 (2)	0.0459 (7)

H2	1.034 (5)	0.097 (6)	0.437 (4)	0.11 (2)*
O3	0.8642 (2)	0.0735 (3)	0.53184 (18)	0.0403 (6)
C1	0.6717 (3)	0.4365 (3)	0.5848 (2)	0.0252 (7)
C2	0.5483 (3)	0.3918 (3)	0.6122 (2)	0.0247 (7)
C3	0.4702 (3)	0.4454 (4)	0.6824 (2)	0.0327 (8)
H3	0.4934	0.5304	0.7255	0.039*
C4	0.3580 (3)	0.3667 (4)	0.6845 (3)	0.0374 (9)
C5	0.3184 (3)	0.2392 (4)	0.6226 (3)	0.0387 (9)
H5	0.2404	0.1907	0.6280	0.046*
C6	0.3949 (3)	0.1847 (4)	0.5531 (2)	0.0334 (8)
H6	0.3711	0.0992	0.5107	0.040*
C7	0.5087 (3)	0.2634 (3)	0.5496 (2)	0.0251 (7)
C8	0.6966 (3)	0.3365 (4)	0.5101 (2)	0.0263 (7)
C9	0.8058 (3)	0.3237 (4)	0.4507 (2)	0.0344 (8)
H9A	0.8578	0.4190	0.4625	0.041*
H9B	0.7742	0.3219	0.3801	0.041*
C10	0.8882 (3)	0.1785 (4)	0.4735 (2)	0.0290 (7)
C11	0.8469 (4)	0.5118 (4)	0.7462 (3)	0.0505 (11)
H11A	0.8860	0.5981	0.7871	0.061*
H11B	0.7840	0.4618	0.7836	0.061*
C12	0.9460 (4)	0.3907 (5)	0.7297 (3)	0.0584 (12)
H12A	0.9069	0.2989	0.6959	0.088*
H12B	0.9889	0.3583	0.7932	0.088*
H12C	1.0061	0.4369	0.6892	0.088*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S	0.0381 (5)	0.0222 (4)	0.0500 (5)	-0.0057 (4)	-0.0124 (4)	0.0003 (4)
F	0.0489 (13)	0.0634 (15)	0.0605 (14)	0.0130 (12)	0.0265 (11)	0.0092 (12)
O1	0.0296 (12)	0.0246 (11)	0.0286 (12)	0.0014 (10)	-0.0018 (10)	-0.0065 (9)
O2	0.0306 (14)	0.0502 (17)	0.0602 (17)	0.0095 (13)	0.0200 (13)	0.0200 (14)
O3	0.0360 (14)	0.0379 (14)	0.0499 (15)	0.0090 (11)	0.0177 (12)	0.0116 (12)
C1	0.0288 (17)	0.0182 (15)	0.0268 (16)	0.0005 (13)	-0.0051 (13)	0.0020 (12)
C2	0.0282 (16)	0.0197 (15)	0.0245 (16)	0.0045 (13)	-0.0046 (13)	0.0024 (13)
C3	0.041 (2)	0.0254 (17)	0.0309 (18)	0.0074 (15)	0.0003 (16)	0.0013 (14)
C4	0.036 (2)	0.039 (2)	0.040 (2)	0.0126 (16)	0.0109 (17)	0.0143 (16)
C5	0.0277 (18)	0.0320 (19)	0.056 (2)	-0.0019 (15)	0.0017 (17)	0.0157 (17)
C6	0.0317 (19)	0.0238 (16)	0.042 (2)	0.0001 (15)	-0.0079 (16)	0.0053 (15)
C7	0.0270 (17)	0.0192 (15)	0.0278 (17)	0.0021 (13)	-0.0029 (14)	0.0036 (13)
C8	0.0256 (17)	0.0233 (15)	0.0294 (17)	0.0018 (14)	-0.0003 (14)	0.0020 (13)
C9	0.0333 (19)	0.0324 (18)	0.0375 (19)	0.0064 (15)	0.0047 (16)	0.0048 (15)
C10	0.0265 (18)	0.0307 (17)	0.0298 (18)	-0.0012 (15)	0.0032 (14)	-0.0001 (14)
C11	0.062 (3)	0.042 (2)	0.042 (2)	-0.002 (2)	-0.0234 (19)	-0.0088 (18)
C12	0.051 (2)	0.059 (3)	0.060 (3)	0.002 (2)	-0.017 (2)	0.020 (2)

Geometric parameters (Å, °)

S—C1	1.751 (3)	C5—C6	1.376 (5)
S—C11	1.815 (4)	C5—H5	0.9300
F—C4	1.371 (4)	C6—C7	1.379 (4)
O1—C8	1.379 (4)	C6—H6	0.9300
O1—C7	1.380 (4)	C8—C9	1.477 (4)
O2—C10	1.303 (4)	C9—C10	1.504 (4)
O2—H2	0.85 (5)	C9—H9A	0.9700
O3—C10	1.217 (4)	C9—H9B	0.9700
C1—C8	1.349 (4)	C11—C12	1.491 (5)
C1—C2	1.445 (4)	C11—H11A	0.9700
C2—C3	1.391 (4)	C11—H11B	0.9700
C2—C7	1.395 (4)	C12—H12A	0.9600
C3—C4	1.362 (5)	C12—H12B	0.9600
C3—H3	0.9300	C12—H12C	0.9600
C4—C5	1.385 (5)		
C1—S—C11	101.79 (15)	C1—C8—O1	112.0 (3)
C8—O1—C7	105.8 (2)	C1—C8—C9	132.1 (3)
C10—O2—H2	112 (4)	O1—C8—C9	115.9 (3)
C8—C1—C2	106.5 (3)	C8—C9—C10	114.9 (3)
C8—C1—S	125.9 (3)	C8—C9—H9A	108.6
C2—C1—S	127.5 (2)	C10—C9—H9A	108.6
C3—C2—C7	119.4 (3)	C8—C9—H9B	108.6
C3—C2—C1	135.2 (3)	C10—C9—H9B	108.6
C7—C2—C1	105.5 (3)	H9A—C9—H9B	107.5
C4—C3—C2	116.3 (3)	O3—C10—O2	124.3 (3)
C4—C3—H3	121.8	O3—C10—C9	123.5 (3)
C2—C3—H3	121.8	O2—C10—C9	112.2 (3)
C3—C4—F	118.1 (3)	C12—C11—S	114.3 (3)
C3—C4—C5	124.5 (3)	C12—C11—H11A	108.7
F—C4—C5	117.4 (3)	S—C11—H11A	108.7
C6—C5—C4	119.7 (3)	C12—C11—H11B	108.7
C6—C5—H5	120.2	S—C11—H11B	108.7
C4—C5—H5	120.2	H11A—C11—H11B	107.6
C5—C6—C7	116.6 (3)	C11—C12—H12A	109.5
C5—C6—H6	121.7	C11—C12—H12B	109.5
C7—C6—H6	121.7	H12A—C12—H12B	109.5
C6—C7—O1	126.2 (3)	C11—C12—H12C	109.5
C6—C7—C2	123.5 (3)	H12A—C12—H12C	109.5
O1—C7—C2	110.3 (3)	H12B—C12—H12C	109.5
C11—S—C1—C8	-101.3 (3)	C8—O1—C7—C2	1.0 (3)
C11—S—C1—C2	83.6 (3)	C3—C2—C7—C6	-0.1 (4)
C8—C1—C2—C3	179.5 (3)	C1—C2—C7—C6	179.3 (3)
S—C1—C2—C3	-4.6 (5)	C3—C2—C7—O1	179.8 (3)
C8—C1—C2—C7	0.4 (3)	C1—C2—C7—O1	-0.8 (3)

S—C1—C2—C7	176.2 (2)	C2—C1—C8—O1	0.2 (3)
C7—C2—C3—C4	-0.2 (4)	S—C1—C8—O1	-175.7 (2)
C1—C2—C3—C4	-179.3 (3)	C2—C1—C8—C9	179.1 (3)
C2—C3—C4—F	-179.1 (3)	S—C1—C8—C9	3.2 (5)
C2—C3—C4—C5	0.2 (5)	C7—O1—C8—C1	-0.7 (3)
C3—C4—C5—C6	0.0 (5)	C7—O1—C8—C9	-179.8 (2)
F—C4—C5—C6	179.3 (3)	C1—C8—C9—C10	109.0 (4)
C4—C5—C6—C7	-0.2 (5)	O1—C8—C9—C10	-72.1 (4)
C5—C6—C7—O1	-179.6 (3)	C8—C9—C10—O3	4.1 (5)
C5—C6—C7—C2	0.3 (4)	C8—C9—C10—O2	-175.1 (3)
C8—O1—C7—C6	-179.1 (3)	C1—S—C11—C12	72.7 (3)

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
O2—H2...O3 ⁱ	0.85 (5)	1.81 (5)	2.654 (3)	177 (5)

Symmetry code: (i) $-x+2, -y, -z+1$.