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2-(5-Isopropyl-3-methylsulfanyl-1-benzofuran-2-yl)acetic acid

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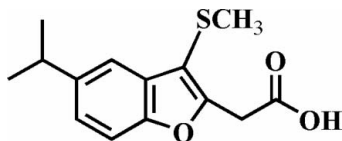
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Key indicators: single-crystal X-ray study; $T = 173$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.052; wR factor = 0.139; data-to-parameter ratio = 14.1.

There are two molecules in the asymmetric unit of the title compound, $\text{C}_{14}\text{H}_{16}\text{O}_3\text{S}$. 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 a axis by aromatic $\pi-\pi$ interactions between the furan rings of adjacent molecules [centroid-centroid distance = $3.430(4)$ Å] and by additional $\text{C}-\text{H}\cdots\pi$ and $\text{C}-\text{H}\cdots\text{O}$ interactions.

Related literature

For the crystal structures of similar 2-(3-methylsulfanyl-1-benzofuran-2-yl)acetic acid derivatives, see: Choi *et al.* (2009); Seo *et al.* (2007). For the biological and pharmacological activity of benzofuran compounds, see: Howlett *et al.* (1999); Ward (1997).



Experimental

Crystal data

 $\text{C}_{14}\text{H}_{16}\text{O}_3\text{S}$
 $M_r = 264.33$

Monoclinic, $P2_1/c$
 $a = 17.160(2)$ Å
 $b = 8.7773(7)$ Å
 $c = 17.819(2)$ Å
 $\beta = 93.905(2)^\circ$
 $V = 2677.6(5)$ Å³

$Z = 8$
 Mo $K\alpha$ radiation
 $\mu = 0.24$ mm⁻¹
 $T = 173$ K
 $0.30 \times 0.20 \times 0.20$ mm

Data collection

Bruker SMART CCD diffractometer
 Absorption correction: none
 19182 measured reflections

4727 independent reflections
 3284 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.066$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.052$
 $wR(F^2) = 0.139$
 $S = 1.09$
 4727 reflections
 336 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.35$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.24$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-\text{H}\cdots A$ | $D-\text{H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D-\text{H}\cdots A$ |
|--|--------------|--------------------|-------------|----------------------|
| $\text{O}2-\text{H}2\text{O}\cdots\text{O}3^{\text{i}}$ | 0.86 (4) | 1.79 (4) | 2.649 (3) | 174 (4) |
| $\text{O}5-\text{H}5\text{O}\cdots\text{O}6^{\text{ii}}$ | 0.75 (4) | 1.88 (4) | 2.621 (3) | 170 (5) |
| $\text{C}19-\text{H}19\cdots\text{O}5^{\text{iii}}$ | 0.95 | 2.70 | 3.567 (4) | 151 |
| $\text{C}9-\text{H}9\text{B}\cdots\text{C}g4$ | 0.99 | 2.57 | 3.350 (4) | 136 |
| $\text{C}23-\text{H}23\text{A}\cdots\text{C}g2$ | 0.99 | 2.58 | 3.299 (4) | 129 |

Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $-x, -y + 1, -z$; (iii) $x, -y + \frac{3}{2}, z + \frac{1}{2}$. $\text{C}g2$ and $\text{C}g4$ are the centroids of the $\text{C}2-\text{C}7$ and $\text{C}16-\text{C}21$ benzene rings, respectively.

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: WM2239).

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supplementary materials

Acta Cryst. (2009). E65, o1527 [doi:10.1107/S1600536809021242]

2-(5-Isopropyl-3-methylsulfanyl-1-benzofuran-2-yl)acetic acid

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Comment

The benzofuran compounds have attracted considerable interest in view of their biological and pharmacological properties (Howlett *et al.*, 1999; Ward, 1997). As a part of our ongoing studies on the synthesis and structures of 2-(3-methylsulfanyl-1-benzofuran-2-yl)acetic acid analogues, the crystal structure of 2-(5-ethyl-3-methylsulfanyl-1-benzofuran-2-yl)acetic acid (Seo *et al.*, 2007) and 2-(3-methylsulfanyl-5-propyl-1-benzofuran-2-yl)acetic acid (Choi *et al.*, 2009) have been described in the literature. Here we report the crystal structure of the title compound, 2-(5-isopropyl-3-methylsulfanyl-1-benzofuran-2-yl)acetic acid which crystallizes with two unique molecules, denoted as A & B, in the asymmetric unit (Fig. 1).

The benzofuran unit is essentially planar, with a mean deviation of 0.003 (2) Å for A and 0.011 (2) Å for B, respectively, 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 (Fig. 2 and Table 1), which link the molecules into centrosymmetric dimers. These dimers are further packed into stacks along the *a*-axis by aromatic π – π interactions between the furan rings from the adjacent molecules. The Cg1···Cg3 distance is 3.430 (4) Å (Cg1 and Cg3 are the centroids of C1/C2/C7/O1/C8 furan ring and C15/C16/C21/O4/C22 furan ring, respectively). In addition, the crystal packing exhibits two different C–H··· π interactions between a methylene H atom and the benzene ring from adjacent molecules (Table 1 and Fig. 2); Cg2 and Cg4 are the centroids of the C2–C7 benzene ring and the C16–C21 benzene ring, respectively, and a non-classical C–H···O hydrogen bond between a benzene H atom and the O atom of the hydroxy group (Table 1 and Fig. 2).

Experimental

Ethyl 2-(5-isopropyl-3-methylsulfanyl-1-benzofuran-2-yl)acetate (292 mg, 1.0 mmol) was added to a solution of potassium hydroxide (337 mg, 6.0 mmol) in water (25 ml) and methanol (25 ml), and the mixture was refluxed for 5h, 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 (hexane-ethyl acetate, 1 : 2 v/v) to afford the title compound as a colorless solid [yield 85%, m.p. 412–413 K; R_f = 0.69 (hexane-ethyl acetate, 1 : 2 v/v)]. 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: ^1H NMR (CDCl_3 , 400 MHz) δ 1.30 (d, J = 6.96 Hz, 6H), 2.33 (s, 3H), 3.01–3.07 (m, 1H), 4.03 (s, 2H), 7.19 (dd, J = 8.44 Hz and J = 1.84 Hz, 1H), 7.38 (d, J = 8.84 Hz, 1H), 7.47 (s, 1H), 10.08 (s, 1H); EI-MS 264 [M^+].

Refinement

Atoms H2O and H5O of the hydroxy groups were 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 = 0.95 Å for the aryl, 0.99 Å for the methylene, 1.00 Å for the methine, and 0.98 Å for the methyl H atoms. $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for the aryl, methine and methylene H atoms, and $1.5U_{\text{eq}}(\text{C})$ for methyl H atoms.

Figures

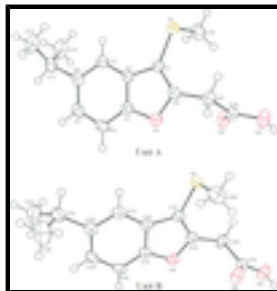


Fig. 1. The molecular structure of the title compound with the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are presented as a small cycles of arbitrary radius.

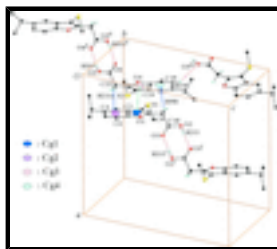


Fig. 2. The O–H...O hydrogen bonds, and π – π , C–H... π , C–H...O interactions (dotted lines) in the title compound. [Symmetry code: (i) $-x + 1, -y + 1, -z + 1$; (ii) $-x, -y + 1, -z$; (iii) $x, -y + 3/2, z + 1/2$.]

2-(5-Isopropyl-3-methylsulfanyl-1-benzofuran-2-yl)acetic acid

Crystal data

$C_{14}H_{16}O_3S$

$M_r = 264.33$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2ybc$

$a = 17.160\ (2)\ \text{\AA}$

$b = 8.7773\ (7)\ \text{\AA}$

$c = 17.819\ (2)\ \text{\AA}$

$\beta = 93.905\ (2)^\circ$

$V = 2677.6\ (5)\ \text{\AA}^3$

$Z = 8$

$F_{000} = 1120$

$D_x = 1.311\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073\ \text{\AA}$

Cell parameters from 5245 reflections

$\theta = 2.4\text{--}28.0^\circ$

$\mu = 0.24\ \text{mm}^{-1}$

$T = 173\ \text{K}$

Block, colorless

$0.30 \times 0.20 \times 0.20\ \text{mm}$

Data collection

Bruker SMART CCD diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

Detector resolution: $10.0\ \text{pixels mm}^{-1}$

$T = 173\ \text{K}$

φ and ω scans

Absorption correction: none

19182 measured reflections

4727 independent reflections

3284 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.066$

$\theta_{\text{max}} = 25.0^\circ$

$\theta_{\text{min}} = 1.2^\circ$

$h = -20 \rightarrow 20$

$k = -10 \rightarrow 10$

$l = -21 \rightarrow 20$

Refinement

| | |
|--|--|
| Refinement on F^2 | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: difference Fourier map |
| $R[F^2 > 2\sigma(F^2)] = 0.052$ | H atoms treated by a mixture of independent and constrained refinement |
| $wR(F^2) = 0.139$ | $w = 1/[\sigma^2(F_o^2) + (0.0613P)^2 + 1.3164P]$ |
| $S = 1.09$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| 4727 reflections | $(\Delta/\sigma)_{\max} < 0.001$ |
| 336 parameters | $\Delta\rho_{\max} = 0.35 \text{ e } \text{\AA}^{-3}$ |
| Primary atom site location: structure-invariant direct methods | $\Delta\rho_{\min} = -0.24 \text{ e } \text{\AA}^{-3}$ |
| | Extinction correction: none |

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 (\AA^2)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|-------------|---------------|----------------------------------|
| S1 | 0.37862 (4) | 0.80938 (8) | 0.21890 (4) | 0.0331 (2) |
| S2 | 0.12907 (4) | 0.14800 (8) | 0.26676 (5) | 0.0351 (2) |
| O1 | 0.33687 (10) | 0.3877 (2) | 0.28508 (10) | 0.0279 (5) |
| O3 | 0.46953 (11) | 0.4873 (3) | 0.40822 (11) | 0.0375 (5) |
| O2 | 0.41120 (12) | 0.6069 (3) | 0.50141 (12) | 0.0371 (6) |
| H2O | 0.449 (2) | 0.570 (5) | 0.530 (2) | 0.076 (14)* |
| O4 | 0.15963 (10) | 0.5807 (2) | 0.21373 (11) | 0.0284 (5) |
| O6 | 0.02448 (11) | 0.4616 (3) | 0.09349 (11) | 0.0416 (6) |
| O5 | 0.09385 (13) | 0.4311 (3) | -0.00875 (13) | 0.0385 (6) |
| H5O | 0.063 (3) | 0.459 (5) | -0.037 (2) | 0.090 (18)* |
| C1 | 0.36056 (14) | 0.6137 (3) | 0.22892 (15) | 0.0225 (6) |
| C2 | 0.35460 (14) | 0.4999 (3) | 0.16827 (15) | 0.0230 (6) |
| C3 | 0.36002 (15) | 0.4995 (3) | 0.08765 (16) | 0.0261 (6) |
| H3 | 0.3698 | 0.5919 | 0.0622 | 0.031* |
| C4 | 0.35082 (15) | 0.3625 (3) | 0.04656 (16) | 0.0289 (7) |
| C5 | 0.33688 (16) | 0.2281 (3) | 0.08780 (18) | 0.0332 (7) |
| H5 | 0.3310 | 0.1346 | 0.0611 | 0.040* |
| C6 | 0.33120 (16) | 0.2260 (3) | 0.16803 (17) | 0.0333 (7) |

supplementary materials

| | | | | |
|------|--------------|------------|---------------|-------------|
| H6 | 0.3217 | 0.1342 | 0.1941 | 0.040* |
| C7 | 0.34024 (14) | 0.3644 (3) | 0.20579 (15) | 0.0250 (6) |
| C8 | 0.34931 (14) | 0.5411 (3) | 0.29642 (16) | 0.0248 (6) |
| C9 | 0.34748 (15) | 0.5971 (3) | 0.37775 (15) | 0.0287 (7) |
| H9A | 0.3422 | 0.7094 | 0.3768 | 0.034* |
| H9B | 0.3000 | 0.5555 | 0.3988 | 0.034* |
| C10 | 0.41644 (15) | 0.5572 (3) | 0.43041 (15) | 0.0244 (6) |
| C11 | 0.35236 (17) | 0.3567 (4) | -0.04190 (17) | 0.0357 (7) |
| H11 | 0.3469 | 0.2475 | -0.0574 | 0.043* |
| C12 | 0.28631 (18) | 0.4423 (4) | -0.08121 (18) | 0.0476 (9) |
| H12A | 0.2894 | 0.5498 | -0.0665 | 0.057* |
| H12B | 0.2366 | 0.3994 | -0.0672 | 0.057* |
| H12C | 0.2896 | 0.4338 | -0.1357 | 0.057* |
| C13 | 0.42626 (19) | 0.4145 (5) | -0.07065 (19) | 0.0541 (10) |
| H13A | 0.4703 | 0.3543 | -0.0490 | 0.065* |
| H13B | 0.4335 | 0.5216 | -0.0563 | 0.065* |
| H13C | 0.4236 | 0.4057 | -0.1256 | 0.065* |
| C15 | 0.14263 (14) | 0.3457 (3) | 0.26341 (15) | 0.0248 (6) |
| C16 | 0.14678 (14) | 0.4533 (3) | 0.32748 (15) | 0.0227 (6) |
| C17 | 0.14295 (15) | 0.4436 (3) | 0.40849 (16) | 0.0288 (7) |
| H17 | 0.1367 | 0.3472 | 0.4316 | 0.035* |
| C18 | 0.14835 (16) | 0.5757 (3) | 0.45287 (17) | 0.0303 (7) |
| C19 | 0.15631 (15) | 0.7170 (3) | 0.41529 (17) | 0.0322 (7) |
| H19 | 0.1585 | 0.8077 | 0.4444 | 0.039* |
| C20 | 0.16123 (16) | 0.7293 (3) | 0.33547 (18) | 0.0323 (7) |
| H20 | 0.1674 | 0.8253 | 0.3120 | 0.039* |
| C21 | 0.15664 (14) | 0.5951 (3) | 0.29375 (16) | 0.0250 (6) |
| C22 | 0.15112 (14) | 0.4274 (3) | 0.19790 (16) | 0.0263 (6) |
| C23 | 0.15319 (15) | 0.3839 (3) | 0.11477 (16) | 0.0312 (7) |
| H23A | 0.2005 | 0.4296 | 0.0952 | 0.037* |
| H23B | 0.1587 | 0.2718 | 0.1115 | 0.037* |
| C24 | 0.08450 (15) | 0.4305 (3) | 0.06474 (16) | 0.0262 (6) |
| C25 | 0.14598 (19) | 0.5682 (4) | 0.54135 (18) | 0.0416 (8) |
| H25 | 0.1474 | 0.4582 | 0.5560 | 0.050* |
| C26 | 0.0728 (2) | 0.6345 (5) | 0.5684 (2) | 0.0606 (11) |
| H26A | 0.0275 | 0.5798 | 0.5453 | 0.073* |
| H26B | 0.0693 | 0.7424 | 0.5545 | 0.073* |
| H26C | 0.0736 | 0.6249 | 0.6233 | 0.073* |
| C27 | 0.21352 (19) | 0.6445 (5) | 0.58342 (19) | 0.0536 (10) |
| H27A | 0.2141 | 0.7528 | 0.5701 | 0.064* |
| H27B | 0.2623 | 0.5966 | 0.5702 | 0.064* |
| H27C | 0.2084 | 0.6340 | 0.6376 | 0.064* |
| C28 | 0.02834 (17) | 0.1368 (4) | 0.2460 (2) | 0.0464 (9) |
| H28A | 0.0014 | 0.1957 | 0.2832 | 0.070* |
| H28B | 0.0117 | 0.0301 | 0.2476 | 0.070* |
| H28C | 0.0153 | 0.1785 | 0.1957 | 0.070* |
| C14 | 0.47646 (16) | 0.8192 (4) | 0.25281 (19) | 0.0407 (8) |
| H14A | 0.4813 | 0.7860 | 0.3054 | 0.061* |
| H14B | 0.4950 | 0.9245 | 0.2494 | 0.061* |

H14C 0.5079 0.7528 0.2226 0.061*

Atomic displacement parameters (Å²)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| S1 | 0.0323 (4) | 0.0251 (4) | 0.0406 (5) | -0.0001 (3) | -0.0085 (3) | 0.0003 (3) |
| S2 | 0.0312 (4) | 0.0236 (4) | 0.0487 (5) | 0.0013 (3) | -0.0087 (3) | -0.0014 (3) |
| O1 | 0.0218 (10) | 0.0294 (11) | 0.0320 (11) | -0.0009 (8) | -0.0012 (8) | 0.0058 (9) |
| O3 | 0.0219 (11) | 0.0604 (15) | 0.0296 (12) | 0.0138 (10) | -0.0040 (9) | -0.0077 (10) |
| O2 | 0.0271 (11) | 0.0563 (15) | 0.0272 (12) | 0.0128 (10) | -0.0046 (9) | -0.0069 (10) |
| O4 | 0.0240 (10) | 0.0284 (11) | 0.0325 (12) | -0.0012 (8) | -0.0002 (8) | 0.0051 (9) |
| O6 | 0.0213 (11) | 0.0693 (16) | 0.0338 (12) | 0.0094 (10) | -0.0006 (9) | -0.0044 (11) |
| O5 | 0.0249 (12) | 0.0597 (16) | 0.0307 (13) | 0.0043 (10) | 0.0001 (10) | 0.0029 (11) |
| C1 | 0.0138 (12) | 0.0261 (15) | 0.0268 (16) | 0.0015 (11) | -0.0037 (11) | -0.0003 (12) |
| C2 | 0.0116 (12) | 0.0262 (15) | 0.0307 (16) | 0.0006 (11) | -0.0025 (11) | -0.0007 (12) |
| C3 | 0.0181 (13) | 0.0282 (16) | 0.0318 (17) | -0.0002 (11) | 0.0002 (12) | 0.0027 (13) |
| C4 | 0.0149 (13) | 0.0359 (17) | 0.0358 (17) | 0.0032 (12) | 0.0012 (12) | -0.0073 (14) |
| C5 | 0.0254 (15) | 0.0276 (16) | 0.046 (2) | 0.0036 (12) | -0.0002 (14) | -0.0101 (14) |
| C6 | 0.0292 (16) | 0.0230 (16) | 0.047 (2) | 0.0012 (12) | -0.0022 (14) | 0.0032 (14) |
| C7 | 0.0143 (13) | 0.0310 (16) | 0.0292 (16) | 0.0019 (11) | -0.0016 (11) | 0.0034 (13) |
| C8 | 0.0139 (13) | 0.0257 (15) | 0.0343 (17) | 0.0028 (11) | -0.0024 (11) | -0.0022 (12) |
| C9 | 0.0180 (14) | 0.0401 (18) | 0.0277 (16) | 0.0056 (12) | -0.0008 (12) | 0.0004 (13) |
| C10 | 0.0204 (14) | 0.0287 (16) | 0.0243 (16) | -0.0009 (12) | 0.0027 (12) | 0.0000 (12) |
| C11 | 0.0315 (16) | 0.0401 (18) | 0.0355 (18) | 0.0025 (14) | 0.0013 (13) | -0.0109 (15) |
| C12 | 0.0338 (18) | 0.077 (3) | 0.0315 (19) | 0.0059 (17) | -0.0015 (14) | -0.0036 (17) |
| C13 | 0.0362 (19) | 0.089 (3) | 0.038 (2) | -0.0022 (19) | 0.0099 (16) | -0.0099 (19) |
| C15 | 0.0141 (13) | 0.0265 (15) | 0.0331 (16) | 0.0025 (11) | -0.0024 (11) | 0.0008 (13) |
| C16 | 0.0091 (12) | 0.0248 (15) | 0.0339 (16) | 0.0004 (10) | -0.0011 (11) | 0.0015 (12) |
| C17 | 0.0212 (14) | 0.0282 (16) | 0.0371 (18) | -0.0008 (11) | 0.0013 (12) | 0.0053 (13) |
| C18 | 0.0217 (14) | 0.0314 (17) | 0.0377 (18) | 0.0001 (12) | 0.0020 (13) | -0.0014 (14) |
| C19 | 0.0241 (15) | 0.0283 (16) | 0.0438 (19) | 0.0030 (12) | 0.0005 (13) | -0.0100 (14) |
| C20 | 0.0277 (15) | 0.0182 (15) | 0.051 (2) | 0.0005 (12) | -0.0010 (14) | 0.0018 (13) |
| C21 | 0.0143 (13) | 0.0262 (15) | 0.0344 (17) | -0.0004 (11) | -0.0001 (11) | 0.0042 (13) |
| C22 | 0.0130 (13) | 0.0274 (15) | 0.0379 (17) | 0.0021 (11) | -0.0031 (12) | 0.0002 (13) |
| C23 | 0.0212 (14) | 0.0380 (18) | 0.0341 (17) | 0.0064 (12) | -0.0005 (12) | -0.0018 (14) |
| C24 | 0.0222 (15) | 0.0285 (16) | 0.0282 (17) | -0.0007 (12) | 0.0038 (12) | -0.0030 (12) |
| C25 | 0.056 (2) | 0.0343 (19) | 0.0361 (19) | 0.0008 (15) | 0.0111 (16) | -0.0042 (15) |
| C26 | 0.044 (2) | 0.088 (3) | 0.052 (2) | -0.018 (2) | 0.0202 (18) | -0.017 (2) |
| C27 | 0.043 (2) | 0.078 (3) | 0.039 (2) | 0.0160 (19) | -0.0024 (16) | -0.0119 (19) |
| C28 | 0.0313 (17) | 0.043 (2) | 0.066 (2) | -0.0109 (15) | 0.0088 (16) | -0.0017 (17) |
| C14 | 0.0276 (16) | 0.047 (2) | 0.048 (2) | -0.0114 (14) | 0.0016 (14) | -0.0024 (16) |

Geometric parameters (Å, °)

| | | | |
|--------|-----------|----------|-----------|
| S1—C14 | 1.747 (3) | C12—H12C | 0.9800 |
| S1—C1 | 1.757 (3) | C13—H13A | 0.9800 |
| S2—C28 | 1.745 (3) | C13—H13B | 0.9800 |
| S2—C15 | 1.752 (3) | C13—H13C | 0.9800 |
| O1—C8 | 1.377 (3) | C15—C22 | 1.387 (4) |

supplementary materials

| | | | |
|------------|-------------|-------------|-----------|
| O1—C7 | 1.432 (3) | C15—C16 | 1.480 (4) |
| O3—C10 | 1.188 (3) | C16—C21 | 1.398 (4) |
| O2—C10 | 1.347 (3) | C16—C17 | 1.452 (4) |
| O2—H2O | 0.86 (4) | C17—C18 | 1.403 (4) |
| O4—C22 | 1.380 (3) | C17—H17 | 0.9500 |
| O4—C21 | 1.436 (3) | C18—C19 | 1.421 (4) |
| O6—C24 | 1.212 (3) | C18—C25 | 1.581 (4) |
| O5—C24 | 1.330 (3) | C19—C20 | 1.435 (4) |
| O5—H5O | 0.75 (4) | C19—H19 | 0.9500 |
| C1—C8 | 1.386 (4) | C20—C21 | 1.392 (4) |
| C1—C2 | 1.470 (4) | C20—H20 | 0.9500 |
| C2—C7 | 1.394 (4) | C22—C23 | 1.533 (4) |
| C2—C3 | 1.446 (4) | C23—C24 | 1.486 (4) |
| C3—C4 | 1.411 (4) | C23—H23A | 0.9900 |
| C3—H3 | 0.9500 | C23—H23B | 0.9900 |
| C4—C5 | 1.419 (4) | C25—C26 | 1.493 (5) |
| C4—C11 | 1.579 (4) | C25—C27 | 1.495 (5) |
| C5—C6 | 1.440 (4) | C25—H25 | 1.0000 |
| C5—H5 | 0.9500 | C26—H26A | 0.9800 |
| C6—C7 | 1.392 (4) | C26—H26B | 0.9800 |
| C6—H6 | 0.9500 | C26—H26C | 0.9800 |
| C8—C9 | 1.532 (4) | C27—H27A | 0.9800 |
| C9—C10 | 1.501 (4) | C27—H27B | 0.9800 |
| C9—H9A | 0.9900 | C27—H27C | 0.9800 |
| C9—H9B | 0.9900 | C28—H28A | 0.9800 |
| C11—C13 | 1.489 (4) | C28—H28B | 0.9800 |
| C11—C12 | 1.494 (4) | C28—H28C | 0.9800 |
| C11—H11 | 1.0000 | C14—H14A | 0.9800 |
| C12—H12A | 0.9800 | C14—H14B | 0.9800 |
| C12—H12B | 0.9800 | C14—H14C | 0.9800 |
| C14—S1—C1 | 100.68 (14) | C21—C16—C17 | 119.6 (2) |
| C28—S2—C15 | 100.39 (14) | C21—C16—C15 | 103.7 (2) |
| C8—O1—C7 | 105.5 (2) | C17—C16—C15 | 136.6 (2) |
| C10—O2—H2O | 110 (3) | C18—C17—C16 | 120.4 (3) |
| C22—O4—C21 | 106.2 (2) | C18—C17—H17 | 119.8 |
| C24—O5—H5O | 123 (4) | C16—C17—H17 | 119.8 |
| C8—C1—C2 | 108.6 (2) | C17—C18—C19 | 117.4 (3) |
| C8—C1—S1 | 125.0 (2) | C17—C18—C25 | 121.5 (3) |
| C2—C1—S1 | 126.4 (2) | C19—C18—C25 | 121.1 (3) |
| C7—C2—C3 | 120.0 (2) | C18—C19—C20 | 123.2 (3) |
| C7—C2—C1 | 103.4 (2) | C18—C19—H19 | 118.4 |
| C3—C2—C1 | 136.6 (2) | C20—C19—H19 | 118.4 |
| C4—C3—C2 | 120.4 (3) | C21—C20—C19 | 117.4 (3) |
| C4—C3—H3 | 119.8 | C21—C20—H20 | 121.3 |
| C2—C3—H3 | 119.8 | C19—C20—H20 | 121.3 |
| C3—C4—C5 | 117.2 (3) | C20—C21—C16 | 121.9 (3) |
| C3—C4—C11 | 122.5 (3) | C20—C21—O4 | 126.9 (2) |
| C5—C4—C11 | 120.3 (3) | C16—C21—O4 | 111.2 (2) |
| C4—C5—C6 | 123.4 (3) | O4—C22—C15 | 110.4 (2) |

| | | | |
|---------------|-------------|-----------------|--------------|
| C4—C5—H5 | 118.3 | O4—C22—C23 | 115.6 (2) |
| C6—C5—H5 | 118.3 | C15—C22—C23 | 134.0 (3) |
| C7—C6—C5 | 117.1 (3) | C24—C23—C22 | 116.2 (2) |
| C7—C6—H6 | 121.4 | C24—C23—H23A | 108.2 |
| C5—C6—H6 | 121.4 | C22—C23—H23A | 108.2 |
| C6—C7—C2 | 122.0 (3) | C24—C23—H23B | 108.2 |
| C6—C7—O1 | 126.2 (2) | C22—C23—H23B | 108.2 |
| C2—C7—O1 | 111.8 (2) | H23A—C23—H23B | 107.4 |
| O1—C8—C1 | 110.6 (2) | O6—C24—O5 | 125.3 (3) |
| O1—C8—C9 | 116.1 (2) | O6—C24—C23 | 118.1 (3) |
| C1—C8—C9 | 133.3 (3) | O5—C24—C23 | 116.6 (2) |
| C10—C9—C8 | 116.8 (2) | C26—C25—C27 | 107.7 (3) |
| C10—C9—H9A | 108.1 | C26—C25—C18 | 112.7 (3) |
| C8—C9—H9A | 108.1 | C27—C25—C18 | 114.2 (3) |
| C10—C9—H9B | 108.1 | C26—C25—H25 | 107.3 |
| C8—C9—H9B | 108.1 | C27—C25—H25 | 107.3 |
| H9A—C9—H9B | 107.3 | C18—C25—H25 | 107.3 |
| O3—C10—O2 | 125.6 (3) | C25—C26—H26A | 109.5 |
| O3—C10—C9 | 120.2 (3) | C25—C26—H26B | 109.5 |
| O2—C10—C9 | 114.3 (2) | H26A—C26—H26B | 109.5 |
| C13—C11—C12 | 107.7 (3) | C25—C26—H26C | 109.5 |
| C13—C11—C4 | 113.9 (3) | H26A—C26—H26C | 109.5 |
| C12—C11—C4 | 112.8 (2) | H26B—C26—H26C | 109.5 |
| C13—C11—H11 | 107.4 | C25—C27—H27A | 109.5 |
| C12—C11—H11 | 107.4 | C25—C27—H27B | 109.5 |
| C4—C11—H11 | 107.4 | H27A—C27—H27B | 109.5 |
| C11—C12—H12A | 109.5 | C25—C27—H27C | 109.5 |
| C11—C12—H12B | 109.5 | H27A—C27—H27C | 109.5 |
| H12A—C12—H12B | 109.5 | H27B—C27—H27C | 109.5 |
| C11—C12—H12C | 109.5 | S2—C28—H28A | 109.5 |
| H12A—C12—H12C | 109.5 | S2—C28—H28B | 109.5 |
| H12B—C12—H12C | 109.5 | H28A—C28—H28B | 109.5 |
| C11—C13—H13A | 109.5 | S2—C28—H28C | 109.5 |
| C11—C13—H13B | 109.5 | H28A—C28—H28C | 109.5 |
| H13A—C13—H13B | 109.5 | H28B—C28—H28C | 109.5 |
| C11—C13—H13C | 109.5 | S1—C14—H14A | 109.5 |
| H13A—C13—H13C | 109.5 | S1—C14—H14B | 109.5 |
| H13B—C13—H13C | 109.5 | H14A—C14—H14B | 109.5 |
| C22—C15—C16 | 108.5 (2) | S1—C14—H14C | 109.5 |
| C22—C15—S2 | 124.3 (2) | H14A—C14—H14C | 109.5 |
| C16—C15—S2 | 127.2 (2) | H14B—C14—H14C | 109.5 |
| C14—S1—C1—C8 | 75.9 (3) | C28—S2—C15—C22 | -83.6 (3) |
| C14—S1—C1—C2 | -104.3 (2) | C28—S2—C15—C16 | 96.2 (2) |
| C8—C1—C2—C7 | -0.3 (3) | C22—C15—C16—C21 | 0.8 (3) |
| S1—C1—C2—C7 | 179.84 (19) | S2—C15—C16—C21 | -178.99 (19) |
| C8—C1—C2—C3 | 179.8 (3) | C22—C15—C16—C17 | -179.4 (3) |
| S1—C1—C2—C3 | 0.0 (4) | S2—C15—C16—C17 | 0.8 (4) |
| C7—C2—C3—C4 | 0.0 (4) | C21—C16—C17—C18 | 0.6 (4) |
| C1—C2—C3—C4 | 179.9 (3) | C15—C16—C17—C18 | -179.1 (3) |

supplementary materials

| | | | |
|---------------|--------------|-----------------|-------------|
| C2—C3—C4—C5 | -0.5 (4) | C16—C17—C18—C19 | 1.0 (4) |
| C2—C3—C4—C11 | 177.2 (2) | C16—C17—C18—C25 | -178.8 (2) |
| C3—C4—C5—C6 | 0.6 (4) | C17—C18—C19—C20 | -1.8 (4) |
| C11—C4—C5—C6 | -177.1 (2) | C25—C18—C19—C20 | 178.0 (3) |
| C4—C5—C6—C7 | -0.2 (4) | C18—C19—C20—C21 | 1.0 (4) |
| C5—C6—C7—C2 | -0.3 (4) | C19—C20—C21—C16 | 0.7 (4) |
| C5—C6—C7—O1 | -179.9 (2) | C19—C20—C21—O4 | 179.5 (2) |
| C3—C2—C7—C6 | 0.4 (4) | C17—C16—C21—C20 | -1.5 (4) |
| C1—C2—C7—C6 | -179.5 (2) | C15—C16—C21—C20 | 178.4 (2) |
| C3—C2—C7—O1 | -180.0 (2) | C17—C16—C21—O4 | 179.5 (2) |
| C1—C2—C7—O1 | 0.1 (3) | C15—C16—C21—O4 | -0.6 (3) |
| C8—O1—C7—C6 | 179.7 (3) | C22—O4—C21—C20 | -178.7 (3) |
| C8—O1—C7—C2 | 0.1 (3) | C22—O4—C21—C16 | 0.3 (3) |
| C7—O1—C8—C1 | -0.3 (3) | C21—O4—C22—C15 | 0.3 (3) |
| C7—O1—C8—C9 | 179.2 (2) | C21—O4—C22—C23 | -179.5 (2) |
| C2—C1—C8—O1 | 0.4 (3) | C16—C15—C22—O4 | -0.7 (3) |
| S1—C1—C8—O1 | -179.74 (17) | S2—C15—C22—O4 | 179.11 (17) |
| C2—C1—C8—C9 | -179.0 (3) | C16—C15—C22—C23 | 179.1 (3) |
| S1—C1—C8—C9 | 0.8 (4) | S2—C15—C22—C23 | -1.1 (4) |
| O1—C8—C9—C10 | 73.6 (3) | O4—C22—C23—C24 | -70.7 (3) |
| C1—C8—C9—C10 | -107.0 (3) | C15—C22—C23—C24 | 109.6 (3) |
| C8—C9—C10—O3 | 1.0 (4) | C22—C23—C24—O6 | -19.0 (4) |
| C8—C9—C10—O2 | -178.9 (2) | C22—C23—C24—O5 | 162.5 (2) |
| C3—C4—C11—C13 | 59.0 (4) | C17—C18—C25—C26 | -110.7 (3) |
| C5—C4—C11—C13 | -123.4 (3) | C19—C18—C25—C26 | 69.5 (4) |
| C3—C4—C11—C12 | -64.2 (4) | C17—C18—C25—C27 | 126.1 (3) |
| C5—C4—C11—C12 | 113.4 (3) | C19—C18—C25—C27 | -53.7 (4) |

Hydrogen-bond geometry (\AA , $^\circ$)

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|------------------------------------|----------|-------------|-------------|---------------|
| O2—H2O \cdots O3 ⁱ | 0.86 (4) | 1.79 (4) | 2.649 (3) | 174 (4) |
| O5—H5O \cdots O6 ⁱⁱ | 0.75 (4) | 1.88 (4) | 2.621 (3) | 170 (5) |
| C19—H19 \cdots O5 ⁱⁱⁱ | 0.95 | 2.70 | 3.567 (4) | 151 |
| C9—H9B \cdots Cg4 | 0.99 | 2.57 | 3.350 (4) | 136 |
| C23—H23A \cdots Cg2 | 0.99 | 2.58 | 3.299 (4) | 129 |

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x, -y+1, -z$; (iii) $x, -y+3/2, z+1/2$.

Fig. 1

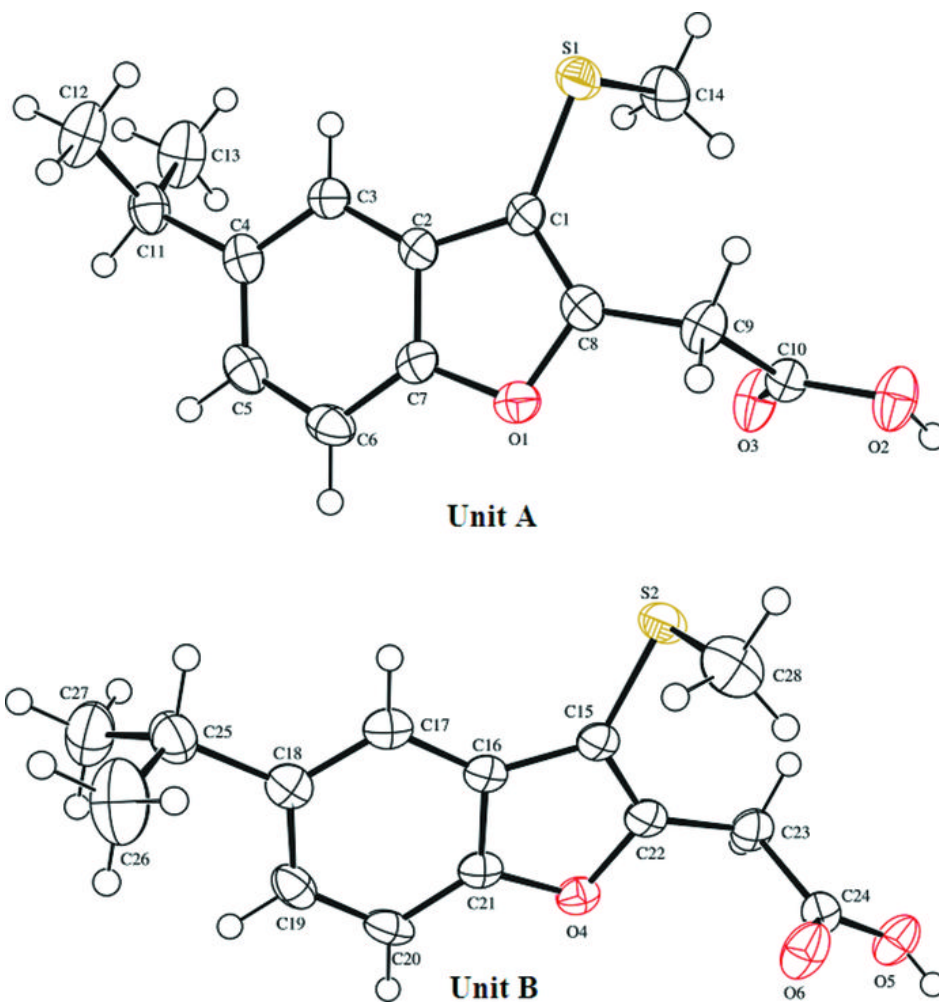


Fig. 2

