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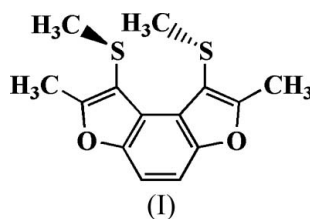
Key indicators

Single-crystal X-ray study
 $T = 298\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.006\text{ \AA}$
 R factor = 0.056
 wR factor = 0.158
Data-to-parameter ratio = 18.6For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.2,5-Dimethyl-3,4-bis(methylsulfanyl)benzo-
[1,2-*b*:4,3-*b'*]difuranIn the molecule of the title compound, $\text{C}_{14}\text{H}_{14}\text{O}_2\text{S}_2$, the benzo[1,2-*b*:4,3-*b'*]difuran group is nearly planar. The molecule possesses a twofold rotation axis. The crystal structure is stabilized by aromatic $\pi-\pi$ stacking and $-\text{CH}_2-\text{H}\cdots\pi$ interactions.

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Comment

Substituted benzodifurans have received considerable interest because of their biological and pharmacological activities, and have important applications in the field of photosensitizers and fluorescent probes (Bilger *et al.*, 1987; Chambers *et al.*, 2001; Rene *et al.*, 1977; 1978). Derivatives bearing such ring systems have been synthesized from the *O*-alkylation of an appropriate dihydroxydibenzoylbenzene and subsequent dehydrative cyclization (Park & Jeong, 2005), and the condensation of 5-hydroxybenzo[*b*]furan with an appropriate α -halocarbonyl compound (Rene *et al.*, 1977). Various structural isomers of benzodifuran systems are known and a few of them have been analyzed by X-ray crystallography (Takahashi & Kobayashi, 2000; Kang *et al.*, 2004). The one-pot reaction of hydroquinone with an excess of α -chloro- α -(methylsulfanyl)acetone in the presence of zinc chloride gave the title compound, (I). We report here the crystal structure of (I), which was isolated by the chromatographic procedure using carbon tetrachloride as an eluant ($R_f = 0.68$).The asymmetric unit of the title structure consists of one half-molecule (Fig. 1). A crystallographic twofold rotation axis passes through the mid-points of the $\text{C}4-\text{C}4^i$ and $\text{C}7-\text{C}7^i$ bonds (symmetry code as in Fig. 1). The bond lengths and angles (Table 1) are within normal ranges (Allen *et al.*, 1987).Rings *A* ($\text{O}/\text{C}1-\text{C}4$) and *B* ($\text{C}3/\text{C}3^i/\text{C}4/\text{C}4^i/\text{C}7/\text{C}7^i$) are each planar, with maximum deviations of 0.0117 (3) ($\text{C}3$) and 0.0119 (2) \AA ($\text{C}7$) from the least-squares planes. They form a dihedral angle of 1.68 (3) $^\circ$. Ring *A* has a local pseudo-twofold axis passing through $\text{C}2$ and the mid-point of the $\text{C}3=\text{C}4$ bond, as evidenced by the torsion angles (Table 1). The benzo[1,2-*b*:4,3-*b'*]difuran group is nearly planar with a puckering amplitude of $Q_T = 0.0863$ (5) \AA (Cremer & Pople, 1975).

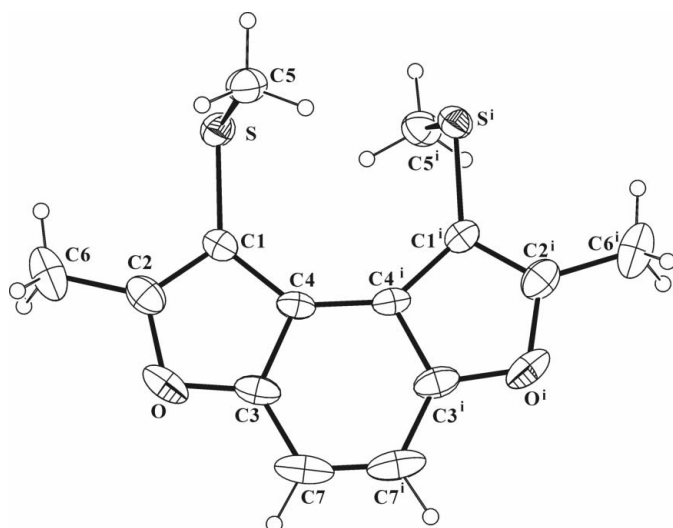


Figure 1

The molecular structure, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry code: (i) $1 - x, y, \frac{1}{2} - z$.]

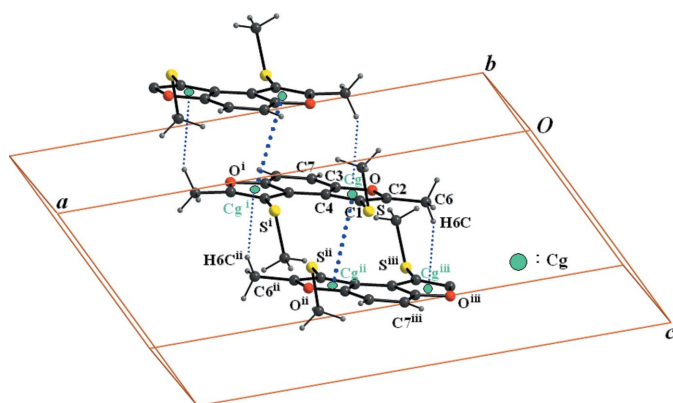


Figure 2

A partial packing diagram of (I). $-\text{CH}_2-\text{H}\cdots\pi$ and $\pi-\pi$ interactions are shown as thin and thick dotted lines, respectively. C_g is the centroid of the (C1–C4/O) ring. [Symmetry codes: (i) $1 - x, y, \frac{1}{2} - z$; (ii) $1 - x, 1 - y, 1 - z$; (iii) $x, 1 - y, \frac{1}{2} + z$.]

The crystal structure is stabilized by aromatic $\pi-\pi$ stacking and $-\text{CH}_2-\text{H}\cdots\pi$ interactions (Fig. 2). The separation of the furan groups, $C_g\cdots C_g^i$, is 3.545 Å (C_g is the centroid of the C1–C4/O ring; symmetry code as in Fig. 2), which clearly indicates the presence of a $\pi-\pi$ stacking interaction. The nearest ring centroid separation of $C_g\cdots C_g^{ii}$ is 3.647 (3) Å (symmetry code as in Fig. 2). The packing of the molecules is additionally stabilized by $-\text{CH}_2-\text{H}\cdots\pi$ interactions between adjacent furan rings, with $-\text{C6}-\text{H6C}\cdots C_g^{iii}$ distances of 2.89 Å (symmetry code as in Fig. 2).

Experimental

The title compound, (I), was prepared by a published method for substituted benzo[*b*]furans (Choi *et al.*, 1998). Zinc chloride (1.50 g, 11.0 mmol) was added at room temperature to a stirred solution of α -chloro- α -(methylsulfanyl)acetone (1.53 g, 11.0 mmol) and hydro-

quinone (0.55 g, 5.0 mmol) in dichloromethane (30 ml) and tetrahydrofuran (5 ml), and the mixture was stirred for 40 min. The mixture was quenched with water, and the organic layer was separated, dried over magnesium sulfate, filtered and concentrated in vacuum. The residue was purified by column chromatography (CCl_4) to afford (I) as a white solid. Crystals suitable for X-ray analysis were grown by slow evaporation of a benzene solution [yield 25%, m.p. 443–445 K; $R_f = 0.68$ (CCl_4)].

Crystal data

$\text{C}_{14}\text{H}_{14}\text{O}_2\text{S}_2$
 $M_r = 278.37$
 Monoclinic, $C2/c$
 $a = 18.106$ (6) Å
 $b = 8.936$ (3) Å
 $c = 9.300$ (3) Å
 $\beta = 117.60$ (3)°
 $V = 1333.5$ (8) Å³

$Z = 4$
 $D_x = 1.387$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 0.39$ mm⁻¹
 $T = 298$ (2) K
 Prism, colorless
 $0.53 \times 0.31 \times 0.19$ mm

Data collection

Stoe Stadi-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: none
 1526 measured reflections
 1526 independent reflections

1138 reflections with $I > 2\sigma(I)$
 $\theta_{\text{max}} = 27.4^\circ$
 3 standard reflections
 frequency: 60 min
 intensity decay: 2.8%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.056$
 $wR(F^2) = 0.158$
 $S = 1.07$
 1526 reflections
 82 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0696P)^2 + 2.3312P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.31$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.39$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

S–C1	1.753 (3)	O–C3	1.374 (5)
S–C5	1.805 (4)	O–C2	1.379 (5)
C1–S–C5	100.4 (2)	C3–O–C2	107.3 (2)
C1–C2–O–C3	0.8 (2)	C3–C4–C1–C2	−1.6 (3)
C2–O–C3–C4	−1.9 (3)	C4–C1–C2–O	0.5 (2)
O–C3–C4–C1	2.1 (2)		

H atoms were positioned geometrically, with C–H = 0.93 and 0.96 Å for aromatic and methyl H, respectively, and constrained to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *STADI4* (Stoe & Cie, 1996); cell refinement: *STADI4*; data reduction: *X-RED* (Stoe & Cie, 1996); 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*.

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