

2,9-Dimethyl-3,8-bis(methylsulfanyl)naphtho-
[2,1-*b*:3,4-*b'*]difuranHong Dae Choi,^a Ji Bong Jang,^a
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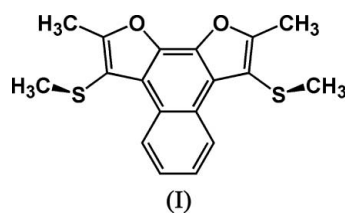
Key indicators

Single-crystal X-ray study
T = 298 K
Mean $\sigma(\text{C}-\text{C}) = 0.006 \text{ \AA}$
R factor = 0.078
wR factor = 0.201
Data-to-parameter ratio = 18.1For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.The title compound, C₁₈H₁₆O₂S₂, was prepared by the Lewis acid-catalysed reaction of 2,3-dihydroxynaphthalene with α -chloro- α -(methylsulfanyl)acetone. The naphtho[2,1-*b*:3,4-*b'*]difuran unit is nearly planar, with a mean deviation from the least-squares plane of 0.028 Å. In the crystal structure, aromatic π - π stacking interactions are observed between adjacent molecules.

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Comment

The naphthodifuran nucleus can be used as a highly reactive diene in Diels–Alder reactions, or to prepare some interesting cyclophane precursors and chrysene derivatives (Thibault *et al.*, 2003; Park *et al.*, 2002; Blank & Haenel, 1983). Although the presence of several structural isomers for naphthodifurans is possible, only naphthodifuran ring systems have been synthesized by the condensation of an appropriate naphthalene diol with ω -bromoacetaldehyde dimethylacetal following cyclization by means of polyphosphoric acid (Dingankar *et al.*, 1971). We report here the crystal structure of the title compound, (I) (Fig. 1), which was obtained from the reaction of 2,3-dihydroxynaphthalene with an excess of α -chloro- α -(methylsulfanyl)acetone in the presence of zinc chloride at room temperature.The S–C bond distances and C–S–C angles in (I) are listed in Table 1. The least-squares plane of naphtho[2,1-*b*:3,4-*b'*]difuran (mean deviation = 0.028 Å) makes a dihedral angle of 6.03 (5)° with the same system related by the symmetry element $(x, \frac{1}{2} - y, z + \frac{1}{2})$, hereafter (i). In the crystal structure, the short intermolecular distances C9···C12ⁱ [3.492 (7) Å] and C10···O1ⁱ [3.487 (6) Å] indicate aromatic π - π stacking interactions (Fig. 2).

Experimental

The title compound was prepared according to the method for substituted benzo[*b*]furans (Choi *et al.*, 1998) and naphtho[*b*]furans (Choi *et al.*, 1999). To a stirred solution of α -chloro- α -(methylsulfanyl)acetone (1.53 g, 11.0 mmol) and 2,3-dihydroxynaphthalene (801 mg, 5.0 mmol) in dichloromethane (30 ml) and tetrahydrofuran (5 ml) was added zinc chloride (1.50 g, 11.0 mmol) at room

temperature, and stirring was continued at the same temperature for 40 min. The mixture was quenched with water and the organic layer was separated, dried over magnesium sulfate, filtered and concentrated. The residue was purified by column chromatography (CCl_4) to afford the title compound in 51% yield. Crystals suitable for an X-ray diffraction study were grown by slow evaporation of a benzene solution (m.p. 457–459 K; $R_f = 0.68$ (CCl_4)).

Crystal data

$\text{C}_{18}\text{H}_{16}\text{O}_2\text{S}_2$ $Z = 4$
 $M_r = 328.43$ $D_x = 1.361 \text{ Mg m}^{-3}$
 Monoclinic, $P2_1/c$ Mo $K\alpha$ radiation
 $a = 7.564$ (2) Å $\mu = 0.34 \text{ mm}^{-1}$
 $b = 20.415$ (5) Å $T = 298$ (2) K
 $c = 11.022$ (1) Å Tetragonal prism, pale red
 $\beta = 109.60$ (1)° $0.42 \times 0.12 \times 0.10 \text{ mm}$
 $V = 1603.4$ (6) Å³

Data collection

Stoe Stadi-4 diffractometer 2179 reflections with $I > 2\sigma(I)$
 $\omega/2\theta$ scans $\theta_{\text{max}} = 27.4^\circ$
 Absorption correction: none 3 standard reflections
 3644 measured reflections frequency: 60 min
 3644 independent reflections intensity decay: 2.4%

Refinement

Refinement on F^2 $w = 1/[\sigma^2(F_o^2) + (0.0635P)^2 + 2.5272P]$
 $R[F^2 > 2\sigma(F^2)] = 0.078$ where $P = (F_o^2 + 2F_c^2)/3$
 $wR(F^2) = 0.201$ $(\Delta/\sigma)_{\text{max}} < 0.001$
 $S = 1.10$ $\Delta\rho_{\text{max}} = 0.51 \text{ e \AA}^{-3}$
 3644 reflections $\Delta\rho_{\text{min}} = -0.34 \text{ e \AA}^{-3}$
 201 parameters
 H-atom parameters constrained

Table 1

Selected geometric parameters (Å, °).

S1—C13	1.760 (4)	O1—C1	1.371 (5)
S1—C17	1.801 (5)	O1—C14	1.379 (5)
S2—C4	1.764 (5)	O2—C2	1.370 (5)
S2—C16	1.804 (6)	O2—C3	1.375 (5)
C13—S1—C17	102.5 (2)	C4—S2—C16	101.1 (2)

All H atoms were positioned geometrically in idealized positions and refined using a riding model, with C—H = 0.93–0.96 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *STADIA* (Stoe & Cie, 1996); cell refinement: *STADIA*; data reduction: *X-RED32* (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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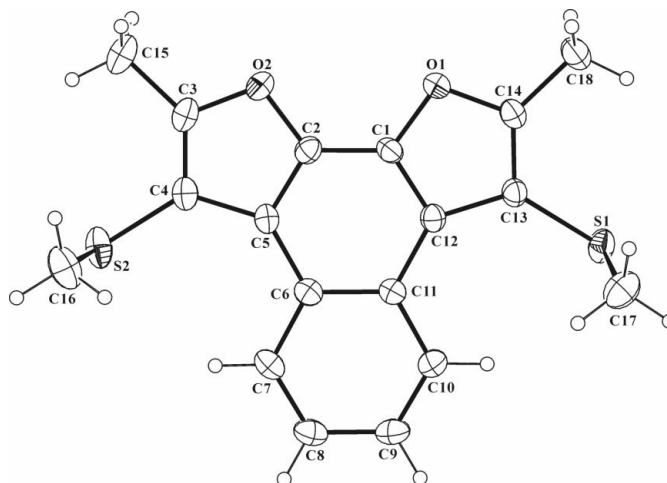


Figure 1
A view of (I), with 30% probability displacement ellipsoids.

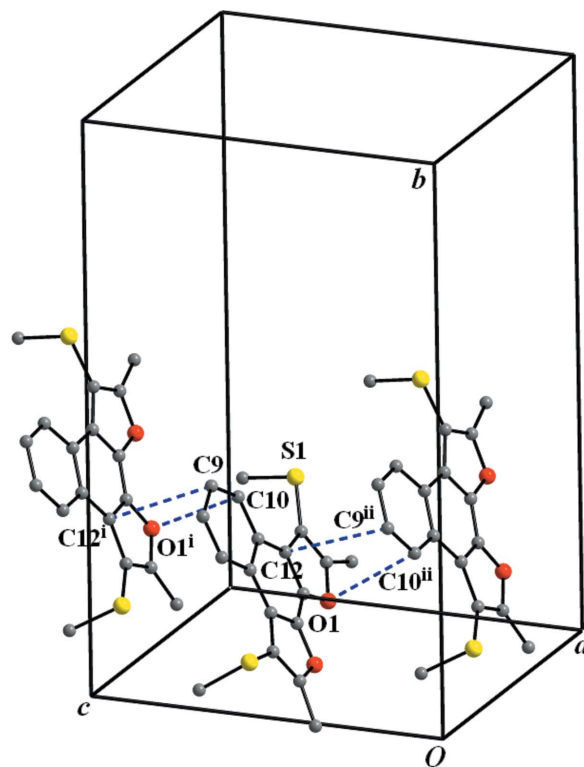


Figure 2
The π - π stacking interactions (dashed lines) in (I) [symmetry codes: (i) $x, \frac{1}{2} - y, z + \frac{1}{2}$; (ii) $x, \frac{1}{2} - y, z - \frac{1}{2}$]. H atoms have been omitted for clarity.

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