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7-Methoxy-2-methylnaphtho[1,2-*b*]thiophene

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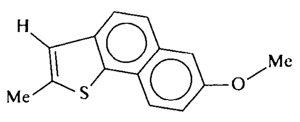
Abstract

The three rings in the molecule of the title compound, $C_{14}H_{12}OS$, are planar, with the methyl and methoxy groups coplanar with the rest of the molecule. The average C—S distance of the thiophene moiety is 1.737 (3) Å. The crystal structure is composed of discrete molecules separated by van der Waals contacts.

Comment

Regioselective alkylation of polycyclic compounds helps to improve the solubilities of these compounds in common organic solvents (Ray *et al.*, 1996). In an attempt to synthesize monoalkylated polycyclic thiophene derivatives having an alkyl group exclusively in the 2-position of the thiophene moiety, which is highly influenced by the position of the heteroatom, we have developed (Pan & Ray, 1999) a new and simple alkylation route using *n*-butyllithium and alkyl iodide. Polycyclic thiophene derivatives with alkyl substituents at specific sites have attracted the attention of medicinal chemists for bioisosterism (Thornber, 1979). Thus, the title compound, (I), was synthesized and its structure analysed.



(I)

The geometry of the molecule in (I) is comparable with that of reported naphthothiophene derivatives (Wilson *et al.*, 1986, 1987). The molecular dimensions in the thiophene moiety [Csp^2—Csp^2 1.400 (2), C═C 1.345 (3) and S—Csp^2 1.740 (2) and 1.734 (2) Å] are relatively short compared with the values of 1.440 (12), 1.353 (12), 1.759 (7) and 1.733 (8) Å, respectively, reported for 2,3,6,7-tetrakis(methylthio)-benzothiophene (Parvez *et al.*, 1996*a*). The C—S distances are slightly longer than the mean value of 1.725 (1) Å for 2,3-bis(ethylsulfonyl)benzothiopene (Parvez *et al.*, 1996*b*) and 1.686 (2) and 1.714(2) Å for 1-(*p*-chlorophenyl)-5α-methoxycarbonylmethyl-4β-(2-thienyl)pyrazolidine-2-one (Sivakumar *et al.*, 1995).

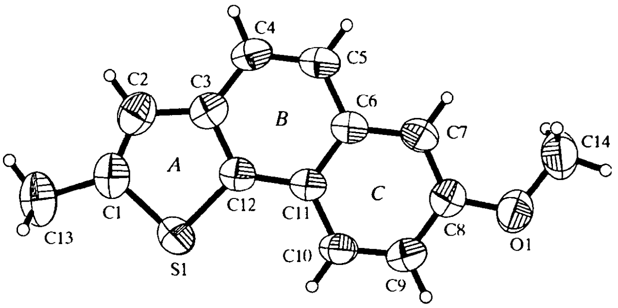


Fig. 1. The structure of (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are drawn as circles of an arbitrary radius.

The whole molecule is strictly planar within experimental error, with a maximum deviation of 0.015 (1) Å for C7. The interplanar angles between the best planes of the rings *A*/*B*, *A*/*C* and *B*/*C* are 0.96 (7), 0.99 (7) and 0.65 (7)°, respectively. The methyl group is in an antiperiplanar orientation with the S1—C1 bond [C12—S1—C1—C13 = −178.5 (2)°] and the methoxy group is coplanar with the molecule [dihedral angle 0.07 (3)°].

As in the benzothiophene structures discussed above, the crystal structure of (I) is composed of discrete molecules separated by van der Waals contacts but with no hydrogen bonds (Olive *et al.*, 1992). The S atoms are in a *trans* orientation, packed along the *ac* diagonal.

Experimental

The preparative method started from 6-methoxy-1-tetralone with Vilsmeir–Haack reagent (phosphorus oxychloride and dimethylformamide), producing 1-chloro-6-methoxy-2,3-dihydronaphthalene-2-carboxaldehyde in excellent yield (Ray *et al.*, 1979) which, on condensation with thioglycollic acid in a basic medium, produced 7-methoxy-4,5-dihydronaphtho-[1,2-*b*]thiophene-2-carboxylic acid in 60% yield (Ghosh *et al.*, 1981). Decarboxylation followed by dehydrogenation (Kar *et al.*, 1991) produced 7-methoxynaphtho[1,2-*b*]thiophene in excellent yield. Treatment with *n*-butyllithium and methyl iodide converted the parent thiophene derivative to the methyl derivative, (I), exclusively (Pan & Ray, 1999). We were able to prepare a crystal of (I) for X-ray analysis by repeated crystallization from a petroleum ether (333–353 K)/chloroform mixture (m.p. 401–403 K).

Crystal data

$C_{14}H_{12}OS$
$M_r = 228.30$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å

Monoclinic
$P2_1/n$
$a = 7.5611$ (2) Å
$b = 8.1393$ (1) Å
$c = 18.9671$ (4) Å
$\beta = 94.798$ (1)°
$V = 1163.18$ (4) Å^3
$Z = 4$
$D_x = 1.304$ Mg m^{-3}
D_m not measured

Cell parameters from 4959 reflections
$\theta = 2.16$–28.33°
$\mu = 0.252$ mm^{-1}
$T = 293$ (2) K
Slab
$0.48 \times 0.34 \times 0.16$ mm
Colourless

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.89$, $T_{\max} = 0.96$
7772 measured reflections
2845 independent reflections

2157 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.034$
$\theta_{\max} = 28.27°$
$h = -10 \rightarrow 9$
$k = -10 \rightarrow 7$
$l = -25 \rightarrow 24$
Intensity decay: negligible

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.121$
$S = 1.043$
2845 reflections
147 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0597P)^2 + 0.1025P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.21$ e Å^{-3}
$\Delta\rho_{\min} = -0.16$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

S1—C12	1.734 (2)	O1—C14	1.432 (2)
S1—C1	1.740 (2)	C1—C13	1.513 (2)
O1—C8	1.366 (2)		
C12—S1—C1	92.1 (1)	C1—C2—C3	114.1 (2)
C8—O1—C14	117.0 (1)	C12—C3—C2	111.8 (1)
C2—C1—S1	111.5 (1)		

All the H atoms were fixed geometrically and allowed to ride on the atoms to which they are attached.

Data collection: *SMART* (Siemens, 1996). Cell refinement: *SAINT* (Siemens, 1996). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1318). Services for accessing these data are described at the back of the journal.

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10,11-Dibromo-3,6-ditosyl-3,6-diazabicyclo[6.4.0]dodeca-1(8),9,11-triene

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Abstract

The molecules of the title compound, $C_{24}H_{24}Br_2N_2O_4S_2$, crystallize in the tetragonal system, space group $P4_12_12$. The compound possesses a crystallographic twofold axis. The dihedral angle between the tosyl

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