All H atoms were located from the difference Fourier map and were refined isotropically; C—H distances are in the range 0.93 (2)–0.96 (2) Å.

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: SK1301). Services for accessing these data are described at the back of the journal.

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(*E*)-1,2-Bis(3,4-dihydro-1-methoxynaphthalen-2-yl)ethylene

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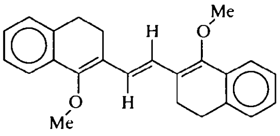
Abstract

In the structure of the title compound, $C_{24}H_{24}O_2$, one of the two types of six-membered rings is planar and the other is in a skew-boat conformation. The ethylene C=C bond distance is 1.345 (3) Å. The substituents at the ethylene are in an *E* configuration. The crystal structure consists of discrete molecules lying about inversion centres, held together by van der Waals contacts.

Comment

Reductive dimerization of carbonyl compounds with the low-valent titanium reagents developed by McMurry & Flaming (1974) has been utilized by synthetic organic chemists. Recently, we have developed a highly stereoselective method for the formation of 1,6-disubstituted 1,3,5-hexatriene derivatives. Use of the technique of reductive dimerization of carbonyl compounds with low-valent titanium reagents to produce stereoselective alkenes is of great use in the synthesis of bioactive molecules, *viz.* retinals and carotenes (Dams & Malinowski, 1982; McMurry *et al.*, 1978). The diastereomeric nature of the new double bond formed during the reaction is dependent on the reagents and reaction conditions. The stereochemistry (*i.e.* whether C1=C10 is *cis* or *trans*) of the title compound, (I), was difficult to assign from ^{1}H NMR data and so determination of the structure by X-ray crystallography was essential.



(I)

The ethylene C=C [C12=C12^i; symmetry code: (i) $2-x$, $-y$, $2-z$] bond distance of 1.345 (3) Å is slightly longer than the reported values of 1.314 (6) Å in unsubstituted ethylene (van Nes & Vos, 1977) and 1.312 Å for a Csp^2—Csp^2 distance of the *trans* type reported in the Cambridge Structural Database (Allen *et al.*, 1987), and is comparable with the value of 1.342 (3) Å for 1,1-bis(*p*-ethoxyphenyl)ethylene reported by Banerjee *et al.* (1985). In the case of polarized ethylenes, an appreciable lengthening of this bond has been reported by Adhikesavalu & Venkatesan (1981, 1982, 1983). The average C—C distance of 1.390 (3) Å within the aromatic ring (*A*) is in agreement with the value of 1.397 Å for C_{aryl}—C_{aryl} distances (Allen *et al.*, 1987). The widening of the angle at C12 [125.9 (2)°] may be due to the weak intramolecular C—H···O interaction between H12*A* and O1 [C12···O1 2.809 (2) Å]. The symmetry-related molecule is in an antiperiplanar orientation, with a torsion angle of 180° through the ethylene bond.

The aromatic ring *A* is essentially planar. The total puckering amplitude Q_T (Cremer & Pople, 1975) of 0.439 (2) shows that the non-aromatic ring (*B*) adopts a skew-boat conformation, with O1 and C12 deviating

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by 0.306 (1) and 0.332 (1) Å, respectively. Rings *A* and *B* have an interplanar angle of 12.47 (7)° between them.

The crystal structure of (I) consists of layers of molecules along the *b* direction held together by van der Waals contacts, while discrete molecules form chain-like structures along the *c* axis.

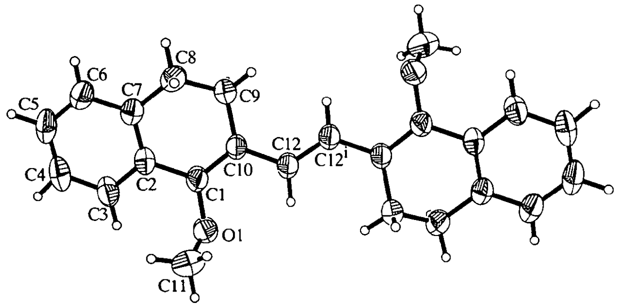

Fig. 1. Displacement ellipsoid plot of (I) at the 50% probability level (*SHELXTL*; Sheldrick, 1997). H atoms are shown as spheres of arbitrary radii [symmetry code: (i) 2 − *x*, −*y*, 2 − *z*].

Experimental

The title compound was prepared from 1-methoxy-2-formyl-3,4-dihydronaphthalene by treatment with titanium tetrachloride and zinc in dimethoxyethane (DME) under an argon atmosphere (Gupta *et al.*, 1999). The starting material was prepared from 1-chloro-2-formyl-3,4-dihydronaphthalene by treatment with sodium methoxide in methanol (Sami *et al.*, 1992). The single crystal used for X-ray analysis was obtained by slow crystallization from chloroform and petroleum ether (m.p. 428–430 K).

Crystal data

$C_{24}H_{24}O_2$
$M_r = 344.43$
Monoclinic
$P2_1/n$
$a = 8.6658\ (4)$ Å
$b = 8.3101\ (4)$ Å
$c = 13.1431\ (5)$ Å
$\beta = 98.336\ (1)°$
$V = 936.48\ (7)$ Å^3
$Z = 2$
$D_x = 1.221$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 3582 reflections
$\theta = 2.65–28.32°$
$\mu = 0.076$ mm^{-1}
$T = 293\ (2)$ K
Parallelepiped
0.44 × 0.24 × 0.20 mm
Yellow

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: none
6151 measured reflections
2290 independent reflections
1676 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.032$
$\theta_{\rm max} = 28.27°$
$h = -11 \rightarrow 11$
$k = -8 \rightarrow 11$
$l = -14 \rightarrow 17$
Intensity decay: negligible

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.140$
$S = 1.051$
2290 reflections
155 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0730P)^2 + 0.0644P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.200$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.153$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

O1—C1	1.386 (2)	C10—C12	1.453 (2)
O1—C11	1.429 (2)	C12—C12ⁱ	1.345 (3)
C1—O1—C11	114.5 (1)	C12—C10—C9	121.3 (1)
C3—C2—C1	121.8 (1)	C12ⁱ—C12—C10	125.9 (2)
C6—C7—C8	122.5 (1)		

Symmetry code: (i) 2 − *x*, −*y*, 2 − *z*.

All H atoms other than the methyl group H atoms were refined isotropically. C—H distances vary in the range 0.92 (2)–1.01 (2) Å.

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: SK1314). Services for accessing these data are described at the back of the journal.

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

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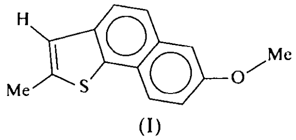
(*Received 7 July 1999; accepted 12 July 1999*)

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).

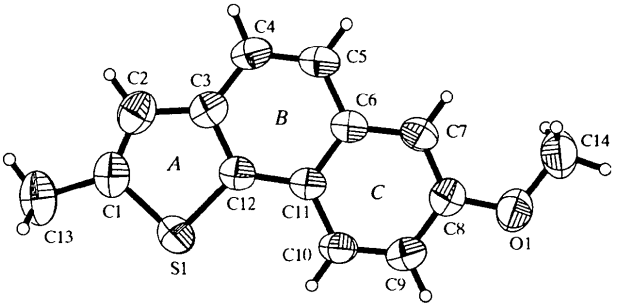


Fig. 1. The structure of (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are drawn as circles of an arbitrary radius.

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

$C_{14}H_{12}OS$	Mo $K\alpha$ radiation
M_r = 228.30	λ = 0.71073 Å