The unit-cell parameters were checked for the presence of higher lattice symmetry (Spek, 1988). Data were collected during 31 h of X-ray exposure time, with scan angle $\Delta\omega = (1.24 + 0.14\tan\theta)^\circ$, horizontal aperture 3.83 mm, vertical aperture 6.00 mm. The space group was derived from observed systematic absences. R is calculated for 1115 reflections with $F > 4\sigma(F)$; wR is based on F^2. H atoms were introduced at calculated positions, riding on their carrier atoms. The methyl group was refined as a rigid group, allowing for rotation around the C—C bond. H atoms were refined with a fixed isotropic displacement parameter related to the value of the equivalent isotropic displacement parameter of the carrier atom by a factor of 1.5 for the methyl H atoms and 1.2 for all other H atoms.

Data collection: locally modified *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *SET*4 (de Boer & Duisenberg, 1984). Data reduction: *HELENA* (Spek, 1993). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *PLUTON* (Spek, 1995). Software used to prepare material for publication: *PLATON* (Spek, 1990).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1205). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Methyl 3-(4-Methoxyphenylmethylene)dithiocarbazate

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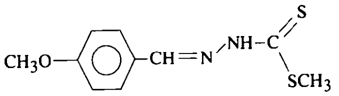
(*Received 9 May 1995; accepted 19 July 1995*)

Abstract

The molecular conformation of the title compound, $C_{10}H_{12}N_2OS_2$, is almost planar. The structure is governed by N—H···S hydrogen bonds, leading to the formation of centrosymmetric dimers.

Comment

In recent years, many metal complexes of sulfur–nitrogen chelating agents have been studied (Ali & Bose, 1984; Ali, Hossain, Majumder & Uddin, 1987; Simon, 1994). Aside from showing interesting physicochemical properties, some of these complexes have been found to display carcinostatic activity (Sunl, 1985). This work is a continuation of our studies on metal complexes with ligands containing S and N as donor atoms (Fun, Sivakumar, Yip, Tian, Duan, Lu & You, 1995), and we now report the synthesis and crystal structure of a new Schiff-base compound derived from 4-methoxybenzaldehyde and methyl dithiocarbazate, *i.e.* methyl 3-(4-methoxyphenylmethylene)dithiocarbazate, (I).



(I)

Fig. 1 shows an *ORTEP* plot (Johnson, 1965) of (I) with the atom-numbering scheme used. The molecule adopts an almost planar conformation. The largest torsion angle involving non-H atoms is 6.4 (2)° for C1—N1—N2—C2. Bond lengths and angles are normal except that the N1—C1 distance of 1.329 (2) Å is shorter than the value typical of a single bond (*International Tables for Crystallography*, Vol. C, 1995). This is due to electron delocalization and was also observed in benzyl 3-(4-dimethylaminophenylmethylene)dithiocarbazate (Fun *et al.*, 1995).

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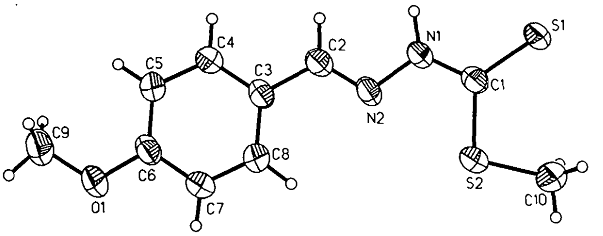

Fig. 1. *ORTEP* (Johnson, 1965) plot of (I) with the atom-numbering scheme showing 50% probability displacement ellipsoids.

In the crystal lattice, molecules are linked by N—H···S hydrogen bonds [N1—H1N 0.96 (2), N1···S1^i 3.439 (1), H1N···S1^i 2.51 (2) Å and N1—H1N···S1^i 164 (2)°; symmetry code (i): $-x, -y+2, -z$] into planar dimers (Fig. 2), which lie parallel to the (122) plane.

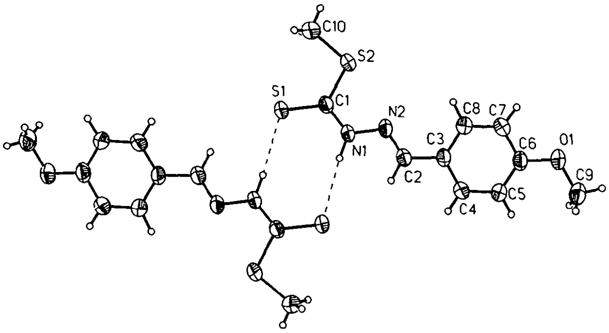

Fig. 2. *ORTEP* plot of the dimer showing the hydrogen bonds.

Experimental

The title compound was prepared by refluxing a 1:1 molar ratio of *S*-methyl dithiocarbazate and 4-methoxybenzaldehyde in methanol. Colourless crystals appeared and single crystals suitable for X-ray diffraction analysis, grown from ethanol at room temperature, were obtained after several days.

Crystal data

$C_{10}H_{12}N_2OS_2$
$M_r = 240.34$
Triclinic
$P\overline{1}$
$a = 4.5834\,(5)$ Å
$b = 11.6598\,(8)$ Å
$c = 12.0208\,(9)$ Å
$\alpha = 65.239\,(6)°$
$\beta = 84.621\,(8)°$
$\gamma = 89.296\,(8)°$
$V = 580.52\,(8)$ Å^3
$Z = 2$
$D_x = 1.375$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 37 reflections
$\theta = 5$–$12.5°$
$\mu = 0.433$ mm^{-1}
$T = 293\,(2)$ K
Needle
0.56 × 0.26 × 0.10 mm
Colourless

Data collection

Siemens *P*4 four-circle diffractometer
θ–2θ scans
Absorption correction: none
3506 measured reflections
2559 independent reflections
1850 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int} = 0.0189$
$\theta_{\rm max} = 27.49°$
$h = -1 \rightarrow 5$
$k = -13 \rightarrow 13$
$l = -15 \rightarrow 15$
3 standard reflections monitored every 97 reflections
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0326$
$wR(F^2) = 0.0869$
$S = 0.925$
2559 reflections
184 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0494P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.17$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.24$ e Å^{-3}
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
S1	0.05893 (10)	0.80812 (4)	0.14197 (4)	0.04739 (14)
S2	−0.29213 (11)	0.80367 (4)	0.37096 (4)	0.0547 (2)
N1	−0.3033 (3)	0.97969 (13)	0.15131 (12)	0.0422 (3)
N2	−0.5066 (3)	1.02865 (13)	0.21075 (13)	0.0427 (3)
O1	−1.4278 (3)	1.39124 (12)	0.32204 (12)	0.0604 (4)
C1	−0.1797 (4)	0.87040 (14)	0.21348 (13)	0.0376 (3)
C2	−0.6301 (4)	1.1269 (2)	0.1406 (2)	0.0424 (4)
C3	−0.8467 (4)	1.19226 (15)	0.18823 (14)	0.0399 (4)
C4	−0.9724 (4)	1.2991 (2)	0.1068 (2)	0.0441 (4)
C5	−1.1695 (4)	1.3680 (2)	0.1468 (2)	0.0451 (4)
C6	−1.2447 (4)	1.3286 (2)	0.2718 (2)	0.0440 (4)
C7	−1.1280 (5)	1.2188 (2)	0.3547 (2)	0.0528 (5)
C8	−0.9305 (4)	1.1516 (2)	0.3143 (2)	0.0484 (4)
C9	−1.5419 (6)	1.5071 (2)	0.2408 (2)	0.0643 (6)
C10	−0.0990 (6)	0.6592 (2)	0.4242 (2)	0.0640 (6)

Table 2. *Selected geometric parameters (Å, °)*

S1—C1	1.6703 (15)	C2—C3	1.461 (2)
S2—C1	1.746 (2)	C3—C4	1.381 (2)
S2—C10	1.788 (2)	C3—C8	1.401 (2)
N1—C1	1.329 (2)	C4—C5	1.385 (2)
N1—N2	1.382 (2)	C5—C6	1.384 (2)
N2—C2	1.268 (2)	C6—C7	1.389 (2)
O1—C6	1.365 (2)	C7—C8	1.374 (2)
O1—C9	1.423 (2)		
C1—S2—C10	102.02 (9)	C4—C3—C2	119.30 (14)
C1—N1—N2	120.52 (13)	C8—C3—C2	122.5 (2)
C2—N2—N1	114.96 (13)	C3—C4—C5	121.9 (2)
C6—O1—C9	117.84 (15)	C6—C5—C4	119.2 (2)
N1—C1—S1	120.97 (11)	O1—C6—C5	124.4 (2)
N1—C1—S2	113.56 (11)	O1—C6—C7	115.99 (15)
S1—C1—S2	125.47 (9)	C5—C6—C7	119.59 (14)
N2—C2—C3	122.21 (15)	C8—C7—C6	120.8 (2)
C4—C3—C8	118.25 (15)	C7—C8—C3	120.2 (2)

The structure was solved by direct methods and refined by the full-matrix least-squares method. All H atoms were located from difference Fourier maps and refined isotropically. *PARST* (Nardelli, 1983) was used for geometrical calculations.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*a*). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990*b*). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1198). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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α-Phenylselenomethoxycarbonylmethyl(triphenyl)arsorane

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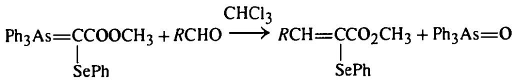
Abstract

The crystal structure of α-phenylselenomethoxycarbonylmethyl(triphenyl)arsorane, $[Ph_3AsC(COOCH_3)SePh]$, has been determined by X-ray diffraction. The compound is a stable α-organoselenoarsonium ylide. Delocalization of electronic density appears to be restricted from atoms O(1) to Se including the As atom. The As—C(1) and Se—C(1) bonds have double-bond characteristics.

Comment

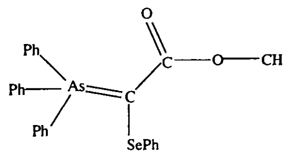
As the Wittig reaction played an important role in olefination, a number of relevant investigations have been performed. Although α-selenophosphonium ylides have been synthesized, α-seleno-substituted phosphonium ylides containing an α-electron-attracting group cannot undergo a Wittig reaction (Petragnani, Rodrigues & Comasseto, 1976; Braga, Comasseto & Petragnani, 1984). Considering that the reactivity of arsonium ylides is higher than that of corresponding phosphonium ylide, we recently synthesized α-phenylselenomethoxycarbonylmethyltriphenylarsorane, which is the first example of an α-seleno-substituted arsonium ylide. Moreover, we found that the compound had sufficient activity to undergo a Wittig-type reaction and so developed the first method of stereoselective synthesis of (*Z*)-α-phenylseleno-α,β-unsaturated esters (Huang, Huang & Huang, 1995).



$$\mathrm{Ph_3As{=}\underset{\substack{|\\ SePh}}{C}COOCH_3} + R\mathrm{CHO} \xrightarrow{\mathrm{CHCl_3}} R\mathrm{CH{=}\underset{\substack{|\\ SePh}}{C}CO_2CH_3} + \mathrm{Ph_3As{=}O}$$

$R = C_6H_5$-, 4-ClC_6H_4-, 4-$CH_3C_6H_4$-, 4-$NO_2C_6H_4$-, $(CH_3)_2CHCH_2$-, CH_3CHCH-

The molecular structures of arsonium ylides have been studied previously (Shao, Jin, Tang, Huang & Huang, 1982; Fan & Shen, 1984; Ferguson & Rendle, 1975, 1976; Hu, Shi, Huang, Dong & Huang, 1989). To our knowledge, however, no information on the structure of an α-selenoarsonium(phosphonium) ylide has been reported. The present investigation was undertaken in order to characterize the stability and reactivity of the title compound, (I).



(I)

Fig. 1 is an *ORTEP* (Johnson, 1965) diagram of the molecule $[Ph_3AsC(COOCH_3)SePh]$. As can be seen, the geometry at the As atom is a distorted tetrahedron. There are two kinds of As—C bond: As—C(Ph) has a mean length of 1.931 (9) Å and As—C(1) a mean length of 1.824 (9) Å. The former is in good agreement with the reported value [1.932 (6) Å] for 1-acetyl-2,3,4-triphenyl-5-(triphenylarsonio)cyclopentadienide (Ferguson & Rendle, 1975). The latter is approximately equal to the mean length of the As—C_{sp^2} single bond (1.897 Å;