ein Hinweis auf den *trans*-Effekt der Pd-C(11)-σ-Bindung (Maitlis, 1971). Die gefundenen Abstände Pd—O sind vergleichbar denen in anderen acetatüberbrückten dimeren Pd-Komplexen (Churchill, Wasserman & Young, 1980; Hiraki, Fuchita & Takechi, 1981; Pfeffer, Wehman & Van Koten, 1985; Ruger, Rittner, Jones, Isenberg & Sheldrick, 1981). Im Vergleich zur Summe der Kovalenzradien (Pauling, 1960) ist der Pd—C(11)-Bindungsabstand mit 1,962 (5) Å um 0,09 Å leicht verkürzt, die Pd—N-Bindungslänge 2,013 (4) Å entspricht dagegen dem erwarteten Wert. Eine deutliche Verzerrung der quadratisch-planaren Koordinationssphäre ist an dem Winkel N—Pd—C(11) [80,8 (2)°] zu erkennen, ein ähnlicher Wert [81,2 (1)°] ist auch in Pd($C_{10}H_9N_2$)(acac) (Hiller, Castineiras, Strähle, Suarez, Vila, Gayoso, Gayoso & Garcia Fernandez, 1986) zu beobachten. Der Abstand Pd$\cdots$Pd^i beträgt 3,194 (1) Å, in analog gebauten bis(μ-carboxylato)Pd-Verbindungen variieren diese Werte von 2,84 Å bis 2,96 Å und werden als nichbindend betrachtet (Churchill, Wasserman & Young, 1980; Wong-Ng, Cheng, Kocman, Lüth & Nyburg, 1979; Zocchi, Tieghi & Albinati, 1973).

Die Geometrie des Schiffsche Base-Liganden ist in guter Übereinstimmung mit den Literaturwerten (Alyea, Dee & Ferguson, 1985; Castineiras, Hiller, Strähle, Sousa, Rodriguez, Bastida & Sanchez-Bermudez, 1986). Die Ebenen [Pd, C(3), N, C(21)] und [N, C(21), C(22), C(26)] bilden einen Diederwinkel von 71,5 (8)°.

Literatur

ALYEA, E. C., DEE, T. D. & FERGUSON, G. (1985). *J. Cryst. Spectrosc. Res.* **15**, 29–38.
CASTINEIRAS, A., HILLER, W., STRÄHLE, J., SOUSA, A., RODRIGUEZ, A., BASTIDA, R. & SANCHEZ-BERMUDEZ, A. (1986). *Acta Cryst.* In Druck.
CHURCHILL, M. R., WASSERMAN, H. J. & YOUNG, G. J. (1980). *Inorg. Chem.* **19**, 762–770.
FRENZ, B. A. (1978). *The Enraf–Nonius CAD-4 SDP – A Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Solution.* In *Computing in Crystallography,* herausgegeben von H. SCHENK, R. OLTHOF-HAZEKAMP, H. VAN KONINGSVELD & G. C. BASSI. Delft Univ. Press.
HILLER, W., CASTINEIRAS, A., STRÄHLE, J., SUAREZ, A., VILA, J. M., GAYOSO, E., GAYOSO, M. & GARCIA FERNANDEZ, M. E. (1986). *Z. Anorg. Allg. Chemie.* In Druck.
HIRAKI, K., FUCHITA, Y. & TAKECHI, K. (1981). *Inorg. Chem.* **20**, 4316–4320.
International Tables for X-ray Crystallography (1974). Bd. IV. Tabelle 2.2B. Birmingham: Kynoch Press. (Gegenwertiger Verteiler D. Reidel, Dordrecht.)
MAITLIS, P. M. (1971). *The Organic Chemistry of Palladium.* Bd. 1. S. 37–41. New York: Academic Press.
MAUGH, T. H. II (1983). *Science,* **220**, 592–595.
NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
PAULING, L. (1960). *Die Natur der chemischen Bindung,* 3. Aufl. S. 224. Weinheim: Verlag Chemie.
PFEFFER, M. M., WEHMAN, E. & VAN KOTEN, G. (1985). *J. Organomet. Chem.* **282**, 127–131.
RUGER, R., RITTNER, W., JONES, P. G., ISENBERG, W. & SHELDRICK, G. M. (1981). *Angew. Chem. Int. Ed. Engl.* **20**, 382–383.
VILA, J. M., PEREIRA, M. T., GAYOSO, E. & GAYOSO, M. (1985). 8th Ann. Meet. Chem. Soc. Portugal, Braga. Abstr. 277–278.
WONG-NG, W., CHENG, P. T., KOCMAN, V., LÜTH, H. & NYBURG, S. C. (1979). *Inorg. Chem.* **18**, 2620–2623.
ZACHARIASEN, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.
ZOCCHI, M., TIEGHI, G. & ALBINATI, A. (1973). *J. Chem. Soc. Dalton Trans.* S. 883–885.

Diphenyl[8-quinolinethiolato(1−)-S]antimony(III)

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Abstract. [Sb(C_9H_6NS)(C_6H_5)$_2$], $M_r = 436 \cdot 18$, monoclinic, $P2_1/n$, $a = 13 \cdot 441$ (4), $b = 9 \cdot 314$ (4), $c = 15 \cdot 178$ (4) Å, $\beta = 109 \cdot 47$ (5)°, $V = 1791$ Å^3, $Z = 4$, $D_x = 1 \cdot 618$ Mg m^{-3}, λ(Mo $K\alpha) = 0 \cdot 71069$ Å, $\mu = 1 \cdot 67$ mm^{-1}, $F(000) = 864$, $T = 294$ (1) K. Final $R = 0 \cdot 032$ for 2630 unique observed X-ray diffractometer data. The 8-quinolinethiolato(1−) ligand chelates Sb *via* S [Sb—S: $2 \cdot 444$ (1) Å] and N [Sb—N: $2 \cdot 767$ (3) Å]. Angles around Sb: N—Sb—C(phenyl I) = $156 \cdot 7$ (1), S—Sb—C(phenyl II) = $99 \cdot 2$ (1), N—Sb—C(phenyl II) = $80 \cdot 5$ (1), S—Sb—N = $70 \cdot 7$ (1), S—Sb—C(phenyl I) = $87 \cdot 4$ (1), C(phenyl I)—Sb—C(phenyl II) = $95 \cdot 8$ (2)°. Each molecule has a close Sb$\cdots$Sb contact [$3 \cdot 884$ (1) Å] to a neighbouring symmetrically equivalent molecule. The Sb atom of the neighbouring molecule is in a *trans* position to S [Sb$\cdots$Sb—S

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= 168·30 (3)°], and *trans* to C(phenyl II) there is ample space for the lone pair. A distorted pseudo-octahedral environment around Sb can therefore be inferred. Intermolecular Sb⋯Sb interaction is proposed to occur *via* quasi-annular four-electron-two-centre bonding.

Introduction. Rather few structures of organoantimony(III) compounds are known, and a better knowledge of the structural chemistry of such compounds should be rewarding with respect to stereochemical implications of the lone pair and for reasons of comparison with inorganic antimony(III) compounds of which more structural data exist. We report here the structure of [Sb(C_6H_5)$_2$(8-mc)] (8-mcH = 8-mercaptoquinoline) as a first example of an organoantimony(III) compound with a weak intermolecular Sb⋯Sb interaction.

Experimental. [SbPh$_2$(8-mc)] was prepared by adding a filtered solution of Na(8-mc) in 40 ml ethanol (from 10 mmol Na and 5 mmol 8-mcH.HCl) and 5 mmol [Ph$_2$SbCl] in 100 ml ethanol and boiling the suspension for 30 min. The mixture was brought to dryness at max. 303 K. [SbPh$_2$(8-mc)] was extracted with 100 ml CHCl$_3$ and crystallized on evaporating the solution to 5 ml (yield 56%, analysis: C found/calc. 57·63/57·83; H 3·76/3·67; Sb 27·82/27·94; N 3·15/3·21; m.p. 430–431 K). Single crystals obtained by recrystallization from Me$_2$SO. Crystal size 0·26 × 0·30 × 0·43 mm, $\omega/2\theta$ scan, scan speed 0·04–0·01° s^{-1} in θ, Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation; lattice parameters from least-squares fit with 25 reflexions in range 8·7 ≤ θ ≤ 14·4°, four standard reflexions recorded every 5 h, only random deviations; 3538 reflexions, 2 ≤ θ ≤ 25°, 0 ≤ h ≤ 16, 0 ≤ k ≤ 11, −18 ≤ l ≤ 18 after averaging 3289 unique reflexions (R_{int} = 0·01, 249 reflexions averaged), 2630 with $I > 3\sigma(I)$; Lorentz and polarization correction, absorption correction *via* ψ scans, max./min. transmission 1·00/0·92; systematic absences ($h0l$) $h + l = 2n + 1$, ($0k0$) $k = 2n + 1$, space group $P2_1/n$; crystal structure solved *via* Patterson function and subsequent ΔF syntheses; refined by full-matrix least squares with anisotropic temperature factors for all non-H atoms, H atoms placed in geometrically calculated positions (C–H 1·08 Å), not included in F calculations, refinement based on F and 217 refined parameters, no extinction correction, $R = 0·032$, $S = 1·96$, unit weights; maximum and average shift over e.s.d. lower than 0·00, largest peak in final ΔF map ±1·0 (2) e Å^{-3} near Sb; calculations with Enraf–Nonius *SDP* (Enraf–Nonius, 1979), complex neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974), figures drawn with *ORTEP*II (Johnson, 1976) and *POP*1 (van de Waal, 1976).

Discussion. The structure of the title compound is shown in Fig. 1 and in a stereoview in Fig. 2. Positional parameters and equivalent values of the anisotropic temperature factors are given in Table 1.* Bond lengths and bond angles are given in Table 2. In the molecule the central Sb atom is bound to two phenyl groups and to the S atom and the N atom of the 8-quinolinethiolato(1−) ligand. The Sb–N distance is longer than the sum of the covalent radii of Sb and N (1·41 and 0·70 Å; Pauling, 1970), whereas the Sb–C and the Sb–S bond lengths agree fairly well with the corresponding sums of the covalent radii: C 0·77, S 1·04 Å. In the title compound the Sb–S bond distance seems to be somewhat shorter and the Sb–N bond length somewhat longer than those in Sb(8-mc)$_3$ (Sb–S: 2·48, 2·50 Å; Sb–N: 2·71, 2·73 Å; σ is not given; Pecs, Ozols & Ievins, 1973). Sb–C distances correspond to those in other phenylantimony compounds (Kuz'mina, Bokii, Timofeeva, Struchkov, Kravtsov & Pombrik, 1978; Bone & Sowerby, 1980). C–C and C–N bond lengths in the quinoline ring are in the range of those in
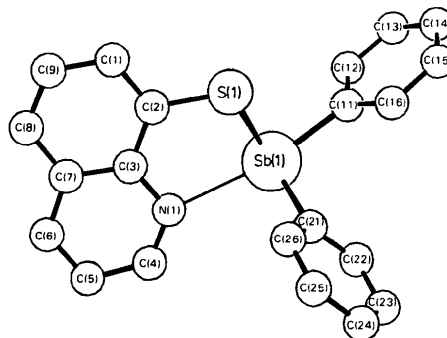

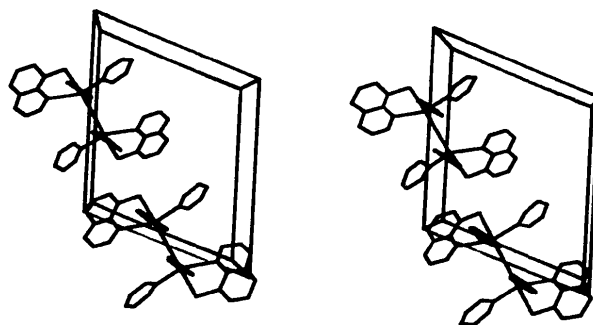Fig. 1. General view of the molecule showing atom numbering.

Fig. 2. Stereoscopic view of the unit cell. The short intermolecular Sb⋯Sb contact is shown by a line drawn connecting the Sb atoms of neighbouring molecules. The a axis is approximately horizontal and the c axis vertical.

other metal(8-mc) compounds (Ievins, Ozola, Ozola & Pecs, 1973); C(3)—C(7) is significantly longer than 1·40 Å as in other (8-mc) compounds of metals with complete d orbitals (Ievins *et al.*, 1973).

Table 1. *Final fractional atomic coordinates and equivalent isotropic thermal parameters* (Å² × 10³)

$$U_{eq} = \frac{1}{24\pi^2} \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	U_{eq}
Sb(1)	0·42007 (2)	0·03002 (4)	0·08401 (2)	43
S(1)	0·3183 (1)	0·1188 (2)	0·17946 (9)	50
N(1)	0·2070 (3)	−0·0021 (5)	−0·0134 (3)	37
C(1)	0·1443 (4)	0·2867 (6)	0·1218 (4)	58
C(2)	0·1973 (4)	0·1749 (6)	0·0975 (3)	44
C(3)	0·1530 (4)	0·1038 (6)	0·0096 (3)	47
C(4)	0·1661 (5)	−0·0703 (7)	−0·0927 (4)	73
C(5)	0·0628 (6)	−0·0369 (8)	−0·1574 (5)	84
C(6)	0·0081 (5)	0·0734 (8)	−0·1362 (4)	76
C(7)	0·0508 (4)	0·1491 (6)	−0·0515 (4)	58
C(8)	−0·0011 (4)	0·2641 (7)	−0·0255 (4)	73
C(9)	0·0444 (4)	0·3313 (7)	0·0592 (4)	73
C(11)	0·5606 (3)	0·0578 (6)	0·2060 (4)	48
C(12)	0·6199 (4)	0·1819 (7)	0·2081 (5)	70
C(13)	0·7071 (5)	0·2112 (8)	0·2897 (5)	84
C(14)	0·7328 (4)	0·1194 (8)	0·3652 (5)	75
C(15)	0·6755 (5)	−0·0040 (8)	0·3620 (4)	73
C(16)	0·5881 (4)	−0·0348 (7)	0·2818 (4)	62
C(21)	0·4047 (4)	−0·1968 (5)	0·1021 (3)	41
C(22)	0·4819 (4)	−0·2866 (6)	0·0908 (4)	56
C(23)	0·4711 (5)	−0·4360 (6)	0·0969 (4)	66
C(24)	0·3837 (5)	−0·4926 (6)	0·1138 (4)	65
C(25)	0·3080 (5)	−0·4021 (7)	0·1264 (4)	65
C(26)	0·3181 (4)	−0·2541 (6)	0·1205 (4)	53

Table 2. *Bond distances* (Å) *and angles* (°) *in* [Sb(C₉H₆NS)(C₆H₅)₂]

Sb(1)—C(11)	2·176 (4)	Sb(1)—S(1)	2·444 (1)
Sb(1)—C(21)	2·149 (5)	Sb(1)···N(1)	2·767 (3)
Sb(1)···Sb(1)(1−x,ȳ,z̄)	3·884 (1)		
S(1)—C(2)	1·765 (4)	C(6)—C(7)	1·409 (8)
C(2)—C(3)	1·430 (7)	C(7)—C(8)	1·404 (8)
C(3)—N(1)	1·338 (6)	C(8)—C(9)	1·377 (9)
N(1)—C(4)	1·308 (8)	C(9)—C(1)	1·423 (7)
C(4)—C(5)	1·442 (8)	C(1)—C(2)	1·380 (7)
C(5)—C(6)	1·363 (9)	C(3)—C(7)	1·440 (6)
S(1)—Sb(1)—N(1)	70·7 (1)	N(1)—Sb(1)—C(11)	156·7 (1)
S(1)—Sb(1)—C(11)	87·4 (1)	N(1)—Sb(1)—C(21)	80·5 (1)
S(1)—Sb(1)—C(21)	99·2 (1)	C(11)—Sb(1)—C(21)	95·8 (2)
Sb(1)—C(11)—C(12)	116·4 (4)	Sb(1)—C(21)—C(22)	118·0 (3)
Sb(1)—C(11)—C(16)	123·2 (3)	Sb(1)—C(21)—C(26)	121·7 (3)
Sb(1)—C(2)—C(2)	104·4 (2)	C(2)—C(3)—N(1)	119·4 (4)
S(1)—C(2)—C(1)	118·2 (4)	C(6)—C(7)—C(8)	123·3 (5)
S(1)—C(2)—C(3)	121·3 (3)	C(3)—N(1)—C(4)	120·0 (4)
C(1)—C(2)—C(3)	120·5 (4)	N(1)—C(4)—C(5)	122·3 (5)
C(2)—C(3)—C(7)	118·5 (4)	C(4)—C(5)—C(6)	118·4 (6)
C(3)—C(7)—C(8)	119·9 (5)	C(5)—C(6)—C(7)	120·3 (5)
C(7)—C(8)—C(9)	120·2 (5)	C(6)—C(7)—C(3)	116·9 (5)
C(8)—C(9)—C(1)	121·1 (5)	C(7)—C(3)—N(1)	122·1 (4)
C(9)—C(1)—C(2)	119·9 (5)		
Sb(1)···Sb(1)—C(11)	93·6 (1)	Sb(1)···Sb(1)—S(1)	168·30 (3)
Sb(1)···Sb(1)—C(21)	92·3 (1)	Sb(1)···Sb(1)—N(1)	109·52 (8)

The C—C distances and the C—C—C angles in the phenyl groups are in the ranges 1·376 (9) to 1·419 (9) Å [mean value 1·393 (9) Å] and 118·5 (6) to 120·8 (6)° [mean value 120·0 (5)°].

Each molecule has a short Sb···Sb(1−x,ȳ,z̄) contact [3·884 (1) Å] to a neighbouring symmetrically equivalent molecule (Fig. 2). A van der Waals radius derived from nonbonded contact distances in crystals has not been determined for Sb. Following the results given by Bondi (1964) this value should be close to 2·09 Å. That means the observed Sb···Sb distance is significantly shorter than the corresponding sum, indicating weak intermolecular interaction. Still shorter intermolecular Sb···Sb distances have been observed in the inorganic Sb^{III} compounds tris(1-pyrrolidinecarbodithioato)Sb [3·517 (9) Å; Kavounis, Kokkou, Rentzeperis & Karagiannidis, 1980] and tris(2-pyridinethiolato)Sb [3·657 (1) Å; Bozopoulos, Kokkou, Rentzeperis & Karagiannidis, 1984]. If the Sb atom of the neighbouring molecule is assumed to form part of the coordination sphere of Sb a distorted pyramid is formed with the C(21) atom in the apical and C(11), S(1), N(1) and Sb (neighbouring) in the basal plane. The stereochemically active 5s electron pair can then be considered to occupy the position opposite to the C(21) atom such that a distorted octahedron is formed. The interaction between the neighbouring Sb atoms could be understood as a consequence of an overlapping of the lone pair of one Sb atom and an empty orbital of the other Sb atom, and *vice versa*, so that a weak quasi-annular four-electron-two-centre bonding involving the Sb atoms results.

References

BONDI, A. (1964). *J. Phys. Chem.* **68**, 441–451.
BONE, S. P. & SOWERBY, D. B. (1980). *J. Organomet. Chem.* **184**, 181–188.
BOZOPOULOS, A. P., KOKKOU, S. C., RENTZEPERIS, P. J. & KARAGIANNIDIS, P. (1984). *Acta Cryst.* C**40**, 944–946.
Enraf–Nonius (1979). *Structure Determination Package.* Enraf–Nonius, Delft.
IEVINS, A., OZOLA, F., OZOLA, A. & PECS, L. (1973). *Latv. PSR Zinat. Akad. Vestis, Kim. Ser.* pp. 668–676, and references therein.
International Tables for X-ray Crystallography (1974). Vol. IV, Tables 2.2B and 2.3.1. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
JOHNSON, C. K. (1976). *ORTEPII.* Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.
KAVOUNIS, C. A., KOKKOU, S. C., RENTZEPERIS, P. J. & KARAGIANNIDIS, P. (1980). *Acta Cryst.* B**36**, 2954–2958.
KUZ'MINA, L. G., BOKII, N. G., TIMOFEEVA, T. V., STRUCHKOV, YU. T., KRAVTSOV, D. N. & POMBRIK, S. I. (1978). *J. Struct. Chem. (USSR)*, **19**, 279–285.
PAULING, L. (1970). *General Chemistry*, 3rd ed. San Francisco: W. H. Freeman.
PECS, L., OZOLS, J. & IEVINS, A. (1973). *Latv. PSR Zinat. Akad. Vestis, Kim. Ser.* pp. 259–266.
WAAL, B. W. VAN DE (1976). *POP1.* Plot of packing program. Twente Univ. of Technology, Enschede, The Netherlands.