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Bis(*O*,*O*-diethyl dithiophosphato)diphenyltin

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Abstract. $(C_6H_5)_2Sn[S_2P(OC_2H_5)_2]_2$, monoclinic, $P2_1/c$, $a = 14{\cdot}137$ (2), $b = 14{\cdot}299$ (7), $c = 15{\cdot}759$ (5) Å, $\beta = 112{\cdot}33$ (2)°, $Z = 4$, $D_x = 1{\cdot}44$ g cm^{-3}, μ(Ag $K\alpha$) = 6·26 cm^{-1}. $R = 7{\cdot}6\%$ for 1081 counter reflexions (20°C). The six-coordinated Sn is surrounded by two C at ~ 2·1 Å and four S atoms, two of which are at ~ 2·5 Å and two at ~ 3·2 Å. With the two C and the two S atoms at ~2·5 Å a deformed tetrahedron with approximate *mm*2 symmetry is observed. When the two remaining S atoms at ~3·2 Å are added, the coordination sphere is a strongly distorted octahedron.

Introduction. Organotin dithiophosphates are of interest because of their possible relationship with inorganic ring systems (Haiduc, 1970). Dithiophosphato groups are usually ring-forming bidentate ligands, but examples of monodentate behaviour are also known. In general, no regular patterns are known for the geometries of dithiophosphate and dithioalkyl compounds of non-transition metals. Several structural investigations of Sn complexes with dialkyl dithiocarbamates have been reported (Sheldrick & Sheldrick, 1970; Furue, Kimura, Yasuoka, Kasai & Kakudo, 1970; Kimura, Yasuoka, Kasai & Kakudo, 1972; Potenza & Mastropaolo, 1973; Lindley & Carr, 1974; Potenza, Johnson & Mastropaolo, 1976), whereas, to our knowledge, no structure of an organometallic dithiophosphate has been studied. In order to contribute to the knowledge of S-coordinated Sn, the structure of the title compound (TINSP) has been determined. Details of the chemical preparation will be published elsewhere (Haiduc, 1978).

A colourless crystal was studied on a Philips PW1100 automatic diffractometer (ω–2θ scan, $6 < 2\theta < 70°$, graphite monochromator, Ag $K\alpha$ radiation, $\lambda = 0{\cdot}5608$ Å). 1212 measurements were made; 1041 were considered as observed $[F > 3\sigma(F)]$ and used in the structure determination. Data were corrected for Lp factors but not for absorption. Cell dimensions were determined by least squares. The structure was solved by the heavy-atom technique and refined by full-matrix least-squares with *CRYLSQ* (XRAY system, 1976), the quantity minimized being $\Sigma\, w(\Delta F_o)^2$ with weights $w = 1/\sigma^2(F_o)$. Scattering factors were those of Cromer & Mann (1968) for all atoms except H which were from Stewart, Davidson & Simpson (1965). Anomalous

Table 1. *Atomic positional parameters* (×10^4 *for* Sn, P *and* S; ×10^3 *for* O, C *and* H) *of* $(C_6H_5)_2Sn[S_2P(OC_2H_5)_2]_2$

The e.s.d.'s are given in parentheses, except for C(2), C(4), C(6), C(7) and H, whose positions were kept fixed.

	x	*y*	*z*
Sn	2893 (1)	5504 (1)	5889 (1)
P(1)	1714 (7)	4293 (6)	7077 (8)
P(2)	3097 (7)	7162 (7)	4408 (7)
S(1)	1460 (6)	5556 (6)	6442 (6)
S(2)	3069 (6)	3808 (6)	7292 (6)
S(3)	4059 (7)	6160 (6)	4600 (7)
S(4)	2145 (6)	6983 (6)	5093 (6)
O(1)	82 (1)	360 (1)	653 (1)
O(2)	141 (2)	440 (1)	794 (2)
O(3)	357 (1)	817 (1)	464 (1)
O(4)	239 (2)	738 (1)	339 (1)
C(1)	77 (3)	309 (3)	569 (3)
C(2)	61	206	585
C(3)	203 (3)	502 (3)	869 (3)
C(4)	153	503	939
C(5)	436 (2)	834 (2)	561 (2)
C(6)	460	930	553
C(7)	196	655	277
C(11)	426 (2)	588 (2)	697 (2)
C(12)	519 (3)	563 (2)	695 (2)
C(13)	612 (2)	596 (2)	765 (3)
C(14)	605 (3)	652 (2)	833 (2)
C(15)	516 (3)	680 (2)	832 (2)
C(16)	425 (2)	649 (2)	763 (2)
C(21)	245 (2)	446 (2)	486 (2)
C(22)	149 (2)	450 (2)	419 (2)
C(23)	117 (2)	382 (2)	351 (2)
C(24)	182 (3)	311 (3)	353 (2)
C(25)	275 (3)	304 (2)	420 (2)
C(26)	309 (2)	372 (2)	487 (2)
H(12)	524	519	644
H(13)	684	574	767
H(14)	673	677	883
H(15)	510	724	882
H(16)	353	667	761
H(22)	100	506	422
H(23)	45	386	300
H(24)	157	260	302
H(25)	320	248	417
H(26)	381	367	540

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dispersion corrections were applied for the Sn, S and P atoms. The final $R = \Sigma|\Delta F|/\Sigma|F_o| = 7{\cdot}6\%$ for 1081 reflexions with $F > 3\sigma(F)$ (including those calculated greater than the threshold). Most of the atoms belonging to the ethyl groups were difficult to locate, probably because of their large thermal motion. As a consequence, the observed values for the C—C lengths are inaccurately determined in the terminal chains. For this reason, C(8) was not included in the final refinement and C(2), C(4), C(6) and C(7) were kept fixed. The thermal parameters were refined isotropically for the other C atoms, anisotropically for O, S, P and Sn.* H atoms were generated at expected positions for the phenyl rings but not for the ethyl groups. Positional parameters are listed in Table 1.

Discussion. Interatomic distances and angles and the numbering scheme are given in Fig. 1 and Table 2. Deviations of atoms from least-squares planes are shown in Table 3. The molecular geometry and conformation appear in Fig. 2. Earlier reports have also shown that dialkyl or diphenyl dithiophosphate and dithiocarbamate complexes of Sn, Pb and Zn show large distortions from the ideal geometries. Some of them can be classified as distorted tetrahedra (Ito, Igarashi & Hagihara, 1969), others as distorted pyramids and bipyramids (Ito, 1972; Furue *et al.*, 1970) or distorted octahedra (Lindley & Carr, 1974; Potenza, Johnson & Mastropaolo, 1976).

In TINSP the ligands can be described as anisobidentate (Potenza, Johnson & Mastropaolo, 1976). Each ligand has one normal covalent S—Sn bond of ~2·5 Å and one S···Sn distance of ~3·2 Å which could be explained by a weak interaction. The marked difference observed for the P—S distances of each ligand can probably be ascribed to the predominance of single- or double-bond character. All the S atoms lie approximately in an equatorial plane around Sn. This plane is probably best described by a least-squares

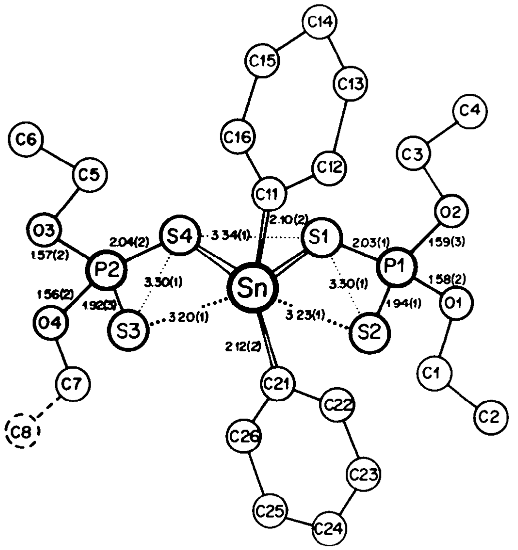

Fig. 1. Schematic drawing illustrating the atomic numbering scheme and giving some important distances (Å). The values for Sn—S(1), Sn—S(4) are respectively 2·49 (1) and 2·481 (8) Å.

Table 2. *Bond angles* (°) *for some non-hydrogen atoms*

The e.s.d.'s are given in parentheses.

C(11)—Sn—C(21)	135 (1)	S(1)—P(1)—O(1)	109·5 (9)
C(11)—Sn—S(1)	109 (1)	S(1)—P(1)—O(2)	106·2 (9)
C(11)—Sn—S(2)	80·2 (8)	S(2)—Sn—S(3)	136·9 (2)
C(11)—Sn—S(3)	84 (1)	S(2)—P(1)—O(1)	114 (1)
C(11)—Sn—S(4)	106·0 (8)	S(2)—P(1)—O(2)	117·3 (9)
C(21)—Sn—S(1)	104·2 (8)	S(3)—Sn—S(4)	69·7 (3)
C(21)—Sn—S(2)	85·2 (7)	S(3)—P(2)—S(4)	113·2 (6)
C(21)—Sn—S(3)	78·2 (8)	S(3)—P(2)—O(3)	115·7 (9)
C(21)—Sn—S(4)	105·7 (7)	S(3)—P(2)—O(4)	117 (1)
S(1)—Sn—S(2)	69·2 (3)	S(4)—P(2)—O(3)	108 (1)
S(1)—Sn—S(4)	84·5 (3)	S(4)—P(2)—O(4)	106 (1)
S(1)—P(1)—S(2)	112·4 (7)		

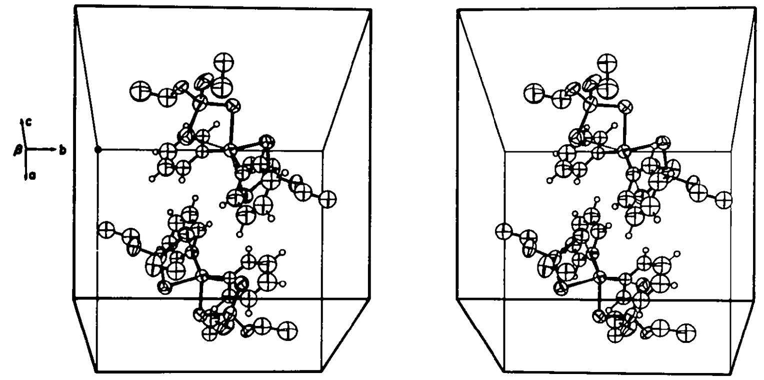

Fig. 2. Stereoscopic *ORTEP* drawing (XRAY system, 1976), showing two centrosymmetrically related molecules in the unit cell.

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No SUP 33192 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, CH1 1NZ, England.

Table 3. *Deviations* (Å) *of atoms from least-squares planes through different sets of atoms*

Plane 1: C(11), Sn, C(21)

S(1)	−1·622	S(2)	−3·036	S(3)	2·932
S(4)	1·719	P(1)	−3·307	P(2)	3·363

Plane 2: S(1), Sn, S(4)

S(2)	0·208	S(3)	−0·316	P(1)	−0·203
P(2)	−0·157	C(11)	1·919	C(21)	−1·987

Plane 3: S(2), S(3), C(11), C(21)

S(2)	0·188	S(3)	0·193	C(11)	−0·189
C(21)	−0·192	Sn	−0·991	P(1)	−1·666
P(2)	−1·686	S(1)	−2·828	S(4)	−2·833

Plane 4: S(1), S(2), S(3), S(4)

S(1)	−0·112	S(2)	0·062	S(3)	−0·062
S(4)	0·112				

Angles (°) between planes

1/2	88·3	1/3	88·2
2/3	88·3	Benzene ring 1/Benzene ring 2	27·5
3/4	89·3		

plane through S(1), S(4) and Sn with slight positive and negative deviations from the plane for S(2) and S(3) respectively. S(1)···S(4) (3·34 Å) is close in value to S(3)···S(4) and S(1)···S(2), whereas S(2)···S(3) is nearly twice as long. The related angles S(4)—Sn—S(3), S(1)—Sn—S(2) and S(1)—Sn—S(4) are 69·7, 69·2 and 84·5°, respectively, while S(2)—Sn—S(3), 136·9°, is considerably greater. A similar disposition of S atoms around the metal has been reported for $\mathrm{Te[S_2C(morpholino)_2]_2}$ and $\mathrm{Se[S_2CN(C_2H_5)_2]_2}$ (Husebye, 1970; Husebye & Helland-Madsen, 1970), with respectively two short and two long Te/Se···S distances. Similar features are also found in $\mathrm{Pb[S_2P(O\text{-}\mathit{i}\text{-}C_3H_7)_2]_2}$ (Lawton & Kokotailo, 1969). These authors have suggested that for this $\mathrm{Pb^{II}}$ compound the geometrical aspects of the observed coordination are due to the presence of a lone pair of electrons in the equatorial plane. Despite this similarity, in TINSP the Sn atom is bound to two additional phenyl groups. A still closer resemblance is therefore observed between TINSP and $\mathrm{(CH_3)_2Sn[S_2CN(CH_3)_2]_2}$ in which Sn is also bound to two additional methyl groups.

S(1), S(4), C(11) and C(21) form a distorted tetrahedron around Sn with approximate *mm*2 symmetry. C(11)—Sn—C(21) and S(1)—Sn—S(4), 135·4 and 84·5° respectively, show marked deviations from the ideal tetrahedral value. S(1) and S(4), as well as S(2)/S(3) and P(1)/P(2), are nearly equidistant from the plane through C(11), Sn and C(21). The dihedral angle shows that this plane is nearly perpendicular to the plane through S(1), Sn and S(4).

S(2), S(3), C(21), C(11) and Sn form a distorted square pyramid with Sn at the apex and at only 1 Å from the plane through the atoms forming the base. The latter plane forms angles of about 90° with planes 1, 2 and 4.

The phenyl groups are planar within experimental error and have normal distances and angles. The dihedral angle between the two rings is 27·5°. As seen in Fig. 2, the geometry of the molecule does not allow efficient packing, which is a possible explanation for both the low density and the large vibrational motion of the side chains.

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