DIPHENYLANTIMONY(III) DIPHENYLPHOSPHINATE AND DIPHENYLMONOTHIOPHOSPHINATE: SYNTHESIS, SPECTRA AND CRYSTAL STRUCTURE

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Summary

Infrared data suggest that in diphenylantimony(III) diphenylphosphinate and diphenylthiophosphinate, $Ph_2Sb[OP(X)Ph_2]$, where X = O (1) or S (2), the ligands are symmetrically bonded, either as chelating or bridging groups, and the presence of the latter has been confirmed by X-ray diffraction. $Ph_2SbO_2PPh_2$ (1) is orthorhombic, space group $P2_12_12_1$, with a 9.185(4), b 11.075(4), c 21.099(7) Å and Z 4. $Ph_2SbOSPPh_2$ (2) is monoclinic, space group $P2_1/n$ with, a 9.842(4), b 10.561(4), c 21.182(7) Å, β 93.19(4)° and Z 4. In both compounds diphenylantimony(III) groups are linked into chains by bridging phosphinate or thiophosphinate groups and antimony achieves pseudotrigonal bipyramidal coordination with the two phenyl groups in equatorial positions. The axial positions are occupied by oxygen and sulphur atoms of the ligands. The independent Sb–O and P–O bond lengths in 1 are very similar, (2.23, 2.29 and 1.49, 1.51 Å), while in 2 the P–O and P–S distances, 1.503 and 2.010 Å respectively, also point to symmetrical coordination. Stereochemical activity of the lone pair is considered.
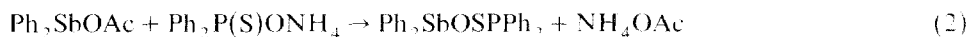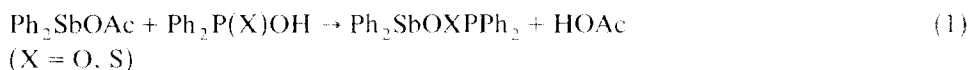
Introduction

The structural chemistry of antimony exhibits many peculiarities and within our range of interests we have previously found that the geometry about antimony can exhibit remarkable variations. Thus, while the central atom in $Sb[S_2P(OR)_2]_3$ is in distorted octahedral coordination [1], pentagonal pyramidal geometry is observed in $Sb(S_2PPh_2)_3$ [2]. In diorganoantimony(III) derivatives the presence within the molecule of both a coordinatively unsaturated central atom and a ligand with a marked tendency to exhibit varying coordination patterns, may lead to interesting

structures. This stimulated the structural investigation of diphenylantimony(III) acetate, Ph_2SbOAc [3], the diphenyldithiophosphinate, $Ph_2SbS_2PPh_2$ [4] and diphenyldithioarsinate, $Ph_2SbS_2AsPh_2$ [4]. The last two compounds are weak dimers containing eight-membered $Sb_2S_4E_2$ rings (E = P, As), in which transannular $Sb \cdots S$ interactions raise the antimony coordination to five. In view of these unusual features, it was of interest to investigate any structural changes resulting from replacement of one or both sulphur atoms of the ligand by oxygen, and we now report the preparation and the crystal structures of $Ph_2SbO_2PPh_2$ (**1**) and $Ph_2SbOSPPh_2$ (**2**).

Results and discussion

The two new compounds were prepared from diphenylantimony acetate and either the free acid or the ammonium salt of the diphenylthiophosphinic acid (eqs. 1 and 2) as white solids which can be recrystallised from acetonitrile. The diphenyl-

$$Ph_2SbOAc + Ph_2P(X)OH \rightarrow Ph_2SbOXPPh_2 + HOAc \qquad (1)$$
$$(X = O, S)$$

$$Ph_2SbOAc + Ph_2P(S)ONH_4 \rightarrow Ph_2SbOSPPh_2 + NH_4OAc \qquad (2)$$

phosphinate **1** is stable in air, but the thio derivative **2** is sensitive to moisture and if stored in contact with the atmosphere it slowly hydrolyses to **1**. **2** should therefore be recrystallised from dry acetonitrile and stored under nitrogen.

Infrared spectra

IR spectra of the two compounds are summarised in the Experimental section, but a number of important bands are given in Tables 1 and 2 which for comparison also include analogous bands from a number of related compounds. The P–O stretching modes for **1** compared with those for diphenylphosphinic acid, its methyl ester [7] and the ammonium [8] and potassium [7,8] salts suggest that both oxygen atoms are coordinated and that the ligand is either bidentate or bridging. In fact, the close similarity between the positions of the P–O modes in **1** and those in the salts indicate that the ligand is coordinated symmetrically (or nearly so).

TABLE 1

INFRARED DATA FOR DIPHENYLPHOSPHINIC ACID DERIVATIVES

Compound	$\nu(P-O)$	$\nu(P=O)$	Reference
$Ph_2P(O)OH$	960vs	1121m	this work
		1128s	
$Ph_2P(O)OMe$	1032	1230	[7]
$Ph_2P(O)ONH_4$	1018s	1152vs	this work
	1037vs	1161vs	
		1154s	[8]
		1164s	
$Ph_2P(O)OK$	1038	1191	[7,8]
$Ph_2P(O)OSbPh_2$	1010s	1133vs	this work
	1035m	1142vs	

TABLE 2

INFRARED DATA FOR DIPHENYLTHIOPHOSPHINIC ACID DERIVATIVES

Compound	ν(PO)			ν(PS)		References
	ν(P–O)		ν(P=O)	ν(P–S)	ν(P=S)	
Ph$_2$P(S)OH	892vs		–	–	633vs	[9] and this work
	896vs		–	–	633s	[10]
Ph$_2$P(S)OMe			–	–	638 [a]	[11]
Ph$_2$P(O)SMe	–		1202s	565s 568 [a]	–	[11]
Ph$_2$P(S)ONH$_4$	1045s 1051s			628vs		this work
Ph$_2$P(S)ONa	1125vs			611s		[10]
Ph$_2$P(S)OSbPh$_2$	1050vs 1061vs			593vs		this work

[a] Raman band.

For the thiophosphinate 2, comparison of the phosphorus–oxygen and phosphorus–sulphur stretching modes with those in diphenylthiophosphinic acid [9,10], its O- and S-methyl esters [11], and the ammonium and sodium salts [10] again point to involvement of both oxygen and sulphur atoms with the ligand behaving as either a chelate or bridging group.

Dithiophosphato and dithiophosphinato ligands are known to show great diversity in their modes of coordination [12] and a number of different examples have been identified in their antimony compounds [1,2,4]. Equally diverse behaviour is to be expected with phosphinato and monothiophosphinato groups and to determine the exact method of coordination X-ray structures were carried out for the two new compounds.

Crystal structure

Important bond distances and angles for compounds 1 and 2 are listed in Table 3 and their structures with atom numbering schemes are illustrated in Figs. 1 and 2. Both compounds have polymeric chain structures with bridging phosphinate and thiophosphinate groups respectively, in agreement with the conclusions from IR spectroscopy; the structures are similar to those of Ph$_2$SbOAc [3], Ph$_2$SbF [13], and a number of related triorgano tin compounds [14–16].

The antimony–oxygen distances in 1 are more closely equal, 2.23 and 2.29 Å, than in Ph$_2$SbOAc, 2.14 and 2.55 Å [3], pointing to a higher degree of secondary Sb–O bonding in the former. This should lead to close similarity in the two P–O distances, 1.49 and 1.51 Å, as the π-component will be almost equally shared. The P–O distances are comparable with those in the cyclic hexamer [Ph$_3$SnO$_2$P(OPh)$_2$]$_6$ (1.487 Å) [14] and in α-phenylphosphonatotrimethyl tin (1.492 and 1.516 Å) [15].

Bonding in Ph$_2$Sb(OSPPh$_2$) is similar but the primary bond is to oxygen (Sb–O 2.299 Å) with secondary Sb–S bonding at 2.753 Å. Oxygen is also the primary bonded atom in Sb(OSPR$_2$)$_3$ where R = phenyl or cyclohexyl [17] but significantly in Sb(SOCMe)$_3$ [18], PhSb(SOCMe)$_2$ [19] and Sb(SOCPh)$_3$ [20] primary interaction is with sulphur. Mattes and Ruhl [20] have ascribed this change in coordination mode to the fact that Sb^{III} is a hard-soft borderline acid and small changes in ligand

TABLE 3

BOND LENGTHS (Å) AND ANGLES (°) FOR $Ph_3Sb[OXPPh_2]$ FOR X = O(2) (1) OR S(1) (2) (with estimated standard deviations in parentheses)

	X = O(2) (1)	X = S(1) (2)
Sb(1)–O(1)	2.23(1)	2.299(3)
Sb(1)–C(11)	2.10(2)	2.143(5)
Sb(1)–C(21)	2.17(2)	2.153(4)
Sb(1)–X	2.29(1)	2.753(1)
P(1)–O(1)	1.49(1)	1.504(3)
P(1)–X	1.51(1)	2.010(3)
P(1)–C(31)	1.79(2)	1.812(5)
P(1)–C(41)	1.78(2)	1.807(4)
O(1)–Sb(1)–C(11)	84.9(6)	83.7(2)
O(1)–Sb(1)–C(21)	85.0(6)	84.0(2)
C(11)–Sb(1)–C(21)	98.1(6)	95.4(2)
O(1)–Sb(1)–X	166.7(5)	168.7(1)
X–Sb(1)–C(11)	87.4(6)	90.1(1)
X–Sb(1)–C(21)	85.3(6)	87.2(1)
O(1)–P(1)–X	117.5(8)	116.5(1)
O(1)–P(1)–C(31)	109.6(8)	110.2(2)
O(1)–P(1)–C(41)	105.7(8)	106.9(2)
X–P(1)–C(31)	106.6(8)	108.9(2)
X–P(1)–C(41)	111.0(8)	108.9(2)
C(31)–P(1)–C(41)	105.8(8)	105.0(2)
Sb(1)–O(1)–P(1)	136.7(8)	135.7(2)
Sb(1)–X–P(1)	129.0(8)	97.59(6)
Sb(1)–C(11)–C(12)	118(1)	122.8(4)
Sb(1)–C(11)–C(16)	123(1)	118.5(4)
Sb(1)–C(21)–C(22)	119(2)	118.9(3)
Sb(1)–C(21)–C(26)	118(1)	121.6(4)
P(1)–C(31)–C(32)	122(2)	122.8(4)
P(1)–C(31)–C(36)	121(2)	117.3(4)
P(1)–C(41)–C(42)	121(2)	120.9(4)
P(1)–C(41)–C(46)	120(2)	120.5(4)

TABLE 4

Sb–O AND Sb–S DISTANCES (Å) IN 2 AND RELATED COMPOUNDS

	Sb–O	Sb–S	Reference
$Ph_2Sb(OSPPh_2)$	2.299	2.753 [a]	this work
$Sb(OSPPh_2)_3$	2.063	3.223	[17]
	2.037	3.001 (3.554) [a]	
	2.061	3.164	
$Sb(OSP^cHex_2)_3$	2.026	3.286	[17]
	2.031	3.183	
	2.027	3.218	
$Sb(SOCMe)_3$	2.763	2.479	[18]
	2.745	2.466	
	2.918 (3.043) [a]	2.461	
$PhSb(SOCMe)_2$	2.808	2.451	[19]
	2.818	2.471 (3.802) [a]	
$Sb(SOCPh)_3$	2.802 (3.463) [a]	2.493	[20]

[a] Distance to a symmetry-related antimony atom.
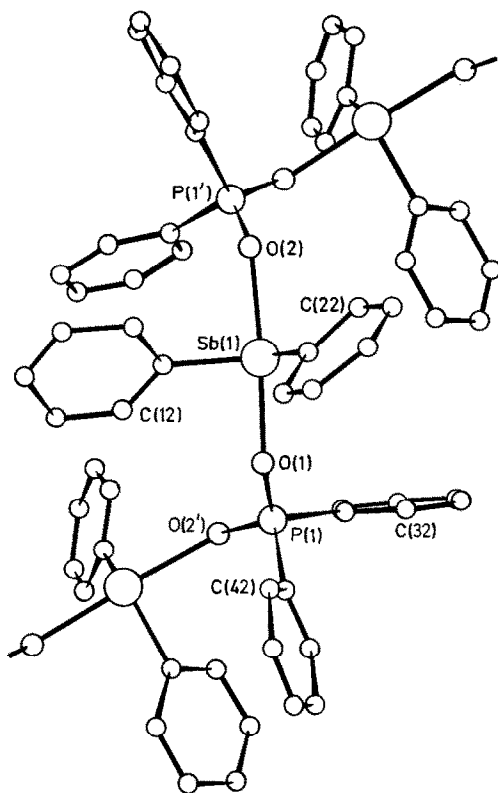
Fig. 1. Part of the chain structure of $Ph_2Sb(O_2PPh_2)$ (1) showing the atom numbering scheme.

electronegativity and geometry can promote either Sb–O or Sb–S primary bonding. The Sb–O and Sb–S distances in a number of compounds with mixed oxygen-sulphur ligands are collected in Table 4 showing that as for **1** coordination in **2** is highly symmetrical; the data also point to antimony (III) softening as an acid on substitution by phenyl groups.

Angles at antimony in **1** and **2** show small variations but in general there is a set of four between phenyl carbon atoms and either oxygen or sulphur atom (83.7–90.1°), one between the phenyl carbon atoms (ca. 97°) and the O–Sb–O(S) angle (ca. 168°). This gives a basic structure which can be described in two different ways depending on whether or not the antimony lone pair is stereochemically active. With an active lone pair, the structure would be based on a trigonal bipyramid with phenyl groups and the lone pair in equatorial sites and the more electronegative Group VI atoms in apical positions. Deviations from the expected 90 and 120° angles would result from the greater repulsion of the lone pair.

The alternative approach is to consider that antimony is pyramidally bonded (ca. 90° angles) to the phenyl groups and an oxygen of the ligand, i.e. the primary bonded atom. The second oxygen for **1** or the sulphur in **2** then form secondary bonds to antimony. As the Sb–O–P angles (ca. 138°) are characteristically large, this must be via bridging rather than chelation. By contrast, in the $PhSb(SAc)_2$

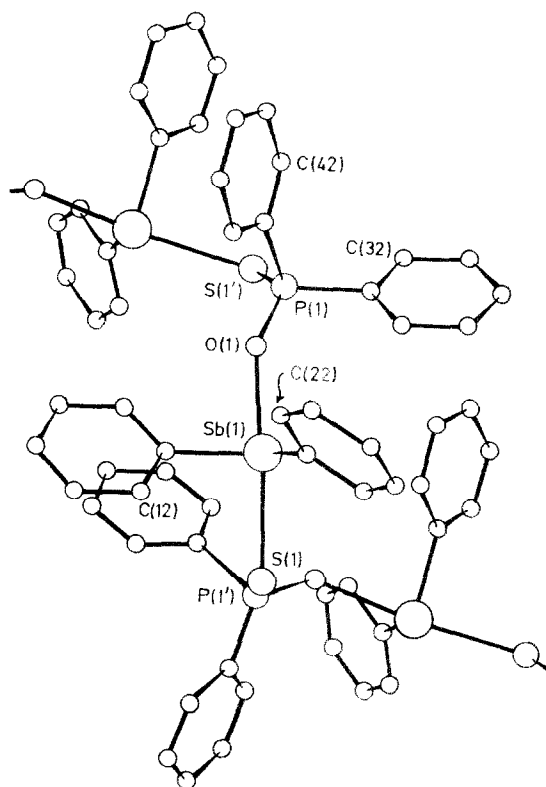Fig. 2. Part of the chain structure of Ph₃Sb(OSPPh₂) (2) showing the atom numbering scheme.

structure [19] where primary bonding is via sulphur. the smaller Sb–S–C angle (ca. 91°) allows secondary bond formation by chelation.

There is strong evidence from the conversion of antimony(III) and phenyl-substituted antimony(III) chlorides and bromides to halogeno anions that secondary bonding at antimony occurs preferentially *trans* to a halogen present in the starting material [19,21]; no structural evidence has yet been adduced for accommodation of a halide ion *trans* to a phenyl group. The rationale for this behaviour is that the ligand charge can be delocalised in a three centre-four electron X–Sb···X system while this mechanism is not possible when a Ph–Sb group is present. The present situation, and incidentally that in both Ph₃SbOAc [3] and Ph₃SbF [13], is related and secondary bonding would be expected *trans* to the oxygen atom not *trans* to a phenyl group. It is thus possible to rationalise the observed structures of **1** and **2** even with no steric activity of the antimony 5s electrons.

Experimental

Preparation of diphenylantimony(III) diphenylphosphinate, Ph₃SbO₂PPh₂ (1)

A solution containing 1.67 g (5 mmol) Ph₃SbOAc and 1.09 g (5 mmol) Ph₂P(O)OH in 50 ml anhydrous methanol was refluxed for 2 h. The white solid deposited was filtered off and recrystallised from acetonitrile. Yield 2.01 g (83%).

m.p. 215–217°C. (Found: C, 58.90; H, 3.98. $C_{24}H_{20}O_2PSb$ calcd.: C, 58.44; H, 4.06%). Major peaks in the IR spectrum (KBr disc, cm^{-1}) are: 1482ms, 1438s, 1434s, 1329w, 1307w, 1133vs, 1094vs, 1070s, 1035s, 1010vs, 995vs, 755ms, 732vs, 696vs, 561vs, 536s, 464ms, 451ms.

Crystal structure of 1

Crystal data. $C_{24}H_{20}O_2PSb$, M 492.8, orthorhombic, a 9.185(4), b 11.075(4), c 21.099(7) Å, U 2146.3 Å^3, Z 4, D_c 1.52 g cm^{-3}, $F(000)$ 984, space group $P2_12_12_1$ from systematic absences, Mo-K_α radiation, λ 0.7107 Å, μ(Mo-K_α) 13.9 cm^{-1}, crystal size $0.15 \times 0.20 \times 0.20$ mm.

Structure determination. Data were collected using a Hilger and Watts four circle diffractometer for 2196 reflections of which 1524 with $I > 3\sigma(I)$ were observed. Corrections were made for Lorentz and polarisation effects but an absorption correction was not necessary. Crystallographic calculations used the CRYSTALS program [22] and scattering factors for neutral atoms [23]. The antimony atom was located by Patterson methods and subsequent Fourier syntheses revealed the other non-hydrogen atoms. Full matrix least-squares refinement converged at $R = 0.087$ with isotropic and 0.063 with anisotropic thermal parameters,

TABLE 5

FRACTIONAL ATOMIC COORDINATES FOR 1 (with estimated standard deviations in parentheses)

Atom	x/a	y/b	z/c
Sb(1)	0.0784(1)	0.2088(1)	0.24613(6)
P(1)	0.0205(5)	−0.0521(5)	0.1590(2)
O(1)	0.111(1)	0.034(1)	0.1964(6)
O(2)	−0.097(1)	−0.120(1)	0.1938(6)
C(11)	0.124(2)	0.110(2)	0.3289(8)
C(12)	0.047(2)	0.002(2)	0.339(1)
C(13)	0.075(3)	−0.065(2)	0.394(1)
C(14)	0.167(3)	−0.026(2)	0.440(1)
C(15)	0.243(3)	0.079(2)	0.430(1)
C(16)	0.223(2)	0.145(2)	0.373(1)
C(21)	0.301(2)	0.247(2)	0.2181(8)
C(22)	0.336(3)	0.359(2)	0.198(2)
C(23)	0.480(3)	0.381(3)	0.177(2)
C(24)	0.582(3)	0.293(3)	0.185(1)
C(25)	0.545(2)	0.183(3)	0.208(1)
C(26)	0.403(2)	0.157(2)	0.224(1)
C(31)	−0.067(2)	0.027(1)	0.0956(7)
C(32)	0.012(3)	0.087(2)	0.049(1)
C(33)	−0.049(3)	0.146(2)	0.001(1)
C(34)	−0.198(4)	0.146(3)	−0.004(1)
C(35)	−0.285(3)	0.092(2)	0.040(1)
C(36)	−0.219(2)	0.030(2)	0.091(1)
C(41)	0.145(2)	−0.154(2)	0.122(1)
C(42)	0.286(3)	−0.165(4)	0.145(2)
C(43)	0.372(4)	−0.257(4)	0.119(2)
C(44)	0.322(4)	−0.331(3)	0.072(1)
C(45)	0.186(4)	−0.318(2)	0.048(2)
C(46)	0.099(3)	−0.230(2)	0.073(1)

the hydrogen atoms placed (but not refined) at their calculated positions and application of a four coefficient Chebyshev weighting scheme. Refined values for the atomic coordinates are listed in Table 5.

Preparation of diphenylantimony(III) diphenylthiophosphinate, Ph$_2$SbOSPPh$_2$ (2)

(a) A solution of 0.84 g (2.5 mmol) Ph$_2$SbOAc in 20 ml dry benzene was added to a suspension of 0.63 g (2.5 mmol) Ph$_2$P(S)ONH$_4$ in 30 ml benzene. The mixture was stirred under reflux for 2 h and then the ammonium acetate was filtered off. The clear filtrate was evaporated in vacuum and the oily residue recrystallised from acetonitrile. Yield 1.1 g (87%), m.p. 159–161°C. (Found: C, 56.45; H, 4.01. C$_{24}$H$_{20}$OPSSb calcd.: C, 56.60; H, 3.93%).

(b) The same compound was obtained by reaction of 0.84 g (2.5 mmol) Ph$_2$SbOAc and 0.59 g (2.5 mmol) Ph$_2$P(S)OH in 50 ml of dried benzene, after 2 h of reflux and concentration of the solution. Yield 1.0 g (78%). Major peaks in the IR spectrum (KBr disc, cm^{-1}) are: 1474s, 1434s, 1425s, 1323w, 1304w, 1177w, 1150w, 1115vs, 1109sh, 1078sh, 1061vs, 1050vs, 1040sh, 1021s, 992s, 750m, 732ms, 723s, 711s, 700vs, 691vs, 615s, 593vs, 518vs, 498m, 457m, 448m.

TABLE 6

FRACTIONAL ATOMIC COORDINATES FOR **2** (with estimated standard deviations in parentheses)

Atom	x/a	y/b	z/c
Sb(1)	0.36005(3)	0.37652(3)	0.26226(1)
P(1)	0.2822(1)	0.6203(1)	0.14930(5)
O(1)	0.3605(3)	0.5609(3)	0.2046(1)
S(1)	0.0880(1)	0.6677(1)	0.16246(6)
C(11)	0.4203(5)	0.4981(4)	0.3398(2)
C(12)	0.5284(5)	0.4707(5)	0.3821(2)
C(13)	0.5629(6)	0.5511(6)	0.4324(3)
C(14)	0.4872(8)	0.6595(6)	0.4401(3)
C(15)	0.3802(8)	0.6884(6)	0.3990(3)
C(16)	0.3461(6)	0.6078(5)	0.3485(2)
C(21)	0.5618(5)	0.3534(4)	0.2296(2)
C(22)	0.6473(5)	0.4584(5)	0.2286(2)
C(23)	0.7709(6)	0.4507(6)	0.2017(3)
C(24)	0.8105(6)	0.3365(7)	0.1756(3)
C(25)	0.7266(6)	0.2329(6)	0.1768(3)
C(26)	0.6020(6)	0.2404(5)	0.2040(3)
C(31)	0.2864(5)	0.5182(4)	0.0807(2)
C(32)	0.1888(6)	0.5223(6)	0.0313(2)
C(33)	0.2044(8)	0.4474(7)	−0.0217(3)
C(34)	0.3141(8)	0.3667(7)	0.0246(3)
C(35)	0.4107(7)	0.3630(6)	0.0244(3)
C(36)	0.3989(6)	0.4384(5)	0.0770(2)
C(41)	0.3744(4)	0.7609(4)	0.1285(2)
C(42)	0.3249(5)	0.8400(5)	0.0801(2)
C(43)	0.3958(6)	0.9467(6)	0.0639(3)
C(44)	0.5172(7)	0.9753(6)	0.0955(3)
C(45)	0.5678(6)	0.8990(6)	0.1434(3)
C(46)	0.4966(6)	0.7916(5)	0.1605(3)

Crystal structure of **2**

Crystal data. $C_{24}H_{20}OPSSb$, *M* 508.8, monoclinic, *a* 9.842(4), *b* 10.561(4), *c* 21.182(7) Å, β 93.19(4)°, *U* 2198.3 Å^3, *Z* 4, D_c 1.54 g cm^{-3}, *F*(000) 1016, space group $P2_1/n$ from systematic absences, Mo-K_α radiation, μ(Mo-K_α) 14.4 cm^{-1} crystal size = 0.10 × 0.15 × 0.30 mm.

Structure determination. Data were measured for 4087 reflections (3031 observed) and treated as above. Refinement converged at *R* = 0.060 with isotropic and 0.031 with anisotropic thermal parameters, placement of hydrogen atoms at their calculated positions and inclusion of anomalous dispersion contributions. Unit weights were appropriate. Final values of the atomic coordinates are collected in Table 6.

Tables of bond distances and angles in the phenyl groups, anisotropic thermal parameters, calculated hydrogen atom positions and observed and calculated structure factors for both compounds can be obtained from D.B.S.

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