Tin-119 Mössbauer and Nuclear Magnetic Resonance Studies of Organotin Compounds. Part 2.[1] Sterically Crowded Organotin Halides and Carboxylates†

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Tin-119 Mössbauer and ^{119}Sn NMR data have been obtained for a number of novel organotin halides and carboxylates containing bulky organic ligands (adamantyl, triptycyl). The Mössbauer spectra are discussed in terms of distortions from tetrahedral geometries as a result of steric crowding. The largest distortions occur for the adamantyl derivatives. A detailed study of ^{119}Sn NMR shifts revealed correlations with Mössbauer quadrupole splittings and with the electronegativities of the ligands concerned. The crystal structure of (*E*)-(but-2-enyl)triphenyltin was determined: triclinic, space group $P\bar{1}$, with a = 9.892(3), b = 10.196(4), c = 11.637(5) Å, α = 107.16(2), β = 103.40(2), γ = 109.77(2)°. The crystals are composed of discrete non-interacting molecules. The structure was refined to R 0.035 and R' = 0.043. The geometry around the tin centres is only slightly distorted from tetrahedral with bond angles ranging between 107.5(2) and 112.8(2)°, average 109.5°. The Sn–C(but-2-enyl) bond is significantly longer than the three Sn–C(phenyl) bonds. The structure is compared to those of other similar compounds.

We have reported on the effects of packing bulky organic ligands around tin(IV) centres.[1] There have been many studies on organotin halides using ^{119}Sn Mössbauer spectroscopy (for reviews see refs. 2–5), but these were severely hampered by the restricted structural information available when they were carried out, which made parameter interpretation difficult and often speculative. However, in the last few years, the number of crystal structures[6] of organotin halides has doubled (Tables 1 and 2). This has allowed us to correlate the Mössbauer parameters with structure, enabling the assignment of co-ordination numbers to a number of new organotin halides which contain bulky organic ligands. The Mössbauer parameters for the new organotin halides SnR(R′)R″X appear to be the first recorded for compounds containing mixed-ligand triorganotin compounds except for $SnMe[CH(SiMe_3)_2]_2I$.[7]

The original reason for synthesising the sterically hindered organotin derivatives described here was to produce optically stable chiral tin compounds. The rationale was that such bulky groups as adamantyl (ad) and triptycyl (tr) (9,10-dihydro-9,10-benzenoanthracen-1-yl) should prevent racemising five-co-ordination by solvent molecules. Thus it was hoped that cleavage of diallyl(methyl)triptycyltin **I** by optically active chloropropionic acid (Scheme 1) would produce a diastereomeric chloropropionate which could be converted into the corresponding chiral organotin bromide with LiBr. This did not, however, occur and only racemic material was obtained. The rates of cleavage of **I** were also studied with (+)-chloropropionic acid and the (±) form. The second-order rate constants obtained were identical within experimental error showing that kinetic asymmetric synthesis had not occurred. In view of the novel nature of these compounds and their precursors, it was decided to investigate their structure using ^{119}Sn Mössbauer[8] and ^{119}Sn NMR spectroscopy.[9–12]

$$\underset{\textbf{I}}{(CH_2{=}CHCH_2)_2SnMe(tr)} \xrightarrow{(i)}$$

$$(CH_2{=}CHCH_2)(tr)MeSn{-}OCOCH(Me)Cl + CH_2{=}CHMe$$

Scheme 1 (*i*) $MeCH(Cl)CO_2H$

The crystal structure of (E)-(but-2-enyl)triphenyltin **1** was also studied in the light of our earlier work.[1,23] and to see whether an (*E*)-but-2-enyl group caused more steric distortion to the $SnPh_3$ entity than did a phenyl group. We previously reported[1] the preparation of tetraadamantyltin(IV) for which Mössbauer spectroscopy gave evidence for a very distorted-tetrahedral tin environment, but we were unable to obtain crystals of the compound. To further our understanding of the latter complex, we include here a comparison of the structure of **1** with those of other organotin(IV) molecules containing bulky ligands.

Results and Discussion

Organotin Halides.—The Mössbauer parameters for the new organotin halides are listed in Table 3, and may be compared to parameters for a number of other organotin halides with both known and unknown crystal structures (Tables 1 and 2). We have grouped these according to formula and known structures. The Mössbauer data for the known four-co-ordinate slightly distorted-tetrahedral structures $SnPh_3Cl$ and $SnPh_3Br$ are quite similar (δ ≈ 1.35, Δ ≈ 2.52 mm s^{-1}) to those of $SnPh_3I$ (δ 1.26, Δ = 2.30 mm s^{-1}). It is therefore reasonable to suggest that the iodide has a slightly distorted-tetrahedral structure. The crystal structure–Mössbauer parameter correlation is further supported by the data for $Sn[CH(SiMe_3)_2]_3Cl$ (δ = 1.27, Δ = 2.18 mm s^{-1}).[4] The compounds $SnPh_2(tr)Br$, $SnPh_2(ad)Br$ and $SnPh_2(ad)I$ all have isomer shifts of about 1.4 mm s^{-1} and quadrupole splittings in the range 2.24–2.56 mm s^{-1} and thus are also likely to have slightly distorted-tetrahedral co-ordination. These three complexes each contain two phenyl ligands and either a triptycyl or an adamantyl group. The last two are both considerably larger than the phenyl group and so a distorted four-co-ordinate structure is reasonable. This is also

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 Selected literature ^{119}Sn Mössbauer parameters,[a] ^{119}Sn NMR chemical shifts,[b] and structures, where known, for triorganotin halides

Compound	Co-ordination number[c]	δ(BaSnO$_3$)/mm s^{-1}	Δ/mm s^{-1}	Mössbauer ref.	δ(^{119}Sn)
$SnMe_3F$	5	1.27	3.90	13	164.2
		1.26[d]	4.10[d]	13	
$SnPh_3F$	—	1.25	3.52(1)	14, 15	0.5[e]
$SnMe_3Cl$	5	1.43	4.24	16	158
$SnEt_3Cl$		1.62	3.72	16	153.4
$SnBu^n{}_3Cl$	—	1.38	3.56	16	141.2
$Sn(C_6H_{11})_3Cl$	4/5[f]	1.64	3.49	17	—
$SnMe_3Br$	—	1.30	3.95	16	128
$SnEt_3Br$	—	1.62	3.31	16	148
$SnBu^n{}_3Br$	—	1.33	3.32	16	134
$SnMe_3I$	—	1.48	3.05	18	38.6
$SnEt_3I$	—	1.55	3.07	16	—
$SnPh_3Cl$	4[g]	1.31	2.56	14	−44.7
$Sn(C_6H_4Cl\text{-}p)_3Cl$	—	1.37	2.49	19	—
$SnPh_3Cl$	—	1.33(3)[h]	2.53(7)[h]	2	—
$Sn[CH(SiMe_3)_2]_3Cl$	—	1.27	2.18	7	—
$SnPh_3Br$	4[g]	1.37(2)[h]	2.51(5)[h]	2	−59.8
$Sn(CH_2CMe_2Ph)_3Br$	—	1.42	2.65	18	—
$Sn(C_6H_4CF_3\text{-}m)_3$	—	1.22	1.94	18	—
$Sn(C_6F_5)_3Br$	—	1.06	1.60	20	—
$Sn[CH(SiMe_3)_2]_3Br$	—	1.24	2.05	7	—
$SnBu^n{}_3I$	—	1.39	2.54	16	—
$SnPh_3I$	—	1.26(6)[h]	2.30(4)[h]	2	−112.8
$Sn(C_6H_4F\text{-}p)_3I$	—	1.23	1.92	18	—
$SnMe[CH(SiMe_3)_2]_2I$	—	1.48	2.24	7	—

[a] Isomer shift data all normalised relative to BaSnO$_3$ using the appropriate conversion factors [α-Sn, + 1.2, β-Sn, + 2.56; and Pd/Sn, + 1.46 mm s^{-1}]. All measurements at 80 K unless otherwise stated. [b] δ(^{119}Sn) relative to SnMe$_4$, negative sign indicating upfield shift. Data from refs. 8–12 using, where possible, data for dilute solutions in inert solvents. [c] Ref. 6. [d] Data at 298 K. [e] This work. [f] Distorted away from tetrahedral to a trigonal-bipyramidal configuration. [g] Slightly distorted tetrahedral. [h] Average of values quoted in ref. 2.

Table 2 Literature ^{119}Sn Mössbauer and ^{119}Sn NMR data[a] for some diorganotin dihalides

Compound	Co-ordination number	δ[b]/mm s^{-1}	Δ/mm s^{-1}	Ref.	δ(^{119}Sn)
$SnMe_2F_2$	6[c]	1.34	4.65	21	—
		1.23	4.52	13	—
		1.20[d]	4.47[d]	13	—
$SnMe_2Cl(F)$	—	1.32	3.80	13	—
		1.27[d]	3.79[d]	13	—
$SnMe_2Cl_2$	6[c]	1.60	3.52	14	140
$SnEt_2Cl_2$	6[c]	1.63	3.81	14	125
$SnBu^n{}_2Cl_2$	—	1.63	3.45	22	123.4
$SnMe_2Br_2$	—	1.60	3.30	14	70
$SnEt_2Br_2$	6[c]	1.70	3.27	14	96
$SnEt_2I_2$	6[c]	1.72	2.97	14	53
$SnPh_2Cl_2$	4[e]	1.38	2.90	14	−32

[a] See footnotes *a*, *b* in Table 1. [b] Relative to BaSnO$_3$ as 0.0 mm s^{-1}. [c] Distorted *trans*-SnR$_2$X$_4$. [d] Data at 298 °K. [e] Distorted tetrahedral.

Table 3 Tin-119 Mössbauer (130 K) and ^{119}Sn NMR data[a] for some novel organotin compounds containing bulky groups

Compound	δ[b]/mm s^{-1}	Δ/mm s^{-1}	Γ/mm s^{-1}	δ(^{119}Sn)
$SnPh_2(tr)Br$	1.35(1)	2.24(1)	0.86(2)	−50.2
$SnPh_2(ad)Br$	1.43(1)	2.56(2)	1.38(2)	−45.3
$SnMe(Ph)(tr)Br$	1.62(1)	2.40(4)	0.91(3)	15.5
$SnMe(Ph)(ad)Br$	1.32(1)	2.89(1)	1.29(2)	28.7
$SnMe(tr)(CH_2CH{=}CH_2)Br$	1.47(1)	2.58(2)	1.06(2)	56.1
$Sn(tr)(CH_2CH{=}CH_2)_2Br$	1.49(1)	2.40(1)	0.96(2)	−31.9 −40.7
$SnPh_2(ad)I$	1.44(2)	2.38(2)	0.97(2)	−61.0
$SnPh(ad)Br_2$	1.56(1)	2.58(1)	0.96(2)	−22.0
$SnMe(tr)Br_2$	1.22(1)	2.14(1)	1.04(1)	+24.6[c]
$SnMe(Ph)(tr)[OCOCH(OH)Ph]$	1.28(2)	2.53(2)	0.91(2)	—

[a] Data for CS$_2$ solutions, this work. [b] Relative to SnO$_2$, this work. [c] In (CD$_3$)$_2$SO.

the case for the allyl derivatives SnMe(tr)(CH$_2$CH=CH$_2$)Br and Sn(tr)(CH$_2$CH=CH$_2$)$_2$Br. Both have almost identical δ values (1.47 and 1.49 mm s^{-1} respectively) and similar Δ values (2.58 and 2.40 mm s^{-1} respectively). Molecular models of these compounds demonstrate the space-filling property of the triptycyl ligand which would strongly discourage a co-ordination number of greater than four.

The compound SnMe(Ph)(ad)Br has a larger Δ (2.89 mm s^{-1}) than the other compounds discussed above. This might indicate that the material is five-co-ordinate like SnMe$_3$F and SnMe$_3$Cl.

However these two have significantly larger quadrupole splittings (3.90 and 4.24 mm s^{-1} respectively). The quadrupole splitting of $SnPh_2Cl_2$ is identical to that of SnMe(Ph)(ad)Br. The structure of the former has been described as distorted tetrahedral,[6,14] but also as a tetramer of centrally six-coordinate and terminally four-co-ordinate units.[6] Thus $SnPh_2Cl_2$ should be described as extremely distorted tetrahedral.

Parish and Platt[24] presented a table of the then known tin(IV) structures listing their Δ values. They concluded that: (*a*) imbalance in the polarity of the σ bonds is the dominant factor in determining the size of Δ; (*b*) the geometrical arrangement of the ligands is important, and (*c*) π bonding is a secondary factor. The second conclusion has been assessed on the basis of the point-charge model. Fitzsimmons and co-workers[25] presented point-charge models for *cis* and *trans* trigonal-bipyramidal geometries of the type SnR_3X_2; the quadrupole splitting calculated for *cis* was 1.57 and for *trans* 3.12 mm s^{-1}. The point-charge calculation for SnR_3X tetrahedra gave an expected Δ of 1.66 mm s^{-1}. These values are not very different from those of Parish and Platt[24] who gave a Δ of 2.0 mm s^{-1} for tetrahedral SnR_3X and 3–4.0 mm s^{-1} for *trans* trigonal-bipyramidal SnR_3X_2 geometries.

These calculations agree well for the structures of the complexes we have already discussed. It is worth noting that $Sn(C_6F_5)_3Cl$ and $Sn(C_6F_5)_3Br$ have the smallest quadrupole splittings (≈1.6 mm s^{-1}) recorded[20] for triorganotin halides likely to contain tetrahedral tin(IV), and both these materials have small isomer shifts.

The compound $SnMe(tr)Br_2$ has a Δ value which is the smallest yet reported for an SnR_2X_2 material and is similar to those reported for slightly distorted-tetrahedral complexes (of the SnR_3X type), and we thus assign its structure.

The Δ value for $SnPh(ad)Br_2$ is also low compared to other SnR_2X_2 compounds though the isomer shift (1.56 mm s^{-1}) is typical. As previously stated, materials containing the adamantyl group appear to have higher chemical shifts reflecting the electron-donating power of the adamantyl ligand.[1] It is therefore probable that $SnPh(ad)Br_2$ contains distorted-tetrahedral molecules.

From this work it would appear that when bulky ligands such as triptycyl, phenyl, adamantyl and $(SiMe_3)_2CH$ are present in SnR_3X and SnR_2X_2 (X = Br or I) materials, then tetrahedral structures are preferred.

It must be borne in mind that all the Mössbauer data referred to in this paper were obtained at low temperatures (80, 130 K), whereas the crystal structures were determined at room temperature. The only relevant known structure which has been investigated at low temperature (138 K) is $SnMe_3Cl$.[26] Suggestions[27] that $SnPh_3Cl$ may have a similar structure at low temperature as judged from the sign of the electric field gradient (e.f.g.) have been refuted.[28] Room-temperature crystal structures of $SnPh_3Cl$[29] and $SnPh_3Br$[30] show them to be slightly distorted tetrahedral. The crystal structure of $Sn(C_6H_{11})_3Cl$ has been reported[31] in which the molecule has been described as distorted tetrahedral. The average C–Sn–C bond angle in the structure is 108.9° which is close to the tetrahedral angle, whereas the average value for an ideal trigonal bipyramid is 100°. The authors show that from a simple point-charge model a Δ value of −2.74 mm s^{-1} can be derived assuming tetrahedral geometry. Using the known geometry it was estimated as −3.64 mm s^{-1}, in good agreement with the observed value of 3.49 mm s^{-1}. Thus in certain cases, cyclohexyl ligands[31–33] prevent five-co-ordination though $Sn(C_6H_{11})_3(OCOMe)$[33] and $Sn(C_6H_{11})_3(OCCF_3)$[33] appear five-co-ordinate. Adamantyl is a very much larger and conformationally rigid group which would act as a strong barrier to higher co-ordination.

The complex SnMe(Ph)(tr)Br has a Δ of 2.40 mm s^{-1} which is very similar to those of other complexes of general formula SnR(R′)(tr)Br(R = R′ = Ph; R = R′ = allyl; R = allyl, R′ = Me) (Table 3) and would suggest it is also close to tetrahedral in structure. However, this complex has an anomalous chemical shift (of 1.62 mm s^{-1}) compared to the other complexes, which we are unable to explain at present.

The Mössbauer data presented in Table 3 of complexes of the type SnR(R′)R″(Br), $SnR(R')Br_2$ and SnR(R′)R″(I) provide evidence for all these compounds being tetrahedral in structure.

Tin–Oxygen Bonded Components.—Tables 3 and 4 list Mössbauer and ^{119}Sn NMR data for a series of carboxylates and related species. These may be divided into four- and five-co-ordinated species on the basis of their crystal structure and/or Mössbauer parameters. The known five-co-ordinate species which have intermolecular Sn–O bonding are characterised by large Δ values (2.98–4.18 mm s^{-1}) whereas those with monomeric structures generally have much lower values (1.94–2.36 mm s^{-1}). The exception is $Sn(C_6H_{11})_3(OCOMe)$[16] the structure of which is intermediate between the above two extremes and is best described as a weakly co-ordinated polymeric material. From the above it is probable that the chlorinated esters[37] $SnPh_3(OCOCH_nCl_{3-n})$ also have a polymeric structure. The trichloroacetate is however anomalous, having a slightly lower Δ value of 2.97 mm s^{-1} and is considered to be a tetrahedral monomeric species. Plots of both Δ and δ(^{119}Sn) NMR shifts *vs.* group electronegativity (χ_g 2.27, CH_3; 2.47, CH_2Cl; 2.66, $CHCl_2$; 2.84, CCl_3)[41] are linear for $n = 0–2$ (r = 0.989, 0.992 respectively, see below). The trichloroacetate is again anomalous, having a more shielded tin nucleus [δ(^{119}Sn) −80] than expected on the basis of the χ_g correlation (≈ −58). Since triaryltin carboxylates are monomeric in solution,[42] the high-field shift is probably due to intramolecular co-ordination of the type detected in the corresponding arylazobenzoates.[39] The triptycyltin carboxylate SnMe(tr)-$(CH_2CH{=}CH_2)$[OCOCH(Cl)Me] has a low Δ value of 2.41 mm s^{-1}. This value is typical of a four-co-ordinated species. The possibility of intramolecular co-ordination can be ruled out in view of the significant *downfield* shift (δ 0.0) of the ^{119}Sn NMR resonance compared with other alkyl carboxylates. The origin of this shift probably lies in distortion of the tetrahedral bond angles.[43]

^{119}Sn *NMR Spectroscopy.*—Several reviews on ^{119}Sn NMR spectra of organotin compounds have appeared.[8–12] In spite of this our understanding of the factors governing δ(^{119}Sn) values is poor, although some general trends have proved useful. In particular for four-co-ordinate organotin derivatives the resonances occur significantly downfield from those of five- and six-co-ordinated species. This has been of considerable value in structural work, as amply illustrated in a study of triphenyltin compounds.[44] The shifts of the compounds described in this work appear in Table 3.

For species $SnPh_2R(Br)$ the observed shifts are close to those expected, assuming additivity and taking $SnPh_3Br$ as the reference halide. For SnPhR(R′)Br rather large upfield deviations (*ca.* 30–40 ppm) occur from the predicted values. Since Mössbauer data suggest that all the structures are tetrahedral, these anomalies probably arise from distortions from the normal tetrahedral bond angles. Angle deformation has previously been shown to contribute significantly to the shielding (or deshielding) of the tin nucleus.[1,43] The presence of bulky groups such as adamantyl and triptycyl mitigates against halide-bridged structures.[45,46] The observed upfield shifts indicate that the central tin atom has developed some sp^2 character.

Correlations of Δ with NMR chemical shifts have been reported in both tin[47] and ferrocene chemistry.[48] However great care must be exercised in the analysis of such correlations in organotin compounds since the co-ordination number in the solid phase is frequently not the same as that in solution.[49] More recently it has been shown that, even for molecules with the same geometry, rather small changes in bond angles can have a marked effect on tin-119 shifts in the solid state.[50] A good example of structural differences in the solution and solid phases is to be found in the alkyltin halides (SnR_3X) which

Table 4 Tin-119 Mössbauer, ^{119}Sn NMR[a] and structural data for some triorganotin derivatives with Sn–O bonds

Compound	Co-ordination number	δ^b/mm s^{-1}	Δ/mm s^{-1}	Ref.	$\delta(^{119}Sn)$
$SnMe_3(OMe)$	5[c]	1.23	3.04	34	121
$SnMe_3(OCOMe)$	5[c]	1.31	3.57	35	129
		1.30	−3.68	36	
$SnMe_3(OCOCF_3)$	5[c]	1.42	4.18	35	
$SnPh_3(OH)$	5[c]	1.24	2.98	15	−86
$SnPh_3(OCOMe)$	—	1.28	3.36	37	−121
$SnPh_3(OCOCH_2Cl)$	—	1.32	3.53	37	−95
$SnPh_3(OCOCHCl_2)$	—	1.35	3.81	37	−79
$SnPh_3(OCOCCl_3)$	—	1.30	2.97	37	−80
$SnPh_3[OCH(Ph)CH_2COPh]$	5[d]	1.13	2.25	38	—
$SnPh_3[ON(Ph)COPh]$	5[d]	1.26	1.94	39, 40	—
$SnPh_3[OCC_6H_4N_2C_6H_3(OH)Me]$	5[d]	1.28	2.36	33	—
$(Ph_3Sn)_2O$	4	1.14	2.27	15	−80.6
$Sn(C_6H_{11})_3(OCOMe)$	4/5	1.57	3.27	16	—

[a] Data from refs. 8–12. [b] Relative to SnO_2. [c] Polymeric chains. [d] Monomeric.

are five-co-ordinate in the solid[5] but four-co-ordinate in solution.[49] On the other hand, triaryl- and trialkyl-tin halides with bulky R groups are four-co-ordinate in both solid and solution phases (*viz.* tricyclohexyltin chloride[17,31]).

Such Δ *vs.* $\delta(^{119}Sn)$ correlations are not unexpected. From a study of a series of unsymmetrical tetraorganotin derivatives, Parish and Platt[18] concluded that Δ values are controlled by imbalances in the polarity of the tin–ligand σ bonds due to electronegativity differences between the ligands and that π-bonding effects are less important. Although a theory of heavy-nuclei shielding is still not available, it is generally accepted that NMR chemical shifts are controlled mainly by the paramagnetic contribution, σ_p. For a related series of tin compounds, σ_p will depend on the imbalance of p-electron distribution resulting from electronegativity differences. Thus it is anticipated that Δ and $\delta(^{119}Sn)$ should be linearly related since they measure the same property of the nucleus.

If the data in Table 1 are separated into groups of the same co-ordination number in the solid phase, some interesting observations may be made. For the simple triphenyltin derivatives known to be four-co-ordinate [$SnPh_3X$ (X = Cl, Br or I)]* an excellent linear correlation between Δ and $\delta(^{119}Sn)$ exists (r = 0.999), equation (1) (N = 3, standard deviations in

$$\delta(^{119}Sn) = 234(4)\Delta - 641(10) \qquad (1)$$

parentheses). It has recently been shown[52] for $SnPh_3Cl$ that tin-119 shifts in solution and the solid state differ by only about 10 ppm, which clearly indicates a lack of association in the solid state. This is in contrast to the SnR_2Cl_2 species which show significant tetrahedral distortion as evidenced by the observation of extensive sideband patterns[52] and also marked differences in $\delta(^{119}Sn)$ for the solution and solid phases.[53]

For both five- and six-co-ordinate species, relationship (1) is, at best, very tenuous, indeed the latter series shows no significant correlation.

It is interesting to compare correlation (1) with that for the $(R_3Sn)_2E$ (E = chalcogen) series of derivatives obtained by Einstein *et al.*[47], which results in equation (2) (r = 0.981, N = 6

$$\delta(^{119}Sn) = 549(54)\Delta - 857(80) \qquad (2)$$

points). The two sets of data lie on very different lines in spite of the fact that all the compounds are basically tetrahedral. The ^{119}Sn NMR shifts appear to be very much more sensitive to changes in the chalcogen than in the halogen. The reason for this difference in behaviour is obscure. However, the crystal structures of $SnPh_3Cl$[28] and $SnPh_3Br$[29] show that the average C–Sn–C bond angles (112.4 and 113.8° respectively) are distorted away from the true tetrahedral angle, whereas those of the chalcogenides are much closer (E = S, 110.3; Se, 109.1; Te, 109.4°). Thus, for the $SnPh_3X$ species, the hybridisation of the central tin atom is tending towards sp^2 with concomitant increase in s-electron density resulting in greater shielding of the tin nucleus. This is supported by the generally higher isomer shifts of the $SnPh_3X$ series[2] compared with the chalcogenides.[47]

For the halide series $SnPh_3X$ there are good correlations of both Δ (r = 0.992, N = 4) and $\delta(^{119}Sn)$ (r = 0.997, N = 3) with Allred–Rochow electronegativities (χ). Similar correlation occurred with the chalcogenides. The dangers of using limited data in such correlations is highlighted when $(Ph_3Sn)_2O$ is included in the latter series. From the correlation of χ with $\delta(^{119}Sn)$ a value of about +150 is predicted for $\delta(^{119}Sn)$. The measured value is −80.6. It is also significant that $SnPh_3F$ lies off the δ *vs.* χ line. A closer examination of the δ and χ data for the $SnMe_3X$ series reveals some interesting trends. Plots of $\delta(^{119}Sn)$ *vs.* $\Delta\chi$ ($=\chi_x - \chi_{Sn}$) are linear for first-row elements (see Table 5) yielding the relationship (3) (r = 0.974, N = 8).

$$\delta = 121(11)\Delta\chi - 103(17) \qquad (3)$$

For heavier elements, again the plot was reasonably linear giving equation (4) (r = 0.962, N = 9). The slopes of the above

$$\delta = 242(26)\Delta\chi - 112(19) \qquad (4)$$

lines are markedly different and point towards spin–orbit coupling (heavy atom) effects.[54] Plots for the $SnPh_3X$ series show similar trends, the first-row elements again being anomalous. The correlations for the first-row and heavier elements are given by equations (5) (r = 0.929, N = 5) and (6)

$$\delta = 65(15)\Delta\chi - 178(24) \qquad (5)$$

$$\delta = 100(19)\Delta\chi - 153(14) \qquad (6)$$

(r = 0.921, N = 7) respectively. The slope of (6) is quite close to that of equation (3). The presence of polarisable electron clouds in the R_3Sn moiety appears to discourage d-orbital involvement by the heteroatom X.

Correlations of $\delta(^{119}Sn)$ with group electronegativities[41] based on the Pauling scale show greater scatter as do those with σ_I Hammett constants, though for both plots first-row elements lie on different lines from those of the heavier elements. This behaviour is mirrored in the relationship of χ_p *vs.* σ_I where slopes for the first-row elements are over twice as large as those for heavy elements.

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* $(Ph_3Sn)_2O$ is not included since literature values of Δ vary widely.[2,5,51]

Table 5 Variation of ^{119}Sn chemical shifts (δ^a in ppm from $SnMe_4$) with $\Delta\chi^b$ for $SnMe_3X$ and $SnPh_3X$ derivatives

$SnMe_3X$ X	$\delta^{119}Sn$	χ	$\Delta\chi$
Li	−183	0.97	−0.75
H	−104.5	2.20	0.48
CMe_3	18.5	2.50	0.78
NMe_2	75.5	3.07	1.35
OH	128	3.50	1.78
OMe	121	3.50	1.78
$OSnMe_3$	113	3.50	1.78
F	164.2	4.10	2.38
$SnMe_3$	−113	1.72	0.00
$TeSnMe_3$	−66.8	2.01	0.29
I	38.6	2.21	0.49
SMe	90	2.44	0.72
$SSnMe_3$	86.5	2.44	0.72
SeMe	45.6	2.48	0.76
$SeSnMe_3$	44.5	2.48	0.76
Br	128	2.74	1.02
Cl	158	2.83	1.11
$SnPh_3X$ X			
H	−148	2.20	0.48
C_6H_{11}	−113.7	2.50	0.78
OH	−86	3.50	1.78
$OSnPh_3$	−86.6	3.50	1.78
F	$+0.5^c$	4.10	2.38
$SnPh_3$	−143.6	1.72	0.00
$TeSnPh_3$	−143	2.01	0.29
I	−114.5	2.21	0.49
$SSnPh_3$	−48.7	2.44	0.72
$SeSnPh_3$	−76	2.48	0.76
Br	−59.8	2.74	1.02
Cl	−44.7	2.83	1.11

[a] High-field shifts are negative. Taken from refs. 8, 10, 11 and 47. [b] $\Delta\chi$ is the electronegativity difference (Allred–Rochow scale) between X and Sn. [c] This work in $HCONMe_2$ at 60 K.

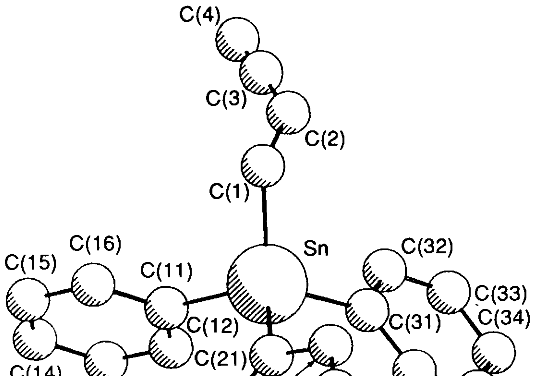

Fig. 1 A view of complex **1** showing the atom labelling

Crystal Structure of Complex **1**.—Table 6 presents the crystal data for complex **1**, positional parameters and selected bond lengths and angles are given in Table 7, and the molecule and its atomic numbering scheme are shown in Fig. 1.

The thermal parameters of the but-2-enyl group are large, and we infer that these groups are either vibrating over a fairly large distance or that there are a number of closely related stable positions possible for the group. The bond lengths and angles for this group are not ideal but structural features that are presented and the chemical understanding gained justifies their inclusion.

Table 6 Crystal data and data collection/refinement parameters for complex **1**

Crystal data	
Molecular formula	$C_{22}H_{22}Sn$
M	405.11
Crystal system	Triclinic
Crystal habit	Plate
Space group	$P\bar{1}$
Z	2
a/Å	9.892(3)
b/Å	10.196(4)
c/Å	11.637(5)
α/°	107.16(2)
β/°	103.40(2)
γ/°	109.77(2)
U/Å^3	981.0(7)
D_c/g cm^{-3}	1.371
μ(Mo-Kα)/mm^{-1}	1.3035
θ Range for lattice parameters (°)	22.2–24.5
Data collection	
Absorption correction	Empirical ψ scans of nine reflections
No. of independent reflections	3457
Ranges of *h*, *k*, *l*	−1 to 11, −12 to 12, −13 to 13
Variation of standards (average) (%)	1.8
Refinement	
Refinement on	*F*
Minimum difference peak, Δ_{min}/e Å^{-3}	−0.139
Maximum shift/error, $(\Delta/\sigma)_{max}$	<0.01
Weighting scheme, *w*	$1/[\sigma^2(F) + (0.02F)^2 + 1]$
S	0.912

The tin atom is in a slightly distorted-tetrahedral environment. The Sn–C phenyl bond lengths are two of 2.132(5) Å and one of 2.144(4) Å. These are on average [2.136(5) Å] slightly smaller than those of the other known triphenyltin(IV) compounds including tetraphenyltin (compound **5**, Table 8) where the average length is 2.144(14) Å. The Sn–C bond length for the but-2-enyl group is 2.164(6) Å. Such longer bonds are common as in structures **2**, **3**, **6** and **7**. The fact that the tin–alkyl bond is not always longer than the tin–phenyl bond can be seen in structure **4**. The question arises as to why should it be either longer or shorter? The hypothesis that we put forward is that if the group is bulky then it will be longer whether it is electron donating or attracting. Previously we suggested that such differences in bond lengths may be due either to the tin atom being bonded to sp^2- or sp^3-hybridised carbons with the latter being longer,[23] or that longer bonds were caused by steric hindrance of bulky groups. The results in Table 8 for compound **4** (which is sp^3 on the iodomethyl carbon, yet the bond is clearly not long), are in keeping with the main lengthening effect being the presence of a bulky or sterically demanding group. In **1** the but-2-enyl being *trans* is more sterically demanding while in **7** the adamantyl group necessitates longer bonds for both itself and the methyl group. It therefore appears that the evidence to date supports a very distorted-tetrahedral structure for the previously reported tetraadamantyltin.[1]

Finally, it is worthwhile to examine the angles in structures **1**–**7** (Table 8). Compound **1** has three angles around the (*E*)-but-2-enyl which average to 110.2°, which is slightly larger than the ideal tetrahedral angle, and the three C(phenyl)–Sn–C(phenyl) angles average to slightly less than the ideal. The same finding is apparent for compounds **2**, **3** and **6**. In tetraphenyltin(IV) the average angle is 109.5°, thus compounds **1**–**3** and **6** all show distorted-tetrahedral arrangements as was previously found for **7**.

Experimental

Preparation of Organotin Derivatives.—(E)-(*But-2-enyl*)*triphenyltin* **1**. This was prepared in 23% yield from the reaction of $Na(SnPh_3)$ and (*E*)-1-bromobut-2-ene in liquid ammonia. The product was recrystallised twice from methanol. Its ^{13}C NMR parameters (in $CDCl_3$) agreed precisely with those previously reported.[60,61]

Table 7 Positional parameters and selected interatomic distances (Å) and angles (°)

Atom	*x*	*y*	*z*
Sn	0.141 82(3)	0.271 91(3)	0.429 14(3)
C(1)	0.249 3(6)	0.121 1(6)	0.381 1(5)
C(2)	0.158 3(8)	−0.009 0(8)	0.259 4(8)
C(3)	0.147 7(9)	−0.046 4(9)	0.151 0(8)
C(4)	0.139(2)	−0.075(2)	0.060(1)
C(11)	0.178 7(4)	0.414 8(4)	0.326 7(4)
C(12)	0.062 2(5)	0.440 4(5)	0.262 6(4)
C(13)	0.085 8(5)	0.532 0(6)	0.195 8(5)
C(14)	0.227 3(6)	0.601 3(6)	0.193 0(5)
C(15)	0.346 8(6)	0.579 3(6)	0.256 3(5)
C(16)	0.323 1(5)	0.487 8(6)	0.323 2(5)
C(21)	0.239 2(4)	0.403 0(4)	0.633 1(4)
C(22)	0.307 7(5)	0.561 8(5)	0.688 1(5)
C(23)	0.369 0(6)	0.642 8(6)	0.820 4(6)
C(24)	0.363 0(6)	0.567 0(7)	0.900 0(5)
C(25)	0.296 0(6)	0.411 4(6)	0.848 3(5)
C(26)	0.235 3(5)	0.329 5(5)	0.716 8(4)
C(31)	−0.102 9(4)	0.151 2(4)	0.376 1(4)
C(32)	−0.199 5(6)	0.048 8(6)	0.252 1(5)
C(33)	−0.360 5(7)	−0.021 8(7)	0.219 9(7)
C(34)	−0.421 3(6)	0.011 7(6)	0.312 3(7)
C(35)	−0.328 4(6)	0.111 5(6)	0.433 2(5)
C(36)	−0.169 9(5)	0.181 6(5)	0.466 0(4)

Sn–C(1)	2.164(6)	C(21)–C(22)	1.391(7)
Sn–C(11)	2.132(4)	C(21)–C(26)	1.393(6)
Sn–C(21)	2.132(5)	C(22)–C(23)	1.377(8)
Sn–C(31)	2.144(4)	C(23)–C(24)	1.370(9)
C(1)–C(2)	1.44(1)	C(24)–C(25)	1.363(9)
C(2)–C(3)	1.17(1)	C(25)–C(26)	1.371(8)
C(3)–C(4)	0.99(1)	C(31)–C(32)	1.372(7)
C(11)–C(12)	1.369(6)	C(31)–C(36)	1.379(7)
C(11)–C(16)	1.387(6)	C(32)–C(33)	1.408(9)
C(12)–C(13)	1.377(7)	C(33)–C(34)	1.36(1)
C(13)–C(14)	1.351(8)	C(34)–C(35)	1.335(9)
C(14)–C(15)	1.364(8)	C(35)–C(36)	1.385(7)
C(15)–C(16)	1.377(8)		
C(1)–Sn–C(11)	108.7(2)	C(11)–Sn–C(21)	111.3(2)
C(1)–Sn–C(21)	109.0(2)	C(11)–Sn–C(31)	107.6(2)
C(1)–Sn–C(31)	112.8(2)	C(21)–Sn–C(31)	107.5(2)

Numbers in parentheses are estimated standard deviations in the least significant digits.

Adamantyl(*methyl*)*phenyltin bromide*. Adamantyl(methyl)diphenyltin[1] (1.9 g, 2.36 mmol) was dissolved in AR acetone (10 cm^3) and treated with solid mercury(II) bromide (0.853 g, 2.36 mmol). The mixture was refluxed overnight. The solid which had precipitated was filtered off and the filtrate evaporated to give an oily white solid. Some carbon tetrachloride was added and the whole stirred for a while, filtered and the solvent removed. The resulting oily material was then treated with a mixture of methanol and light petroleum and allowed to stand overnight. The crystals were triturated with methanol and filtered off, m.p. 66–67 °C, yield 65%. ^1H NMR (in CCl_4 from $SiMe_4$): δ 7.6–7 (m, aromatic, 5 H), 2.5–1.5 (m, adamantyl, 13 H); and 0.7 (s, methyl, 3 H, J ^{117,119}Sn 48 Hz) (Found: C, 47.9; H, 5.5; Br, 18.4. Calc. for $C_{17}H_{23}BrSn$: C, 47.9; H, 5.4; Br, 18.7%).

Methyl(*phenyl*)*triptycyltin bromide*. Methyldiphenyltriptycyltin (1.3 g, 2.4 mmol) was dissolved in AR chloroform (10 cm^3) and a solution of bromine (0.385 g, 2.4 mmol) in chloroform (10 cm^3) was added dropwise at 0 °C. The solvent was removed *in vacuo* to give a white, slightly oily solid. It was stirred with a little methanol, filtered off and dried, then recrystallised from acetone and dried in an oven at 110 °C, m.p. 269–270 °C, yield 75%, ^1H NMR (in $CDCl_3$ from $SiMe_4$): δ 8–6.8 (m, aromatic, 5 H), 5.5 (s, methine), 1.25 (s, methyl, 3 H, $J^{117,119}$Sn, 52 Hz) (Found: C, 58.65; H, 4.05; Br, 14.70. Calc. for $C_{27}H_{21}BrSn$: C, 59.6; H, 3.90; Br, 14.70%).

Allyl(*methyl*)*triptycyltin chloropropionate*. The compound $SnMe(tr)(CH_2CH{=}CH_2)_2$[1] (0.2 g, 0.43 mmol) was dissolved in AR CCl_4 (2 cm^3). Chloropropionic acid (0.108 cm^3, 1.29 mmol) was added. The mixture was heated briefly to reflux then allowed to stand for 1 h at room temperature. The CCl_4 was removed and the remaining white solid was recrystallised from methanol, m.p. 144–147 °C, yield 80%. ^1H NMR (in CCl_4 from $SiMe_4$): δ 7.7–6.8 (m, aromatic, 12 H), 5.3 (s, methine), 6.2 (m, olefinic CH=), 4.4 (q, aliphatic CH of propionate), 2.7 (d, aliphatic CH_2, J ^{117,119}Sn 64), 1.7 (d, methyl of propionate group), and 1.07 (s, methyl, $J^{117,119}$Sn 52 Hz) (Found: C, 61.2; H, 4.8; Cl, 7.1. Calc. for $C_{27}H_{25}ClO_2Sn$: C, 60.55; H, 4.70; Cl, 6.65%).

Allyl(*methyl*)*triptycyltin bromide*. Allyl(methyl)triptycyltin chloropropionate (1 g, 1.86 mmol) and LiBr (0.161 g, 1.86 mmol) were dissolved in AR acetone (15 cm^3) at room temperature and the mixture shaken for 0.5 h. The solvent was removed, AR CCl_4 (10 cm^3) added, and the whole shaken again

Table 8 Comparison of the known $SnRPh_3$ (R = alkyl, aryl or metal) structures

	1	**2**	**3**	**4**	**5**	**6**	**7**
Bond length (Å)							
Sn–C(Ph)	2.132(4)	2.16(1)	2.16(1)	2.143(6)	2.144(14)	2.145(14)	2.139(10)
	2.132(5)	2.15(1)	2.16(1)	2.135(6)	2.144(14)	2.157(14)	2.144(10)
	2.144(4)	2.12(1)	2.16(1)	2.120(5)	2.144(14)	2.197(17)	2.163(10)
average	2.136	2.16	2.16	2.134(6)	2.144	2.17	2.148
Sn–R	2.164(6)	2.23(2)	2.21(1)	2.134(6)	2.144(14)	2.590(2)	2.175(9)
Bond angles (°)							
C(Ph)–Sn–C(Ph)	107.6(2)	108.94(6)	104.2(0.9)	106.3(2)	110.8(9)	99.7(5)	109.8(4)
	107.5(2)	107.13(5)	106.8(1.0)	111.8(2)	110.8(9)	99.4(6)	113.1(3)
	111.3(2)	107.26(5)	107.2(1.0)	110.7(2)	108.8(4)	98.2(6)	108.5(4)
average	108.8	107.8	106.1	109.6		99.1	
C(Ph)–Sn–R	108.7(2)	108.27(5)	107.2(1.3)	107.5(3)	108.8(4)	115.4(4)	109.2(5)
	109.0(2)	113.57(5)	113.4(1.4)	110.7(3)	108.8(4)	118.4(4)	109.4(5)
	112.8(2)	111.38(5)	117.1(1.5)	109.7(3)	108.8(4)	121.6(4)	106.8(5)
average	110.2	110.8	112.56	109.3	109.5*	118.47	109.5*

Complexes: (*E*)-But-2-enyltriphenyltin **1** (this work); butyltriphenyltin **2**;[55] (cyclohepta-1,3,5-trienyl)triphenyltin **3**;[56] (iodomethyl)triphenyltin **4**;[57] tetraphenyltin **5**;[58] (trimethylphosphine)(triphenylstannyl)cobalt **6**;[59] adamantyl(methyl)diphenyltin **7**.[23] * Average of all six angles.

for a few minutes, then filtered. The solvent was removed and the remaining white solid was recrystallised from ethanol, m.p. 204 °C, yield: 80%. ^{1}H NMR (in CCl$_4$ from SiMe$_4$): δ 7.6–6.7 (m, aromatic), 6.1–5.4 (m, olefinic CH=), 5.23 (s, methine), 5.2–4.9 (t, olefinic =CH$_2$), 2.73 (d, aliphatic CH$_2$, $J\,^{117,119}$Sn 64), and 1.15 (s, methyl, $J\,^{117,119}$Sn 52 Hz) (Found: C, 56.7; H, 4.0; Br, 15.6. Calc. for $C_{24}H_{21}BrSn$: C, 56.7; H, 4.1; Br, 15.7%).

Adamantyl(phenyl)tin dibromide. Adamantyl triphenyltin[1] (12 g, 0.024 mol) was dissolved in the minimum volume of AR CCl$_4$ then treated with a 1 mol dm^{-3} solution of bromine (0.048 mol, 48 cm^3) in the same solvent. The solution decolourised rapidly and after 5 min the solvent was removed, leaving an oily liquid. On standing overnight at 0 °C white crystals were obtained. These were triturated with methanol and filtered off. The product was recrystallised from methanol and dried, giving 9 g (75%) white crystals, m.p. 110 °C. ^{1}H NMR (in CCl$_4$ from SiMe$_4$): δ 7.5 (m, aromatic, 5 H) and 2.7–1.4 (m, adamantyl, 15 H) (Found: C, 38.9; H, 4.0; Br, 32.2. Calc. for $C_{16}H_{20}Br_2Sn$: C, 39.15; H, 4.10; Br, 32.55%).

Adamantyldiphenyltin bromide. Adamantyltriphenyltin[1] (2.45 g, 5 mmol) was dissolved in AR acetone (100 cm^3), treated with mercury(II) bromide (1.80 g, 5 mmol), and the mixture refluxed for 4 h. On cooling to room temperature a white solid appeared which was filtered off. This was shown by NMR spectroscopy and its melting point (276 °C) to be phenylmercury(II) bromide. The filtrate was evaporated *in vacuo* to give a white oily solid. A little methanol was added and on standing overnight at −15 °C crystallisation occurred,. The crystals were filtered off to give 2.1 g (85%) of white solid. The crude material was extracted with CCl$_4$ and the insoluble material filtered off. The solvent was removed and an oily solid again obtained, which on trituration with methanol at 0 °C gave white crystals, m.p. 93–95 °C. ^{1}H NMR (in CCl$_4$ from SiMe$_4$): δ 8–7 (m, aromatic, 10 H), and 2.65–1.5 (m, adamantyl, 15 H) (Found: C, 54.4; H, 5.2; Br, 16.2. Calc. for $C_{22}H_{25}BrSn$: C, 54.15; H, 5.15; Br, 16.35%).

The iodo derivative of the above compound was also prepared by cleavage with iodine (in CCl$_4$ or CHCl$_3$) or by HgI$_2$ (in acetone), m.p. 109–111 °C.

Diphenyltriptycyltin bromide. Triphenyltriptycyltin[1] (2 g, 3.3 mmol) was dissolved in AR CHCl$_3$ (40 cm^3) and placed in an ice-bath. A solution of bromine in CHCl$_3$ (13.5 cm^3, 0.25 mol dm^{-3}, 3.4 mmol) was added dropwise over 2 h at 0 °C with rapid stirring. The bromine colour had disappeared completely after 3 h. The solvent was then removed *in vacuo* to give a slightly off-white solid. This was stirred with a little methanol, filtered off and dried, then recrystallised from benzene, m.p. 311–312 °C. ^{1}H NMR (in CDCl$_3$ from SiMe$_4$): δ 8.3–6.5 (aromatic, 22 H) and 5.5 (methine) (Found: C, 64.2; H, 3.9; Br, 12.6. Calc. for $C_{32}H_{23}BrSn$: C, 63.4; H, 3.8; Br, 13.2%).

Diallyltriptycyltin bromide. Triallyltriptycyltin[1] (4 g, 8.08 mmol) was dissolved in AR acetone (100 cm^3). Solid mercury(II) bromide (3.67 g, 8.08 mmol) was added under dry argon with stirring and the mixture refluxed gently overnight. On cooling allylmercury(II) bromide was obtained (m.p. 125–126 °C). The filtrate was evaporated leaving a white solid. This was triturated with CCl$_4$ and filtered to remove any residual allylmercury bromide. Evaporation of the filtrate gave a white solid which was recrystillised from methanol. Yield: 2.8 g (65%), m.p. 188–189 °C. ^{1}H NMR (in CDCl$_3$ from SiMe$_4$): δ 7.8–6.8 (m, aromatic, 12 H), 6.1 (m, olefinic, 1 H), 5.3 (s, methine, 1 H), 5.2–4.65 (t, olefinic, 2 H), and 2.88 (aliphatic, 2 H, $J\,^{117,119}$Sn 64 Hz) (Found: C, 57.6; H, 4.2; Br, 15.8. Calc. for $C_{26}H_{23}BrSn$: C, 58.4; H, 4.3; Br, 14.9%).

Methyl(phenyl)triptycyltin mandelate. Methyldiphenyltriptycyltin (0.50 g, 0.92 mmol) and (S)(+)-mandelic acid (α-hydroxybenzeneacetic acid) (0.14 g, 0.92 mmol) were finely ground together, then heated on an oil-bath at 110–120 °C for 40 min. On cooling the resultant solid was extracted with hot CCl$_4$ (15 cm^3). After filtration and cooling at −15 °C over 4 d unreacted mandelic acid crystallised. The filtrate was evaporated and extracted with light petroleum (b.p. 30–40 °C) and stored at 0 °C for 2 h. The resultant solid was filtered off. Proton NMR analysis showed that the desired compound had been made but was contaminated with 10–15% mandelic acid. The latter proved impossible to remove and the product appeared to decompose on standing.

^{119}Sn *NMR and Mössbauer Measurements*.—^{119}Sn NMR data were obtained using a Bruker WP 80 SY spectrometer as described previously.[1] Mössbauer data were obtained as in Part 1 of this series.[1]

Crystal Structure Determination of Complex **1**.—A colourless single crystal having approximate dimensions 0.5 × 0.5 × 0.08 mm was mounted on a glass fibre in a random orientation. All geometric and intensity data were taken from this sample at 18 °C using an Enraf-Nonius CAD4 computer-controlled kappa-axis diffractometer equipped with Mo-Kα radiation (λ = 0.7107 Å). The Kα band was isolated using a graphite-crystal incident-beam monochromator. Twenty-five reflections were located and measured using the CAD4 search routine which utilised the computer-controlled diagonal slit method of centring. Cell constants and an orientation matrix for the data collection were obtained by application of the CAD4 automatic indexing routine to the positions of these 25 reflections. The ω–2θ scan technique was used to measure 4254 reflections in the range $3 \leqslant 2\theta \leqslant 50$. The scan rate varied from 1 to 7° min (in ω). The variable scan rate allows rapid data collection for intense reflections and assures good counting statistics for weak reflections. The three standard reflections (remeasured every 60 min) showed a small linear loss in intensity which was corrected for. Intensity data were corrected for Lorentz, polarisation and absorption effects (ψ scans) in the usual manner. The 2986 unique data with $I > 3\sigma(I)$ were used to solve and refine the structure. There were no systematic absences and the space group was determined to be $P\bar{1}$ (no. 2).

The structure was solved by conventional Patterson and Fourier-difference methods. Hydrogen atoms were placed in ideal positions with a fixed isotropic thermal parameter (U = 0.080 Å^2). All other atoms were refined with anisotropic thermal parameters. The final cycle of least-squares refinement included 208 parameters and did not shift any parameter by more than 0.01 times its standard deviation. The final R and R' values were 0.034 95 and 0.042 74, and the final Fourier map was featureless with no peaks greater than 0.96 e Å^{-3}. All calculations were carried out on a DEC Micro-VAX computer using SHELXS 86[62] or MOLEN;[63] structures were drawn using ORTEP.[64] Atomic scattering factors were taken from ref. 65.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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