Crystal and Molecular Structure of 1,2;3,4-Di-μ-*o*-aminobenzoato-*OO′*-1,3-bis(*o*-aminobenzoato-*O*)-1,2,4; 2,3,4-di-μ_3-oxo-tetrakis[di-n-butyltin(IV)]†

Suraj P. Narula,* Shashi K. Bharadwaj, and Hemant K. Sharma
Chemistry Department, Panjab University, Chandigarh 160 014, India
Gaetan Mairesse, Pierre Barbier, and Guy Nowogrocki
Equipe de Cristallochimie UAU 52 CNRS, 1004, Ecole Nationale Superieure de chimie de Lille, 59652, Ville neuve, D'Ascq cedex, France

The crystal structure of $[\{[\mathrm{SnBu^n_2(O_2CC_6H_4NH_2}\text{-}o)]_2\mathrm{O}\}_2]$ has been determined by single-crystal *X*-ray diffraction (298 K); space group $P\bar{1}$, a = 17.278(9), b = 15.890(9), c = 14.154(8) Å, α = 71.80(9), β = 68.67(8), γ = 82.02(6)°, Z = 2, and R = 0.050 for 2 038 reflections [$I > 3\sigma(I)$]. This dimer incorporates two bridging, one effectively isobidentate, and one nearly unidentate carboxy groups. The Sn–O and C–O bond distances, OCO bond angles (non-bridging carboxy groups), ^{119m}Sn Mössbauer, i.r., and n.m.r. (^{1}H, ^{13}C, and ^{119}Sn) spectral data reveal that one molecule, (**I**), in the dimer has one six-co-ordinate and one five-co-ordinate tin atom while the other, (**II**), has two six-co-ordinate tin atoms. This stannoxane is the first example of its kind so far reported.

The commercial viability of organotin carboxylates has necessitated understanding of the bonding in these compounds to establish the relationship between their biocidal, antifouling, wood preservation, *etc.* activity with structure. Consequently, in recent years there has been an upsurge in the synthesis and structural elucidations of various organotin esters of well known carboxylic acids. Among many such compounds, triorganotin esters of substituted benzoic acids and other derivatives have received much attention[1–5] and each report has revealed a new structural possibility. Trimethyltin glycinate[6] is different from the known carboxylates in having electron-lone-pair donation through nitrogen. The carbonyl oxygen is only hydrogen bonded, thereby giving a cross-weave structure to this polymeric compound. Thus the presence of amino group(s) in the ligands attached to tin has assumed importance as the prospective donor site and/or source of hydrogen bonding in/or between the molecules.[1,3–7] A survey of the literature, however, reveals that diorganotin esters in general and dicarboxystannoxanes carrying ligands with functional substituents, in particular, have not received attention commensurate with the structural possibilities.[8–10] The dimer $[\{[\mathrm{SnBu^n_2(O_2CC_6H_4NH_2}\text{-}o)]_2\mathrm{O}\}_2]$ is one such example. Therefore, a detailed structural study of this compound has been attempted and the results obtained are now reported.

Discussion

The compound is obtained by azeotropic removal of water from the reaction between di-n-butyltin oxide and *o*-aminobenzoic acid in the molar ratio 1 : 1 in benzene. Single-crystal *X*-ray data (see Experimental section) are consistent with the molecular structure shown in the Figure. This reveals the association of two similar molecules through Sn–O linkages with crystallographically imposed $\bar{1}$ symmetry. The compounds $[\{[\mathrm{SnMe_2(O_2CCH_2Cl)]_2O}\}_2]$,[8] $[\{[\mathrm{SnBu_2(O_2CCCl_3)]_2O}\}_2]$,[9] and $[\{[\mathrm{SnMe_2(NCS)]_2O}\}_2]$[11] also contain a planar four-membered $\mathrm{Sn_2O_2}$ ring. The atoms Sn(1) and Sn(2) as well as Sn(40) and Sn(41) are linked by carboxy bridges. The remaining two carboxy groups are non-bridging. The butyl groups are shown to subtend angles of 137(4) and 149(4)° at Sn(1) and Sn(2), but 136(3) and 140(3)° at Sn(40) and Sn(41) respectively.

The deviation from linearity of the axial angles O(14)–Sn(1)–O(4) and O(15)–Sn(2)–O(3$^\mathrm{I}$) [165(7) and 170(7)° respectively] and O(53)–Sn(40)–O(43) and O(54)–Sn(41)–O(42$^\mathrm{I}$) [each 169(7)°] may be due to interactions between Sn(2$^\mathrm{I}$) and O(4) and Sn(41$^\mathrm{I}$) and O(43).[8] The bond distances O(4)–Sn(2$^\mathrm{I}$) and O(43)–Sn(41$^\mathrm{I}$) [2.72(1) and 2.79(2) Å respectively] are considerably less than the sum of the van der Waals radii (3.70 Å), greater than the commonly occurring Sn–O covalent bond (2.0 ± 0.05 Å),[3,12] but near to the Sn–O bond distance (2.69 Å) observed in a 1 : 1 adduct of dichlorodimethyltin(IV) and salicylaldehyde.[13] These data may suggest co-ordinate bond formation between these atoms giving Sn(2) and Sn(41) distorted octahedral environments in the dimer.

Table 1 shows that the CSnC bond angles at Sn(2) and Sn(41) [149(4) and 140(3)° respectively] are relatively wider than those at the other two tin atoms. This may lead to greater exposure of these tin atoms to oxygens O(4) and O(43) respectively and comparatively stronger association (or six-co-ordination) as mentioned above. On the other hand, Sn(1) and Sn(40) have relatively narrow CSnC angles [137(4) and 136(3)°] and therefore are expected to have reduced but nearly equal (from the angle values) interactions. The bond distances O(5)–Sn(1) and O(44)–Sn(40) [3.11(2) and 2.84(1) Å respectively] do indicate reduced interactions but these are by no means equal. The CSnC bond angles along with n.m.r.[14] and Mössbauer[5] spectral data have been used to predict the co-ordination number in organotin compounds. However, angles in the range 130—150° (as well as parameters dependent on these angles) have predicted both bipyramidal and octahedral geometry around tin.[14] Therefore these angles in isolation cannot be used to ascertain the co-ordination number of tin.

The interactions due to other oxygens as well as the angles subtended at tin in the $\mathrm{Sn_2O_2}$ ring are essentially as reported previously.[8,9,15]

The present compound differs from carboxystannoxanes reported[9–11] in respect of the CO bond lengths and OCO bond angles in the non-bridged carboxy ligands. Whereas O(4)–C(6) [1.31(3) Å] and C(6)–O(5) [1.22(2) Å] in molecule (**I**) are unequal, the corresponding O(43)–C(45) and C(45)–O(44) distances in molecule (**II**) are 1.30(3) and 1.28(4) Å respectively. This discrepancy is further reflected in the intramolecular distances such as O(5) • • • Sn(1) [3.11(2) Å] and O(44) • • • Sn(40) [2.84(1) Å]. The latter distance is near to those observed between carboxy oxygens O(4) and O(43) and the

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

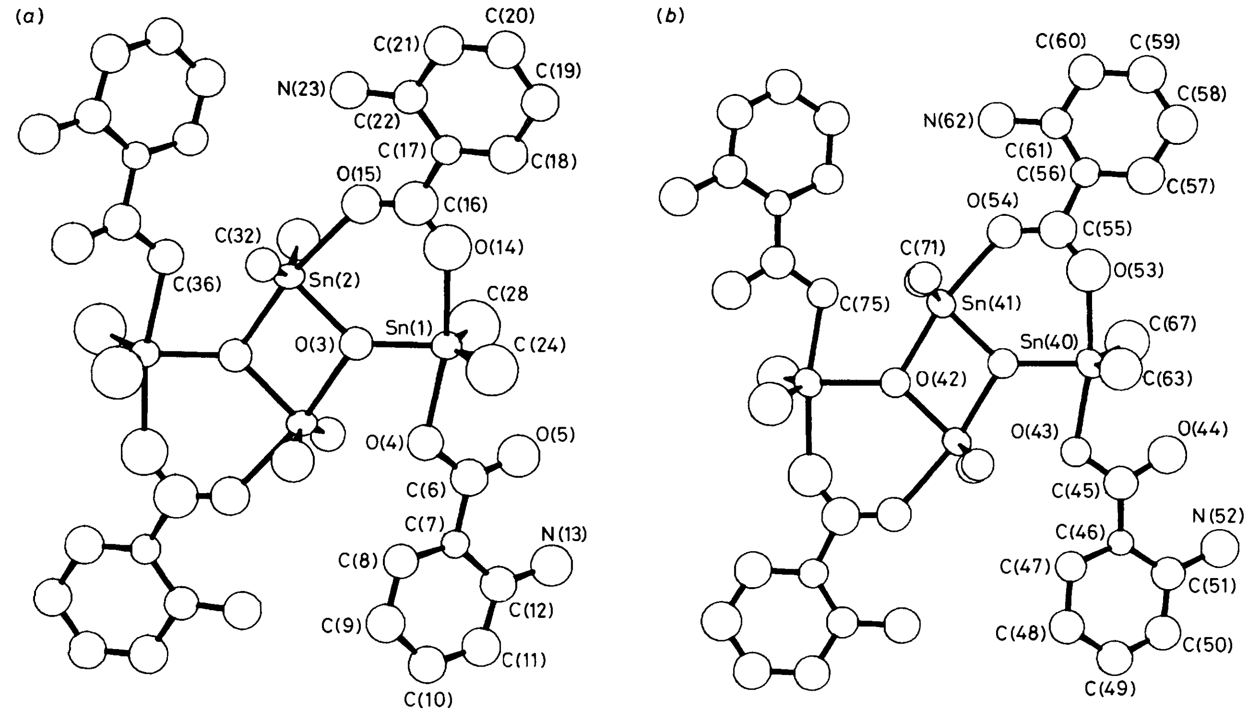

Figure. Perspective drawings of molecules (**I**) (*a*) and (**II**) (*b*) showing the numbering scheme. For clarity, only the first carbon atoms of the butyl chain linked to Sn shown

neighbouring atoms Sn(2^{I}) and Sn(41^{I}) which are proposed to be co-ordinately linked.

The longer bond distance Sn(1)–O(4) [2.23(2) Å] relative to Sn(40)–O(43) [2.15(2) Å] is at variance with weaker association between Sn(1) and O(5) atoms. This anomaly may be explained by the simultaneous stronger interaction O(4) ··· Sn(2^{I}) [2.72(1) Å] than O(43) ··· Sn(41^{I}) [2.79(2) Å]. Further support to the differing interactions between O(5) and O(44) and their respective tin atoms comes from OCO bond angles. Whereas O(4)–C(6)–O(5) is 123(4)°, O(43)–C(45)–O(44) is 114(4)°, assignable to unidentate and chelate bidentate carboxy groups respectively. Molloy *et al.*[4] have also suggested a unidentate character for a carboxy group with similar crystallographic data to those for O(4)–C(6)–O(5).

Holmes and co-workers[2] reported that isobidentate character of a carboxy group towards tin is opposed by intramolecular hydrogen bonding of carbonyl oxygen in triphenyltin *o*-amino/hydroxybenzoates, *etc.* All the intramolecular O ··· (H)N bond distances [2.69(2) Å] recorded here (Table 2) are shorter than the sum of van der Waals radii of these atoms (2.9 Å), indicating the existence of hydrogen bonding in the dimer. The presence of intramolecular hydrogen bonding is confirmed by i.r. and n.m.r. spectral data (see below). However, the almost equivalent O ··· (H)N distances obtained here are intriguing as the expected stronger interaction O(5) ··· HN(13) cannot permit this equality. However, in the absence of crystallographically determined positions for the hydrogen atoms and the presence of other supporting crystal data it is difficult completely to rule out the possibility of the carboxy group being unidentate resulting from intramolecular hydrogen bonding.

The ^{119m}Sn Mössbauer spectrum of the dimer gave an isomer shift (δ) 1.34 and a quadrupole splitting (q.s.) of 3.50 mm s^{-1} (ρ = q.s./δ = 2.6), indicating an average co-ordination number for tin of greater than four. With the availability of crystallographically determined bond angles RSnR, the q.s. values can be calculated for each tin atom using Sham and Bancroft's equation.[16] The average value obtained is in good agreement with the observed value, testifying to the applicability of the equation. Davies *et al.*[17] also calculated q.s.

Atom	RSnR angle/°	Q.s./mm s^{-1}
Sn(1)	136	3.32
Sn(2)	149	3.68
Sn(40)	137	3.34
Sn(41)	140	3.42
		Av. 3.44

values for tin atoms in a few dibutyldioxastannolanes and their derivatives in the same way and these are in good agreement with the experimental values. It may be pointed out that although the CSnC angles and q.s. values (which depend upon these angles) in isolation cannot be used to predict the geometry of each tin atom in the dimer, the available literature values support the structure proposed. For example CSnC 136 ± 1° and q.s. = 3.33 ± 1 mm s^{-1} are commonly found for five- and six-co-ordinate tin and indicate both these geometries here.

The i.r. spectrum of the solid dimer gave bands at 3 475 and 3 370 cm^{-1} [ν(NH)] along with one band (unresolved) at 3 470 cm^{-1} attributable to ν(NH ··· O); ν(CO_2) modes are observed at 1 605 and 1 530 cm^{-1}. In dilute CCl_4 solutions, these bands shift to 3 505, 3 390, 1 625, and 1 520 cm^{-1} respectively. The ν(CO_2) bands are assigned to co-ordinated, bridging, or non-bridging carboxy groups[18,19] while the absorption due to hydrogen bonding (H ··· O) at 3 470 cm^{-1} disappears in carbon tetrachloride solution. These spectral shifts in solution support the cleavage of hydrogen bonds in the dimer.

The following n.m.r. spectral data (δ) were obtained: ^{1}H (for each organotin moiety), 0.8 (t, 6 H, CH_3), 1.70—1.80 (m, 12 H, CH_2), 5.75 (s, 2 H, NH_2), 6.6, 6.72, 7.2, and 7.35 (m, 4 H, C_6H_4); ^{13}C, 13.5 (CH_3), 26.9, 27.7, 27.9 (3CH_2), 116.2, 116.7, 132.6, 133.4 (C_6H_4), 150.6 [C(NH_2)], and 174.8 (very weak, CO_2) p.p.m.; ^{119}Sn, −210.9 and −220.6 p.p.m. The ^{1}H n.m.r.

Table 1. Main bond lengths (Å) and angles (°) within the two molecules of $[\{[SnBu^n{}_2(O_2CC_6H_4NH_2\text{-}o)]_2\}_2]$

Sn(1)–O(3)	1.97(1)	Sn(2)–O(3)	2.09(1)	Sn(40)–O(42)	2.05(1)	Sn(41)–O(42)	2.01(1)
Sn(1)–O(4)	2.23(2)	Sn(2)–O(3^{I})	2.17(2)	Sn(40)–O(43)	2.15(2)	Sn(41)–O(42)	2.17(2)
Sn(1)–O(14)	2.26(2)	Sn(2)–O(15)	2.29(2)	Sn(40)–O(53)	2.22(2)	Sn(41)–O(54)	2.28(2)
Sn(1)–C(24)	2.17(3)	Sn(2)–C(32)	2.14(2)	Sn(40)–C(63)	2.22(2)	Sn(41)–C(71)	2.15(2)
Sn(1)–C(28)	2.14(4)	Sn(2)–C(36)	2.14(2)	Sn(40)–C(67)	2.14(3)	Sn(41)–C(75)	2.17(2)
O(4)–C(6)	1.31(3)	O(14)–C(16)	1.22(4)	O(43)–C(45)	1.30(3)	O(53)–C(55)	1.25(3)
O(5)–C(6)	1.22(2)	O(15)–C(16)	1.21(3)	O(44)–C(45)	1.28(4)	O(54)–C(55)	1.26(4)
C(6)–C(7)	1.53(4)	C(16)–C(17)	1.51(5)	C(45)–C(46)	1.46(4)	C(55)–C(56)	1.51(4)
C(7)–C(8)	1.39(3)	C(17)–C(18)	1.39(4)	C(46)–C(47)	1.39(4)	C(56)–C(57)	1.42(4)
C(8)–C(9)	1.46(4)	C(18)–C(19)	1.44(4)	C(47)–C(48)	1.42(4)	C(57)–C(58)	1.45(5)
C(9)–C(10)	1.40(3)	C(19)–C(20)	1.42(3)	C(48)–C(49)	1.40(3)	C(58)–C(59)	1.42(4)
C(10)–C(11)	1.37(3)	C(20)–C(21)	1.37(4)	C(49)–C(50)	1.38(4)	C(59)–C(60)	1.40(4)
C(11)–C(12)	1.45(4)	C(21)–C(22)	1.45(4)	C(50)–C(51)	1.42(4)	C(60)–C(61)	1.44(4)
C(12)–C(7)	1.46(3)	C(22)–C(17)	1.44(3)	C(51)–C(46)	1.39(3)	C(61)–C(56)	1.36(3)
N(13)–C(12)	1.35(3)	N(23)–C(22)	1.36(3)	N(52)–C(51)	1.40(4)	N(62)–C(61)	1.40(3)
O(3)–Sn(1)–O(4)	79(1)	O(3)–Sn(2)–O(3^{I})	78(1)	O(42)–Sn(40)–O(43)	81(1)	O(42)–Sn(41)–O(42^{I})	75(1)
O(3)–Sn(1)–O(14)	89(1)	O(3)–Sn(2)–O(15)	91(1)	O(42)–Sn(40)–O(53)	89(1)	O(42)–Sn(41)–O(54)	94(1)
O(3)–Sn(1)–C(24)	117(3)	O(3)–Sn(2)–C(32)	103(1)	O(42)–Sn(40)–C(63)	108(2)	O(42)–Sn(41)–C(71)	109(1)
O(3)–Sn(1)–C(28)	107(2)	O(3)–Sn(2)–C(36)	105(1)	O(42)–Sn(40)–C(67)	114(2)	O(42)–Sn(41)–C(75)	110(1)
O(4)–Sn(1)–O(14)	165(7)	O(3^{I})–Sn(2)–O(15)	170(7)	O(43)–Sn(40)–O(53)	169(7)	O(42^{I})–Sn(41)–O(54)	169(7)
O(4)–Sn(1)–C(24)	88(2)	O(3^{I})–Sn(2)–C(32)	101(1)	O(43)–Sn(40)–C(63)	93(1)	O(42^{I})–Sn(41)–C(71)	100(1)
O(4)–Sn(1)–C(28)	99(2)	O(3^{I})–Sn(2)–C(36)	97(1)	O(43)–Sn(40)–C(67)	104(2)	O(42^{I})–Sn(41)–C(75)	96(1)
O(14)–Sn(1)–C(24)	89(2)	O(15)–Sn(2)–C(32)	79(1)	O(53)–Sn(40)–C(63)	87(1)	O(54)–Sn(41)–C(71)	86(1)
O(14)–Sn(1)–C(28)	93(2)	O(15)–Sn(2)–C(36)	87(1)	O(53)–Sn(40)–C(67)	84(1)	O(54)–Sn(41)–C(75)	86(1)
C(24)–Sn(1)–C(28)	137(4)	C(32)–Sn(2)–C(36)	149(4)	C(63)–Sn(40)–C(67)	136(3)	C(71)–Sn(41)–C(75)	140(3)
Sn(1)–O(3)–Sn(2)	135(1)	Sn(1)–O(3)–Sn(2^{I})	122(1)	Sn(40)–O(42)–Sn(41)	135(1)	Sn(40)–O(42)–Sn(41^{I})	120(1)
Sn(2)–O(3)–Sn(2^{I})	102(1)	Sn(1)–O(14)–C(16)	142(6)	Sn(41)–O(42)–Sn(41^{I})	105(1)		
Sn(1)–O(4)–C(6)	116(3)	Sn(2)–O(15)–C(16)	136(5)	Sn(40)–O(43)–C(45)	116(2)	Sn(40)–O(53)–C(55)	140(5)
O(4)–C(6)–O(5)	123(4)	O(14)–C(16)–O(15)	123(5)	O(43)–C(45)–O(44)	114(4)	O(53)–C(55)–O(54)	123(5)
O(4)–C(6)–C(7)	115(4)	O(14)–C(16)–C(17)	115(5)	O(43)–C(45)–C(46)	124(4)	C(55)–O(54)–Sn(41)	133(4)
C(6)–C(7)–C(8)	115(4)	C(16)–C(17)–C(18)	117(6)	O(44)–C(45)–C(46)	122(5)	O(53)–C(55)–C(56)	120(5)
C(6)–C(7)–C(12)	119(4)	C(17)–C(18)–C(19)	117(5)	C(45)–C(46)–C(47)	114(5)	O(54)–C(55)–C(56)	117(5)
C(8)–C(7)–C(12)	125(4)	C(18)–C(19)–C(20)	118(5)	C(45)–C(46)–C(51)	121(4)	C(55)–C(56)–C(57)	111(5)
C(7)–C(8)–C(9)	119(4)	C(19)–C(20)–C(21)	123(5)	C(47)–C(46)–C(51)	124(5)	C(55)–C(56)–C(61)	125(5)
C(8)–C(9)–C(10)	117(4)	C(20)–C(21)–C(22)	121(5)	C(46)–C(47)–C(48)	118(5)	C(56)–C(57)–C(58)	117(5)
C(9)–C(10)–C(11)	124(4)	C(21)–C(22)–C(17)	114(4)	C(47)–C(48)–C(49)	118(3)	C(57)–C(58)–C(59)	119(5)
C(10)–C(11)–C(12)	122(5)	C(21)–C(22)–N(23)	119(5)	C(48)–C(49)–C(50)	123(5)	C(58)–C(59)–C(60)	121(5)
C(11)–C(12)–C(7)	113(5)	C(22)–C(17)–C(16)	117(5)	C(49)–C(50)–C(51)	119(5)	C(59)–C(60)–C(61)	119(5)
C(11)–C(12)–N(13)	125(5)			C(50)–C(51)–C(46)	117(4)	C(60)–C(61)–N(62)	117(5)
N(13)–C(12)–C(7)	122(4)			C(50)–C(51)–N(52)	120(5)	C(60)–C(61)–C(56)	119(5)
				N(52)–C(51)–C(46)	123(5)		

The superscript I refers to atoms with symmetry $\bar{x}, \bar{y}, \bar{z}$ in the first molecule (atoms 1—39) and $1 - x, 1 - y, 1 - z$ in the second (atoms 40—78).

spectrum was also recorded at four different temperatures (300—360 K) and concentrations (1.7—15 mg cm^{-3}). The NH_2 signal was invariant with temperature and concentration, confirming intramolecular hydrogen bonding in the dimer. The ^{13}C n.m.r. spectrum reveals a very weak peak assignable to the CO_2 group, even at relatively high concentrations and higher Fourier-transform peak accumulations, possibly suggesting that carboxy groups are not free in this molecule. The ^{119}Sn n.m.r. spectrum of a saturated solution in chloroform showed two types of tin atoms.[20] Holeček *et al.*[21] have suggested (δ) values from +200 to −60 for four-co-ordinated, −90 to −190 for five-co-ordinated, and −210 to −400 p.p.m. for six-co-ordinated tin atoms in solution. Thus the signal at −220.6 p.p.m. is due to six-co-ordinated tin atoms. If there is no change in the structure* of the compound in saturated solutions, this value may be assigned to Sn(2) and Sn(41) in the dimer (from crystal data). The other value (−210.9 p.p.m.) is at the extreme end of the range for five-co-ordinated tin. This absorption may be taken as the unresolved signals of the other two tin atoms, one of which, Sn(40), is six-co-ordinated while the other, Sn(1), is five-co-ordinated. More light could be thrown on this aspect of the structure from magic angle spinning solid-state ^{119}Sn n.m.r. spectroscopy.

Conclusions

From the foregoing discussion, it may be concluded that in the dimer one molecule, (**I**), has one six-co-ordinate and one five-co-ordinate tin atom while the other molecule, (**II**), has two six-co-ordinate tin atoms. In this compound there are two bridging, one effectively isobidentate, and one nearly unidentate carboxy groups. No such structure for a stannoxane has previously been reported.

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* Very weak signals at −200, −194, and −161 p.p.m. also appear which increase in intensity on dilution. This may be due to dedimerisation of the compound.

Table 2. Contact distances (Å)

Intramolecular

Sn(1) ··· Sn(2)	3.758(2)	Sn(40) ··· Sn(41)	3.761(2)
Sn(1) ··· Sn(2$^{\mathrm{I}}$)	3.619(2)	Sn(40) ··· Sn(41$^{\mathrm{I}}$)	3.647(3)
Sn(2) ··· Sn(2$^{\mathrm{I}}$)	3.299(3)	Sn(41) ··· Sn(41$^{\mathrm{I}}$)	3.315(3)
Sn(2) ··· O(4$^{\mathrm{I}}$)	2.72(1)	Sn(41) ··· O(43$^{\mathrm{I}}$)	2.79(2)
Sn(1) ··· O(5)	3.11(2)	Sn(40) ··· O(44)	2.84(1)
O(5) ··· N(13)	2.67(3)	O(44) ··· N(52)	2.70(2)
N(23) ··· O(15)	2.69(2)	N(62) ··· O(54)	2.70(2)
N(23) ··· C(9$^{\mathrm{I}}$)	3.42(4)	N(62) ··· C(48$^{\mathrm{I}}$)	3.84(4)

Intermolecular

O(5) ··· C(19)	2/001	3.56(4)	C(21) ··· C(45)	1/010	3.71(3)
O(5) ··· C(60)	2/001	3.52(2)	C(21) ··· C(46)	1/010	3.65(3)
O(5) ··· N(62)	2/001	3.46(2)	C(21) ··· C(47)	1/010	3.64(3)
C(7) ··· C(78)	1/100	3.66(4)	N(23) ··· O(44)	1/010	3.56(2)
C(8) ··· C(78)	1/100	3.70(4)	N(23) ··· C(50)	2/110	3.55(3)
C(10) ··· N(52)	2/010	3.59(4)	C(49) ··· N(52)	2/120	3.59(3)
C(11) ··· C(56)	1/100	3.53(3)	C(50) ··· C(50)	2/120	3.52(5)
C(11) ··· C(61)	1/100	3.60(3)	C(50) ··· N(51)	2/120	3.63(3)
N(13) ··· N(62)	1/100	3.63(2)	C(50) ··· N(52)	2/120	3.53(3)
N(13) ··· N(62)	2/001	3.63(3)			

Coding of equivalent positions (see Table 1): 1 x, y, z; 2 $\bar{x}, \bar{y}, \bar{z}$. C(19) 2/001 means that atom C(19) is in position 2, translated by 1*c*.

Experimental

Preparation of Complex.—Di-n-butyltin(IV) oxide (2.49 g, 10 mmol) in benzene (50 cm^3) was added to *o*-aminobenzoic acid (1.37 g, 10 mmol) dissolved in benzene (30 cm^3). The mixture was heated under reflux for 4 h to complete the reaction and water was removed using a Dean and Stark separator. The solvent was evaporated and the residue extracted with light petroleum (b.p. 40—60 °C). The crude product was obtained as a white solid (yield 90%). It was recrystallised from a mixture of diethyl ether and light petroleum (b.p. 40—60 °C), m.p. 134 °C (Found: C, 47.8; H, 6.6; N, 3.5; Sn, 31.4. Calc. for $C_{60}H_{96}N_4O_{10}Sn_4$: C, 47.7; H, 6.3; N, 3.7; Sn, 31.5%).

Crystallography.—Crystal data. $C_{60}H_{96}N_4O_{10}Sn_4$, M = 1 508.2, triclinic, space group $P\bar{1}$, a = 17.278(9), b = 15.890(9), c = 14.154(8) Å, α = 71.80(9), β = 68.67(8), γ = 82.02(6)°, U = 3 680 Å^3, Z = 2, D_c = 1.36 g cm^{-3}, $F(000)$ = 1 528, μ(Mo-K_α) = 14 cm^{-1}, λ = 0.7107 Å, T = 298 K.

Data collection and processing. The irregular shaped crystal selected (*ca.* 0.25 × 0.40 × 0.35 mm) was coated with dried paraffin and then sealed in a quartz capillary. The unit-cell parameters were obtained from a least-squares refinement of the setting angles of 25 reflections carefully centred on a four-circle Philips PW100 automatic diffractometer using Mo-K_α radiation and a graphite monochromator. Intensities were

Table 3. Atomic coordinates (× 10^4)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Sn(1)	−666(1)	98(1)	2 465(1)	Sn(40)	4 418(1)	5 485(1)	2 899(1)
Sn(2)	881(1)	−507(1)	92(1)	Sn(41)	4 691(1)	3 966(1)	5 401(1)
O(3)	−176(8)	77(8)	977(10)	O(42)	4 745(8)	5 095(8)	4 233(9)
O(4)	−1 679(10)	768(9)	1 849(11)	O(43)	4 983(8)	6 679(9)	2 704(11)
O(5)	−2 562(10)	417(11)	3 506(14)	O(44)	4 723(10)	7 104(10)	1 247(13)
C(6)	−2 416(17)	792(16)	2 563(23)	C(45)	5 012(15)	7 312(19)	1 853(22)
C(7)	−3 085(14)	1 319(13)	2 126(18)	C(46)	5 370(12)	8 172(15)	1 579(18)
C(8)	−2 804(14)	1 777(15)	1 056(19)	C(47)	5 441(13)	8 369(16)	2 431(17)
C(9)	−3 396(17)	2 327(15)	592(18)	C(48)	5 719(14)	9 226(17)	2 254(19)
C(10)	−4 223(16)	2 342(15)	1 269(20)	C(49)	5 909(14)	9 816(15)	1 236(21)
C(11)	−4 494(15)	1 882(16)	2 318(20)	C(50)	5 868(14)	9 591(17)	393(18)
C(12)	−3 941(16)	1 331(16)	2 838(21)	C(51)	5 553(14)	8 754(17)	564(20)
N(13)	−4 166(12)	872(13)	3 875(16)	N(52)	5 487(11)	8 531(12)	−287(15)
O(14)	569(13)	−379(12)	2 676(14)	O(53)	3 814(10)	4 191(13)	3 424(14)
O(15)	1 413(9)	−885(10)	1 437(13)	O(54)	4 145(9)	3 181(9)	4 702(12)
C(16)	1 233(21)	−730(19)	2 276(26)	C(55)	3 882(15)	3 402(20)	3 933(22)
C(17)	1 845(15)	−853(13)	2 851(18)	C(56)	3 546(12)	2 675(17)	3 721(18)
C(18)	1 561(15)	−632(15)	3 799(20)	C(57)	3 342(15)	3 004(16)	2 783(19)
C(19)	2 133(17)	−760(16)	4 366(18)	C(58)	3 053(16)	2 362(20)	2 458(20)
C(20)	2 946(16)	−1 106(15)	3 925(20)	C(59)	2 982(15)	1 466(18)	3 079(21)
C(21)	3 213(15)	−1 301(15)	2 979(20)	C(60)	3 179(14)	1 185(16)	4 009(19)
C(22)	2 665(15)	−1 193(14)	2 376(19)	C(61)	3 486(13)	1 814(17)	4 319(19)
N(23)	2 952(11)	−1 434(12)	1 462(15)	N(62)	3 709(11)	1 484(12)	5 226(15)
C(24)	−561(20)	1 321(19)	2 783(22)	C(63)	3 148(16)	6 091(17)	3 300(20)
C(25)	143(31)	1 524(32)	2 851(37)	C(64)	2 660(26)	5 814(25)	2 802(30)
C(26)	−92(33)	2 341(37)	3 476(43)	C(65)	1 533(52)	6 068(53)	3 070(63)
C(27)	329(34)	2 911(37)	2 674(45)	C(66)	1 594(44)	6 445(46)	3 467(55)
C(28)	−1 224(18)	−1 156(20)	3 354(23)	C(67)	5 242(18)	4 998(18)	1 625(21)
C(29)	−808(25)	−1 852(29)	3 967(31)	C(68)	6 038(20)	5 388(20)	1 100(23)
C(31)	−1 354(29)	−2 784(33)	4 327(38)	C(69)	6 514(21)	4 957(20)	75(24)
C(31)	−1 069(42)	−3 157(45)	4 927(54)	C(70)	7 387(22)	5 293(22)	−421(26)
C(32)	618(15)	−1 890(16)	731(19)	C(71)	3 480(13)	3 886(14)	6 604(16)
C(33)	475(21)	−2 296(24)	71(27)	C(72)	2 821(15)	4 446(15)	6 155(18)
C(34)	286(22)	−3 374(25)	839(29)	C(73)	1 965(17)	4 389(17)	7 131(21)
C(35)	165(27)	−3 817(30)	131(36)	C(74)	1 322(18)	5 044(19)	6 681(22)
C(36)	1 768(12)	519(13)	−695(16)	C(75)	5 811(13)	3 160(13)	4 960(16)
C(37)	1 794(14)	1 097(16)	−9(18)	C(76)	6 258(14)	3 483(14)	3 744(17)
C(38)	2 237(15)	1 946(17)	−771(20)	C(77)	7 130(15)	2 966(15)	3 491(18)
C(39)	2 335(18)	2 533(19)	−115(23)	C(78)	7 612(15)	3 326(16)	2 291(20)

collected by the ω—2θ technique with a ω-scan speed of 0.03° s^{-1} and a scan width of 1.20° over the range $4 \leqslant 2\theta \leqslant 40°$; $-15 \leqslant h \leqslant 15$, $-14 \leqslant k \leqslant 14$, and $0 \leqslant l \leqslant 13$. Three standard reflections 003, $0\overline{23}$, and $1\overline{41}$ were monitored every hour to check crystal stability, but no trends were observed. 6 753 Reflections were collected and corrected for Lorentz and polarization effects, 2 038 being considered observed $[I > 3\sigma(I)]$. The net intensities I were calculated as $I = CT - (B_1 + B_2)$ where CT is the total integrated peak count obtained in the scan time $t_c/2$; $\sigma(I)$ is given by $[CT + (B_1 + B_2) + (pI)^2]^{\frac{1}{2}}$ where p is the 'ignorance factor' included to avoid overweighting very strong reflections; a value of 0.04 was used.

Structure analysis and refinement. The structure was determined by the heavy-atom method (Patterson function) which revealed the relative positions of the Sn atoms. Several subsequent Fourier difference maps and least-squares refinements were necessary to obtain the skeleton of the structure. Furthermore, location of the atoms of the butyl chains proved to be difficult, because some of the carbon atoms, not bonded to the Sn atoms, probably freely oscillate in relatively large holes in the packing. This problem, which is characteristic of such compounds,[8,9] led to poor resolution of the corresponding atomic co-ordinates, associated with the large thermal vibrations of these atoms. No special significance therefore should be attached to the positions characterising the butyl chains (Table 3). Limitations of core memory precluded full-matrix refinement of the entire structure. The parameters of each crystallographically independent molecule were therefore refined separately and alternatively, using anisotropic thermal coefficients for the Sn atoms and isotropic ones for the others. In the last cycle the largest parameter shift/standard deviation was 0.05 for the butyl atoms, and 0.005 for the skeleton atoms. The final R and R' values were 0.050 and 0.054, respectively, with unit weights assigned to all reflections used. Absorption corrections were applied, using the DIFABS method,[22] but did not markedly improve the refinement. No attempt was made to locate the hydrogen atoms. Scattering factors were taken from ref. 23, with anomalous dispersion effects for Sn atoms.[24] All computations were carried out on a CII Honeywell Bull Mini 6 computer.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Spectroscopy.—The ^{119m}Sn Mössbauer spectrum was obtained at 77 K using a Harwell spectrophotometer equipped with a 256 multi-channel analyser and a $Ba^{119m}SnO_3$ source. Data reduction of the Lorentzian line shapes was done by the usual least-squares method. I.r. spectra were recorded in KBr pellets and CCl_4 solution on a Perkin-Elmer 621 spectrophotometer. Proton n.m.r. spectra were taken in $CDCl_3$ on a Varian (EM 390) 90-MHz spectrophotometer using $SiMe_4$ as an internal standard. The spectrum at variable temperatures was recorded on a Brüker (AM 500) 500 MHz instrument at the Tata Institute of Fundamental Research (TIFR) Bombay. The ^{13}C n.m.r. spectrum was obtained in saturated $CDCl_3$ solution (77.00 p.p.m.) on a 22.49-MHz JEOL FX60Q spectrophotometer using $SiMe_4$ as an internal standard. The ^{119}Sn n.m.r. spectrum was recorded in a 10-mm tube in a very saturated solution in chloroform on a JEOL FX60Q spectrophotometer with D_2O as field-frequency lock. The chemical shifts, $\delta(^{119}Sn)$, are relative to $SnMe_4$.

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