Structural Study of 3-Oxypropyltin Compounds†

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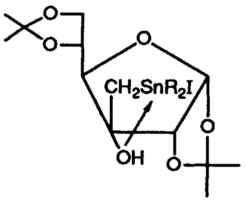
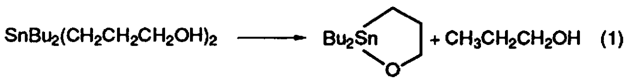
The structures of (3-hydroxypropyl)iododiphenyltin **3** and 2,7-diiodo-2,7-diphenyl-1,6-dioxa-2,7-distannacyclodecane **6** have been determined by single-crystal X-ray diffraction. Compound **6**, obtained by controlled thermolysis of **3**, has a tricyclic structure, with a central Sn_2O_2 ring arising from transannular, Sn–O [*i.e.* Sn(2)–O(6) and Sn(7)–O(1)] interactions. The terminal rings in centrosymmetric **6** are in a transoid arrangement with respect to the central Sn_2O_2 ring, *i.e.* there is a stepped geometry. The tin atoms have trigonal-bipyramidal geometries being bonded in equatorial sites to two carbons and one oxygen [Sn–O′, *i.e.* Sn(2)–O(1) 2.060(7) Å] and in axial sites to iodine [Sn–I 2.776(1) Å] and to oxygen [Sn–O, *i.e.* Sn(2)–O(6) 2.268(7) Å]: I–Sn–O 161.7(2)°. In C_6H_6 and in chlorocarbon solutions, **6** exists as a 4.2 : 1 mixture of two isomers: the major one has the solid-state structure while the minor one has the terminal rings in an umbrella configuration, *i.e.* the terminal rings are cisoid with respect to the central Sn_2O_2 ring. Two sets of tin couplings to C(3) [C_β] and to C(4) [C_α] of each isomer were observed. Compound **3** exists as a chelate complex, with trigonal-bipyramidal tin: three equatorial C, with I[Sn–I 2.857(1) Å] and O[Sn–O 2.487(8) Å] axial [I–Sn–O 168.3(2)°]. Chelation persists in chlorocarbon solvents.

Alcohols can act both as Lewis bases (electron donors) and as Brönsted acids.[1] Both features have been illustrated with appropriate organotin compounds. The donor ability can be seen in the stannyl-carbohydrate derivative **1**: the intramolecular Sn ··· O(H) co-ordination persists in solution as well as in the solid state.[2] An example of the Brönsted acidity of alcohols in organotin chemistry is illustrated by the intramolecular protonolysis of a Bu–Sn bond[3] in $SnBu_2(CH_2CH_2CH_2OH)_2$ on heating, equation (1).



1 R = Bu, Me or Ph



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Further work, as we now report, on $SnPh_2I(CH_2CH_2CH_2OH)$ **3** has provided additional examples of these properties of the alcohol group in organotin chemistry.

Experimental

Melting points are uncorrected and were measured on a Kofler hot-stage apparatus. Mass spectra were obtained on an AEI M30 instrument; *m/z* for tin-containing peaks are based on ^{120}Sn. NMR spectra were obtained on a Bruker 250 MHz instrument and are reported in Table 1. IR spectra were recorded on a Philips Analytical PU 9800 Fourier-transform spectrometer.

The compound $SnPh_3(CH_2CH_2CH_2OH)$ was prepared by a published procedure.[4]

(3-Hydroxypropyl)iododiphenyltin **3**.—To a solution of $SnPh_3(CH_2CH_2CH_2OH)$ (5.00 g, 0.0122 mol) in CCl_4 (50 cm^3) was added slowly a solution of I_2 (3.10 g, 0.0122 mol) in CCl_4 (50 cm^3). After addition was complete, the reaction mixture was gently heated until the solution became colourless. The solution was cooled, rotatory evaporated to remove CCl_4 and finally evacuated at 1 Torr and 60 °C for 5 h to remove PhI. The resulting solid was recrystallised from light petroleum (b.p. 60–80 °C)–benzene (3:1). Yield 4.33 g (77%), m.p. 119 °C. Alternatively, the oil resulting from the rotary evaporation of CCl_4 was crystallised from benzene–light petroleum (b.p. 60–80 °C). Mass spectrum (20 eV): *m/z* 401 (Ph_2SnI, 18), 333 ($Ph_2SnCH_2CH_2CH_2OH$, 58), 324 (PhSnI, 45), 304 (Ph_2SnOCH_2, 45), 274 (Ph_2Sn, 100), 247 (SnI, 18), 197 (PhSn, 80), 128 (HI, 85) and 120 (Sn, 75%). IR (KBr): 3412 (OH), 3065, 3042 and 3023 (CH_{aryl}), 2990 and 2948 (CH_{alkyl}), 1480 (C═C), 1431, 1074, 1049, 972, 729, 696, 536 and 451 cm^{-1} (Sn–C).

2,7-Diiodo-2,7-diphenyl-1,6-dioxa-2,7-distannacyclodecane **6**.—The procedure was the same as that described for the preparation of **3**, except that the final evacuation of the reaction mixture was carried out at 120 °C for 10 h. The solid residue was initially recrystallised from light petroleum (b.p. 60–80 °C)–benzene (3:1) (m.p. 199 °C), and then from CH_2Cl_2. The final product had a m.p. of 209 °C. Mass spectrum (20 eV): *m/z* 354 ($PhISnCH_2O$, 40), 324 (PhISn, 100), 247 (SnI, 40), 197 (PhSn, 86), 128 (HI, 26) and 120 (Sn, 15%). IR (KBr): 306 and 3044 (CH_{aryl}), 2965 and 2924 (CH_{alkyl}), 1476 (C═C), 1429, 1065, 1040, 978, 959, 858, 739, 695 (aryl), 613, 534 and 444 cm^{-1} (Sn–O).

Crystal Structure Determinations.—Data were obtained for compounds **3** and **6** with a Nicolet P3 four-circle diffractometer with graphite monochromator and Mo-Kα radiation (λ = 0.710 69 Å). Intensities were measured at ambient temperature for reflections with 2θ in the range 0–60°, corresponding to

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Non-SI units employed: Torr ≈ 133 Pa, eV ≈ 1.6×10^{-19} J, cal ≈ 4.184 J.

Table 1 NMR spectra of compounds **3**, **6** and $SnPh_3(CH_2CH_2CH_2OH)$ at 25 °C, *J* in Hz*

^1H NMR

Compound (solvent)	$\delta(H_\alpha)$ $[J(H_\alpha H_\beta)]$ $\{J(SnH)\}$	$\delta(H_\beta)$ $[J(H_\beta H_\gamma)]$ $\{J(SnH)\}$	$\delta(H_\gamma)$ $[J(H_\gamma OH)]$	$\delta(OH)$	δ(Ph–Sn)	
					o-H	*m*-, *p*-H
$SnPh_3(CH_2CH_2CH_2OH)$ ($CDCl_3$)	1.58 (m) [—] {56}	2.04 (m) [6.38] {56}	3.69 [—]	1.58	7.64 (m) *J ca.* 45	7.45 (m)
$SnPh_2I(CH_2CH_2CH_2OH)$ ($CDCl_3$)	1.89 [6.45] {68.4}	2.04 [5.50] {126}	3.71 (br) [3.30]	2.15	7.75 (m) *J ca.* 55	7.41 (m)
$[SnPhI(CH_2CH_2CH_2O)]_2$ (CD_2Cl_2)	1.8–2.2 (m)	Major isomer	3.79 (m) 3.97 (m)		8.00 (m)	7.54 (m)
		Minor isomer	3.88 (m) 4.36 (m)		7.64 (m)	7.23 (m)

^{13}C NMR

Compound (solvent)	$\delta(C_\alpha)$ $[J(^{119}Sn^{13}C)]$ $\{J(^{117}Sn^{13}C)\}$	$\delta(C_\beta)$ $[J(^{119}Sn^{13}C)]$	$\delta(C_\gamma)$ $[J(^{119}Sn^{13}C)]$	δ(Ph)			
				o-C $[J(^{119}Sn^{13}C)]$	*m*-C $[J(^{119}Sn^{13}C)]$	*p*-C $[J(^{119}Sn^{13}C)]$	*ipso*-C $[J(^{119}Sn^{13}C)]$ $\{J(^{117}Sn^{13}C)\}$
$SnPh_3(CH_2CH_2CH_2OH)$ ($CDCl_3$)	6.59 [398] {380}	29.23 [21.4]	65.49 [66.4]	136.95 [35]	128.59 [57]	129.00 [12]	138.91 [491] {469}
$SnPh_2I(CH_2CH_2CH_2OH)$ ($CDCl_3$)	17.47 [493] {470}	27.60 [33.0]	63.64 [33.5]	135.68 [46]	128.56 [62.5]	129.34 [13.5]	140.06 [605] {579}
$[SnPhI(CH_2CH_2CH_2O)]_2$ (CD_2Cl_2) Major isomer	24.94 [631] {603}	27.81 [*ca.* 11] [37.1]	63.68 [17.5] [59.9]	136.69 [60.5]	129.70 [78.1]	131.53 [15.8]	138.31 [727]
Minor isomer	25.71 [*ca.* 625]	28.78 [—]	66.58 [—]	136.43 [—]	128.91 [—]	130.94 [—]	139.65 [—]
$[SnPhI(CH_2CH_2CH_2O)]_2$ (C_6H_6) Major isomer	24.50 [628] {600}	27.58 [11.2] [36.9]	63.59 [17.5] [61.4] {58.7}				
Minor isomer	25.51	28.44 [12] [36]	66.13 [18.6] [58.7]				

* Tin-119 NMR: $SnPh_3(CH_2CH_2CH_2OH)$ ($CDCl_3$) δ −100.0; $SnPh_2I(CH_2CH_2CH_2OH)$ ($CDCl_3$) δ −113.1, $[SnPhI(CH_2CH_2CH_2O)]_2$ (CD_2Cl_2) δ −168.9 (major) and −158.6 (minor).

$\sin\theta/\lambda \leqslant 0.704$, using the θ–2θ scan technique. Scan rates determined from a pre-scan intensity (I_p) were in the range 5.33 ($I_p < 150$) to 58.6 ($I_p > 2500$)° 2θ min^{-1}. Scan widths, dependent upon 2θ, were in the range 2.4–2.8 2θ.

Unit-cell parameters were, in each case, based upon accurate diffractometer angles obtained for 14 reflections with 2θ in the range 20–25°. For both crystals, the intensities of two standard reflections monitored at intervals of 50 measurements remained constant to within about 2% [1 × estimated standard deviation (e.s.d.)] and no correction for crystal decomposition was applied. For **3**, however, the data were corrected for absorption by an empirical method based upon ψ scans on three reflections. Both structures were solved by application[5] of SHELXS 86 and refined[6] with SHELX 76 minimising $\Sigma w(\Delta F)^2$. In the final stages of refinement, hydrogen atoms were included in calculated positions [*d*(C–H) 1.08 Å] and refined riding on the non-hydrogen atoms to which they are attached with separate group isotropic thermal parameters for each of alkyl, aryl and (in **6**) hydroxyl H. The scattering factors for neutral atoms used were those built into the programs except for iodine for which the necessary data were taken from ref. 7. All calculations were performed on the Honeywell DPS/8 computer (CP6 operating system) of the Computing Centre of the University of Aberdeen. Unit-cell parameters, space groups, and values pertinent to the data collection and refinement of the structures are given in Table 2. Non-hydrogen atomic coordinates are given in Tables 3 and 4, and bond lengths and angles in Tables 5 and 6, for compounds **3** and **6**, respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

Results and Discussion

Synthesis.—(3-Hydroxypropyl)triphenyltin **4** reacts readily with I_2 to form thermally labile $SnPh_2I(CH_2CH_2CH_2OH)$ **3**, equation (2). It had been previously established that **4** reacts

$$\underset{\mathbf{4}}{SnPh_3(CH_2CH_2CH_2OH)} + I_2 \longrightarrow \underset{\mathbf{3}}{SnPh_2I(CH_2CH_2CH_2OH)} + PhI \quad (2)$$

with I_2 in chlorocarbon solutions *ca.* 100 times faster than does $SnPh_3(CH_2CH_2CH_2CH_3)$ **5**, both reactions leading to Ph–Sn bond cleavage.[8] The difference in reactivities of Ph–Sn bonds in **4** and **5** was considered to arise from the nucleophilic assistance afforded by the OH group in the reaction of **4**: nucleophilic assistance by remote donor groups has been detected in various reactions of other organotin compounds with electrophilic reagents.[9–12] Compound **3** exists both in the solid state and in chlorocarbon solutions as a chelate complex with Sn–O co-

Table 2 X-Ray data collection and structure refinement parameters for compounds **3** and **6**

Compound	**3**	**6**
Formula	$C_{15}H_{17}IOSn$	$C_{18}H_{22}I_2O_2Sn_2$
M	458.90	761.56
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbca* (no. 61)	*C*2/*c* (no. 15)
a/Å	11.90(1)	12.360(6)
b/Å	16.50(3)	11.838(6)
c/Å	16.55(2)	15.870(5)
β/°	(90)	104.77(3)
U/Å^3	3249(7)	2245(2)
Z	8	4
D_c/Mg m^{-3}	1.872	2.253
μ/mm^{-1}	3.44	4.96
F(000)	1744	1408
Crystal size/mm	0.24 × 0.28 × 0.8	0.6 × 0.22 × 0.22
Transmission, min. (max.)	0.07 (0.33)	—
Max. |*h*| (|*k*|,|*l*|)	16 (23, 23)	17 (16, 22)
Reflections measured	5301	3575
No. unique reflections	4765	3298
R_{int}	0.02	0.04
No. observed reflections	2279 [$I > 2\sigma(I)$]	2380 [$I > 2\sigma(I)$]
No. refined parameters	170	111
Weighting scheme coefficient, *g**	3.26 × 10^{-4}	1.64 × 10^{-3}
R	0.064	0.066
R′	0.055	0.075
Max. shift/e.s.d.	0.19	0.07
Min. (max.) Δρ/e Å^{-3}	−1.1 (1.4)	−1.0 (5.5)

* g in $w = 1/[\sigma^2(F) + gF^2]$.

Table 3 Atomic coordinates ($\times 10^4$) for non-hydrogen atoms with estimated standard deviations (e.s.d.s) in parentheses for compound **3**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Sn	656(1)	2217(1)	534(1)
I	2211(1)	1583(1)	1688(1)
C(1)	1876(9)	2383(9)	−389(6)
C(2)	1357(11)	2492(17)	−1199(9)
C(3)	405(11)	2988(11)	−1264(9)
O	−347(7)	2824(7)	−638(5)
C(11)	−523(8)	1253(7)	527(7)
C(12)	−917(10)	942(9)	−197(8)
C(13)	−1701(13)	290(10)	−178(11)
C(14)	−2127(11)	15(10)	506(13)
C(15)	−1723(12)	323(10)	1237(11)
C(16)	−923(10)	929(9)	1241(8)
C(21)	134(9)	3246(8)	1251(7)
C(22)	−706(11)	3158(10)	1792(8)
C(23)	−1039(13)	3822(13)	2265(10)
C(24)	−502(16)	4532(14)	2188(14)
C(25)	309(17)	4619(13)	1644(18)
C(26)	642(14)	2958(11)	1165(14)

Table 4 Atomic coordinates ($\times 10^4$) for non-hydrogen atoms with e.s.d.s in parentheses for the unique set of atoms constituting one half of the centrosymmetric molecules of compound **6**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Sn	543(1)	6373(1)	5181(1)
I	−486(1)	8370(1)	5466(1)
C(1)	1814(8)	6183(9)	6366(6)
C(2)	1964(9)	6987(9)	7030(7)
C(3)	2849(10)	6886(12)	7775(7)
C(4)	3564(11)	5964(12)	7861(7)
C(5)	3432(11)	5193(12)	7212(8)
C(6)	2517(9)	5270(10)	6458(7)
O	811(6)	4596(6)	4738(4)
C(7)	882(12)	6689(11)	3949(9)
C(8)	1541(22)	5671(16)	3766(14)
C(9)	1249(11)	4577(11)	3966(8)

Table 5 Interatomic distances (Å) and angles (°) for compound **3**

I–Sn	2.857(1)	C(1)–Sn	2.123(10)
O–Sn	2.487(8)	C(11)–Sn	2.122(11)
C(21)–Sn	2.16(1)	C(2)–C(1)	1.49(2)
C(3)–C(2)	1.40(2)	O–C(3)	1.40(2)
C(12)–C(11)	1.39(2)	C(16)–C(11)	1.38(2)
C(13)–C(12)	1.43(2)	C(14)–C(13)	1.32(2)
C(15)–C(14)	1.40(2)	C(16)–C(15)	1.38(2)
C(22)–C(21)	1.35(2)	C(26)–C(21)	1.33(2)
C(23)–C(22)	1.41(2)	C(24)–C(23)	1.34(2)
C(25)–C(24)	1.33(3)	C(26)–C(25)	1.41(2)
C(1)–Sn–I	94.9(3)	O–Sn–I	168.3(2)
O–Sn–C(1)	73.5(4)	C(11)–Sn–I	99.0(3)
C(11)–Sn–C(1)	123.0(5)	C(11)–Sn–O	88.9(4)
C(21)–Sn–I	96.1(3)	C(21)–Sn–C(1)	119.4(5)
C(21)–Sn–O	88.5(4)	C(21)–Sn–C(11)	113.6(4)
C(2)–C(1)–Sn	112(1)	C(3)–C(2)–C(1)	118(2)
O–C(3)–C(2)	110(1)	C(3)–O–Sn	110.4(7)
C(12)–C(11)–Sn	120(1)	C(16)–C(11)–Sn	121.0(9)
C(16)–C(11)–C(12)	119(1)	C(13)–C(12)–C(11)	119(1)
C(14)–C(13)–C(12)	122(1)	C(15)–C(14)–C(13)	119(1)
C(16)–C(15)–C(14)	120(2)	C(15)–C(16)–C(11)	121(1)
C(22)–C(21)–Sn	120(1)	C(26)–C(21)–Sn	120(1)
C(26)–C(21)–C(22)	120(1)	C(23)–C(22)–C(21)	120(2)
C(24)–C(23)–C(22)	120(2)	C(25)–C(24)–C(23)	120(2)
C(26)–C(25)–C(24)	120(2)	C(25)–C(26)–C(21)	120(2)

ordination as shown by X-ray crystallography and by NMR spectroscopy: this provides some foundation for the view that the remote OH group is enhancing the reactivity of a Ph–Sn bond in **4** *via* co-ordination with tin in the transition state of the cleavage step.

Of interest, the two $SnCH_2$ protons in **4**, while chemically equivalent are magnetically inequivalent, as shown by their complex absorptions in the ^1H NMR spectrum.[13]

The thermal instability of **3** was initially realised during attempts to remove, by heating under vacuum, the iodobenzene formed as a co-product in the synthesis of **3** [equation (2)]. Subsequently, the procedure detailed in the Experimental section was established as an efficient route to **6**. The formation of **6**, a dimer in the solid state and in solution, formally arises from protonolysis of a Ph–Sn bond of **3** by the internal OH group [equation (3)].

$$\underset{\mathbf{3}}{2SnPh_2I(CH_2CH_2CH_2OH)} \xrightarrow{\text{heat}} 2PhH + \underset{\mathbf{6}}{[SnPhI(CH_2CH_2CH_2O)]_2} \quad (3)$$

As reported in the Introduction, intramolecular protonolysis of an alkyl–tin bond occurs readily in $SnBu_2(CH_2CH_2CH_2OH)_2$ to provide **2**. As Ph–Sn bonds are generally more reactive than alkyl–tin bonds, cleavage of a Ph–Sn bond in (3-hydroxypropyl)phenyltin compounds should be anticipated. Although the strength of a Ph–Sn bond is less than that of an I–Sn bond (*e.g.* bond dissociation energies for $Me_3Sn–I$ and $Me_3Sn–Ph$ are estimated to be 80 and 57 kcal mol^{-1}),[14] it is still striking that Ph–Sn protonolysis occurs rather than reaction at the iodo group in **3** [*i.e.* to give $Ph_2\overline{SnCH_2CH_2CH_2O}$].

Compound **2** has a high melting point (220–224 °C) and was reported[3,15] as being insoluble in organic solvents; it therefore appears to be aggregated in the solid state. However no structure determination was attempted. Compound **2** can also be prepared[3,15] from SnH_2Bu_2 and $CH_2{=}CHCH_2OH$.

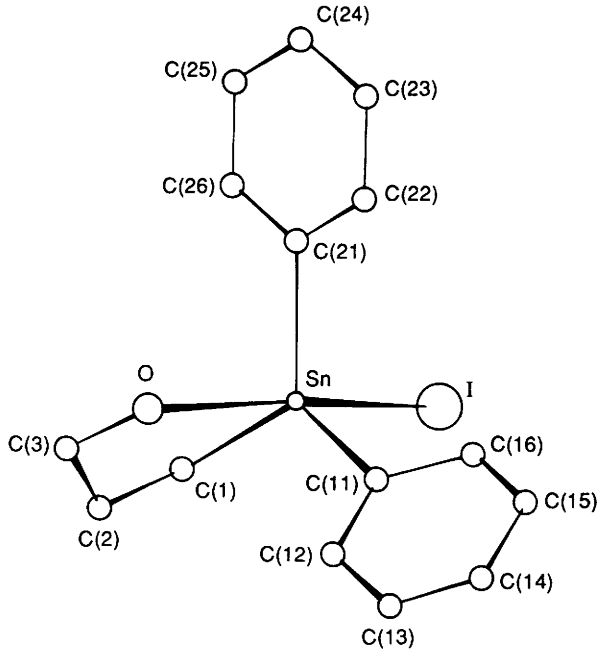


Fig. 1 Structure of compound **3**

Table 6 Interatomic distances (Å) and angles (°) for compound **6***

I–Sn	2.776(1)	C(1)–Sn	2.13(1)
O–Sn	2.268(7)	C(7)–Sn	2.13(1)
C(2)–C(1)	1.40(1)	C(6)–C(1)	1.37(2)
C(3)–C(2)	1.40(2)	C(4)–C(3)	1.39(2)
C(5)–C(4)	1.35(2)	C(6)–C(5)	1.43(2)
C(9)–O	1.46(1)	C(8)–C(7)	1.52(2)
C(9)–C(8)	1.40(2)	Sn–O′	2.060(7)
C(1)–Sn–I	102.2(3)	O–Sn–I	161.7(2)
O–Sn–C(1)	92.4(3)	C(7)–Sn–I	101.8(3)
C(7)–Sn–C(1)	123.6(5)	C(7)–Sn–O	78.5(4)
C(2)–C(1)–Sn	121.4(8)	C(6)–C(1)–Sn	118.7(7)
C(6)–C(1)–C(2)	120(1)	C(3)–C(2)–C(1)	120(1)
C(4)–C(3)–C(2)	120(1)	C(5)–C(4)–C(3)	120(1)
C(6)–C(5)–C(4)	121(1)	C(5)–C(6)–C(1)	119(1)
C(9)–O–Sn	112.9(7)	C(8)–C(7)–Sn	105.9(9)
C(9)–C(8)–C(7)	121(2)	C(8)–C(9)–O	110(1)
I–Sn–O′	92.9(2)	C(7)–Sn–O′	120.5(4)
C(1)–Sn–O′	108.3(3)	Sn–O–Sn′	108.2(3)
O–Sn–O′	71.8(3)	C(9)–O–Sn′	121.7(7)

* Prime indicates atoms subject to the symmetry operation $-x, 1-y, 1-z$.

Table 7 Comparison of selected bond angles and lengths in compounds **1** and **3**

Bond length/ or angle	1	3
Sn–O/Å	2.681(2)	2.487(8)
Sn–I/Å	2.764(2)	2.857(1)
I–Sn–O/°	158.3(4)	168.3(2)
O–Sn–$C_{chelate}$°	74.3	73.5(4)

Crystal Structure of Compound **3**.—The single-crystal data for **3** are consistent with the atomic arrangement in Fig. 1. Compound **3** in the solid state exists as a chelate complex with a distorted trigonal-bipyramidal tin co-ordination; iodine and oxygen occupy axial sites with I–Sn–O 168.3(2)°. The sum of the C–Sn–C bond angles is 356.0(5)° and the bite angle of the chelate group is 73.5(4)°. The shape of the $SnCH_2CH_2CH_2OH$ ring is that of an envelope with C(2) as the flap, C(2) being 0.46 Å out of the best plane of the other ring atoms. The axial Sn–I bond length is 2.857(1) Å, which is somewhat greater than values found for tetrahedral four-co-ordinate tin iodides [2.69(3)–2.729(3) Å].[16] The Sn–O bond length in **3** is 2.487(8) Å, compared to the sum of the covalent bond radii of Sn and O of 2.06 Å. A normal Sn–O covalent bond length is taken[17] to be *ca.* 2.0 Å, although a value[18] of 1.940(1) Å has been determined for $(Me_3Sn)_2O$. Intramolecular Sn • • • O distances in the range of 2.263(6)–3.071(2) Å have been confidently reported to indicate Sn–O bonding.[19]

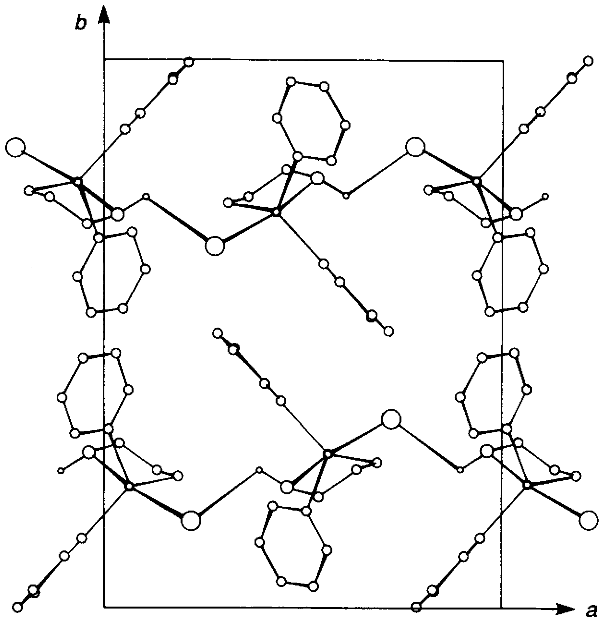


Fig. 2 One layer of packed molecules of **3** shown in (001) projection with $-\frac{1}{4} < Z < \frac{1}{4}$. The atoms are identified as in Fig. 1, with the addition of hydroxyl H (smaller circles). The chains of molecules linked by I • • • H–O interactions running parallel to *a* are clearly seen

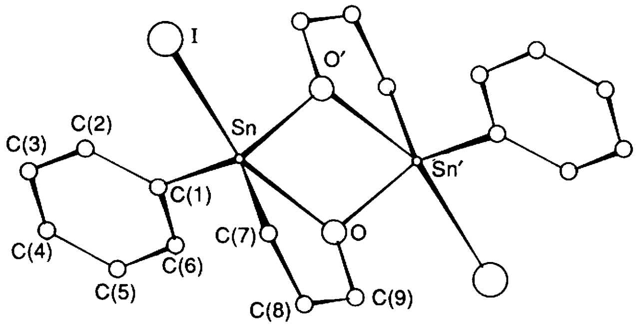


Fig. 3 Structure of the centrosymmetric molecule of **6**

Comparison of selected bond lengths and bond angles within the two hydroxy co-ordinated complexes, **1** and **3**, is of interest (Table 7). The four-membered chelate ring in **1** is much more strained than is the five-membered ring in **3**; the approach by the OH group to Sn in the polycyclic compound **1** is more hindered than in **3**. The more ideal approach of oxygen to tin in **3** is reflected by a shorter Sn–O bond length and an I–Sn–O bond angle closer to 180°.

A packing diagram of the molecules of **3** is shown in Fig. 2.

Solution Structure of Compound **3**.—The chelation in **3** is maintained in solution, as gleaned from the coupling constants $^1J(^{119}Sn^{13}C)$ 493 and $^2J(^{119}Sn^1H)$ 68.4 Hz: these are slightly greater than the corresponding values of 450 and 65 Hz normally taken as indicative of five-co-ordinate tin.[20,21]

Crystal Structure of Compound **6**.—The single-crystal data for **6** are consistent with the atomic arrangements shown in Fig.

3. The packing of the molecules is shown in Fig. 4. Compound **6** has a centre of symmetry and is in essence a tricyclic compound, which can be considered as either (*i*) a dimer of the five-membered heterocycle, 2-iodo-2-phenyl-1-oxa-2-stannacyclopentane, with Sn–O inter-monomer associations or (*ii*) a ten-membered $Sn_2O_2C_6$ heterocycle, 2,7-diiodo-2,7-diphenyl-1,6-dioxa-2,7-distannacyclodecane, with transannular interactions, Sn(2)–O(6) and Sn(7)–O(1) (crystallographically Sn–O and Sn′–O′, respectively, where primed atoms are those in the equivalent position $-x, 1-y, 1-z$ relative to those given in Table 4). The fact that the shortest Sn–O bonds are Sn–O′ and Sn′–O [*i.e.* Sn(2)–O(1) and Sn(7)–O(6)] suggests that the latter designation may be the more apt. The formation of **6** most probably arises by dimerisation of initially formed $\mathrm{IPh\overline{SnCH_2CH_2CH_2O}}$ moieties.

A feature of the structure of **6** is the central Sn_2O_2 planar (by crystallographic symmetry) ring—a unit also found in several other organotin compounds.[22] The two terminal five-membered rings are in a *trans* arrangement about the Sn_2O_2 ring, *i.e.* there is a step-like geometry. The best description of these five-membered rings is as half-chairs: the plane best fitting any four of the five atoms of these rings is defined by Sn and atoms C(7)–C(9) with O 0.363 Å out of the plane.

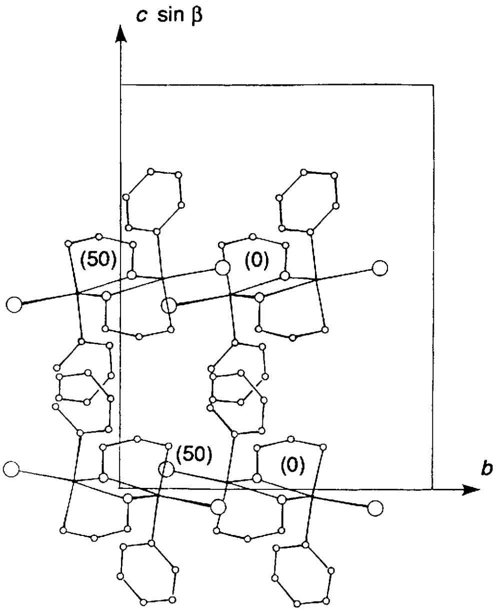


Fig. 4 The cell content of **6** viewed down *a*. The heights of the centroids of the molecules are given in parentheses in units of *a*/100

The tin atoms in **6** have distorted trigonal-bipyramidal arrangements, being bonded to 2 C (both equatorial), 2 O [Sn–O′ 2.060(7) (equatorial); Sn–O 2.268(7) Å (axial)] and I (axial), with I–Sn–O 161.7(2)°. The equatorial Sn–O′ bond length is close to a normal Sn–O covalent bond, while the axial Sn–O bond is short for a Sn–O co-ordinate linkage. The transannular Sn–O and Sn′–O′ interactions are clearly very strong.

The solid state structure of **6** makes an interesting comparison with those of other compounds containing ten-membered distannaheterocycles, *viz.* compounds **7**,[23] **8**[23] (Table 8) and **9**.[24] Both **7** and **8** contain trigonal-bipyramidal tin co-ordination. Compounds **7**–**9** (like **6**) were obtained from reactions which formally should provide their monomeric five-membered hetero-cyclic counterparts, $\mathrm{R_2\overline{SnOCH_2CH_2O}}$ **10**, $\mathrm{R_2\overline{SnOCH_2CH_2S}}$ **11** and $\mathrm{R_2\overline{SnCH_2CH_2CH_2CH_2}}$ **12**. There are apparent similarities between **6**–**8**, in that all three compounds have tricyclic structures. However in **7** and **8** the weaker Sn–O bonds (the axial bonds) in the Sn_2O_2 central rings are those which are also in the outer ten-membered heterocycles (*i.e.* these weaker bonds are the 'inter-monomer' Sn–O contacts). It appears that compounds **7** and **8** could properly be considered as dimers of the 1,3,2-dioxa- and 1,3,2-oxathia-stannolanes **10** ($R = Bu^t$) and **11** ($R = Bu^t$), respectively. In contrast, for **6** the Sn–O bonds in the outer ten-membered heterocycle are the stronger ones: the transannular interactions, Sn(1)–O(7) and Sn(6)–O(2), being axial bonds are weaker.

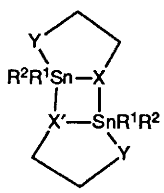
In general, the propensity for aggregation, for a given R group, decreases in the sequence **10** > **11** > $\mathrm{R_2\overline{SnSCH_2CH_2S}}$ **13**. The degree of association of these heterocycles in the solid state (and in solution) also depends on R: *e.g.* **10** (R = Bu) exists[25] as an infinite ribbon polymer with six-co-ordinate tin, in contrast to dimeric **7**. In addition to the more simple 1,3,2-dioxastannolanes **10**, there are also some diorganostannyl carbohydrate derivatives whose associations depend markedly on the bulk or hindrance of the sugar unit.[26,27]

Unlike dimeric **8**, compound **11** (R = Bu) exists in the solid state as a linear polymer (strong Sn–O and weak Sn ··· S inter-monomer associations).[28] Solid **13** ($R = Bu^t$) is monomeric,[23] **13** (R = Bu) consists of weak (Sn ··· S) symmetrically associated monomers, which provide six-co-ordinate tin,[29] and **13** (R = Me) exists as a linear five-co-ordinate polymer.[30,31]

As well as compound **9**, monomeric **12** (R = Ph) can also be isolated[24] from the reaction between $BrMg(CH_2)_4MgBr$ and $SnPh_2Cl_2$.

It would be of interest to investigate the structures of analogues of **6** to see the effects of substituents on the degree of aggregation and also on the Sn–O associations.

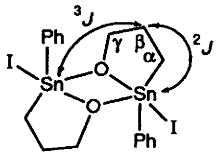
Table 8 Tin–oxygen bond lengths and Sn–O–Sn and O–Sn–O angles in compounds **6**–**8**

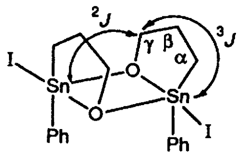


6–**8**

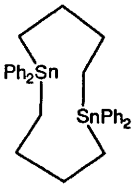
	Sn–X/Å	Sn–X′/Å	Sn–Y/Å	X–Sn–X′/°	Sn–X–Sn′/°
6 $R^1 = Ph, R^2 = I$ $X = O, Y = CH_2$	2.268(7)	2.060(7)		71.8(3)	108.2(3)
7 $R^1 = R^2 = Bu$	2.086(8)	2.244(7)	2.047(7)	67.3(3)	112.3(3)
$X = Y = O$	2.090(7)	2.253(7)	2.049(7)	67.7(4)	112.3(3)
8 $R^1 = R^2 = Bu$	2.079(5)	2.291(5)		66.9(2)	112.8(2)
$X = O, Y = S$	2.084(5)	2.297(5)		67.0(2)	113.2(2)

Table 9 Comparison of NMR parameters δ and *J*/Hz for isomers of **6** in solution





Major isomer ≡ *trans* isomer		Minor isomer ≡ *cis* isomer	
$\delta(C_\alpha)$ 24.50		$\delta(C_\alpha)$ 25.51	
$\delta(C_\beta)$ 27.58	$^2J(^{119}Sn^{13}C)$ 11.2	$\delta(C_\beta)$ 28.44	$^2J(^{119}Sn^{13}C)$ 12.0
	$^3J(^{119}Sn^{13}C)$ 36.9		$^3J(^{119}Sn^{13}C)$ 36.0
$\delta(C_\gamma)$ 63.59	$^2J(^{119}Sn^{13}C)$ 17.5	$\delta(C_\gamma)$ 66.13	$^2J(^{119}Sn^{13}C)$ 18.6
	$^3J(^{119}Sn^{13}C)$ 61.4		$^3J(^{119}Sn^{13}C)$ 58.7



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Solution Structures of Compound **6**.—The NMR spectra (^1H, ^{13}C and ^{119}Sn) of compound **6** in solution (see Table 1) indicate the presence of two species. The similarity between their spectra (especially the ^{13}C NMR spectra) suggest that these two species are isomers. Thus, dissolution of the single solid-state species in solvents leads to the immediate formation of a pair of isomers. The isomers are present in a *ca.* 4.2:1 mole ratio in both chlorocarbon and benzene solutions at ambient temperature. The major isomer is taken to have the solid-state structure* (*i.e. trans*-**6**) with the minor one having a *cis* arrangement of the terminal rings (Table 9).

A model of the minor isomer shows that the two phenyl rings face each other in a partially opened butterfly-wing fashion (an umbrella like arrangement). Of interest, the phenyl protons in the *cis* isomer appear in the ^1H NMR spectrum at higher field compared to the major isomer (the *trans* isomer) (*e.g.* the *ortho* protons in *trans*-**6** in CD_2Cl_2 solution appear as a multiplet centred at δ 8.0 whereas those in *cis*-**6** are centred at δ 7.6; the *meta* and *para* protons shift from δ 7.6 to 7.2). A similar shift to higher field has been found for the aryl protons (*i*) in [2,2]-paracyclophane (δ 6.5), compared to those, for example,[32] in 1,4-dimethylbenzene (δ 7.0),[32] and (*ii*) in *syn*-sesqui- and sester-benzobicyclo[2.2.2]octenes, molecules with stacked benzene rings.[33]

The isomerisation process for the conversion of *trans*-**6** into *cis*-**6** (and *vice versa*) involves an inversion of configuration at one tin centre in dimeric **6**. In *trans*-**6**, the solid-state structure, the tin centres could be classified as (*R*),(*S*) [or (*S*),(*R*)] (*i.e. trans*-**6** is a *meso* compound), whereas in *cis*-**6** the tin centres are either (*R*),(*R*) or (*S*),(*S*). Thus, isomerisation does not simply involve the separation of the two monomers of a dimeric **6** unit and their recombination.

No NMR evidence was found for monomeric or high-aggregated species in solution.

From the ^{13}C NMR spectrum, it can be established that there are two tin atoms in each of the two isomers of **6** from the two sets of $J(^{119}Sn^{13}C)$ values for each C_β and C_γ (see Table 9 and Fig. 5), *i.e.* these carbon atoms view each tin atom as a different entity.

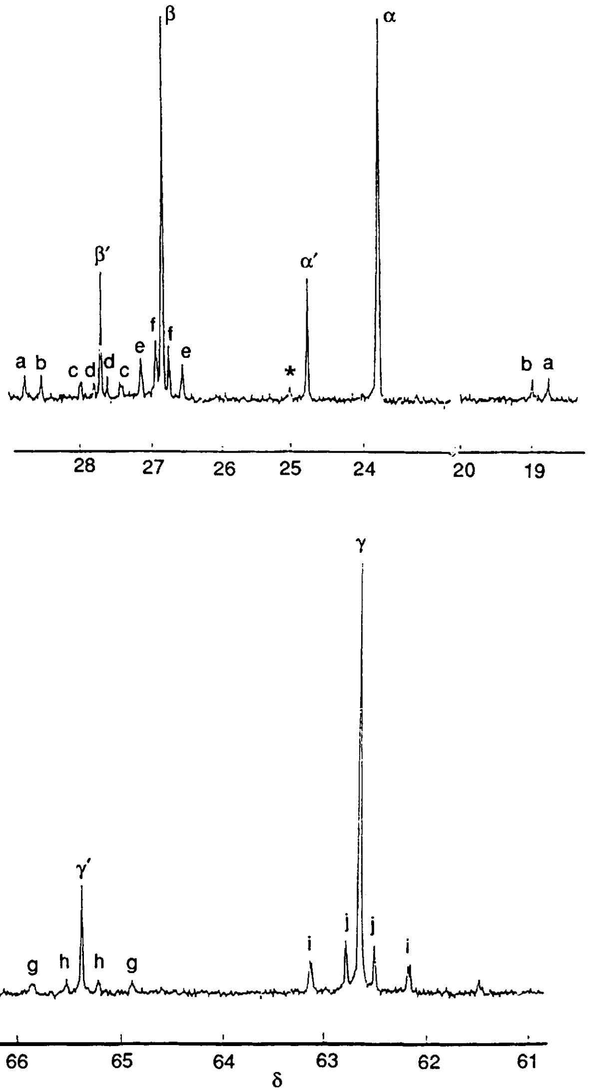

Fig. 5 Carbon-13 NMR spectrum of compound **6**: C_α, C_β and C_γ correspond to the major isomer and C_α', C_β' and C_γ' to the minor isomer: signal a, ^{119}Sn coupling to C_α; b, ^{117}Sn coupling to C_α; c, $^{117,119}Sn$ coupling (^3J) to C_β; d, $^{117,119}Sn$ coupling (2*J*) to C_β'; e, $^{117,119}Sn$ coupling (^3J) to C_β; f, $^{117,119}Sn$ coupling (^2J) to C_β; g, $^{117,119}Sn$ coupling (^3J) to C_γ; h, $^{117,119}Sn$ coupling (^2J) to C_γ'; i, $^{117,119}Sn$ coupling (^3J) to C_γ'; j, $^{117,119}Sn$ coupling (^2J) to C_γ; * = impurity

Davies *et al.*[24] reported for compound **9** that $\delta(C_\beta)$ also exhibits two pairs of satellites due to coupling in the two tin nuclei: $^2J(^{119}Sn^{13}C)$ 19 and $^3J(^{119}Sn^{13}C)$ 38 Hz.

Compound **7** also maintains its dimeric structure in solution,[23] however some dissociation of dimeric **8** occurs in solution. Dissociation of aggregated **10** (R = Bu)[22] and **11** (R = Bu)[28] (both into dimers) and **13** (R = Bu) (into monomers)[29] also occurs in solution.

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* ^{13}C NMR: δ 22.5 (C_α), 27.6 (C_β) and 63.7 (C_γ).

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