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Synthesis and spectroscopic studies of triorganostannyl esters of amic acids. Crystal structure of the triphenylstannyl ester of citraconic acid monopyrrolidide

Areila Samuel-Lewis, Peter J. Smith
International Tin Research Institute, Kingston Lane, Uxbridge, Middlesex UB8 3PJ (UK)

John. H. Aupers
Department of Biological and Chemical Sciences, Whitelands College, Roehampton Institute, West Hill, London SW15 3SN (UK)

and David C. Povey
Chemistry Department, University of Surrey, Guildford, Surrey GU2 5XH (UK)

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Abstract

Reaction of seven amic acids with triphenyltin hydroxide, tricyclohexyltin hydroxide or bis(tributyltin) oxide has given eighteen new triorganostannyl esters. The ^{119m}Sn Mössbauer spectra, at 80 K, show them all to be polymers containing pentacoordinate tin atoms and the infrared data at room temperature indicate that the amido carbonyl groups bridge intermolecularly between planar R_3Sn moieties. The polymeric structure of the triphenylstannyl ester of citraconic acid monopyrrolidide has been confirmed by an X-ray study.

Introduction

In the course of our work on the synthesis and structure of amic acids derived from symmetrical and unsymmetrical cyclic acid anhydrides [1], we have studied the reactions of *N*-phenylsuccinamic acid (**1a**), *N,N*-diethylphthalamic acid (**2a**), maleic acid monomorpholide (**3a**), citraconic acid monopyrrolidide (**3e**), *N*-phenylcitraconamic acid (**3i**), *N*-propylphenylmaleamic acid (**3m**) and *N*-tert-butyl-phenylmaleamic acid (**3p**) with bis(tributyltin) oxide, triphenyltin hydroxide and tricyclohexyltin hydroxide to form their triorganostannyl esters (**1b**–**1d**, **2b**–**2d**, **3b**–**3d**, **3f**–**3h**, **3j**–**3l**, **3n**, **3o** and **3q**). The triphenyl-, tributyl- and tricyclohexyl-tin groups were chosen, since they are known [2] to confer biological (fungicidal and acaricidal) properties on the resulting compounds. The only previously reported compound of

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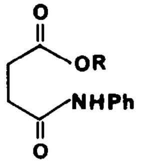
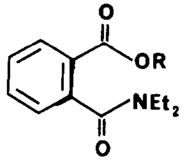


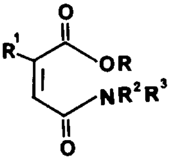
(1)

(1a) $R = H$
(1b) $R = SnBu_3$
(1c) $R = SnPh_3$
(1d) $R = Sn(\underline{c}\text{-}C_6H_{11})_3$



(2)

(2a) $R = H$
(2b) $R = SnBu_3$
(2c) $R = SnPh_3$
(2d) $R = (\underline{c}\text{-}C_6H_{11})_3$



(3)

(3a) $R^1 = R = H$, NR^2R^3 = morpholino
(3b) $R^1 = H$, $R = SnBu_3$, NR^2R^3 = morpholino
(3c) $R^1 = H$, $R = SnPh_3$, NR^2R^3 = morpholino
(3d) $R^1 = H$, $R = Sn(\underline{c}\text{-}C_6H_{11})_3$, NR^2R^3 = morpholino
(3e) $R^1 = Me$, $R = H$, NR^2R^3 = pyrrolidino
(3f) $R^1 = Me$, $R = SnBu_3$, NR^2R^3 = pyrrolidino
(3g) $R^1 = Me$, $R = SnPh_3$, NR^2R^3 = pyrrolidino
(3h) $R^1 = Me$, $R = Sn(\underline{c}\text{-}C_6H_{11})_3$, NR^2R^3 = pyrrolidino
(3i) $R^1 = Me$, $R = R^2 = H$, $R^3 = Ph$
(3j) $R^1 = Me$, $R = SnBu_3$, $R^2 = H$, $R^3 = Ph$
(3k) $R^1 = Me$, $R = SnPh_3$, $R^2 = H$, $R^3 = Ph$
(3l) $R^1 = Me$, $R = Sn(\underline{c}\text{-}C_6H_{11})_3$, $R^2 = H$, $R^3 = Ph$
(3m) $R^1 = Ph$, $R = R^2 = H$, $R^3 = Pr$
(3n) $R^1 = Ph$, $R = SnBu_3$, $R^2 = H$, $R^3 = Pr$
(3o) $R^1 = Ph$, $R = Sn(\underline{c}\text{-}C_6H_{11})_3$, $R^2 = H$, $R^3 = Pr$
(3p) $R^1 = Ph$, $R = R^2 = H$, $R^3 = {}^tBu$
(3q) $R^1 = Ph$, $R = Sn(\underline{c}\text{-}C_6H_{11})_3$, $R^2 = H$, $R^3 = {}^tBu$

this type, which is in the patent literature [3], appears to be the triphenylstannyl ester of *N*,*N*-bis(2-cyanoethyl)maleamic acid.

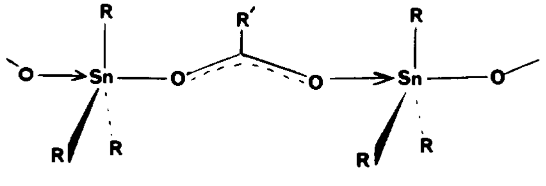
Results and discussion

The tributylstannyl and tricyclohexylstannyl esters were synthesised by mixing toluene solutions of the amic acids with bis(tributyltin) oxide (2 : 1 molar ratio) or tricyclohexyltin hydroxide (1 : 1 molar) and refluxing for 1–2 h, using a Dean and Stark trap to remove the water formed by azeotropic dehydration. The triphenylstannyl esters were prepared by heating equimolar amounts of triphenyltin hydroxide and the appropriate amic acid in a lower boiling solvent (acetone), to minimise any thermolysis of the Sn–C bonds, and using molecular sieves to effect the dehydration.

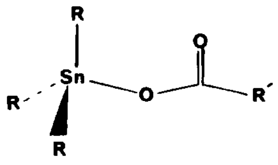
The analytical, IR and Mössbauer data for the isolated amic acid esters are collected in Table 1. In the ^{119m}Sn Mössbauer spectra of the triorganostannyl esters, all of which consist of two well-resolved quadrupole split lines, the isomer shift (δ) values increase in the order Ph_3Sn ester < Bu_3Sn ester < $(c\text{-}C_6H_{11})_3Sn$ ester, indicating a progressive increase in the total *s*-electron density at the tin nucleus, in accord with the known electronic effects of the organic groups.

The quadrupole splitting (ΔE_Q) values for the triorganostannyl esters fall within the range 2.58–3.70 mm s^{-1}, and these are characteristic [2] of a pentacoordinate trigonal bipyramidal tin atom geometry, at 80 K, with equatorial organic groups and a planar (or near-planar) R_3Sn unit. Studies on the IR spectra of tributylstannyl esters of heterocyclic and substituted aromatic carboxylic acids have shown [4,5] that compounds in which the tin atom is five coordinate with an intermolecular bridging carboxyl group (**4**, R = Bu) have ν_{max}(CO) absorptions at 1570–1615 cm^{-1}, whereas ν_{max}(CO) stretching frequencies of 1635–1653 cm^{-1} are associated with a free carbonyl group in a monomeric ester containing tetrahedral tin (**5**, R = Bu). Hence, in the tributylstannyl amic acid esters (**1b**–**3b**, **3f**, **3j** and **3n**), the $\nu_{max}(CO)_{acid}$ bands at 1630–1655 cm^{-1} (Table 1) indicate a non-bridging carbonyl group, whereas the lower-frequency $\nu_{max}(CO)_{amide}$ absorptions (1590–1615 cm^{-1}) are characteristic of an intermolecularly bridging amido carbonyl group (**6**, R = Bu).

The IR spectra of triphenylstannyl carboxylates have been investigated by Molloy and co-workers [6], who found that ν_{max}(CO) values of 1605–1640 cm^{-1} were associated with a non-bridging CO group (**5**, R = Ph) and frequencies of 1540–1550 cm^{-1} with a bridging CO (**4**, R = Ph). The $\nu_{max}(CO)_{acid}$ and $\nu_{max}(CO)_{amide}$ stretching bands of 1612–1649 cm^{-1} and 1570–1615 cm^{-1}, respec-



(4)



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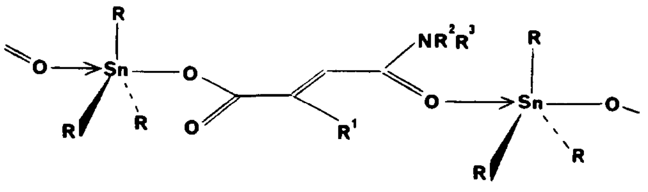

(6)

tively, for the triphenylstannyl amic acid esters (**1c–3c**, **3g** and **3k**) would again favour the associated structure (**6**, R = Ph). A similar pattern is found in the IR spectra of the tricyclohexylstannyl esters (**1d–3d**, **3h**, **3l**, **3o** and **3q**), where $\nu_{max}(CO)_{acid}$ = 1619–1668 cm^{-1} and $\nu_{max}(CO)_{amide}$ = 1598–1622 cm^{-1}; tricyclohexyltin carboxylates containing an uncoordinated carbonyl group show [5,7] $\nu_{max}(CO)$ = 1630–1640 cm^{-1}.

The reason for the preferential intermolecular bridging of the amido carbonyl group is probably that the electron-donating NR^2R^3 moiety renders this a stronger donor towards the tin atom than the ester CO. An additional factor worthy of consideration is the degree of steric inhibition offered by the three organic groups bound to the tin atom.

Description of structure 3g

Figure 1 is a schematic diagram of the molecule showing the numbering adopted and the approximate disposition of the atoms. Figure 2 is a stereo-drawing of the molecule viewed along the unit cell *a* axis.

Table 2 gives positional parameters for non-hydrogen atoms with their estimated standard deviations. Selected bond lengths and angles, together with their estimated standard deviations, are listed in Table 3. Futher details of the molecular geometry are presented in Table 4.

The stereochemistry about the tin atom is approximately trigonal bipyramidal, the equatorial plane being defined by C(11), C(21) and C(31) [plane (v), Table 4]

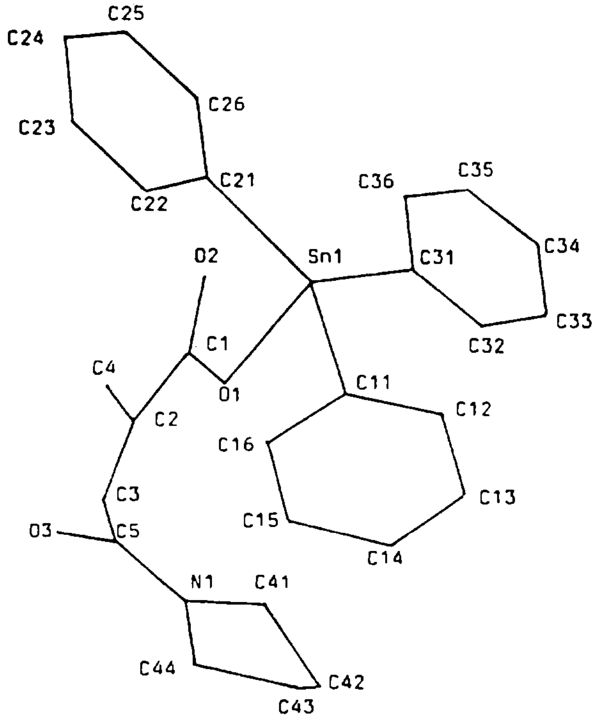

Fig. 1. Schematic drawing of molecule **3g** showing the numbering adopted

with axial bonds involving O(1) of the same molecule and O(3′) from the amido carbonyl group of the molecule related by the *n*-glide. The latter interaction is somewhat weaker, as indicated by the Sn(1)–O(3′) separation of 2.418(3) Å as compared with 2.139(2) Å for Sn(1)–O(1). The Sn(1)–O(2) separation of 2.991(3) Å is less than the sum of the van der Waals' radii of the atoms and implies a very weak interaction. The equatorial plane has a dihedral angle of 88.7(2)° with plane (i). To facilitate bonding by Sn(1) to O(1) and O(3′) and to accommodate the bulky triaryltin group, the Sn(1)–O(1) direction is reciprocally related to the postulated [1] O(1)–H direction in the free acid. If the molecule is viewed along the axis Sn(1)–C(3), a roughly staggered arrangement is observed, with phenyl(2) *trans* to the pyrrolidine ring. There are no other intermolecular distances that require comment. The intermolecular bridging by the amic acid residue via its amido carbonyl group gives rise to a one-dimensional chain polymer, a structure which is adopted by many triorganotin carboxylates [2]. It is interesting that, in **3g**, the amido carbonyl group functions as the intermolecular bridging ligand rather than the CO from the carboxylate moiety (cf. **4** and **6**).

The structure of the free acid **3e** has already been discussed [1]. The main differences to be noted are related to the replacement of the acid hydrogen by the triphenyltin group. The carbon skeleton C(1)–C(5) is still essentially planar [plane (i), Table 4], but the absence of the hydrogen bond has released the constraints which held O(1) and O(3) in the molecular plane. A slight rotation about C(2)–C(1) has the plane of the acid group [plane (ii), Table 4] making a dihedral angle of 9.8(1)° with the skeletal plane. A rotation about C(3)–C(5) yields a dihedral angle of 89.4(2)° between the plane about C(5) [plane (iii), Table 4] and the carbon chain. The π-interaction between N(1) and C(5):O(3) is preserved by a concomitant rotation which has the plane about N(1) [plane (iv), Table 4] making a dihedral angle of 85.5(2)° with plane (i) and 11.2(2)° with plane (iii). There are no significant differences in the bond lengths associated with the carbon skeleton between **3e** and **3g**, except for a slight lengthening of the C(2)–C(4) bond from 1.481(6) Å to 1.519(6) Å. There is disorder associated with the pyrrolidine ring which was treated by the use of site occupation factors for C(42) and C(43). This procedure yielded two half-chair conformations (a) and (b) with site occupation

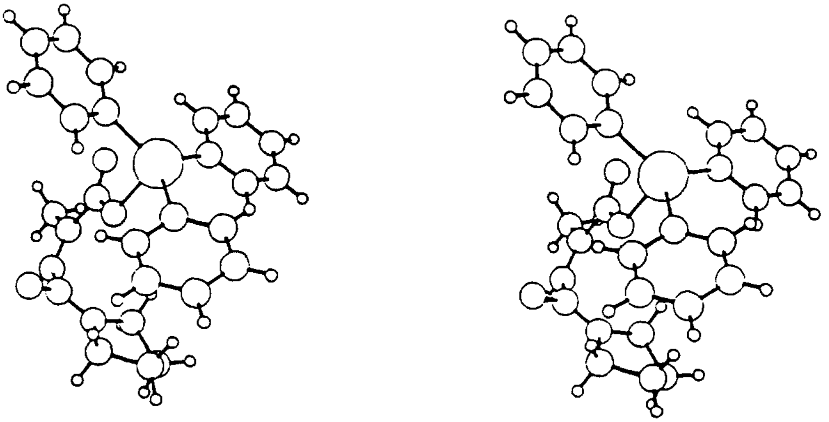

Fig. 2. Stereo-drawing of molecule **3g** viewed along the unit cell *a* axis

Table 1

Analytical, IR and Mössbauer data for the esters

Compound (formula)	Solvent	M.p. (°C)	Found (%) (Required)			IR (cm^{-1})		Mössbauer ($mm\ s^{-1}$)	
			C	H	N	$\nu_{max}(CO)_{acid}$	$\nu_{max}(CO)_{amide}$	δ	ΔE_Q
1b ($C_{22}H_{37}NO_3Sn$)	toluene	61– 62	54.8 (54.8	7.8 7.7	2.9 2.9)	1655 (1695	1615 1661) [a]	1.50	3.55
1c ($C_{28}H_{25}NO_3Sn$)	Me_2CO	75– 78	62.2 (62.0	4.7 4.6	2.6 2.6)	1645	1615	1.30	2.58
1d ($C_{28}H_{43}NO_3Sn$)	toluene	156–158	60.0 (60.0	7.7 7.7	2.5 2.5)	1665	1622	1.60	3.41
2b ($C_{24}H_{41}NO_3Sn$)	light petroleum	88– 90	56.4 (56.5	8.1 8.0	2.7 2.7)	1630 (1702	1591 1575) [a]	1.49	3.60
2c ($C_{30}H_{29}NO_3Sn$)	light petroleum/EtOAc	117–120	62.3 (63.2	5.1 5.1	2.4 2.5)	1633	1588	1.31	3.20
2d ($C_{30}H_{47}NO_3Sn$)	toluene	128–129	61.4 (61.2	8.0 8.0	2.3 2.4)	1619	1599	1.56	3.46
3b ($C_{20}H_{39}NO_5Sn$)	[b]	67– 70	49.0 (48.8	8.1 7.9	2.7 2.8)	1642 (1715	1595 1648) [a]	1.47	3.64
3c ($C_{26}H_{25}NO_4Sn$)	EtOAc	145–148	58.4 (58.4	4.6 4.7	2.6 2.6)	1612	1582	1.29	3.05

3d	EtOAc	140–142	57.1	7.8	2.4	1630	1601	1.53	2.85
($C_{26}H_{43}NO_4Sn$)			(56.5	7.8	2.5)				
3f	[c]	59– 64	53.3	8.1	3.0	1655	1600	1.46	3.51
($C_{21}H_{39}NO_3Sn$)			(53.4	8.3	3.0)	(1697	1622) [a]		
3g	EtOAc	195–198	60.8	5.2	2.5	1620	1570	1.27	2.98
($C_{27}H_{27}NO_3Sn$)			(60.9	5.1	2.6)				
3h	light petroleum/toluene	181–184	59.0	8.1	2.6	1634	1600	1.58	3.52
($C_{27}H_{45}NO_3Sn$)			(58.9	8.2	2.5)				
3j	light petroleum	61– 63	56.0	7.6	2.9	1651	1590	1.49	3.64
($C_{23}H_{37}NO_3Sn$)			(55.9	7.5	2.8)	(1703	1629) [a]		
3k	Me_2CO	158–161	63.0	4.6	2.6	1649	1609	1.32	3.26
($C_{29}H_{25}NO_3Sn$)			(62.8	4.5	2.5)				
3l	toluene	188–191	60.6	7.5	2.5	1642	1598	1.54	2.95
($C_{29}H_{43}NO_3Sn$)			(60.8	7.5	2.4)				
3n	light petroleum	57– 60	57.0	7.8	2.8	1635	1605	1.51	3.70
($C_{25}H_{41}NO_3Sn$)			(57.5	7.8	2.7)	(1655	1620) [a]		
3o	[c]	50– 60	61.4	7.9	1.8	1638	1615	1.54	3.13
($C_{31}H_{47}NO_3Sn$)			(62.0	7.8	2.3)				
3q	light petroleum/toluene	159–162	62.7	8.3	2.0	1668	1605	1.50	2.83
($C_{32}H_{49}NO_3Sn$)			(62.5	8.0	2.3)	(1659	1610) [a]		

[a] Free acid. [b] Viscous oil, which crystallised as monohydrate: $\nu_{max}(OH) = 3420\ cm^{-1}$. [c] Oil, which crystallised on standing.

Table 2

Positional parameters for non-hydrogen atoms in **3g** with estimated standard deviations in parentheses

Atom	x	y	z	$\bar{U} \times 10^4$ [a]
Sn(1)	0.3181 1(2)	0.1061 6(2)	0.2158 7(2)	383(1)
O(1)	0.360 7(2)	−0.034 6(2)	0.288 4(2)	481(9)
O(2)	0.483 2(2)	−0.046 4(2)	0.187 2(2)	593(10)
O(3)	0.238 9(2)	−0.235 9(2)	0.362 9(2)	545(10)
N(1)	0.311 5(2)	−0.142 3(3)	0.478 8(2)	505(11)
C(1)	0.437 9(3)	−0.080 4(3)	0.253 9(3)	448(12)
C(2)	0.470 3(3)	−0.178 9(3)	0.302 1(3)	481(13)
C(3)	0.415 7(3)	−0.227 1(3)	0.365 9(3)	524(14)
C(4)	0.567 0(4)	−0.226 6(4)	0.270 2(4)	711(18)
C(5)	0.315 9(3)	−0.198 6(3)	0.400 7(3)	443(12)
C(11)	0.203 7(3)	0.127 8(3)	0.313 6(3)	450(12)
C(12)	0.192 6(3)	0.222 2(3)	0.360 6(3)	544(14)
C(13)	0.118 2(4)	0.236 3(4)	0.425 8(3)	667(17)
C(14)	0.052 1(4)	0.154 4(5)	0.442 0(4)	752(20)
C(15)	0.061 7(4)	0.062 0(5)	0.395 0(4)	703(18)
C(16)	0.137 7(3)	0.045 8(4)	0.331 6(3)	560(15)
C(21)	0.275 9(4)	0.038 3(3)	0.083 5(3)	429(12)
C(22)	0.183 3(3)	−0.009 1(4)	0.071 8(3)	590(15)
C(23)	0.154 0(4)	−0.052 7(4)	−0.013 5(4)	716(19)
C(24)	0.215 7(4)	−0.048 6(4)	−0.089 8(3)	692(18)
C(25)	0.306 3(4)	−0.002 1(4)	−0.079 3(3)	679(18)
C(26)	0.336 5(3)	0.039 9(4)	0.006 0(3)	598(15)
C(31)	0.447 2(3)	0.199 0(3)	0.240 4(3)	448(12)
C(32)	0.459 5(4)	0.257 2(4)	0.321 8(4)	720(19)
C(33)	0.542 2(4)	0.319 8(5)	0.338 1(4)	910(24)
C(34)	0.616 0(4)	0.324 5(5)	0.272 7(4)	816(21)
C(35)	0.646 5(4)	0.265 1(5)	0.191 5(4)	855(22)
C(36)	0.522 4(4)	0.203 6(4)	0.176 1(3)	696(18)
C(41)	0.217 8(3)	−0.125 9(4)	0.526 8(3)	631(17)
C(42a)	0.241 4(7)	−0.030 1(8)	0.588 5(9)	296(6) [b]
C(42b)	0.249 5(11)	−0.064 6(12)	0.614 7(7)	
C(43a)	0.351 4(7)	−0.041 3(11)	0.611 6(6)	
C(43b)	0.336 8(10)	−0.001 8(9)	0.579 8(11)	
C(44)	0.392 9(4)	−0.078 1(4)	0.519 5(4)	814(21)

[a] Spherically averaged $U_{ij} \times 10^4$ (Å^2). [b] These four atomic positions were only refined isotropically.

factors of 0.554 and 0.446, respectively. The torsion angle data are given in Table 4 and the associated pseudo-rotational phase parameters [8] are (a) $\Delta = -4.8°$, $\phi_m = 40.5°$ and (b) $\Delta = -3.0°$, $\phi_m = -41.3°$ ($\Delta = 0$ and 36° for idealised half-chair and envelope conformations, respectively).

Experimental

Spectroscopy

IR spectra were recorded as Nujol mulls on a Perkin Elmer 1330 spectrophotometer.

^{119m}Sn Mössbauer spectra were obtained using a Cryophysics microprocessor spectrometer with a 512-channel data store. A 10 mCi Ba^{119m}SnO$_3$ source was used

Table 3

Selected bond lengths (Å) and angles (°) for **3g** with estimated standard deviations in parentheses

C(21)-Sn(1)-O(1)	98.2(1)	Sn(1)-O(1)	2.139(2)
C(21)-Sn(1)-C(11)	116.7(2)	Sn(1)···O(3′)	2.418(3)
C(31)-Sn(1)-C(11)	115.3(2)	Sn(1)···O(2)	2.991(3)
C(21)-Sn(1)-O(3′)	82.0(1)	Sn(1)-C(11)	2.123(4)
C(11)-Sn(1)-O(3′)	88.1(1)	Sn(1)-C(21)	2.128(4)
C(31)-Sn(1)-O(3′)	81.7(1)	Sn(1)-C(31)	2.124(4)
O(1)-Sn(1)-O(2)	47.9(1)	O(1)-C(1)	1.301(5)
O(1)-Sn(1)-O(3′)	176.9(5)	O(2)-C(1)	1.222(5)
O(2)-Sn(1)-C(11)	137.0(1)	O(3)-C(5)	1.246(5)
O(2)-Sn(1)-C(21)	78.1(1)	C(1)-C(2)	1.490(6)
O(2)-Sn(1)-C(31)	77.1(1)	C(2)-C(3)	1.335(6)
O(2)-Sn(1)-O(3′)	134.9(1)	C(2)-C(4)	1.519(6)
		C(3)-C(5)	1.492(6)
		C(5)-N(1)	1.322(5)

at room temperature and samples were cooled to 80 K, using a liquid nitrogen cryostat. The experimental error in the measured values of isomer shift (δ) and quadrupole splitting (ΔE_Q) parameters is ± 0.05 mm s^{-1}.

Table 4

Molecular geometry

a. Least-squares planes defined by atomic positions and distances of atoms from the plane (Å).

Plane (i): C(1)-C(5)
C(1) 0.00(0), C(2) 0.03(1), C(3) 0.03(1), C(4) −0.04(1), C(5) −0.02(1), Sn(1) 0.14(1), O(1) 0.19(1), O(2) −0.19(1), O(3) −1.11(1), N(1) 1.12(1)

Plane (ii): O(1), O(2), C(1), C(2)
O(1) 0.00(0), O(2) 0.00(1), C(1) 0.00(1), C(2) 0.00(1)

Plane (iii): O(3), N(1), C(3), C(5)
O(3) 0.01(1), N(1) 0.01(1), C(3) 0.01(1), C(5) −0.04(1)

Plane (iv): N(1), C(5), C(41) C(44)
N(1) 0.04(1), C(5) −0.02(1), C(41) −0.02(1), C(44) −0.03(1),C(42a) −0.41(1), C(43a) 0.22(1), C(42b) 0.17(2), C(43b) −0.48(1)

Plane (v): Sn(1), C(11), C(21), C(31)
Sn(1) −0.219(2), C(11) 0.010(5), C(21) 0.011(5), C(31) 0.011(5), O(1) −2.341(5), O(3′) 2.192(4)

b. Torsion angles (°) for the pyrrolidine ring

N(1)-C(41)-C(42a)-C(43a)	−31.2(8)
C(41)-C(42a)-C(43a)-C(44)	40.5(9)
C(42a)-C(43a)-C(44)-N(1)	−33.2(8)
C(43a)-C(44)-N(1)-C(41)	14.0(6)
C(44)-N(1)-C(41)-C(42a)	10.8(6)
N(1)-C(41)-C(42a)-C(43b)	31.9(10)
C(41)-C(42b)-C(43b)-C(44)	−41.3(11)
C(42b)-C(43b)-C(44)-N(1)	33.6(10)
C(43b)-C(44)-N(1)-C(41)	−13.4(7)
C(44)-N(1)-C(41)-C(42b)	−11.8(7)

Synthesis of amic acids

The amic acids (**1a**, **2a**, **3a**, **3e**, **3i**, **3m** and **3p**) were prepared by the reaction of the primary or secondary amine with the appropriate acid anhydride; the melting points were in good agreement with literature values [9–13].

Synthesis of triorganostannyl esters

The tributyl- and tricyclohexylstannyl esters were prepared by refluxing a mixture of bis(tributyltin) oxide (1 mol) and the appropriate amic acid (2 mol), or tricyclohexyltin hydroxide (1 mol) and amic acid (1 mol), in toluene and removing the water azeotropically using a Dean and Stark trap. A typical preparation is given below.

A mixture of **3e** (1.83 g, 100 mmol) and tricyclohexyltin hydroxide (3.85 g, 100 mmol) were refluxed in toluene (150 ml) under a Dean and Stark trap for 2 h. On cooling, the slightly cloudy solution was filtered and the solvent removed using a rotary evaporator. The white residual solid was heated in light petroleum, and toluene was added to the resulting suspension until dissolution occurred, whereupon **3h** (2.66 g, 69%) crystallised at room temperature. It had m.p. 181–184°C.

A representative synthesis of the triphenylstannyl esters is as follows. A mixture of **3e** (1.83 g, 100 mmol) and triphenyltin hydroxide (3.67 g, 100 mmol) was refluxed in acetone (150 ml) over molecular sieves for 2 h. The solvent was removed from the cloudy solution using a rotary evaporator and the white solid residue recrystallised from ethyl acetate—filtration of the hot solution being necessary—to form **3g** (2.50 g, 47%). It had m.p. 195–198°C.

The microanalytical data for, and the melting points of, the new esters are collected in Table 1, together with the solvents used for their recrystallisation.

Single crystals of **3g** were prepared by dissolving the ester in warm ethyl acetate and allowing the solvent to evaporate slowly at room temperature.

Crystal data

$C_{27}H_{27}NO_3Sn$, $M = 532.2$. Monclinic. $a = 13.467(2)$, $b = 12.764(4)$, $c = 14.181(2)$ Å, $\beta = 91.85(1)°$, $V = 2436$ Å^3 (by least-squares refinement on diffractometer angles for 15 automatically centred reflections, $\lambda = 0.71069$ Å), space group $P2_1/n$ (alt. $P2_1/c$, No. 14), $Z = 4$, $D_c = 1.451$, $D_o = 1.449$ g cm^{-3}, F(000) = 1080. Colourless needles. $\mu(\text{Mo-}K_\alpha) = 9.76$ cm^{-1}.

Data collection and processing

CAD4 diffractometer, ω–2θ mode with ω scan width = 0.7 + 0.35 tan θ, ω scan speed 3.3 deg min^{-1}: 5229 reflections measured ($1 < \theta < 26°$, h, k, $\pm l$), 4191 unique (merging $R = 0.014$ after empirical absorption correction by ψ scans to calculate transmission values), giving 3496 with $I > 3\sigma(I)$. No significant decay was detected. Lorentz and polarisation corrections were applied to all reflections. The reflection data were collected by Dr D.C. Povey in the Crystallography Department of the University of Surrey.

Stucture analysis and refinement

The structure was solved using the heavy atom technique (Sn), followed by iterative Fourier synthesis using the programme SHELX-76, and refined by the method of full-matrix least-squares. Initially, all atoms were treated isotropically.

The two carbon atoms, C(42) and C(43), of the pyrrolidine ring showed large thermal vibration parameters which, when considered in conjunction with the geometry of the ring, strongly suggested disorder. Alternative positions were calculated for both atoms and the structure refinement continued using constrained bond lengths for the ring obtained from the structure of the free acid. Site occupation factors for the two atomic positions of each atom were also refined. A difference Fourier synthesis revealed the hydrogen atoms as diffuse electron-density maxima and, in subsequent cycles, these atoms were placed in calculated positions assuming a C–H bond length of 1.0 Å. Further refinement proceeded with all non-hydrogen atoms, save C(41) and C(42), refined anisotropically. No attempt was made to refine either the hydrogen atom positional or thermal parameters. Final R values were 0.034 for the significant reflections and 0.042 for all reflections. Weights were assigned to the observed structure factors during the refinement using the scheme $w = 1.1104/[\sigma^2(F) + 0.000780F^2]$. A final difference Fourier synthesis confirmed the refinement to be correct.

Throughout the structure factor calculations, the atomic scattering factors used were those embodied in the SHELX-76 programme package. Computations were performed initially on the Prime computer at the University of Surrey and the refinement was completed on the VAX 11/750 at the Roehampton Institute.

Lists of observed and calculated structure factors, anisotropic thermal parameters and calculated hydrogen atom coordinates are available from the authors.

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