Journal of Organometallic Chemistry, 437 (1992) 131–144
Elsevier Sequoia S.A., Lausanne
JOM 22845

Preparation, spectroscopic studies and structure of bis(triorganostannyl) esters of substituted aliphatic dicarboxylic acids *

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

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

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

(Received October 17, 1991)

Abstract

Bis(triorganostannyl) esters of phenylmaleic acid, citraconic acid, maleic acid, phenylsuccinic acid, methylsuccinic acid and succinic acid, $R_3SnO_2CCR^1:CHCO_2SnR_3$ (R = Bu, Ph, Cy; R^1 = Ph, Me, H) and $R_3SnO_2CCHR^1\cdot CH_2CO_2SnR_3$ (R = Bu, Ph; R^1 = Ph and R = Bu, Ph, Cy; R^1 = Me, H), have been prepared from R_3SnOH or $(Bu_3Sn)_2O$ and the dicarboxylic acid or its anhydride. The structures of these compounds in the solid state are discussed with reference to their IR and Mössbauer spectra. The crystal structures of the bis(triphenylstannyl) esters of phenylmaleic acid and citraconic acid have been determined by single crystal X-ray diffraction. In the first diester, both tin atoms are occupying tetrahedral geometries, with no short intermolecular O ··· Sn contacts. In bis(triphenyltin) citraconate, the carboxylatotin attached to the substituted olefinic carbon is also four coordinate, but the second tin atom is five coordinate, due to intermolecular coordination by a carboxylate group from a neighbouring molecule [Sn ··· O 2.397(3) Å], thereby giving rise to a polymeric chain structure. The tributylstannyl monoester of citraconic acid has been synthesized and its structure in solution assigned by ^{13}C and ^{119}Sn NMR spectroscopy and, in the solid state, by IR and Mössbauer spectroscopy.

Introduction

Although a large number of structural studies have been carried out on the triorganostannyl esters of monofunctional carboxylic acids [1,2], relatively little work has so far been undertaken on the organotin esters of dicarboxylic acids.

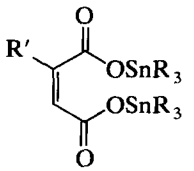
Correspondence to: Dr. P.J. Smith.

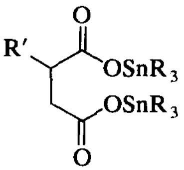
* Dedicated to Professor Alwyn G. Davies in recognition of his distinguished contributions to organotin chemistry, as well as being a good teacher and friend.

In 1967, Mufti and Poller [3] proposed from IR studies on the bis(triphenylstannyl) and bis(tributylstannyl) esters of maleic and fumaric acids that, in the solid state, these diesters had polymeric structures with all tin atoms pentacoordinate and bridging carboxyl groups. Subsequent X-ray crystallographic investigations of the bis(trimethylstannyl) esters of malonic [4], terephthalic [5] and acetylenedicarboxylic [5] acids have demonstrated this polymeric structure. A recent X-ray study of the tributylstannyl(oxalato) salt, $[Cy_2NH_2]_2^+$ $[EtOH \cdot Bu_3SnO(CO_2)(O)Bu_3Sn\text{-}OC(O)^-]_2^{2-}$, has shown that, in this complex ester, the anion contains a central bis(tributylstannyl) oxalate moiety in which both tin atoms are again pentacoordinate via two additional coordinated oxalate anions [6].

Recently, the synthesis of a series of bis(triorganostannyl)esters of 4-(trialkylstannyloxysulphonyl)phthalic acids has been reported [7] by Shcherbakov and co-workers.

In this work, the influence of the acid substituent, R^1, on the structure of the organotin diester in the solid state has been investigated by IR and Mössbauer spectroscopy for the following compounds:





R^1 = Ph, R = Bu (**1**), Ph (**2**) or Cy (**3**)
R^1 = Me, R = Bu (**4**), Ph (**5**) or Cy (**6**)
R^1 = H, R = Bu (**7**), Ph (**8**) or Cy (**9**)

R^1 = Ph, R = Bu (**10**) or Ph (**11**)
R^1 = Me, R = Bu (**12**), Ph (**13**) or Cy (**14**)
R^1 = H, R = Bu (**15**), Ph (**16**) or Cy (**17**)

The structures of (**2**) and (**5**) have been determined by X-ray crystallography.

Experimental

Cy_3SnOH, Ph_3SnOH, $(Bu_3Sn)_2O$, citraconic anhydride, maleic acid, phenylsuccinic acid, methylsuccinic acid and succinic acid were commercial products and were used without further purification. Phenylmaleic anhydride was prepared using a modified version of the method of Hill [8], in which the reflux time was reduced from 3 h to 30 min.

Compounds **1–6** were prepared by refluxing a 1:1 molar mixture of $(Bu_3Sn)_2O$ and the acid anhydride in toluene or a 2:1 mixture of R_3SnOH and the anhydride for 2 h (with Ph_3SnOH, acetone was used as solvent and molecular sieves were added to remove the water formed as by-product whilst, with Cy_3SnOH, the water was removed by azeotropic dehydration in toluene using a Dean and Stark separator).

The diesters, **7**, **9**, **10**, **12**, **14**, **15** and **17**, were synthesized by refluxing a 1:1 molar mixture of $(Bu_3Sn)_2O$ and the dicarboxylic acid, or a 2:1 mixture of Cy_3SnOH and the acid, in toluene for 2 h, the water formed being removed azeotropically. The bis(triphenylstannyl) esters, **8**, **11**, **13** and **16**, were prepared by refluxing a 2:1 mixture of Ph_3SnOH and the dicarboxylic acid in acetone for 2 h over molecular sieves.

The solvents used for recrystallization, where appropriate, were: acetone (for **2**, **8** and **16**), light petroleum (for **6**), light petroleum/acetone (for **5**), light petroleum/ethyl acetate (for **13**) and toluene (for **9**, **10**, **12**, **14**, **15** and **17**).

The tributylstannyl half ester of citraconic acid (**18**) was prepared by refluxing a 2:1 molar mixture of citraconic acid and bis(tributyltin) oxide for 2 h in ethyl acetate over molecular sieves. The resulting cloudy solution was filtered and the solvent removed on a rotary evaporator, to leave an oily residue. This was pumped at high vacuum, to form a white solid.

Analytical data are summarized in Table 1. C and H microanalyses were carried out by the Microanalytical Laboratory, University College London.

IR spectra (nujol mulls) were recorded on a Perkin–Elmer 1330 spectrometer. ^{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 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}. ^{119}Sn NMR spectra, recorded under nuclear Overhauser suppressed conditions, and ^{13}C NMR spectra, were determined using a Jeol FX60Q spectrometer. ^{119}Sn chemical shifts, $\delta(^{119}Sn)$, are relative to Me_4Sn and are accurate to ± 0.1 ppm.

Crystals of **2** and **5** suitable for X-ray diffraction experiments were obtained from solutions of ethyl acetate and acetone/petroleum ether, respectively, over a prolonged period at room temperature.

Crystal data for 2

$C_{46}H_{36}O_4Sn_2$, $M = 890.2$. Triclinic, $a = 8.54(3)$, $b = 13.40(4)$, $c = 17.98(6)$ Å, $\alpha = 76.9(1)°$, $\beta = 75.4(2)°$, $\gamma = 86.6(8)°$, $V = 1940(18)$ Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections in the range $10 \le \theta \le 12°$, $\lambda = 0.71069$ Å), space group $P\bar{1}$ (No. 2), $Z = 2$, $D_c = 1.525$ g cm^{-3}, $F(0, 0, 0) = 888$. Colourless needles, $\mu(\text{Mo-}K_\alpha) = 13.3$ cm^{-1}.

Data collection and processing for 2

Reflection data were collected on an Enraf–Nonius CAD4 diffractometer. The intensity data were measured in the range $1 \le \theta \le 24°$ ($0 \le h \le 9$, $-15 \le k \le 15$, $-20 \le l \le 20$), for a hemisphere of reciprocal space using the ω–2θ scan mode with scan width $= 0.7 + 0.35 \tan \theta$, ω scan speed 3.3 deg min^{-1}; 6003 reflections were measured, 4864 having $I \ge 3\sigma(I)$. An empirical absorption correction was applied using ψ scans to calculate transmission values. No significant decay was detected. Lorentz and polarization corrections were applied to all reflections. The reflection data were collected by Dr. D.C. Povey in the Chemistry Department, University of Surrey.

Structure analysis and refinement for 2

The structure was solved using the heavy-atom technique (Sn), followed by iterative Fourier synthesis using the programme SHELX-76 [11] on the VAX 11/750 at the Roehampton Institute. The structure was refined by the method of full-matrix least-squares using the Enraf–Nonius Structure Determination Package SDP [12] in the Chemistry Department at the University of Surrey (by JHA whilst on study leave). Initially, all atoms were treated isotropically. As the refinement

Table 1

Analytical data for bis(triorganostannyl) esters

Compound	Yield (%)	m.p. (°C)	Analytical data [Found (calc.) (%)]	
			C	H
1	84	43–44	52.99 (52.99)	7.66 (7.79)
2	62	156.5–158	61.53 (62.02)	4.24 (4.04)
3 [a]	53	72–76	58.25 (58.47)	7.76 (7.63)
4	–	Oil [b]	49.23 (49.15)	7.93 (8.19)
5	53	122.5–123.5	59.15 (59.42)	4.21 (4.11)
6	5	138.5–141	57.01 (56.94)	8.07 (8.10)
7	–	45–48 [c]	48.12 (48.41)	7.83 (8.07)
8	72	123–126 [d]	58.51 (58.97)	4.33 (3.93)
9	38	149–151	56.65 (56.47)	7.70 (8.00)
10	–	82–84	52.66 (52.85)	8.03 (8.13)
11	11	270–276	61.73 (61.88)	4.38 (4.26)
12	78	77.5–78.5	49.18 (49.01)	8.30 (8.45)
13	36	98–101	58.58 (59.28)	4.54 (4.34)
14	55	166–168	57.50 (56.81)	8.61 (8.31)
15	76	97–99 [e]	48.18 (48.28)	8.20 (8.33)
16	22	160–162	58.87 (58.82)	4.25 (4.17)
17	78	186–191	55.95 (56.34)	8.21 (8.22)
18	–	83–85 [f]	48.84 (48.69)	7.83 (7.64)

[a] Compound isolated as the monohydrate [ν(OH) 3400 cm^{-1}]. [b] Ref. 9 reports a solid, m.p. 65–68°C. [c] Ref. 3 reports 44–46°C; ref. 10 reports 42–43°C. [d] Ref. 3 reports 118–120°C. [e] Ref. 10 reports 91–93°C. [f] Ref. 9 reports 75–77°C.

progressed, the tin atoms and, subsequently, the oxygen and carbon atoms, were refined anisotropically. A difference Fourier synthesis revealed some hydrogen atoms as diffuse electron density maxima and, in subsequent cycles, all hydrogen atoms were placed in calculated positions assuming a C–H bond length of 1.0 Å. Full anisotropic refinement converged at $R = 0.021$, $R_w = 0.024$, estimated standard deviations of observations of unit weight = 1.09, using the weighting scheme [13] $w^{-1} = (\sigma F)^2 + (0.01F)^2 + 1.0$, where the coefficients were adjusted to give a near linear δR *versus* normal probability plot [14] of slope 1.04. A final difference Fourier synthesis revealed no significant outstanding electron density maxima.

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

Crystal data for 5

$C_{41}H_{34}O_4Sn_2$, $M = 828.1$. Orthorhombic, $a = 17.204(4)$, $b = 18.153(4)$, $c = 11.488(6)$ Å, $V = 3588(3)$ Å^3, space group $P2_12_12_1$ (No. 19), $Z = 4$, $D_c = 1.538$ g cm^{-3}, $F(0,0,0) = 1648$. Colourless needles. μ(Mo-K_α) = 14.4 cm^{-1}.

Data collection and processing for 5

As for **2**, except that cell parameters were determined using 25 reflections in the range $9 \leq \theta \leq 11°$. Intensity data were measured in the range $1 \leq \theta \leq 26°$ ($0 \leq h \leq 21$, $0 \leq k \leq 22$, $0 \leq l \leq 14$) for an octant of reciprocal space, 3955 reflections were measured, 3382 having $I \geq 3\sigma(I)$. Corrections were applied for Lorentz and polarization effects and for an 8.3% decay in the monitored reflection over the period of data collection. No suitable reflections were available for ψ measurements and, consequently, no empirical absorption correction could be applied.

Structure analysis and refinement for 5

As for **2**, except that the programme DIFABS [15] was used to apply an absorption correction before anisotropic refinement commenced. Full anisotropic refinement converged at $R = 0.024$, $R_w = 0.029$, estimated standard deviation of an observation of unit weight = 1.104 using the weighting scheme $w^{-1} = (\sigma F)^2 + (0.013F)^2 + 1.3$, where the coefficients were adjusted to give a near linear δR *versus* normal probability plot of slope 1.01.

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

Results and discussion

Mössbauer and IR spectra

Table 2 shows the Mössbauer and IR spectroscopic data for the bis(triorganostannyl) esters **1**–**17**.

The bis(triorganostannyl) esters of the phenyl-substituted dicarboxylic acids, with the exception of the phenylmaleate derivative, **2**, show Mössbauer ΔE_Q values in the range 2.92–3.63 mm s^{-1}, indicating that, at 80 K, both tin atoms are occupying a trigonal bipyramidal geometry with planar R_3Sn moieties and the carboxylate ligands bridging axially, as found earlier by X-ray crystallography for bis(trimethylstannyl) esters [4,5]. The significantly lower quadrupole splitting observed for bis(triphenylstannyl) phenylmaleate (**2**) together with its high frequency ν_{as}(CO) IR bands, suggest a monomeric structure with tetrahedral tin atoms, which has been confirmed by X-ray crystallography. The IR spectra of the other phenyl-substituted diesters show that **1** and **3** contain uncoordinated carbonyl groups and are therefore monomers with four coordinate tin atoms at room temperature. It is interesting to note here that tributyltin benzoate has been found [16] to contain four coordinate tin at room temperature and five coordinate tin at 140 K. It may therefore be concluded that, for the bis(triorganostannyl) phenylmaleates, **1**–**3**, the

Table 2

Mössbauer and IR data for the esters

Compound	δ (mm s^{-1})	ΔE_Q (mm s^{-1})	ν_{as}(CO) (cm^{-1})
1	1.50	3.48	1612, 1650
2	1.17	2.46	1620, 1650
3	1.37	2.92	1612, 1650
4	1.47	3.63	1570, 1640
5	1.33 [a]	3.32 [a]	1529, 1648
	1.13 [b]	2.93 [b]	
6	1.50	3.00	1625
7	1.48	3.72	1580
8	1.45 [a]	3.47 [a]	1570, 1640
	1.11 [b]	2.78 [b]	
9	1.47	2.72	1613, 1656
10	1.45	3.63	1589
11	1.10	3.09	1553
12	1.44	3.71	1562
13	1.22	3.30	1540
14	1.49	2.96	1650
15	1.43	3.70	1640
16	1.19	2.27	1635
17	1.47	2.84	1640
18	1.50	3.94	1570

[a] Outer doublet. [b] Inner doublet.

greatest steric effect is found in **2**, which is a monomer at 80 K as well as at room temperature. The Mössbauer and IR data indicate that the phenylsuccinates, **10** and **11**, on the other hand, are pentacoordinate at room temperature and at 80 K, demonstrating the contribution of the (shorter) double bond in the maleates to the steric effect.

The methyl-substituted diesters, again with the exception of the bis(triphenylstannyl) maleate derivative, **5**, show large ΔE_Q values consistent with pentacoordinate polymeric structures at 80 K. In contrast to **2**, however, the Mössbauer spectrum of **5** consists of two overlapping doublets and its IR spectrum contains both low and high frequency ν_{as}(CO) bands, indicative of four and five coordinate tin sites in the molecule. This has been confirmed by X-ray crystallography in the present work. The bis(tricyclohexylstannyl) esters of citraconic and methylsuccinic acids, **6** and **14**, show only uncoordinated carbonyl bands in their IR spectra and are therefore likely to be monomeric species at room temperature with essentially tetrahedral tin atom geometries. The bis(triphenylstannyl) and bis(tributylstannyl) esters of methylsuccinic acid, **12** and **13**, from their IR and Mössbauer data, are five coordinate polymers at room temperature, as well as at 80 K. This could be due to steric effects, which would favour intermolecular coordination by both CO groups in the succinates, compared to the corresponding citraconates which contain a double bond and in which such an association would be restricted. Interestingly, bis(tributylstannyl) citraconate (**4**), which is a viscous liquid at room temperature, shows two ν_{as}(CO) bands at 1570 and 1640 cm^{-1}, and this is in accord with the presence of associated and free carbonyl groups at room temperature. The observation of a single low field ^{119}Sn NMR signal for this compound (+92.8 ppm as a 10% w/v solution in CCl_4) suggests that the polymeric structure is broken down in CCl_4. A similar effect has been noted previously [17] for bis(tributyltin) carbonate, $(Bu_3SnO)_2CO$, which shows $\delta(^{119}Sn)$ +104.9 ppm, as a 10% w/v solution in $CDCl_3$.

The unsubstituted diesters, at 80 K, are all five coordinate, except the bis(triphenylstannyl) derivatives, **8** and **16**. Compound **8** is similar to **5**, in that it contains both four and five coordinate tin atoms in the same molecule, its Mössbauer spectrum showing two overlapping doublets with similar parameters to **5**. The IR data are consistent with this, since two $\nu_{as}(CO)$ bands are observed at 1570 cm^{-1} and 1640 cm^{-1}, the latter band being clearly apparent when a strong mull is used. Mufti and Poller, however, concluded on the basis of its IR spectrum [3] that **8** has a polymeric structure with all tin atoms pentacoordinate and bridging carboxyl groups. Their assignments for $\nu_{as}(CO)$ were 1540 cm^{-1} and 1560 cm^{-1}, and the higher frequency (1640 cm^{-1}) band, which is also observed (1648 cm^{-1}) in the closely related diester **5** (Table 2), was not reported.

Interestingly, bis(triphenylstannyl) succinate (**16**) has tetrahedral tin atom environments, although its methyl- and phenyl- substituted analogues, **11** and **13**, both contain pentacoordinate tin sites, as discussed above, and it is not immediately evident why this is so. Finally, at room temperature, the IR data indicate that **9**, **16** and **17** are unassociated molecules containing tetrahedral tin atoms.

X-Ray structure of bis(triphenylstannyl) phenylmaleate (2)

Table 3 gives positional parameters for non-hydrogen atoms with their estimated standard deviations, whilst Table 4 gives selected bond lengths and angles for **2**, together with their estimated standard deviations. The atom numbering is shown in Fig. 1, which is a stereo-diagram of the molecule, viewed to give minimum overlap of atoms.

The two tin atoms, Sn(1) and Sn(2), are both occupying essentially tetrahedral geometries, the average bond angles around each metal atom being 109.3° and 110.8°, respectively. The carbonyl group, C(1):O(2), is sterically encumbered by the three phenyl groups attached to Sn(1), as well as by the phenyl substituent on the maleate group, all of which act as a barrier preventing the approach to the tin atom in a neighbouring molecule by the carbonyl oxygen, to form an associated polymeric structure. The carbonyl group, C(5):O(3), is similarly inhibited by the phenyl groups on Sn(2) although, in this case, a weak intramolecular interaction is observed [Sn(2)...O(3) = 2.613(2) Å].

The two acid groups are oriented with respect to the plane including the carbon–carbon double bond, C(2):C(3), such that one is approximately perpendicular to the skeletal plane and the other almost parallel. The dihedral angle for the parallel relationship is 8.2° and that for the perpendicular relationship 91.5°; the dihedral angle between the two acid group planes is 98.1°. The dihedral angle between phenyl(4) and the skeletal plane is 15.3°, thus enabling some π-interaction between the ethenic double bond and the aromatic system to be preserved. If it is assumed that this interaction varies as $\cos^2 \psi$, where ψ is the dihedral angle, then this interaction will be 93% of that for zero dihedral angle [18].

X-Ray structure of bis(triphenylstannyl) citraconate (5)

Table 5 gives positional parameters for non-hydrogen atoms, with their estimated standard deviations, selected bond lengths and angles for **5** are listed in

Table 3

Positional parameters for non-hydrogen atoms in **2** with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	B_{eq} (Å^2)
Sn(1)	0.32119(3)	0.17845(2)	0.35061(1)	3.434(5)
Sn(2)	0.50514(2)	0.63632(1)	0.13540(1)	3.062(4)
O(1)	0.4957(3)	0.2791(2)	0.3518(1)	3.91(5)
O(2)	0.2787(3)	0.3455(2)	0.4212(1)	4.58(6)
O(3)	0.4280(3)	0.4942(2)	0.2647(1)	3.90(5)
O(4)	0.6016(2)	0.6219(2)	0.2332(1)	3.62(5)
C(1)	0.4240(4)	0.3457(2)	0.3919(2)	3.62(7)
C(2)	0.5383(4)	0.4173(2)	0.4057(2)	3.16(6)
C(3)	0.5793(4)	0.5072(2)	0.3563(2)	3.20(7)
C(5)	0.5284(4)	0.5400(2)	0.2823(2)	3.19(7)
C(11)	0.4857(4)	0.0924(2)	0.2780(2)	3.43(7)
C(12)	0.6393(4)	0.1294(3)	0.2398(2)	4.66(8)
C(13)	0.7442(5)	0.0778(3)	0.1889(2)	6.1(1)
C(14)	0.6977(5)	−0.0112(3)	0.1761(2)	5.6(1)
C(15)	0.5477(5)	−0.0502(3)	0.2139(2)	5.6(1)
C(16)	0.4403(5)	0.0021(3)	0.2644(2)	4.88(9)
C(21)	0.1577(4)	0.2534(2)	0.2838(2)	3.59(7)
C(22)	0.0341(4)	0.3165(3)	0.3117(2)	5.11(9)
C(23)	−0.0725(5)	0.3586(3)	0.2658(3)	6.3(1)
C(24)	−0.0560(4)	0.3408(3)	0.1925(2)	5.8(1)
C(25)	0.0659(5)	0.2785(3)	0.1644(2)	5.28(9)
C(26)	0.1712(4)	0.2342(3)	0.2097(2)	4.33(8)
C(31)	0.2330(4)	0.0921(3)	0.4673(2)	4.04(8)
C(32)	0.2935(5)	−0.0053(3)	0.4891(2)	5.6(1)
C(33)	0.2360(6)	−0.0638(3)	0.5644(3)	7.2(1)
C(34)	0.1196(5)	−0.0249(4)	0.6178(2)	7.2(1)
C(35)	0.0585(6)	0.0697(4)	0.5971(2)	7.3(1)
C(36)	0.1138(5)	0.1292(3)	0.5219(2)	5.8(1)
C(41)	0.6030(4)	0.3782(2)	0.4763(2)	4.06(7)
C(42)	0.5282(6)	0.2963(3)	0.5340(2)	6.0(1)
C(43)	0.5895(7)	0.2599(3)	0.6000(2)	8.2(1)
C(44)	0.7226(6)	0.3029(4)	0.6086(2)	8.6(1)
C(45)	0.7969(5)	0.3824(4)	0.5519(2)	8.0(1)
C(46)	0.7377(5)	0.4208(3)	0.4860(2)	5.9(1)
C(51)	0.5915(4)	0.5083(2)	0.0850(2)	3.26(7)
C(52)	0.7273(4)	0.5220(3)	0.0218(2)	4.40(8)
C(53)	0.7948(5)	0.4411(3)	−0.0108(2)	5.33(9)
C(54)	0.7268(5)	0.3453(3)	0.0187(2)	5.36(9)
C(55)	0.5910(5)	0.3305(3)	0.0804(2)	5.26(9)
C(56)	0.5240(4)	0.4115(3)	0.1138(2)	4.41(8)
C(61)	0.2632(4)	0.6842(2)	0.1765(2)	3.49(7)
C(62)	0.2290(4)	0.7872(3)	0.1726(2)	4.35(8)
C(63)	0.0754(5)	0.8189(3)	0.2075(2)	5.8(1)
C(64)	−0.0443(5)	0.7482(4)	0.2441(2)	6.9(1)
C(65)	−0.0125(5)	0.6469(4)	0.2472(3)	7.2(1)
C(66)	0.1397(4)	0.6137(3)	0.2139(2)	5.12(9)
C(71)	0.6486(4)	0.7655(2)	0.0631(2)	3.16(7)
C(72)	0.8099(4)	0.7733(2)	0.0655(2)	3.75(7)
C(73)	0.9068(4)	0.8534(3)	0.0161(2)	4.58(8)
C(74)	0.8449(5)	0.9263(2)	−0.0356(2)	4.92(9)
C(75)	0.6865(5)	0.9202(3)	−0.0396(2)	4.93(9)
C(76)	0.5887(4)	0.8401(2)	0.0099(2)	3.95(8)

Table 4

Selected bond lengths (Å) and bond angles (deg) in **2** with e.s.d.s in parentheses

Sn(1)-C(11)	2.140(3)	O(1)-Sn(1)-C(11)	96.9(3)
Sn(1)-C(21)	2.129(3)	O(1)-Sn(1)-C(21)	111.2(1)
Sn(1)-C(31)	2.125(3)	O(1)-Sn(1)-C(31)	108.2(1)
Sn(1)-O(1)	2.077(2)	C(11)-Sn(1)-C(21)	106.8(1)
Sn(2)-C(51)	2.129(3)	C(11)-Sn(1)-C(31)	112.3(1)
Sn(2)-C(61)	2.125(3)	C(21)-Sn(1)-C(31)	120.5(1)
Sn(2)-C(71)	2.149(3)	O(4)-Sn(2)-C(51)	106.4(1)
Sn(2)-O(4)	2.090(2)	O(4)-Sn(2)-C(61)	103.1(1)
Sn(2)...O(3)	2.613(2)	O(4)-Sn(2)-C(71)	109.7(1)
C(1)-O(1)	1.303(4)	C(51)-Sn(2)-C(61)	129.3(1)
C(1)-O(2)	1.220(4)	C(51)-Sn(2)-C(71)	106.6(1)
C(5)-O(3)	1.224(4)	C(61)-Sn(2)-C(71)	109.7(1)
C(5)-O(4)	1.318(3)	Sn(1)-O(1)-C(1)	107.9(2)
C(1)-C(2)	1.509(5)	Sn(2)-O(4)-C(5)	103.2(2)
C(2)-C(3)	1.392(4)	O(1)-C(1)-O(2)	123.2(3)
C(2)-C(41)	1.486(4)	O(1)-C(1)-C(2)	114.1(3)
C(3)-C(5)	1.469(4)	O(2)-C(1)-C(2)	122.5(3)
		C(1)-C(2)-C(3)	121.4(3)
		C(1)-C(2)-C(41)	114.9(2)
		C(3)-C(2)-C(41)	123.7(3)
		C(2)-C(3)-C(5)	123.1(3)
		O(3)-C(5)-O(4)	120.8(3)
		O(3)-C(5)-C(3)	123.5(2)
		O(4)-C(5)-C(3)	115.7(3)

Table 6. The atom numbering is shown in Fig. 2, which is a stereo-diagram of the molecule viewed to give minimum overlap of atoms.

In **5**, one of the carbonyl groups, C(5):O(3), is involved in intermolecular bonding. The bulk of the molecule is directed away from this carbonyl group, thereby enabling the CO to form an intermolecular bond with a tin atom of an

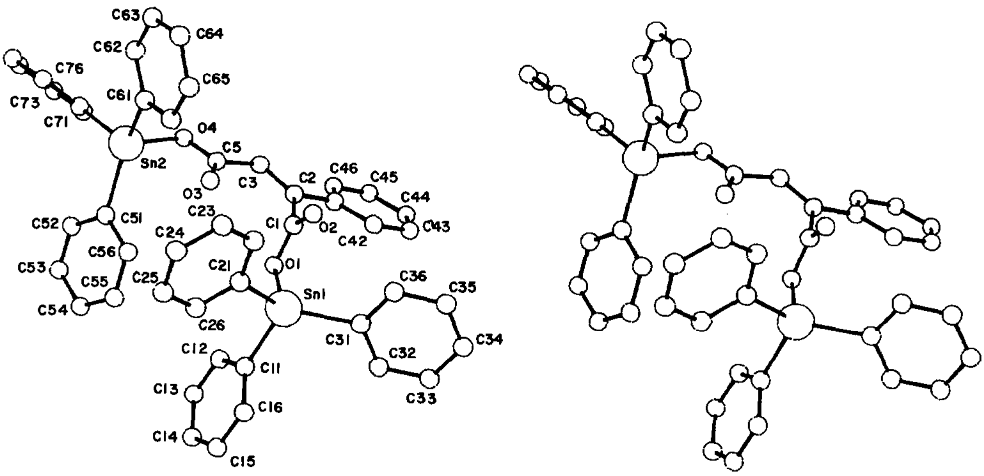


Fig. 1. Stereo-drawing of molecule **2**, showing atom numbering and viewed to give minimum overlap of atoms.

Table 5

Positional parameters for non-hydrogen atoms in **5** with e.s.d.s in parentheses

Atom	x	y	z	B_{eq} (Å^2)
Sn(1)	0.21091(2)	0.16520(2)	0.46698(3)	4.077(7)
Sn(2)	0.21767(2)	0.48703(2)	0.78898(3)	3.302(5)
O(1)	0.1340(2)	0.2364(2)	0.3824(3)	4.52(8)
O(2)	0.2057(2)	0.3033(2)	0.4976(3)	4.52(8)
O(3)	0.2454(2)	0.4739(2)	0.4805(3)	3.55(7)
O(4)	0.1665(2)	0.4437(2)	0.6281(3)	4.26(8)
C(1)	0.1518(3)	0.2992(3)	0.4273(4)	3.9(1)
C(2)	0.1033(3)	0.3637(3)	0.3965(4)	3.7(1)
C(3)	0.1182(3)	0.4292(3)	0.4396(4)	3.6(1)
C(4)	0.0394(5)	0.3538(5)	0.3110(7)	5.4(2)
C(5)	0.1832(3)	0.4497(2)	0.5204(4)	3.20(9)
C(11)	0.3323(3)	0.1792(3)	0.4383(5)	4.6(1)
C(12)	0.3731(3)	0.2413(4)	0.4728(6)	5.3(1)
C(13)	0.4514(3)	0.2478(4)	0.4467(6)	6.1(2)
C(14)	0.4886(3)	0.1927(4)	0.3866(6)	6.1(2)
C(15)	0.4500(4)	0.1309(4)	0.3542(6)	6.5(2)
C(16)	0.3713(3)	0.1236(3)	0.3777(6)	5.5(1)
C(21)	0.1687(3)	0.1554(3)	0.6400(5)	4.8(1)
C(22)	0.1942(4)	0.2010(3)	0.7276(5)	6.6(2)
C(23)	0.1640(6)	0.1922(4)	0.8382(6)	10.1(2)
C(24)	0.1125(7)	0.1404(5)	0.8637(7)	13.5(3)
C(25)	0.0849(6)	0.0946(5)	0.7793(8)	10.5(2)
C(26)	0.1148(5)	0.1015(4)	0.6668(7)	7.2(2)
C(31)	0.1788(3)	0.0721(3)	0.3641(6)	5.1(1)
C(32)	0.1482(4)	0.0803(4)	0.2532(6)	6.6(2)
C(33)	0.1355(5)	0.0187(5)	0.1845(7)	9.8(2)
C(34)	0.1518(4)	−0.0504(4)	0.2230(8)	9.5(2)
C(35)	0.1809(4)	−0.0585(4)	0.3306(8)	8.4(2)
C(36)	0.1944(4)	0.0015(4)	0.4014(6)	6.6(2)
C(41)	0.1175(3)	0.4477(3)	0.8760(4)	3.18(9)
C(42)	0.0707(3)	0.4909(3)	0.9477(5)	4.6(1)
C(43)	0.0084(4)	0.4606(4)	1.0063(5)	5.6(1)
C(44)	−0.0077(4)	0.3878(4)	0.9945(6)	6.0(2)
C(45)	0.0368(3)	0.3432(4)	0.9246(6)	5.7(1)
C(46)	0.0992(3)	0.3740(3)	0.8647(5)	4.7(1)
C(51)	0.3148(3)	0.4149(3)	0.7908(4)	3.51(9)
C(52)	0.3665(4)	0.4128(4)	0.6999(5)	6.1(1)
C(53)	0.4317(4)	0.3698(5)	0.7046(6)	7.7(2)
C(54)	0.4447(4)	0.3257(4)	0.7980(7)	7.4(2)
C(55)	0.3953(5)	0.3272(4)	0.8869(7)	8.8(2)
C(56)	0.3302(4)	0.3714(4)	0.8864(6)	6.7(2)
C(61)	0.2217(3)	0.5962(3)	0.7233(5)	3.78(9)
C(62)	0.1580(4)	0.6417(3)	0.7327(5)	5.2(1)
C(63)	0.1596(4)	0.7134(3)	0.6900(6)	6.2(2)
C(64)	0.2261(5)	0.7396(3)	0.6414(5)	6.6(2)
C(65)	0.2892(5)	0.6954(3)	0.6297(5)	6.1(1)
C(66)	0.2878(4)	0.6240(3)	0.6689(4)	4.5(1)

adjacent molecule. This results in a polymeric structure (Fig. 3), in which planar triphenyltin units involving Sn(2) are linked *via* C(5) : O(3). Sn(2) is occupying an almost regular trigonal bipyramidal geometry, where the average C–Sn–C bond

Table 6

Selected bond lengths (Å) and bond angles (deg) in **5** with e.s.d.s in parentheses

Sn(1)-O(1)	2.089(4)	O(1)-Sn(1)-C(11)	118.4(2)
Sn(1)-C(11)	2.129(5)	O(1)-Sn(1)-C(21)	105.7(2)
Sn(1)-C(21)	2.124(6)	O(1)-Sn(1)-C(31)	93.9(2)
Sn(1)-C(31)	2.135(6)	C(11)-Sn(1)-C(21)	119.3(2)
Sn(2)-O(4)	2.193(3)	C(11)-Sn(1)-C(31)	105.2(2)
Sn(2)...O(3′)	2.397(3)	C(21)-Sn(1)-C(31)	111.3(2)
Sn(2)-C(41)	2.117(5)	O(4)-Sn(2)-C(41)	87.2(2)
Sn(2)-C(51)	2.123(5)	O(4)-Sn(2)-C(51)	95.9(2)
Sn(2)-C(61)	2.122(5)	O(4)-Sn(2)-C(61)	92.8(2)
O(1)-O(2)	2.178(5)	C(41)-Sn(2)-C(51)	115.3(2)
O(1)-C(1)	1.287(6)	C(41)-Sn(2)-C(61)	120.7(2)
O(2)-C(1)	1.231(6)	C(51)-Sn(2)-C(61)	123.6(2)
O(3)-C(5)	1.244(6)	O(3′)-Sn(2)-O(4)	170.4(1)
O(4)-C(5)	1.274(5)	O(3′)-Sn(2)-C(41)	83.2(1)
C(1)-C(2)	1.481(7)	O(3′)-Sn(2)-C(51)	88.0(2)
C(2)-C(3)	1.315(7)	O(3′)-Sn(2)-C(61)	92.4(1)
C(2)-C(4)	1.484(9)	Sn(2′)-O(3)-C(5)	132.1(3)
C(3)-C(5)	1.500(7)	Sn(1)-O(1)-O(2)	72.8(2)
		Sn(1)-O(1)-C(1)	102.2(3)
		Sn(2)-O(4)-C(5)	134.2(3)
		O(1)-C(1)-O(2)	119.7(5)
		O(1)-C(1)-C(2)	118.0(4)
		O(2)-C(1)-C(2)	122.2(5)
		C(1)-C(2)-C(3)	121.1(5)
		C(1)-C(2)-C(4)	118.7(5)
		C(3)-C(2)-C(4)	120.2(5)
		C(2)-C(3)-C(5)	127.1(5)
		O(3)-C(5)-O(4)	125.6(4)
		O(3)-C(5)-C(3)	120.0(4)
		O(4)-C(5)-C(3)	114.3(4)

angle is 119.9° and the average C–Sn–O(4) and C–Sn–O(3) angles are 92.0° and 87.9°, respectively. In contrast to this, the carbonyl group, C(1):O(2), is impeded by one of the phenyl groups [phenyl(1)] and this prevents its association with a tin atom of a neighbouring molecule. Sn(1) occupies an almost regular tetrahedral stereochemistry, with the average angle around the tin atom being 109.0°, and is located on a side-arm roughly perpendicular to the direction of the polymer chain (Fig. 3).

The two acid groups are oriented with respect to the plane including the C(2):C(3) double bond, such that one is approximately perpendicular to the skeletal plane and the other approximately parallel. The dihedral angle for the parallel relationship is 0.8° and that for the perpendicular relationship 86.7°; the dihedral angle between the two acid group planes is 87.1°. The Sn(2)–O(4) bond length of 2.193(3) Å is significantly longer than the equivalent Sn(1)–O(1) bond length of 2.089(4) Å and this may be related to the higher coordination number of Sn(2).

Comparison of 2 with 5

In structure **2**, the acid group nearest to the substituted carbon is perpendicular to the skeletal plane whilst, in **5**, that acid group is approximately parallel to the

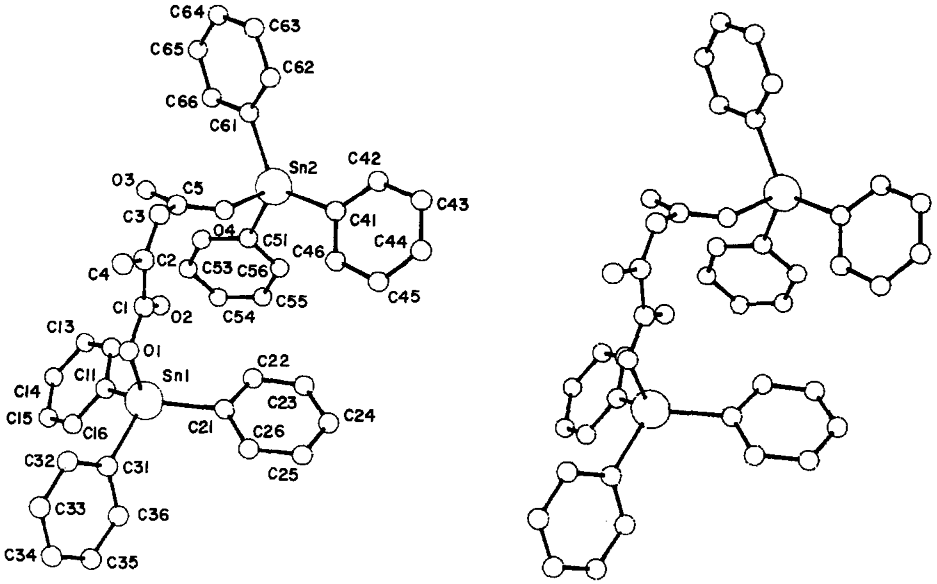


Fig. 2. Stereo-drawing of molecule 5, showing atom numbering and viewed to give minimum overlap of atoms.

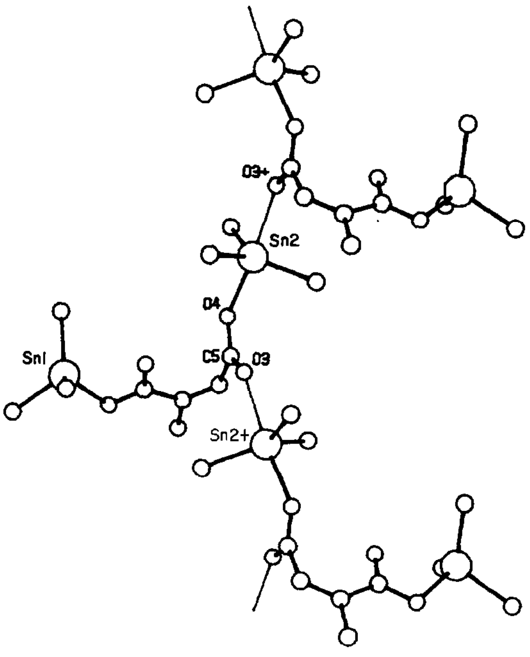
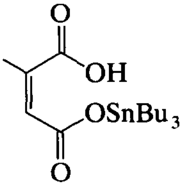


Fig. 3. View down the x-axis of a fragment of the polymeric chain of 5 (+ signs indicate atoms of adjacent molecules).

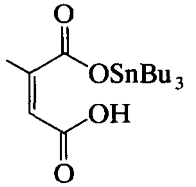
skeletal plane. The difference may arise from the need to have the substituted phenyl plane approximately parallel to the skeletal plane, which would require rotation of the adjacent acid plane out of the skeletal plane. The arrangement in **5** is similar to that in the amic reported by us previously [19].

Tributyltin monoester of citraconic acid

Very few studies have been carried out on the organotin monoesters of dibasic acids. Kochkin and co-workers reported the synthesis of monotriethylstannyl and monotributylstannyl esters of citraconic and itaconic acids [9]. In the present work, the tributylstannyl half ester of citraconic acid (**18**) has been prepared by the reaction of 2 mol of the carboxylic acid with 1 mol of bis(tributyltin) oxide, in ethyl acetate, as a white air-stable powder. Kochkin assigned this compound structure **18a**, although no supporting spectroscopic or X-ray data were given [9].



(**18a**)



(**18b**)

In the solid state, the monoester shows a well resolved Mössbauer doublet with $\delta = 1.50$, $\Delta E_Q = 3.94$ mm s^{-1} and a $\nu_{as}(CO)$ IR band at 1570 cm^{-1}, indicative of a pentacoordinate carboxyl-bridged polymer. Recent X-ray studies have shown [20] that the trimethylstannyl half ester of glutamic acid, $Me_3SnO \cdot CO \cdot CH(NH_3^+)CH_2CH_2CO_2^-$, is a helical chain polymer with trigonal bipyramidal tin atoms and bridging carboxylate groups. The ^{119}Sn NMR spectrum of **18**, as a dilute solution in CCl_4, showed a sharp singlet at +20.1 ppm, which is *ca.* 70 ppm upfield of that in the diester **4**. In order to distinguish between the two possible isomers, **18a** and **18b**, the ^{13}C NMR spectra, as concentrated solutions in toluene, of **18** and **4** have been compared. Two well separated carboxyl resonance signals were observed in the diester, at +174.4 ppm and +170.8 ppm, the latter peak being assigned to the carboxyl group adjacent to the electron donating methyl substituent. In contrast to **4**, the half ester displays two closely separated carboxyl singlets at +172.0 ppm and +171.6 ppm, the higher field resonance again being assigned to the more shielded carboxylic group. It is therefore reasonable to conclude that, since the higher field signals in **4** and **18** have not shifted significantly, the carboxyl moiety adjacent to the methyl group is always attached to a tributylstannyl radical, suggesting structure **18b** for the half ester.

Further studies on these organotin half esters are under way and will be reported at a later date.

Acknowledgments

The International Tin Research Institute, Uxbridge, is thanked for permission to publish this paper. We are grateful to Dr. C.K. Yap, formerly of the Forest Research Institute Malaysia, Kuala Lumpur, for assistance with recording the

Mössbauer spectra, Mrs. B.C. Patel, ITRI, for the NMR spectra, and Drs. G.A. Webb and R. Bolton, University of Surrey, for helpful comments.

References

1 E.R.T. Tiekink, Appl. Organomet. Chem., 5 (1991) 1.
2 A.G. Davies and P.J. Smith, in G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Pergamon, Oxford, 1982, p. 519.
3 A.S. Mufti and R.C. Poller, J. Chem. Soc. C, (1967) 1362.
4 U. Schubert, J. Organomet. Chem., 155 (1978) 285.
5 A. Glowacki, F. Huber and H. Preut, Recl. Trav. Chim. Pays-Bas, 107 (1988) 278.
6 S.W. Ng., V.G. Kumar Das, M.B. Hossain, F. Goerlitz and D. van der Helm, J. Organomet. Chem., 390 (1990) 19.
7 V.I. Shcherbakov, I.P. Malysheva, O.N. Druzhkova and T.N. Chulkova, J. Organomet. Chem., 407 (1991) 181.
8 R.K. Hill, J. Am. Chem. Soc., 83 (1961) 4745.
9 D.A. Kochkin and M.M. Koton, J. Gen. Chem. USSR, 43 (1973) 2709.
10 P. Dunn and T. Norris, Australian Defence Stand. Labs., Report No. 269 1964.
11 G.M. Sheldrick, SHELX-76, Programme for Crystal Structure Determination, University of Cambridge, 1976.
12 B.A. Frenz and Associates, Enraf–Nonius Structure Determination Package, SDP Users Guide, version 1.1a, Delft, 1983.
13 R.C.G. Killean and J.L. Lawrence, Acta Crystallogr. Sect. B, 25 (1969) 1750.
14 S.C. Abraham, Acta Crystallogr., Sect. B 30 (1974) 261.
15 N. Walker and D. Stuart, Acta Crystallogr., Sect. A, 39 (1983) 158.
16 D.W. Allen, J.S. Brooks, R. Formstone, A.J. Crowe and P.J. Smith, J. Organomet. Chem., 156 (1978) 359.
17 D.W. Allen, J.S. Brooks, S. Bailey and B.F. Taylor, Appl. Organomet. Chem., 1 (1987) 393.
18 P.B.D. de la Mare, E.A. Johnson and J.S. Lomas, J. Chem. Soc., (1964) 5317.
19 A. Samuel-Lewis, P.J. Smith, J.H. Aupers and D.C. Povey, J. Organomet. Chem., 402 (1991) 319.
20 F. Huber, B. Mundus-Glowacki and H. Preut, J. Organomet. Chem., 365 (1989) 111.