Crystal Structure of Trichloroacetatotrivinyltin and Mössbauer Spectroscopic Characterization of Trivinyl- and Divinyl-n-butyltin Carboxylates

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The structure of the title compound has been determined by *X*-ray analysis. It consists of $Sn(CH{=}CH_2)_3(O_2CCCl_3)$ units linked by *syn–anti* trichloroacetate bridges giving five-co-ordinate tin atoms. The compound crystallizes in space group *I*2/*a* with a = 16.686(9), b = 10.267(6), c = 15.866(9) Å, β = 107.08(8), and Z = 8. A comparison of these structural data with those available for $SnMe_3(O_2CMe)$, $SnMe_3(O_2CCF_3)$, and $Sn(CH_2Ph)_3(O_2CMe)$ reveals that distortions of the SnC_3 group and the asymmetry of the two Sn–O distances are in the order benzyl > vinyl > methyl. The influence of the vinyl groups around the tin atom has also been examined by Mössbauer spectroscopy. The Mössbauer parameters of two series of compounds, $Sn(CH{=}CH_2)_3(O_2CR')$ and $SnBu(CH{=}CH_2)_2(O_2CR')$ (R' = Me, CH_2Br, CH_2Cl, $CHCl_2$, CCl_3, or CF_3), have been determined. The quadrupole-splitting data, compared with those available for other series of organotin carboxylates having a trigonal-bipyramidal geometry, are consistent with the structural information. These values decrease with increasing distortion and asymmetry of the lattice.

THE organic R groups around the tin atom in triorganotin carboxylates $SnR_3(O_2CR')$ (R' = Me or halogenomethyl) have a profound influence on their structures. A *trans*-trigonal-bipyramidal structure with quasi-planar SnC_3 groups is exhibited by the two trimethyltin derivatives $SnMe_3(O_2CMe)$ and $SnMe_3(O_2CCF_3)$.[1] Greater distortions of this geometry occur in the case of $Sn(CH_2Ph)_3(O_2CMe)$,[2] whereas bulky organic groups lead to a distorted tetrahedral geometry in tricyclohexyltin acetate.[3] Vinyl groups seem to affect the planarity of the SnC_3 moiety, as evidenced by the i.r. pattern of the Sn–C region which does not change on passing from the solid to the solution where the trivinyltin carboxylates are found monomers.[4–8] On the other hand, no crystal structure of a trivinyltin derivative is available in order to specify the configuration of the SnC_3 group.

In this study an *X*-ray analysis has been carried out on $Sn(CH{=}CH_2)_3(O_2CCCl_3)$. The stereochemistry at tin in this class of compound has been examined by Mössbauer spectroscopy of the two series $Sn(CH_2{=}CH)_3(O_2CR')$ and $SnBu(CH{=}CH_2)_2(O_2CR')$ (R' = Me, CH_2Br, CH_2Cl, $CHCl_2$, CCl_3, or CF_3). The results are compared with those for the corresponding methyltin derivatives [9–11] and are interpreted in the light of the *X*-ray structures.

EXPERIMENTAL

Preparation of the Triorganotin Carboxylates.—n-Butyldivinyltin bromide was prepared by adding bromine (22 g, 137 mmol) with stirring at 20 °C to n-butyltrivinyltin (35 g, 136 mmol) prepared as previously described.[12] Distillation under reduced pressure gave $SnBu(CH{=}CH_2)_2Br$ (37.5 g, 89%) boiling at 89—90 °C (0.8 mmHg).†

Allyltrivinyltin (1) and allyl-n-butyldivinyltin (2) were prepared by treating trivinyltin chloride (32 g, 136 mmol) and $SnBu(CH{=}CH_2)_2Br$ (37 g, 119 mmol) respectively with an excess of allylmagnesium bromide in diethyl ether. Distillation under reduced pressure gave 28 g (85.3%) of compound (1), b.p. 69—71 °C (18 mmHg), and 23 g (71%) of (2), b.p. 73—74 °C (7 mmHg).

Trivinyltin (3) and n-butyldivinyltin carboxylates (4) were prepared by protolysis of the allyl–tin bond.[13] Equimolecular amounts (8—10 mmol) of compound (1) or (2) and the appropriate acid $R'CO_2H$ (R' = Me, CH_2Br, CH_2Cl, $CHCl_2$, CCl_3, or CF_3) were allowed to react under the experimental conditions (see also Table 1) given in the following scheme:

$$(1) + R'CO_2H \xrightarrow{(i)} (3)$$

$$(2) + R'CO_2H \xrightarrow{(ii)} (4)$$

(*i*) Acetone–water (50—100 cm³, 1 : 1 v/v), 30 °C; (*ii*) ethanol (50—100 cm³), under reflux.

After removing the solvent under reduced pressure, the solid residues were crystallized from chloroform–n-hexane to give the carboxylates.

Of the vinyltin derivatives, suitable crystals for *X*-ray analysis were formed by trivinyltin trichloroacetate: colourless crystals were obtained on cooling a hot chloroform solution. Analytical and physical data of the prepared carboxylates are listed in Table 1 together with the carboxyl stretching frequencies recorded in Nujol mulls and in chloroform solution, using a Perkin-Elmer model 457 spectrometer equipped with KBr optics. Molecular weights were determined in chloroform with a Mechrolab model 302B vapour-phase osmometer. The data for some representative compounds are given in Table 2.

Trivinyltin Trichloroacetate.—*Crystal and intensity data.* $C_8H_9Cl_3O_2Sn$, M = 362.2, Monoclinic, a = 16.686(9), b = 10.267(6), c = 15.866(9) Å, β = 107.08(8)°, U = 2 598.2 Å³, D_m = 1.87 (by flotation in a 1,2-dibromoethane–1,4-dibromobutane), Z = 8, D_c = 1.85 g cm⁻³, $F(000)$ = 1 392, λ(Mo-K_α) = 0.710 7 Å, μ(Mo-K_α) = 25.6 cm⁻¹, space group *I*2/*a* (a non-standard orientation of *C*2/*c*) from systematic absences *hkl* for $h + k + l$ odd and *h*0*l* for $h(l)$ odd with equivalent positions $(0,0,0;\ \tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2}) \pm (x,y,z;\ \tfrac{1}{2}+x,\ -y,\ z)$. A centric space group was assumed on the basis of intensity tests, and was shown to be correct by the successful refinement of the structure.

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† Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

TABLE 1

Preparation of trivinyl- [a] and butyldivinyl-tin [b] carboxylates: analytical and physical data [c]

Compound	M.p. (θ_c/°C)	Analysis (%) [d] C	H	Cl	Br	F	$\nu_{asym}(CO_2)$ (cm^{-1}) in Nujol	in $CHCl_3$
$Sn(CH=CH_2)_3(O_2CMe)$	160—161 [e]						1 565, 1 540	1 645,[f] 1 618
$Sn(CH=CH_2)_3(O_2CCH_2Br)$ [g]	117—118	28.5	3.2		23.7		1 590, 1 550	
		(28.4)	(3.3)		(23.6)			
$Sn(CH=CH_2)_3(O_2CCH_2Cl)$	129—130 [h]						1 595, 1 555	1 670
$Sn(CH=CH_2)_3(O_2CCHCl_2)$ [g]	89—90	29.2	3.1	21.7			1 625	1 680, 1 625 [f]
		(29.3)	(3.1)	(21.6)				
$Sn(CH=CH_2)_3(O_2CCCl_3)$ [g]	127—128	26.3	2.5	29.1			1 650	1 690, 1 665, 1 650 [f]
		(26.5)	(2.5)	(29.3)				
$Sn(CH=CH_2)_3(O_2CCF_3)$	127—128 [i]						1 660	1 710, 1 655 [f]
$SnBu(CH=CH_2)_2(O_2CMe)$ [g]	93—94	41.4	6.4				1 570, 1 545	1 640,[f] 1 615
		(41.5)	(6.3)					
$SnBu(CH=CH_2)_2(O_2CCH_2Br)$ [g]	64—65	32.7	4.6		21.6		1 585, 1 555	
		(32.6)	(4.7)		(21.7)			
$SnBu(CH=CH_2)_2(O_2CCH_2Cl)$ [g]	77—78	37.1	5.4	11.1			1 590, 1 560	1 670
		(37.1)	(5.3)	(11.0)				
$SnBu(CH=CH_2)_2(O_2CCHCl_2)$ [g]	49—50	33.3	4.3	19.9			1 655	
		(33.5)	(4.5)	(19.8)				
$SnBu(CH=CH_2)_2(O_2CCCl_3)$ [g]	78—79	30.7	3.8	27.2			1 655	
		(30.6)	(3.8)	(27.1)				
$SnBu(CH=CH_3)_2(O_2CCF_3)$ [g]	64-65	34.9	4.3			16.7	1 670	1 715, 1 655 [f]
		(35.0)	(4.4)			(16.6)		

[a] Time of reaction: 110—150 h for R′ = Me, CH_2Br, or CH_2Cl_2, 50 h for CCl_3, and 20 h for CF_3. [b] Time of reaction; 20 h for all compounds. [c] Yields are in the range 70—95%. For the divinylbutyltin acetate the yield is very low (20%). [d] Calculated values are given in parentheses. [e] Lit.,[4] 161—162 °C. [f] Only band present at infinite dilution. [g] New compound. [h] Lit.,[4] 127—128 °C. [i] Lit.,[4] 127—129 °C.

Preliminary Weissenberg photographs indicated that the compound was highly decomposed in the X-ray beam. In order to collect a sufficient number of reflections, four crystals were mounted on a Philips computer-controlled four-circle diffractometer, equipped with a graphite monochromator. The dimensions of the largest crystal were 0.5 × 0.5 × 0.25 mm, while the other three crystals were smaller (*ca.* 0.25 × 0.25 × 0.12 mm). Accurate lattice and orientation parameters were obtained by least-squares treatment of 25 symmetry-related reflections.

Intensity data were measured by use of the θ—2θ scan method. The intensities of several reflections (3—8, depending on the crystal) monitored after every 60 reflections showed a steady decrease in intensity and the collected data were rescaled according to the equation $I_t = I_0(1 - qt)$. The values of q for the four crystals, deduced from plots of I_t against I_0 for the monitored reflections, are 0.000 30, 0.000 30, 0.000 20, and 0.000 32 min^{-1} respectively. After 480 min the intensities had decreased to nearly 86% of the initial intensity. Since the variation in intensity was not strictly the same for all reflections, each crystal was used for <8 h. Moreover, the intensity decrease was linear only within the first 10 h and then was probably exponential with time. After 10 d of exposure to the X-ray beam the crystals appeared opaque and albuminous, while those not subject to irradiation did not show any deterioration. After 1 year some deterioration in the latter was observed, but this was only superficial and the crystals were still suitable for X-ray work.

TABLE 2

Molecular weights of some triorganotin carboxylates in $CHCl_3$ (37 °C)

Compound	Concentration/ mg cm^{-3}	M Found	Calc.	i [a]
$Sn(CH=CH_2)_3(O_2CMe)$	11.3	349.2	258.8	1.35
	5.6	320.9		1.24
	2.8	311.6		1.20
	1.4	299.5		1.15
		271.3 [b]		1.05
$Sn(CH=CH_2)_3(O_2CCF_3)$	38.0	487.7	312.8	1.56
	19.0	448.3		1.43
	9.5	417.6		1.33
	4.7	383.8		1.23
		381.6 [b]		1.22
$SnBu(CH=CH_2)_2(O_2CMe)$	38.5	300.5	288.9	1.04
	19.2	300.5		1.04
	9.6	300.5		1.04
	4.8	300.5		1.04
		300.5 [b]		1.04
$SnBu(CH=CH_2)_2(O_2CCF_3)$	40.9	456.0	342.9	1.33
	20.4	449.2		1.31
	10.2	452.6		1.32
	5.1	442.3		1.29
		452.6 [b]		1.32

[a] i = Ratio of Found to Calc. values of M. [b] Extrapolated to infinite dilution.

The intensities were corrected for Lorentz and polarization effects and scaled using nearly 100 common reflections. No absorption corrections were made. The data were then scaled to give 2 288 independent F_{hkl} values. Using the criterion $I > 2\sigma(I)$, 403 of these were rejected as not being significantly above background.

Solution and refinement of the structure. The position of the Sn atom was determined from a three-dimensional Patterson synthesis and confirmed by least-squares refinement to R 0.35. A difference electron-density synthesis based upon the Sn signs revealed the positions of all the non-hydrogen atoms. Four cycles of isotropic refinement (with unit weights) then reduced R to 0.11. Anisotropic temperature factors of the form $\exp -[2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + \ldots + 2U_{12}hka^*b^* + \ldots)]$ were assigned to the tin atom and to the three chlorine atoms, and three more cycles of least squares reduced R to 0.058; another cycle gave no further decrease. Thereafter, the weighting scheme used was of the form $w^{-1} = a_i|F_o|^i$ where a_i were calculated using the program PESO.[14,15] Two cycles of refinement converged at R 0.054. At this point a difference-Fourier synthesis clearly indicated that the atoms vibrated anisotropically. Two further cycles with anisotropic temperature factors for all atoms reduced R to 0.046. The four scale factors were then allowed to vary independently, but all the other parameters were fixed (including calculated hydrogen-atom positions), whereupon R decreased to 0.039. A final difference-Fourier map contained some peaks, four of which had densities of 0.5—1.0 e Å^{-3}.

Scattering factors for neutral non-hydrogen atoms were taken from Cromer and Waber,[16] and that of Sn was corrected for the real and imaginary parts of the anomalous dispersion.[17] Final atomic co-ordinates are listed in Table 3, bond lengths and angles in Table 4. Table 5 gives the molecular planes, and the atom-numbering system used and a view of the polymeric chain are given in Figure 1. Observed and calculated structure factors, thermal parameters from the final least-squares cycle, calculated hydrogen co-ordinates, and shortest approaches between polymeric chains are listed in Supplementary Publication No. SUP 22472 (17 pp.).* All computations were carried out on a CDC Cyber 76 computer, using the program of ref. 18.

TABLE 3

Fractional atomic co-ordinates ($\times 10^4$) with standard deviations in parentheses for $Sn(CH=CH_2)_3(O_2CCCl_3)$

Atom	x	y	z
Sn	−219(4)	2 003(5)	2 794(4)
Cl(1)	954(3)	2 089(3)	1 051(3)
Cl(2)	2 263(3)	395(4)	1 990(3)
Cl(3)	1 303(3)	−216(4)	216(3)
O(1)	255(4)	196(6)	2 013(5)
O(2)	762(5)	−1 552(6)	1 538(5)
C(1)	1 264(6)	479(8)	1 210(7)
C(2)	688(6)	−358(8)	1 634(6)
C(3)	−964(8)	2 562(11)	1 533(7)
C(4)	−1 753(10)	2 776(15)	1 353(10)
C(5)	−664(7)	477(9)	3 448(7)
C(6)	−1 009(9)	674(11)	4 055(9)
C(7)	1 031(7)	2 532(10)	3 351(8)
C(8)	1 612(10)	1 820(15)	3 875(9)

TABLE 4

Selected interatomic distances (Å) and angles (°) with standard deviations in parentheses

(*a*) Lengths			
Sn–O(1)	2.49(1)	C(7)–C(8)	1.30(3)
Sn–O(2)	2.17(2)	C(1)–C(2)	1.58(2)
Sn–C(3)	2.10(3)	C(1)–Cl(1)	1.73(2)
Sn–C(5)	2.13(2)	C(1)–Cl(2)	1.76(3)
Sn–C(7)	2.08(3)	C(1)–Cl(3)	1.75(2)
C(3)–C(4)	1.28(3)	C(2)–O(1)	1.21(2)
C(5)–C(6)	1.28(3)	C(2)–O(2)	1.25(2)
(*b*) Angles			
O(1)–Sn–O(2^{I})	173.4(3)	Sn–C(5)–C(6)	123.4(8)
C(3)–Sn–C(5)	118.1(5)	Sn–C(7)–C(8)	126.1(10)
C(3)–Sn–C(7)	124.8(5)	O(1)–C(2)–O(2)	128.2(10)
C(5)–Sn–C(7)	115.7(5)	O(1)–C(2)–C(1)	118.9(8)
O(1)–Sn–C(3)	85.1(4)	O(2)–C(2)–C(1)	112.9(10)
O(1)–Sn–C(5)	84.3(4)	C(2)–O(1)–Sn	157.4(7)
O(1)–Sn–C(7)	88.9(4)	C(2)–O(2)–Sn^{II}	122.8(8)
O(2^{I})–Sn–C(3)	93.6(4)	Cl(1)–C(1)–C(2)	112.9(8)
O(2^{I})–Sn–C(5)	90.6(4)	Cl(2)–C(1)–C(2)	104.0(7)
O(2^{I})–Sn–C(7)	97.1(4)	Cl(3)–C(1)–C(2)	110.5(7)
Sn–C(3)–C(4)	122.7(11)		

Atom positions derived by transformation of the asymmetric unit (x, y, z) are defined by the superscript Roman numerals: I $-x, \frac{1}{2}+y, \frac{1}{2}-z$; II $-x, -\frac{1}{2}+y, \frac{1}{2}-z$.

TABLE 5

Least-square planes, with, in square brackets, deviations (Å) of the most relevant atoms. The equation of a plane in direct space is given by $Px + Qy + Rz = S$, where x, y, z are the crystallographic non-orthogonalized fractional co-ordinates

Plane (1): C(3), C(5), C(7)

$$-8.480x + 7.439y + 9.428z = 4.169$$

[Sn 0.14, C(4) 0.66, C(6) 1.01, C(8) −0.53]

Plane (2): C(1), C(2), O(1), O(2)

$$8.554x - 0.403y + 10.618z = 2.345$$

[C(1) 0.0, C(2) −0.01, O(1) 0.0, O(2) 0.0, Sn 0.35, Sn^{II} 0.31, Cl(1) −0.50, Cl(2) 1.69, Cl(3) −0.99]

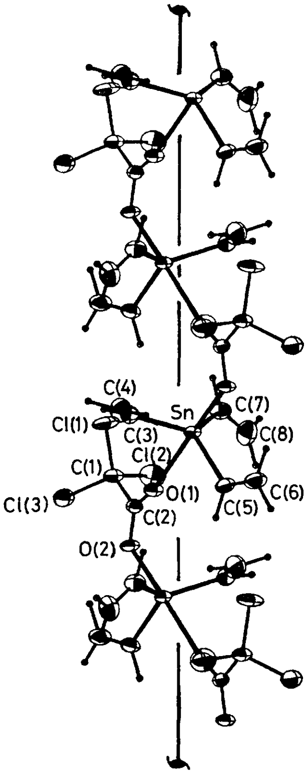

FIGURE 1 Perspective view of one polymeric *syn–anti* trichloroacetate-bridged chain in $Sn(CH=CH_2)_3(O_2CCCl_3)$, developing along the screw axis parallel to b. The drawings were made using the program ORTEP (Johnson, 1970) and the thermal-vibration ellipsoids are scaled to enclose 32% probability; for clarity, hydrogen atoms are artificially reduced

Mössbauer Parameters.—Mössbauer spectra were recorded on a conventional constant-acceleration spectrometer using a 15-mCi $Ca^{119m}SnO_3$ source (Radiochemical Centre, Amersham) at room temperature. The velocity scale was calibrated by means of the spectrum of an enriched iron foil. The isomer-shift values are reported relative to SnO_2 at room temperature. Absorption envelopes were fitted to two lorentzian lineshapes by an iterative squares program [19] adapted for use with a CDC Cyber 76 computer. The data are accurate to ± 0.03 mm s^{-1}. The computed full width ranges from 1.00 to 1.30 mm s^{-1}. In no case was a detectable Mössbauer effect observed at room temperature. All the spectra consist of simple quadrupole-split doublets showing that there is only one kind of tin environment. Table 6 lists the Mössbauer isomer shifts (δ) and the quadrupole splittings (Δ) together with the Herber ρ values [20] for both the examined series of organotin carboxylates. Calculated

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

Δ and η parameters shown in the Table were obtained from the point-charge model (see below).

TABLE 6

Mössbauer data (80 K) for $SnR_3(O_2CR')$ compounds

R_3	R'	$\delta^{a,b}$,	$\Delta_{obs.}{}^{a}$	$\Delta_{calc.}$	η	ρ
		mm s^{-1}				
$(CH=CH_2)_3$	Me	1.25	3.60	−3.24	0	2.88
	CH_2Br	1.27	3.65	−3.46	0	2.87
	CH_2Cl	1.28	3.66	−3.46	0	2.86
	$CHCl_2$	1.30	3.72	−3.64	0	2.86
	CCl_3	1.32	3.77	−3.70	0	2.85
	CF_3	1.36	3.84	−3.78	0	2.82
$Bu(CH=CH_2)_2$	Me	1.30	3.43	−3.40	0.13	2.63
	CH_2Br	1.30	3.48	−3.62	0.12	2.67
	CH_2Cl	1.32	3.52	−3.62	0.12	2.66
	$CHCl_2$	1.34	3.55	−3.80	0.12	2.65
	CCl_3	1.34	3.56	−3.86	0.12	2.65
	CF_3	1.41	3.60	−3.94	0.11	2.55

[a] ± 0.03 mm s^{-1}. [b] Relative to SnO_2.

DISCUSSION

Structure of Trivinyltin Trichloroacetate.—The crystal structure (Figure 1) consists of $Sn(CH=CH_2)_3(O_2CCCl_3)$ units linked by *syn–anti* trichloroacetate bridges, giving five-co-ordinate tin atoms in approximately D_{3h} geometry. Chains are possible because the carboxyl group has the *syn–anti* conformation:[21] the C(2)–O(1)–Sn angle is 157.4°(7) while C(2)–O(2)–Sn^{II} is 122.8°(8); moreover, the Sn atom is out of the trichloroacetate plane by 0.35 Å, while Sn^{II} is out by 0.31 Å (see Table 5). Similar *syn–anti* bridges are also observed for the analogous organotin carboxylates $SnMe_3(O_2CMe)$, $SnMe_3(O_2CCF_3)$, and $Sn(CH_2Ph)_3(O_2CMe)$.[1,2] The co-ordination of tin atom is distorted trigonal bipyramidal: each tin atom is surrounded by two axial oxygen atoms of two O_2CCl_3 groups and by the equatorial carbon atoms of the vinyl groups. The two Sn–O bond lengths are 2.17(2) and 2.49(2) Å and are related to C(2)–O(2) [1.25(2) Å] and C(2)–O(1) [1.21(2) Å]. This asymmetry is typical of these compounds and increases with decreasing pK_a of the acid $R'CO_2H$.[1,9] The long Sn–O bond (2.49 Å) is associated with the *anti*-oxygen while the shorter bond (2.17 Å) is associated with the *syn*-oxygen.* The three Sn–C lengths [2.10(2), 2.13(2), and 2.08(3) Å] are in good agreement with those found in quinolin-8-olato(trifluoroacetato)divinyltin [22] (mean Sn–C 2.10 ± 0.024 Å).

The distances in the vinyl groups are all <1.33 Å, the value of a C=C double bond, probably due to their thermal motion; this precludes any discussion of the dimensions of these groups. The thermal motion of this molecule is relatively high and may be due to the decomposition of the sample or to a too large correction for the crystal decay; moreover, the thermal activity of atoms in the outer part of the molecule is due to the fact that there is little interaction between individual polymeric chains, there being no opportunity for hydrogen bonding. Similar contacts and thermal motion are observed for the other polymeric organotin carboxylates.

Distortion in the trans-*trigonal-bipyramidal* SnR_3O_2 *moiety.* The five-co-ordinate tin carboxylates of the type $SnR_3(O_2CR')$ possess a trigonal-bipyramidal structure distorted to different degrees. Figure 2 shows the geometry around the carboxyl groups in these compounds: the long Sn–O bond is always associated with the *anti*-oxygen, and there seems to be a relationship between the Sn–*anti*-O–C angle and the Sn–*anti*-O bond length, except for tribenzyltin acetate where the Sn–O bond is exceptionally long probably due to steric effects of the fairly bulky benzyl groups.

The distortion was evaluated by performing the test of Muetterties and Guggenberger,[23] forcing the Sn–L distances to be 1 Å but preserving the values of the bond angles at tin. (For a discussion of the need for this modification see ref. 24.) The calculated *e* and *a* angles together with those of the D_{3h} trigonal bipyramid and C_{4v} square pyramid ($\theta = 102°$) are shown in Table 7. The departure from D_{3h} geometry is due to the different distances of approach of the oxygens to the Sn atom (*e.g.* the asymmetry of the two Sn–O bonds); the O–Sn–C angles associated with the short Sn–O bond are all $>90°$, while those associated with the long Sn–O bond are all $<90°$ (see Table 4). Consequently, the nature of the distortions in this class of compounds may be determined using the method of Burgi and Dunitz.[25] The test above [23] shows that $SnMe_3(O_2CMe)$ and $SnMe_3(O_2CCF_3)$ are approximate to D_{3h} symmetry; nevertheless C_{2v} symmetry is also maintained at Sn, since the Sn, O(1), O(2), and C(2) atoms are in the mirror plane, and the SnC_3 moiety is almost planar.

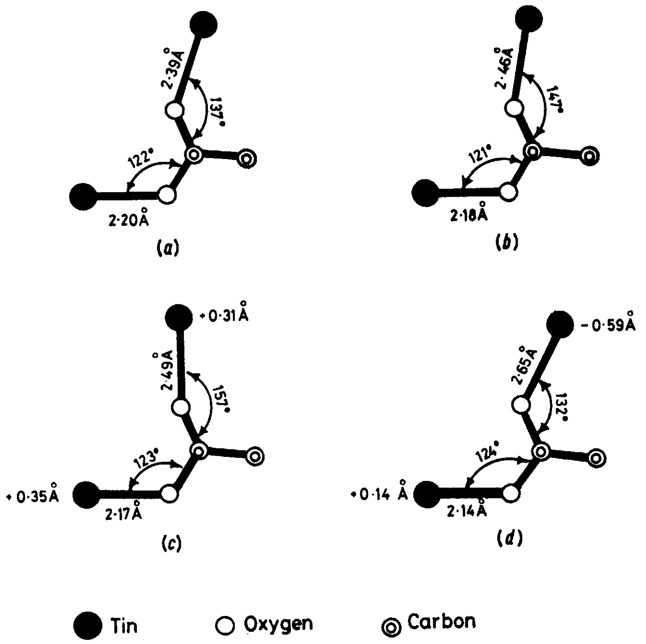

FIGURE 2 *syn–anti* configuration of the carboxylate group in the compounds $SnMe_3(O_2CMe)$ (*a*), $SnMe_3(O_2CCF_3)$ (*b*), $Sn(CH=CH_2)_3(O_2CCCl_3)$ (*c*), and $Sn(CH_2Ph)_3(O_2CMe)$ (*d*). For (*c*) and (*d*) the deviations of the tin atoms from the carboxylate plane are also indicated; these are zero for (*a*) and (*b*)

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* The *syn*-oxygen is that associated with the Sn-O bond parallel to the acetate C–C bond.

TABLE 7

Calculated *e* and *a* angles, together with those for the D_{3h} trigonal bipyramid and C_{4v} square pyramid (refs. 23 and 24)

	e/°			a/°					
Compound	e_1	e_2	e_3	a_1	a_2	a_3	a_4	a_5	a_6
D_{3h} trigonal bipyramid	53.1	53.1	53.1	101.5	101.5	101.5	101.5	101.5	101.5
C_{4v} square pyramid ($\theta = 102°$)	75.7	75.7	0.0	119.8	75.7	119.8	119.8	75.7	119.8
SnMe$_3$(O$_2$CMe)	50.5	50.5	58.4	99.9	101.0	99.9	102.2	103.6	102.2
SnMe$_3$(O$_2$CCF$_3$)	52.1	52.1	55.2	100.3	99.9	100.3	103.1	102.2	103.1
Sn(CH=CH$_2$)$_3$(O$_2$CCCl$_3$)	53.6	56.6	49.2	102.3	99.0	97.6	105.6	102.6	101.9
(with crystallographic co-ordinates)	49.2	51.9	44.6	107.0	103.5	102.9	106.2	103.0	103.0
Sn(CH$_2$Ph)$_3$(O$_2$CMe)	64.1	55.4	39.7	109.1	90.1	102.2	109.3	101.1	98.6

Tribenzyltin acetate is the most distorted of these compounds, but the reduction of the angle e_3 and the increase of angles e_1 and e_2 with respect to 53.1° show that the distortion is towards C_{4v}; moreover, C_{2v} symmetry is not maintained (this demands that $e_1 = e_2$, $a_2 = a_5$, and $a_1 = a_3 = a_4 = a_6$).

Trivinyltin trichloroacetate is also distorted away from D_{3h} geometry towards C_{4v}, as can be seen from the fact that angle $e_3 < 53.1°$ and e_1 and $e_2 > 53.1°$. However, C_{2v} symmetry is approximately maintained in the Sn–O(1)–O(2$^{\text{I}}$)–C(7) * plane: $\chi^2 = 3.56$ with three degrees of freedom, whereas the Sn–O(1)–O(2$^{\text{I}}$)–C(3) and Sn–O(1)–O(2$^{\text{I}}$)–C(5) planes have $\chi^2 = 21.66$ and 9.47 respectively; this is also supported by the angles *a*.

The extent of asymmetry (as measured by the difference between the two Sn–O distances [1,9] and departure from planarity of the SnC$_3$ group) also follows the same sequence, *i.e.* methyl < vinyl < benzyl (Table 8).

TABLE 8

Structural distortions of the *trans*-trigonal bipyramid for SnR$_3$(O$_2$CR′) compounds

Compound	Asymmetry (Å)	Displacement (Å) of tin out of the ideal SnC$_3$ plane
SnMe$_3$(O$_2$CMe)	0.186	0.09
SnMe$_3$(O$_2$CCF$_3$]	0.281	0.10
Sn(CH=CH$_2$)$_3$(O$_2$CCCl$_3$)	0.320	0.14
Sn(CH$_2$Ph)$_3$(O$_2$CMe)	0.510	0.21

The distortion of the trivinyltin carboxylates is also supported by the i.r. spectra in the Sn–C region, both in the solid state and in chloroform solution.[4]

It is interesting to note that the trivinyl- and divinyl-n-butyltin compounds have similar spectra in chloroform solution. The value of the ν_{asym}(CO$_2$) at very low concentrations is *ca.* 1 640—1 650 cm^{-1} (*cf.* Table 1), typical of a chelated COO configuration.[26,27] Thus, independently of the electron-withdrawing power of the R′ organic group, it seems that the preferred form of the tin carboxylates, at infinite dilution, is a five-co-ordinated monomeric species with bidentate carboxylate.

Influence of the R *and* R′ *Groups on the Mössbauer Parameters.*—To test the geometry of the vinyltin derivatives at the tin atom the point-charge model was employed. The following trigonal-bipyramidal, equatorial, partial quadrupole splittings (p.q.s./mm s^{-1}) were used:[28] CO$_2$Me (0.075), CO$_2$CH$_2$Br and CO$_2$CH$_2$Cl (0.13), CO$_2$CHCl$_2$ (0.175), CO$_2$CCl$_3$ (0.19), and CO$_2$CF$_3$ (0.21). For the Bu$^{\text{n}}$ and CH$_2$=CH ligands the p.q.s. values of alkyl ligands (−0.94) [28,29] and of phenyl (−0.89) [28] were used. Bancroft's relation, $3(\text{p.q.s.})^{\text{t.b.e.}} - 4(\text{p.q.s.})^{\text{t.b.a.}} = 0.58$ mm s^{-1}, equates the p.q.s. values of trigonal-bipyramidal equatorial (t.b.e.) and apical (t.b.a.) configurations.[28]

A FORTRAN program based on the diagonalization of the electric-field gradient (e.f.g.) tensor was used to calculate the Mössbauer parameters. For the equatorial, *mer*, and *cis* geometrical isomers of the Sn(CH=CH$_2$)$_3$(O$_2$CR′) series and for the five geometrical isomers of the SnBu(CH=CH$_2$)$_2$(O$_2$CR′) series, the tolerance-limit criterion indicates an equatorial geometry with two *trans*-oxygen atoms and three equatorial groups for all the compounds, taking ±0.4 mm s^{-1} as satisfactory agreement between measured and calculated quadrupole splittings.[29] For brevity, only the calculated asymmetry parameter (η) and the calculated quadrupole splittings for the equatorial geometrical isomers are reported in Table 6. Within the limits of the point-charge model, a negative sign may be assigned to all the measured Δ values of the vinyl compounds.

Substitution at the R′ group by halide has little effect on the isomer shifts of both series of vinyltins, whose δ values fall in the narrow ranges 1.30 ± 0.06 and 1.34 ± 0.07 mm s^{-1}. Thus, for these series, the *s*-electron density at the tin nucleus is essentially the same despite the change in electronegativity of the R′ groups. This trend has also been observed for SnMe$_3$(O$_2$CR′) [9] (δ 1.39 ± 0.05 mm s^{-1}) and for SnBu$_3$(O$_2$CR′) (δ 1.49 ± 0.13 mm s^{-1}).[10]

The dependence of the quadrupole splitting on the substitution by halide is more significant and an increase is observed on replacing R′ by groups of increasing electron-acceptor ability. This trend may be described by a linear correlation,[11,30] $\Delta = \Delta_0 + p\sigma^*$, between the Δ values and the Taft inductive factor σ^* of the R′ groups. The following values of p are found: 0.072 ± 0.008 and 0.065 ± 0.007 mm s^{-1} for trivinyl- and divinyl-n-butyltins respectively. A comparison of these data with those of the trimethyltin halogenoacetate series [9–11] (p 0.182 ± 0.021 or 0.213 ± 0.010 mm s^{-1}) shows that substitution by halide has a greater influence on the Δ values of the methyl- than on the vinyl-tin derivatives. As a consequence, it may be concluded that in the case of the trimethyltin halogenoacetates the electronic effects of the R′ groups greatly increase the asymmetry (*cf.* Table 8) and consequently the Δ values on passing from the acetate to the other homologues.

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* The O(2$^{\text{I}}$) atom is that bonded to tin at 2.17 Å and then normalized.

On the other hand, in the trivinyltin series, the electronic contribution of the R′ groups to the asymmetry should be less pronounced. Due to this fact substitution by halide operates in a more distorted lattice structure. Thus, as previously reported,[11,30] the parameter assumes a value which may take into account the structural features.

These conclusions are in agreement with data for compounds of known structure (*cf.* Table 8): thus, (*i*) trivinyltin trichloroacetate exhibits greater distortions than trimethyltin derivatives having R′ = Me and CF_3; (*ii*) the SnC_3 moiety in $Sn(CH{=}CH_2)_3(O_2CCl_3)$ is less planar than that in the trimethyltin compounds; and (*iii*), in terms of asymmetry, the vinyl group results in a greater degree of distortion of the *trans*-trigonal-bipyramidal structure than methyl and both less than that of benzyl. It is suggested that the Δ values of the tribenzyltin halogenoacetates should not be much different from that of the acetate ($\Delta = 3.15$ mm s^{-1}) [31] since the asymmetry in this compound [2] is very high (0.51 Å) and will not be influenced greatly by halide substitution.

We thank Dr. A. Zanotti for access to the Philips diffractometer, and the C.N.R., Rome, for support.

[8/1350 *Received*, 20*th July*, 1978]

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