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X-RAY CRYSTAL ANALYSIS OF TRICYCLOHEXYLTIN TRIFLUOROACETATE AND MÖSSBAUER DATA FOR (cyclo-$C_6H_{11})_3SnO_2CR'$ ($R' = CH_3, CH_2Cl, CHCl_2, CCl_3$ AND CF_3)

SANDRO CALOGERO,

Laboratorio di Chimica e Tecnologia dei Radioelementi del CNR, Corso Stati Uniti, Padova (Italy)

PAOLO GANIS,

Istituto Chimico, Universita' di Napoli, Via Mezzocannone, 4, Napoli (Italy)

VALERIO PERUZZO and GIUSEPPE TAGLIAVINI *

Istituto di Chimica Analitica, Universita' di Padova, Via Marzolo 1, Padova (Italy)

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Summary

The halogenocarboxylates (cyclo-$C_6H_{11})_3SnO_2CR'$, ($R' = CH_3, CH_2Cl, CHCl_2, CCl_3$ and CF_3) have been prepared, and characterized by Mössbauer and IR spectroscopy. The crystal structure of (cyclo-$C_6H_{11})_3SnO_2CCF_3$ has been determined by X-ray analysis. The crystals are orthorhombic, space group *Pcmn*, with unit cell parameters *a* 14.390 ± 0.004, *b* 13.427 ± 0.004, *c* 11.516 ± 0.003 Å. The structure was resolved by Patterson methods and refined to an *R* value of 0.147. The coordination about the tin atom can be considered distorted trigonal-pyramidal or distorted tetrahedral. Mössbauer data are explained in terms of distortions of bond angles about the tin atom.

Introduction

Recently we have undertaken systematic studies on organotin carboxylates by means of Mössbauer spectroscopy and X-ray crystal analysis. The following compounds have been studied: $[R_2SnO_2CR']_2O$ and $R_2Sn(O_2CR')OSn(OH)R_2$ [1,2] (R = n-Bu, $CH_2{=}CH$, $CH_2CH{=}CH_2$), $(CH_2{=}CH)_3SnO_2CR'$ and $(CH_2{=}CH)_2(n\text{-}C_4H_9)SnO_2CR'$ ($R = CH_3, CH_2Cl, CHCl_2, CCl_3, CF_3$) [3] and (cyclo-$C_6H_{11})_3$-SnCl [4]. We noted that the crystal data of some tricyclohexyltin derivatives [4,5] do not agree well with the structure assigned on the basis of the Mössbauer quadrupole splitting values [6]. The bulky cyclohexyl groups substanti-

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* To whom inquiries should be directed.

ally modify the general structural pattern of compounds of the R_3SnO_2CR' type, which usually have polymeric structures involving five-coordinated tin atoms [7—10].

Thus we decided to carry out Mössbauer spectroscopic studies on the series of tricyclohexyltin halocarboxylates (cyclo-$C_6H_{11})_3SnO_2CR'$ with $R' = CH_3$, CH_2Cl, $CHCl_2$, CCl_3 and CF_3, and to carry out an X-ray analysis of the trifluoroacetate derivative, so that the results could be compared with those for the corresponding acetate [5].

Experimental

Tricyclohexyltin carboxylates

By the method previously described for the acetate [11], tricyclohexyltin carboxylates were prepared by heating (110—150° C) tricyclohexyltin hydroxide and the appropriate acid in a 1/1 molar ratio. Analytical and physical data for the carboxylates are listed in Table 1, together with the COO asymetric stretching frequencies recorded on Nujol mulls or chloroform solutions, using a Perkin-Elmer Model 457 spectrophotometer equipped with KBr optics.

Molecular weights were determined in chloroform with a Mechrolab Model 302 B Vapour Phase Osmometer; and all the compounds were found to be monomeric in that solvent. For the acetate and trifluoroacetate, results at various concentrations are given in Table 2.

IR data for the chloroform solutions indicate that the only band present at very high dilution is centered in the range 1640—1655 cm^{-1} (cf. Table 1).

Mössbauer data

The Mössbauer spectra were recorded on a conventional constant acceleration spectrometer using a 15 mCi Ca $^{119}SnO_3$ source and were fitted by an iterative least squares program. In no case was a detectable Mössbauer effect

TABLE 1

ANALYTICAL AND PHYSICAL DATA FOR (cyclo-$C_6H_{11})_3SnO_2CR$ [a]

R'	M.P. (°C)	Analysis found (calc)(%)				$\nu_a(COO)(cm^{-1})$	
		C	H	Cl	F	in Nujol	in $CHCl_3$
CH_3	63— 64 [c]					1640	1640 [d]
CH_2Cl [b]	102—103	52.00 (52.03)	7.80 (7.64)	7.77 (7.67)		1675	1655 [d]
$CHCl_2$ [b]	138—139	48.39 (48.42)	6.85 (6.90)	14.31 (14.29)		1690, 1655	
CCl_3 [b]	113—115	45.85 (45.79)	6.40 (6.34)	19.23 (19.13)		1650	
CF_3 [b]	116—117	49.84 (49.92)	6.85 (6.91)		11.90 (11.84)	1690	1715, 1655 [d]

[a] Yields are in the range 70—95%. [b] New compound. [c] Lit. [11] 61—63. [d] Only band present at infinite dilution.

TABLE 2

MOLECULAR WEIGHTS OF THE TRICYCLOHEXYLTIN ACETATE AND TRIFLUOROACETATE (37°C)

Compound (Mol. wt. calcd.)	Concn. (mg/ml)	Mol. wt. found	i [a]
(cyclo-$C_6H_{11})_3SnO_2CCH_3$ (427.19)	30.20	474.1	1.11
	15.10	414.3	0.97
	7.55	414.3	0.97
	3.77	418.6	0.98
		427.2 [b]	1.00
(cyclo-$C_6H_{11})_3SnO_2CCF_3$ (481.16)	39.87	485.9	1.01
	19.94	485.9	1.01
	9.97	471.5	0.98
	4.98	471.5	0.98
		471.5 [b]	0.98

[a] i = Mol. wt. found/Mol. wt. calcd. [b] Extrapolated value (concn. → 0).

observed at room temperature. Mössbauer parameters, isomer shifts (δ), and quadrupole splittings (Δ) at liquid nitrogen temperature are listed in Table 3.

Structure analysis of (*cyclo*-$C_6H_{11})_3SnO_2CCF_3$

The structure of (cyclo-$C_6H_{11})_3SnO_2CCF_3$ was elucidated by a three-dimensional X-ray structural analysis. The intensity data were collected at 25°C on a Philips PW 1100 computer-controlled four-circle diffractometer with graphite monocromator; the $\theta - 2\theta$ scan method was used. Since the compound was found to decompose in the X-ray beam two crystals were used for the collection of intensity data. The intensities dropped to ~10% after half data collection. The structure was refined by eight cycles of full-matrix least-squares assuming isotropic thermal parameters to an R value of 0.17; six more cycles were calculated with anisotropic thermal parameters for Sn and F (owing to the small number of reflections with respect to the atomic parameters to be refined, the calculations with anisotropic thermal parameters for all atoms were not attempted). The final R value is 0.147.

TABLE 3

MÖSSBAUER DATA AT LIQUID NITROGEN TEMPERATURE FOR THE (cyclo-$C_6H_{11})_3SnO_2CR'$ SERIES

R′	δ [a,b] (mm s^{-1})	Δ [a] (mm s^{-1})	Δ [c] (mm s^{-1})	O—Sn—C [d] (°)
CH_3 [e]	1.39	3.33	−2.96	106
CH_2Cl	1.42	3.38	−3.12	107
$CHCl_2$	1.83	3.60	−3.26	107
CCl_3	1.90	3.70	−3.30	106
CF_3	1.97	3.78	−3.36	106

[a] ±0.03 mm s^{-1}. [b] Relative to SnO_2 at room temperature. [c] Predicted by simple point-charge model. [d] Values predicted taking into account distortions in the treatment of the point charge model. [e] Lit. [6, 12] δ = 1.57, Δ = 3.27.

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TABLE 4

CRYSTAL DATA FOR TRICYCLOHEXYLTIN TRIFLUOROACETATE

Molecular formula	$C_{20}H_{33}O_2F_3Sn$
Molecular weight	481.1
Crystal size (mm)	0.2 × 0.3 × 0.9
Space group (confirmed by refinement)	*Pcmn*
Cell constants (25°)	
a (Å)	14.390 ± 0.004
b (Å)	13.427 ± 0.004
c (Å)	11.516 ± 0.003
Unit cell volume (Å^3)	2225.1 ± 0.2
Density (calcd)(g cm^{-3})	1.443 (Z = 4)
Linear absorption coeff. (Mo-K$_\alpha$)(cm^{-1})	11.92
No. of reflections measured	1201
No. of reflections with $I \geqslant 3\sigma(I)$	665
$R = \Sigma[\lvert Fo\rvert - \lvert Fd\rvert]/\Sigma\lvert Fo\rvert$	0.147

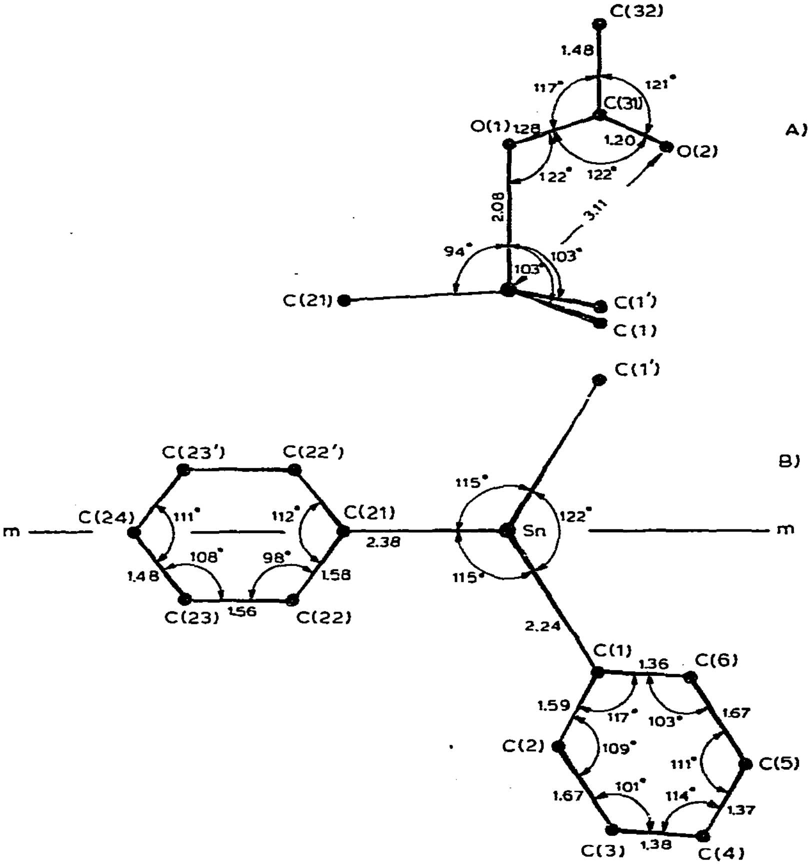

Fig. 1. Some internal conformational parameters of $(\text{cyclo-}C_6H_{11})_3SnO_2CCF_3$.

TABLE 5

FRACTIONAL ATOMIC CO-ORDINATES ($\times 10^4$) AND THERMAL PARAMETERS ($\times 10^3$) [a,b]

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sn	1748(4)	2500	2125(5)	108(4)	51(3)	159(6)	−14(8)	−24(5)	−3(14)
F(1)	9503(114)	3436(111)	5174(132)	151(208)	278(140)	393(192)	32(153)	71(178)	9(136)
F(2)	9966(61)	2230(109)	6024(42)	233(74)	699(324)	50(34)	218(108)	121(43)	34(102)
F(3)	9022(56)	2153(34)	4289(84)	205(71)	62(24)	305(110)	55(36)	−8(70)	21(32)
O(1)	615(31)	2500	3253(39)	112(16)					
O(2)	1475(38)	2500	4801(44)	173(20)					
C(1)	2435(39)	3960(38)	2524(44)	120(18)					
C(2)	1708(42)	4780(43)	2932(52)	148(20)					
C(3)	2281(42)	5765(45)	3456(53)	149(22)					
C(4)	2838(47)	5977(49)	2514(6)	161(25)					
C(5)	3523(60)	5283(69)	2319(76)	240(38)					
C(6)	3087(55)	4247(60)	1740(67)	208(32)					
C(21)	804(46)	2500	427(56)	96(21)					
C(22)	195(36)	3472(37)	541(43)	113(17)					
C(23)	9709(33)	3407(35)	9336(42)	100(16)					
C(24)	9122(48)	2500	9321(57)	95(23)					
C(31)	721(25)	2500	4357(62)	126(29)					
C(32)	986(31)	2500	5066(48)	120(35)					

[a] Estimated standard deviations in parentheses. [b] The anisotropic thermal parameters U_{ij}(Å^2) are in the form $\exp[-2\pi^2(\Sigma_i\Sigma_j h_i h_j a_i a_j U_{ij})]$.

TABLE 6

BOND DISTANCES (Å) AND BOND ANGLES (°) WITH THE ESTIMATED STANDARD DEVIATIONS

Atoms	Bond distances (Å)	Atoms	Bond angles (°)
Sn—C(1)	2.24(4)	C(21)—Sn—C(1)	115(1)
Sn—C(21)	2.38(6)	C(21)—Sn—O(1)	94(2)
Sn—O(1)	2.08(4)	C(1)—Sn—O(1)	103(1)
C(1)—C(2)	1.59(6)	C(1)—Sn—C(1′)	122(2)
C(2)—C(3)	1.67(6)	Sn—C(1)—C(2)	112(3)
C(3)—C(4)	1.38(6)	Sn—C(1)—C(6)	115(4)
C(4)—C(5)	1.37(8)	C(1)—C(2)—C(3)	109(4)
C(5)—C(6)	1.67(9)	C(2)—C(3)—C(4)	100(5)
C(1)—C(6)	1.36(7)	C(3)—C(4)—C(5)	114(6)
C(21)—C(22)	1.58(5)	C(4)—C(5)—C(6)	111(6)
C(22)—C(23)	1.56(5)	C(5)—C(6)—C(1)	103(6)
C(23)—C(24)	1.48(5)	C(6)—C(1)—C(2)	117(5)
C(31)—O(1)	1.28(4)	Sn—C(21)—C(22)	104(3)
C(31)—O(2)	1.20(5)	C(21)—C(22)—C(23)	97(4)
C(31)—C(32)	1.48(5)	C(22)—C(23)—C(24)	108(4)
		C(23)—C(24)—C(23′)	111(4)
		C(22′)—C(21)—C(22)	112(4)
		Sn—O(1)—C(31)	122(2)
		O(1)—C(31)—O(2)	122(3)
		O(1)—C(31)—C(32)	117(2)
		O(2)—C(31)—C(32)	121(2)

The most relevant crystal data are given in Table 4.

Final atomic coordinates and temperature factors are listed in Table 5; bond distances and angles are given in Table 6 and in Fig. 1.

All calculations were carried out on a CDC Cyber 76 computer using the program of ref. 13. Lists of the observed and calculated structure factors are available from the authors on request.

Results and discussion

The salient features of the structure of (cyclo-$C_6H_{11})_3SnO_2CCF_3$, compared with those of the corresponding acetate [5], are:

(i) The structure consists of discrete units of $(C_6H_{11})_3SnO_2CCF_3$ (cf. Fig. 2). The coordination number is best considered to be four: O(2) is at 3.11 Å from Sn (cf. Fig. 1). In the acetate the corresponding Sn···O distance is 2.85 Å, and was assumed to indicate a weak chelation [8].

(ii) The bond angles around the tin atom (see Fig. 1 and Table 7) are, within the standard deviations, very close to those found for the acetate and are equally consistent with a distorted trigonal-pyramidal or a distorted tetrahedral coordination at tin. It is interesting to compare these values with those for tribenzyltin acetate [14] (see Table 7), where the coordination of tin has been described as trigonal bipyramidal; in this latter case the second apical position is occupied by an oxygen atom 2.65 Å from tin, compared with the 3.70 Å of the present structure (see Fig. 2). In our opinion the bond angles around tin in tribenzyltin acetate are not much different from those found in the tricyclohexyltin acetate and trifluoroacetate (cf. Table 7);

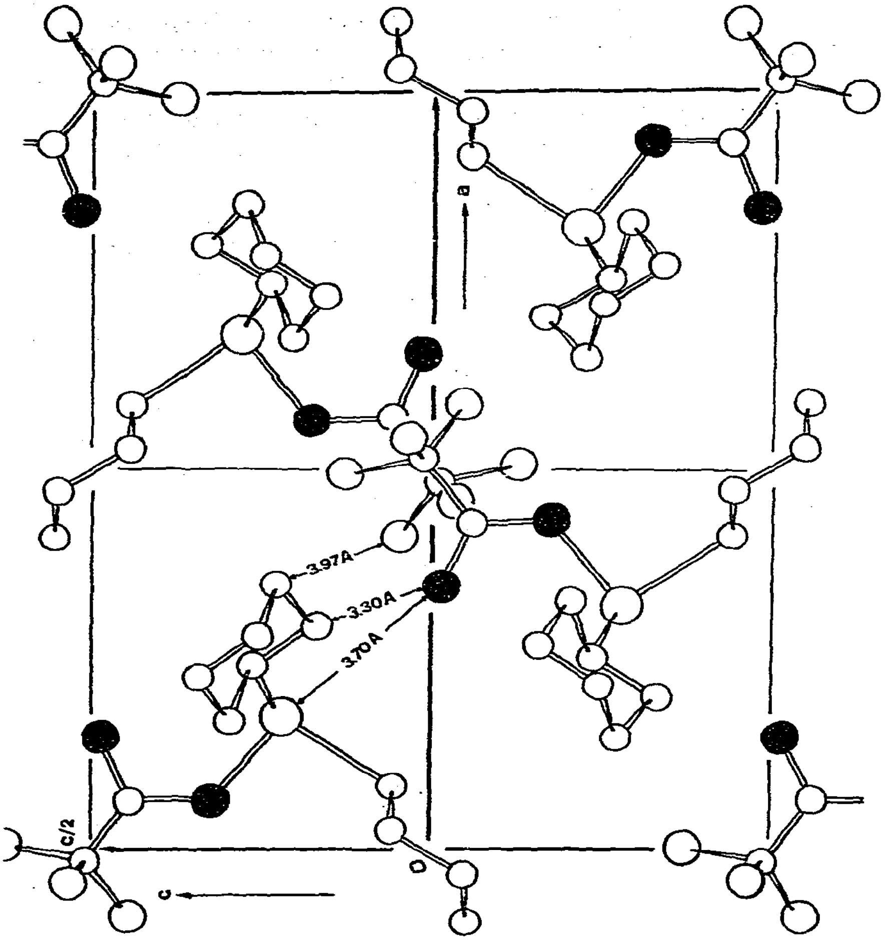

Fig. 2. Molecular packing of (cyclo-$C_6H_{11})_3SnO_2CCF_3$ as viewed along the *b* axis. Intermolecular contact distances shorter than 4.00 Å are reported.

(iii) The high temperature factors for some carbon atoms of the cyclohexyltin groups indicate a large libration of these groups about the Sn—C bonds; the corresponding geometrical parameters are also affected by this dynamic disorder; the CF_3 groups are statistically disposed about the space-group mirror

TABLE 7

BOND ANGLES (°) ABOUT TIN FOR TRICYCLOHEXYLTIN ACETATE AND TRIFLUOROACETATE AND FOR TRIBENZYLTIN ACETATE

Bond angles	(cyclo-$C_6H_{11})_3SnO_2CCH_3$	(cyclo-$C_6H_{11})_3SnO_2CCF_3$	$(PhCH_2)_3SnO_2CCH_3$
C(21)—Sn—C(1')	122	113	124
C(21)—Sn—C(1)	115	118	126
C(1)—Sn—C(1')	115	118	108
C(21)—Sn—O(1)	94	95	91
C(1')—Sn—O(1)	103	105	96
C(1)—Sn—O(1)	103	105	99

plane, but we believe that a very high libration is also occurring about the C(31)—C(32) bond. This would account for the observed exceptionally high anisotropic temperature factors for the fluorine atoms. The relatively low melting point of this compound 116—117° C, is noteworthy. Similar effects were noted in analogous compounds, such as tricyclohexyltin chloride [4] and acetate [5] and trimethyltin trifluoroacetate [15].

The relatively high disorder in the present structure (see the high R value) apparently does not affect the main skeleton of the molecule, as proved by the corresponding good geometry and by the relatively low temperature factors of the relevant atoms.

The knowledge of the crystal structure of tricyclohexyltin acetate and of tricyclohexyltin trifluoroacetate, the two extremes of the tricyclohexyltin carboxylate series, enables us to attempt a correlation between X-ray and Mössbauer data. The higher the electron withdrawing ability of the R′ group the larger is the s-electron density on the tin atom. The linear relation between δ values and σ^* Taft inductive factors of R′ groups is $\delta = 1.33 + 0.22\,\sigma^*$. As a consequence the isomer shift range is larger in this series than in the case of the R_3SnO_2R' series with R = Me [16—18], Ph [17,18] or $CH_2{=}CH$ [3], which have a polymeric trigonal bipyramidal structure [15,17,18,3].

Moreover, the increase in the asymmetry of the p-electron distribution due to the R′ group gives rise to the linear dependence of the quadrupole splitting on σ^* i.e. $\Delta = 3.29 + 0.15\,\sigma^*$.

The additivity of the quadrupole splitting was analysed by assuming a tetrahedral geometry for all the carboxylate series. Tentatively we assumed a partial quadrupole splitting (p.q.s) for the cyclohexyl group the same as that for alkyl groups: i.e. -1.37 mm s^{-1} [19]. The working p.q.s.'s for the CH_3CO_2, $ClCH_2CO_2$, Cl_2CHCO_2, Cl_3CCO_2 and F_3CCO_2 (0.11; 0.19; 0.26; 0.28 and 0.31 mm s^{-1}, respectively) were evaluated from those reported in the literature for the trigonal bipyramidal arrangement [20]. We used the ratio of the tetrahedral and the bipyramidal trigonal apical p.q.s. expressions given by Clark et al. [21]. There is poor agreement between the predicted and observed quadrupole splitting values (cf. Table 3); the large discrepancy might be attributable to distortions from a tetrahedral geometry, and so a qualitative treatment of a point charge model including distortions was performed as described in ref. 22. The quadrupole splitting values and asymmetry parameters (η) were calculated as a function of one or more angular distortions. As an example, Figs. 3a and 3b show the plots of Δ and η as function of the angles C—Sn—O and C—Sn—C, respectively, for $(cyclo\text{-}C_6H_{11})_3SnO_2CCF_3$: especially noteworthy is the remarkable dependence of Δ and η on the C—Sn—O angle. From Fig. 3a the value of the C—Sn—O angle, which reproduces the observed quadrupole splitting value of 3.78 mm s^{-1}, is 106°; the C—Sn—O values found in the crystal structure are 94° ± 2, 103° ± 2 and 103° ± 2. Analogous calculations have been carried out also for the other carboxylates (cf. Table 3).

The approximations involved in the quadrupole splitting calculations together with the high standard deviations in the structural data preclude quantitative comparison of the above values. However it seems reasonable to ascribe the high value of the quadrupole splitting for the trifluoroacetate derivative to the strong dependence of this parameter on the deviation of the C—Sn—O

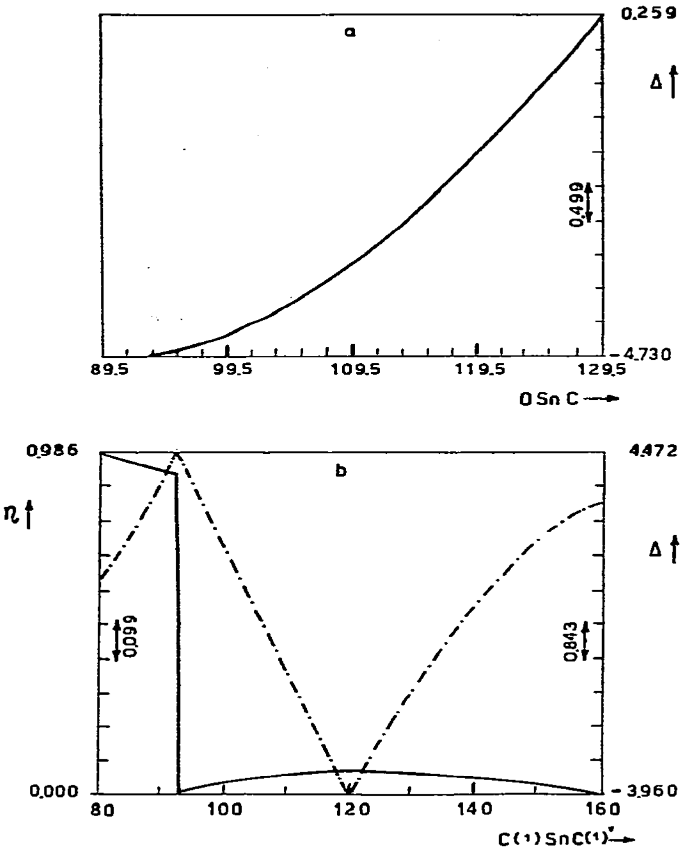

Fig. 3. Plot of Δ and η for (cyclo-C_6H_{11})$_3$SnO_2CCF_3 vs. a) OSnC and b) CSnC angles (Δ = ———; η = ·—·—·).

angles from tetrahedral values. A similar conclusion may be drawn in the case of the acetate derivative. Moreover we have previously pointed out [4] that the high Δ value (3.49 mm s^{-1}) of (cyclo-C_6H_{11})$_3$SnCl, which has a distorted tetrahedral geometry, can be accounted for by the distortion of the C—Sn—Cl angle. Thus we believe that analogous results are to be expected for all the tricyclohexyltin carboxylates.

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