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MÖSSBAUER STUDY OF SOME DISUBSTITUTED DISTANNOXANES $(R'COO)R_2SnOSnR_2(OOCR')$ AND $(R'COO)R_2SnOSnR_2(OH)$

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Summary

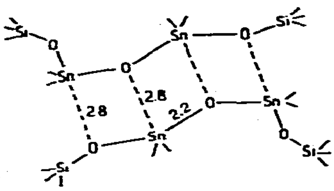
Mössbauer parameters have been determined for a series of disubstituted distannoxanes of type A, $(R'COO)R_2SnOSnR_2(OOCR')$, and of type B, $(R'COO)R_2SnOSnR_2(OH)$, (R = n-C_4H_9, $CH_2{=}CH$, $CH_2{=}CHCH_2$ and R' = CH_3, CH_2Cl, $CHCl_2$, CCl_3, CF_3). A treatment of the data by the point-charge method has been carried out. Taken together with the published literature X-ray, IR, NMR and molecular weight data, the results are consistent with dimeric structures in which the tin atoms are in a trigonal-bipyramidal geometry.

The quadrupole splitting, with fixed R′, increases on passing from the allyl- and butyl- to vinyl-haloacetate derivatives. It is inferred that this trend might be correlated with the structural packing of the skeleton of the very similar ladder-type dimeric structures formed by inter- and intra-molecular Sn—O bonds.

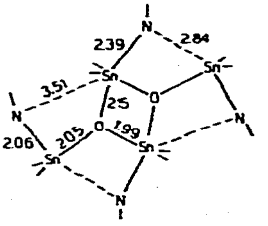
Introduction

Many investigations on disubstituted distannoxanes of type A, $(XR_2SnOSnR_2X)$, and of type B, $(XR_2SnOSnR_2OH)$ by means of X-ray analysis [1—3], IR, Mössbauer and NMR spectra and molecular weight determinations [1,4—10], have revealed the tendency of these compounds to exist as dimers both as solids and in organic solvents. In such dimers the various functional ligands X, which have different bonding modes, are able to influence the packing of the dimeric skeleton formed by the Sn—O and Sn—X bonds. This can be seen by comparing the structures of the following compounds: $\{[Me_2SnOSiMe_3]_2O\}_2$ [1], $\{[Me_2SnNCS]_2O\}_2$ [2] and $\{[n\text{-}Bu_2SnOOCCCl_3]_2O\}_2$ [3], schematically represented by structures I, II and III together with some significant bond length data (Å).

It has been suggested that the varying lengths of the inter- and intra-molecular Sn—O and Sn—functional ligand bonds affect the Mössbauer quadrupole splitting



(I)



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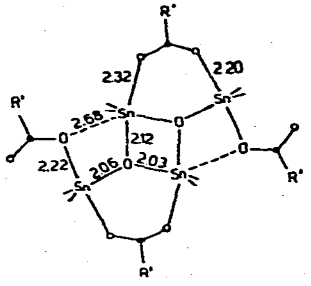


(III)

values [4]. Thus we have undertaken a Mössbauer study on disubstituted haloacetate distannoxanes of both types A and B [5—7], (Type A: R = n-C_4H_9, R' = CH_3, CH_2Cl, $CHCl_2$, CCl_3; R = CH_2=CH, R' = CH_2Cl, $CHCl_2$, CCl_3, CF_3; R = CH_2=$CHCH_2$, R' = CH_2Cl, $CHCl_2$, CCl_3. Type B: R = n-C_4H_9, R' = CH_3, CH_2Cl, CCl_3, CF_3; R = CH_2=CH, R' = $CHCl_2$, CCl_3). In addition to examining how the different functional ligands influence the dimer skeleton packing, it has been our aim to determine how the organic groups R are acting. The vinyl group is considered to interact with tin by p_π—d_π bonding [11] and to make the Sn—O bonds stronger and more covalent [12] in the trivinyltin carboxylates than in the trimethyltin carboxylates [13]. On the other hand, the allyl group, through an hyperconjugation-like interaction between the Sn—C bond and the allylic double bond, decreases the electron density at the tin atom [14,15]. Thus it is thought that these organic ligands with fixed R', can differ in their effects on the electron density and the electric field gradient [16] at the tin nucleus, leading to differences in the Mössbauer parameters.

Experimental

The distannoxanes used have been prepared as previously reported [5—7] by treating tetraallyl-, dibutyldiallyl- and divinyldiallyltin substrates with the appropriate carboxylic acids in methanol or aqueous acetone media. The compounds were crystallized twice from chloroform/n-hexane mixture, giving melting points and IR spectra as previously reported.

IR spectra were recorded on a Perkin—Elmer Model 457 spectrophotometer equipped with KBr optics, using dispersed Nujol mulls or carbon tetrachloride solutions.

Molecular weights were determined in CCl_4 with a Mechrolab Model 302B Vapour Phase Osmometer.

^{119m}Sn Mössbauer spectra were recorded at 80 K by a conventional constant-acceleration spectrometer using a $Ca^{119m}SnO_3$ source at room temperature. The velocity scale was calibrated and its linearity checked by use of an enriched standard iron foil. An RSG-60 Reuter—Stokes proportional counter was used. Centre shift values are relative to SnO_2 at room temperature.

Powdered samples, mixed with an inert matrix of perspex, were encapsulated between mylar windows held by high purity aluminium containers. The absorber thickness was approximately 50 mg/cm^2.

A Hofman liquid helium cryostat equipped with a self-feeding liquid nitrogen supply was used. The temperature was checked by a constantan—iron thermocouple.

900 channels of the 4096 channel analyzer were used. The contents were collected by a teleprinter (HP 3752A) and by an X—Y recorder (HP 7004B).

All spectra, corrected for solid angle effects, were fitted, without constraints to two Lorenzian line shapes by a program [17] adapted by us for use with a CDC Cyber 76 computer.

Results

In no case was a detectable Mössbauer effect observed at room temperature. Most of the spectra were found to be asymmetric, the average area ratio being, for random polycrystalline samples, less than 1.3. Representative spectra of three of the compounds examined are given in Fig. 1.

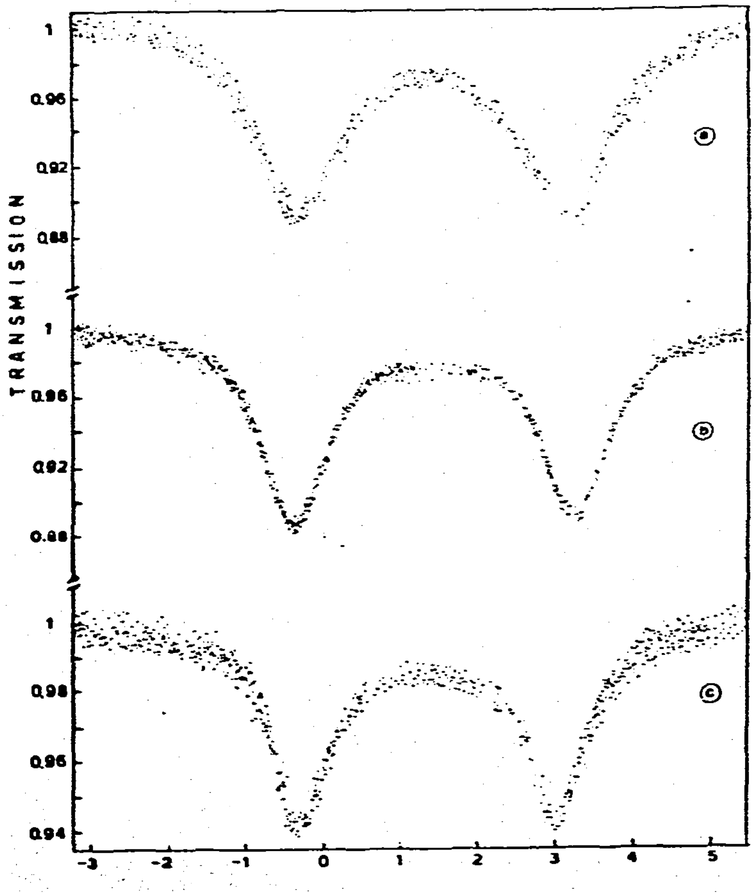


Fig. 1. Mössbauer spectra at 80 K. (a) $[(CH_2{=}CH)_2SnOOCCHCl_2]_2O$, (b) $[(n\text{-}C_4H_4)_2SnOOCCHCl_2]_2O$, (c) $[(CH_2{=}CHCH_2)_2OOCCHCl_2]_2O$.

TABLE 1

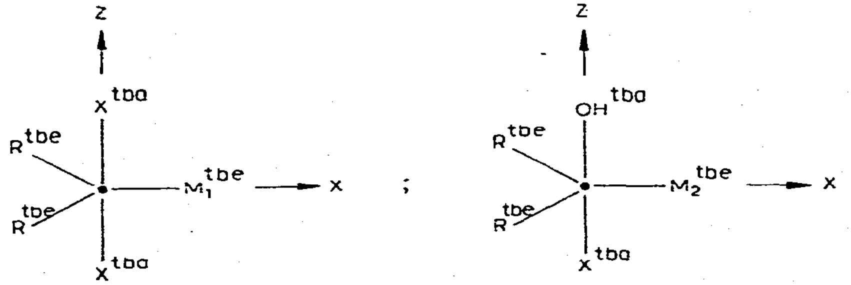
MÖSSBAUER (80 K) AND IR DATA FOR $[R_2SnX]_2O$ AND $XR_2SnOSnR_2OH$ COMPOUNDS

Number	Compound	$\delta^{a,b}$ (mm/sec)	Δ^b (mm/sec)	ρ^c	Γ^d (mm/sec)	$\nu_a(COO)^e$ (cm^{-1})	$\nu(OH)^e$ (cm^{-1})
1	$[(CH_2{=}CH)_2SnOOCCF_3]_2O$	1,47	3,92	2,67	1,29	1660s	
2	$[(CH_2{=}CH)_2SnOOCCl_3]_2O$	1,46	3,91	2,68	1,28	1645vs	
3	$[(CH_2{=}CH)_2SnOOCCHCl_2]_2O$	1,37	3,72	2,72	1,28	1625s	
4	$[(CH_2{=}CH)_2SnOOCCH_2Cl]_2O$	1,35	3,71	2,75	1,18	—	
5	$[(n\text{-}C_4H_9)_2SnOOCCCl_3]_2O$	1,42	3,61	2,54	1,02	1650s	
6	$[(n\text{-}C_4H_9)_2SnOOCCHCl_2]_2O$	1,42	3,60	2,53	1,00	1625s(br)	
7	$[(n\text{-}C_4H_9)_2SnOOCCH_2Cl]_2O$	1,38	3,48	2,52	1,16	1605s	
8	$[(n\text{-}C_4H_9)_2SnOOCCH_3]_2O$	1,32[f]	3,26[f]	2,44	1,08	1560s	
9	$[(CH_2{=}CHCH_2)_2SnOOCCCl_3]_2O$	1,41	3,52	2,50	1,10	1650s	
10	$[(CH_2{=}CHCH_2)_2SnOOCCHCl_2]_2O$	1,40	3,42	2,49	1,08	1635s	
11	$[(CH_2{=}CHCH_2)_2SnOOCH_2Cl]_2O$	1,19	3,30	2,77	1,15	1585s	
12	$(Cl_3COO)(CH_2{=}CH)_2SnOSn(CH{=}CH_2)_2(OH)$	1,25	3,13	2,50	1,25	1660vs	3360s(br)
13	$(Cl_2HCOO)(CH_2{=}CH)_2SnOSn(CH{=}CH_2)_2(OH)$	1,25	3,05	2,44	1,23	1655vs	3340s(br)
14	$(F_3COO)(n\text{-}C_4H_9)_2SnOSn(n\text{-}C_4H_9)_2(OH)$	1,34	2,98	2,22	1,28	1680s(br)	3420m(br)
15	$(Cl_3COO)(n\text{-}C_4H_9)_2SnOSn(n\text{-}C_4H_9)_2(OH)$	1,33	2,96	2,23	1,06	1665s	3500m(br)
16	$(ClH_2COO)(n\text{-}C_4H_9)_2SnOSn(n\text{-}C_4H_9)_2(OH)$	1,29	2,79	2,16	0,98	1645s	3380m(br)
17	$(H_3COO)(n\text{-}C_4H_9)_2SnOSn(n\text{-}C_4H_9)_2(OH)$	1,18	2,64	2,24	1,20	1605s(br)	3280m(br)

[a] Relative to SnO_2 at room temperature. [b] ±0,03 mm/sec. [c] $\rho = \Delta/\delta$. [d] Computed FWHM. [e] positions of the asymmetric stretching vibration band of the intramolecular bridging carboxylate group and the OH stretching vibration band in Nujol mull, KBr optics (see also ref. 5—7). [f] See ref. 4 and 9 for previous values: 1,32, 1,30 mm/sec and 3,22, 3,24 mm/sec, for δ and Δ respectively.

Table 1 lists the Mössbauer centre shift (δ) and the quadrupole splitting (Δ) parameters together with the Herber ρ-values [18], the Γ_{av} computed full width at half maximum (FWHM), the ν_a(COO) and ν(OH) stretching frequencies of the distannoxanes examined. These have been divided into five groups (cf. Table 1) with the aim of listing and distinguishing them by compound type and by the organic groups (R). For each group the δ, Δ and ν_a(COO) values increase in the order, $CH_3 < CH_2Cl < CHCl_2 < CCl_3 < CF_3$. Looking at the compounds having fixed R and R′ groups, it is notable that the δ and Δ values are greater for a compound of type A than of type B; in addition, for compounds with the same R′, the quadrupole splitting trend is in the order, vinyl > butyl > allyl. The ρ-values are in the range 2.16—2.77.

Using the additive point-charge method [16,19], we have obtained a good fit by taking into account models in which the tin atoms are arranged in a regular trigonal bipyramidal geometry. We used the models represented below, which represent the distannoxanes of types A and B, respectively:



(R = n-C_4H_9 , $CH_2{=}CH$, $CH_2{=}CH{-}CH_2$,
X = R′COO, M_1 = $(OSnR_2)_2SnR_2X_2$)

(R = n-C_4H_9 . $CH_2{=}CH$.
X = R′COO , M_2 = $(OSnR_2)_2SnR_2XOH$)

The components of the electric field gradient (EFG) tensor are given by equations 1—3 for compounds of type A and 4—6 for compounds of type B with $|V_{XX}| > |V_{YY}| > |V_{ZZ}|$:

$$V_{XX} = [2\{M_1^{tbe}\} - \tfrac{1}{2}\{R^{tbe}\} - 2\{X^{tba}\}]e \tag{1}$$

$$V_{YY} = [-\{M_1^{tbe}\} + \tfrac{5}{2}\{R^{tbe}\} - 2\{X^{tba}\}]e \tag{2}$$

$$V_{ZZ} = [-\{M_1^{tbe}\} - 2\{R^{tbe}\} + 4\{X^{tba}\}]e \tag{3}$$

$$V_{XX} = [2\{M_2^{tbe}\} - \tfrac{1}{2}\{R^{tbe}\} - \{OH^{tba}\} - \{X^{tba}\}]e \tag{4}$$

$$V_{YY} = [-\{M_2^{tbe}\} + \tfrac{5}{2}\{R^{tbe}\} - \{OH^{tba}\} - \{X^{tba}\}]e \tag{5}$$

$$V_{ZZ} = [-\{M_2^{tbe}\} - 2\{R^{tbe}\} + 2\{OH^{tba}\} + 2\{X^{tba}\}]e \tag{6}$$

We used the trigonal-bipyramidal apical (tba) and equatorial (tbe) partial quadrupole splitting values as reported by Bancroft et al. [20], as follows. Apical parameters: $CH_3COO = 0.075$, $CH_2ClCOO = 0.13$, $CHCl_2COO = 0.175$, $CCl_3COO = 0.19$, $CF_3COO = 0.21$, OH = −0.13 mm/sec; equatorial parameters: for the butyl group the value −1.13 mm/sec is assumed, as reported for other alkyl groups.

TABLE 2

OBSERVED AND CALCULATED QUADRUPOLE SPLITTINGS

Compounds [a]	Δ_{obs} (mm/sec)	Δ_{calcd} (mm/sec)	η
1	3.92	—4.17	0.52
2	3.91 [b]	—	—
3	3.72	—4.03	0.54
4	3.71	—3.86	0.56
5	3.61 [c]	—	—
6	3.60	—3.67	0.46
7	3.48	—3.50	0.48
8	3.26	—3.28	0.51
9	3.52 [d]	—	—
10	3.42	—3.55	0.43
11	3.30	—3.38	0.45
12	3.13 [e]	—	—
13	3.05	—3.41	0.80
14	2.98	—3.10	0.71
15	2.96	—3.06	0.72
16	2.79	—2.95	0.75
17	2.64	—2.85	0.78

[a] References number of Table 1. [b] Used to derive $\{M_1^{tbe}\}$ — 0.59 mm/sec. [c] Used to derive $\{CH_2{=}CH^{tbe}\}$ — 1.28 mm/sec. [d] Used to derive $\{CH_2{=}CHCH_2^{tbe}\}$ — 1.08 mm/sec. [e] Used to derive $\{M_2^{tbe}\}$ — 0.45 mm/sec.

From equation 3, taking into account the observed quadrupole splittings of the compounds 5, 2, and 9 of Table 2, $\{M_1^{tbe}\} = -0.59$ mm/sec, $\{CH_2{=}CH^{tbe}\} = -1.28$ mm/sec, $\{CH_2{=}CHCH_2^{tbe}\} = -1.08$ mm/sec were calculated. Analogously from equation 6 and the observed quadrupole splitting of the compound 12, $\{M_2^{tbe}\} = -0.45$ mm/sec is calculated.

Table 2 shows the quadrupole splittings and the asymmetry parameters η calculated by means of these values in equation 1—6 for thirteen of the compounds examined.

The fitting of the $|\Delta_{calcd}|$ against the $|\Delta_{obs}|$ gives a straight line of slope 1.01, intercept 0.13 mm/sec and a correlation coefficient 0.97, showing a good agreement with the ideal values.

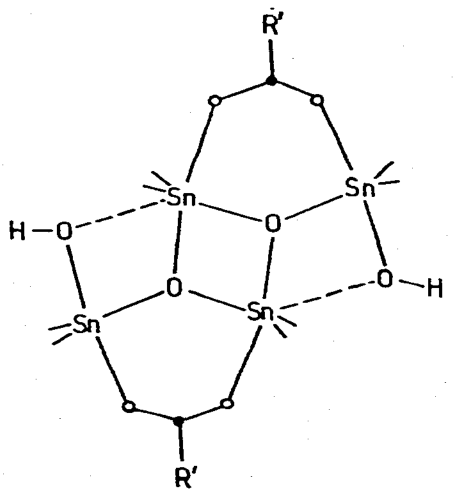
The difference $||\Delta_{obs}| - |\Delta_{cald}|| << 0.4$ mm/sec [20], for all the compounds examined, allows us to assign the tin atoms to a trigonal bipyramidal geometry.

Discussion

On the basis of the previous IR (cf. Table 1) and molecular weight data [1,5—7,21] and the X-ray structure of $\{[n\text{-}Bu_2SnOOCCCl_3]_2O\}_2$ [3], all the distannoxanes examined may be regarded as isostructural dimeric compounds.

Distannoxanes of type B may be thought to have the structure IV.

This is in agreement with data from the present work listed in Table 3. These refer to tetrabutyl-1-trichloroacetoxy-3-hydroxydistannoxane, which, in solution, behaves in a similar way to the corresponding haloacetate of type A [3]. It is a dimer in CCl_4, and in the solid state or in solution it gives $\nu_a(COO)$ stretching frequency values typical of a bridging carboxylate group. An additional interac-



(IV)

tion seems to exist between the tin atoms and the OH ligand, since the OH stretching frequency shifts from 3500 cm^{-1} in the solid to 3650 cm^{-1} in solution, whereas the ν_a(COO) frequencies are practically unchanged.

The interactions of the haloacetate ligand in structure III or those of the hydroxy ligand in IV with the endocyclic tin atoms seem not to contribute to the hexacoordinated environment of these tin atoms [3]. This point of view is supported by the present data: all Mössbauer spectra show the presence of simple doublets, providing no evidence for distinguishable tin atoms. Whether from Herber's criterion [18] or from point charge calculations, the tin atoms must be considered to lie in a pentacoordinated geometry.

The centre shift trend (cf. Table 1) increases with the increase of the electronegativity of the functional ligands [22]. In the present class of compounds, as with the class of triorganotin haloacetates previously examined [23—25]. Introduction of haloacetate groups having increasing electron-acceptor properties tends to remove electron density from the tin atom through the carboxylate group. Thus halo-substitution increases the positive charge on the tin atom and the result is a deshielding of the 5s-orbital which leads to an increase of the effective nuclear charge. The deshielding effect is more pronounced for compounds

TABLE 3

IR DATA FOR TETRABUTYL-1-TRICHLOROACETOXY-3-HYDROXYDISTANNOXANE IN THE SOLID STATE AND IN SOLUTION AND MOLECULAR WEIGHT IN CCl_4 (37°C)

Medium	Concentration (g/ml)	ν_a(COO) (cm^{-1})	ν(OH) (cm^{-1})	Mol. wt. found	i [a]
Nujol	—	1650sh, 1665s	3500m(br)		
CCl_4	6.44 [b]	1655s, 1680s	3650m	1342	2.03

[a] i = Mol.wt. found/mol.wt. calcd. (662.02). [b] Concentration near to a saturated solution.

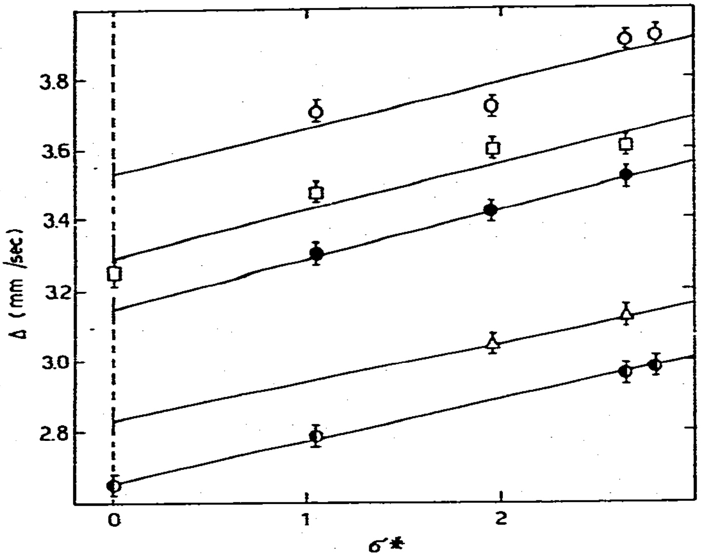


Fig. 2. Plot of quadrupole splitting against Taft inductive factor. ○ vinyl-, □ butyl-, ● allyl-distannoxanes of type A; △ vinyl-, ◉ butyl-distannoxanes of type B.

of type A than for type B, since in the former four haloacetate groups are present.

On considering the quadrupole splitting values, we have found a linear correlation between the Δ values and the Taft factor σ^* of the R′ groups (cf. Fig. 2), consistent with the behaviour previously demonstrated for a series of triorganotin haloacetates $R_3SnOOCR'$ (R = Me and Ph) [23–25]. In Table 4 are listed the values of the slopes p and the intercepts Δ_0 (calculated quadrupole splitting value of the acetate) involved in the equation $\Delta = \Delta_0 + p\sigma^*$ for the five groups of compounds examined and for those previously reported. It will be seen that no significant differences, within the standard deviations, appear in the p-values

TABLE 4

LINEAR CORRELATION ($\Delta = \Delta_0 + p\sigma^*$) BETWEEN THE Δ-VALUES AND THE σ^* TAFT FACTOR OF THE R′ GROUPS.

Series of isostructural compounds	p (mm/sec)	Δ_0 [a] (mm/sec)	Δ_0 [b] (mm/sec)
$[(CH_2{=}CH)_2SnOOCR']_2O$	0.131 ± 0.04	3.53 ± 0.09	—
$[(n\text{-}C_4H_9)_2SnOOCR']_2O$	0.135 ± 0.03	3.29 ± 0.05	3.26 ± 0.03
$[(CH_2{=}CHCH_2)_2SnOOCR']_2O$	0.137 ± 0.005	3.15 ± 0.00	—
$(R'COO)(CH_2{=}CH)_2SnOSn(CH{=}CH_2)_2OH$	0.113	2.83	—
$(R'COO)(n\text{-}C_4H_9)_2SnOSn(n\text{-}C_4H_9)_2OH$	0.119 ± 0.01	2.65 ± 0.05	2.64 ± 0.03
$(CH_3)_3SnOOCR'$	0.213 ± 0.01 [c]	3.59 ± 0.02 [c]	3.57 ± 0.04
$(CH_3)_3SnOOCR'$	0.182 ± 0.0210 [d]	3.69 [d]	3.68 ± 0.03
$(C_6H_5)_3SnOOCR'$	0.231 ± 0.045 [d]	3.34 [d]	3.36 ± 0.03

[a] Calculated value for the acetate. [b] Observed value for the acetate. [c] Our calculation from data of ref. 23. [d] Reported values in ref. 24; see also ref. 25.

inside each series of compounds; the values for the isostructural chain polymeric triorganotin derivatives [24] are greater than those of the dimeric distannoxanes.

The linear correlation found is significant in establishing that only electronic effects are important in determining the trend of the Δ values [24]. For trimethyltin derivatives it has been proposed [24] that the Δ trend arises from an increasing asymmetry of the two Sn—O bonds with the increase of the σ^* of the haloacetate groups. This is consistent with structural data on the trimethyltin acetate and trifluoroacetate [24—26].

Starting from this point of view, we suggest that within an isostructural series of compounds, the slope p assumes a value which is in account for different structural parameters. It seems to us that the regular increase in the splitting quadrupole values for all the five groups of compounds examined can be related to the variation of parameters which characterise the isostructural skeleton of the very similar ladder-type dimeric structure formed by the Sn—O bonds. In these compounds the influence of groups of increasing electron-acceptor ability might reinforce the carboxylate C—O bonds (cf. trend of the ν_a(COO) values, Table 1) and reduce the Sn···OOCR′ bonding. As a consequence the intra- and inter-molecular Sn—O bonds become stronger.

The effect of the structure packing is also revealed by comparing the Δ_0 values of the distannoxanes of type B, which are lower than those of the distannoxanes of type A, this lowering probably being due to the presence of only two carboxylate groups in the former.

Support for the above arguments comes also from analysing the trend of the Δ_0 values which concern acetate derivatives having different R groups around the tin atoms. In order to discuss this trend, the intercept values Δ_0 (cf. Table 4) must be taken into consideration. On the basis of these values we obtain the following Δ_0 trend order, vinyl (3.53) > butyl (3.29) > allyl (3.15) for type A and vinyl (2.83) > butyl (2.65) for type B. The differences between these values do appear to be significant. It is notable that introduction of the different alkyl groups in an homologous series of distannoxanes does not cause any variation in the Δ values. Tetrabutyl-, tetraoctyl- and tetramethyl-1,3-(trimethylsiloxy)distannoxanes have been found to have the following values: 2.46, 2.45 and 2.42 mm/sec, respectively [4].

In the introduction we predicted the effects which could be produced by the organic groups employed. In our opinion, the vinyl group makes the Sn—O bonds stronger and more covalent [12,13], whereas the allyl group has the opposite effect. In other words, by comparison with the butyl group, these groups seem to promote a different packing in the dimeric molecule.

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