ELSEVIER

Journal of Organometallic Chemistry 558 (1998) 19–33

Journal of Organometallic Chemistry

Existence of an intradimeric rearrangement in monofunctional tetrabutyldistannoxanes $[Bu_4Sn_2X_2O]_2$ probed by multinuclear NMR spectroscopy in solution and in solid state

Odile Primel [1], Marie-France Llauro [2], Roger Pétiaud[2], Alain Michel *

Laboratoire des Matériaux Organiques à Propriétés Spécifiques, CNRS, BP 24, 69390 Vernaison, France

Received 23 May 1997; received in revised form 30 October 1997

Abstract

A set of 1-D and 2-D, ^{13}C- and ^{119}Sn-NMR experiments—both in solution and in the solid state—exhibit a common peculiarity of the monofunctional tetrabutyldistannoxanes of general formulae $R_4Sn_2X_2O$ in comparison with the no problematic NMR data of difunctional tetrabutyldistannoxanes R_4Sn_2XYO. Relying on the support of these observations, the existence of a dynamic process is evidenced in solution. This process, rapid and equilibrated at ambient temperature, is shown to be frozen both in solution at 188 K and in the solid state. A mechanism of intramolecular rearrangement of the distannoxane dimeric form is discussed on the basis of modelisation of the movements required. It accounts for all spectroscopic observations and is not expected to occur with the dimer form of the difunctional distannoxanes ($X \neq Y$). © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Tin; Distannoxanes; Rearrangement; NMR; Catalysts

1. Introduction

Many organic tin compounds have long been used as catalysts in various kinds of reactions, namely the synthesis of polyurethanes [1,2], the polymerisation of butyrolactones [3,4], the transesterification reactions [5,6] and others. Besides, we have recently shown that dibutyltinoxide reacts with esters leading to 1-alkoxy-3-acyloxytetrabutyldistannoxanes [7] which are the true catalytic entities in reactions dealing with esters. Moreover, in the field of chemical modifications of polymer blends, in situ during processing operations, leading to new morphologic features of the blend, we have compared the catalytic efficiency of different tin compounds including dimeric tetrabutyldistannoxanes. These last one have shown to be particularly efficient in redistributive transesterification [8–10] but also in other exchange reactions like ester/carbonate [11] and ester/amide. Both difunctional $[Bu_4Sn_2XYO]$ and monofunctional derivatives with general formulae $[Bu_4Sn_2X_2O]$ have been tested. This led us to study the structure of distannoxanes, using multinuclear ^1H-, ^{13}C- and ^{119}Sn-NMR [7,8](Table 1). In the frame of these NMR studies we focused our attention on some particular and still incompletely explored features of the NMR spectra of monofunctional tetrabutyldistannoxanes.

Concerning the structure of distannoxanes in solution many reports have been published by different authors using various techniques. In particular, Otera et al. related the dimeric structure of distannoxanes, proposed by Okawara [12], to the general aspect of the ^{119}Sn solution NMR spectra [13,14]. Several authors [8,15,16] also considered the exchange reactions which may occur between different distannoxane dimers, and observed, in certain conditions, monomer exchanges between dimer entities or ligand exchanges on tin atoms. Furthermore, various distannoxanes inclined to

* Corresponding author.

[1] Present address: RHOVYL; 55310 Tronville-en-Barrois; France.

[2] Service de RMN du Réseau des Polymèristes Lyonnais, LMOPS, CNRS, BP 24, 69390 Vernaison, France.

0022-328X/98/$19.00 © 1998 Elsevier Science S.A. All rights reserved.
PII S0022-328X(97)00706-7

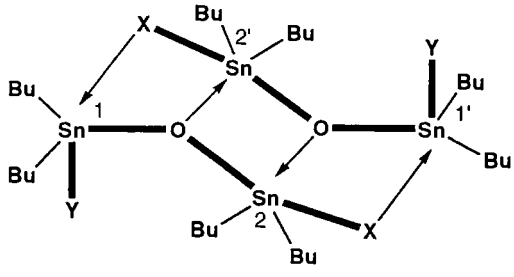
Table 1
Characteristic NMR spectral features of dimeric 1,3-diphenoxytetrabutyldistannoxane and 1,3-dichlorotetrabutyldistannoxane (C)

Diphenoxy	Dichloro (C)
^{13}C-NMR	
δ C1Bu = 13.60 and 13.75	δ C1Bu = 13.70 and 13.80
δ C2Bu = 27.25 and 27.45 (^3J = 108, 119)	δ C2Bu = 26.75 and 26.90 (^3J = 100, 122)
δ C3Bu = 27.55 and 27.65 (^2J = 33)	δ C3Bu = 27.40 and 27.60 (^2J = 30)
δ C4Bu = 23.20 (^1J = 577, 605)	δ C4Bu = 32.15 (^1J = 552, 577)
δ C4Bu = 25.10 (^1J = 588, 615)	δ C4Bu = 32.90 (^1J = 577, 605)
δ SnOCOPh (para) = 118.50	
δ SnOCOPh (ortho) = 118.95	
δ SnOCOPh (meta) = 129.55	
δ SnOCOPh (quaternary) = 160.85	
^{1}H-NMR	
δ CH$_3$Bu = 0.820 and 0.880	δ CH$_3$Bu = 0.920 and 0.955
δ CH$_2$(2)[a]Bu = 1.285 and 1.375	δ CH$_2$(2)[a]Bu = 1.350 and 1.415
δ CH$_2$(3 and 4)[a]Bu = 2.1–1.5 region	δ CH$_2$(3 and 4)[a]Bu = 2.1–1.5 region
δ SnOCOPh (o,m,p) = 6.615, 7.100, 6.705	
^{119}Sn-NMR (cf Table 3)	

Chemical shifts (δ) are given in ppm and coupling constants (J) in Hertz.
[a] Unresolved multiplets.

yield monocrystals, were studied by X-ray diffraction and sometimes by both X-ray and NMR techniques [18,19].

The first crystalline structure of a dimeric distannoxane compound was evidenced by Harrison et al. [20]. This two dimensional centrosymmetric structure with an essentially planar [–R$_2$Sn–O–SnR$_2$–O–] central ring and a global 'staircase' structure or 'ladder-like' (entirely planar) in some cases is represented in Scheme 1. Later on, it has been evidenced that other crystalline forms exist, but the above structure is by far the predominant one. In a recent review concerning the crystalline state of dimeric dicarboxylatotetraorganodistannoxanes, Tiekink [17] describes five types of structures for these organotincarboxylates. In type IV, i.e. {[Ph$_2$Sn(O$_2$CCCl$_3$]$_2$O}$_2$ all tin are six coordinate, in



Scheme 1.

type III, i.e. {[Me$_2$Sn(O$_2$CCH$_3$]$_2$O}$_2$ there are four non equivalent tin atoms, two pentacoordinated and two hexacoordinated. Two other structural types have been evidenced (type I and II) which are very similar both having the two dimensional centrosymmetric structure shown on Scheme 1 which can be considered as the reference structure for dimeric distannoxane compounds. For example, Tiekink [18] has shown that the two following dimeric distannoxanes, namely {[Bu$_2$Sn(O$_2$CCH$_2$C$_6$F$_5$]$_2$O}$_2$ and {[Bu$_2$Sn(O$_2$CCH$_2$C$_6$H$_4$F-*p*]$_2$O}$_2$, adopt two slightly different crystalline structures: in the first one (I) both oxygen atoms of the carboxylate are involved in the bidentate bridging whereas in the second one (II) a less common structure is adopted where the two bidentate bridging carboxylate ligands utilise only one O atom involving the presence of three condensed Sn$_2$O$_2$ rings in a ladder like structure. But the ^{119}Sn-NMR data for these compounds in solution allowed the authors to conclude to similar structures in solution.

The predominant centrosymetric structure shown on Scheme 1 (which includes types I and II described by Tiekink [18]) is built up around a four-membered cyclic [–R$_2$Sn–O–SnR$_2$–O–] central core and presents four pentacoordinate tin atoms with two types of non equivalent sites, namely [1 and 1′] and [2 and 2′]. Each type of tin site [1 for example] is linked to two tin sites [2 and 2′] through different type of links Sn$_1$–O–Sn$_2$ and Sn$_1$–O→Sn$_{2'}$ so that in the ^{119}Sn-NMR spectrum two doublet satellite peaks are expected related to two different $^2J_{endo-exo}$ coupling constants. In fact, in the general case where X differs from Y, these compounds give a ^{119}Sn-NMR spectrum of the same type as the spectrum presented in Fig. 1, showing indeed two $^2J_{Sn-Sn}$ coupling constants on each of both tin sites. However, Otera [14] noticed a first exception to this observation: the diacetoxytetrabutyldistannoxane (A) spectrum only shows one single coupling constant. Later on, different authors observed only a single carbonyl resonance on this distannoxane (A) and on others dicarboxylatotetraalkyldistannoxanes. Owing to these observations, Tiekink evokes first the existence of a dynamic equilibrium between tetraorganodistannoxanes [19], by analogy with exchange reactions previously evidenced by Gross [15], and more recently proposes an intramolecular [18] dynamic process shown on Scheme 2 which should lead to equivalence of the carboxylate ligands while preserving the non equivalence of the exocyclic and endocyclic tin sites.

In the present work, we will attempt to clarify the dynamic process suggested by Tiekink [18] concerning dicarboxylatotetraorganodistannoxanes and see if it holds for all monofunctionnal (X = Y) tetrabutyldistannoxanes. For that purpose we investigated four monofunctional distannoxanes with X = Y = chloro, acetoxy,

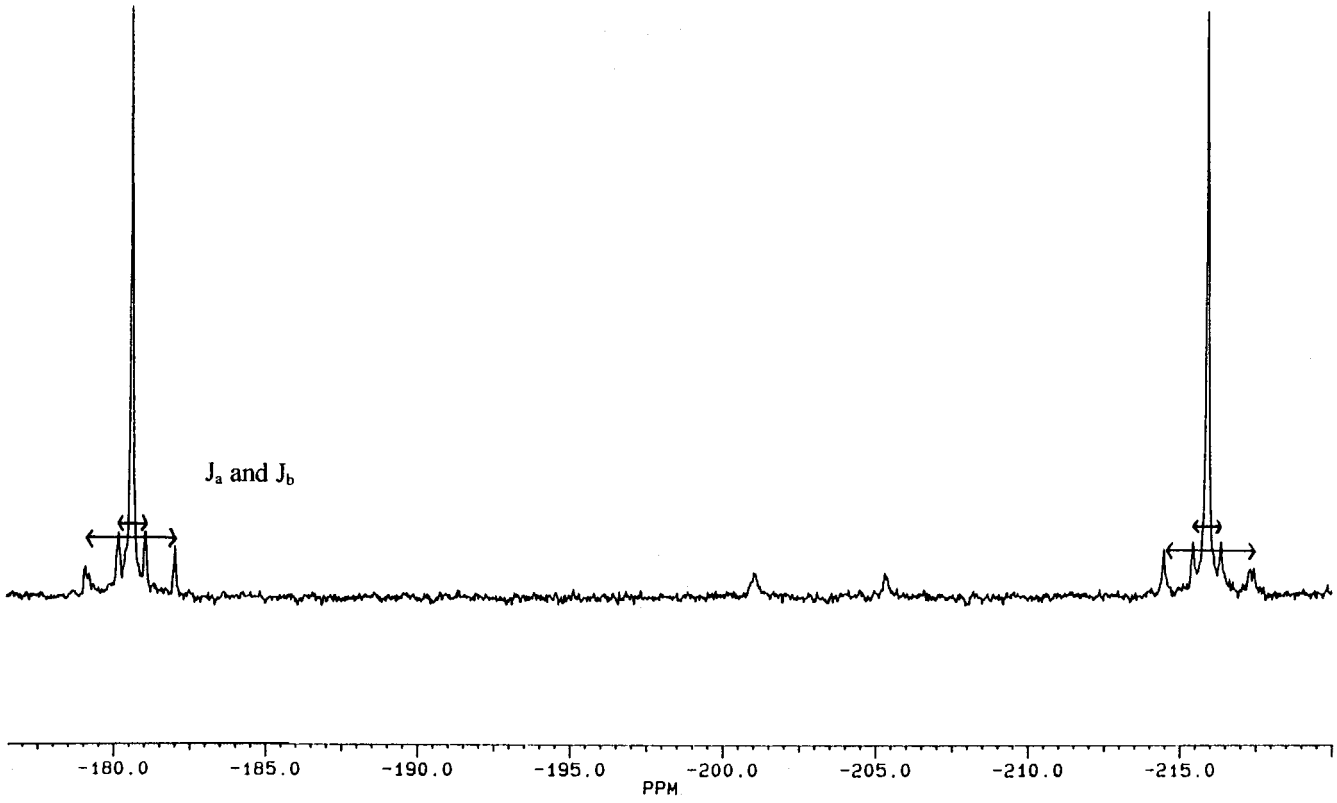


Fig. 1. ^{119}Sn-NMR spectrum of the reaction products of dibutyltinoxide with methyl benzoate (initial oxide/ester molar ratio R = 1:1).

methoxy and phenoxy groups and called for ^{1}H-, ^{13}C- and ^{119}Sn-NMR. In order to prove the dynamic origin of the phenomenon we worked both in solution—at different temperatures—and in solid state. We focused our attention on both coupling constants between tin sites and chemical shift values (^{13}C and ^{119}Sn). We compared our NMR observations with previous and no problematic data we obtained with difunctional l-alcoxy 3-acyloxy tetrabutyldistannoxanes [7–9].

2. Results and discussion

Otera [14], in a view to explain the special feature observed concerning the $^{2}J_{Sn-O-Sn}$ couplings on the diacetoxytetrabutyldistannoxane (A) suggests that the two coupling values $J_{Sn1-Sn2} = J_b$ and $J_{Sn1-Sn2'} = J_a$ should be fortuitously equal. Another hypothesis could be done according to which the value of one coupling constant would be so weak that the corresponding doublet would be overlapped by the base of the main peak.

But, as we mentioned above this is not the only peculiarity of this compound. In previous studies [7], we noticed, on the ^{13}C-NMR spectrum of compound A, the presence of a single carbonyl peak at 176.9 ppm and only one methyl peak at 22.85 ppm, which may be assigned to acetoxy groups. However, the structure presented in Scheme 1 and confirmed by X-ray studies on similar compounds [19] has two different types of acetoxy groups: on one hand, a group bridging between two different tin sites, one endocyclic and one exocyclic, and on the other hand, a ligand acetoxy group on exocyclic tin site (Sn exo). We should therefore observe two chemical shifts for the >C=O and two chemical shifts for the $-CH_3$. It is also possible to suppose that two carbonyl resonances fortuitously overlap, but this becomes very unlikely if we keep in mind that many other diacyloxytetraorganodistannoxanes, with different acyloxy groups also show a single carbonyl resonance.

So, the recent suggestion of Tiekink [18] of a dynamic intramolecular process concerning diacyloxydistannoxanes has to be clarified and spectral features of other monofunctional distannoxanes have to be examined. For that purpose we set up various NMR techniques.

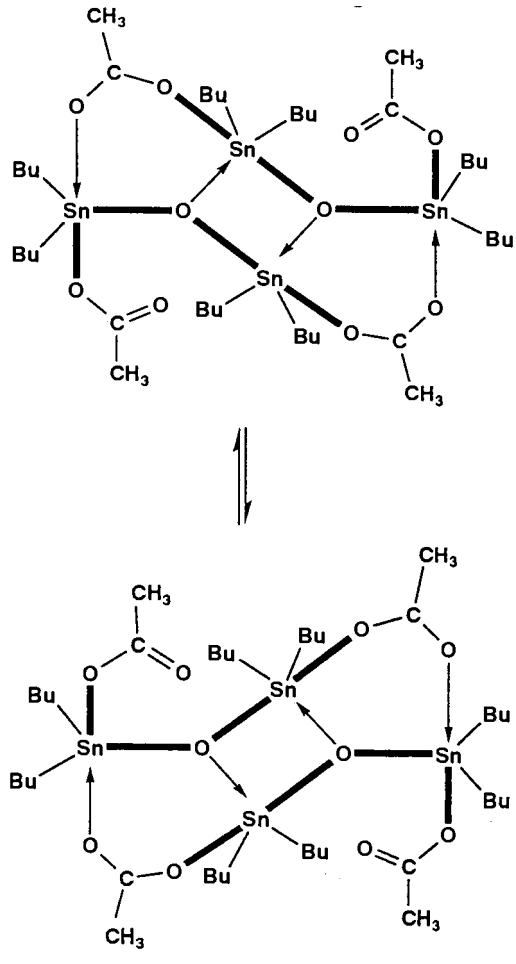
Before starting on it seems useful for the further discussion to mention some questions about tin sites assignments in distannoxanes compounds and to summarise some chemical shifts and coupling constants values observed previously [7–9] with a family of difunctional 1-alcoxy-3-acyloxy tetrabutyldistannoxanes.

First of all we notice that, observing the variation of the chemical shift of tin with the chemical nature of its neighbors in compounds of type $R_{4-n}SnX_n$ when n

varies, Mc Farlane [21] often observed bell curves. As an increase in the electron-withdrawing ability of groups bound to tin is generally admitted to lead to a decrease of the tin shielding, well explained by a change in electron density (diamagnetic contribution), the authors attribute these rather surprising observations to an additional paramagnetic contribution. They notice that the chemical shift changes are too large to be due to a change in electron density.

All ^{119}Sn-NMR investigations made later on have clearly shown that the coordination number of the tin site is of a major importance on chemical shift. So, differences in the ability to associate in a dimeric form—giving pentacoordinated tin sites—may explain strong differences in a given family described wrongly as being of $R_{4-n}SnX_n$ [21].

Concerning the more recent assignments of tin sites in distannoxanes, when endo and exo ^{119}Sn tin sites are precisely attributed it is on the basis of the coordination type of the sites and so it takes into account the dimeric structure or more exactly the proximity of two of the four tin sites (1 and 2′ Scheme 1). At least in symetrical distannoxanes and when large differences are observed



Scheme 2.

($\Delta\delta > 10$ ppm) these assignments have not been debated.

For example, in the 1,3-dichlorotetrabutyldistannoxane where endo and exo sites differ by 51 ppm, due to the strong electron withdrawing effect of the chlorine atom the exo site of Bu_2SnCl_2O coordination type has been assigned to the more deshielded resonance by comparison with the endo site of Bu_2SnClO_2 coordination type.

When the difference between endo and exo chemical shifts is about 10 ppm (or < 10 ppm) the attribution based on the type of tin site coordination may be questionable (or impossible) mainly because it does not take into account the effect of the two other tin sites (1′ and 2) on the chemical shift of both sites 1 and 2′.

For example in the 1,3-diacetoxytetrabutyldistannoxane the more deshielded resonance is assigned to the $Bu_2SnO_2(OAc)$ endocyclic tin site by Otera [14] and Michel [7], whereas on the contrary Gross [15] assigned this resonance to the $Bu_2SnO(OAc)_2$. Later on, Tiekink [18,19], referring to Gross, applies this type of assignment to other diacyloxytetrabutyldistannoxanes presenting in some cases a chemical shift difference between tin sites of 3.3 ppm.

The observations made by Gross [15] and Jain [16] on asymetric distannoxanes, obtained in solution by addition of monofunctional and difunctional centrosymetric distannoxanes, show clearly that changes of substituents on sites 2 and 1′ can strongly affect the difference in chemical shift between unmodified sites 1 and 2′. For example Jain [16] observed the same chemical shift ($\delta = -213.1$ ppm) for both $Bu_2SnO_2(OAc)$ and $Bu_2SnO(OAc)_2$ tin sites (2′ and 1, respectively) when 2 and 1′ tin sites are respectively Bu_2SnO_2F and Bu_2SnOF_2. On the contrary, strong differences between the same 2′ and 1 tin sites ($\Delta\delta = 51.3$ with $\delta = -221.4$ and -170.1) are observed by Gross [15] when 2 and 1′ are respectively Bu_2SnO_2Cl and Bu_2SnOCl_2. But, nevertheless, these strong modifications are imputable to strong effects (due to F or Cl which are quite different from OAc group) at longer distances which are not taken into account in the coordination description.

So, looking backward at the attribution of endo and exo sites in 1,3-diacetoxy distannoxane, that is to say with the same substituents on all four sites, and assuming the effect of a given substituent at longer distance is lower, we consider that with a donor group X (OAc is the present case), joined to the fact that the donor group has a shielding effect on the tin site, then $Bu_2SnO_2(OAc)$ should be expected at lower field compared to $Bu_2SnO(OAc)_2$. Both are expected at higher field than Bu_2SnO_3 which is the coordination type corresponding to Bu_2SnO ($\delta = -172.2$ in the same solvent). This argument may appear questionable, but our assignment seems to be reinforced by the comparison with chemical shift values of a family of l-alcoxy-3-

Table 2
Chemical shift [δ (ppm)] and coupling constant [J (Hz)] values determined by ^{119}Sn and ^{13}C solution NMR in [TCE/C_6D_6], for various difunctional dimeric 1-alcoxy-3acetoxytetrabutyldistannoxanes [$Bu_4Sn_2XYO]_2$ compared with monofunctional 1,3diacetoxytetrabutyldistannoxane (A)

Distannoxane compound		$\delta_{(Sn\ endo)}$	$\delta_{(Sn\ exo)}$	$^2J_{endo-exo}$	$\delta_{(CO)}$
X	Y				
Benzoyl	OCH_3	−215.9	−180.6	67 and 221	171.90
Methylphthalate	OCH_3	−209.6	−180.7	770 and 224	172
O–CO–CH_3	OC_8	−214.5	−182.5	72 and 205	176
O–CO–CH_3	OC_{18}	−214.5	−182	70 and 204	
O–CO–C_8	OCH_3	−218.2	−181.4	72.5 and 217	
X≡Y					
O–CO–CH_3		−219.4	−229.8	122	

acetoxy tetrabutyldistannoxanes. As shown in Table 2 two parent distannoxanes have been prepared [9] by reaction of methylbenzoate and dimethylphthalate in excess with Bu_2SnO, as previously described [7] and have been completely characterised. They differ only by a slight difference on the carboxylic group (X). So, their exo $Bu_2SnO(OCH_3)(OCOPh)$ and endo $Bu_2SnO_2(OCOPh)$ tin sites can be assigned, a difference in chemical shift being expected mainly on the endo sites. The exo sites are therefore assigned at $\delta = -180.6$ and -180.7 in these two compounds. Then tin sites assignments of the last three alcoxyacyloxytetrabutyldistannoxanes of Table 2 may be done by comparison with the previous ones. As for the monofunctional 1,3-diacetoxytetrabutyldistannoxane (A) it seems therefore logical to assign its endo site $Bu_2SnO_2(OAc)$ in the same region as the endo site in the previous family since the nature of the site itself is not modified and as a consequence the exo site $Bu_2SnO(OAc)_2$ should be at $\delta = -229.8$ that is to say more shielded than the endo site. Although these assignments seem supported by some arguments, we do not consider that the tin sites in all diacyloxy distannoxanes can easily be assigned, since in some cases the difference in chemical shift values is particularly small.

As for $^2J_{Sn-Sn}$ coupling constant values (Table 2) we notice that the single coupling observed on the diacetoxytetrabutyldistannoxane(A) is between the two distinct values observed for the family of the 1-alcoxy-3-acyloxytetrabutyldistannoxanes.

2.1. 1-D-^{119}Sn solution NMR

Fig. 2 shows the spectra obtained for various symmetrical (X = Y) distannoxanes. Chemical shift and coupling constant values are given in Table 3. Concerning the assignments it is not debated for the dichloro compound, it remains questionable for the diacetoxy and is discussed in this text, and dimethoxy and diphenoxy compounds are tentatively assigned on the basis of the following observation: exo sites give broader (and less intense) peaks for both chloro and acetoxy compound (Fig. 2a,b) and this feature is unexplained, at now. As for dimethoxy and diphenoxy distannoxanes, for which the difference between exo and endo tin sites chemical shift values are very small, the broader peak is tentatively assigned to the exo tin site by analogy with the above observation. Moreover, the broader peak is sometimes modified in chemical shift and width by temperature and field strength variation so that the broader peak of the diphenoxy compound which is the more deshielded at ambient temperature moves when the temperature raises and becomes the less deshielded. With the four monofunctional distannoxanes investigated, only one coupling constant is observed between the endocyclic and exocyclic sites. The integration value of each peak of the doublet satellite peaks is in the range expected for the coupling of a ^{119}Sn with two Sn sites, namely two times the natural abundance [$^{119}Sn + {}^{117}Sn$].

Since the $^{119}Sn-{}^{119}Sn$ and $^{119}Sn-{}^{117}Sn$ doublets are very poorly or not resolved, and according to the ^{119}Sn and ^{117}Sn natural abundances (respectively 8.58 and 7.61% and a total of 16.2%) the satellites lines corresponding to the scalar couplings between one ^{119}Sn exo site and the endo sites should give a central line with an expected intensity of 0.715 [$0.715 = (1-0.162)^2 + 0.5 \times (0.162)^2$, the last term being the central line of the triplet corresponding to the AX_2 isotopomer] and a satellite doublet with a global intensity of 0.272 [$0.162 \times (1-0.162)$ for each line]. The outside lines of the AX_2 isotopomer are expected to have an intensity of 0.0065 (each) and are not detected. Each peak of the doublet satellite is compared to the global intensity for the different compounds observed, the values obtained are in the range 13–16.4% of the total intensity, which is in rather good agreement with the expected value (0.272/2).

Some distortions of the intensities of the satellite doublets are observed. Figs. 1 and 2e clearly show that

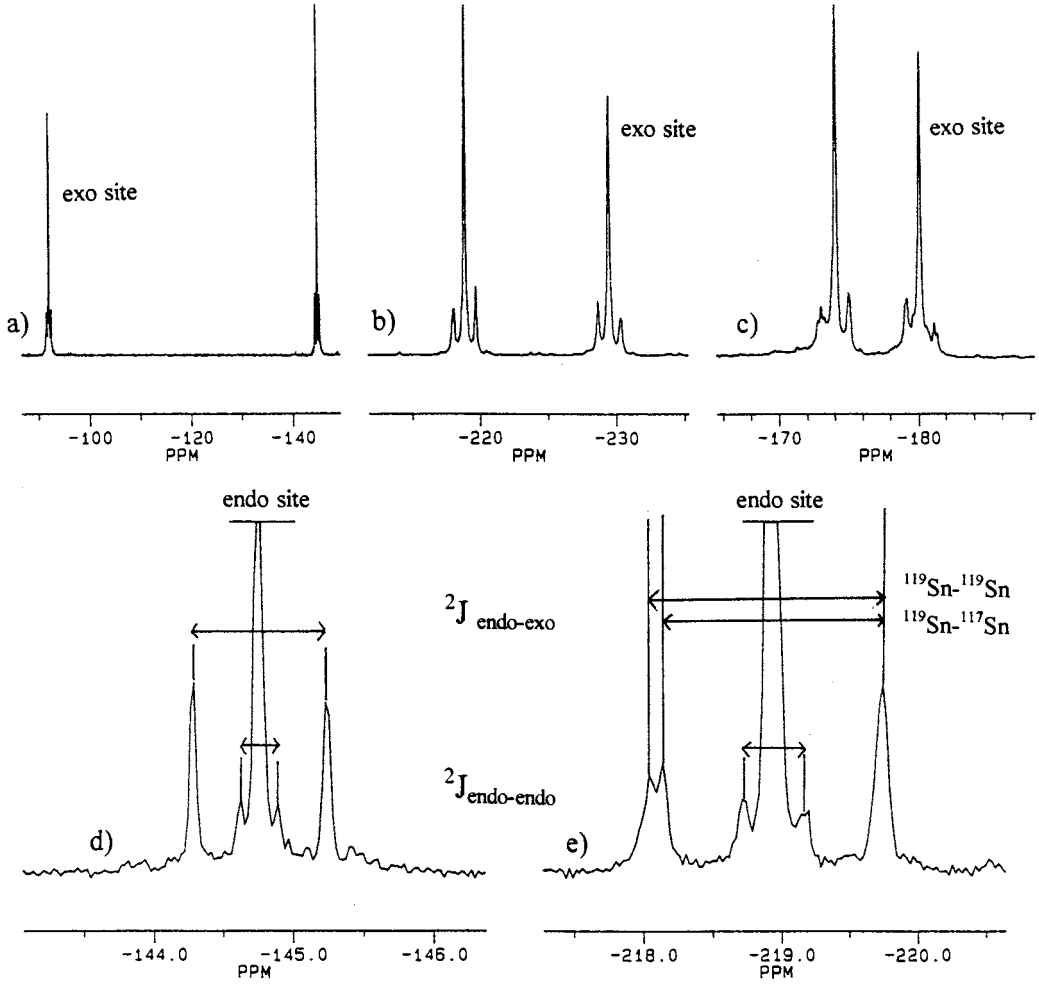


Fig. 2. ^{119}Sn-NMR spectra of various monofunctional dimeric distannoxanes of general formulae $[Bu_4Sn_2X_2O]_2$. (a) X = Cl (C), (b) X = CH_3COO (A), (c) X = OCH_3, (d) enlargement of Sn endo region for X = Cl, (e) enlargement of Sn endo region for X = CH_3COO.

the external component of the satellite doublet is broader and splitted in two peaks attributed to the slight difference (isotopic effect) on both chemical shift and coupling constant values. When $\Delta\nu/J$ is sufficiently low some second order effect can add to the previous effect, but this is not generally the case (the lower values are observed for diacetoxy and dimethoxy compounds as shown on Fig. 2b,c, with $\Delta\nu/J = 6.1$ and 2.7, respectively).

Moreover, the existence of the distannoxane dimer structure (Scheme 1) implies the existence of a $^2J = {}^{119}$Sn endo–^{117}Sn endo coupling as well as a $^4J = {}^{119}$Sn exo–^{117}Sn exo coupling; the corresponding doublets are expected to have a total intensity of 7.6% (natural ^{117}Sn abundance) of the total observed site. It could indeed be the small peaks noticeable, but poorly resolved, at the base of some main peaks of the spectra. Fig. 2d,e show the endo tin resonances of the dichloro and diacetoxy compounds. The measurement of the $^4J_{exo-exo}$ coupling constants—which are found in the same range as the $^2J_{endo-endo}$ (20–30 Hz)—is more difficult on the exo site, because this peak is broader and the though the resolution is not so good. The coupling constants values obtained are reported in Table 3. The fact that $^4J > {}^2J$ for the dichloro compound (C) is rather surprising and since the assignment of the tin sites is not debated for this compound—it is worth noticing that this compound shows a particularly low value (71.5 Hz) of the $^2J_{endo-exo}$ coupling constant—these two features remain unexplained.

2.2. 2-D $^{119}Sn-^{119}Sn$ solution NMR

The ^{119}Sn–^{119}Sn homonuclear correlation of the chemical shifts which we had already used is a way to get out from the lack of resolution already noticed. It allows us, like Otera did but without argumentation [16], to reject definitely the hypothesis according to which one of the two ^2J constants [$^{119}Sn_1$–$^{119}Sn_{2\ or\ 2'}$] is too small for the corresponding satellite doublet to be detected. The 2-D map presented in Fig. 3 was obtained with distannoxane A. It clearly shows the existence of a

Table 3
Chemical shift [δ (ppm)] and coupling constant [J (Hz)] values determined by ^{119}Sn solution NMR in [TCE/C_6D_6], for various monofunctional dimeric distannoxanes [$Bu_4Sn_2X_2O$]

X	δ (ppm)		$^2J_{endo-exo}$ (Hz)		$J_{exo-exo}$	$J_{endo-endo}$
	Sn endo	Sn exo	^{119}Sn–^{119}Sn	^{119}Sn–^{117}Sn	(^4J)	(^2J)
Acetoxy (A)	−219.4	−229.8[a]	127	121	19	34.5
Chloro (C)	−144.6	−92.1		71.5*	31	20
Methoxy	−174.1	−180.1[b]	164[c]			
Phenoxy	−179.5	−178.5[b]		95*		

[a] This assignment first proposed by Otera [14] and first discussed by Michel [7] is supported in the present text by new arguments, it is not in agreement with assignment made by Gross [15].
[b] Tentative assignment, see text.
[c] From 2-D spectrum, the 1-D spectrum being too complex.
* Mean value.

single coupling constant between the endo and exocyclic sites, with $J = 127$ Hz. The correlation peaks only form two sets of four cross peaks due to the intersection between two doublets. This is contrary to the general case represented in Fig. 4 which shows the 2-D map obtained with 1-methoxy-3-benzoxytetrabutyldistannoxane (B), a difunctional (X = Y) compound for which the correlation peaks form sets of eight peaks due to the intersection of two times two doublets.

2.3. CP-MAS ^{13}C solid state NMR

Solid state NMR experiments have been done in a view to evidence—or to rule out—the dynamic origin of the phenomena observed with monofunctional distannoxanes in solution.

Fig. 5 shows the CP-MAS ^{13}C spectrum obtained for A. Contrarily to the spectrum recorded in solution [7], each type of carbon (CH_3 and CO) of the acetoxy groups shows two main resonances (Fig. 5a) situated on both sides of the corresponding chemical shift observed in solution at ambient temperature. Chemical shift values are reported in Table 4. These two regions should correspond to bidentate bridging acetoxy and unidentate acetoxy ligand. Precise assignment is not possible, at present, but whatever it is, this confirms the existence of a dynamic phenomena in solution as suggested by Tiekink. The above observations prove that this exchange reaction no more occurs in solid state.

But a splitting occurs for one of the CO site, as for one of the CH_3 site, poorly resolved in the last case (as shown in Fig. 5b,c, respectively). This indicate two different environments in the crystal for one type of acetoxy group. This second observation has to be correlated with ^{119}Sn-NMR.

2.4. CP-MAS ^{119}Sn solid state NMR

The spectra of several solid state tin carboxylates have already been reported [23,24] but we have not found any concerning distannoxanes.

Fig. 6 shows the CP-MAS ^{119}Sn spectrum obtained for A. Two main resonance regions are observed with nearly the same chemical shifts as previously observed in solution (Table 4). But we notice that the higher field region is split in the solid state and give two well resolved peaks separated by 3 ppm. This is in good agreement with ^{13}C previous observations and allows us to precise that there are two non-equivalent environments for the exocyclic tin atoms if our tin site assignment—discussed herein—is considered as unambiguously established.

This may be due to the crystalline structure of the product. Similar phenomenona have already been observed. For example, Komoroski [23] observed with tributyltinacetate two ^{119}Sn lines ($\delta = -48$ and -54 ppm) of equal intensity which was attributed to two non equivalent environments of the tin atoms in the crystal, they correspond to tin probably pentacoordinated [23,24] due to the observed chemical range which is more shielded than that observed in solution. It should be pointed out that tributyltinacetate provides a CP-MAS ^{13}C spectrum which also exhibits a splitting of the acetyl carbonyl resonance, at 178.6 and 177.9 ppm ($\delta = 175.85$ in solution). The CH_3 of the butyl groups also shows different environments since it is split into two peaks at 14.7 and 14 ppm ($\delta = 13.80$ ppm in solution). Similarly, we observe for A at least three CH_3 (butyl) as shown in Table 4 which indicates in the crystal a more complex situation than a simple differenciation between butyl exo and butyl endo.

So, these solid state NMR experiment allows two different conclusions: a first set of observations (^{13}C) shows the existence of two types of acetyl groups whereas only one is observed in solution which indicate a rapid dynamic phenomenon in solution, no longer possible in solid state. A second set of observations (^{13}C and ^{119}Sn) indicates two types of environments in the crystal for the tin exo site and their acetate ligand, whereas the same type of splittings on the endo site and their bidentate acetate are not detected.

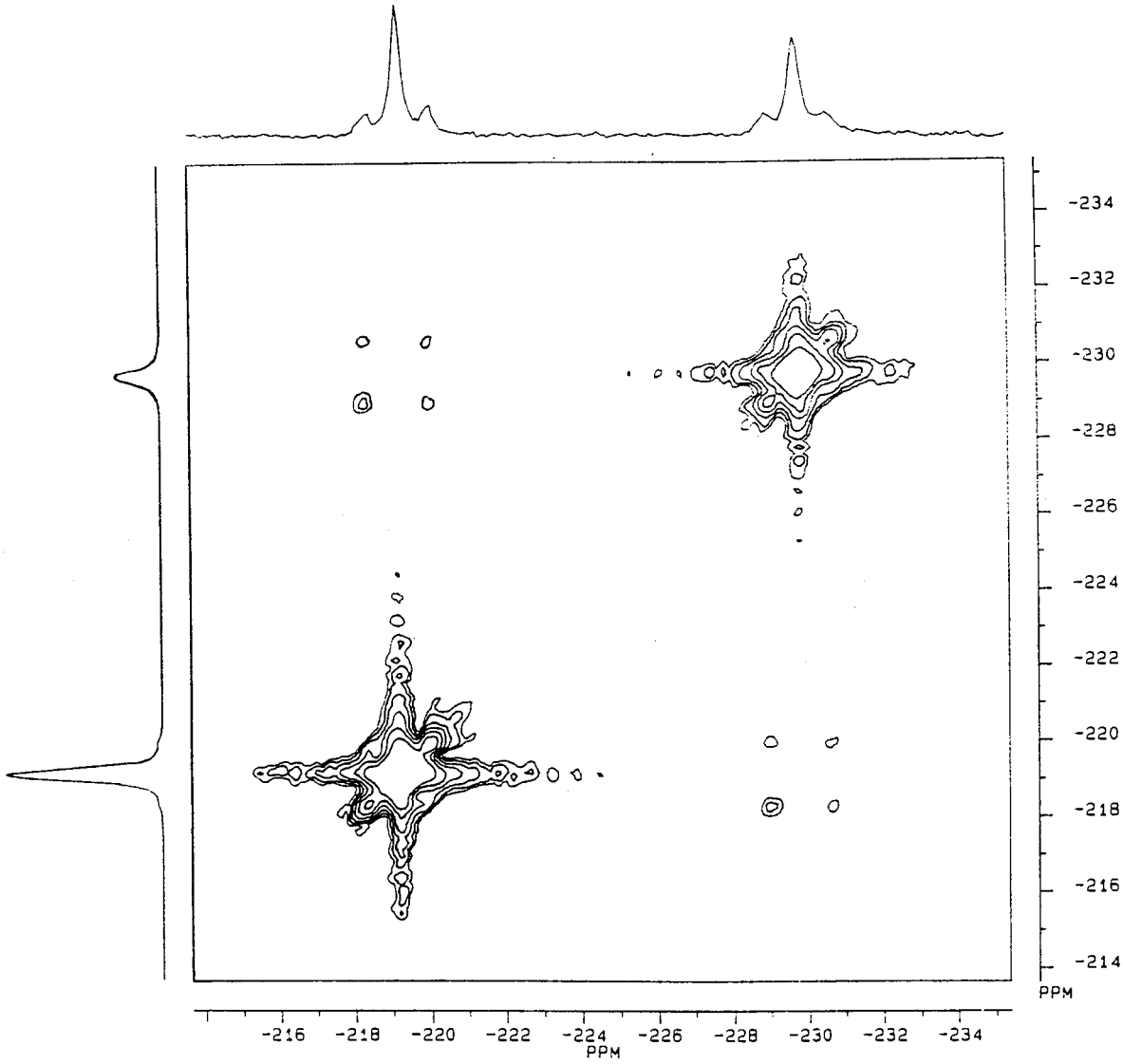


Fig. 3. Contour plot of the 2-D Sn–Sn COSY spectrum of the diacetoxy tetrabutyldistannoxane. Homonuclear chemical shift correlation.

2.5. Nature of the dynamic process and relation with the characteristic NMR spectral features

The dynamic process which is at the origin of the characteristic NMR spectral features is most probably an intradimeric one since it does not seem to be concentration dependent, chemical shift values observed in solution being nearly constant. It is worthy of note that, for the same reasons, we have previously concluded [7] that the equilibrium between monomeric and dimeric forms in distannoxanes is almost completely shifted towards the dimeric entity and also because the tin chemical shifts observed correspond to particularly highly shielded pentacoordinated sites.

This intramolecular dynamic exchange, first suggested by Tiekink with monofunctional 1,3-acyloxydistannoxanes and which has been evidenced here with four monofunctional tetrabutyldistannoxanes, is represented more generally by Scheme 3.

The characteristics of this exchange are such that:

- endocyclic tin sites always remain endo, the same for related butyl groups
- exocyclic tin sites always remain exo, the same for related butyl groups. In ^{119}Sn- and ^{13}C-NMR as well no chemical shift modifications are observed on main tin resonances and on butyl carbons
- the X group bridging two tin sites in one form becomes an X ligand in the other form and reversely. So, in ^{13}C-NMR average chemical shifts are observed for typical carbons of X groups (as we have shown with $X = CH_3COO$ and X = phenoxy)
- the most striking observations concern the averaging of $^2J_{endo-exo}$ couplings observed in all cases.

An exocyclic tin 1 coupled with a coupling constant ^2J_a, through two covalent bonds [Sn_1–O–Sn_2] to an endocyclic tin 2, becomes an exocyclic tin coupled

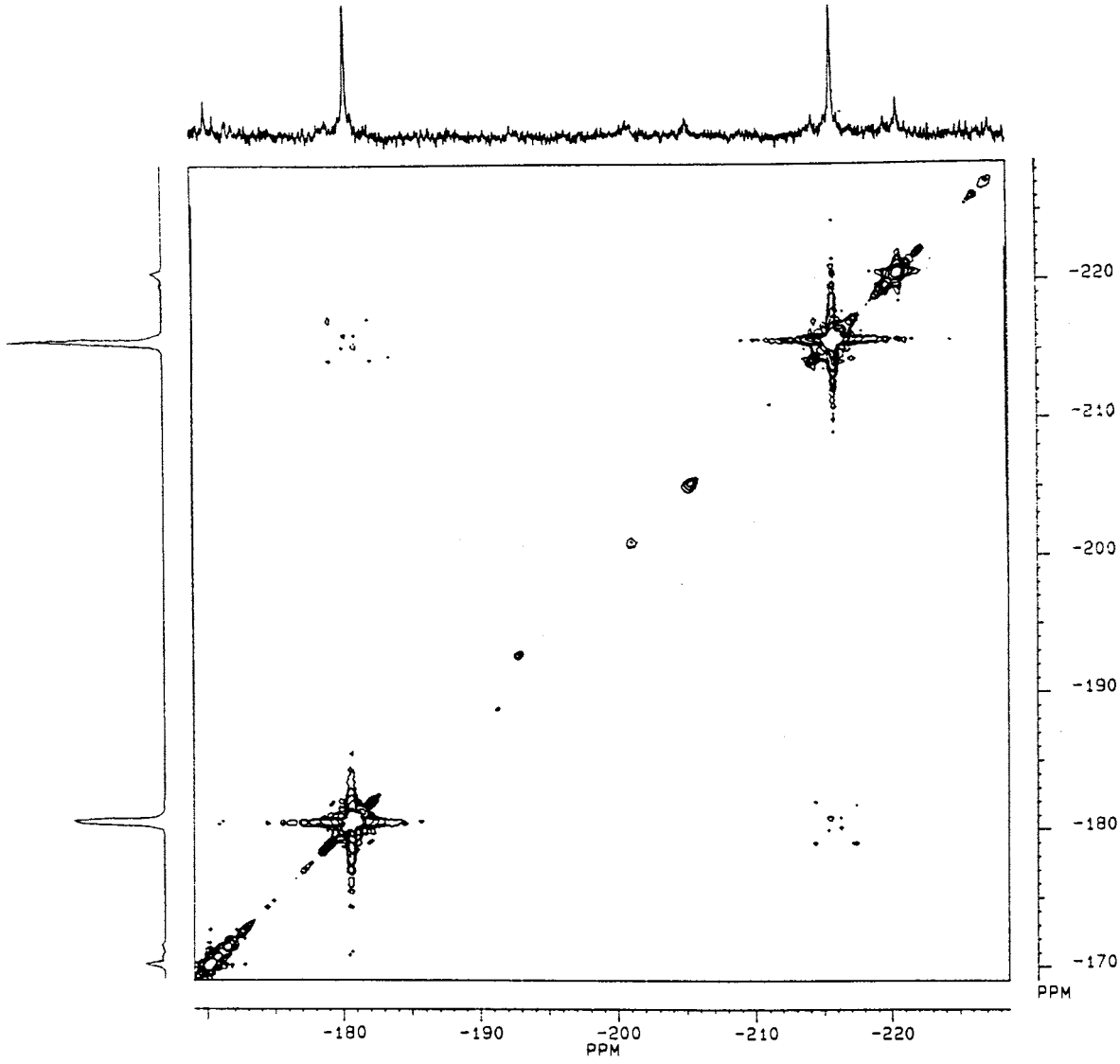


Fig. 4. Contour plot of the 2-D Sn–Sn COSY spectrum of the 1-methoxy-3-benzoxytetrabutyldistannoxane (B) obtained by reaction of dibutyltinoxide with methylbenzoate. Homonuclear chemical shift correlation.

with a constant ^2J_b, through a covalent and a coordination bond [Sn_1–O→Sn_2] to the same endocyclic tin, and the same holds for [$Sn_{1'}$–O–$Sn_{2'}$] which becomes [$Sn_{1'}$–O→$Sn_{2'}$]. Reversely [Sn_1–O→$Sn_{2'}$] becomes [Sn_1–O–$Sn_{2'}$]. The rearrangement being rapid the apparent Sn–Sn coupling observed is an averaged value between ^2J_a and ^2J_b, the two satellite doublets merging into a single one.

The satellite doublet observed on both endo and exo sites of the ^{119}Sn-NMR spectra allows to calculate the averaged $^2J_{exo-endo}$ value [($^2J_a + {}^2J_b$)/2]. Generally ^{119}Sn–^{119}Sn and ^{119}Sn–^{117}Sn couplings are poorly or not resolved.

This equilibrium may occur since all ligands of the dimer tin atoms (other than the butyls) are identical (X≡Y). Therefore, they are interchangeable. This holds for monofunctional distannoxanes [$Bu_4Sn_2X_2O$] but not for the general case of difunctional distannoxanes [Bu_4Sn_2XYO] in which the structure is frozen since the best donor ligand (X) automatically bridges the exo and endo tin atoms.

Moreover, this equilibrium requires changes in the interatomic distances and bonding angles, and thus mobility, so it may only occur in the liquid state, therefore in solution. In the solid state, everything is frozen, the exchange does not take place and the CP-MAS spectrum agrees with X-ray observations of homologous compounds. For the same reason the dynamic process is probably influenced by steric hindrance of X groups.

In the case of compound (A) the equilibrium is represented in Scheme 2 which shows the change from bridging acetoxy to ligand acetoxy. A confirmation of this intramolecular dynamic process in solution is given

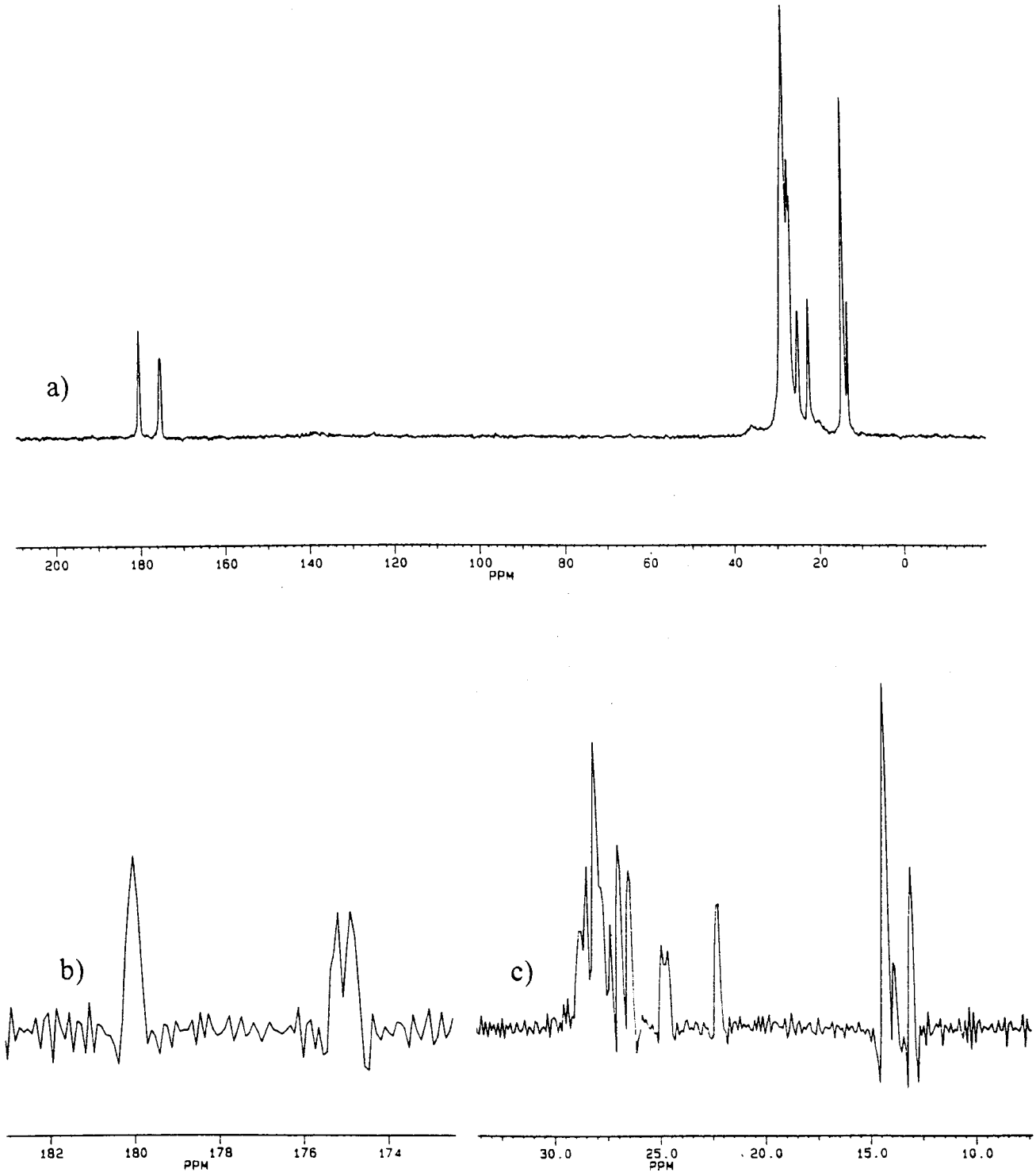


Fig. 5. CP-MAS ^{13}C solid state NMR spectrum of the 1,3-diacetoxytetrabutyldistannoxane (A). (a) Global spectrum obtained by FID processing with an exponential window function, (b) enlargement of the carbonyl resonances obtained by FID processing with a Lorentz-Gauss function for resolution enhancement, (c) enlargement of the aliphatic resonances obtained by FID processing with a Lorentz-Gauss function for resolution enhancement.

by the spectroscopic observations at different temperatures. As shown in Fig. 7 two methyl resonances are observed at $T = 188$ K, corresponding to a slow exchange process, whereas two signals can no longer be distinguished at $T = 243$ K the rate of exchange being sufficiently rapid.

The existence of this equilibrium shed light on others observations.

Table 4
Comparison between ^{119}Sn and ^{13}C-NMR chemical shift values, measured in solution and in the solid state, for dimeric 1,3-diacetoxytetrabutyldistannoxane (A)

	δ Liquid state (ppm), 293 K		δ Solid state (ppm), 293 K	
	endo	exo[a]	endo	exo
^{119}Sn	−219.4	−229.8	−213	−226; −229
^{13}C			Bridging acetoxy endo–exo	Acetoxy ligand exo
>C=O	176.9		180	175.1; 174.8[a]
$\underline{C}H_3$–COO	22.85		22.15	24.8; 24.6[a]
CH_3 (butyl)	13.85		14.2; 13.8; 13.0	

[a] Tentative assignment, see text.

2.6. Intermolecular dimeric equilibrium between two different monofunctional distannoxanes

While the reaction between two bifunctional distannoxanes leads to the following equilibrium [8]:

$$[X'Bu_2SnOBu_2SnY']_2 + [XBu_2SnOBu_2SnY]_2 \rightleftharpoons 2[(Y'Bu_2SnOBu_2SnX')\ (XBu_2SnOBu_2SnY)]$$

Gross showed that two monofunctional distannoxanes irreversibly react according to the following equation [15]:

$$[XBu_2SnOBu_2SnX]_2 + [X'Bu_2SnOBu_2SnX']_2 \rightarrow 2[XBu_2SnOBu_2SnX']_2$$

This reaction implies a ligand exchange on tin atoms, for which the mechanism has not yet been clearly elucidated. From our studies hereby reported, we can propose the mechanistical Scheme 4. The first step consists in forming a new dimer—by an interdimeric process—unstable if X and X′ have not the same donor ability. Let us suppose X is a better donor than X′, X_a will then link onto Sn_b, while X'_b will become a simple ligand of Sn_a. Then a configurational rearrangement will yield irreversibly to the stable dimer of the new bifunctional distannoxane. When an equimolar quantity of 1,3-diacetoxytetrabutyldistannoxane in solution is added to a solution of 1,3-dimethoxytetrabutyldistannoxane the ^{119}Sn-NMR spectrum shows instantaneously two new resonances ($\delta = -179.35$ and -214.74) each of them with two different ^2J couplings

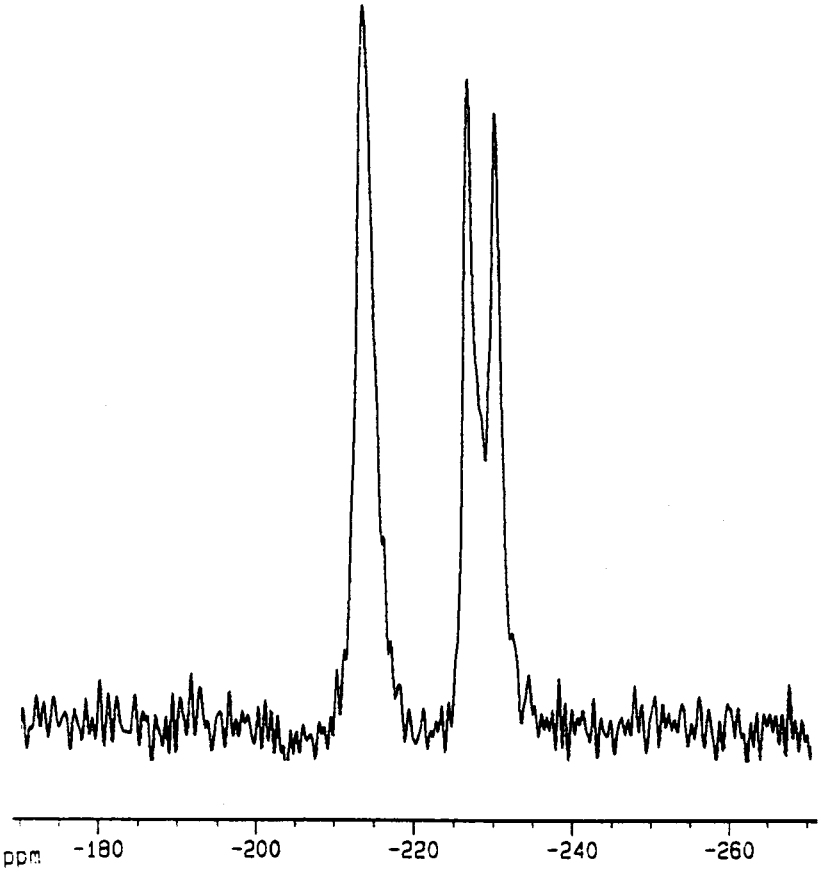
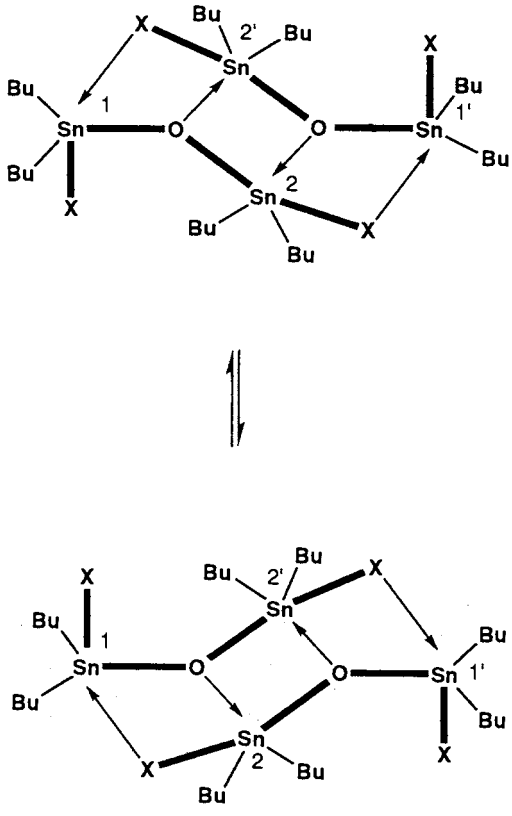


Fig. 6. CP-MAS ^{119}Sn solid state NMR spectrum of the 1,3-diacetoxydibutyldistannoxane (A): enlargement of σ iso region.



Scheme 3.

($^2J = 209$ and 64 Hz). The spectrum obtained is typical of pure, difunctional l-alcoxy-3-acetoxytetrabutyldistannoxane as previously obtained [7–9] by reaction of an ester with Bu_2SnO (Fig. 1). The individual solutions of the parent monofunctional distannoxanes, have already been fully characterised [8] and show only a mean $^2J_{exo-endo}$ value (Table 3). Then we can conclude that both the ligand exchange and the intradimeric rearrangement are very rapid, at the NMR scale, so that the intermediate species postulated by Scheme 4 cannot be evidenced.

2.7. Intradimeric distannoxane rearrangement and catalytic efficiency in redistributive transesterification

In the frame of a comparative study of catalytic efficiency of different tin compounds in the redistributive transesterification reaction at 413 K, without any solvent, we observed differences between different types of distannoxanes [8]. Fig. 8 shows the reaction rate of the transesterification between methyl myristate and stearyl acetate *versus* time, with various catalysts. We notice a catalytic activity almost identical for diacetoxytetrabutyldistannoxane (A) and dichlorotetrabutyldistannoxane (C), whereas 1-acetoxy-3-octyloxytetrabutyldistannoxane (D) exhibits a considerably higher activity than the previous compounds. The corresponding rate constants are 4.2, 4.1 and 13.5 l mol^{-1} min^{-1}, respectively. It has been shown [8] that, for the last distannoxane, alcoxy ligand exchange occurs in presence of an ester at the exocyclic alcoxytin site, whereas no ligand exchange occurs with compound A and B at this temperature, then Espinasse et al. [8] concluded to a catalytic activity based on a complexation of the carbonyl group of the ester by the dimeric distannoxane noticeably favoured by the preliminary alcoxy ligand exchange in the last case. These two types of contributions were in good agreement with previous important works in the field of catalytic activity of organometallic compounds [25–27].

However, A and C are monofunctional distannoxanes (X≡Y) for which the equilibrium depicted in Scheme 3 occurs in solution, contrarily to D which is a difunctional distannoxane (X ≠ Y) in which the acetoxy ligand has a much higher donor ability than the alcoxy one and the distannoxane has a more stiff structure. The same difference probably holds in bulk at 413 K. The intramolecular rapid rearrangement of dimers A and C is a factor of reduction of the catalytic efficiency since it should disturb the carbonyl ester complexation on neighbouring exo and endo tin sites.

2.8. Modelisation of the movements required for this rearrangement

From the rigid crystalline distorted trigonal bipyramidal structure established by X-ray analysis for this type of compounds by other authors [17–19] and using a modelisation program to simulate the rearrangement (BIOSYM-MSI crystal builder module) it appears that this rearrangement requires only slight bond angle and distance modifications as shown in Fig. 9. This figure is deduced from the crystalline structure of 1,3-di-*t*-butylcarboxylatotetraethyldistannoxane previously established by Tiekink [19]. It shows that the major movements required are (1) a twisting of the central diamond –Sn–O–Sn–O– (schematically represented as ⇔ and in which d_2 becomes equal to d_1, and reversely, α angle becomes equal to β angle and reversely and (2) a rotation (↷) around Sn–O bond of the free Sn–OCO*t*-butyl ligand.

3. Experimental

3.1. Reagents

Dibutyltin oxide, n-octyl acetate and diphenylcarbonate were commercial products (Aldrich).

3.2. Reaction of dibutyltin oxide with model esters (typical procedure)

Equimolar amounts (0.032 mol) of dibutyltin oxide

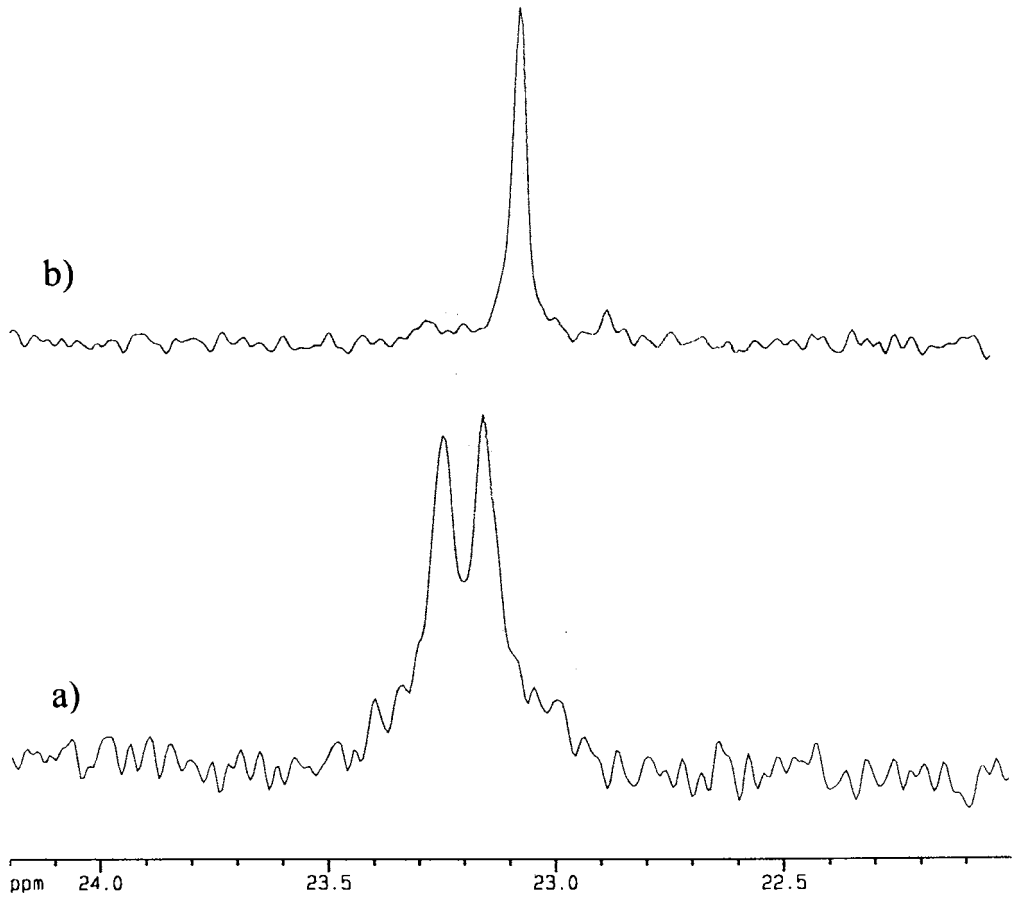


Fig. 7. ^{13}C-NMR spectra of 1,3-acetoxytetrabutyldistannoxane (A) in toluene-d8 at different temperatures: enlargement of CH_3 resonance region, (a) $T = 188$ K, (b) $T = 243$ K.

and ester (n-octyl acetate) were mixed in a reactor equipped with a magnetic stirrer and a reflux condenser. The mixture was heated at 200°C. After a few minutes the mixture became clear. After cooling, an oily, colourless, translucent liquid which is not crystallisable was obtained. Characteristic NMR (^{1}H-, ^{13}C- and ^{119}Sn-) spectral features of this distannoxane have been given previously [8].

3.3. Preparation of 1,3-diacetoxytetrabutyldistannoxane (A)

Two methods are available [22], reaction of acetic acid with dibutyltin oxide and partial hydrolysis of dibutyltin diacetate. The second method was used and a white, crystalline distannoxane was obtained. $C_{20}H_{42}O_5Sn_2$ (599.4) requires C, 40.04; H, 7.01; Sn, 39.60; found: C, 40.05; H, 7.09; Sn, 40.42%. All characteristic NMR chemical shifts have been given previously [8].

3.4. Preparation of 1,3-dimethoxytetrabutyldistannoxane (in dilute solution)

This distannoxane was prepared by addition of water (0.031 g, 1.74 mM) to a solution of dimethoxy dibutyltin (10.25 g, 3.48 mM) in 10 ml of tetrachloroethylene. Methyl alcohol formed during the reaction was not eliminated. There was a rapid exchange (at the NMR scale, 250 MHz) between free methyl alcohol and methoxy tin ligands, at room temperature. An average chemical shift value for methoxy protons was observed. All characteristic NMR chemical shifts have been given previously [8].

3.5. Preparation of 1,3-dichlorotetrabutyldistannoxane(C)

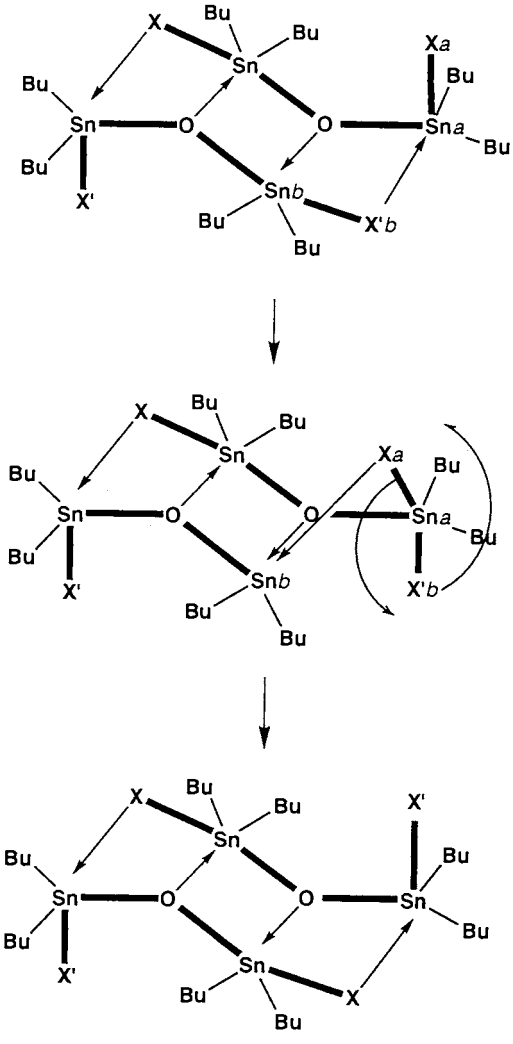
This crystalline compound is obtained by partial hydrolysis of Bu_2SnCl_2. All characteristic NMR spectral features are given in Tables 1 and 3.

3.6. Preparation of 1,3-diphenoxytetrabutyldistannoxane

This crystalline compound is obtained by reaction at 160°C of diphenylcarbonate (0.100 mol) and dibutyltinoxide (0.200 mol). After 15 min the mixture became clear and the carbon dioxide is completely evolved. After cooling, a white, crystalline product is obtained. $C_{28}H_{46}O_3Sn_2$ (668) requires C, 50.34; H, 6.94, O, 7.18; Sn, 35.54; found: C, 50.17; H, 7.00; O, 7.20; Sn, 35.63%. $P_F = 146$°C. All characteristic NMR spectral features are given in Tables 1 and 3.

3.7. NMR spectroscopy

High-resolution liquid NMR spectroscopy was carried out with a Bruker AC 200, Bruker AC250 or Bruker DRX400 instrument. ^1H was observed at 200, 250 or 400 MHz, ^{13}C was observed at 62.9 or 100.6 MHz and ^{119}Sn was observed at 74.6 or 149.2 MHz. Tetrachloroethylene (TCE)/deuterated benzene (C_6D_6) mixtures (2:1 by volume) were used as solvents. Chemical shifts values (δ) are in ppm with reference to internal tetramethylsilane (TMS) for ^1H and ^{13}C, and to external tetramethyltin for ^{119}Sn. Coupling constants values (J) are given in Hertz.



Scheme 4.

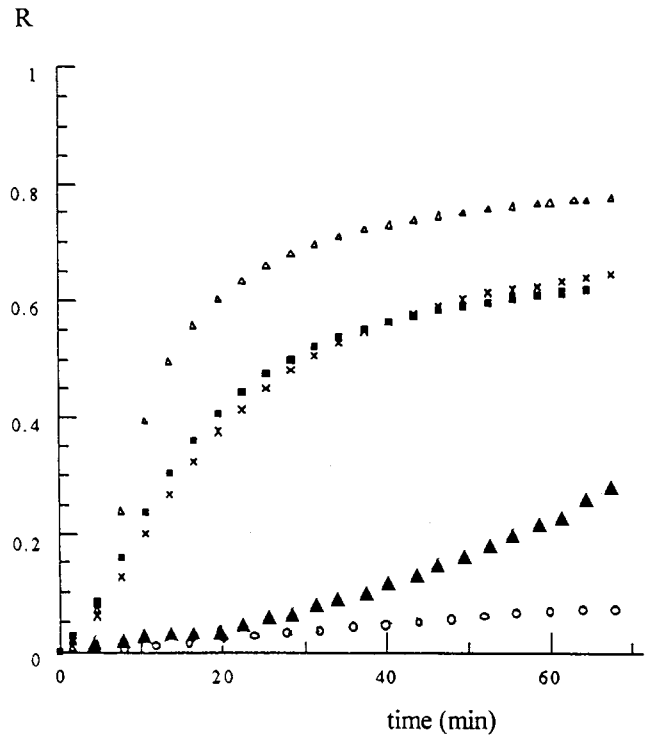


Fig. 8. Reaction rate versus time in the transesterification between methyl myristate and stearyl acetate at 413 K with different catalysts: (○) without catalyst, (▲) dibutyltindiacetate, (x) 1,3-diacetoxytetrabutyldistannoxane (A), (■) 1,3-dichlorotetrabutyldistannoxane (C), (△) 1-acetoxy-3-octyloxytetrabutyldistannoxane.

The Broker COSYX.AU microprogram was used for the $^{119}Sn-^{119}Sn$ COSY spectrum, 128 experiments were used to create the F1 domain, with 288 scans for each; 512 data points were used for acquisition with no zero-filling in the F2 dimension. A fixed delay of 3.448 ms was added to the variable delay between the two 90° pulses. A square sine-bell filter or a Lorentz-Gauss was used in both dimensions.

Solid-state NMR spectra were obtained with CP-MAS (cross polarisation, magic angle spinning) techniques with a Bruker AC200 at 50.3 MHz for ^{13}C and and Bruker DSX 300 at 111.9 MHz for ^{119}Sn.

For ^{13}C typical conditions were: 90 RF pulse, 5.4 μs; contact time, 2 ms; pulse repetition time, 6 s; MAS rate 4 KHz; 1024 scans were run.

For ^{119}Sn, dibutyltinoxide is used to set Hartman-Hahn condition for cross polarisation; typical conditions were: 90 RF pulse, 2.8 μs; contact time, 10 ms; pulse repetition time, 10 s; MAS rate, 8 KHz. σ iso was determined after variation of the spinning rate in order to discriminate it from the spinning side bands. Chemical shift values are given in ppm relative to Me_4Sn; for

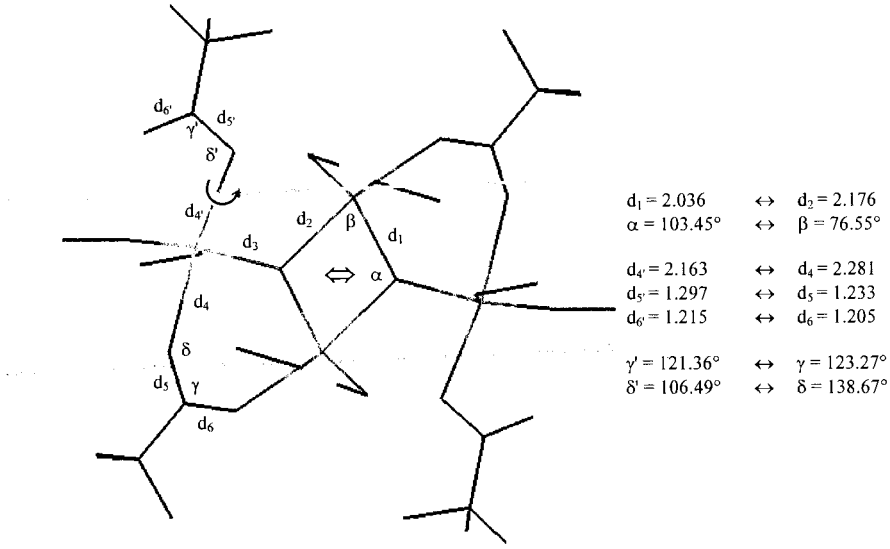


Fig. 9. Molecular structure of solid dimeric 1,3-di-*t*-butylcarboxylato-tetraethyldistannoxane (from reference [17]) and schematic representation of bond angles and distances.

that purpose the two peaks observed for $Bu_3SnOCOCH_3$ were assigned to $\delta = -48$ and -54 ppm, which are the chemical shift values previously evidenced by Komoroski [23] relative to Me_4Sn.

4. Conclusion

Owing to the analysis of a set of 1-D and 2-D ^{13}C- and ^{119}Sn-NMR experiments—both in solution and in solid state—it has been established that dimers of monofunctional tetrabutyldistannoxanes $[R_4Sn_2X_2O]_2$ rapidly rearrange in solution by an intradimeric dynamic process. In solution at 188 K and in solid state this rearrangement is frozen. This rearrangement probably reduces the ability of these monofunctional tetrabutyl distannoxane to activate carbonyl reactivity by complexation with exo and endo tin sites. It contributes then to explain the lower catalytic activity of these monofunctional distannoxanes compared to 1-alcoxy-3-acyloxytetrabutyldistannoxanes observed in the redistributive transesterification of EVA and EMA polymers in bulk.

Acknowledgements

The authors acknowledge Dr Patrick Masson (Institut de Physique et Chimie des Materiaux de Strasbourg) for crystalline patterns obtained from literature data (BIOSYM-MSI crystal builder module).

References

[1] I. Descheres, Q.T. Pham, Makromol. Chem. 188 (1987) 1909.
[2] I. Descheres, Q.T. Pham, Makromol. Chem. 191 (1990) 891.
[3] Y. Hori, M. Suzuki, A. Yamaguchi, T. Nishishita, Macromolecules 26 (1993) 5533.
[4] J.E. Kemnitzer, S.P. McCarthy, R.A. Gross, Macromolecules 26 (1993) 6143.
[5] G.H. Hu, Y.J. Sun, M. Lambla, Makromol. Chem. Macromol. Chem. Phys. 194 (1993) 665.
[6] P. Cassagnau, M. Bert, V. Verney, A. Michel, Polymer 34 (1993) 124.
[7] J. Bonetti, C. Gondard, R. Pétiaud, M.F. Llauro, A. Michel, J. Organomet. Chem. 481 (1994) 7.
[8] I. Espinasse, R. Pétiaud, M.F. Llauro, A. Michel, Int. J. Polymer Anal. Charact. 1 (1995) 137.
[9] C. Lacroix, M. Bousminá, P. Carreau, M.F. Llauro, R. Petiaud, A. Michel, Polymer 37 (1996) 2949.
[10] I. Pesneau, M.F. Llauro, M. Gregoire, A. Michel, J. Appl. Polymer Sci. 65 (1997) 2457.
[11] O. Primel, Doctorate Thesis, University of Lyon, France, 1996.
[12] R. Okawara, M. Wada, J. Organomet. Chem. 8 (1967) 261.
[13] J. Otera, T. Yano, K. Nakashima, R. Okawara, Chem. Lett. (1984) 2109.
[14] T. Yano, K. Nakashima, J. Otera, R. Okawara, Organometallics 4 (1985) 1501.
[15] D.C. Gross, Inorg. Chem. 28 (1989) 2355.
[16] V.K. Jain, V.B. Mokal, P. Sandor, Magn. Reson. Chem. 30 (1992) 1158.
[17] E.R.T. Tiekink, Appl. Organomet. Chem. 5 (1991) 1.
[18] E.R.T. Tiekink, M. Gielen, A. Bouhdid, M. Biesemans, R. Willem, J. Organomet. Chem. 494 (1995) 247.
[19] C. Vatsa, V.K. Jain, T. Kesavadas, E.R.T. Tiekink, J. Organomet. Chem. 408 (1991) 157.
[20] P.G. Harrison, M.J. Begley, K.C. Molloy, J. Organomet. Chem. 186 (1980) 213.
[21] R.K. Harris, J.D. Kennedy, W. McFarlane, NMR and the Periodic Table, Academic Press, London, 1978, p. 348.
[22] Y. Maeda, R. Okawara, J. Organomet. Chem. 10 (1967) 247.
[23] R.A. Komoroski, R.G. Parker, A.M. Mazany, T.A. Early, J. Magn. Reson. 73 (1987) 389.
[24] K.C. Molloy, Inorg. Chim. Acta 141 (1988) 151.
[25] M. Pereyre, G. Colin, J.P. Delvigne, Bull. Soc. Chim. Fr. 262, (1969).
[26] K. Tomita, Polymer 17 (1976) 221.
[27] J. Otera, N. Dan-oh, H. Nozaki, J. Org. Chem. 56 (1991) 5307.