Group 4 Organometallic Reagents. A ^{1}H, ^{13}C, and ^{119}Sn Nuclear Magnetic Resonance Study on 2,2-Dibutyl-1,3,2-dioxastannolane Structure in Solution

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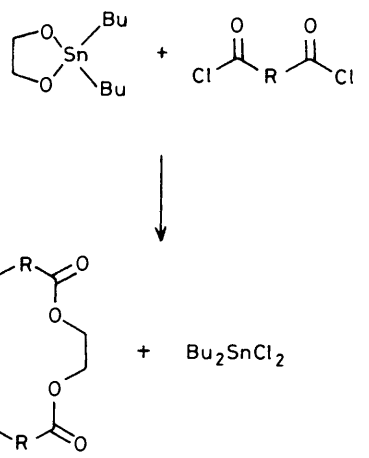
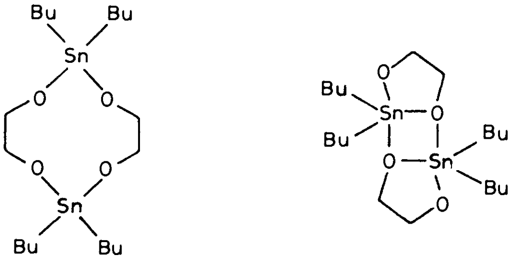
The behaviour of 2,2-dibutyl-1,3,2-dioxastannolane (DOS) in chloroform solution has been investigated by concerted ^{1}H, ^{13}C, and ^{119}Sn n.m.r. spectroscopy at variable temperatures; the results are compared with previous reports. A complex pattern of association equilibria involving the five-membered DOS is evident. The controversy about the dimeric structure of the title compound has been composed assigning to the dimer a 'fluxional type' structure in which a fast intramolecular shift with inversion at tin is responsible for the apparent high symmetry features of the molecule. The energy barrier relative to fluxional exchange is of the order of 42 kJ mol^{-1}. The interconversion of four-, five-, and six-co-ordinate tin species represents a new example of configurational instability of the organotin compounds.

Dioxastannolanes are useful intermediates in synthesis[1] because of their high selectivity in reactions with electrophiles; for this reason they have been widely used by the organic chemist in the past few years. As a recent and original application, the use of the Shanzer reaction of stannoxanes with dicarboxylic acid dichlorides in apolar solvents[2] [equation (1)] has been proved to be a very powerful tool for obtaining macrocyclic tetraesters in a single-step procedure, with remarkable yields and outstanding regio- and stereo-selectivity.



(1)

Fully developing the scope of such reaction is highly desirable because of its versatility in organic synthesis; this requires a somewhat more detailed study on the reaction mechanism, which appears to be complex and intriguing, to understand better the origin of stannoxane selectivity. In this contest, we needed to establish the structure of the reactant in solution. Despite the fact that the structure of 2,2-dibutyl-1,3,2-dioxastannolane (DOS) has been widely studied,[3,4] there are some basic points about its structure still unexplained. Many authors[5–12] have established a dimeric structure for 1,3,2-dioxastannolane and substituted analogues in apolar non-co-ordinating solvents as the only species present in solution and a higher aggregated polymeric structure in the solid state. Monomeric DOS appears in solution in detectable concentration only when bulky substituents are present in the molecule;[10] the same effect seems to be induced by increasing the temperature and dilution. While high concentrations are believed to give rise to aggregation greater than dimeric,[3] the molecule is still dimeric in the gas phase.[8]



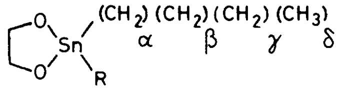
(1) (2)

Scheme 1.

These interpretations rest on a wide variety of data measured in solution, *i.e.* osmometric molecular weights, i.r., ^{1}H and ^{119}Sn n.m.r. spectroscopy, as well as in gas phase, *i.e.* field-desorption mass spectrometry and in solid state, *i.e.* ^{119}Sn Mössbauer spectroscopy and a fair choice of *X*-ray crystallographic data, mostly of DOS derivatives of carbohydrates.

To the dimeric species two different types of general structures have been assigned, as shown in Scheme 1. Structure (**1**), equivalent to that generally adopted by Shanzer and his co-workers,[2] suffers from the basic disadvantage that does not account for the pentaco-ordination of tin, as shown by ^{119}Sn n.m.r. and Mössbauer spectroscopy.[3] Structure (**2**), instead, at first glance, is in excellent agreement with all the physical data found by different workers. Moreover, it is similar to the crystallographic structures so far found.[5,7] The ^{119}Sn behaviour resulted from symmetry, showing only a single resonance for most compounds considered. It is relevant that for ^{119}Sn n.m.r. both chemical shifts and linewidths are markedly dependent on concentration and temperature: downfield shifts are observed in cases where the dissociation to monomer is favoured. This seems to be strongly suggestive of chemical exchange phenomena. Moreover, in the case of unsubstituted DOS, there is a striking discrepancy with the proposed structures in ^{1}H and ^{13}C n.m.r. spectra. The chemical difference arising from the well established regioselectivity towards electrophiles[1,12] of the two pairs of oxygen atoms in the dimer (**2**) should be reflected in the magnetic non-equivalence of the adjacent methylenes; in fact, as observed for

Table 1. ^1H, ^{13}C, and ^{119}Sn n.m.r. spectral data for 2,2-dibutyl-1,3,2-dioxastannolane (DOS)[a]



				CH_2O	Sn	$(CH_2)_\alpha$	$(CH_2)_\beta$	$(CH_2)_\gamma$	$(CH_3)_\delta$
^1H[b]	Ass.	δ	(Linewidth)	3.611 (1.2)		1.287{t(m)}	1.624 (m)	1.362 (sept.)	0.907 (t)
		^nJ		31 (^1H $^{117/119}Sn$)		8.2 (8.8)		7.5	7.5
	Mon.	δ	(Linewidth)	3.674 (1.8)					
^{13}C[c]	Ass.	δ		62.89		22.27	27.27	26.76	13.34
		$^nJ(^{13}C\ ^{117/119}Sn)$		38		643	31	101	38
	Mon.	δ		64.06					
^{119}Sn[d]		δ	(Linewidth)		−181 (180)				

[a] Spectra were performed at 33 °C on a 0.85M solution in $CDCl_3$ at 20 MHz for ^{13}C, 29.648 MHz for ^{119}Sn, and on a 0.2M solution at 300 MHz for ^1H. [b] Values are from Me_4Si, using $CHCl_3$ as a secondary internal reference at δ 7.26. Half-height linewidths given in Hz where measured. [c] δ Values given in p.p.m. from Me_4Si, using $CDCl_3$ as a secondary internal reference at δ 76.89 p.p.m. Data attributions were based on ref. 14. Spectra recorded under proton-noise decoupling conditions. [d] δ Values given in p.p.m. from Me_4Sn in $CDCl_3$ as external reference. Half-height linewidths in Hz. Spectra were recorded under proton-noise decoupling conditions.

(2), they cannot give rise to a single resonance on the basis of pure geometry or symmetry considerations: ^1H Spectra should therefore show two coupled signals while proton-decoupled ^{13}C spectra should consist of two different resonances. Preliminary spectra, surprisingly, revealed sharp single resonances for both nuclei, both flanked by well resolved satellite bands corresponding to coupling of ^{13}C and ^1H with $^{117/119}Sn$ nuclei. This evidence is only consistent with a monomeric structure for DOS, which has been ruled out by all other physical data.* To overcome these inconsistencies and to give a clearer basis to our mechanistic and synthetic objective, we decided to investigate the unsubstituted DOS system in the same medium (*i.e.* in chloroform solution) used in Shanzer's reaction and we chose n.m.r. as the appropriate technique for the purpose.

We report here the results obtained in this study using combined ^1H, ^{13}C, and ^{119}Sn n.m.r. spectroscopy.

Results and Discussion

Table 1 reports n.m.r. spectral data for DOS obtained at 33 °C. In the ^1H spectrum we could observe a single, sharp resonance for the ring methylene groups, flanked by tin satellites. At 0.065 p.p.m. downfield is a smaller single signal, which we assigned to monomeric DOS, in line with the general interpretation. The small but definite down-field shift of the monomer is in agreement with the expected deshielding effect due to 'free' oxygen with respect to 'ligated' oxygen. The signal is somewhat broad and, together with the observation of two separated lines, it leads to the conclusion that dissociation into monomeric DOS should be slow on the ^1H n.m.r. time scale. The two $^{117/119}Sn$ satellite bands (^3J average coupling constant is 31 Hz with every field applied) arise from very similar coupling of ^1H with both tin nuclei.

From the ^{13}C n.m.r. spectra we obtained basically the same kind of information: associated DOS presents one single sharp signal for each butyl carbon and for the ring methylenes, all coupled with $^{117/119}Sn$ nuclei: this can only be due to high 'average' symmetry and stable bonding of tin to carbon and oxygen, at least on the ^{13}C time scale. A small signal due to monomeric DOS is also present at 1.17 p.p.m. downfield from the main signal, just as observed in the ^1H spectrum. The ^{119}Sn n.m.r. spectrum shows a single band at a chemical shift in the range for pentaco-ordinate tin, but much shifted towards the upper limits of this range. The large linewidth value of 180 Hz is noteworthy: David and his co-workers[8] have reported linewidth values of 3 Hz for substituted DOS and, since accidental causes for line broadening were carefully avoided in our experiments, it was concluded that the linewidth observed cannot be the 'natural' linewidth.

Table 2. Effect of increasing magnetic field on the ^1H n.m.r. signal of CH_2O moiety of DOS[a]

Field[b]	80	90	300	400
$\Delta\nu^c_{(mon.-ass.)}$	not resolved	6	19	26
Linewidth$^d_{mon.}$		broad	1.8	1.7
Linewidth$^d_{ass.}$		1.8—2.0	1.2	1.5

[a] Data measured for a 0.2M solution of DOS in $CDCl_3$ at room temperature. [b] Applied magnetic field in MHz. [c] Values in Hz for the separation between monomeric and associated DOS signals. [d] Half-height linewidth in Hz.

All these experimental data, while supporting the existence of association equilibria and of associate species being the major component in solution, namely dimeric DOS with pentaco-ordinate tin atoms, at the same time showed fast 'averaging' dynamic processes which required further investigation.

To verify the consistency of the dissociative scheme, ^1H spectra were performed at increasing dilution from an initial saturated solution at 33 °C and the most representative spectral features are shown in the Figure. The resulting pattern is typical for a dissociative equilibrium, with increasing amounts of monomer upon dilution. Obviously, separate signals imply slow exchange, but at 90 MHz of applied field the monomer line is broad. Applying increasing magnetic field was an experimental device to study this equilibrium without affecting constants and results obtained from a 0.2M solution are reported in Table 2.

While at 80 MHz the two signals are badly resolved, they separate and narrow with increasing Δν separation induced by higher fields: scattering is obviously due to different instrumental homogenity conditions, but a common difference between monomeric and dimeric linewidth is evident, both greater than instrumental linewidth. Data are consistent with a slow but still exchanging equilibrium on the n.m.r. time scale.

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* Although in more recent papers[13a,b] Shanzer has adopted structural type (2) for the dimer of some substituted DOS derivatives and given a more detailed and correct interpretation of data, no explanations can be deduced for the ambiguities of the unsubstituted system.

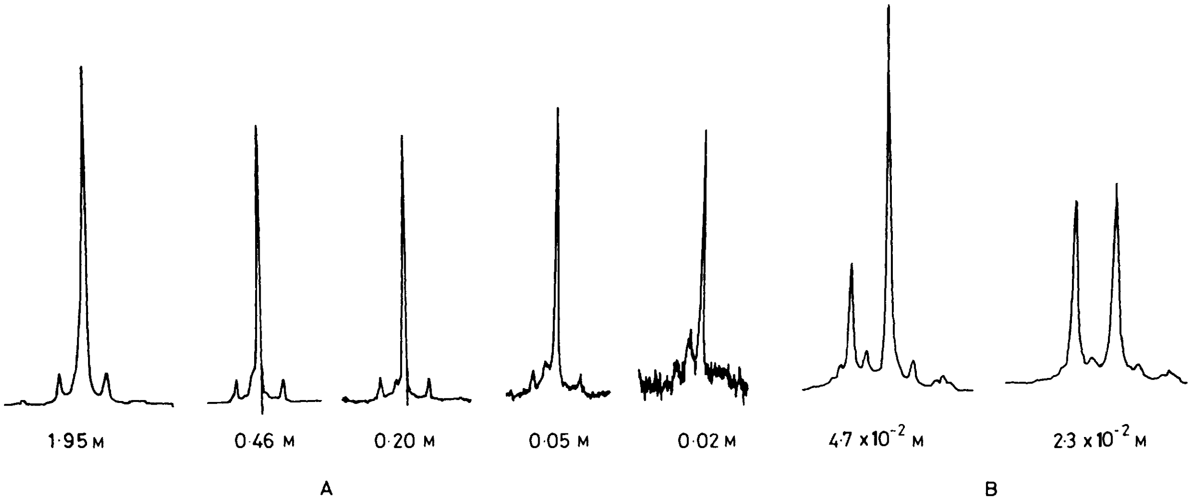


Figure Concentration effect on ^{1}H n.m.r. spectra of DOS ring methylene groups. All spectral data measured at 33 °C. A, Spectra recorded at 90 MHz; B, spectra recorded at 300 MHz. At 4.7 × 10^{-2}M, $\Delta\nu$ was *ca.* 24 Hz and linewidth 3 Hz for monomer and 2.4 Hz for associate. At 2.3 × 10^{-2}M, $\Delta\nu$ 26.3 Hz and corresponding linewidth values were 3.3 and 4.2 Hz. In both cases the $(CH_3)_6$ and the $CHCl_3$ signals showed a linewidth of 1.1 and 0.6 Hz, respectively.

Table 3. Effect of concentration on ^{119}Sn n.m.r. spectral data for DOS[a]

Concentration (M)	0.20	0.30	0.60	0.85	1.45	1.95[b]
δ[c]	−164	−171	−178	−181	−186	−189
Linewidth[d]	(very broad)	(*ca.* 600)	(280)	(180)	(120)	(110)

[a] Spectra recorded at 33 °C in $CDCl_3$ solution under proton-noise decoupling conditions. [b] Supersaturated solution at room temperature. [c] δ Values are given in p.p.m. from Me_4Sn as external reference. [d] Half-height linewidths in Hz.

Table 4. Effect of varying temperature on ^{119}Sn n.m.r. spectral data of DOS[a]

T (°C)	−60[b]				−46[b]			−20	0	33	57
δ	−128	−132.9	−266.8	−284	−132	−265	−280	Not detected	−189	−178	−174
Linewidth	(35)	(24)	(28)	(57)	(190)	Very broad	Very broad	Not detected	(1 200 *ca.*)	(280)	(100)

[a] Spectra were recorded on a 0.6M solution in $CDCl_3$. δ values in p.p.m. from Me_4Sn as external reference. Half-height linewidths in Hz. [b] Measured at 0.2M to avoid solubility problems.

From the Figure (spectra at 300 MHz at low concentration) we can also appreciate the line broadening as a function of concentration, further support for the existence of exchange, between the two signals: the effect is simply due to the variation of the relative mole fraction with dilution.

In all cases, at constant concentration (0.2M) the separation Δδ was *ca.* 0.065 p.p.m., which increased at 300 MHz with dilution up to 0.088 p.p.m. for a 2.3 × 10^{-2}M solution, where the line broadening was the highest observed.

The effect of concentration was also investigated on ^{119}Sn n.m.r. spectra at 33 °C. Table 3 shows experimental results. An up-field shift is evident with increasing concentration, but it is coupled to a very marked band narrowing; because of the large linewidth and nucleus sensitivity, 0.2M is a limiting concentration for obtaining spectra.

Since the chemical shift is approaching the six-co-ordinate tin range, but only a single resonance is evident, it is concluded that the signal must be an average resonance arising from a fast exchange between five- and six-co-ordinate tin in the system, *i.e.* fast equilibria between dimeric DOS and higher aggregates, with chemical shifts depending on the relative mole fraction.

Together with the above monomer $\rightleftarrows$ dimer system, this higher association generates a very complex series of subsequent equilibria.

Variable-temperature experiments were thought to be the appropriate tool for obtaining further information on the system. Unfortunately, a severe limitation was set by the solubility of DOS, sufficient for a wide temperature range only in chloroform; this prevented spectral data from being obtained outside the −60 to +60 °C range. With this limitation ^{1}H spectra could not relay useful data, while partial results were obtained for ^{13}C and ^{119}Sn for dilute solutions. Data from Table 4 show the behaviour exerted by ^{119}Sn. Decreasing temperature induced first an up-field shift caused by aggregation and a line broadening up to a coalescence, then a splitting into two sets of signals in the typical ranges of penta- and hexa-co-ordinate tin respectively. Further cooling gave rise, at the lower temperatures obtainable, to splitting of the penta-co-ordinate tin signal, the hexa-co-ordinate tin being already present in two bands. All signals are still broad, but further cooling resulted in freezing the solution. Slowing of penta/hexa-co-ordinate tin exchange was evident, *i.e.* an intermolecular

Table 5. Effect of temperature variation on ^{13}C n.m.r. spectra of DOS[a]

T^b (°C)	33	0	−19	−27	−46	−55	−62
CH_2O δ[d] (Linewidth)[e]	63.10 (2.4)	62.92 (2.9)	62.77 (4.3)	62.65 (8.2)	62.49 (15)	62.00 (45)	62.00 (54)[c]
$(CH_2)_\alpha$	22.04 (3.1)	22.16 (3.9)	22.15 (10)	22.20 (16)	Not measured (above coalescence)	24.34 19.54 (40) Δν 96 Hz	24.45 19.34 (23) Δν 102 Hz
$(CH_2)_\beta$	27.37 (1.6)	27.35 (1.6)	27.34 (2.3)	27.33 (2.3)	27.30 (3.8)	27.27 (Not measured)	27.14 (7)
$(CH_2)_\gamma$	26.89 (1.4)	26.93 (1.6)	26.98 (2.2)	27.02 (2.1)	27.05 (3.5)	27.10 (Not measured)	
$(CH_3)_\delta$	13.49 (1.6)	13.57 (1.6)	13.65 (2.2)	13.71 (1.7)	13.76 (2.7)	13.81 (2.8)	13.84 (3.4)

[a] Data obtained for 0.2M solution in $CDCl_3$ with proton-noise decoupling. [b] In the temperature range investigated, linewidth for $CDCl_3$ increased from 2.0 to 2.7 Hz. [c] Near coalescence point from band shape. [d] δ Values given in p.p.m. from Me_4Si using $CDCl_3$ as internal secondary reference at δ 76.89 p.p.m. [e] Half-height linewidths in Hz.

exchange between dimeric and higher associated DOS, but not enough could be learned from the dimer itself.

About ^{13}C variable-temperature experiments, the results are summarized in Table 5. The effect was especially evident on ring methylene and on butyl methylene carbons in the position α to the tin atom. Both these signals, single at room temperature, broadened with cooling to a coalescence point. For the CH_2O moiety, whose chemical shift going upfield with decreasing temperature reflected increasing aggregation, coalescence happened at the lowest temperature, so that no further information could be gained. For the α-methylene group coalescence at *ca.* −40 °C allowed further cooling, with subsequent splitting into two signals. At −62 °C these signals showed Δν 102 Hz and the linewidth decreased to 23 Hz for the upper field band.

What these data show is the slowing down of an exchange process responsible for the apparent 'averaging' of the two different ring methylene signals and leading to an 'averaging' of the two butyl groups. A similar effect seems to be exerted by the more distant carbons in the butyl groups, but probably due to smaller Δδ, it did not emerge in this temperature range. Indeed this process can be observed for the β- and γ-CH_2 moieties.

Experimental data ruled out the possibility of 'symmetry averaging' and nicely support the evidence of 'fast exchange averaging' for the two different sets of groups. This whole set of experiments brought about a much more complicated situation in solutions for DOS than commonly accepted. Physical limitations and multiple association equilibria are enough to discourage any quantitative investigation; nevertheless a qualitative but still useful description of this system was attempted, to obtain a clearer understanding of its behaviour.

The Multiple Equilibria System.—The pattern emerging from experimental data can be described in terms of equilibria (2) where DOS_{pol} represents a series of subsequent equilibria (3) involving *n* molecules of DOS. We shall attempt to analyse single steps on the basis of available data.

$$\mathrm{DOS_{mon}} \overset{K_{dim}}{\rightleftharpoons} \mathrm{DOS_{dim}} \overset{K_{pol}}{\rightleftharpoons} \mathrm{DOS_{pol}} \tag{2}$$

$$\mathrm{DOS_{trim}} \rightleftharpoons \mathrm{DOS_{tetr}} \rightleftharpoons \mathrm{DOS}_n \tag{3}$$

Dimerization equilibrium. The first dimerization equilibrium is slow enough to be observed on the ^{1}H n.m.r. time scale. Since only a single average signal of the CH_2O moiety is observed for dimeric and higher polymeric DOS, matching the fast exchange observed in the ^{119}Sn spectra, attempts to measure the K_{dim} constant failed, because of the different contribution of DOS_{pol} at every concentration. This fact was clearly shown by the fact that the increase in the relative amount of monomer with dilution was steeper than expected. However, a rough estimate would place the order of magnitude of K_{dim} between 10^2 and 10^3, and the range of existence of monomer as a major component below 2×10^{-2}M. From the concentration range where the highest linewidth could be measured for the monomer signal, an approximate rate constant was obtained, corresponding to the pseudo-first-order k_{dim}, as $k_{app.}$ *ca.* 10 s^{-1}, giving a lifetime τ *ca.* 10^{-1} s at 33 °C for a single species; k_{dim} would then be *ca.* 10^3 l mol^{-1} s^{-1}.

Higher association equilibria. ^{119}Sn Spectral data are most useful in describing higher aggregation equilibria. These are demonstrated by the increasing contribution of hexaco-ordinate tin in the average signal, but physically obtainable concentrations never led to 'pure' hexaco-ordinate tin in solution at room temperature. The same was true for the lower limit of 'pure' pentaco-ordinate tin since it was not possible to have spectra below 0.2M. To obtain limiting chemical shift values, low-temperature experiments were partially successful, setting the Sn^V chemical shift at δ *ca.* −130 p.p.m. and those of Sn^{VI} at δ *ca.* −270 p.p.m.; since the signals were still broad, these values are merely indicative. This enabled us to evaluate approximately the mole fraction of pentaco-ordinate tin at various concentrations and room temperature, *e.g.* 0.75 at 0.2M and 0.65 at 0.85M.

Although this approximation does not reflect the effective molar ratio of dimer to polymer, nevertheless these figures show that, for normal working concentrations, the dimer is to be considered the predominant species in the fast exchange. This obviously holds at room temperature, since the lower temperature showed a marked increase in association phenomena.

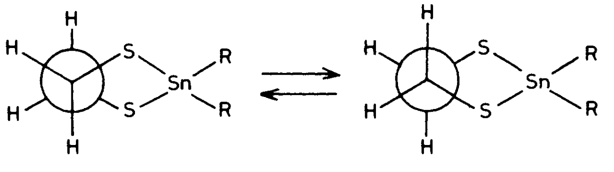
The upfield shift of the broadening signal with cooling is indeed consistent with increasing aggregation induced by decreasing temperature.

To give an order of magnitude to the fast exchange, the ^{119}Sn chemical shift range for Sn^V and Sn^{VI} indicated a lifetime for single species $\tau < 10^{-4}$ s, corresponding to $k_{app.} > 10^4$ s^{-1}, while the coalescence is occurring at *ca.* −20 °C.

The 'Dimeric' DOS System.—Some experimental evidence for dimeric DOS deserved more careful study.

The average CH_2O signal in the ^{1}H spectrum is insensitive to dilution with regard to splitting behaviour: at concentrations where DOS_{pol} has been shown to be negligible, the 'associated' CH_2O signal is still a sharp singlet.

With increasing dilution, the ^{119}Sn resonance broadens instead of narrows, as if it resulted from averaging of the sharp



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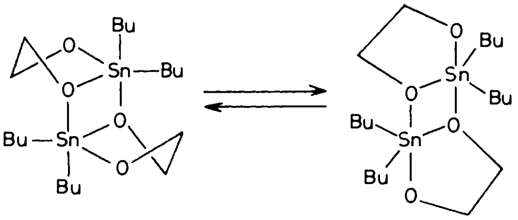
Scheme 2.



(4) (4′)

Scheme 3. Berry pseudorotation

(for Sn^{VI}) and broad (for Sn^{V}) lines. This fact is in agreement with an 'exchange' for five-co-ordinate tin, *i.e.* intramolecular fast tin exchange involving the dimer only.

The satellites of the CH_2O moiety in the ^1H n.m.r. spectrum are strong evidence of tin atoms being linked to oxygens for long enough to relay coupling information, in contrast to the fast exchange cited above. These facts suggested that some kind of internal motional feature should be responsible for the dimer behaviour.

Abel and his co-workers[15] studied the structural properties of the thia-analogue of DOS, *i.e.* the di-thiastannolane (3), and clearly demonstrated, at variance with previous work,[16,17] that the compound is monomeric at all concentrations and is a rapidly equilibrating half-chair system, with an interconversion barrier of 30—32 kJ mol^{-1} as shown in Scheme 2.

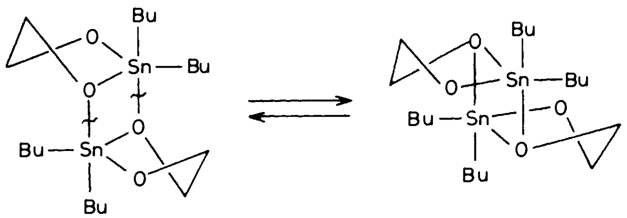
Assuming an analogous equilibrating system for monomeric DOS, a description of the dimer was attempted; it is evident however that conformational equilibration cannot be responsible for averaging ring methylene signals; this would require Sn–O bond breaking and forming by a low-energy process. Such processes are quite common for tin compounds[18,19] and fluxional character has been demonstrated in several cases of metallotropic shifts for stannyl derivatives.[20]

By analogy with structurally similar stannolidines,[19] as a possible mechanism for dimeric DOS, the Berry pseudorotation[21] was considered: this consists of a fast intramolecular tunnelling process, but from Scheme 3 we note that scrambling of equatorial and axial positions at tin has occurred, not of the CH_2 centres.

A second motion exhibited by stannolidines is the dissociation–inversion mechanism: applied to the dimer, this correspond to dissociation into monomeric DOS and statistical recombination (see Scheme 4). This equilibrium has already been discussed and shown to be slow on the n.m.r. time scale, and hence unable to give an average signal.

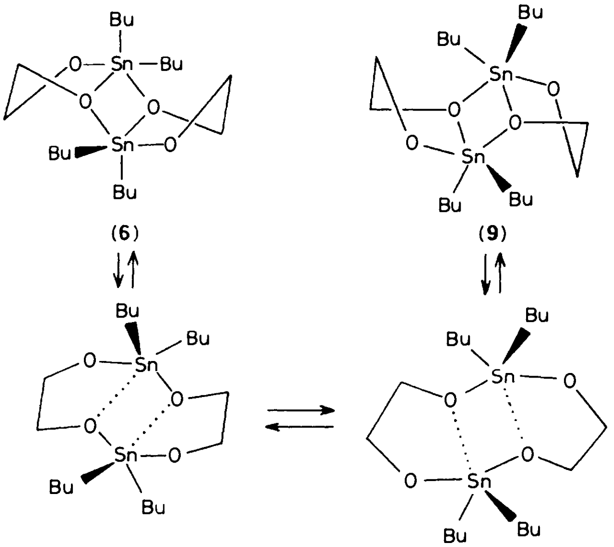
We propose here that experimental data are best accounted for by a third motional feature, namely an intramolecular dissociation–inversion mechanism, described in Scheme 5, superimposed on the conformational 'libration'. This mechanism implies fast intramolecular tin exchange, with inversion at the tin centre, while still bonded to oxygen atoms, hence transmitting coupling information to other nuclei.*

The fluxional character of the dimer is thus consistent with



(5) (5′)

Scheme 4. Dissociation–inversion



(6) (9) (7) (8)

Scheme 5. Intramolecular dissociation–inversion

scrambling of CH_2O and butyl moieties, through symmetrical intermediates (7) and (8). The broad ^{119}Sn resonance is a direct consequence of inversion at tin: pentaco-ordinate tin in crystalline substituted DOS is a distorted trigonal bipyramid;[5,7] three oxygens can occupy two axial and one equatorial positions or *vice-versa* and the two isomers racemize by fast tin inversion. Thus two different n.m.r. signals coalesce to one at room temperature. This interpretation is nicely supported by the low-temperature ^{13}C n.m.r. experiments presented above. At the coalescence point of the CH_2O signals, the linewidth value and $\Delta\nu$ *ca.* 80 Hz, extrapolated from the monomeric DOS chemical shift as a limiting value, gave an approximate life-time and rate constant as follows: $7 \times 10^{-3} < \tau < 10^{-2}$ s; $150 < k < 200$ s^{-1} at -62 °C.

Data from the ^1H spectra, extrapolated to coalescence, gave a k value of 200 s^{-1}, which compares very well with the ^{13}C figures.

These values correspond roughly to an exchange barrier of 42 kJ mol^{-1} between the two interconverting species. Similar approximation about the splitting of $(CH_2)_\alpha$ gave a $\Delta G^{\neq}$ value between 42 and 46 kJ mol^{-1}, leading to the conclusion that they belong to the same phenomenon. The case of butyl groups is interesting. At room temperature, the dimer molecule has an average symmetry plane due to fluxionality, as in Scheme 5;

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* This phenomenon is not surprising if we consider that in ten-membered rings transannular interactions are well known to be strong[22] and in the present case are even 'attractive'.

hence the butyl groups are isochronous. When fluxional exchange becomes slow and the structure rigid, the symmetry plane is lost and the butyls should become anisochronous, *i.e.* the tin atom can be a prochiral probe for the molecule. The observed data reflect nicely the expected trend, with the magnitude of the effect decreasing with the distance from $(CH_2)_\alpha$ to $(CH_3)_\delta$.

An important point should be made here. Although both conformers deriving from inversion at tin are present in stannolidines in solution, 'freezing' the system in the crystalline state gives only one conformer,[19] probably the more stable, *i.e.* that with butyl groups in the equatorial position. In the same way a single conformer is present in crystalline substituted DOS.[13b] Hence it is possible that by cooling the fluxional equilibrium, only one conformer could be formed. Our present data, although in agreement, are not sufficient to support this hypothesis.

^{119}Sn Low-temperature data emphasize the point. The broad line at −164 p.p.m. (see Tables 3 and 4), after splitting in penta- and hexa-co-ordinate tin bands, curiously shifts to −132 p.p.m.: this effect could be due to the disappearance of one conformer. The subsequent splitting of the band could in fact depend not only on two different conformers, but also on two different pentaco-ordinate tin atoms, namely that from the dimer and that from end-groups of higher aggregates, which are present at that temperature.

An unequivocal attribution does not seem feasible and some ambiguity affects our conclusions because of the possible occurrence of polymeric DOS in the exchange.

Finally we can predict the fluxional exchange to be sensitive to steric hindrance. Steric constraint imposed by bulky substituents or rigid groups on the dimer should in principle dramatically affect not only further association, but the occurrence of fluxional behaviour as well. This could be a reasonable explanation for the sharp ^{119}Sn signal obtained in DOS structures from carbohydrates[8] while, when co-ordinated by pyridine, they would take part in fluxional equilibria. For the same reason polymeric aggregates should be fluxionally stable; as a consequence, the two triplets, observable in very small amounts in ^{1}H n.m.r. spectra for the CH_2O moiety on both sides of the main signals, clearly evident at 400 MHz, could be suggestive of polymer end-groups unable to undergo exchange and could indicate limiting chemical shift values for CH_2O protons.

Conclusions

This work has outlined the very complex behaviour of DOS in solution. The compound exerted a series of aggregation equilibria in addition to a peculiar intramolecular fluxionality, responsible for fast tin exchange in the system. The results give new insight into a system whose structure has been debated in recent years. The relevance of the structural information obtained from this study for mechanistic and synthetic aspects of the Shanzer reaction will be an object of a forthcoming paper.

Experimental

Instruments.—N.m.r. spectra were performed on the following instruments: Perkin-Elmer R 32, 90 MHz; Varian FT 80 A equipped with a variable-temperature control apparatus, 80 MHz; Bruker CXP 300, 300 MHz; Bruker AM 400, 400 MHz. Recording conditions are indicated in the text and Tables.

Materials.—Commercial samples of $CDCl_3$ were used: Carlo Erba 99.5% and Merck 99.8% (for diluted solutions). 2,2-Dibutyl-1,3,2-dioxastannolane (DOS) was prepared according to a known procedure.[23] A fresh solution was prepared before each experiment.

Acknowledgements

We thank Professor L. Mandolini, University of Roma, Professor L. Lunazzi, University of Bologna, and Dr. C. Luchinat, University of Firenze, for suggestions. We are also indebted to Mr. D. Macciantelli, CNR Ozzano-Emilia, Bologna, and Dr. M. Nicoletti, University of Roma, for the operation of the high-field spectrometers.

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Received 17th *July* 1984; *Paper* 4/1233