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^{119}Sn NMR SPECTROSCOPIC INVESTIGATION OF TETRABUTYLDISTANOXANES

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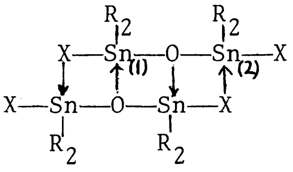
^{119}Sn FT NMR spectra proved to differentiate tin atoms in dimeric tetrabutyldistanoxanes successfully. Tentative assignment of ^{119}Sn NMR spectra was achieved for the first time.

Tetraorganodistanoxanes 1, one of the most unique classes of organotin compounds, have been extensively studied for long time1) and are still receiving much recent attention.2) Despite the early observation3) of the dimeric nature for 1, their structure has long been the subject of controversy. However, recent X-ray analyses1,2,4) have led to the definite conclusion that 1 possess the ladder structure shown below as proposed first by Okawara et al.5) Although their studies



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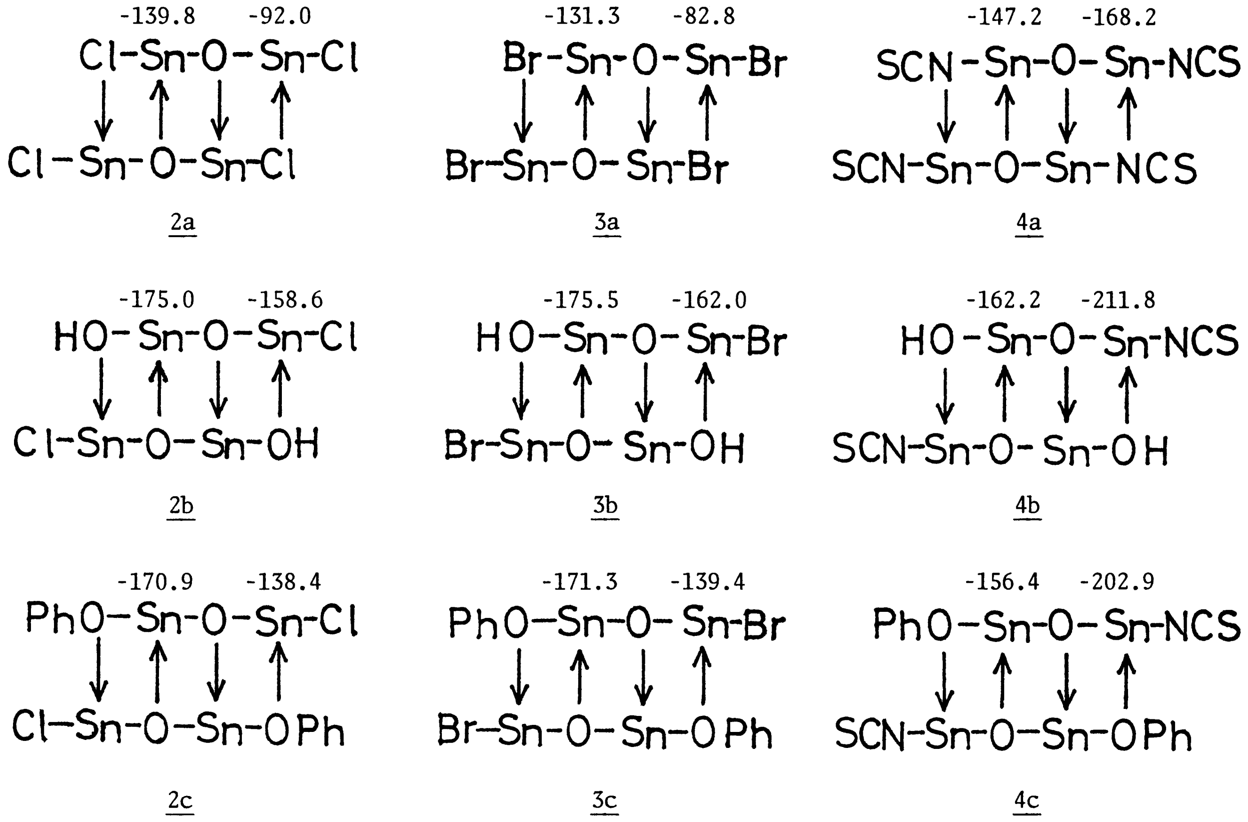
were based on IR spectra both in the solid state and in solution, it seems rather surprising that solution work of 1 has been limited except molecular weight measurements. Davies et al. have reported ^{119}Sn NMR spectroscopic studies of tetrabutyldistanoxanes by means of the heteronuclear double magnetic resonance technique.6) They observed only broad singlets for these compounds except for 1,3-dihalo derivatives which exhibit a pair of signals as expected from the dimeric formulation.

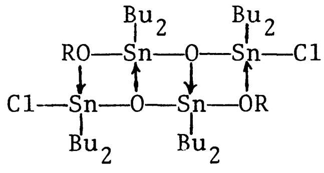
In the course of our studies on ^{119}Sn NMR spectra,7) we expected that FT NMR spectroscopy should afford more improved resolution. This is indeed the case. A pair of signals were observed for all of compounds 2-4.8) Here we wish to report on these results in which the tentative assignment of ^{119}Sn chemical shifts (δ(^{119}Sn)) can be successfully achieved for the first time.9)

The typical examples of ^{119}Sn NMR spectra of tetrabutyldistanoxanes are illustrated in Fig. 1 and whole results with probable assignment are given in Scheme 1.10) Apparently, well-resolved two singlets are observed in every case except for isothiocyanates 4. As pointed out by Davies et al.,5) the observed δ(^{119}Sn) values are in good agreement with occurrence of five-coordination about tin,11) thus the ladder structure 1 being confirmed.



Scheme 1.[12)]

For the assignment of signals, let us consider first the chloro derivatives 2b and 2c. For these compounds, two dimeric formulations 5 and 6 are possible. Since previous X-ray studies have revealed the oxygen-bridged structure for $[\mathrm{Cl}{}^{i}\mathrm{Pr}_2\mathrm{SnOSn}{}^{i}\mathrm{Pr}_2\mathrm{OH}]_2$,[4d)] $[\mathrm{Cl(Me_3SiCH_2)_2SnOSn(CH_2SiMe_3)_2OH}]_2$,[4d)] and $[\mathrm{ClPh_2SnOSnPh_2OH}]_2\cdot 2(\mathrm{CH_3})_2\mathrm{CO}$,[2)] 5 is presumed to be preferable in the present case as well. Comparison of 2b and 2c obviously indicates that the highfield signals with comparable $\delta(^{119}\mathrm{Sn})$ values (-175.0 and -170.9 ppm, respectively) are attributable to Sn(1) which is coordinated by three oxygens and two butyl groups in common. The others at -158.6 and -138.4 ppm are thus assigned to Sn(2).



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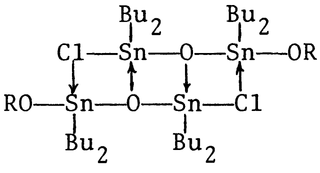

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R = H or Ph

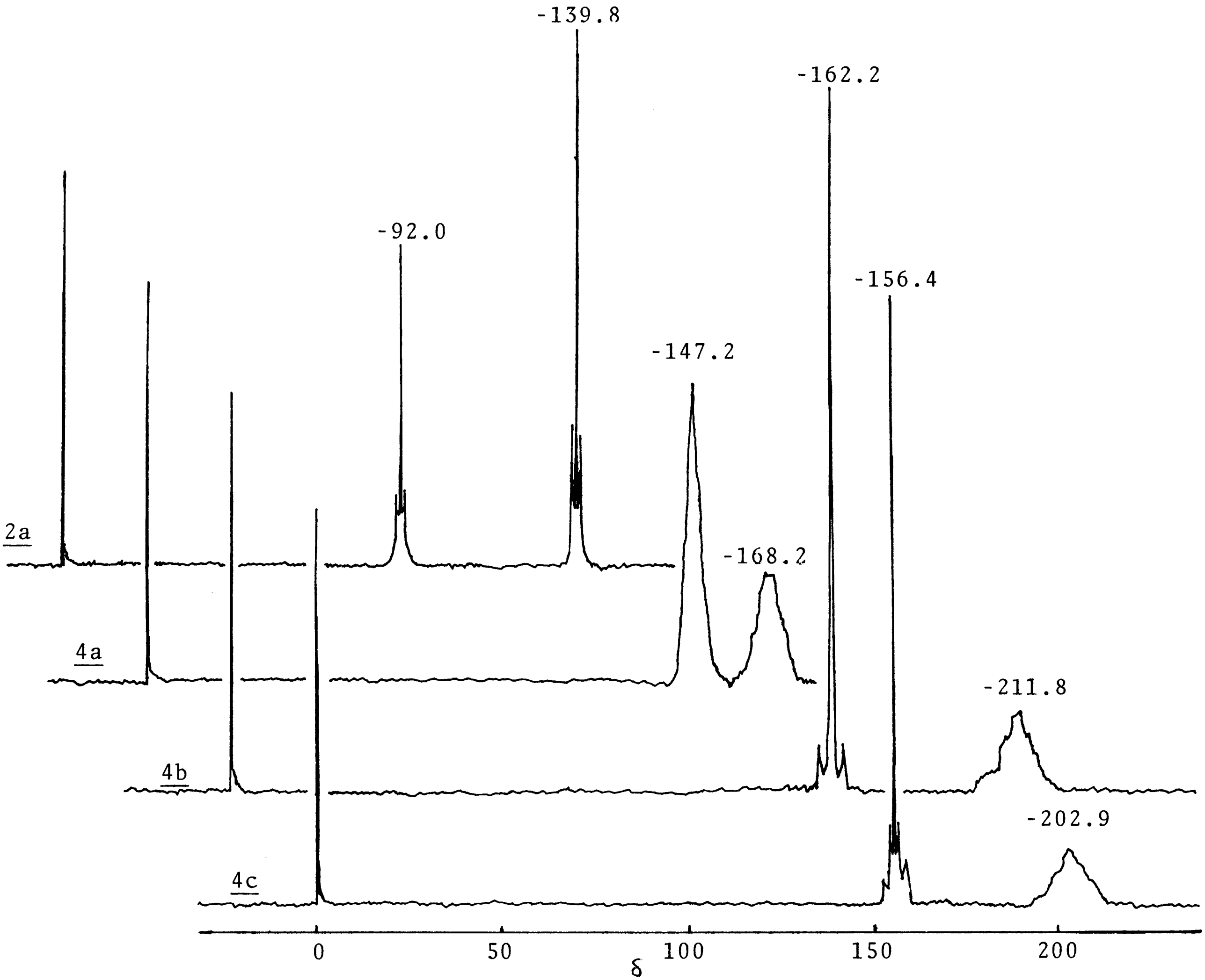

Fig. 1. ^{119}Sn NMR spectra of tetrabutyldistanoxanes.

The dichloro compound 2a gives rise to an unusually lowfield signal (-92.0 ppm) in addition to one at -139.8 ppm. It is well recognized that the chloro organotin compounds exhibit $\delta(^{119}Sn)$ at a significantly lowerfield than the corresponding alkoxy derivatives.[13)] Accordingly, the highfield signal is attributed to Sn(1) since this atom is bonded to less chlorine atoms than Sn(2). In accord with this postulate, either of signals of 2a lie downfield from the corresponding ones of 2b and 2c in which both tin atoms possess less chlorine substituents.

The results of the bromo derivatives 3a-c are quite analogous to the corresponding chloro derivatives so that the assignment can be made straightforwardly.

As shown in Fig. 1, the diisothiocyanate compound 4a exhibits characteristic broad signals. It is seen, however, that the lowerfield signal changes dramatically to a sharp and well-resolved one by replacing one of isothiocyanato groups by a hydroxy or phenoxy group. Broadening is therefore ascribed to the isothiocyanato group bonded to tin. For 4b and 4c, the structure involving a bridging isothiocyanato group can be ruled out on the basis of IR spectra which show no band around 1960 cm^{-1} attributable to bridging ν(N=C).[5b)] Alternatively, the oxygen bridged structure may well be supported. On this basis, the assignment for 4b and 4c was made as shown in Scheme 1. These assignment are consistent with the observation that Sn(1) gives rise to a well-resolved sharp signal since no isothiocyanato group is bonded to Sn(1) in these structures.

As for 4a, the broader signal at -168.2 ppm may be attributed to Sn(2) which is bonded to two isothiocyanato groups.

In summary, ^{119}Sn FT NMR spectra proved to differentiate successfully tin atoms in dimeric distanoxanes providing a powerful tool for structural elucidation of these compounds. These applications are now in progress in our laboratory.

References

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7) For the preceding paper of this series: J. Otera, T. Yano, E. Kunimoto, and T. Nakata, Organometallics, 3, 426 (1984).
8) Moreover, tin-tin coupling also was observed in most cases. Detailes will be discussed in a forthcoming full paper.
9) In this text, the tin atom coordinated by the central oxygen atom between two tin atoms of another chain designated as Sn(1) and the other as Sn(2).
10) ^{119}Sn FT NMR spectra with complete proton noise decoupling were obtained by using a JEOL FX-100 spectrometer operating at 37.08 MHz. Field-frequency control was made with a deuterium-labelled solvent ($CDCl_3$) lock. The chemical shifts were determined relative to internal Me_4Sn, negative signs indicating highfield shifts from the reference.
11) J. Otera, J. Organomet. Chem., 221, 57 (1981).
12) Butyl groups are deleted in this scheme for simplicity.
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