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The Proton Magnetic Resonance Spectra of Tris-*para*chlorophenyltin Chloride Adducts

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*The 1:1 addition compounds formed between tris-*para*-chlorophenyltin chloride and the Lewis bases, acetone and dimethyl sulfoxide, have been investigated. It is observed that as the base strength increases, there is a shift of electron density towards the tin atom as measured via the phenyl ring coupling constants. The results support the previous suggestion that long range coupling constants may be used to determine qualitatively the extent of d_π–p_π interaction in aryltin compounds. A method for calculating the chemical shifts and coupling constants of the aromatic protons without the aid of computerized pmr analyses is also described.*

Introduction

It has been established that triorganotin halides form 1:1 addition compounds with Lewis bases [1]. Depending on the basicity of the Lewis base, the configuration of the adducts range from a distorted tetrahedral structure to a trigonal bipyramidal configuration with three coplanar alkyl groups [1, 2]. Our interest in the bonding in aryltin compounds has led us to investigate the interaction between tris-*para*-chlorophenyltin chloride and the Lewis bases, acetone and dimethyl sulfoxide (DMSO), in an inert solvent, such as carbon tetrachloride. An aromatic organotin compound containing a substituent in the *p*-position was chosen in order to obtain a simplified pmr spectrum. Except for the effects due to the magnetic tin isotopes, tris-*para*chlorophenyltin chloride would be expected to give an AA′BB′ spectrum.

Experimental

Reagents

Fisher Spectroanalyzed Grade carbon tetrachloride and acetone were used without further purification. Spectroquality Grade dimethyl sulfoxide, obtained from Matheson, Coleman and Bell Co., was used without further purification. The solvents contained no impurities which could be detected by pmr spectroscopy. Except for acetone, the solvents were stored over Linde 4A molecular sieve.

Reagent grade starting materials were used without purification in all synthetic work.

Analyses

The elemental analyses were done by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

*Preparation of Tris-*para*chlorophenyltin Chloride*

A mixture of 8.57 g (15 mmol) of tetrakis-*para*-chlorophenyltin and 1.25 g (4.8 mmol) of anhydrous stannic chloride was heated at 205–215 °C for 3 hours and subsequently at 180–190 °C for another 3 hours. Recrystallization of the reaction product from 95% EtOH yielded 4.0 g of the pure compound. M.p. 110–111 °C (Lit. [3] 110–111 °C). *Anal.* Calculated: C, 44.23; H, 2.47; Cl, 29.01%. Found: C, 44.33; H, 2.46; Cl, 28.83%.

*Preparation of Tris-*para*methylphenyltin Chloride*

Tris-paramethylphenyltin chloride was prepared from the tetrakis-*para*methylphenyltin using similar experimental conditions. M.p. 99 °C (Lit. [4] 97.5–98.0 °C). *Anal.*: Calculated: C, 58.99; H, 4.95; Cl, 8.29%. Found: C, 59.03; H, 5.18; Cl, 7.69%.

PMR Spectra

The pmr spectra were obtained on Varian Model A-60 and Model HA-100 spectrometers using carbon tetrachloride, acetone or dimethyl sulfoxide as solvents. The spectra were traced both ways using a sweep width of 500 cps and were found to be reproducible to ±0.5 cps. The spectra were calibrated using TMS as the internal standard.

The $J(^{119}Sn–C–C–H_A)$ coupling constants were determined from spectra that were traced both ways using sweep width of 100 cps and were found to be reproducible to ±0.2 cps.

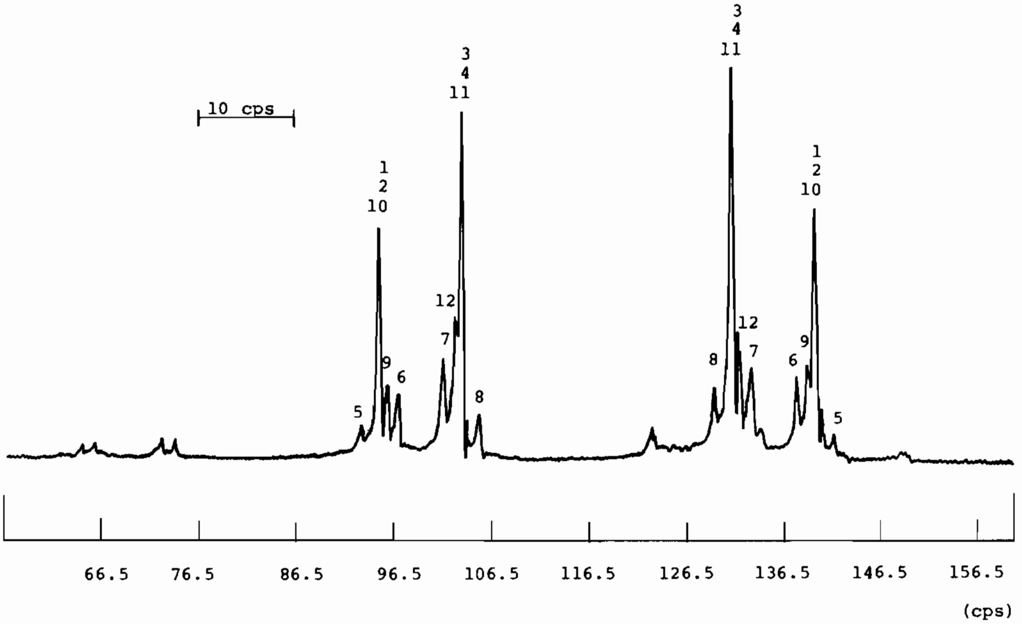


Figure 1. The ^{1}H NMR resonance spectrum at 100 Mc sec^{-1} of tris-*para*chlorophenyltin chloride in acetone. Line assignments are indicated on the respective peaks.

Results and Discussion

A typical proton nmr spectrum for tris-*para*chlorophenyltin chloride is shown in Figure 1. The spectrum consists of two groups of peaks; the downfield and upfield groups of peaks were attributed to the protons *ortho* to the tin atom, designated as H_A and the protons *ortho* to the chlorine atom designated as H_B respectively. The downfield group of peaks assigned to the H_A protons was confirmed by decoupling experiments on the analogous compound, tris-*para*methylphenyltin chloride. A pair of satellites resulting from the coupling of the ^{117}Sn and ^{119}Sn with the *ortho* protons was observed on the downfield side. The separation between the satellites and the chemical shift of the H_A proton did not change when the spectrum was obtained on a 60Hz or 100Hz instrument. This confirms that these satellites were indeed the $J(^{117}Sn–C–C–H_A)$ and $J(^{119}Sn–C–C–H_A)$ coupling constants. Previous studies on phenyltin chlorides have also found that the downfield peaks are due to the protons *ortho* to the tin atom [5, 6].

One method of obtaining the chemical shifts of the H_A and H_B protons in an AA′BB′ spectrum without the aid of a computer is to find the center of the AA′ or BB′ multiplet and use this as the resonance frequencies, H_A and H_B, respectively. However, the center of a multiplet is not always easy to assign since the outermost lines are sometimes of very weak intensity. Also the center of a multiplet is equal to the chemical shift only when the multiplet is perfectly symmetrical. As shown in Figure 1, the pmr spectrum obtained in this investigation contains two intense lines which are characteristic of an AA′BB′ system when $J_{AB} \gg J_{AB'} > 0$ and $J_{BB'} > J_{AA'} > 0$. The more intense line is labeled as line 3, ν_3, while the less intense line is labeled as line 1, ν_1 [7]. By assigning the two most intense lines in the experimental spectrum as lines 1 and 3, $\nu_0\delta$, the difference between the chemical shift of the H_A and H_B protons, can be calculated using the following derived equations [7]:

$$N = \nu_1 - \nu_3 \qquad (1)$$

$$[(\nu_0\delta)^2 + N^2]^{1/2} = \nu_1 + \nu_3 \qquad (2)$$

Since in an AA′BB′ spectrum the AA′ transitions are a mirror image of the BB′ transitions, the resonance frequencies H_A and H_B can be obtained because the distance $\nu_0\delta$ must be centered on the center of the observed spectrum.

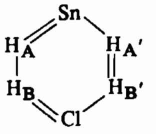
Once the chemical shift of the AA′ protons has been determined, the $J(^{119}Sn–C–C–H_A)$ coupling constants may be obtained because the distance between the chemical shift of the AA′ protons and the observed satellites is ½$J(^{117}Sn–C–C–H_A)$ and ½$J(^{119}Sn–C–C–H_A)$.

In order to confirm this method for calculating the chemical shifts of the H_A and H_B protons detailed pmr analyses were carried out on tris-*para*chlorophenyltin chloride. The analyses were obtained using the LAOCOON III program and the difference between the experimental and computed frequencies are within ±0.2 cps. The assignments of the various transition frequencies as shown in Figure 1 are achieved

TABLE I. Comparison between Observed and Calculated Chemical Shifts for Tris-*para*chlorophenyltin Chloride.

Solvent	H$_B$ – H$_A$ (obs.)	H$_B$ – H$_A$ (calc.)
CCl$_4$	11.25 cps	11.25 cps
(CH$_3$)$_2$CO	35.42	35.42
(CH$_3$)$_2$SO	20.87	21.10

TABLE II. NMR Analyses of Tris-*para*chlorophenyltin Chloride in CCl$_4$, (CH$_3$)$_2$CO, and (CH$_3$)$_2$SO Solutions.



	Solvent		
	CCl$_4$^{a}	Acetone^a	DMSO^b
H$_A$	100.051 ± 0.032	99.801 ± 0.020	99.819 ± 0.025
H$_A$'	100.051 ± 0.032	99.801 ± 0.020	99.819 ± 0.025
H$_B$	111.302 ± 0.032	135.223 ± 0.020	120.923 ± 0.025
H$_B$'	111.302 ± 0.032	135.223 ± 0.020	120.923 ± 0.025
J$_{AA'}$	0.464 ± 0.056	1.573 ± 0.035	1.627 ± 0.075
J$_{A'B}$	0.537 ± 0.036	0.426 ± 0.031	0.358 ± 0.035
J$_{A'B'}$	7.996 ± 0.040	8.052 ± 0.030	8.036 ± 0.036
J$_{AB}$	7.996 ± 0.040	8.052 ± 0.030	8.036 ± 0.036
J$_{AB'}$	0.537 ± 0.036	0.426 ± 0.031	0.358 ± 0.035
J$_{BB'}$	3.146 ± 0.041	2.345 ± 0.033	2.106 ± 0.070

^{a}Analysis done on 100 Hz instrument. ^{b}Analysis done on 60 Hz instrument.

TABLE III. Comparison of the Tin *Ortho*-hydrogen and Tin Methyl Hydrogen Coupling Constants in Tris-*para*chlorophenyltin Chloride and Trimethyltin Chloride Adducts.

Solvent	J(^{119}Sn–C–C–H$_A$)	J(^{119}Sn–CH$_3$)^a
CCl$_4$	61.6 cps	57.6 cps
(CH$_3$)$_2$CO	63.4	66.1
(CH$_3$)$_2$SO	66.7	69.2

^{a}Ref. 2.

by comparing the observed spectrum with a theoretical spectrum typical for a *para*disubstituted aromatic compound.

Table I list the differences of the chemical shifts of the H$_A$ and H$_B$ protons – those calculated from the pmr analyses using the LAOCOON III program as well as those observed from the pmr spectra. The agreement of the calculated and observed differences between the H$_A$ and H$_B$ protons indicate that the method described for calculating the chemical shifts is valid.

Tabulated in Table II are the computerized values for the chemical shifts and coupling constants for tris-*para*chlorophenyltin chloride in Lewis bases as well as in an inert solvent. Examination of the table reveals that in a solution of acetone or dimethyl sulfoxide the J$_{BB'}$ coupling constants decreases relative to those from carbon tetrachloride solution while the J$_{AA'}$ coupling constants increase when a coordinating solvent is employed. Although the interpretation of coupling constants is not a simple procedure, these results imply as a result of coordination, there is a shift of electron density toward the tin atom as the base strength increases.

In Table III, the J(^{119}Sn–C–C–H$_A$) coupling constants in the tris-*para*chlorophenyltin chloride complexes obtained in the present study are compared with the J(^{119}Sn–CH$_3$) coupling constants in trimethyltin chloride adducts [2]. In the case of the J(^{119}Sn–C–C–H$_A$) coupling constants there is a change of only 5.1 cps in going from the non-donating solvent, CCl$_4$, to the strong Lewis base, DMSO, as compared with a change of 11.6 cps observed for the J(^{119}Sn–CH$_3$) coupling constants in the same series of solvents. In the latter case there is a linear correlation between the coupling constants and the per cent *s*-character in the tin–carbon bond [2]. On the other hand, no such correlation is observed in the present study.

It has been suggested [5] that the long range coupling constants in (C$_6$H$_5$)$_n$SnCl$_{4-n}$ depend on the amount of *pi* electron interaction. A reexamination of Table II indicates that as the strength of the Lewis base increases, the J(^{119}Sn–C–C–H$_A$) coupling constants also increase. Thus, the results support the suggestion that the long range coupling constants may be used to determine qualitatively the extent of d$_\pi$–p$_\pi$ interaction in aryltin compounds.

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