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NMR Studies of Triorganotin Aminobenzoates

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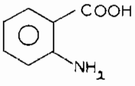
Introduction

Although *o*-aminobenzoic acid (anthranilic acid, I)



I

has been extensively used as a ligand in studies of the coordination chemistry of a variety of metal ions [1–3] including tin(IV) [4] and also diorganotin (IV) [5] species, no triorganotin (IV) derivatives have so far been reported.

The anion of I is ideally suited to behave as a bidentate chelating agent *via* one of the carboxylate oxygen atoms and the amino nitrogen atom, forming a six-membered chelate ring with the metal. Such bidentate behaviour for the anion of I has been described by Curran and her co-workers [1, 2]. In other situations, the anthranilate anion has been found to behave as a unidentate ligand *via* one carboxylate oxygen [5], whereas the free acid can apparently act as a unidentate ligand *via* the amino nitrogen atom [4].

We report here the synthesis of the trimethyltin, tri-n-butyltin and triphenyltin derivatives of both anthranilic acid and its isomer *p*-aminobenzoic acid. Proton NMR results indicate that in its triorganotin derivatives, the anthranilate anion behaves as a bidentate chelating agent, through a carboxylate oxygen atom and the amino nitrogen atom.

Experimental

Tributyltin and triphenyltin derivatives were prepared by heating a mixture of bistriorganotin oxide with the appropriate aminobenzoic acid (2 mol) in benzene and removing the water azeotropically using a Dean–Stark apparatus. After all the water had been removed from the reaction mixture (*ca.* 2 hours) the solvent was removed on a rotary evaporator and the residue distilled *in vacuo* or recrystallised from petroleum ether (60–80°).

Trimethyltin anthranilate and trimethyltin *p*-aminobenzoate were prepared from trimethyltin chloride and the appropriate carboxylate anion generated from sodium methoxide in absolute methanol.

C and H Microanalyses were carried out by the Australian Microanalytical Service – CSIRO Melbourne. Sn analyses were carried out with a Varian Techtron, Model 1000 A.A.

The physical, analytical and NMR data for all the compounds, together with the literature value where known, are shown in Table I.

The NMR spectra were obtained with TMS as internal reference on a Perkin-Elmer R12B spectrometer. Dilution studies were recorded by adding a known volume of carbon tetrachloride with a syringe to the preweighed NMR tubes containing the triorganotin aminocarboxylates.

Results and Discussion

The NMR data for the triorganotin anthranilates and *p*-aminobenzoates investigated are given in Table I. The chemical shifts of the amino protons of the anthranilates are displaced to considerably lower fields than those of the *p*-aminobenzoates. We consider that the greater deshielding observed for the amino protons of the anthranilates compared to that of the *p*-aminobenzoates, is an indication that intramolecular tin-nitrogen bonding is present in the triorganotin anthranilates.

The results of the NMR dilution studies have been summarised in Fig. 1, and provide additional evidence for the presence of intramolecular tin-nitrogen bonding in the triorganotin anthranilates. The most significant feature of the concentration – dependence studies is that the chemical shift values for the amino protons of the *p*-aminobenzoates (in which intramolecular tin-nitrogen bonding is not possible) show large shifts on dilution, not displayed by the triorganotin anthranilates.

Similar conclusions concerning the existence of intramolecular bonding interactions, and based on proton chemical shift values have been reported previously [6, 7, 8].

The value of the coupling constant $^2J(^{119}SnCH)$ has also been used in the elucidation of the structures of methyltin derivatives [9–11]. An increase in the coordination number of the tin atom should give rise to an increase in the value of $^2J(^{119}SnCH)$. The coupling constants determined for trimethyltin anthranilate and trimethyltin *p*-aminobenzoate in carbon tetrachloride solution are 58.67 cps and 56.72 cps respectively. These values are of the order for carboxylic organotin esters [12], and the larger value for the *ortho*-derivative further substantiates the

TABLE I. Analytical, Physical and NMR Data for Triorganotin Aminobenzoates.

Compound	Analysis: Found (Calcd) %			M.P. (°C) or b.p. (°C mm/Hg)	δNH$_2$ (ppm from TMS)	
	C	H	Sn		CCL$_4$ Soln	CHCL$_3$ Soln
PABSnBu$_3$[a]	53.61 (53.56)	7.70 (7.75)	28.1 (27.88)	172–174°/0.02	4.14	4.20
PABSnPh$_3$[b]	61.86 (61:77)	4.48 (4.32)	24.3 (24.44)	158–159[c]	3.65	3.70
PABSnMe$_3$	40.20 (40.07)	5.12 (5.01)	39.9 (39.60)	155–156	3.95	4.02
OABSnBu$_3$	53.60 (53.56)	7.60 (7.75)	27.6 (27.88)	165–166/0.02	5.70	5.75
OABSnPh$_3$	62.08 (61.77)	4.44 (4.32)	24.5 (24.44)	108–109	5.60	5.65
OABSnMe$_3$	40.22 (40.07)	5.22 (5.01)	40.0 (39.60)	134–135	5.55	5.65

[a] PAB = *para*-aminobenzoate.
[b] OAB = *ortho*-aminobenzoate.
[c] Lit (Ref. 14) 158–160 °C.

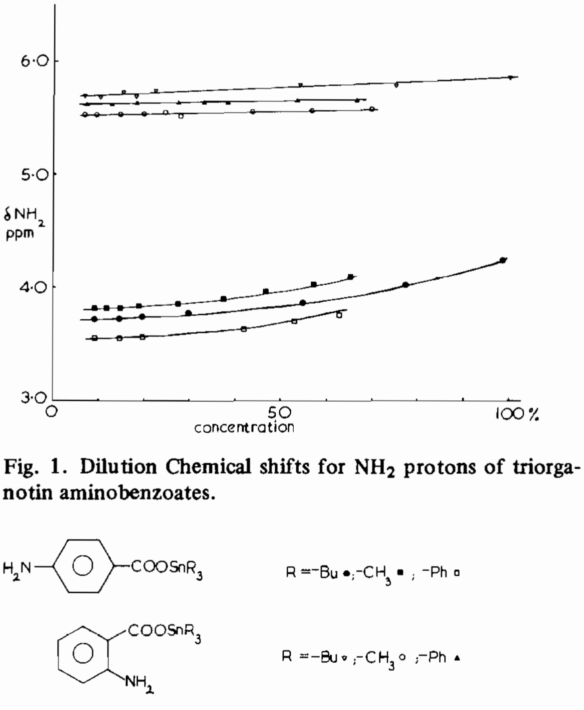
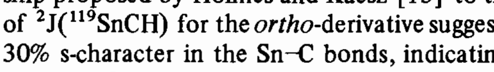


Fig. 1. Dilution Chemical shifts for NH$_2$ protons of triorganotin aminobenzoates.



presence of intramolecular tin-nitrogen bonds in these compounds. Furthermore, application of the relationship proposed by Holmes and Kaesz [13] to the value of $^2J(^{119}SnCH)$ for the *ortho*-derivative suggest almost 30% s-character in the Sn–C bonds, indicating *quasi*-planarity for the SnC$_3$ skeleton in this compound.

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