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^{13}C AND ^{119}Sn NMR STUDY OF SOME TRIPHENYLTIN(IV) CARBOXYLATES

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Summary

The ^{13}C and ^{119}Sn NMR spectra of $CDCl_3$ solutions of aliphatic and aromatic triphenyltin(IV) carboxylates of the type $Ph_3SnOCOR$ (Ph = phenyl; R = H, CH_3, C_2H_5, $C(CH_3)_3$, CF_3, CH_2Cl, $CHCl_2$, CCl_3, CH_2Br and $CHBr_2$) and of the type $Ph_3SnOCOC_6H_4X$ (X = H, 4-NH_2, 4-OCH_3, 4-$C(CH_3)_3$, 4-CH_3, 4-$NHCOCH_3$, 4-OH, 4-SH, 4-I, 4-Cl, 4-CN, 4-NO_2, 2-OH and 2-NH_2) have been recorded. The values of the chemical shifts $\delta(^{119}Sn)$ and $\delta(^{13}C)_{ipso}$ and the coupling constants $^1J(^{119}Sn^{13}C)$ of the triphenyltin(IV) group provide evidence that the compounds are monomeric species in the solutions irrespective of their structure in the solid state.

Introduction

Solid triorganotin(IV) carboxylates form either linear polymers with *trans*-trigonal bipyramidal geometry around the five-coordinate tin atom (the carbonyl groups forming bridges between tin atoms in planar SnC_3 groups) or tetrahedral monomers [1–4]. The decisive role in the corresponding bonding and coordination type of the structure is played by steric effects between substituents of the tin atom and the carboxyl groups. The solutions of these compounds in nonpolar (noncoordinating) solvents contain monomeric molecules with almost tetrahedral-coordinate tin atoms. Of course, a little association dependent on the concentration of the solution, cannot be excluded [5].

Information on the structure and bonding in triorganotin(IV) carboxylates in the solid state has been obtained mostly from the study of their vibrational spectra in the frequency regions of the carboxylate and SnC_3 groups [1]. The structures were verified in some cases using Mössbauer spectra [2,3] and diffraction methods [4,6]. Information on the structure of these compounds in solutions of nonpolar solvents was hitherto available only from the vibrational spectra.

Recently we reported [7] an application of ^{13}C and ^{119}Sn NMR spectra to the study of the coordination and structure of triphenyltin(IV) compounds in solutions. Results of the study of the structure of triphenyltin(IV) carboxylates of the type $Ph_3SnOCOR$ (Ph = phenyl; R = H, CH_3, C_2H_5, $C(CH_3)_3$, CF_3, CH_2Cl, $CHCl_2$, CCl_3, CH_2Br and $CHBr_2$) and the type $Ph_3SnOCOC_6H_4X$ (X = H, 4-NH_2, 4-OCH_3, 4-$C(CH_3)_3$, 4-CH_3, 4-$NHCOCH_3$, 4-OH, 4-SH, 4-I, 4-Cl, 4-CN, 4-NO_2, 2-OH and 2-NH_2) in solutions of noncoordinating solvent (deuteriochloroform) are reported in this paper.

Results and discussion

The majority of the studied aliphatic carboxylates (compounds. **1**–**3**, **5**–**9**, Table 1) in the solid state are known to form linear polymers [8,9]. The only exception is compound **4**, which is monomeric in the solid state due to the bulky substituent on the carboxyl group. Compound **8** can be regarded a transition species between polymeric and monomeric carboxylates [10]. Compound **10**, studied here for the first time, is probably also monomeric, as indicated by the frequencies of the carboxyl groups (Table 4). All the aromatic triphenyltin(IV) carboxylates studied (**11**–**24**, Table 2) are monomeric in the solid state; the frequencies ν_a and ν_s of the carboxyl group in infrared spectra lie in the spectral region typical of monodentate group COO (Table 4, ref. 11) for all the compounds, including those studied for the first time (**14**, **16**, **18**–**21**, **23** and **24**).

The frequencies ν_a and ν_s of infrared spectra of all the studied compounds in chloroform solution have values typical of the monodentate group COO (Table 4, ref. 8, 9, 11) and thus provide evidence for the monomeric nature of the compounds in this solution regardless of their structure in the solid state. The measured parameters of ^{13}C and ^{119}Sn NMR spectra (Table 1–3) are in agreement with the data of infrared spectra. Although the chemical shifts $\delta(^{119}Sn)$ lie in a broad range from -64.4 to -120.9 ppm, they never exceed the maximum value of -128.1 ppm (tetraphenyltin) of the range typical of the four-coordinate tin atom in triphenyltin(IV) compounds [7]. For the compounds studied we have found a relation between $\delta(^{119}Sn)$ of the carboxylates and pK_a [12] of the corresponding carboxylic acids, of the form $\delta(^{119}Sn) = \alpha(pK_a) + \beta$; $\alpha = -11.81 \pm 0.53$ ppm, $\beta = -58.27 \pm 2.07$ ppm, $r = 0.980$, $N = 22$.

A similar relation was noted earlier by McFarlane and Wood [5] for a substantially smaller group of aliphatic triphenyltin(IV) carboxylates. The existence of such a relation indicates the mutual dependence of the two physical properties. Both the strength of the acid and the chemical shift $\delta(^{119}Sn)$ are controlled by the same factors, and depend on the electron density on the hydrogen or tin atoms, respectively. Thus the chemical shift $\delta(^{119}Sn)$ depends mainly on the overall electron density on the central tin atom. For the aromatic carboxylates with exception of the compounds **17**, **18**, **23** and **24** we have found the dependence of the chemical shift $\delta(^{119}Sn)$ on the Hammett constants σ_p [13] to be $\delta(^{119}Sn) = \rho\sigma_p + \delta_o$; $\rho = 17.88 \pm 0.60$, $\delta_o = -109.75 \pm 0.25$, $r = 0.996$, $N = 10$.

The monomeric form of the triphenyltin(IV) carboxylates in $CDCl_3$ is indicated mainly by the obtained values of the coupling constants $^1J(^{119}Sn^{13}C)$ which lie in the narrow range 637.8–650.4 Hz for all the studied compounds and in the upper part of the range (550–650 Hz) appropriate to the *s*-electron density of sp^3 hybrid orbitals

TABLE 1

^{13}C AND ^{119}Sn NMR PARAMETERS OF ALIPHATIC TRIPHENYLTIN(IV) CARBOXYLATES $(C_6H_5)_3SnOCOR$

No	R	$\delta(^{119}Sn)$ (ppm)	$^1J(^{119}Sn^{13}C)$ (Hz)[a]	$\delta(^{13}C)$ (ppm)[b]					
				C(*i*)	C(*o*)	C(*m*)	C(*p*)	COO	other
1	H	−91.4[c]	650.4	137.47	136.81	129.01	130.34	166.99	
2	CH_3	−113.7	648.2	138.16	136.75	128.76	130.03	178.32	20.56(CH_3)
3	C_2H_5	−114.0	648.2	138.26	136.80	128.81	130.03	181.30	27.34(CH_2), 9.84(CH_3)
4	$C(CH_3)_3$	−117.7	647.0	138.60	136.75	128.76	129.93	185.68	38.60(C), 27.82(CH_3)
5	CF_3	−64.4	638.7	135.95	136.73	129.32	131.00	161.53	115.37(CF_3)
6	CH_2Cl	−89.8[c]	644.5	137.24	136.80	129.00	130.42	172.67	41.47(CH_2Cl)
7	$CHCl_2$	−75.7[c]	641.0	136.8[d]	136.8[d]	129.17	130.71	169.01	65.40($CHCl_2$)
8	CCl_3	−65.1	637.8	136.12	136.65	129.25	130.85	165.80	91.40(CCl_3)
9	CH_2Br	−91.1[c]	643.9	137.09	136.75	129.00	130.42	172.57	27.14(CH_2Br)
10	$CHBr_2$	−77.5[c]	[e]	136.46	136.70	129.10	130.61	[e]	30.90($CHBr_2$)

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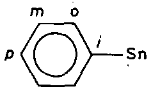
[a] $^nJ(^{119}Sn^{13}C)$ ($n = 2$–4) are almost the same for all the compounds, ^2J 48.8–49.3 Hz, ^3J 64.0–64.5 Hz, ^4J 13.4–13.7 Hz. [b] . [c] Saturated solution. [d] Overlapped. [e] Non-observed (low solubility).

TABLE 2

^{119}Sn NMR PARAMETERS OF AROMATIC TRIPHENYLTIN(IV) CARBOXYLATES $(C_6H_5)_3$-$SnOCOC_6H_4X$

No	X	$\delta(^{119}Sn)$ (ppm)	$^1J(^{119}Sn^{13}C)$ [a] (Hz)
11	H	−109.9	648.4
12	4-NH_2	−120.9	650.4
13	4-OCH_3	−115.0	649.4
14	4-$C(CH_3)_3$	−112.4	648.2
15	4-CH_3	−112.6	649.4
16	4-$NHCOCH_3$	−110.2 [b]	649.4
17	4-OH	−111.0 [b]	648.0
18	4-SH	−102.8	648.2
19	4-I	−105.2	647.0
20	4-Cl	−104.9	647.5
21	4-CN	−97.4	648.2
22	4-NO_2	−96.1	646.5
23	2-OH	−94.9 [b]	647.0
24	2-NH_2	−116.8 [b]	650.4

[a] Identical values of $^nJ(^{119}Sn^{13}C)$ ($n = 2$–3) were obtained within the limits of experimental error for all the compounds 48.8 Hz (^2J), 64.4 Hz (^3J), 13.7 Hz (^4J). [b] Saturated solution.

of tin atoms bonded to sp^2 hybrid orbitals of three carbon atoms in the group $SnPh_3$ [7].

It is noteworthy that the chemical shifts $\delta(^{13}C)_{ipso}$ of phenyl groups in the $SnPh_3$ lie in the range 135.95–138.7 ppm [7], which also corresponds to the tetrahedral coordination of Sn atoms.

Although the chemical shifts $\delta(^{119}Sn)$ were measured over a wide concentration region 0.1–0.5 mol l^{-1} (up to the full saturation of the solution), they show only a very small concentration dependence. The maximum variation in $\delta(^{119}Sn)$ was 0.3 ppm. The NMR parameters measured at about 0.5 mol l^{-1} concentration are summarized in Tables 1–3. The small concentration dependence indicates that there is negligible autoassociation of molecules of the studied compounds in deuteriochloroform under the conditions used. No perceptible association was found even with compounds containing an electron pair donor group as a substituent of the carboxyl group (e.g. NH_2 in the compounds **12** and **24**, OH in **17** and **23**, etc.). Our measurements do not confirm the formation of a chelate complex in compound **23** reported by Khoo and Smith [14] on the basis of the ^{1}H NMR spectrum. Formation of a chelate complex should change the chemical shift $\delta(^{119}Sn)$ by −80 ppm [15] and the shift should approach the value of −200 ppm associated with five-coordinated triphenyltin(IV) compounds [7]. We suggest that the incorrect interpretation of the chemical shifts $\delta(^1H)$ of amino groups in the compounds **12** and **24** [14] was caused by the neglect of substantial variations in the values of $\delta(^1H)$ in the parent 2- or 4-aminobenzoic acids.

Experimental

All the triphenyltin(IV) carboxylates (Tables 1 and 2) were prepared by the reaction of triphenyltin(IV) hydroxide with equimolar amounts of the corresponding

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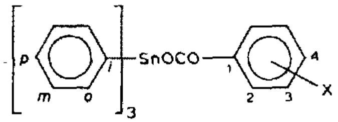
TABLE 3

^{13}C NMR CHEMICAL SHIFTS OF AROMATIC TRIPHENYLTIN(IV) CARBOXYLATES $(C_6H_5)_3SnOCOC_6H_4X$

Compound No [a]	δ(^{13}C) (ppm) [b]									
	C(*i*)	C(*o*)	C(*m*)	C(*p*)	C(1)	C(2)	C(3)	C(4)	COO	X
11	138.24	136.80	128.81	130.06	130.07	130.53	128.07	132.59	172.79	
12	138.79	136.80	128.73	129.87	119.18	132.63	113.49	150.84	173.02	
13	138.52	136.81	128.78	129.99	122.69	132.64	113.30	163.16	172.56	55.17(CH_3O)
14	138.41	136.85	128.81	130.03	128.27	130.51	125.10	156.25	172.82	34.99(C), 31.09(CH_3)
15	138.41	136.85	128.81	130.03	[c]	130.61	128.80	143.18	172.86	21.54(CH_3)
16	138.41	136.85	128.90	130.12	125.93	131.88	118.67	142.06	172.38	168.53(CO), 24.56(CH_3)
17	138.51	136.85	128.90	130.12	122.57	133.00	115.06	160.19	172.86	
18	137.87	136.80	128.90	130.22	[c]	130.66	127.93	134.66	171.45	
19	137.97	136.85	128.90	130.22	[c]	132.07	137.38	100.44	171.99	
20	138.06	136.81	128.89	130.14	129.09	131.93	128.35	138.91	171.59	
21	137.53	136.80	129.00	130.37	134.61	130.95	131.97	118.13	170.72	115.94(CN)
22	137.47	136.77	128.97	130.37	136.42	131.43	123.16	150.10	170.10	
23	137.63	136.80	129.00	130.37	113.31	161.66	[d]	[d]	175.06	
24	138.71	136.80	128.77	129.98	111.07	150.48	[e]	[e]	174.31	

[a] See Table 2. [b]



[c] Overlapped. [d] 135.48, 131.49, 118.81, 117.11. [e] 134.11, 133.06, 116.34, 116.14.

TABLE 4

MELTING POINTS, ANALYTICAL DATA AND INFRARED CARBONYL FREQUENCIES OF TRIPHENYLTIN(IV) CARBOXYLATES

Compound [a]	m.p. (°C)	Analytical data (found/(calcd.) (%))				Frequency ν(CO) (cm^{-1})			
						KBr		CHCl$_3$	
		C	H	Sn	other	ν_a	ν_s	ν_a	ν_s
10	184–185	42.80 (42.38)	2.96 (2.84)	20.95 (20.85)	30.23 [b] (28.19)	1640	1380	1680	1333
14	124–129	65.87 (66.07)	5.62 (5.35)	22.79 (22.51)	– –	1622	1340	1623	1338
16	97–99 (decomposition)	61.83 (61.40)	4.18 (4.39)	22.95 (22.47)	2.83 [c] (2.65)	1625	1338	1640	1352
18	148–151	59.36 (59.67)	4.12 (4.01)	24.02 (23.59)	6.74 [d] (6.37)	1680	1325	1675	1335
19	147–153	50.37 (50.29)	3.78 (3.21)	19.78 (19.88)	21.55 [e] (21.29)	1632	1330	1640	1345
20	131–135	59.52 (59.39)	3.95 (3.79)	23.84 (23.48)	7.68 [f] (7.01)	1640	1330	1650	1340
21	133–135	63.26 (62.94)	3.18 (3.86)	24.05 (23.92)	3.02 [c] (2.82)	1650	1332	1632	1338
23	120–122	61.20 (61.64)	4.30 (4.13)	(25.34 (24.37)	– –	1630	1380	1635	1370
24	[g]		[g]			1623	1353	1640	1354

[a] See Tables 1 and 2. [b] Br. [c] N. [d] S. [e] I. [f] Cl. [g] Ref. 13.

acids in benzene [11]. The product was identified by chemical analysis, and by comparison of the melting points and infrared spectra with literature data [8,9,11,14,16–19]. Physical and chemical data for compounds **10, 14, 16, 18–21, 23** and **24**, studied here for the first time, are given in Table 4.

Infrared spectra were measured on a Perkin–Elmer spectrometer type 684 in KBr pellets and in chloroform (10%) solution. ^{13}C and ^{119}Sn NMR spectra were measured on a JNM-FX 100 spectrometer (JEOL, Japan) at 25.047 and 37.14 MHz, respectively, at 300 K. The ^{13}C and ^{119}Sn chemical shifts were relative to internal $(CH_3)_4Si$ and external $(CH_3)_4Sn$, respectively. The basis of the interpretation of the NMR spectra has been described elsewhere [7].

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