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TRIORGANOTIN(IV) BENZOATES AND AMINOBENZOATES

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Summary

Complexes of the general formula R_3SnX, where X is the anion of benzoic acid, *o*-, *m*-, *p*-amino- or *N*-phenyl-*o*-amino-benzoic acid, have been prepared and characterised. A combination of molecular weight, infrared, ^1H NMR and ^{119}Sn Mössbauer measurements show that, the amino-nitrogen atoms are not coordinated to tin. When R = phenyl or cyclohexyl, the compounds are monomeric and four-coordinate, and when R is alkyl (Me, Pr^n, Bu^n) they are monomeric and five-coordinate, with a bidentate carboxylate in the equatorial position of a trigonal bipyramidal structure.

Introduction

The coordination chemistry of *o*-aminobenzoic acid with transition metals has been investigated [1–3] and derivatives of tin(IV) chloride [4] and diorganotin(IV) have been reported [5,6]. Triorganotin(IV) derivatives appear to be restricted to benzoic acid itself [7,8], arylazo- and benzoyl-substituted benzoic acid [9,10], and *o*- and *p*-aminobenzoic acid [11]. It has been suggested, on the basis of NMR data, that the anthranilic acid derivatives involve an Sn–N bond [11], which we have previously disputed [6]. We now report further examination of a range of triorganotin benzoates and aminobenzoates, including characterisation by Mössbauer spectroscopy.

Experimental

Benzoic acid (BAH) and the isomeric amino-benzoic acids (*o*-, *m*-, and *p*-BAH) and *N*-phenyl-*o*-aminobenzoic acid (N-PABAH) were purified by recrystallisation from hot water. The tin compounds R_3SnCl (R = Me, Bu^n, Bz (= benzyl)) were

(*Continued on p. 22*)

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TABLE 1

PHYSICAL AND ANALYTICAL DATA

No.	Compound	Yield (%)	M.p. (°C)	Analysis (Found (calcd.) (%))					Mol. wt.		
				C	H	N	Sn	Cl	Cryos-copically	Rast method	Calcd.
1	$(CH_3)_3Sn \cdot BA$	80	138–140	41.95 (42.14)	5.09 (4.91)	–	41.32 (41.69)	17.65 (17.82)	269.4	272.6	284.7
2	$(CH_3)_3Sn \cdot o$-ABA	75	135–137 (134–135) [b]	39.75 (40.04)	5.45 (5.00)	4.90 (4.67)	39.38 (39.60)	17.55 (17.82)	213.3	277.2	299.7
3	$(CH_3)_3Sn \cdot m$-ABA	80	156	39.80 (40.04)	4.72 (5.00)	5.10 (4.67)	39.38 (39.60)	17.55 (17.82)	253.5	280.4	299.7
4	$(CH_3)_3Sn \cdot p$-ABA	80	159 (155–156) [b]	39.90 (40.04)	5.25 (5.00)	4.93 (4.67)	39.50 (39.60)	17.60 (17.82)	273.9	275.5	299.7
5	$(CH_3)_3Sn \cdot$N-PABA	80	155	51.45 (51.10)	5.40 (5.05)	3.95 (3.72)	31.26 (31.59)	17.65 (17.82)	307.2	340.2	375.7
6	$(n\text{-}C_3H_7)_3Sn \cdot BA$ [a]	75	(58–60)	52.20 (52.07)	6.90 (7.95)	–	31.80 (32.19)	12.25 (12.53)	292.9	340.4	368.7
7	$(n\text{-}C_3H_7)_3Sn \cdot o$-ABA [a]	70	–	49.67 (50.03)	6.67 (7.03)	4.04 (3.64)	30.52 (30.93)	12.30 (12.53)	340.04	347.4	383.7
8	$(n\text{-}C_3H_7)_3Sn \cdot m$-ABA [a]	80	–	49.65 (50.03)	6.90 (7.03)	4.10 (3.64)	30.62 (30.93)	12.35 (12.53)	348.6	363.3	383.7
9	$(n\text{-}C_3H_7)_3Sn \cdot p$-ABA [a]	85	–	51.25 (50.03)	7.30 (7.03)	3.95 (3.64)	30.79 (30.93)	12.30 (12.53)	366.7	368.5	383.7
10	$(n\text{-}C_3H_7)_3Sn \cdot$N-PABA [a]	80	–	57.15 (57.42)	6.52 (6.74)	3.40 (3.04)	25.64 (25.82)	12.30 (12.53)	425.9	430.2	458.7
11	$(n\text{-}C_4H_9)_3Sn \cdot BA$ [a]	80	–	55.30 (55.51)	7.45 (7.79)	–	28.51 (28.90)	10.60 (10.91)	382.05	390.5	410.7
12	$(n\text{-}C_4H_9)_3Sn \cdot o$-ABA [a]	78	– (165–166/0.02) [b]	54.01 (53.55)	7.55 (7.75)	3.55 (3.28)	27.74 (27.88)	10.55 (10.91)	402.6	408.7	425.7
13	$(n\text{-}C_4H_9)_3Sn \cdot m$-ABA [a]	80	–	53.45 (53.55)	7.40 (7.75)	3.65 (3.28)	27.47 (27.88)	10.65 (10.91)	394.9	408.7	425.7

14	$(n\text{-}C_4H_9)_3Sn\cdot p\text{-ABA}$ [a]	80	(172–174) [b]	53.80	7.55	3.60	27.65	10.70	412.3	410.5	425.7
				(53.55)	(7.75)	(3.28)	(27.88)	(10.91)			
15	$(n\text{-}C_4H_9)_3Sn\cdot$N-PABA [a]	80	–	60.15	6.98	3.38	23.33	10.70	470.2	489.8	501.7
				(59.79)	(7.37)	(2.79)	(23.65)	(10.91)			
16	$(C_6H_5)_3Sn\cdot$BA	82	86–87	63.45	4.45	–	24.87	9.10	[c]	[c]	470.7
			(84–84.5) [b]	(63.73)	(4.24)		(25.21)	(9.21)			
17	$(C_6H_5)_3Sn\cdot o\text{-ABA}$	70	106–107	62.04	4.25	3.26	24.22	9.09	[c]	[c]	485.7
			(108–109) [b]	(61.76)	(4.32)	(2.88)	(24.43)	(9.21)			
18	$(C_6H_5)_3Sn\cdot m\text{-ABA}$	75	105	61.35	4.10	3.35	24.20	9.10	[c]	[c]	485.7
				(61.76)	(4.32)	(2.88)	(24.43)	(9.21)			
19	$(C_6H_5)_3Sn\cdot p\text{-ABA}$	80	156–157	61.84	4.21	3.35	24.23	8.95	[c]	[c]	485.7
			(158–159) [b]	(61.76)	(4.32)	(2.88)	(24.43)	(9.21)			
20	$(C_6H_5)_3Sn\cdot$N-PABA	80	145	66.49	4.70	2.90	20.96	8.95	[c]	[c]	561.7
				(66.22)	(4.45)	(2.49)	(21.13)	9.21)			
21	$(C_6H_5CH_2)_3Sn\cdot$BA	70	285	65.20	5.30	–	22.90	8.15	467.1	490.3	512.7
			(dec.)	(65.53)	(5.07)		(23.15)	(8.30)			
22	$(C_6H_5CH_2)_3Sn\cdot m\text{-ABA}$	75	90–92	63.90	5.07	2.74	22.15	8.20	–	467.1	527.7
				(63.67)	(5.11)	(2.65)	(22.49)	(8.30)			
23	$(C_6H_5CH_2)_3Sn\cdot p\text{-ABA}$	70	72–75	63.40	4.97	2.74	22.20	8.15	–	480.2	527.7
				(63.67)	(5.11)	(2.65)	(22.49)	(8.30)			
24	$(c\text{-}C_6H_{11})_3Sn\cdot$BA	80	75–77	61.65	7.40	–	24.06	8.55	465.5	473.6	488.7
				(61.38)	(7.75)		(24.28)	(8.80)			
25	$(c\text{-}C_6H_{11})_3Sn\cdot o\text{-ABA}$	75	95–96	59.90	7.35	3.04	23.25	8.50	484.07	492.5	503.7
				(59.55)	(7.74)	(2.77)	(23.56)	(8.80)			
26	$(c\text{-}C_6H_{11})_3Sn\cdot m\text{-ABA}$	70	150–152	59.87	7.52	2.45	23.35	8.60	480.5	490.2	503.7
				(59.55)	(7.74)	(2.77)	(23.56)	(8.80)			
27	$(c\text{-}C_6H_{11})_3Sn\cdot p\text{-ABA}$	78	135–137	59.15	7.63	2.95	23.30	8.55	480.9	285.2	503.7
				(59.55)	(7.74)	(2.77)	(23.56)	(8.80)			
28	$(c\text{-}C_6H_{11})_3Sn\cdot$N-PABA	80	97–98	63.97	7.35	2.15	20.14	8.60	498.2	520.2	579.7
				(64.17)	(7.41)	(2.41)	(20.47)	(8.80)			

[a] liquid. BAH = Benzoic acid; *o*-ABAH = *o*-aminobenzoic acid; *m*-ABAH = *m*-aminobenzoic acid; *p*-ABA = *p*-aminobenzoic acid; N-PABAH = *N*-phenyl-*o*-aminobenzoic acid. [b] literature value. Ref. 11 and 7. [c] Insoluble both in benzene and camphor.

TABLE 2

INFRARED SPECTROSCOPIC DATA (cm^{-1}) [a]

No. Compound	ν(Sn–O)	ν(Sn–C)	$\nu(COO)_{asym}$	$\nu(COO)_{sym}$	$\Delta\nu$ [b]	ν(N–H)			
BAH	–	–	1715vs,sp	1290vs,sp	425		–		
BANa	–	–	1600vs,sp	1405vs	195		–		
o-ABAH	–	–	1675vs	1295s	380	3480sp	3380sp	3320sp	3240b
o-ABANa	–	–	1605vs,sp	1385s	220	3400s	3330sp		
m-ABAH	–	–	1635s,sp	1385s,sp	250	3430b,w			
m-ABANa	–	–	1630vs,sp	1410vs,sp	220	3440m,sp	3350m,sp	3220w	
p-ABAH	–	–	1670vs,sp	1290s,sp	380	3460m,sp	3370s,sp	3240w	
p-ABANa	–	–	1630s,sp	1410s,b	220	3450sh	3400sh	3335s	3220sh
N-PABAH	–	–	1655vs,sp	1250s,sp	405	3330sp			
N-PABANa	–	–	1610vs,sp	1385vs,sp	225	3320s,sp	3260sh		
1 $(CH_3)_3Sn\cdot BA$	450, 410 ms,sp sh	555, 520 vs,sp sh	1605vs,sp	1380vs,sp	225	–	–		
2 $(CH_3)_3Sn\cdot$ *o*-ABA	440, 410 vw m,sp	545, 530 ms, sh	1620vs	1400sh	220	3470w	3380sp	3260sp	
3 $(CH_3)_3Sn\cdot$ *m*-ABA	450, 405 m w,b	545, 520 ms,sp m	1620vs	1400sh	220	3460m,sp	3370s,sp	3220w	
4 $(CH_3)_3Sn\cdot$ *p*-ABA	425 m,b	550, 505 s,sp m,sp	1650vs	1440s	210	3480sh	3440s	3360s,sp	3240s,sp
5 $(CH_3)_3Sn\cdot$ N-PABA	455 m,sp	550, 505 m,sp m,sp	1615sh	1360s,sp	255	3400m			
6 $(n\text{-}C_3H_7)_3Sn\cdot BA$ [c]	460m,sp	590m,sp	1620s,sp	1380sh	240	–	–		
7 $(n\text{-}C_3H_7)_3Sn\cdot ABA$ [c]	450m,sp w,b w,b	600, 535	1630s,sp	1380sh	250	3490ms,sp	3360m,sp		
8 $(n\text{-}C_3H_7)_3Sn\cdot$ *m*-ABA [c]	460m,sp	590, 520 m,b m,b	1620s,sp	1370sh	250	3460m	3370m,sp	3230w	
9 $(n\text{-}C_3H_7)_3Sn\cdot$ *p*-ABA [c]	435, 385 m,sp w	590, 500 w,b m,sp	1610s,sp	1380s	230	3480m,b	3370s,sp	3270s,sp	3240m
10 $(n\text{-}C_3H_7)_3Sn\cdot$ n-PABA	495, 460 m	580, 520 m,sp w	1625s,sp	1380s	240	3280m	3340sh		

11 $(n\text{-}C_4H_9)_3Sn\cdot BA$	455m,sp	590, 515 m w,b	1620vs,sp	1380sh	250	–	–	
12 $(n\text{-}C_4H_9)_3Sn\cdot o\text{-}ABA$ [c]	455m,sp	590, 520 m,s m,b	1620s,sp	1380sh	240	3460m	3360s,sp	3220w
13 $(n\text{-}C_4H_9)_3Sn\cdot m\text{-}ABA$ [c]	470m,sp	610, 515 w,b sh	1620s,sp	1380sh	240	3460m	3360s,sp	3230w
14 $(n\text{-}C_4H_9)_3Sn\cdot p\text{-}ABA$ [c]	445w,sp	605, 510 sh w,sp	1615s,sp	1370sh	245	3500m	3390s,sp	3270m
15 $(n\text{-}C_4H_9)_3Sn\cdot N\text{-}PABA$ [c]	470m,sp	590, 505 m,sp m	1630s,sp	1385s	245	3300m,sp		
16 $(C_6H_5)_3Sn\cdot BA$	345m,sp	–	1625s,sp	1345vs,sp	280	–	–	–
17 $(C_6H_5)_3Sn\cdot o\text{-}ABA$	335, 325 w,sp w,b	–	1620 s,sp	1390	230	3500m,sp	3390m,sp	
18 $(C_6H_5)_3Sn\cdot m\text{-}ABA$	340m,sp	–	1610s,sp	1350s,sp	260	3450m,sp	3380s,sp	
19 $(C_6H_5)_3Sn\cdot p\text{-}ABA$	340sh	–	1600s,sp	1345s,sp	255	3460m	3380s,sp	3220w
20 $(C_6H_5)_3Sn\cdot N\text{-}PABA$	370, 330 w,sh,w	–	1600s,sp	1360s,sp	240	3320m,sp		
21 $(C_6H_5CH_2)_3Sn\cdot BA$	365, 310 s,sp m,sp	475, 450 s,sp sh	1605s,sp	1410s,sp	195	–	–	–
22 $(C_6H_5CH_2)_3Sn\cdot m\text{-}ABA$	360vw,sp	445, 410 m,sp w	1560s,sp	1370s,sp	190	3380s,sp		
23 $(C_6H_5CH_2)_3Sn\cdot p\text{-}ABA$	385w	450, 415 m,sp sh	1595s,sp	1390m	205	3380		
24 $(c\text{-}C_6H_{11})_3Sn\cdot BA$	410m,sp	480m,sp	1620vs,sp	1330vs,sp	290	–		
25 $(c\text{-}C_6H_{11})_3Sn\cdot o\text{-}ABA$	430sh	490, 415 m,sp m	1625vs,sp	1360vs,sp	265	3470s,sp	3360 s,sp	
26 $(c\text{-}C_6H_{11})_3Sn\cdot m\text{-}ABA$	465s,sp	490, 415 w,sp m,sp	1625vs,sp	1350vs,sp	275	3480m,sp	3380 vs,sp	
27 $(c\text{-}C_6H_{11})_3Sn\cdot p\text{-}ABA$	440s,sp	490, 420 sh w,sp	1620s,sp	1350s,sp	270	3480s,sp	3380 vs,sp	
28 $(c\text{-}C_6H_{11})_3Sn\cdot N\text{-}PABA$	460m,sp	495, 420 m,sp w,sp	1620s,sp	1360s,sp	260	3290s,sp		

[a] In KBr disc unless otherwise noted. s = strong; b = broad; m = medium; w = weak; sp = sharp; sh = shoulder. [b] $\Delta\nu = \nu(COO)_{asym} - \nu(COO)_{sym}$. [b] Liquid film, between polythene strips.

TABLE 3

^{1}H NMR DATA [a,b]

No.	Compound	δ(COOH)	δ(NH)	δ (Ring protons)		δ (Sn–R)			
	BAH	10.88 (m,1H)	–	8.03 (q,2H)	7.38 (q,3H)		–		
	o-ABAH [c]	–	5.60 (m,2H)	7.70 (q,1H)	7.12 (m,1H)	6.53 (m,2H)	–		
	m-ABAH [c]	–	9.05 (bm,2H)	8.30 (m,2H)	7.78 (m,2H)		–		
	p-ABAH	–	[h]	8.35 (t,2H)	7.70 (m,2H)		–		
	N-PABAH	9.53 (b,1H)	7.95 (d,1H)	7.18 (m,9H)			–		
1	$(CH_3)_3$SnBA	–	–	8.08 (m,2H)	7.43 (bm,3H)		1.78–0.38 (bm,9H)		
2	$(CH_3)_3$Sn·*o*-ABA	–	5.63 (bm,2H)	8.00–7.50 (bp,2H)	7.35–6.45 (bp,2H)		2.00–0.63 (bm,9H)		
3	$(CH_3)_3$Sn·*m*-ABA	–	3.70 (s,2H)	7.20 (m,2H)	6.80–6.30 (bp,2H)		2.10–0.75 (bm,9H)		
4	$(CH_3)_3$Sn·*p*-ABA	–	–	7.85 (m,2H)	6.55 (t,2H)		4.38–0.58 (bm,9H)		
5	$(CH_3)_3$Sn·N-PABA	–	9.55 (bp,1H)	7.15 (m,9H)			1.63–0.5 (bm,9H)		
6	$(n\text{-}C_3H_7)_3$·SnBA	–	–	7.95 (m,2H)	7.38 (m,3H)		1.65 (bp,6H)	1.28 (q,6H)	0.98 (t,9H)
7	$(n\text{-}C_3H_7)_3$Sn·*o*-ABA	–	5.43 (m,2H)	7.08 (m,2H)	6.50 (m,2H)		1.65 (m,6H)	1.23 (t,6H)	0.90 (t,9H)
8	$(n\text{-}C_3H_7)_3$Sn·*m*-ABA	–	3.70 (s,2H)	7.20 (m,2H)	6.90–6.50 (bp,2H)		1.55 (t,6H)	1.20 (t,6H)	0.93 (t,9H)
9	$(n\text{-}C_3H_7)_3$Sn·*p*-ABA	–	4.00 (m,2H)	7.80 (m,2H)	6.53 (t,2H)		1.70 (m,6H)	1.30 (m,6H)	0.95 (t,9H)
10	$(n\text{-}C_3H_7)_3$Sn·N-PABA	–	8.05 (m,1H)	7.10 (bp,9H)			1.70 (t,6H)	1.35 (t,6H)	1.05 (t,9H)

11	$(n\text{-}C_4H_9)_3Sn\cdot BA$	–	–	8.05 (m,2H)	7.33 (m,3H)		1.38 (bm,18H)	0.88 (t,9H)	
12	$(n\text{-}C_4H_9)_3Sn\cdot o\text{-}ABA$	–	5.50 (m,2H)	7.20 (m,2H)	6.60 (m,2H)		1.50 (t,18H)	0.85 (t,9H)	
13	$(n\text{-}C_4H_9)_3Sn\cdot m\text{-}ABA$	–	3.70 (s,2H)	7.20 (t,2H)	6.95–6.55 (m,2H)		1.53 (t,18H)	0.83 (t,9H)	
14	$(n\text{-}C_4H_9)_3Sn\cdot p\text{-}ABA$	–	3.88 (bs,2H)	7.83 (m,2H)	6.33 (m,2H)		1.53 (bp,18H)	0.95 (t,9H)	
15	$(n\text{-}C_4H_9)_3Sn\cdot$N-PABA	–	7.95 (m,1H)	7.30–6.45 (bp,9H)			1.88–1.05 (bp,18H)		0.70 (t,9H)
16	$(C_6H_5)_3Sn\cdot BA$ [c]	–	–	–			–		–
17	$(C_6H_5)_3Sn\cdot o\text{-}ABA$ [d]	–	3.25 (s,2H)	7.70–7.30 (m,19H)			–		
18	$(C_6H_5)_3Sn\cdot m\text{-}ABA$ [e]	–	–	–			–		
19	$(C_6H_5)_3Sn\cdot p\text{-}ABA$	–	3.35 (t,2H)	7.95–6.25 (m,19H)			–		
20	$(C_6H_5)_3Sn\cdot$N-PABA	–	9.53 (s,1H)	8.25–6.25 (m,24H)			–		
21	$(C_6H_5CH_2)_3Sn\cdot BA$ [e]	–	–	–			–		
22	$(C_6H_5CH_2)_3Sn\cdot o\text{-}ABA$ [f]	–	3.27 (bm,2H)	7.69–6.30 (m,19H)			–		
23	$(C_6H_5CH_2)_3Sn\cdot p\text{-}ABA$ [g]	–	3.88 (bm,2H)	7.80–6.10 (m,19H)			–		
24	$(c\text{-}C_6H_{11})_3Sn\cdot BA$	–	–	7.95 (m,2H)	7.38 (m,3H)		2.13–1.30 (m,33H)		
25	$(c\text{-}C_6H_{11})_3Sn\cdot o\text{-}ABA$	–	5.60 (m,2H)	7.88 (bm,1H)	7.20 (t,1H)	6.60 (bm,2H)	2.25–0.98 (m,33H)		
26	$(c\text{-}C_6H_{11})_3Sn\cdot m\text{-}ABA$	–	6.27 (m,2H)	7.10 (m,2H)	6.80–6.50 (m,2H)		2.30–1.03	(bm,33H)	
27	$(c\text{-}C_6H_{11})_3Sn\cdot p\text{-}ABA$	–	3.90 (m,2H)	7.80 (d,2H)	6.55 (d,2H)		2.25–0.98 (m,33H)		
28	$(c\text{-}C_6H_{11})_3Sn\cdot$N-PABA	–	6.27 (bp,1H)	7.21 (m,9H)			2.20–0.87 (m,33H)		

[a] s = singlet; d = doublet, t = triplet; q = quartet; m = multiplet; bp = broad peak. [b] In $CDCl_3$ unless otherwise noted. [c] In Trifluoroacetic acid. [d] In DMSO-d_6. [e] Insoluble in $CDCl_3$, TFA or DMSO. [f] $\delta(CH_2) = 2.72–2.50$ (m,6H). [g] $\delta(CH_2) = 2.95–3.03$ (m,6H). [h] Overlapping with phenyl protons.

commercially available and were used as received, those with R = Pr^n, Ph and Cy (= cyclohexyl) were prepared by reported methods [12]. The sodium salts were prepared by addition of ethanolic sodium hydroxide followed by azeotropic distillation with benzene.

Tin complexes. The triorganotin(IV) chloride (1.0 mmol) and the sodium salt of the acid (1.04 mmol) were refluxed together in absolute ethanol (30 cm^3) for 3–4 h. The mixture was reduced in volume, cooled, and filtered to remove sodium chloride. Thiophene-free dry benzene (20 cm^3) was added and the mixture refluxed for about 2 h in a Dean and Stark apparatus. Any separated sodium chloride was removed by filtration, and the process repeated until no further separation occurred. The solvent was then removed completely and the residue purified by recrystallisation from ethanol (compounds **1–5**, **24–28** of Table 1) or, in the case of compounds **16–23**, which were insoluble in the common solvents, by washing with light petroleum (b.p. 40–60°C). The triphenyl derivatives (**6–15**) were viscous liquids, and were purified by extraction with light petroleum. Tripropyltin(IV) benzoate, which is a liquid, solidified on prolonged standing.

Physical methods. Melting points were determined in open capillaries, and are uncorrected. Tin was estimated as SnO_2 and other elemental analyses were carried out by the Microanalytical Service, Calcutta University. Molecular weights were determined both cryoscopically in benzene and by the Rast method (in molten camphor at 175°C). Infrared spectra were recorded on a Pye Unicam SP3-300 spectrometer with neat liquids or KBr discs. ^1H NMR spectra were obtained on a Tesla B487 spectrometer at 80 MHz, with TMS as internal standard. ^{119}Sn Mössbauer spectra were recorded with a Harwell 6000 Series spectrometer, with samples cooled by liquid nitrogen (ca. 80 K) and the source (Pd/Sn) at room temperature. Isomer shifts are quoted relative to SnO_2 at room temperature.

Results

Twenty-eight triorganotin derivatives of benzoic acid, *o*-, *m*-, *p*-aminobenzoic acid, and *N*-phenyl-*o*-aminobenzoic acid have been prepared. Analytical and molecular-weight data are given in Table 1. With the exception of the triphenyl derivatives, which were insoluble, the compounds are monomeric both in molten camphor and freezing benzene.

The infrared spectra of the free acids, their sodium salts, and the tin derivatives are presented in Table 2. Following previous workers [6,13–27], assignments have been made for ν(N–H), ν(COO), ν(Sn–C), and ν(Sn–O). The deprotonation of the carboxyl group on complexation is shown by the disappearance of the broad O–H stretching band of the acid in the region 2500–2900 cm^{-1}. The N–H stretching frequency of the free acids, in the range 3330–3480 cm^{-1}, moves to 3260–3400 cm^{-1} for the anhydrous sodium salts, suggesting the formation of strong hydrogen bonds. In the tin derivatives, this band has the same frequency as the acid, or is slightly raised in frequency, indicating that the nitrogen atom of the amino acids is not coordinated to tin.

The value of $\Delta\nu$ ($= \nu(COO)_{asym} - \nu(COO)_{sym}$) can be used to determine the mode of coordination of the carboxyl group [13–15]. For the straight-chain trialkyltin derivatives, $\Delta\nu$ is in the range 235–245 cm^{-1}, indicating a bidentate or bridging ligation. The triphenyl and tricyclohexyl compounds show higher values (255–27 cm^{-1}), which are consistent with unidentate bonding to tin.

TABLE 4

TIN-119 MÖSSBAUER DATA (at 80 K; mm s^{-1})

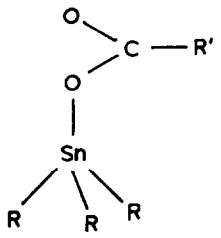
No.	Compound	IS ± 0.03	QS ± 0.03	L_1 ± 0.06	L_2 ± 0.06
1	$(CH_3)_3Sn \cdot BA$	1.36	3.59	0.98	1.11
2	$(CH_3)_3Sn \cdot o$-ABA	1.34	3.40	1.04	1.12
3	$(CH_3)_3Sn \cdot m$-ABA	1.43	3.49	1.13	1.08
4	$(CH_3)_3Sn \cdot p$-ABA	1.38	3.02	2.11	2.57
5	$(CH_3)_3Sn \cdot$N-PABA	1.36	3.76	1.00	1.03
6	$(n\text{-}C_3H_7)_3Sn \cdot BA$	1.49	3.67	0.93	1.04
7	$(n\text{-}C_3H_7)_3Sn \cdot o$-ABA	1.45	3.16	0.91	0.89
8	$(n\text{-}C_3H_7)_3Sn \cdot m$-ABA	1.48	3.30	0.94	1.02
9	$(n\text{-}C_3H_7)_3Sn \cdot p$-ABA	1.43	3.22	0.94	1.07
10	$(n\text{-}C_3H_7)_3Sn \cdot$N-PABA	–	–	–	–
11	$(n\text{-}C_4H_9)_3Sn \cdot BA$	1.41	3.40	0.93	1.03
12	$(n\text{-}C_4H_9)_3Sn \cdot m$-ABA	1.46	3.16	0.98	1.00
13	$(n\text{-}C_4H_9)_3Sn \cdot m$-ABA	1.47	3.24	0.93	1.01
14	$(n\text{-}C_4H_9)_3Sn \cdot p$-ABA	1.42	2.99	0.97	1.04
15	$(n\text{-}C_4H_9)_3Sn \cdot$N-PABA	–	–	–	–
16	$(C_6H_5)_3Sn \cdot BA$ [a]	–	–	–	–
17	$(C_6H_5)_3Sn \cdot o$-ABA	0.92	2.16	0.90	0.91
18	$(C_6H_5)_3Sn \cdot m$-ABA	1.16	2.60	1.48	1.56
19	$(C_6H_5)_3Sn \cdot p$-ABA	1.01	2.46	1.66	2.26
20	$(C_6H_5)_3Sn \cdot$N-PABA	0.92	2.16	0.90	0.90
21	$(C_6H_5CH_2)_3Sn \cdot BA$	–	–	–	–
22	$(C_6H_5CH_2)_3Sn \cdot m$-ABA	–	–	–	–
23	$(C_6H_5CH_2)_3Sn \cdot p$-ABA	1.17	2.62	1.34	2.09
24	$(c\text{-}C_6H_{11})_3SnBA$ [a]				
25	$(c\text{-}C_6H_{11})_3Sn \cdot o$-ABA	1.52	2.77	0.92	0.99
26	$(c\text{-}C_6H_{11})_3Sn \cdot m$-ABA	1.49	2.68	0.97	0.95
27	$(c\text{-}C_6H_{11})_3Sn \cdot p$-ABA	1.53	2.70	0.84	0.91
28	$(c\text{-}C_6H_{11})_3Sn \cdot$N-PABA	1.48	2.66	0.89	0.96

[a] Decomposed before measurement could be made.

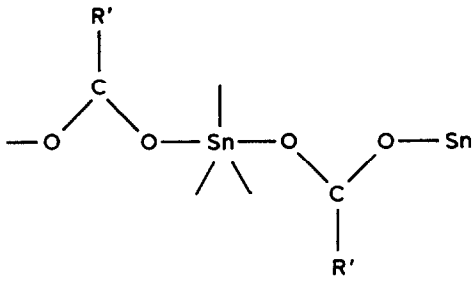
The number of Sn–C stretching bands can be used to deduce the geometry of the triorganotin moiety [17–22]. Bridged polymeric species would be expected to have roughly planar SnC_3 skeletons, and to give only a single strong band. The observation of two bands, as here, indicates monomeric structures, with mono- or bi-dentate carboxylate groups.

The ^1H NMR spectra of the free acids and the soluble tin complexes are reported in Table 3. The signal due to the carboxylic proton of the free acid is not present in the spectra of the complexes. The position of the NH signal of *o*-aminobenzoic acid (δ 5.60 ppm) is little changed in the complexes, which indicates that the amino group is not coordinated. Similar observations were made in our earlier studies of dibutyltin(IV) *o*-aminobenzoate [6], but contrast with the report of Khoo and Smith [11] for the triorganotin derivatives. The position of the amino-proton resonance in the other complexes is also consistent with the lack of coordination of this group expected for monomeric structures. The methyl groups give multiple signals, indicating non-equivalence of these groups which, in turn, implies bidentate bonding for the carboxylate.

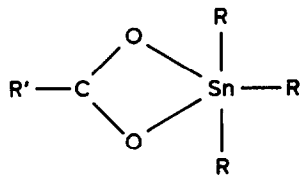
The ^{119}Sn Mössbauer data (Table 4) are best interpreted on the basis of the quadrupole splitting (QS) values, which allow ready distinction between four- and



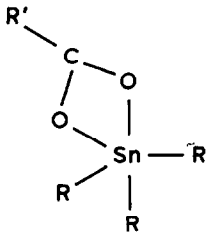
(I)



(II)



(III)



(IV)

five-coordinate structures [36,37]. For a tetrahedral molecule R_3SnX (I), where X is a carboxylate group, the expected QS is about 2.4 mm s^{-1} for R = alkyl and 2.2 mm s^{-1} for R = Ph, while five-coordination normally gives values in excess of 3.0 mm s^{-1}. On this basis, the triphenyl and tricyclohexyl derivatives are four-coordinate and the remainder five-coordinate. The distinction between polymeric, carboxylate-bridged (II) and monomeric five-coordination (III, IV) is more difficult. Structure IV is expected to give a smaller QS (ca. 1.7 mm s^{-1}, R = alkyl) than any observed here, but calculated values for II and III are 3.1 and 3.6 mm s^{-1}, respectively. The majority of the trialkyltin compounds give values close to latter range, and are similar to those of the carboxylates previously reported by us to have structure III [13].

Conclusion

The combination of IR, NMR and Mössbauer spectroscopic data indicates that the compounds $R_3Sn(O_2CR)$ (R = amino-substituted benzoate) have monomeric structures in which the amino group is not coordinated to tin. They are structurally very similar to the complexes of diamino-ethane and -propane tetracarboxylic acids studied previously [13], in that the triphenyl- and tricyclohexyl-tin derivatives are four-coordinate, with monodentate carboxylate groups, while the trialkyl (straight-chain) compounds are chelated with the carboxylate group in the equatorial position of trigonal-bipyramidal structures.

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