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Preparation and the infrared, Mössbauer and ^{1}H, ^{13}C and ^{119}Sn NMR spectra of some triorganotin(IV) derivatives of *N*-benzoyl-DL-alanine and *N*-benzoyl-DL-alanylglycine

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Abstract

The triorganotin(IV) derivatives of *N*-benzoyl-DL-alanine (HA), R_3SnA, and *N*-benzoyl-DL-alanylglycine (HDP), R_3SnDP (R = methyl, n-propyl, n-butyl, phenyl and cyclohexyl, respectively,) have been prepared from the triorganotin(IV) chlorides R_3SnCl and the appropriate *N*-benzoylamino acid. The compounds are five-coordinate and polymeric in the solid state. The tin atoms in triorganotin(IV) groups R_3Sn are coordinated by the unidentate carboxylic group and by the oxygen atom of the amidocarbonyl group of adjacent molecule. The compounds are essentially monomeric in non-coordinating solvents ($CHCl_3$, benzene, nitrobenzene and camphor, respectively), in coordinating solvents (dimethyl sulphoxide, hexamethylphosphortriamide) coordination by one molecule of solvent occurs to form *trans*-trigonal bipyramid five-coordinate complexes.

Introduction

Organotin(IV) compounds R_nSnX_{4-n} are toxic to various organisms and are used to a significant extent as biocidal agents in agriculture and technology [1]. Most

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desirable are compounds whose biocidal properties are not only due to the organotin(IV) part of the molecule (R_4Sn group), but also to the group X, because the effects are mutually combined and complemented. The anions of *N*-acylamino acids in the place of the polar group X in organotin(IV) compounds R_nSnX_{4-n} also have biological importance. Several triorgano- and diorganotin(IV) derivatives of protected and unprotected amino acids and dipeptides have been prepared and some results of X-ray and spectral studies of the structure of these compounds have been previously reported [2–11]. In this paper we describe the synthesis, the infrared, Mössbauer and ^1H, ^{13}C and ^{119}Sn spectra of a series of triorganotin(IV) derivatives of *N*-benzoyl-DL-alanine (protected amino acid) and its dipeptide *N*-benzoyl-DL-alanylglycine.

Experimental

Standard procedures were used to prepare tri-n-propyltin(IV), triphenyltin(IV) and tricyclohexyltin(IV) chlorides [12–14]; *N*-benzoyl-DL-alanine [15]; and *N*-benzoyl-DL-alanylglycine [16–18]. Trimethyltin(IV) and tri-n-butyltin(IV) chlorides were obtained from Alfa Products (U.S.A.) and used without purification.

Melting points were determined in open capillaries, and are uncorrected. Elemental analysis was carried out by the Micro-analytical Service of Calcutta University. The tin content was determined gravimetrically as SnO_2. Molecular weights were determined by the Rast method (in camphor) and cryoscopically in benzene and nitrobenzene. Infrared spectra were recorded on Pye-Unicam P 321 and Perkin–Elmer 684 spectrometers in KBr disks, Nujol suspensions and chloroform solutions in KBr (4000–400 cm^{-1}) or polyethylene (600–200 cm^{-1}) cells. The Mössbauer spectra were measured with a KFKI apparatus (Budapest, Hungary) at room temperature using $Ba^{119m}SnO_3$ as the source. Spectral parameters were obtained by computer treatment of the experimental data by use of the least-squares method for the best fit of the measured values with a simple symmetrical doublet of Lorentzian lines. ^1H, ^{13}C and ^{119}Sn NMR spectra were measured on JEOL JNM-FX 100 spectrometer at 99.602, 25.047 and 37.14 MHz, respectively, in pulse mode with Fourier transformation at 300 K, selective INEPT [19] on a Bruker AM 400 instrument. Saturated solutions of the compounds ($\leqslant$ 150 mg/ml) were studied in deuteriochloroform, hexadeuteriodimethyl sulphoxide and hexamethylphosphortriamide solutions, respectively. ^1H chemical shifts were referred to internal tetramethylsilane. Chemical shifts $\delta(^{119}Sn)$ were related to external neat tetramethylstannane, chemical shifts $\delta(^{13}C)$ were referred to a solvent signal and converted to the δ-scale: deuteriochloroform (δ 77.00 ppm), hexadeuteriodimethyl sulfoxide (δ 39.00 ppm), hexamethylphosphortriamide (δ 36.00 ppm). Positive values of the chemical shifts denote downfield shifts. The signals of the carbon atoms were assigned on the basis of relative integral intensities, the values of coupling constants $^nJ(^{119}Sn, {}^{13}C)$ and multiplicity in proton-coupled spectra. Chemical shifts $\delta(^{13}C)$ of carbonyl carbon atom in C_6H_5CONH group were assigned unambiguously (and distinguished from COOSn) after selective decoupling from aromatic *ortho*-protons in compounds **1–5** and HA. ^{13}C chemical shifts of carbonyl carbon in C_6H_5CONH in compounds **6–10** and HDP were assigned as described above. ^{13}C chemical shifts of carbonyl carbons in $CH(CH_3)CONH$ and CH_2COOSn were differentiated using selective INEPT [19]. ^{13}C chemical shifts of carbonyl carbons of C_6H_5CONH and

CH(CH$_3$)CONH were assigned after selective transfer from C*H*(CH$_3$) via $^2J(^{13}$CO,H) while ^{13}C signals of carbonyl carbons of CH(CH$_3$)CONH and CH$_2$COOSn were observed in selective INEPT spectra by pulsing proton C*H*$_2$COOSn.

Preparation of compounds

To a solution of the sodium salt of *N*-benzoylalanine (5 mmol) or *N*-benzoylalanylglycine (5 mmol) in a dry solvent mixture of benzene (30 ml) absolute ethanol (10 ml) was added the triorganotin(IV) chloride (5 mmol). The reaction mixture was refluxed for 6–8 h during which a white solid (NaCl) separated. The contents were then cooled and filtered. The process of refluxing and filtration was repeated two or three times until all the sodium chloride is separated. Then all of the solvent was removed by distillation under reduced pressure to leave a solid syrup. Trimethyltin(IV), tri-n-propyltin(IV) and tri-n-butyltin(IV) compounds (syrups), were washed with petroleum ether (40–60 °C) in which trialkyltin(IV) chlorides are soluble. The compounds solidify after three to six months in a vacuum desiccator. Tricyclohexyltin(IV) derivatives were recrystallized from dry methanol, and triphenyltin(IV) derivatives from dry benzene. Analytical data and melting points of compounds are listed in Table 1.

Table 1

Physical and analytical data of triorganotin(IV) derivatives of *N*-benzoyl-DL-alanine and *N*-benzoyl-DL-alanylglycine

Compound[a]	Yield (%)	M.p. (°C)	Analysis (Found (calc) (%))				Mol. wt.
			C	H	N	Sn	Found (calc)
$(CH_3)_3$SnA (1)	71	95–105	43.11	4.62	3.78	33.84	278[b]
			(43.86)	(5.32)	(3.90)	(33.35)	(335.6)
(n-$C_3H_7)_3$SnA (2)	80	58– 70	65.09	6.95	3.01	27.04	323[c]
			(65.51)	(7.05)	(3.18)	(26.97)	(439.6)
(n-$C_4H_9)_3$SnA (3)	85	65– 70	55.11	7.23	1.95	24.43	456[b]
			(54.81)	(7.68)	(2.90)	(24.62)	(418.6)
$(C_6H_5)_3$SnA (4)	74	195	61.68	4.40	–	21.28	[d]
			(62.04)	(4.46)		(21.89)	
(c-$C_6H_{11})_3$SnA (5)	70	124–128	59.39	8.03	1.58	21.08	490[b]
			(60.04)	(7.68)	(2.50)	(21.19)	(559.6)
$(CH_3)_3$SnDP (6)	80	85– 90	40.38	5.09	–	28.65	328[c]
			(40.18)	(5.33)		(28.74)	(412.6)
(n-$C_3H_7)_3$SnDP (7)	85	95–100	50.76	7.06	4.89	23.76	512[c]
			(50.74)	(6.80)	(5.60)	(23.88)	(496.6)
(n-$C_4H_9)_3$SnDP (8)	75	93–107	52.95	6.81	–	21.85	455[c]
			(53.47)	(7.10)		(22.05)	(538.6)
$(C_6H_5)_3$SnDP (9)	73	182–184	59.56	4.52	–	19.57	[d]
			(60.14)	(4.67)		(19.81)	
(c-$C_6H_{11})_3$SnDP (10)	72	88– 95	57.58	8.11	–	19.57	576[b]
			(58.38)	(7.46)		(19.23)	(616.6)

[a] Abbreviations HA = *N*-benzoyl-DL-alanine (C_6H_5CONHCH(CH$_3$)COOH), HDP = *N*-benzoyl-DL-alanylglycine (C_6H_5CONHCH(CH$_3$)CONHCH$_2$COOH). [b] Nitrobenzene. [c] Benzene. [d] Separate at low temperature in nitrobenzene and are insoluble in benzene and camphor.

Results and discussion

The triorganotin(IV) derivatives of *N*-benzoyl-DL-alanine and *N*-benzoyl-DL-alanylglycine listed in Table 1 were prepared by the conversion of the appropriate triorganotin(IV) chloride and the sodium salt of the amino acids. In all cases, the composition showed a 1/1 molar ratio. The compounds were identified by chemical analysis and by infrared and ^{1}H, ^{13}C and ^{119}Sn NMR spectroscopy (Tables 2–5). The compounds (excluding triphenyltin(IV) derivatives) are highly soluble in chloroform. The solubility of triphenyltin(IV) derivatives in chloroform and other non-polar solvents is very low (sufficient for the infrared measurements, but not for NMR spectra). Molecular weight measurements showed that all the derivatives are monomers in benzene, nitrobenzene and camphor. All the compounds react with bromoform.

Structural proposals are based on infrared, Mössbauer and ^{13}C and ^{119}Sn NMR data.

Infrared spectra

Frequencies, shapes and relative strengths of the majority of absorption bands in the infrared spectra of compounds **1**–**10** both in the solid state and in chloroform solutions are practically identical. This is especially true for the frequencies due to the substituent R (CH_3, n-C_3H_7, n-C_4H_9, C_6H_5 and C_6H_{11}) of the organotin part (R_3Sn) of the molecule; to the carbon–carbon and carbon–hydrogen bonds in the groups of CH_3, CH_2, and CH of substituents A and DP, and also to Sn–O bonds, with frequencies in the range of 470–480 cm^{-1}. The absorption bands important for the estimation of structure of the compounds in solid state and in solution are summarized in Table 2.

All the studied compounds reveal a very strong band at ~ 1650 cm^{-1} in the infrared spectra of chloroform solutions, which can be obviously assigned to ν_{as}(COO) and ν(CO$_{\text{amide}}$). This band in the infrared spectra of the compounds in solid state extends towards lower frequencies. In the spectra of compounds **1**, **4**, **6** and **9**, a new band develops in the range of 1606–1616 cm^{-1}. A broad band at ~ 1370–1395 cm^{-1} corresponding to the stretching vibration ν_s(COO) does not change with a change in the aggregate state. On the other hand, the band corresponding to ν(CN) + δ(NH) absorption in chloroform solutions lies at 1516–1520 cm^{-1} and in the solid state of compounds **1**,**4** it shifts to higher frequencies (1537 and 1540 cm^{-1}, respectively). In the infrared spectra of compounds **7**,**8** and **10** in the solid state in this region we observed a broad band (1520–1550 cm^{-1}) with distinct splitting features, whereas two bands were found there for compounds **6** and **9** (1548, 1525 and 1535, 1526 cm^{-1}, respectively). As the frequencies of ν_s(COO) do not change significantly with a change in the R_3Sn substituent or with a change in the aggregate state, it is most likely that ν_{as}(COO) will not change either and so we have assigned it the value of ~ 1650 cm^{-1}, as shown in Table 2. The values ν_{as}(COO), ν_s(COO), their differences, (being ~ 250–270 cm^{-1} for all compounds which are substantially higher than the 115 and 140 cm^{-1} found for sodium salts of the acids HA and HDP, respectively) and their non-dependence on the aggregate state of the compound correspond to the monodentate function of the carboxyl group. The oxygen atom of C=O in carboxyl group shows no participation in the coordination of the central tin atom either in solid state or in solution. The

Table 2

Infrared spectral data (cm^{-1})

Compound[a]	ν(NH)	$\nu(\mathrm{CO}_{\mathrm{amide}})$	ν(CN)+δ(NH)	ν_{as}(COO)	ν_s(COO)	ν_{as}(SnC)	ν_s(SnC)
NaA[b]	3420s,b	1630s	1520m,b	1575m,b	1405s		
	330w,b						
EtA[b]	3300s,b	1660s	1516vs	1740s,b	1385s		
1[c]	3420s,b	1653vs	1516vs	1653vs	1396s	551m	519w
	3330m,b						
1[b]	3300m,b	1606s	1537vs	1647vs	1390s	554m	(510vw)
2[c]	3380m,b	1655s	1520s	1655s	1395s	570m	519w
3[c]	3400m,b	1640s	1518s	1640s	1390s	580m	524w
4[c]	3425m,b	1651vs	1517vs	1651vs	1395s	269m	235w,sh
	3314m,b						
4[b,d]	3280s,b	1612s	1540s	1646vs	1387s	272m	231vw
5[b]	3300m,b	1600m	1540m	1635s	1370s	475m	415w
NaDP[b]	3360s,b	1630s	1530m,b	1600s	1390s		
EtDP[c]	3410s,b	1630–1660s,b	1510m,b	1725s	1265s		
	3310s,b						
EtDP[b]	3260m,b	1620–1670m,b	1515m,b	1740s	1285s		
6[c]	3430m,b	1646vs	1519vs	1646vs	1388s	552m	519w
6[b]	3419w	1616vs	1548vs	1647vs	1395s	554m	518vw,sh
	3288s	1639vs	1525vs				
7[b]	3360m,b	1610–1640vs,b	1520–1550s,b	1651vs	1388s	595m	510w
8[b]	3300m,b	1610–1640vs,b	1520–1550s,b	1655vs	1388s	600m	520vw
9[c]	3430m,b	1649vs	1519s	1649vs	1386s	268s	238w,sh
9[b,d]	3300m,b	1650s	1526s	1659vs	1386s	273s	234w
		1606s	1539s				
10[b,d]	3300vs,b	1620–1650vs,b	1530s,b	1655s	1386s	475m	415w

[a] For compounds see Table 1. [b] KBr disc. [c] Solution of $CHCl_3$. [d] Nujol suspension.

formation of intramolecular chelates or intermolecular bridges by the bidentate carboxylic group is excluded. A marked shift of the ν(CN) + δ(NH) band towards higher frequencies of compounds **1** and **4** and simultaneous shift of $\nu(\mathrm{CO}_{\mathrm{amide}})$ band towards lower frequencies with the change from solid → solution are consistent with the idea of participation of the CONH group in the coordination bonding with the tin atom via donor oxygen atom in the solid state. The presence of doublets for $\nu(\mathrm{CO})_{\mathrm{amide}}$) and ν(CN) + δ(NH) in the compounds **6** and **9** and broad bands in the same region at the compounds of **7**, **8** and **10** give evidence for the participation of only one CONH group in the NHCO · · · Sn donor–acceptor connection. From the above analysis we can conclude that in chloroform solutions compounds **1**–**10** are present in the form of simple molecules having tetrahedral coordination of tin atom. In the solid state, however, the coordination number of the tin atom increases owing to the formation of a NHCO · · · Sn donor–acceptor bond and thus in compounds **1**–**10** the tin atom is five-coordinated. The presence of both stretching vibrations, ν_{as}(SnC) and ν_s(SnC), in the infrared spectra of all compounds both in the solid state and in solution excludes, however, an exactly planar arrangement of the three Sn–C bonds and thus a precisely symmetrical shape of the *trans*-trigonal bipyramid arrangement of bonds around central tin atom in compounds **1**–**10** in the solid state. The values of ν(NH) are evidence for the formation of hydrogen bonds of NHCO · · · H in the solid compounds and their disintegration during dissolution of the compounds is chloroform.

Mössbauer spectra

Five-coordinate geometry around the central tin atom of compounds in the solid state has been confirmed in two compounds studied by means of Mössbauer spectroscopy. Mössbauer spectra parameters relevant to the determination of structure, i.e. isomer shift (IS) and quadrupole splitting (QS) were determined (always with an accuracy of ± 0.03 mm s^{-1}) as 1.34 and 2.93 mm s^{-1}, respectively, for compound **6** and 1.23 and 2.80 mm s^{-1}, respectively, for compound **9**. That the QS/IS ratio is 2.19 and 2.28 for compounds **6** and **9**, respectively, indicates tin atom coordination to be higher than four. The values of isomer shifts lie in the range typical of triorganotin(IV) carboxylates, while quadrupole splitting values are slightly lower than those typical for *trans*-trigonal bipyramid coordination of tin in R_3SnO_2 fragment (3.00–4.00 mm s^{-1}), but substantially higher than that for *cis*-trigonal bipyramid (1.70–2.40 mm s^{-1}) and pseudotetrahedral (1.00–2.40 mm s^{-1}) arrangements [20]. The values of QS in the region 2.8–3.0 mm s^{-1} were also found in triorganotin derivatives of amino acids with *trans*-trigonal bipyramid geometry around tin atom [21] and for other triorganotin carboxylates with $O \cdots Sn(R)_3O$ intermolecular interaction [22]. It indicates that weak intermolecular bonding results in an increase of the coordination number of tin atom and the formation of a deformed *trans*-trigonal bipyramid coordination around the tin atom. A different strength of Sn–OCO and Sn–OCNH bonds in intermolecular aggregates in solid compounds **1–10** also results in the deviation of Sn–C bonds out of the equatorial plane towards the Sn–OCNH bond as was manifested in the infrared spectra. Polymer-like structure of compounds **1–10** in the solid state and intermolecular $O \cdots Sn$ coupling and thus *trans*-trigonal bipyramid coordination of the tin atom is also supported by the fact that parameters of Mössbauer spectra were determined at room temperature.

NMR spectra

The ^1H NMR spectra of the compounds **1–8** and ethyl esters of HA and HDP acids were recorded in deuteriochloroform and are given in Table 3. The number of

Table 3

^1H NMR data of compounds **1–8** in $CDCl_3$ (δ (ppm))

Compound [a]	C_6H_5	$N\mathit{H}$ [b]	$C\mathit{H}(CH_3)$	$NHC\mathit{H}_2$	$(CH)C\mathit{H}_2$	SnR_3	
						CH_2	CH_3
EtA [c]	7.40–7.84	6.82	4.77	–	1.51	–	–
1 [d]	7.36–7.78	7.00	4.46	–	1.50	–	0.59
2	7.39–7.84	6.96	4.69	–	1.51	1.13–1.83	0.97
3	7.36–7.84	7.02	4.74	–	1.51	1.05–1.78	0.89
5	7.36–7.86	7.05	4.71	–	1.52	0.95–2.03	–
EtDP [e]	7.26–7.82	7.30	4.84	4.00	1.47	–	–
6 [f]	7.28–7.85	6.95;7.10	4.75	3.96	1.52	–	0.60
7	7.28–7.85	6.85;7.16	4.75	3.97	1.52	1.10–1.76	0.96
8	7.36–7.84	6.12;7.09	4.74	3.99	1.50	1.00–1.78	0.89

[a] For compounds see Table 1. [b] Concentration dependent. [c] (OCH_2CH_3): 4.23(CH_2), 1.29(CH_3). [d] $^2J(^{119}Sn,H)$: 59.1 Hz. [e] (OCH_2CH_3): 4.15(CH_2), 1.23(CH_3). [f] $^2J(^{119}Sn,H)$: 59.3 Hz.

Table 4

^{13}C and ^{119}Sn NMR parameters of R_3Sn groups in compounds 1–9

Compound [a]	Solvent	$\delta(^{119}Sn)$	$\delta(^{13}C)$ (ppm) ($^{n}J(^{119}Sn, ^{13}C)$ (Hz))			
			C(1)	C(2)	C(3)	C(4)
1	$CDCl_3$	142.4	−2.04 (405.9)			
2	$CDCl_3$	129.8	19.61 (351.6)	19.14 (22)	18.44 (64.4)	
3	$CDCl_3$	129.2	16.68 (353.5)	27.74 (22)	26.92 (64)	13.58
4	dmso-d_6 [b]	−263.0	143.15 [c]	136.36 (47)	128.23 (70.4)	128.87 [c]
5	$CDCl_3$	31.4	34.06 (331.2)	30.96 [c]	28.79 [c]	26.80 [c]
6	$CDCl_3$	147.4	−2.10 (401.5)			
7	$CDCl_3$	127.4	19.59 (351.6)	19.00 [c]	18.27 (64.6)	
8	$CDCl_3$	129.0	16.80 (349.4)	27.62 (21.50)	26.86 (64.5)	13.52 [c]
8	hmpa [d]	−58.6				
9	dmso-d_6	−269.0	144.20 (832.4)	136.25 (47.0)	128.59 (70.4)	128.59 [c]

[a] For compounds see Table 1. [b] Hexadeuteriodimethyl sulfoxide. [c] Not found. [d] Hexamethylphosphortriamide.

protons calculated from integration curves is equal to that calculated from the molecular formula of each compound. Thus, the studied compounds have been fully identified by analysis of the ^{1}H NMR spectra.

^{119}Sn and ^{13}C NMR spectroscopy has been employed to obtain further information about the structure of compounds in solution.

The chemical shifts $\delta(^{119}Sn)$ of the alkyltin(IV) derivatives **1**–**3** and **6**–**8** are in the range 129.0 to 147.4 ppm (Table 4), which is typical of quasi-tetrahedral arrangement [23,24] of simple trialkyltin(IV) compounds with four-coordinate central tin atom. The value of $\delta(^{119}Sn)$ for compound **5** (31.4 ppm) corresponds well to the tetrahedral configuration of $(C_6H_{11})_3SnOCO$ [25]. The chemical shifts $\delta(^{119}Sn)$ of compound **8** in hexamethylphosphortriamide (−58.6 ppm) and those of the compounds **4** and **9** in hexadeuteriodimethyl sulfoxide (−269.0 and −263.0 ppm, respectively) are typical of tri-n-butyl- and triphenyltin(IV) complexes with one molecule of coordinating solvent bonded through the donor atom to the central tin atom [23,26]. The tin atom assumes a coordination number of five.

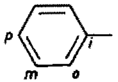
The values of $\delta(^{13}C)$ for the carboxylic and amide carbonyl carbon atoms are practically unchanged relative to the ethyl esters of HA and HDP, which is consistent with the absence of $C{=}O\cdots SnR_3$ interaction.

The values of the coupling constants $^{1}J(^{119}Sn, ^{13}C)$ are directly associated with the structure of organotin(IV) compounds. The compounds **1**–**3** and **5**–**8** in $CDCl_3$ solution exhibit $^{1}J(^{119}Sn, ^{13}C)$ in the range 331.2 to 405.9 Hz which corresponds to that of the pseudotetrahedral structure of R_3SnO configuration with four-coordinating tin(IV) atom [23]. The coupling constant $^{1}J(^{119}Sn, ^{13}C)$ for the compound **9** in

Table 5

^{13}C chemical shifts (δ (ppm)) of A ($C_6H_5CONHCH(CH_3)COO$) and DP ($C_6H_5CONHCH(CH_3)CONHCH_2COO$) in compounds **1–9**

Compound [a]	COOSn	$C_6H_5\mathit{C}ONH$	CH	$CH\mathit{C}H_3$	C_i [b]	C_o	C_m	C_p	CH_2	$CH_2\mathit{C}ONH$
EtA [c,d]	173.12	166.86	48.45	18.32	133.75	126.96	128.37	131.52	–	–
1 [c]	177.68	166.86	49.27	19.20	134.27	126.96	128.42	131.47	–	–
2 [c]	177.68	166.45	49.27	19.30	134.33	126.96	128.42	131.40	–	–
3 [c]	177.62	166.39	49.33	19.38	134.39	126.96	128.42	131.35	–	–
4 [f]	175.44	165.61	49.37	18.07	134.60	126.41	128.23	131.16	–	–
5 [c]	177.21	166.39	49.45	19.55	134.45	126.96	128.37	131.35	–	–
EtDP [c,g]	169.37 [e]	167.08	48.85	17.78	133.45	126.93	127.98	131.19	40.99	173.07
6 [c]	173.88	167.10	49.21	18.73	133.98	127.14	128.48	131.64	42.31	172.24
7 [c]	173.69	166.86	48.98	18.47	133.68	127.05	128.22	131.39	41.96	172.28
8 [c]	173.65	166.86	49.03	18.61	133.75	127.08	128.31	131.47	42.02	172.18
9 [f]	172.2	166.03	48.79	18.01	133.20	127.47	128.59	131.22	[h]	172.2

[a] For compounds see Table 1. [b] 

. [c] In deuteriochloroform. [d] $\delta(OCH_2CH_3)$: 61.44(CH_2), 14.00(CH_3). [e] COOEt. [f] In hexadeuteriodimethyl sulfoxide. [g] $\delta(OCH_2CH_3)$: 60.82(CH_2), 13.63(CH_3). [h] Overlapped by the solvent.

hexadeuteriodimethyl sulfoxide (832.4 Hz) is typical of *trans*-trigonal bipyramid arrangement of the tin atom surroundings in Ph_3SnO_2 fragment of the complex $Ph_3SnOC(O)R \cdot (dmso\text{-}d_6)$ [26]. The mean values of the angle θ (angle C–Sn–C) calculated from $^1J(^{119}Sn, ^{13}C)$ according to refs. 27 and 28 are ca. 112° (compounds **1** and **6**) and 109.5° (compound **8**) and 110° (compound **3**). The deformation of tetrahedral geometry of groups Me_3SnO and $n\text{-}Bu_3SnO$ in these compounds is negligible. The almost ideal shape of R_3SnO excludes even a more obvious interaction with nitrogen atoms of the amidic groups and/or oxygen atoms of carbonyl groups (if any interactions exist, they must be very weak).

Conclusion

Triorganotin(IV) derivatives of *N*-benzoyl-DL-alanine and *N*-benzoyl-DL-alanylglycine (**1–10**) in the solid state have a polymeric structure (containing unidentate carboxylic groups). Their molecules are linked together via the weak intermolecular donor–acceptor $NHCO \cdots SnR_3$ bond. The fragment of $O \cdots Sn(R_3)O$ has a slightly deformed *trans*-trigonal bipyramid geometry of atoms linked to the central tin atom with a slightly out of planar arrangement of the R_3Sn group.

In solutions of non-coordinating solvents ($CDCl_3$, benzene, nitrobenzene) the compounds **1–10** are present in the form of simple molecules with nearly ideal tetrahedral configuration of R_3SnOCO groups. In solutions of coordinating solvents (hexamethylphosphortriamide, hexadeuteriodimethyl sulfoxide) compounds **1–10** form complexes with one molecule of the solvent. These complexes reveal *trans*-trigonal bipyramid structure with five-coordinate tin atom.

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