IR AND ^{13}C, ^{17}O, AND ^{119}Sn NMR SPECTRA OF SOME BIS(1-BUTYL)TIN(IV) CARBOXYLATES OF DICARBOXYLIC ACIDS

Jaroslav HOLEČEK[a], Antonín LYČKA[b], Milan NÁDVORNÍK[a] and Karel HANDLÍŘ[a]

[a] *Department of General and Inorganic Chemistry,*
Institute of Chemical Technology, 532 10 Pardubice
[b] *Research Institute of Organic Syntheses, 532 18 Pardubice-Rybitví*

Received January 11, 1991
Accepted February 25, 1991

Infrared spectroscopy and multinuclear (^{13}C, ^{17}O, and ^{119}Sn) NMR spectroscopy have been used to study the structure of bis(1-butyl)tin(IV) carboxylates of dicarboxylic acids $(1\text{-}C_4H_9)_2.Sn(X(COO)_2)$, where $X = (CH_2)_n$ ($n = 0-8$), CH=CH (*cis* and *trans*) and C_6H_4 (*ortho* and *para*). The crystalline compounds are formed by linear or cyclic oligomers or polymers whose basic building units represent a grouping composed of the central tin atom substituted by two 1-butyl groups and coordinated with both oxygen atoms of two anisobidentate carboxylic groups derived from different molecules of a dicarboxylic acid. The environment of the tin atom has a shape of a trapezoidal bipyramid. When dissolved in non-coordinating solvents, the compounds retain the oligomeric character with unchanged structure of environment of the central tin atom. In the media of coordinating solvents the bis(1-butyl)tin(IV) carboxylates of dicarboxylic acids form complexes whose central hexacoordinated tin atom binds two molecules of the solvent trough their donor atoms. Carboxylic groups form monodentate linkages in these complexes.

A number of our earlier communications[1-5] describes results of our studies of structure of particle of tri- and diorganotin(IV) carboxylates of monocarboxylic acids in various types of solvents using infrared spectroscopy and multinuclear (^{13}C, ^{17}O, and ^{119}Sn) NMR spectroscopy. It was found that in non-coordinating solvents the triorganotin(IV) monocarboxylates and diorganotin(IV) dicarboxylates derived from monocarboxylic acids (regardless of their structure in solid state) exist as monomeric chelate complexes with anisobidentate function of carboxylic group. Particles of triorganotin(IV) carboxylates have a shape of deformed *cis*-trigonal bipyramid (the coordination number of the central tin atom is equal to 5 or better to 4 + 1), the environment of central tin atom of diorganotin(IV) dicarboxylates (where the coordination number is equal to 6 or to 4 + 2) having the shape of trapezoidal bipyramid (skew). In coordinating solvents the molecules of triorganotin(IV) carboxylates form complexes containing one coordinated molecule of solvent (*trans*-trigonally bipyramidal arrangement around the tin atom), the complexes of diorganotin(IV) dicarboxylates with two molecules of coordinating solvent being trapezoidally bipyramidal. In both types of complexes the carboxylic group is bound monodentately to the tin atom.

The organotin(IV) carboxylates of dicarboxylic acids and especially the diorganotin(IV) carboxylates have not yet attracted attention in spite of their important application possibilities. A limited number only of this type of compounds have been described[6-8], and the structure of their particles is only derived from analysis of infrared spectra of some of them. The present paper summarizes the results of studies of structure of bis(1-butyl)tin(IV) carboxylates of dicarboxylic acids $(1\text{-}C_4H_9)_2Sn(X(COO)_2)$, where X is $(CH_2)_n$ ($n = 0-8$), i.e. derivatives of oxalic (*I*), malonic (*II*), succinic (*III*), glutaric (*IV*), adipic (*V*), and sebacic (*VI*) acids, or X is CH=CH, i.e. maleic (*VII*) and fumaric (*VIII*) acids, or X is 1,2- or 1,4-C_6H_4, i.e. phthalic (*IX*) and terephthalic (*X*) acids using infrared spectroscopy and ^{13}C, ^{17}O, and ^{119}Sn NMR spectroscopy.

EXPERIMENTAL

All the compounds studied in this work were prepared by the reaction of bis(1-butyl)stannyl oxide $(1\text{-}C_4H_9)_2SnO$ with the corresponding dicarboxylic acids in benzene medium. The water formed in the reaction was removed by azeotropic distillation[6].

The infrared spectra were measured in Nujol suspension and in chloroform solution using a Perkin–Elmer 684 apparatus. The ^{13}C, ^{17}O, and ^{119}Sn NMR spectra were measured at 25·047, 13·505, and 37·14 MHz, respectively, using a JNM-FX 100 (JEOL) apparatus at 300 K; the samples were dissolved in deuteriochloroform. The detailed conditions of the measurements are described in our earlier papers[1-5]. The chemical shifts $\delta(^{13}C)$ are referred to the solvent signal ($\delta = 77\cdot00$), the chemical shifts $\delta(^{17}O)$ and $\delta(^{119}Sn)$ are referred to external neat H_2O and to $(CH_3)_4Sn$, respectively ($\delta = 0\cdot0$).

RESULTS AND DISCUSSION

Syntheses and Identification of Substances

From literature[6-12] it is known that diorganotin(IV) carboxylates of dicarboxylic acids can be obtained either in the form of pseudolinear polymers insoluble in currently used solvents or in the form of low-molecular oligomers, cyclic and perhaps also linear, which are soluble in organic nonpolar or slightly polar solvents.

As already stated all the compounds studied here were prepared in their soluble form[6,9-12] by the well-tried method of azeotropic esterification of bis(1-butyl)stannyl oxide with the respective acids using equimolar ratios of the components in benzene medium[6]. Nevertheless, the compounds *I*, *VIII* and *X* prepared by this reaction (with almost quantitative yields) were completely insoluble in all currently used solvents. The other substances were recrystallized from benzene or its mixtures with petroleum ether. Although elemental analysis (Table I) confirms – for all the compounds – the composition corresponding to the empirical formulas of the respective bis(1-butyl)tin(IV) carboxylates of dicarboxylic acids, some compounds exhibit physical parameters whose values differ from those given in literature. Compound *I*, which in accordance with ref.[6] represents bis(1-butyl)stannyl oxalate monohydrate, shows no melting of its crystals at 195°C (ref.[6]). Our results obtained from thermal and thermogravimetric analyses show that the compound looses one water molecule at ca 165°C and undergoes a three-step decomposition on further heating (250 – 300°C). The three-step decomposition was also observed at the temperatures of c. 280, 400, 460°C and 340, 390, 450°C with compounds *VIII* and *X*, respectively. In all the cases tin(II) oxide is the final decomposition product, which agrees excellently with results by Bruck[10,11]: he found that the only volatile decomposition

TABLE I

Physical and analytical data of the compounds $(1\text{-}C_4H_9)_2Sn(X(COO)_2)$

Compound	X	Calculated/(Found)			Melting temperature, °C	Mol. weight found (calculated)
		% C	% H	% Sn		
I	—	35·43 (34·91)	5·94 (5·82)	35·02 (34·96)	165 dec.	—
II	CH_2	39·44 (40·15)	6·03 (6·40)	35·43 (35·62)	65—67	1 457[a] (1 339·84)[b]
III	$(CH_2)_2$	41·30 (41·18)	6·35 (6·35)	34·01 (33·88)	189—191	1 430[c] (1 396·00)[b,d]
IV	$(CH_2)_3$	43·01 (42·90)	6·66 (6·61)	32·70 (32·84)	166—167	1 482[a] (1 452·08)[b]
V	$(CH_2)_4$	44·60 (45·40)	6·95 (7·00)	31·48 (31·22)	135—136	1 205[a] (1 131·15)[e,f]
VI	$(CH_2)_8$	49·91 (50·02)	7·91 (8·01)	27·40 (26·98)	122—128	870[c] (866·32)[g,h]
VII	CH═CH(*cis*)	41·54 (41·60)	5·82 (5·77)	34·21 (34·37)	136—138	1 390 (1 395·92)[b,i]
VIII	CH═CH(*trans*)	41·54 (40·86)	5·82 (5·70)	34·21 (33·86)	280 dec.	[j]
IX	$1,2\text{-}C_6H_4$	48·40 (48·47)	5·60 (5·55)	29·89 (29·78)	206—207	1 821[c] (1 588·16)[b]
X	$1,4\text{-}C_6H_4$	48·40 (48·47)	5·60 (5·55)	29·89 (30·03)	340 dec.	[j]

[a] Osmometry; [b] tetramer; [c] cryoscopy (camphor); [d] melting temperature 187—187·5°C (ref.[6]); [e] trimer; [f] melting temperature 136—137°C (ref.[6]); [g] dimer. [h] mol. weight 2 950—3 000, melting temperature 78—82°C (ref.[6]); [i] refs[7,8]; [j] polymer.

products from compounds *V*, *VIII*, and *X* are carbon monooxide and a mixture of organic compounds with butane and butenes as predominant components. Compounds *II* – *VII* and *IX* – in accordance with our results of measurements of molecular masses and with comparison with physical data and properties of known substances[6–8] – represent lower oligomers (Table I), which is also true of the compound *VI* which – in contrast to literature data[6] – was prepared in the form of white crystals.

Infrared Spectra

Table II presents the frequence values of both components (symmetrical and antisymmetrical) of valence vibrations of carboxylic group in IR spectra of compounds *I* – *X* which are significant for the estimation of structure of carboxylic group and the way of its bond to the organotin(IV) fragment of these compounds.

In Table II it is particularly noteworthy that both the values ν_{as}(COO) and ν_s(COO) of IR spectra of the crystalline substances (Nujol suspension) are the same or very slightly different from those for the respective solutions in nonpolar (noncoordinating) solvent. Hence it can be stated that the structure of carboxylic group as well as the way of its bond to the central tin atom in compounds *II* – *VII* and *IX* are independent of the state of aggregation of these compounds, and it can also be expected then that both the solid phase and solutions of the compounds in nonpolar solvents contain the same or very much cognate particles as the basic units.

The frequence ν_{as}(COO) of the compounds studied (except *I*) in both solid phase

TABLE II

The frequence values ν_{as}(COO) and ν_s(COO) in the IR spectra of compounds *I*–*X* (cm^{-1})

Compound	Solid phase (Nujol)		Solution in $CHCl_3$	
	ν_{as}(COO)	ν_s(COO)	ν_{as}(COO)	ν_s(COO)
I	1 687	1 307	–	–
II	1 606	1 370	1 610	1 380
III	1 586	1 390	1 610	1 387
IV	1 610	1 380	1 610	1 380
V	1 588	1 360	1 590	1 383
VI	1 620	1 365	1 625	1 365
VII	1 585	1 366	1 585	1 384
VIII	1 566	1 375	–	–
IX	1 600	1 370	1 610	1 370
X	1 598	1 360	–	–

and chloroform solution are distinctly lower than the corresponding values of methyl or ethyl esters of the respective dicarboxylic acids (by 100 – 150 cm^{-1}) and only slightly higher than the corresponding values of their alkaline salts. The values of $\nu_s(\text{COO})$ approach those of the alkaline salts, being shifted towards higher frequences (by 80 – 100 cm^{-1} in average) as compared with the values of $\nu_s(\text{COO})$ of methyl and ethyl esters of the respective acids[13–23]. Thus in compounds *II*–*X* each carboxyl group is bound to a tin atom by both its oxygen atoms; however, it is not excluded that the two Sn—O bonds have different strength (anisobidentate function of carboxylic group). On the basis of ref.[24] the denticity criterion of a carboxylic group is seen in the difference $\nu_{as}(\text{COO}) - \nu_s(\text{COO}) = \Delta\nu$. For derivatives of dicarboxylic acids the value $\Delta\nu < 240\ \text{cm}^{-1}$ indicates the bidentate function and $\Delta\nu > 240\ \text{cm}^{-1}$ indicates the monodentate function[25]. The differences $\Delta\nu$ are 191 to 240 cm^{-1} for compounds *II*–*X* (they are in the range of 374 – 522 cm^{-1} for methyl and ethyl esters and in the range of 162 – 212 cm^{-1} for alkaline salts[13–23]). Thus the $\Delta\nu$ values of compounds *II*–*X* represent a transition step between monodentate and bidentate behaviour of a carboxylic group. The shift in $\nu_{as}(\text{COO})$ and $\nu_s(\text{COO})$ values in the hydrate of compound *I* was explained in ref.[6].

NMR *Spectra*

Except for compounds *I*, *VIII*, and *X*, which are almost insoluble in deuteriochloroform, the solubility of substances – though relatively low – is sufficient for the measurements of most relevant parameters of the ^{13}C and ^{119}Sn NMR spectra to be possible (Table III).

The values of chemical shifts $\delta(^{119}\text{Sn})$ of compounds *II* – *VII* and *IX* in deuteriochloroform solutions vary within the limits from −126·6 to −146·4 ppm, which is a typical region of bis(1-butyl)tin(IV) compounds with the coordination number of the central metal atom equal to five[26] or the so-called coordination 4 + 2 which is found generally e.g. with the diorganotin(IV) dicarboxylates derived from monocarboxylic acids[3–5]. In such cases the central atom is coordinated with six ligands out of which four ligands are firmly bound and the other two ligands exhibit a substantially weaker bond. The increased coordination of the tin atom (the coordination number above 4) is also indicated by the $\delta(^{13}\text{C})$ values of carbon atoms of the 1-butyl substituent which are also comparable with the $\delta(^{13}\text{C})$ values of the analogous bis(1-butyl)tin(IV) dicarboxylates derived from monocarboxylic acids[3–5].

Extremely valuable information about structure of carboxylic group and way of its bond to tin atom is provided by the $\delta(^{13}\text{C})(\text{COO})$ values. These values in the compounds studied are distinctly shifted down field (by c. 10 ppm or even more) as compared with the same values in NMR spectra of organic esters[27], namely to the region where there are the $\delta(^{13}\text{C})(\text{COO})$ values of alkaline salts of the respective dicarboxylic acids[27] (cf. data of Table III). From what was said it follows that carboxylic group is bound bidentately to tin atom, i.e. similarly as it is in the diorganotin(IV) dicarboxylates derived from monocarboxylic acids[3-5,28]. This conclusion is also supported by the fact that – in analogy with the organotin(IV) carboxylates derived from monocarboxylic acids[3-5] – the ^{17}O NMR spectrum of compound *VIII* only exhibits a single signal ($\delta(^{17}O)$ = 280·9), whereas the ^{17}O NMR spectrum of bis(1-butyl)phthalate (neat liquid, 380 K, D_2O in coaxial capillary as

TABLE III

Parameters of the ^{13}C and ^{119}Sn NMR spectra of compounds *II*–*VII* and *IX* in deuteriochloroform, 300 K

Compound	$\delta(^{119}Sn)$	$\delta(^{13}C)^a/(^nJ(^{119}Sn, ^{13}C)$, Hz)							
		C(1)	C(2)	C(3)	C(4)	COO	C(X)	COO[b,c]	COO[c,d]
II	−127·3	25·44 (553·4)	26·31 (34·2)	26·31 (100·1)	13·45 <5	176·32	40·89	167·20	178·46
III	−141·3	25·00 (576·2)	26·56 (34·2)	26·31 (97·1)	13·50 <5	182·22	29·53	172·80	183·67
IV	−143·1	25·00 (578·5)	26·56 (34·5)	26·22 (94·8)	13·45 <5	183·00	33·19 (2C) 21·10 (1C)	171·40[e]	184·24
V	−144·9	24·95 (578·6)	26·61 (35·4)	26·40 (97·7)	13·45 <5	183·59	33·72 (2C) 24·95 (2C)	173·70	184·86
VI	−146·4	25·30 [f]	26·68 [f]	26·28 [f]	13·51 [f]	182·84 [f]	34·04 24·96 29·00 29·10	173·70	
VII	−126·6	26·04 (553·8)	26·63 (27·9)	26·40 (102·6)	13·47 <5	174·76	150·70	165·90	171·82[g]
IX[h]	−135·8	25·40 (559·8)	26·80 (29·4)	26·34 (104·0)	13·43 <5	177·45	135·51 130·71 129·07	167·90	171·10[g]
IX[i]	−230·3	[f]	26·93	26·05	13·74	170·74	134·21 130·38 129·09		

[a] $\overset{4}{C}H_3\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}H_2$; [b] the chemical shift $\delta(^{13}C)$(COO) of dimethyldicarboxylates; [c] ref.[27]; [d] chemical shift $\delta(^{13}C)$(COO) of dianions of dicarboxylic acids; [e] diethylester; [f] the value was not determined due to low solubility of the substance; [g] monoanion; [h] $\delta(^{17}O)$ = 280·9; [i] in hexadeuteriodimethyl sulfoxide.

an external liquid (δ = 0·0)) exhibits two ^{17}O signals: $\delta(^{17}O)$ (C=O) = 377 ($w_{1/2}$ = = 1 000 Hz) and $\delta(^{17}O)$ (C—O) = 161 ($w_{1/2}$ = 880 Hz).

In hexadeuteriodimethyl sulfoxide solutions compound *IX* exhibits the value of chemical shift $\delta(^{119}Sn)$ = −230·3 ppm, which is a value typical of hexacoordinated bis(1-butyl)tin(IV) complex compounds[26]. The ^{13}C NMR spectrum of this compound in hexadeuteriodimethyl sulfoxide exhibits only a single signal for the carbon atom of carboxylic group, which indicates chemical identity of both carboxylic groups in the fragment 1,2-$C_6H_4(COO)_2$. In this coordinating solvent the value $\delta(^{13}C)$ . . (COO) = 170·74 is shifted upfield by almost 7 ppm as compared with that of the same compound in deuteriochloroform solution, i.e. it is shifted to a region characteristic of the shifts $\delta(^{13}C)$ (COO) of organic esters (see Table III) with "monodentate" function of carboxylic group. Hence it is most likely that – as it is the case with the diorganotin(IV) dicarboxylates derived from monocarboxylic acids[3–5] – the environment of the tin atom of compound *IX* (in the medium of coordinating solvent – hexadeuteriodimethyl sulfoxide) includes an octahedral arrangement of six ligands, namely two carbon atoms C(1) of the 1-butyl substituents, two oxygen atoms of two different monodentate carboxylic groups, and two donor atoms from two solvent molecules. Hence compound *IX* is present in hexadeuteriodimethyl sulfoxide solution formally as the disolvate $(1\text{-}C_4H_9)_2Sn(OCOC_6H_4COO).2\,(CD_3)_2.SO$. From the experiments described here it is impossible to decide whether these are monomeric particles with a chelate function of the 1,2-$C_6H_4(COO)_2$ fragment or they are oligomers with a bridge function of the fragment. As we were unable to measure the value of coupling constant $^1J(^{119}Sn, ^{13}C)$ of compound *IX* in hexadeuteriodimethyl sulfoxide, it is impossible to give any detailed description of shape of the coordination polyhedron around the tin atom in the disolvates considered.

CONCLUSION

The environment of tin atom in the bis(1-butyl)tin(IV) dicarboxylates derived from mono- and dicarboxylic acids is not much different – by our results[3–5,28]. The tin atom is coordinated with two organic substituents and with four oxygen atoms of two carboxylic groups. Two Sn—O bonds are relatively strong, the other two are substantially weaker. The resulting coordination polyhedron will necessarily differ from an ideal shape of *trans*-octahedron or *trans*-tetragonal bipyramid because of the different strength of bonds between the tin atom and its various ligands. This conclusion is supported also by the values of $^1J(^{119}Sn, ^{13}C)$ of the compounds studied or by the therefrom calculated values[29] of C—Sn—C angles. The $^1J(^{119}Sn, ^{13}C)$ values within the limits from 553·4 Hz to 578·6 Hz correspond to the values of C—Sn—C angle within the limits from 130° to 133°. The environment of central atom formed by two 1-butyl groups and two anisobidentate chelate carboxylic groups coming from two different molecules of dicarboxylic acid has a shape of trapezoidal bipyramid (skew). These basic building units then agglomerate into linear chains or cyclic formations which can be found in both crystals and solutions of compounds *I*–*X* in noncoordinating solvents.

In the media of coordinating solvents the basic building particles are pseudo-octahedral formations formed by the central tin atom surrounded by two carbon atoms C(1) of 1-butyl substituent, donor atoms of two solvent molecules, and two oxygen atoms of two different monodentate carboxylic groups.

REFERENCES

1. Holeček J., Handlíř K., Nádvorník M., Lyčka A.: J. Organomet. Chem. *258*, 147 (1983).
2. Lyčka A., Nádvorník M., Handlíř K., Holeček J.: Collect. Czech. Chem. Commun. *49*, 2903 (1984).
3. Holeček J., Handlíř K., Lyčka A., Chattopadhyay T. K., Majee B., Kumar A. K.: Collect. Czech. Chem. Commun. *51*, 1100 (1986).
4. Lyčka A., Holeček J., Handlíř K., Pola J., Chvalovský V.: Collect. Czech. Chem. Commun. *51*, 2583 (1986).
5. Lyčka A., Jirman J., Holeček J.: Collect. Czech. Chem. Commun. *53*, 588 (1988).
6. Andrews T. M., Bower A., Laliberte B. R., Montermoso J. C.: J. Am. Chem. Soc. *80*, 4102 (1958).
7. Mufti A. J., Poller R. C.: J. Chem. Soc. C *1967*, 1362.
8. Kizling J., Rattay V., Jakubčck E.: Ropa Uhlie *29*, 199 (1987).
9. Bruck S. D.: J. Polym. Sci., B *4*, 933 (1965).
10. Bruck S. D.: J. Polym. Sci., A1 *5*, 2458 (1967).
11. Bruck S. D.: J. Polym. Sci., A1 *7*, 781 (1969).
12. Frankel M., Gertner D., Wagner D., Zilkha A.: J. Appl. Polym. Sci. *9*, 3383 (1965).
13. Abramovitz R. A.: Can. J. Chem. *37*, 1146 (1959).
14. Matzke P., Chacon O., Andrade C.: J. Mol. Struct. *9*, 255 (1971).
15. Ito K., Bernstein H. J.: Can. J. Chem. *34*, 170 (1956).
16. Felton D. G., Orr S. F. D.: J. Chem. Soc. *1955*, 2170.
17. Abramovitz R. A.: Can. J. Chem. *36*, 151 (1958).
18. Chapman D., Lloyd D. R., Prince R. H.: J. Chem. Soc. *1964*, 550.
19. Savart V. V.: Z. Anorg. Allg. Chem. *385*, 329 (1970).
20. Compton D. A. C., Grow W. D., Porter A. J.: J. Chem. Soc., Perkin Trans 2 *1975*, 400.
21. Pristera F.: Anal. Chem. *25*, 884 (1953).
22. Akihisa M.: Bull. Chem. Soc. Jpn. *30*, 361 (1957).
23. Lindberg B. J.: Acta Chem. Scand. *22*, 571 (1968).
23. Lindberg B. J.: Acta Chem. Scand. *22*, 571 (1968).
24. Deacon G. B., Phillips R. J.: Coord. Chem. Rev. *33*, 227 (1980).
25. Glowacki A., Huber F., Preut H.: Rec. Trav. Chim. Pay-Bas *107*, 278 (1989).
26. Holeček J., Nádvorník M., Handlíř K., Lyčka A.: J. Organomet. Chem. *315*, 299 (1986).
27. Bremser W., Ernst L., Franke B., Gerhards R., Hardt A.: *Carbon-13 NMR Spectral Data.* Verlag Chemie, Weinheim 1981.
28. Lyčka A., Holeček J.: J. Organomet. Chem. *294*, 179 (1985).
29. Holeček J., Lyčka A.: Inorg. Chim. Acta *118*, L15 (1986).

Translated by J. Panchartek.