Journal of Organometallic Chemistry, 415 (1991) 203–209
Elsevier Sequoia S.A., Lausanne
JOM 22011

Structures of the compounds bis(*o*-, *m*-, and *p*-aminobenzoato-*O*,*O'*) di-n-butyltin(IV) in the solid state and in solution

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(Received February 21st, 1991)

Abstract

The structures of the title compounds have been established through variable temperature multinuclei (^{1}H, ^{13}C, ^{119}Sn, ^{17}O) NMR, Mössbauer, infrared and mass spectral studies along with an X-ray diffraction study in the case of the *ortho*-isomer. The compounds are monomeric six-coordinate species in the solid state and in solution.

Introduction

There have been a few reports recently concerning the structures of some bis(substituted benzoato-*O*,*O'*) dialkyltin(IV) compounds, which have been shown to have very similar distorted octahedral geometries in the solid state [1–3]. Intermolecular bonding has been observed only for *ortho*-substituted benzoato derivatives [3,4], and a variant on the structure is presented by bis(*o*-hydroxybenzoato-*O*,*O'*) di-n-butyltin (IV) [4]. Triorganotin carboxylates also show unusual structural features as a result of interactions between donor sites or hydrogen bonding in or between molecules [5,6]. There is, however, uncertainty about whether the structures of diorganotin dicarboxylates established for the solid state also apply in non-interacting solvents [7,8,10] and so it seemed of interest to make detailed structural studies of such compounds in the two phases. Thus the structures (of *ortho*-, *meta*-, and *para*-substituted aminobenzoato derivatives) of ^{n}Bu$_2$Sn(OC(O)-C$_6$H$_4$NH$_2$)$_2$ have been examined in the solid state and in solution, and the crystal structure of the *ortho*-aminobenzoato derivative established by an X-ray diffraction study.

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0022-328X/91/$03.50

Results and discussion

The title compounds were obtained by azeotropic dehydration of a mixture of di-n-butyltin(IV) oxide and the substituted benzoic acids in a 1 : 2 molar ratio in benzene. The elemental analysis and mass spectral data for the products (Table 1) show them to have the composition $^{n}Bu_2Sn(OC(O)C_6H_4NH_2\text{-}x)_2$ (x = *o*, *m*, or *p*).

The IR spectra of the solid compounds have ν(NH) modes at 3470–3490 and 3370–3410 cm^{-1} and unresolved peaks or shoulders for the *o*-aminobenzoato derivative at 3375–3380 cm^{-1}. Other relevant bands such as $\nu(CO_2)$ appear at 1620–1630 cm^{-1} and 1380–1420 cm^{-1}. In CCl_4 solution, the shoulder at 3375–3380 cm^{-1} is absent and the ν(NH) frequencies are higher by ca. 10–15 cm^{-1}, but the positions of the $\nu(CO_2)$ bands are unchanged (~ 1630 ± 5 cm^{-1} and 1400 ± 15 cm^{-1}) in all cases.

Solid state structures

The ^{119m}Sn Mössbauer spectra of the compounds at liquid nitrogen temperature yield chemical isomer shifts (IS) of 1.34–1.51 and quadrupole splittings (QS) of 3.5–3.8 mm s^{-1}. The value of the QS/IS ratio, ca. 2.50, shows [9] the coordination in these compounds to be > 4.

The crystal structure of dimethylbis(*p*-aminobenzoato-*O,O′*)tin(IV) has been reported previously [1], but that of the *o*-amino isomer compounds was nevertheless determined in order to observe the effects of the change in position of the amino group and of the presence of higher alkyl groups on the tin. The X-ray study showed solid $^{n}Bu_2Sn(OC(O)C_6H_4NH_2\text{-}o)_2$ to consist of monomers, the structure of one which is shown in Fig. 1. The compound crystallises in space group $R\bar{3}$. The atomic coordinates are listed in Table 2 and the bond lengths and angles in Table 3. The solid overall structure is essentially the same those recently reported for related species [1–3], but the present compound shows weak intermolecular hydrogen bonding [1] [N(11) [H] ··· O(14) = 3.06(2) Å], and there is also intramolecular hydrogen bonding [N(11) [H] ··· O_4 = 2.67(2) Å, N(21) [H] ··· O(12) = 2.71(3) Å]. IR data also indicate the presence of both types of hydrogen bonding in the solid.

Table 1

Physical, analytical and mass spectral data for bis(aminobenzoato-*O,O′*) di-n-butyltin(IV) compounds

No. [a]	Anal. [b] Found (%)				M.p. (°C)	Mass spectral data [c]
	C	H	H	Sn		*m/z*, assignment, relative intensity (%)
1	52.51	6.10	5.63	23.14	104	506, $[Bu_2Sn(OC(O)C_6H_4NH_2)_2]^+$, 0.06 449, $[BuSn(OC(O)C_6H_4NH_2)_2]^+$, 4.1 256 $[Sn(OC(O)C_6H_4NH_2)]^+$, 1.1 212 $[Sn(C_6H_4NH_2)]^+$, 0.6 137, $(HOOCC_6H_4NH_2)^+$, 50 119, $(OCC_6H_4NH)^+$, 100 92, $(C_6H_4NH_2)^+$, 90.8
2	52.53	6.21	5.80	23.26	86	do
3	52.32	6.01	5.62	23.28	119	do

[a] 1: $Bu_2Sn(OC(O)C_6H_4NH_2\text{-}o)_2$; 2: $Bu_2Sn(OC(O)C_6H_4NH_2\text{-}m)_2$; 3: $Bu_2Sn(OC(O)C_6H_4NH_2\text{-}p)_2$.

[b] Calc. for $C_{22}H_{30}O_4N_2Sn$: C, 52.27; H, 5.94; N, 5.54; Sn, 23.56%. [c] Fragmentation pattern for all the three compounds is the same (mass numbers are based on ^{1}H, ^{12}C, ^{16}O, ^{120}Sn).

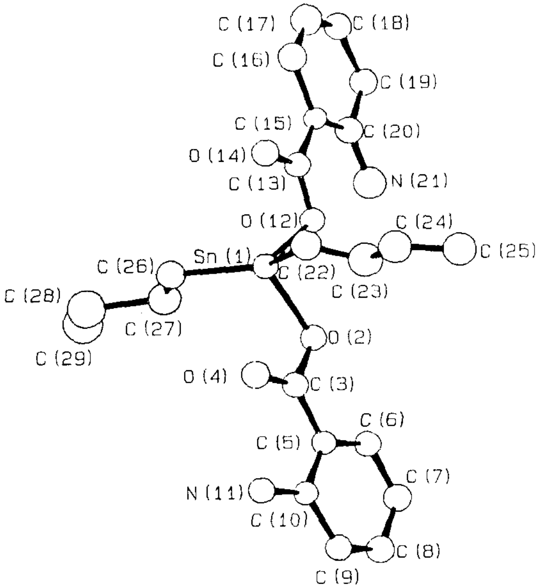

Fig. 1. Perspective diagram showing numbering scheme for bis(*o*-aminobenzoato-*O,O′*) di-n-butyltin(IV).

The hydrogen bonding has no structural effect on bonding characteristics of the carboxy groups and so does not merit discussion.

Structure in solution

Multinuclear magnetic resonance [$\delta(^1H$, ^{13}C, ^{17}O, $^{119}Sn)$] data of the title compounds were as follows: δ ^1H 0.86–0.89 (t, 6H, CH_3), 1.25–1.83 (m, 12H, CH_2), 4.09–5.69 (s, 4H, NH_2), 6.65–8.0 (m, 8H, C_6H_4) ppm; δ ^{13}C, 13.4 (CH_3), 25.3, 26.3, 26.6 ($3CH_2$), 110.9–135.1 (C_6H_4), 146.4–151.1 [$C(NH_2)$], 175.8–177.2 (very weak, CO_2) ppm; δ ^{17}O, 262–272 ppm. ($W_{1/2}$, 800–1200 Hz); δ ^{119}Sn, −150.5 to −157.9 ppm; $^1J(^{119}Sn-^{13}C)$, 584.3–592.1 Hz; C–Sn–C angle (θ) (as calculated from ^1J values [7]), 133.9–134.6°. It is noteworthy that there is no significant change in the C–Sn–C bond angle on going from the solid state to solution.

According to Holeček et al. [7,8], di-n-butyltin(IV) dicarboxylates with δ ^{119}Sn NMR values between −90 and −190 ppm can be considered to contain 5-coordinated tin atoms. It has been suggested that in solutions of such compounds, one dechelated carbonyl oxygen undergoes a rapid fluxional exchange with the chelated one [8]. Lockhart et al. [10], however, have pointed out the uncertainty of conclusions based only on δ ^{119}Sn NMR values. In order to assess the change in structure on going to the solution phase they preferred to compare C–Sn–C bond angles in the solid and solution. For $Me_2Sn(OAC)_2$, they observed no change in the C–Sn–C angle and so concluded that the six-coordinate structure is present in both phases. Kennedy et al. [11] on the other hand observed a fall in the δ ^{119}Sn NMR values upon dilution of solutions of butyltin trialkoxides and also upon raising the temperature, and attributed this to de-oligomerisation of these compounds, with resulting change in the environments of the tin atoms. With the compounds studied in the present work dilution has no observable effect, and so we turned to variable temperature NMR studies in the case of the *o*-amino isomer.

Table 2

Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($\times 10^3$) with esd's

Atom	x	y	z	U
Sn(1)	8334(1)	7789(1)	2569(1)	118
O(2)	7580(9)	7340(9)	1153(9)	123(4)
C(3)	7965(15)	6777(14)	765(15)	124(6)
O(4)	8590(10)	6642(10)	1303(9)	144(5)
C(5)	7622(13)	6383(13)	−246(14)	110(6)
C(6)	6934(14)	6633(14)	−720(15)	127(6)
C(7)	6611(15)	6289(15)	−1698(16)	143(7)
C(8)	7023(16)	5699(15)	−2146(15)	144(7)
C(9)	7706(15)	5471(14)	−1682(15)	129(7)
C(10)	8050(13)	5783(13)	−682(13)	106(6)
N(11)	8715(11)	5539(11)	−195(11)	125(5)
O(12)	7410(8)	8510(8)	2631(9)	114(4)
C(13)	7655(15)	8998(15)	3504(14)	119(6)
O(14)	8381(9)	8979(9)	4037(9)	135(4)
C(15)	7172(13)	9551(13)	3886(12)	99(5)
C(16)	7613(16)	10068(16)	4931(16)	147(7)
C(17)	7063(18)	10463(20)	5192(17)	176(10)
C(18)	6281(17)	10520(16)	4721(15)	138(7)
C(19)	5801(16)	10084(15)	3728(15)	141(7)
C(20)	6328(17)	9559(17)	3311(15)	143(7)
N(21)	5967(15)	9117(15)	2402(16)	196(9)
C(22)	9703(17)	8738(18)	2856(18)	167(9)
C(23)	9700(22)	9167(22)	2261(22)	215(11)
C(24)	10775(20)	9851(20)	2459(20)	196(10)
C(25)	10710(20)	10444(19)	1970(20)	201(11)
C(26)	7859(16)	6659(16)	3002(17)	149(7)
C(27)	6896(20)	6110(19)	2524(20)	194(10)
C(28)	6708(30)	5188(30)	2889(28)	266(12)
C(29)	5928(32)	4814(28)	2554(30)	291(14)

The ^{1}H NMR chemical shifts (δ 5.64 to 5.69 ppm) for the NH protons show no change over the temperature range 298–330 K. The δ ^{13}C NMR shifts also show no significant change, showing that there is no dechelation of the carbonyl group. The ^1J coupling constant values vary only slightly (< 5 Hz) in the range 290–330 K. These data do not indicate any significant change in the structure of the compound in solution over this temperature range. However, the ^{119}Sn NMR chemical shift does vary with temperature (188–385 K) from -154.6 to -143.8 ppm. This change would be consistent with a change in the environment (to 5 coordination) of the tin atom in solution, but this is not supported by the coupling constant (^1J) values at various temperatures or by solution state infrared data ($\nu(CO_2)$ at 1625 and 1380 cm^{-1}). However, the data reported by Kennedy et al. [11] reveal that in the case of butyltin alkoxides for which depoligomerisation occurs, the ^{119}Sn chemical shift changes by > 100 ppm over a 100 °C temperature range, and the change of only 11 ppm over a temperature range of ca. 200 °C observed in the present study is probably too small to indicate major structural changes in diorganotin dicarboxylates. At most it may indicate some long range association of the molecule at lower temperatures without significant effect on the bonding within the molecule.

Table 3

Main bond lengths (Å) and angles (°) and some relevant non-bonded contacts

Sn(1)–C(22)	2.17(2)	Sn(1)–C(26)	2.13(3)
Sn(1)–O(2)	2.09(1)	Sn(1)–O(12)	2.11(1)
Sn(1)–O(4)	2.56(2)	Sn(1)–O(14)	2.58(1)
C(3)–O(2)	1.33(3)	C(13)–O(12)	1.30(2)
C(3)–O(4)	1.25(3)	C(13)–O(14)	1.26(3)
C(3)–C(5)	1.46(3)	C(13)–C(15)	1.44(3)
C(5)–C(6)	1.38(3)	C(15)–C(16)	1.53(3)
C(6)–C(7)	1.41(3)	C(16)–C(17)	1.30(4)
C(7)–C(8)	1.44(4)	C(17)–C(18)	1.32(4)
C(8)–C(9)	1.35(4)	C(18)–C(19)	1.45(3)
C(9)–C(10)	1.45(3)	C(19)–C(20)	1.50(4)
C(10)–N(11)	1.37(3)	C(20)–N(21)	1.33(3)
C(5)–C(10)	1.46(3)	C(15)–C(20)	1.43(3)
O(2)–Sn(1)–O(12)	81.2(8)	O(2)–Sn(1)–C(22)	109(1)
O(2)–Sn(1)–C(26)	106(2)	O(12)–Sn(1)–C(22)	110(2)
O(12)–Sn(1)–C(26)	106(2)	C(22)–Sn(1)–C(26)	132(3)
Sn(1)–O(2)–C(3)	104(2)	Sn(1)–O(12)–C(13)	105(2)
Sn(1)–O(4)–C(3)	84(1)	Sn(1)–O(14)–C(13)	85(1)
O(2)–C(3)–O(4)	116(4)	O(12)–C(13)–O(14)	116(3)
O(2)–C(3)–C(5)	117(3)	O(12)–C(13)–C(15)	125(4)
C(3)–C(5)–C(6)	117(4)	C(13)–C(15)–C(16)	115(3)
C(6)–C(5)–C(10)	125(4)	C(16)–C(15)–C(20)	125(4)
C(5)–C(6)–C(7)	119(4)	C(15)–C(16)–C(17)	108(4)
C(6)–C(7)–C(8)	118(4)	C(16)–C(17)–C(18)	132(7)
C(7)–C(8)–C(9)	123(5)	C(17)–C(18)–C(19)	125(5)
C(8)–C(9)–C(10)	121(4)	C(18)–C(19)–C(20)	110(4)
C(9)–C(10)–C(5)	114(3)	C(19)–C(20)–C(15)	120(4)
C(9)–C(10)–N(11)	123(4)	C(19)–C(20)–N(21)	116(4)
O(2)–Sn(1)–O(4)	55.2(8)	O(12)–Sn(1)–O(14)	54.1(6)
O(4)–Sn(1)–O(14)	169(5)		
Intramolecular distances			
O(4) ··· N(11)	2.67(2)		
O(12) ··· N(21)	2.71(3)		
N(11) ··· O(14)′	3.06(2)	(symmetry element y, z, $-1+x$)	

We conclude that the title compounds are distorted six-coordinated organotin monomers in the solid state and retain their structures in non-interacting solvents.

Experimental

Synthesis

A solution of di-n-butyltin(IV) oxide (2.49 g, 10 mmol) and *o*, *m*- or *p*-amino benzoic acid (2.74 g, 20 mmol) in benzene (50 cm^3) was heated under reflux for 4 h in a Dean and Stark azeotropic distillation apparatus to permit continuous removal of water formed in the reaction. The solvent was evaporated and the residue extracted with light petroleum ether (b.p. 40–60 °C). The extract was evaporated and the product obtained was recrystallised from a mixture of diethyl ether and petroleum ether (b.p. 40–60 °C). Analytical and mass spectral data are given in Table 1.

Spectroscopy

IR spectra were recorded for KBr pellets or CCl_4 solutions on a Perkin–Elmer 621 spectrophotometer. ^{119m}Sn Mössbauer spectra were recorded at 77 K with a Harwell spectrophotometer equipped with a 256 multi-channel analyser and a $Ba^{119m}SnO_3$ source. Data reduction of the Lorentzian line shapes was carried out by the usual least-squares method. The ^{1}H, ^{13}C, ^{119}Sn NMR spectra (at room temperature and at variable temperatures) and ^{17}O spectra at 300 K were recorded with $CDCl_3$ solutions on a Bruker (AM500) 500 MHz instrument at the Tata Institute of Fundamental Research, Bombay. The ^{13}C chemical shifts were determined by reference to the signal from the solvent ($CDCl_3$, δ 77.00 ppm). The ^{1}H, ^{119}Sn and ^{17}O chemical shifts are quoted relative to Me_4Si, Me_4Sn and D_2O, respectively. Elemental analyses were carried out with a Carlo Erba Strumentazione (Italy) elemental analyser model 1106. Mass spectra were obtained with V-G micromass MM 70/70F double-focusing spectrophotometer.

Crystallography

Crystal data (298 K). $C_{22}H_{30}N_2O_4Sn$, $M = 505.4$, trigonal; space group $R\bar{3}$, $a = 16.029(9)$ Å, $\alpha = 105.19(8)°$; $V = 3586$ Å^3, $F(000) = 1554$; $Z = 6$; $D_x = 1.40$ g cm^{-3}, $\lambda = 0.7107$ Å, $\mu(\text{Mo-}K_\alpha) = 11$ cm^{-1}.

The unit cell parameters were obtained from a least-squares refinement of the setting angles of 25 carefully centered reflection with $10 \leqslant 2\theta \leqslant 16°$ on a four-circle Philips PW1100 automatic diffractometer. The maximum value of $\sin \theta/\lambda$ reached in the intensity measurements was 0.60. Data were collected in hexagonal axes: range *hkl*: $0 \leqslant h \leqslant 25$; $0 \leqslant k \leqslant 25$; $-20 \leqslant l \leqslant 20$. 3933 reflections measured, 1482 observed $(I) > 3\sigma(I)$, 1131 unique, 3 standard reflections: 612, $3\bar{1}4$, $\bar{6}\bar{1}\bar{2}$ monitored every other hour; no significant changes were observed. The structure was solved by the heavy atom method (Patterson function). Refinement was by full matrix least squares (involving F) anisotropic thermal parameters for the tin atom, but isotropic parameters for other atoms. Absorption correction by the DIFABS method [12] gave no improvement, $R = 0.062$; $R_w = 0.063$ ($w = 1$). Ratio of maximum least-squares shift to error in final refinement cycle $< 10^{-1}$. Large thermal motions for the whole molecule and bond length variations within the aromatic cycle C(15)–C(20) were observed. Further structural analysis and refinements were carried out as previously reported [13], but hydrogen atoms were omitted. The computer program used was a local version of SFLS5 Pravitt.

Acknowledgement

S.K.B. and Y.S. are grateful to the UGC (India) for the award of Teacher and Senior Research Fellowships, respectively, and H.K.S. to CSIR, New Delhi for a Research Associateship. We thank the Bhabha Atomic Research Centre, the Tata Institute of Fundamental Research, Bombay and the Indian Institute of Science, Bangalore, for Mössbauer and NMR facilities.

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