Journal of Organometallic Chemistry, 453 (1993) 171–174

JOM 23423

X-Ray structure investigation of trimethyltin α-phenyl-α-oxoacetate

T.V. Sizova [a], N.S. Yashina [a], V.S. Petrosyan [a], A.V. Yatsenko [b], V.V. Chernyshev [b] and L.A. Aslanov [b]

[a] *Physical Organic Chemistry Laboratory and* [b] *Structural Chemistry Laboratory, Chemistry Department, M.V. Lomonosov University, Moscow 119899 (Russian Federation)*

(Received October 28, 1992)

Abstract

X-Ray structure investigation of trimethyltin α-phenyl-α-oxoacetate $Me_3SnOC(O)CH(OH)Ph$ was carried out. The unit cell contains two independent molecules with practically identical conformation. Molecules are associated in the chains due to coordination bonds between the oxo-group and the tin atom of the neighbouring molecule. The chains in the crystal are connected with one another by hydrogen bonds between oxo-group protons and carboxyl oxygen atoms.

1. Introduction

Molecules of trialkyl(aryl)tin carboxylates have a tendency to form polymeric chains with bridging carboxylate groups. However if the acid molecule contains another electron-donating centre apart from carboxyl, then chain structure formation can take place with its participation. To determine the type of molecular association in the structure of the organotin derivative of α-phenyl-α-oxoacetic (mandelic) acid, X-ray investigation of $Me_3SnOC(O)CH(OH)Ph$ was carried out.

2. Experimental section

2.1. Synthesis and crystal preparation

Me_3SnOH was prepared according to standard methods. DL-mandelic acid and solvents were commercial products. The solvents were dried before use. $Me_3SnOC(O)CH(OH)Ph$ was obtained in 80% yield by refluxing 1/1 $Me_3SnOH/HOOCCH(OH)Ph$ mixture (10 mmol) in benzene (80 ml) and MeOH (20 ml) and removing the water of neutralization by azeotropic distillation. After 6 h the solvent was evaporated *in vacuo* giving a white residue. The Me_3Sn OC(O) CH(OH)Ph was recrystallized from $CHCl_3$/heptane. M.p. 124–125°C. Analytical data for $Me_3SnOC(O)CH(OH)Ph$: Calcd. for $C_{11}H_{16}O_3Sn$: C, 41.9: H, 5.1. Found: C, 42.0; H, 5.1%. IR spectra were recorded on a Carl Zeiss spectrometer UR-20.

2.2. Crystal data

$C_{11}H_{16}SnO_3$, M = 314.9, monoclinic, space group $P2_1/c$, $a = 7.887(2)$, $b = 22.002(4)$, $c = 15.592(3)$ Å, $\beta = 100.11(2)°$, $U = 2664$ Å^3, $Z = 8$, $D_c = 1.571$ g/cm^3, $\mu = 19.1$ cm^{-1} (Mo Kα radiation).

2.3. Data collection and structure determination

A crystal of approximate dimensions 0.1 × 0.25 × 0.35 mm was used with a CAD-4 diffractometer (ω-scanning, $\theta_{max} = 30°$). The calculations were performed by SDP programs [1] on a MicroVAX-II computer. Of the total 7731 recorded reflections, 4861 reflections with $I > 2.5\sigma(I)$ were used for the structure determination and refinement. Empirical absorbtion correction using ψ-scanning curves of 10 reflections was applied. Approximate coordinates of the tin atom were determined by the Patterson method. The remaining atoms were located from a difference Fourier map. All atoms (except hydrogens) were given anisotropic temperature factors. Hydrogens in phenyl, HO- and HC-groups of ligand were refined isotropically. As determined from the difference Fourier map, all hydrogens attached to tin atom methyl groups are fully disordered, and for these atoms the following procedure was used [2]: 3 methyl hydrogens were assumed to be uniformly distributed on the circle border, and the

---

Correspondence to: Dr. V.S. Petrosyan.

0022-328X/93/$6.00

TABLE 1. Fractional atomic coordinates ($\times 10^5$ for Sn, $\times 10^3$ for H and $\times 10^4$ for other atoms)

Atom	Molecule A			Molecule B		
	x	*y*	*z*	*x*	*y*	*z*
Sn	−8793(4)	55909(2)	33822(2)	47764(4)	28027(2)	43507(2)
O(1)	1753(4)	5305(2)	3477(2)	4505(5)	2908(2)	2963(2)
O(2)	2799(4)	6236(2)	3432(3)	4513(5)	1928(2)	2626(2)
O(3)	5878(4)	5809(2)	3181(2)	5094(4)	2177(2)	997(2)
C(1)	−1539(4)	4741(3)	3872(5)	7297(8)	2436(3)	4509(4)
C(2)	−1194(8)	5749(3)	2035(4)	2688(8)	2234(3)	4436(4)
C(3)	−711(7)	6351(3)	4228(4)	4516(9)	3752(3)	4467(3)
C(4)	2902(6)	5685(2)	3359(3)	4682(6)	2460(2)	2456(3)
C(5)	4451(6)	5404(2)	3041(3)	5215(6)	2669(2)	1603(3)
C(6)	3889(6)	5227(3)	2093(3)	6997(7)	2947(2)	1790(3)
C(7)	3512(9)	4638(3)	1867(5)	7241(9)	3552(3)	1637(5)
C(8)	2891(9)	4482(4)	1028(5)	8934(8)	3798(3)	1827(6)
C(9)	2657(9)	4908(4)	395(5)	10261(9)	3432(4)	2148(5)
C(10)	3055(9)	5498(4)	605(5)	10051(9)	2836(4)	2288(5)
C(11)	3647(8)	5653(3)	1458(4)	8407(8)	2593(3)	2116(4)
H(1)	548(7)	622(2)	293(3)	571(6)	188(2)	123(3)
H(5)	479(6)	505(2)	338(3)	442(6)	297(2)	132(3)
H(7)	377(7)	434(3)	229(4)	625(7)	379(2)	141(3)
H(8)	268(8)	407(4)	83(5)	888(9)	417(4)	174(5)
H(9)	221(9)	481(4)	−16(5)	1139(9)	363(4)	236(5)
H(10)	277(9)	580(3)	19(4)	1113(8)	254(4)	256(5)
H(11)	393(7)	603(3)	159(4)	824(8)	216(3)	222(4)
H(2) [a]	−161(7)	462(2)	394(4)	768(6)	237(3)	458(4)
H(3) [a]	−133(8)	580(3)	183(2)	241(5)	210(2)	445(4)
H(4) [a]	−76(9)	647(2)	431(3)	447(8)	389(2)	446(4)

[a] Coordinates for these atoms correspond to centres of circles of disordered methyl hydrogens (see Experimental section). Values for radii of these atoms differ by 0.85 to 0.90 Å.

TABLE 2. Selected interatomic distance (Å) and angles (°) in molecules A and B

	A	B		A	B
Sn–O(1)	2.149(3)	2.149(3)	O(2)–C(4)	1.223(6)	1.213(6)
Sn–O(3)′	2.566(3)	2.535(3)	O(3)–C(5)	1.422(5)	1.429(6)
Sn–C(1)	2.119(7)	2.119(6)	O(3)–H(1)	1.02(5)	0.86(5)
Sn–C(2)	2.101(6)	2.091(7)	C(4)–C(5)	1.528(7)	1.535(7)
Sn–C(3)	2.119(7)	2.110(6)	C(5)–C(6)	1.517(7)	1.514(7)
O(1)–C(4)	1.269(6)	1.286(6)	Sn · · · O(2)	3.219(4)	3.284(5)
O(1)SnO(3)′	173.1(1)	172.8(1)	SnO(3)C(5)	130.3(3)	129.7(3)
O(1)SnC(1)	90.7(2)	94.8(2)	SnO(3)H(1)	117.(3)	113.(3)
O(1)SnC(2)	93.5(2)	100.9(2)	C(5)O(3)H(1)	109.(3)	110.(3)
O(1)SnC(3)	103.5(2)	89.2(2)	O(1)C(4)O(2)	125.4(5)	125.3(4)
O(3)′SnC(1)	84.6(2)	88.0(2)	O(1)C(4)C(5)	114.4(4)	112.3(4)
O(3)′SnC(2)	84.6(2)	83.4(2)	O(2)C(4)C(5)	120.1(4)	122.3(4)
O(3)′SnC(3)	83.2(2)	83.6(2)	O(3)C(5)C(4)	110.7(4)	110.5(4)
C(1)SnC(2)	120.9(3)	119.9(3)	O(3)C(5)C(6)	113.4(4)	112.7(4)
C(1)SnC(3)	117.7(3)	118.1(3)	C(4)C(5)C(6)	107.8(4)	109.8(3)
C(2)SnC(3)	118.4(3)	119.8(3)	C(5)C(6)C(7)	120.6(5)	120.8(5)
SnO(1)C(4)	120.2(3)	122.2(3)	C(5)C(6)C(11)	121.0(5)	120.3(5)
O(1)C(4)C(5)O(3)	−162.0	−169.5	C(4)C(5)C(6)C(7)	−101.5	−114.6
O(1)C(4)C(5)C(6)	73.4	65.5	C(4)C(5)C(6)C(11)	74.5	65.8
O(2)C(4)C(5)O(3)	22.1	12.8	O(3)C(5)C(6)C(7)	135.6	121.8
O(2)C(4)C(5)C(6)	−102.5	−112.2	O(3)C(5)C(6)C(11)	−48.5	−57.9

In phenyl groups bond lengths are 1.345(11)–1.424(11) Å and angles 118.2(5)–122.3(7)°. Coordinates of atoms O(3)′ are produced by operation *x* − 1, *y*, *z* for molecule A and *x*, 1/2 − *y*, 1/2 + *z* for molecule B.

TABLE 3. Hydrogen bonds in $Me_3Sn(OOCCH(Ph)OH)$

Fragment	H···O	O···O	O–H...O
O(3)A–H(1)A···O(2)B	1.78(5)	2.757(5)	160(5)
O(3)B–H(1)B···O(2)A	1.86(5)	2.705(4)	171(5)

Coordinates of atoms O(2)A and O(2)B are produced by symmetry operations $1-x$, $y-1/2$, $1/2-z$ (O(2)A) and $1-x$, $1/2+y$, $1/2-z$ (O(2)B).

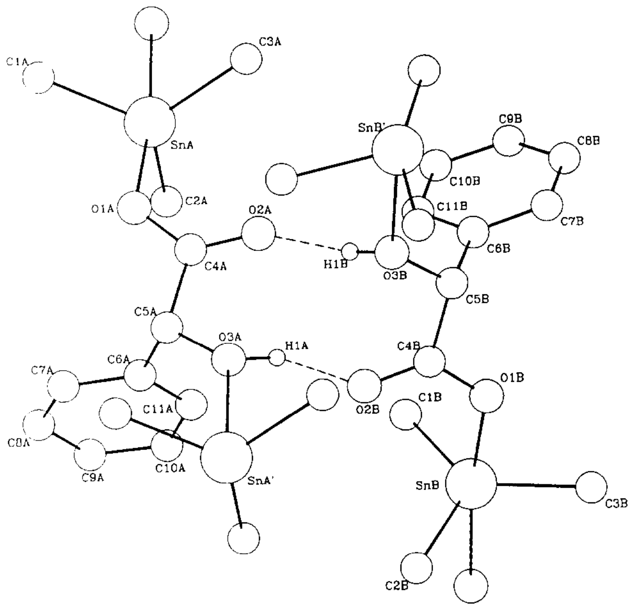

Fig. 1. Structure of the compound showing the two independent molecules.

parameters refined were radius, coordinates of the centre of the circle and isotropic temperature parameter. This model decreases the number of refined parameters per Me-group from 12 to 5. Additional subroutines were written and included in the SDP package by Dr. V.V. Chernyshev. The refinement led to final error indices $R = 0.034$ and $R_w = 0.035$. The scattering factors used were those for neutral atoms. Final fractional atomic coordinates, bond distances and angles and some nonvalent contacts in the structure are given in Tables 1–3.

3. Results and discussion

The structure contains two independent molecules (type A and type B) of $Me_3SnOC(O)CH(OH)Ph$ with practically identical conformation. Tin atoms have a distorted trigonal-bipyramidal environment; in apical positions there are atoms O(1) of carboxylate group and O(3) of hydroxy group from the neighbouring molecule of the same type. The Sn–O(3) bonds are 0.42–0.39 Å longer than Sn–O(1). Tin atoms are displaced from the 3 methyl carbon atoms plane on 0.22 Å (A) and 0.18 Å (B). Bonds C(4)–O(1) in the carboxylate group are on average 0.06 Å longer than C(4)–O(2); this difference is smaller than that in the structure of pure mandelic acid, 0.10 Å [3]. Molecules are bonded in the infinite chains by Sn–O(3) interactions. The chains of type A translationally equivalent molecules are oriented along the *a* axis, and the chains of molecules of type B are oriented along the *c* axis. The chains of each type form alternate layers perpendicular to the *b* axis, forming plywood-like packing. On the other hand, at the crossing points molecules A and B form dimers due to hydrogen bonds H(1)A ··· O(2)B and H(1)B ··· O(2)A (see Table 3). The structure of the dimer is represented in Fig. 1. Such dimers also exist in the structure of mandelic acid [3]. As a result of dimerisation layers perpendicular to the *b* axis are corrugated along the *c* axis: the neighbouring A-chains are on the different altitude, and the B-chains have zigzag form. The coordination of OH group to tin and the formation of H-bonds are also reflected in the IR spectra: after the transition from solution in CH_2Cl_2, THF or DMSO to the solid state, the OH stretching frequency decreases from 3460–3500 cm^{-1} (3400 cm^{-1} in free mandelic acid) to 3200 cm^{-1}. On the other hand the decrease of $\nu_{as}(CO_2)$ frequency observed for solid-state $Me_3SnOC(O)CH(OH)Ph$ compared with its value in solution (see Table 4) could be explained by the formation of H-bonds between the carbonyl and the OH-group of the neighbouring molecule [4]. The presence of very weak ν_s(Sn–C) stretching in the solid state spectrum of $Me_3SnOC(O)CH(OH)Ph$ indicates that 3 methyl carbon atoms form the plane of the distorted trigonal-bipyramidal environment of the tin atom. The low solubility of $Me_3SnOC(O)CH(OH)Ph$ in non-polar solvents has made it impossible for us to investigate by IR or NMR spectroscopy what kind of association — chain formation due to Sn–O interactions or dimerisation due to H-bonding — is predominant at the moment of crystal formation.

Chain-polymerisation of triorganotin carboxylates is usually due to bridging carboxylate groups, but if the acid residue has an additional nucleophilic centre, a chain structure can be formed with its participation. The general geometrical parameters in such structures

TABLE 4. Characteristic IR data for $Me_3SnOC(O)CH(OH)Ph$ (ν, cm^{-1})

	KBr	CH_2Cl_2	THF	DMSO
$\nu_{as}(CO_2)$	1632	1660	1640	1645
ν_{as}(Sn–C)	550	550	550	555
ν_s(Sn–C)	515vw	515	515w	–
ν(OH)	3200	3500	3460	3460

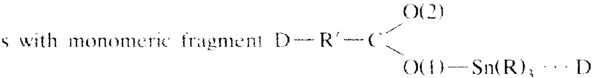

TABLE 5. Selected geometrical parameters in structures of chain-carboxylates with monomeric fragment $D\text{—}R'\text{—}C\begin{smallmatrix} \diagup O(2) \\ \diagdown O(1)\text{—}Sn(R)_3 \cdots D \end{smallmatrix}$ and related compounds: distances Sn–O(1), Sn ··· O(2) and Sn ··· D and deviations of Sn atoms from the planes of three neighbour C atoms Δ(Sn), Å

Compound	Sn–O(1)	Sn ··· O(2)	Sn ··· D	Δ(Sn)	Ref.
Ph_3Sn(2-hydroxybenzoate)	2.08	3.07	3.03(O)	0.38	[6]
Me_3Sn(2-hydroxyphenylacetate)	2.15	3.22	2.57(O)	0.22	^{a}
	2.15	3.28	2.54(O)	0.18	^{a}
Ph_3Sn(3-pyridylcarboxylate)	2.14	3.27	2.57(N)	0.12	[9]
Me_3Sn(glycinate)	2.21	3.23	2.46(N)	0.11	[10]
Me_3Sn(glutaminate)	2.22	3.36	2.30(O)	0.02	[11]
	2.30	3.22	2.22(O)		
in monomeric triorganotincarboxylates	2.06–2.12	2.63–3.11	0.39–0.63		
in polymeric carboxylates with bridgind carboxylic groups:	2.14–2.25	3.11–3.66	0.08–0.21		
Me_3Sn(2-pyridylcarboxylate) H_2O (tetramer)	2.15–2.21	3.15–3.28	2.41–2.44(O)	0.07–0.11	[12]

are listed in Table 5. In the cases of triphenyltin *o*-,*p*-amino- and *o*-methoxybenzoates [5,6] amino and methoxy groups do not play a part in tin atom coordination because of their low nucleophility. In the structure of triphenyltin 2-hydroxo-5-methylphenylazobenzoate [7], potential donor centres — hydroxo and azo groups — are blocked by intramolecular H-bonds. Similarly in triphenyltin 3-benzoylpropionate [8] the benzoylic ketogroup do not participate either in interactions with the tin atom, and the association of molecules here is due to bridging carboxylate groups. The structure of triphenyltin *o*-hydroxobenzoate (see Table 5) represents the transition state between monomeric and polymeric structures. In the structure of monosubstituted trimethyltin glutaminate the acid residue $HGlu^-$ exists in the zwitterionic form (with proton transfer from carboxylic to amino group) and coordination of tin atom is by two monodentate carboxylate groups, leading to regularization of the trigonal bipyramidal environment of the tin atom. The structures of glycinatotrimethyltin and 3-pyridylcarboxylatotriphenyltin are similar to the only known structure of the triorganotincarboxylate adduct with a neutral donor molecule: 2-pyridylcarboxylatotriphenyltin monohydrate (tetramer). The coordination trigonal bipyramid is distorted here: the tin atom is displaced from the equatorial plane towards the carboxylic oxygen atom, and apical bond lengths are essentially different. In the structure discussed here distortion of the coordination polyhedron is even more essential because the hydroxo group has less effective donor properties than the aliphatic amino and pyridyl groups or the water molecule, but they are greater than those of the phenolic hydroxo group.

References

1 B.A. Frenz. *Structure Determination Package, User's guide*. 1985.

2 V.V. Chernyshev. *Kristallographia*. in press (in Russian).

3 K.-T. Wei and D.L. Ward. *Acta Crystallogr., Sect. B*, *33* (1977) 797.

4 K. Nakamoto, P.J. McCarthy and B. Miniatas, *Spectrochimica Acta*, *21* (1965) 379.

5 R.G. Swister, J.F. Vollano V. Chandrasekhar, R.O. Day and R.R. Holmes, *Inorg. Chem.*, *23* (1984) 3147.

6 J.F. Vollano, R.O. Day, D.N. Rau, V. Chandrasekhar and R.R. Homes, *Inorg. Chem.*, *23* (1984) 3153.

7 P.G. Harrison, K. Lambert, T.J. King and B. Majee, *J. Chem. Soc., Dalton Trans.*, (1983) 363.

8 S.W. Ng, V.G. Kumar Das and A. Syed, *J. Organomet. Chem.*, *364* (1989) 353.

9 S.W. Ng, V.G. Kumar Das, F. van Meurs, J.D. Schagen and L.H. Straver, *Acta Crystallogr., Sect. C*, *45* (1989) 570.

10 B.Y. K. Ho, K.C. Molloy, J.J. Zuckerman, F. Reidinger and J.A. Zubieta, *J. Organomet. Chem.*, *187* (1980) 213.

11 F. Huber, B. Mundus-Glowacki and H. Preut, *J. Organomet. Chem.*, *365* (1989) 111.

12 P.G. Harrison and R.C. Philips, *J. Organomet. Chem.*, *182* (1979) 37.