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STRUCTURAL STUDIES IN MAIN GROUP CHEMISTRY

XV *. DI- AND TRI-ORGANOTIN ARYLSULPHONATES

PHILIP G. HARRISON **, ROBIN C. PHILLIPS and JOHN A. RICHARDS
Department of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD (Great Britain)

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Summary

Diorganotin bis(arylsulphonates) and triorganotin monoarylsulphonates are readily obtained in very high yield by the azeotropic dehydration of the organotin oxide and the arylsulphonic acid in boiling benzene. Tin-119*m* Mössbauer data for the compounds are reported. The crystal structure of trimethyltin benzenesulphonate monohydrate has been determined by Fourier and Patterson techniques from diffractometer data. Crystals are monoclinic, space group $P2_1/c$, a 12.166(7), b 8.376(8), c 13.581(7) Å, β 103.71(4)°, $Z = 4$. Crystals are composed of chains of $Me_3SnO_3SPh \cdot H_2O$ molecules connected by hydrogen bonds between water molecules and the arylsulphonate group of an adjacent molecule. Individual molecules enjoy trigonal bipyramidal geometry with planar Me_3Sn moieties. Oxygen atoms from a water molecule and a benzenesulphonate group occupy the apical positions.

Introduction

Previous routes to organotin esters of sulphonic acids have involved solvolysis of tetramethyltin and methyltin chlorides by the sulphonic acid, subsequent ligand redistribution [2—5], and functional group exchange between a diorganotin oxide and the trimethylsilyl ester of an arylsulphonic acid [6]. In this paper we report a facile, high-yield synthesis of di- and tri-organotin derivatives of sulphonic acids, their tin-119*m* Mössbauer spectra, and the results of an X-ray diffraction study of one product, $Me_3SnO_3SPh \cdot H_2O$.

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[*] For part XIV see ref. 1.

[**] To whom correspondence should be addressed.

Experimental

Tin-119*m* Mössbauer spectra were recorded using a Harwell spectrometer equipped with a 256 channel multichannel analyser against a $Ba^{119m}SnO_3$ source. Data reduction to Lorentzian line shapes was accomplished by usual least-squares methods.

The compounds were synthesised by mixing the appropriate diorganotin oxide, triorganotin hydroxide, or bis(triorganotin) oxide with 2 or 1 mol, respectively, of the arylsulphonic acid, and dehydrating the reaction mixture in boiling benzene using a Dean and Stark water separator. The products either separated out of solution during the reaction or on cooling to room temperature. The white amorphous products were filtered off and dried in vacuo. Some of the products showed a tendency to hold water fairly strongly, and where necessary heating to 110°C afforded the anhydrous compound. Analytical and tin-119*m* Mössbauer data are collected in Table 1.

Crystals of $Me_3SnO_3SPh \cdot H_2O$ were obtained by the recrystallisation of the anhydrous material from methanol in air. A crystal of dimensions 0.3 × 0.3 × 0.2 mm^3 was mounted on a fine glass fibre and used to obtain cell data and subsequent intensity measurements.

TABLE 1

ANALYTICAL AND TIN-119*m* MÖSSBAUER DATA FOR R_3SnO_3SAr AND $R_2Sn(O_3SAr)_2$ COMPOUNDS

Compound	Microanalytical data Found (calcd.)(%)		Tin-119*m* Mössbauer data (mm s^{-1})					
	C	H	I.S.	Q.S.	Γ_1	Γ_2	I_1/I_2	M.p. (°C)
$Me_3SnO_3SC_6H_5$	33.84 (33.68)	4.51 (4.40)	1.58	4.17	0.90	1.18	1.04	67-69
$Me_3SnO_3SC_6H_5 \cdot H_2O$	31.40 (31.87)	4.83 (4.76)	1.53	4.20	0.94	0.96	1.02	66-67
$Me_3SnO_3SC_6H_4Me$	35.57 (35.85)	4.70 (4.81)	1.47	4.26	0.81	0.84	0.97	312-314 (decomp.)
$(C_3H_7)_3SnO_3SC_6H_5$	44.20 (44.47)	7.12 (6.47)	1.57	4.18	0.84	0.84	0.98	71-73
$(C_3H_7)_3SnO_3SC_6H_4Me$	44.98 (45.85)	6.57 (6.73)	1.57	4.15	0.88	1.00	1.05	64-65
$(C_6H_{11})_3SnO_3SC_6H_5$	54.34 (54.87)	7.34 (7.29)	1.70	4.31	0.84	0.84	0.87	ca. 240 (decomp.)
$(C_6H_{11})_3SnO_3SC_6H_4Me$	55.01 (55.67)	7.48 (7.48)	1.69	4.32	0.74	0.74	0.96	244-246
$Ph_3SnO_3SC_6H_5$	56.67 (56.84)	4.00 (3.97)	1.38	3.90	0.84	0.83	1.10	254-256
$Ph_3SnO_3SC_6H_4Me$	57.29 (57.61)	4.31 (4.25)	1.44	4.00	0.78	0.86	1.05	213-215
$Me_2Sn(O_3SC_6H_5)_2$	37.05 (36.31)	3.89 (3.48)	1.41	4.70	0.82	0.86	1.01	320
$(C_4H_9)_2Sn(O_3SC_6H_5)_2$	43.36 (43.89)	5.32 (5.16)	1.76	4.91	0.85	0.86	0.99	320
$Ph_2Sn(O_3SC_6H_5)_2$	48.37 (49.09)	3.51 (3.43)	1.52	4.64	0.96	0.88	0.96	ca. 230 (decomp.)

TABLE 2

FINAL FRACTIONAL ATOMIC COORDINATES

Atom	x/a	y/b	z/c
C(1)	0.675(1)	0.191(2)	−0.044(1)
C(2)	0.842(1)	0.182(2)	0.227(1)
C(3)	0.566(1)	0.373(2)	0.173(1)
C(4)	0.802(1)	0.755(2)	−0.018(1)
C(5)	0.784(1)	0.747(2)	−0.121(1)
C(6)	0.860(1)	0.847(2)	−0.161(1)
C(7)	0.949(1)	0.918(2)	−0.095(1)
C(8)	0.968(1)	0.901(2)	0.000(1)
C(9)	0.895(1)	0.808(2)	0.044(1)
O(1)	0.5986(9)	0.0155(12)	0.1438(8)
O(2)	0.6772(11)	0.7446(21)	0.1104(11)
O(3)	0.6173(9)	0.5745(19)	−0.0498(12)
O(4)	0.7713(8)	0.4923(12)	0.0852(8)
S	0.7082(3)	0.6302(5)	0.0361(3)
Sn	0.68885(7)	0.24568(14)	0.11434(6)

Crystal data. $C_9H_6SO_4Sn$, mol. wt. 338.88, a 12.166(7), b 8.376(8), c 13.581(7 Å, β 103.71(4)°, U 1344.3 Å^3, $Z = 4$, $F(000)$ 632. Mo-K_α 0.71069 Å, μ(Mo-K_α) 20.50 cm^{-1}. Space group $P2_1/c$ from systematic absences ($h0l$ for $l = 2n + 1$, and $0k0$ for $k = 2n + 1$).

The space group was determined from oscillation and zero- and frist-layer Weissenberg photographs. The intensities of 3300 independent non-zero reflections were measured on a Hilger and Watts four-circle automatic diffractometer. Reflections with intensities $I < 3\sigma(I)$ were considered non-observed and were

TABLE 3

FINAL ANISOTROPIC THERMAL PARAMETERS [a,b]

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	12.8(16)	7.4(12)	6.3(10)	−3.9(12)	1.7(10)	−1.1(9)
C(2)	6.1(9)	6.1(9)	9.0(12)	−1.4(8)	−3.5(8)	2.0(9)
C(3)	6.0(8)	7.5(10)	5.0(8)	2.2(8)	1.9(7)	0.8(8)
C(4)	4.5(6)	5.6(8)	7.0(8)	−2.0(7)	0.9(5)	−2.8(10)
C(5)	6.0(8)	8.0(11)	7.9(10)	0.6(10)	1.4(7)	5.7(12)
C(6)	6.9(10)	10.1(15)	7.6(11)	1.3(10)	2.2(9)	0.6(11)
C(7)	6.0(9)	7.7(12)	8.6(12)	−1.8(9)	2.3(9)	1.4(10)
C(8)	4.8(9)	8.2(12)	11.0(15)	−3.3(9)	1.4(9)	−0.7(12)
C(9)	5.5(8)	8.8(13)	7.5(10)	−0.4(8)	−0.1(8)	−0.9(9)
O(1)	7.1(6)	4.5(5)	7.1(7)	0.0(5)	0.8(5)	−0.6(5)
O(2)	10.0(9)	10.1(10)	15.4(12)	2.5(10)	7.4(9)	4.7(13)
O(3)	4.0(5)	11.3(11)	14.6(13)	−1.8(7)	−0.9(7)	2.0(10)
O(4)	5.9(5)	4.9(5)	7.0(6)	−0.2(4)	0.1(5)	1.0(5)
S	4.2(1)	5.8(2)	9.8(3)	1.1(1)	1.4(2)	1.2(2)
Sn	4.51(4)	4.88(4)	5.49(4)	0.23(5)	0.04(3)	0.41(6)

[a] Thermal parameters as listed have been multiplied by 10^2. [b] U_{ij} are of the form $\exp -2\pi^2(h^2U_{11}a^{*2}$ $kU_{22}b^{*2} + lU_{33}c^{*2} + hkU_{12}a^*b^* + hlU_{13}a^*c^* + klU_{23}b^*c^*)$.

TABLE 4

INTRAMOLECULAR BOND DISTANCES (Å) AND ANGLES (°)

Bond distances (Å)			
Sn—C(1)	2.17(1)	C(4)—C(5)	1.36(2)
Sn—C(2)	2.18(1)	C(5)—C(6)	1.45(2)
Sn—C(3)	2.13(1)	C(6)—C(7)	1.36(2)
Sn—O(1)	2.30(1)	C(7)—C(8)	1.27(3)
Sn—O(4)	2.37(1)	C(8)—C(9)	1.41(2)
		C(9)—C(4)	1.32(2)
S—O(4)	1.45(1)	O(1)···O(2)	2.54(2)
S—O(2)	1.50(1)		
S—O(3)	1.48(1)		
S—C(4)	1.83(1)		
Bond angles (°)			
C(1)—Sn—C(2)	119.7(7)	O(4)—S—O(2)	112.7(8)
C(1)—Sn—C(3)	125.6(6)	O(4)—S—O(3)	108.9(7)
C(1)—Sn—O(1)	94.0(6)	O(4)—S—C(4)	109.0(6)
C(1)—Sn—O(4)	87.3(6)	O(2)—S—O(3)	118.1(8)
C(2)—Sn—C(3)	114.4(6)	O(2)—S—C(4)	100.7(8)
C(2)—Sn—O(1)	92.3(5)	O(3)—S—C(4)	106.4(8)
C(2)—Sn—O(4)	90.0(5)	Sn—O(4)—S	124.6(5)
C(3)—Sn—O(1)	87.2(5)	C(9)—C(4)—C(5)	125.4(15)
O(1)—Sn—O(4)	176.2(3)	C(4)—C(5)—C(6)	113.0(14)
		C(5)—C(6)—C(7)	118.9(17)
		C(6)—C(7)—C(8)	123.4(19)
		C(7)—C(8)—C(9)	120.1(16)
		C(8)—C(9)—C(4)	116.1(16)

not used, reducing the number of reflections to 1996. Lorentz and polarisation corrections were applied, but none was made for adsorption because of the low μ value.

Structure determination and refinement. The positional parameters of the tin atom in the asymmetric unit were obtained from a Patterson synthesis, and then used to phase the initial structure factor calculation. A fourier synthesis established the positions of the remaining non-hydrogen light atoms. Isotropic, followed by anisotropic, block-diagonal least-squares refinement produced convergence at an R value of 0.111. The scattering factors used were those of neutral atoms. The X-Ray 70 suite of programs was employed for the calculations. Final fractional atomic coordinates and anisotropic thermal parameters are listed in Tables 2 and 3, respectively. Intramolecular bond distances and angles are listed in Table 4.

Discussion

Triorganotin monoarylsulphonates and diorganotin bis(arylsulphonates) are readily obtained in essentially quantitative yield by the azeotropic dehydration of 1 : 1 and 1 : 2 mixtures, respectively, of the appropriate organotin (hydr)-oxide and arylsulphonic acid according to equations 1 and 2. The materials are very stable white amorphous powders, and exhibit only very low, sometimes sparing solubility in the common organic solvents.

$$\left.\begin{array}{l}\frac{1}{2}R_3SnOSnR_3\\ \text{or}\\ R_3SnOH\end{array}\right\} + ArSO_3H \xrightarrow{-H_2O} R_3SnO_3SAr \qquad (1)$$

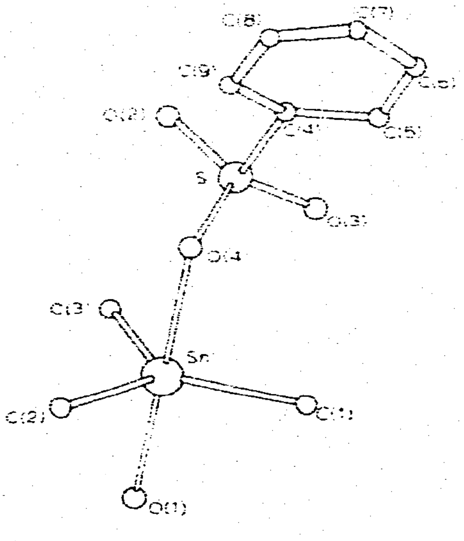
$$R_2SnO + 2\ ArSO_3H \xrightarrow{-H_2O} R_2Sn(O_3SAr)_2 \qquad (2)$$

$Ar = C_6H_5, C_6H_4Me\text{-}4$; $R = Me, C_3H_7, Bu, C_6H_{11}, Ph$

The tin-119*m* Mössbauer spectra of the derivatives consist of two narrow [Γ = 0.74—1.18 mm s^{-1}] lines of equal intensity. The isomer shift values are high compared with other R_3SnX and R_2SnX_2 compounds, indicative of higher tin 5*s* electron density at the nucleus resulting from the ionic nature of the tin—oxygen bonds. The magnitude of the quadrupole splittings of the diorganotin bis(arylsulphonates) (4.64—4.91 mm s^{-1}) is somewhat less than that of the stronger fluoro-, chloro- trifluoromethyl-, and alkylsulphonic acids (4.91—5.54 mm s^{-1}) [2—4], but still serve to suggest that they possess structures similar to that determined by X-ray diffraction for $Me_2Sn(O_3SF)_2$ [7], in which sulphonate groups bridge linear Me_2Sn moieties.

The triorganotin derivatives also exhibit large quadrupole splittings (3.90—4.32 mm s^{-1}), again indicating an infinite chain polymeric structure in which sulphonate groups bridge planar R_3Sn moieties.

Trimethyltin benzenesulphonate readily absorbs a molecule of water on recrystallisation from methanol in air, and the structure of the resultant monohydrate is shown in Fig. 1. The tin enjoys trigonal bipyramidal geometry with the SnC_3 unit being planar. A unidentate benzenesulphonate group and a water mole-



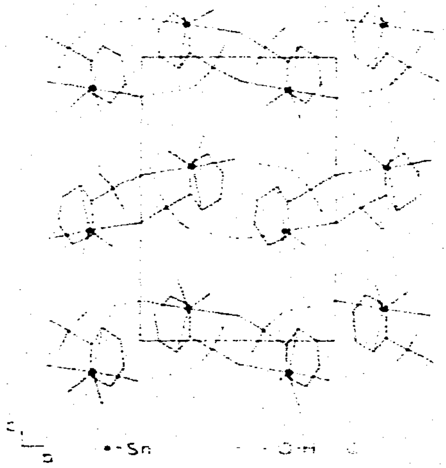


Fig. 1. View of the molecule showing the atomic numbering.

Fig. 2. Projection of the unit cell on to the *bc* plane showing the chains of hydrogen-bonded molecules. Hydrogen bonds are shown by dotted lines.

TABLE 5

WEIGHTED LEAST-SQUARES EQUATIONS ($w = z$) IN THEIR NORMAL FORM OF THE MEAN PLANES THROUGH GROUPS OF ATOMS, AND DEVIATIONS OF THE ATOMS FROM THESE PLANES (Å) (according to ref. 9)

Equations are of the form $pI + qJ + rK = s$, where I, J, and K are orthogonal coordinates related to the monoclinic coordinates in the following way: $I = x + z \cos\beta$; $J = y$; $K = z \sin\beta$.

Plane (i): C(1), C(2), C(3)
$0.46844\,I + 0.87314\,J - 0.13491\,K = 5.39264$
[Sn − 0.0463]

Plane (ii): C(4)—C(9)
$0.56892\,I - 0.82196\,J - 0.02659\,K = 0.48353$
[C(4) − 0.09033; C(5) 0.06502; C(6) − 0.00875; C(7) − 0.02689; C(8) 0.00909; C(9) 0.05148]

cule occupy the two apical positions at distances of 2.37(1) and 2.30(1) Å, respectively. That the Sn—OSO_2Ph bond distance is longer than the Sn—O_{water} distance is a reflection of the highly ionic nature of the tin—sulphonate bond. In the analogous nitrate derivative, $Me_3SnNO_3 \cdot H_2O$ [8], the Sn—O_{water} distance is longer (2.47 Å), whereas the Sn—ONO_2 bond is relatively short (2.22 Å) and more covalent in character. Crystals of $Me_3SnO_3SPh \cdot H_2O$ are made up of infinite chains of molecules connected by hydrogen bonding between water molecules and sulphonate groups of adjacent molecules parallel to the *a* axis (Fig. 2). The intermolecular O···O contact (2.54(2) Å) is much shorter than the similar interaction in $Me_3SnNO_3 \cdot H_2O$ (2.72 Å). The bond distances and angles within the benzenesulphonate group are normal.

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