Arylarsonates of Diorganotin(IV)

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Arylarsonates of diorganotin(IV) of the general formula $X\text{-}C_6H_4AsO_3SnR_2$ ($R = CH_3$, $n\text{-}C_4H_9$, $n\text{-}C_8H_{17}$, $C_6H_5CH_2$; $X = H$, p-CH_3, p-Cl, p-Br, p-OH, p-COOH, o-COOH, o-NH_2, o-NO_2) and $[-CH_2As(C_6H_5)O_2Sn(C_8H_{17})_2]_2$ have been prepared. The complexes are high melting solids, insoluble in the common organic solvents, and have been characterized by elemental analysis, molecular-weight determination, and infrared and Mössbauer spectroscopy. Five- and six-coordinate structures are postulated.

Introduction

In continuation of our earlier studies [1–4], we have isolated and studied fifteen new complexes of diorganotin(IV) with phenylarsonic acid and its derivatives.

Experimental

Materials and Methods

p-Hydroxyphenylarsonic acid was procured from Koch and Light, England. All other arsonic acids were prepared in the laboratory by usual methods [3–8]. Dimethyltin-, dibutyltin-, dibenzyltin- and dioctyltin-oxides were obtained from Alpha Products and used as received.

Elemental analysis was carried out by the Australian Microanalytical Service, Melbourne and the results are reported in Table I.

TABLE I. Analytical and Physical Data for $X\text{-}C_6H_4AsO_3SnR_2$.

S. No.	X	R	Colour	M.P. (°C)	%C[a]	%H[a]	M[a]	
1.	H	Oct	White	239–240	48.62(48.53)	7.25(7.00)	1096(544)	Dimer
2.	p-CH_3	Oct	White	241–243	49.54(49.46)	7.25(7.46)	1845(558)	Trimer
3.	o-NH_2	Oct	White	209–210	46.32(47.23)	7.07(7.15)	1012(544)	Dimer
4.	o-NO_2	Oct	Yellow	168	45.18(44.82)	6.66(6.62)	503(557)	Monomer
5.	p-OH	Oct	Light pink	275 dec	47.04(47.14)	7.02(6.96)	2038(560)	Tetramer
6.	p-Cl	Oct	White	192–193	46.32(45.63)	6.70(6.56)	588(578)	Monomer
7.	p-Br	Oct	White	218	41.46(42.37)	6.48(6.10)	700(623)	Monomer
8.	p-COOH	Oct	White	320dec	47.39(46.99)	6.80(6.65)	Insol.	Polymer
9.	o-COOH	Oct	White	195	47.17(46.99)	6.86(6.65)	1155(588)	Dimer
10.	o-COOH	Me	White	285	30.86(30.13)	3.67(3.87)	Insol.	Polymer
11.	p-COOH	Me	White	320dec	27.63(27.55)	2.85(2.80)	Insol	Polymer
12.	o-COOH	Bu	White	225–227	38.36(37.82)	4.92(4.83)	1019(476)	Dimer
13.	p-COOH	Bu	White	290dec	38.58(37.82)	5.62(4.83)	Insol	Polymer
14.	o-COOH	CH$_2$Ph	White	310dec	45.36(46.14)	3.41(3.49)	1051(544)	Dimer
15.	$[-CH_2As(Ph)O_2]_2$	Oct	White	244	48.41(48.64)	6.71(6.48)	Insol	Polymer

[a]Calculated values in brackets.

Infrared spectra in the ranges 4000–700 cm^{-1} and 600–200 cm^{-1} were recorded on Spectromom and Perkin-Elmer 577 instruments. Mössbauer spectra were recorded with a Harwell 6000 series spectrometer with samples cooled by liquid nitrogen (ca. 80 K) and source (Pd–Sn) at room temperature. Isomer shifts are relative to SnO$_2$ measured at room temperature. Melting points were found in open capillary tubes. Molecular weights were determined by the Rast method at 200 °C.

Preparation of Diorganotin(IV) Arylarsonates

The arylarsonates X-C$_6$H$_4$AsO$_3$SnR$_2$ (R = n-C$_4$H$_9$, n-C$_8$H$_{17}$; X = o-NO$_2$, o-COOH) were prepared by refluxing the ligand (0.10 mol) and the respective diorganotin(IV) oxide (0.11 mol) in absolute ethanol (30 cm^3) for one hour. The resulting solution was filtered to remove any unreacted diorganotin(IV) oxide. The filtrate, after removal of the solvent, gave a solid which was dried under vacuum. All other arylarsonates were prepared by refluxing the ligand (0.11 mol) and the diorganotin(IV) oxide (0.10 mol) in absolute ethanol (30 cm^3) for one hour, when a white solid was obtained, filtered off, dried, powdered, and refluxed for a further half-hour with the filtrate, to ensure complete reaction. The mixture was filtered and the solid washed with hot absolute ethanol three times, and dried in vacuum.

Results and Discussion

In the present study, arylarsonates of diorganotin-(IV) of the general formula X-C$_6$H$_4$AsO$_3$SnR$_2$ have been prepared and characterised by elemental analysis, molecular-weight determination, infrared and Mössbauer spectroscopy.

All the complexes are white except those of dioctyltin(IV) with p-hydroxy- and o-nitro-phenylarsonic acids, which are light pink and light yellow, respectively. The high melting points of the complexes indicate their polymeric nature, which is supported by their insolubility in the common organic solvents. However, when R = n-C$_8$H$_{17}$ and X = o-NO$_2$, p-Cl, p-Br, the compounds show slight solubility in chloroform and benzene. Molecular weight determinations in camphor show that these complexes are monomers at 200 °C; all other complexes are polymers with various degrees of polymerisation at this temperature (Table I).

To judge from the thermal stabilities, polymeric structures are most stable for R = CH$_3$, and the stability decreases in the order R = CH$_3$ > n-C$_4$H$_7$ > CH$_2$Ph > n-C$_8$H$_{17}$. The electronegativity of X also plays an important role in polymerisation. The presence of electron withdrawing groups such as Cl, Br, or NO$_2$ at para or ortho positions to AsO$_3$ facilitates the formation of monomers, while the presence of p-carboxy substituents produces highly stable chain polymers. The effect of o-carboxy substituents is intermediate.

Infrared Spectra

Infrared spectra of the arylarsonic acids and their complexes have been recorded in the ranges 4000–700 cm^{-1} and 600–200 cm^{-1} in nujol. The stretching frequencies of diagnostic interest are those of As=O, As–C, Sn–O, and Sn–C bonds (Table II).

For free arylarsonic acids, ν(As=O) is observed in the range 915–865 cm^{-1}. In most cases, ν(As=O) is lower (by 70 ± 35 cm^{-1}) in the complexes than in the free acids, indicating coordination of As=O to tin. In three cases (R = n-C$_8$H$_{17}$; X = H, p-CH$_3$, o-NH$_2$), slight increases are observed which may be due to the release of arsonic oxygen from hydrogen bonding when hydroxyl groups of X-C$_6$H$_4$AsO$_3$X$_2$ are deprotonated by bonding to tin.

On complex formation, an increase of 70 cm^{-1} in ν(As–C) is noted in all complexes except those of di-octyltin with the acids with X = p-CH$_3$, p-OH. In these cases, a decrease in ν(As–C) of 5–18 cm^{-1} was observed. The increase in ν(As–C) may be attributed to the coordination of the As=O group to tin, while the decrease in ν(As–C) may be due to the electron-releasing effect of p-tolyl and p-hydroxy-phenyl groups. For the carboxy-substituted phenyl-arsonic acids, ν(C=O) is assigned as 1690 cm^{-1} (p-carboxy) and 1655 cm^{-1} (o-carboxy). A decrease in ν(C=O) of 35–105 cm^{-1} in the complexes of these acids shows the participation of the carbonyl group in coordination. Bands of medium intensity, observed around 400 cm^{-1} and 500 cm^{-1} are assigned to ν(Sn–O) and ν(Sn–C), respectively, and are consistent with previous observations [1–4]. The reactions of diorganotin oxides with o-carboxy-phenylarsonic acids involve deprotonation of one hydroxy group of the arsonic acid and one carboxy group. Since a shoulder around 2400 ± 50 cm^{-1} due to As–OH is present in the spectra of the complexes whereas bands due to As–OH at 2650 and COOH at 2850 cm^{-1} present in the spectrum of the acid, are absent in those of the complexes. However, for the other arsonic acids, both hydroxy groups of the AsO$_3$H$_2$ unit are deprotonated during the formation of the complexes. In the spectra of p-carboxyphenylarsonic acid complexes a weak shoulder around 2760 ± 10 cm^{-1} is present while the acid spectrum shows two shoulders around 2775 and 2825 cm^{-1} which indicates presence of the COOH group in the complexes. The infrared data support the polymerisation of the complexes through carbonyl groups and through the As=O groups of the arsonic acid.

^{119}Sn Mössbauer Spectra

On the basis of the Mössbauer data (Table III), the compounds can be divided into five well defined

TABLE II. Infrared Data (cm^{-1}) for X-C$_6$H$_4$AsO$_3$SnR$_2$.[a]

S. No.	X	R	(Sn–O)	(Sn–C)	(As=O)	(As–C)	(C=O)	(As–OH)	(COOH)/NH$_2$
1.	H	Oct	–	–	875s(870bs)	1120m(1077s)	–	–	–
2.	p-CH$_3$	Oct	–	–	885m(865m)	1080m(1085)	–	–	–
3.	o-NH$_2$	Oct	395w	470m(570w)	900s(850bs)	1095w(1070b)	–	–	3350 m (acid 3250m)
4.	o-NO$_2$	Oct	365m	490sh(530m)	840s(905s)	1170m(1108m)	–	–	–
5.	p-OH	Oct	368m	465m(520m)	820s(880s)	1090m(1100m)	–	–	–
6.	p-Cl	Oct	350m	465m(500s)	840m(900s)	1080s(1077s)	–	–	–
7.	p-Br	Oct	400w	495w	822s(915bs)	1065vw(1085)	–	–	–
8.	p-COOH	Oct	–	–	840s(893s)	1070m(1050)	1585w (1690s)	–	2770sh
9.	o-COOH	Oct	355m	475w	810s(890s)	1120m(1077sh)	1585s (1655)	2400sh	–
10.	o-COOH	Me	–	–	880s(893)	1075m(1050m)	1620s (1655s)	–	–
11.	p-COOH	Me	465	540w(575)	880s(893s)	1080m(1050m)	1590s (1690s)	–	2770sh
12.	o-COOH	Bu	360w	500wb	850s(893)	1100s(1077sh)	1590m (1655s)	–	–
13.	p-COOH	Bu	350w	470w(515sh)	830s(893)	1085m(1050m)	1612s (1690s)	–	2770sh
14.	o-COOH	CH$_2$Ph	395	485sh	850s(890s)	1110m(1050m)	1620m (1655s)	2450sh	–
15.	[–CH$_2$As(Ph)O$_2$]$_2$	Oct	425	525	850s(870)	1100s(1095)	–	–	–

[a]Values in brackets are those for the free arsonic acids.

TABLE III. ^{119}Sn Mössbauer Data (mm s^{-1}) for X-C$_6$H$_4$AsO$_3$SnR$_2$.

| S. No.	X	R	IS(SnO$_2$)[a]	QS[a]	Line-widths[b]		Structure
1.	H	Oct	1.16	2.85	0.95	1.02	
2.	p-CH$_3$	Oct	1.15	2.79	0.83[c]		I
3.	o-NH$_2$	Oct	1.17	2.87	0.95	0.99	
4.	o-NO$_2$	Oct	1.24	3.12	1.01[c]		
5.	p-Cl	Oct	1.12	3.00	0.96	1.19	
6.	p-Br	Oct	1.15	2.95	0.95	1.10	II or III
7.	p-OH	Oct	1.19	3.02	0.97	1.07	
8.	p-COOH	Bu	1.29	3.16	0.87	1.03	
9.	o-COOH	Bu	1.33	3.46	0.95	1.22	V
10.	o-COOH	Oct	1.34	3.52	0.92	1.26	
11.	p-COOH	Oct	1.31	3.55	1.00	1.28	VI
12.	o-COOH	Me	1.34	3.96	0.98	1.08	V
13.	o-COOH	CH$_2$Ph	0.62	1.77	1.09	1.26	VII or cis-V
14.	[−CH$_2$As(Ph)O$_2$]$_2$	Oct	1.27	4.04	1.01	1.01	VIII

[a]$\pm$0.05 mm s^{-1}.   [b]$\pm$0.05 mm s^{-1}.   [c]Line widths constrained to be equal.

groups. The data can be discussed in terms of the coordination number and stereochemistry of the tin atom but do not give any direct indication of the degree of polymerisation.

The compounds of the first group (Table III, compounds 1–3) have isomer shifts (IS) of *ca.* 1.16 mm s^{-1} and quadrupole splitting (QS) of *ca.* 2.8 mm s^{-1}, consistent with tetrahedral geometry at the tin atom [9, 10]. For these compounds the coordination shift of ν(As=O) is small and positive, showing that the As=O group is not coordinated. Monomeric structures are possible, but are excluded by the molecular weight data. It is not possible to distinguish dimeric structure (I, n = 1) from higher ring or chain polymers.

The second group of compounds (numbers 4–8) show marginally higher IS, *ca.* 1.2 mm s^{-1}, and rather large QS, *ca.* 3.0 mm s^{-1}. The IR data indicate coordination of the As=O group (negative coordination shifts of ν(As=O), so that the change in Mössbauer parameters, although close to the experimental error, is probably significant. Involvement of the As=O group requires an increase in the coordination number of the tin, and the data are not inconsistent with five-coordination [9–11], a common coordination number for tin(IV) [12]. Five-coordinate diorganotin(IV) compounds usually have trigonal-bipyramidal structures with the organic groups in equatorial positions. The monomeric structure suggested by the molecular weight is unlikely since, if the organic groups were both in equatorial positions, the arsonic acid would have to span the *trans* axial position, while a *fac* configuration for the arsonic acid would require one organic group to be

axial. It is therefore more likely that polymeric structures are adopted which break down at 200 °C in camphor, and satisfactory dimeric(II) or polymeric-(III) structure can be proposed.


(I)

(II)

(III)
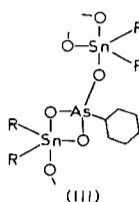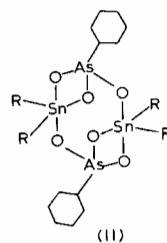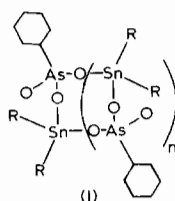
For the compounds of the third group (numbers 9–11), further increases in both parameters are seen, with IS *ca.* 1.3 mm s^{-1} and QS *ca.* 3.5 mm s^{-1}.

Interpretation of these data is more difficult, since other compounds with similar parameters have been attributed five-coordinate [11, 13–15] or *trans* six-coordinate structures [16–19]. In diorganotin(IV) systems where the remaining ligands are highly electronegative, the QS is determined mainly by the C–Sn–C bond angle [9, 20], and distortion from regular six-coordination can give values similar to those for five-coordination [21, 22]. The IS might be expected to be slightly greater for five-coordination, but this difference could easily be offset by an increase due to a widening of the C–Sn–C angle in the six-coordinate system. No firm diagnosis of the structure can thus be made. However, all these compounds contain carboxy substituents which on the basis of the IR data may be involved in coordination [loss or modification of ν(O–H), decrease in the difference ν(C=O) – ν(C–O)], suggesting six-coordination for the tin. Chain structures (IV) seem less likely than three-dimensional polymers (V, VI). A dimeric structure with the organic groups in *trans* positions does not seem possible.

(IV)

(V)

(VI)
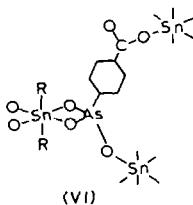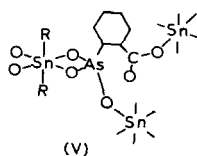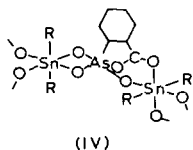
The remaining compounds have Mössbauer parameters characteristic of regular six-coordination. For o-HO$_2$CC$_6$H$_4$AsO$_3$SnMe$_2$ (compound 12), the IR data indicate coordination of the As=O and carboxy groups, suggesting structure (V) in which the smaller bulk of the CH$_3$ group allows a C–Sn–C bond angle close to 180°. In the corresponding dibenzyltin compound (13) the organic groups must be in *cis* positions, and this compound could be dimeric(VIII) or polymeric (analogous to V). The diarsonic acid derivative [–CH$_2$As(C$_6$H$_5$)O$_2$]$_2$Sn-(C$_8$H$_{17}$)$_2$ (14) involves *trans* six-coordination, and

the high insolubility of this compound suggests a polymeric structure (VIII).

(VII)

(VIII)
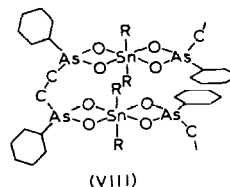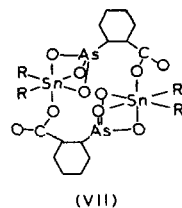
Thus, on the basis of the Mössbauer and IR data, several different solid-state structures seem to be formed. In the majority of cases, all three oxygen atoms of the arsonic acid group are involved in coordination to tin without participation of the ring substituents. Only when those substituents are carboxy groups do they seem to be involved in the coordination with a subsequent rise in the coordination number of tin to six.

Acknowledgements

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