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ORGANOTIN DERIVATIVES OF (ARYLAZO)BENZOIC ACIDS

I. PREPARATION, SPECTROPHOTOMETRIC TITRATIONS AND IR SPECTRA

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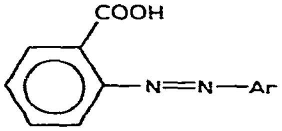
Summary

Organotin derivatives of some (arylazo)benzoic acids have been prepared, and investigated by spectrophotometric titration and IR spectroscopy The organotin (*o*-arylazo)benzoates are generally penta-coordinated, but those containing a hydroxyl group in the 2-position, e g , triorganotin *o*-(2-hydroxy-5-methylbenzeneazo)benzoate, are hexa-coordinated The tetracarboxy derivatives contain two different types of tin—carboxylate bonds, as shown by two IR absorptions, at 1700 (ester-like) and 1620 cm^{-1} (chelated).

Introduction

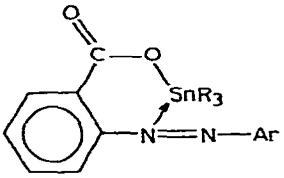
Though *o*-(arylazo)benzoic acids and related compounds (I) have been widely used as ligands in transition metal chemistry [1—6], no organotin derivatives have so far been reported



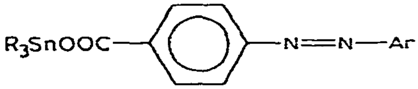
(I)

This group of compounds is well suited for the preparation of a variety of interesting organotin complexes because *(1)* (arylazo)benzoic acids with a wide variety of nuclear substituents can be easily prepared by diazotisation of the aminobenzoic acid followed by coupling with suitable aryl moiety, *(2)* the ligands have a very favourable steric arrangement for the formation of 6-membered chelate ring, *(3)* with —OR or $—NR_2$ type substituent at the *o*-position, the ligands may be made terdentate making it possible to prepare hexa-coordinated triorganotin compounds, and *(4)* the electronic spectra are expected to be sensitive to coordination of the azo-N-atom, making it possible to study the formation and stability of the chelate ring through spectral studies

A number of organotin derivatives of *o*-(arylazo)benzoic acids (II) have been prepared and their properties compared with those of *p*-(arylazo)benzoates (III) to ascertain the effect of chelation on spectral and other properties



(II)



(III)

Results and discussion

For convenience the name of the ligands have been abbreviated as shown in Table 1.

(A) Method of preparation

The organotin derivatives have been prepared either by *(a)* stirring the organotin halide with the sodium salt of the carboxylic acid in methanol or ethanol or *(b)* refluxing the hexa-organodistannoxanes with the carboxylic acid in benzene The conditions, products, m.p., and yields are summarised in Table 2.

Table 2 shows that the yields are dependent on the nature of the aryl group in I. In general triphenyltin derivatives are best prepared by method *a*, while method *b* is better for alkyltin compounds. An interesting feature is that side products are formed by cleavage of alkyl—tin bonds (rcn. no 9, 13, 17) even though the tin—phenyl bonds are not cleaved under similar conditions The cleavage of alkyl—tin bonds under conditions which do not cleave phenyl—tin bonds is very unusual. In contrast to reaction of triphenyltin chloride with sodium (arylazobenzoates), the reaction of diphenyltin dichloride under similar conditions always gave products in which all Ph—Sn bonds had been cleaved (rcn. no. 4, 16 and 21).

Analytical data for the compounds are given in Table 3.

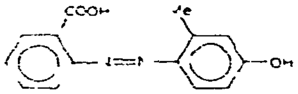
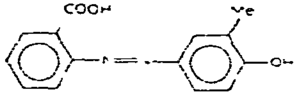
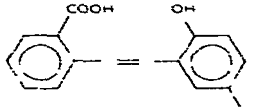
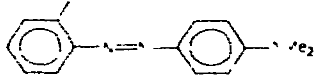
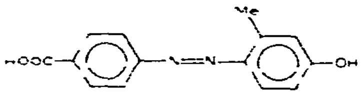
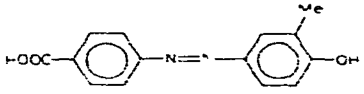
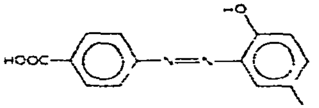
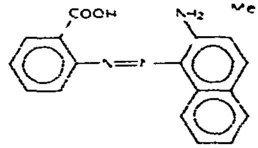
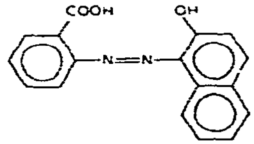
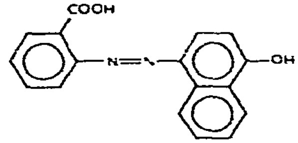
(B) Spectrophotometric titration

The absorption spectra of triorganotin in *p*-(arylazo)benzoates (III) are almost identical with those of the free acids. On the other hand, organotin derivatives of the *o*-(arylazo)benzoic acids (II) show considerably different spectra from the free acid and its sodium salt, as would be expected if chelation through the azo-N-atom occurs. (A detailed discussion of the electronic spectra will be reported later.) The difference between the absorption spectra of the sodium salt and the organotin derivative of *o*-(arylazo) benzoic acids has been used to investigate the nature and stoichiometry of the products through spectrophotometric titrations, In some cases reaction 1 is so fast that the sodium salt in

(continued on p. 43)

TABLE 1

LIGANDS AND THEIR ABBREVIATION

Structure	Name	Abbreviation used [a]
	*o* (2-Methyl-4-hydroxybenzeneazo)-benzoic acid	*o*-2M4HBB
	*o* (3-Methyl-4-hydroxybenzeneazo)-benzoic acid	*o* 3M4HBB
	*o* (2-Hydroxy-5-methyl-benzene-azo)benzoic acid	*o*-2H5MBB
	*o* (4-Dimethyl-aminobenzeneazo)-benzoic acid	*o*-4DABB
	*p* (2-Methyl-4-hydroxybenzene-azo)benzoic acid	*p*-2M4HBB
	*p* (3-Methyl-4-hydroxybenzene-azo)benzoic acid	*p* 3M4HBB
	*p*-(2-Hydroxy-5-methylbenzeneazo)-benzoic acid	*p* 2H5MBB
	*o* (2-Amino-naphthylazo)benzoic acid	*o*-2ANB
	*o* (2-Hydroxy-naphthylazo)benzoic acid	*o* 2HNB
	*o*-(4-Hydroxy-naphthylazo)-benzoic acid	*o* 4HBB

[a] M = methyl, H = hydroxy, A = amino, DA = dimethylamino, BB = benzeneazobenzoic acid and NB = naphthylazobenzoic acid. The numerals in the abbreviations indicate the position of the group

TABLE 2

SUMMARY OF REACTIONS AND PRODUCTS

Reactants (mole ratio)	Expt. condition^a	Product (m p yield (%))
1 Ph_3SnCl + Na-o 2M4HBB (1 1)	a 6 h benzene	Ph_3Sn(o 2M4HBB) (180°C 90—95)
2A Bu_3SnCl + Na-o 2M4HBB (1 1)	a 12 h petr. ether	Bu_3Sn(o 2M4HBB). (136°C 10—15)
2B $(Bu_3Sn)_2O$ + o-2M4HBB (1 2)	b 6 h petr ether	Bu_3Sn(o 2M4HBB) (136°C 75—80)
3 $(Pr_3Sn)_2O$ + o-2M4HBB (1 2)	6 2 h CCl_4	Pr_3Sn(o 2M4HBB) (141°C, 75—80)
4 Ph_2SnCl_2 + Na-o 2M4HBB (1 2)	a 3 h^b	$(o\ 2M4HBB)_4Sn$ (225°C 65—70)
5 Ph_3SnCl + Na-o-3M4HBB (1 1)	a, 8 h benzene/ petr ether mixture	Ph_3Sn(o 3M4HBB) (174°C, 60—65)
6A Bu_3SnCl + Na-o 3M4HBB (1 1)	a 8 h petr ether	Bu_3Sn(o 3M4HBB) (112°C 10—15)
6B $(Bu_3Sn)_2O$ + o 3M4HBB (1 2)	b, 6 h petr ether	Bu_3Sn(o 3M4HBB) (112°C 75—80)
7. $(Pr_3Sn)_2O$ + o 3M4HBB (1 . 2)	b, 3 h benzene/ petr ether mixture	Pr_3Sn(o 3M4HBB) (139°C 85—90)
8 Ph_3SnCl + Na-o-2H5MBB (1 1)	a, 6 h, benzene	Ph_3Sn(o 2H5MBB) (145°C 95)
9 $(C_6H_{11})_3SnBr$ + Na-o 2H5MBB (1 1)	a, 10 h product (i) extracted with ether and (ii) with benzene	(i)$(C_6H_{11})_3Sn$(o 2H5MBB) (140°C 55) (ii)$(C_6H_{11})_2Sn$(o 2H5MBB) OH (184°C 25)
10 Ph_3SnCl + Na-o 2ANB (1 1)	a 8 h benzene	Ph_3Sn(o 2ANB) (158°C, 60—65)
11 Ph_3SnCl + Na-o 4HNB (1 1)	a 3 h benzene	Ph_3Sn(o-4HNB) (224°C, 90—95)
12 Bu_3SnCl + Na-o 4HNB (1 · 1)	a 10 h petr ether	Bu_3Sn(o 4HNB) (150°C 55—60)
12B $(Bu_3Sn)_2O$ + o 4HNB (1 2)	b 4 h petr ether	Bu_3Sn(o 4HNB) (150°C, 85—90)
13 $(C_6H_{11})_3SnBr$ + Na-o 4HNB (1 1)	a 10 h product (i) extracted with petr ether (ii) with benzene	(i)$(C_6H_{11})_3Sn$ (o 4HNB) (187°C 30—35) (ii)$[(C_6H_{11})_2Sn(o\ 4HNB)]_2O$ (232°C, 20)
14 Ph_3SnCl + Na-o-2HNB (1 1)	a 10 h benzene	Ph_3Sn(o-2HNB) (212°C 75—80)
15 Bu_3SnCl + Na-o 2HNB (1 1)	a 12 h fractional crystallisation from benzene	Bu_3Sn(o 2HNB) (180°C, 30)
16 Ph_2SnCl_2 + Na-o-2HNB (1 2)	a 3 h^b	$(o\ 2HNB)_4Sn$ (240°C, 55—60)
17 Bu_3SnCl + Na-o 4DABB (1 · 1)	a, 12 h, product (i) was extracted with petr ether, (ii) with benzene	(i) Bu_3Sn(o-4DABB) (100°C, 75) (ii) $[Bu_2Sn(o\ 4DABB)]_2O$ (200°C 20)
18 Ph_3SnCl + Na-o 4DABB (1 1)	a 1/2 h benzene/ petr ether mixture	Ph_3Sn(o 4DABB) (177°C 90—95)
19 $(C_6H_{11})_3SnBr$ + Na-o 4DABB (1 · 1)	a 2 h petr ether	$(C_6H_{11})_3Sn$(o-4DABB) (145°C, 85)
20 $(Pr_3Sn)_2O$ + o 4DABB (1 2)	b 12 h petr ether	Pr_3Sn(o-4DABB) (130°C 25)
21. Ph_2SnCl_2 + Na-o-4DABB (1 2)	a, 2 h^c	$[(o\text{-}4DABB)_2Sn]_2O$ (260°C 8—10)

(Table to be continued)

TABLE 2 (continued)

Reactants (mole ratio)	Exptl condition [a]	Product (m p yield (%))
22 Ph$_3$SnCl + Na-*p* 3M4HBB (1 1)	a 16 h benzene	Ph$_3$Sn(*p* 3M4HBB) (165°C 65—70)
23 Ph$_3$SnCl + Na *p* 2M4HBB (1 1)	a, 12 h petr ether	Ph$_3$Sn(*p* 2M4HBB) (162°C, 60—65)
24 Ph$_3$SnCl + Na-*p* 2H5MBB (1 1)	a 12 h benzene/ petr ether mixture	Ph$_3$Sn(*p* 2H5MBB) (164°C 60)

[a] Given in the order method time solvent for crystallisation of the product a Stirring at room temperature in methanol except in reaction nos 17—21 for which ethanol was used b refluxing in dry benzene [b] Purified by Soxhlet extraction with benzene [c] Purified by repeated washing with benzene and petroleum ether

methanol can be titrated spectrophotometrically against Ph$_3$SnCl

$$Ph_3SnCl + o\text{-}(ArN{=}N) \cdot C_6H_5COONa \rightarrow \text{Products} \qquad (1)$$

A typical titration curve is shown in Fig 1 As expected, the equivalence point corresponds to the formation of 1 1 product, and this is confirmed by elemental analysis. Such direct titration with organotin halides cannot be used in most cases but the reverse reaction 2 can usually be used for spectrophotometric titration.

TABLE 3

ANALYTICAL DATA

Compound [a]	Found (calcd) (%)		
	C	H	Sn
Ph$_3$Sn(*o* 2M4HBB)	63 87(63 50)	4 40(4 30)	19 62(19 63)
Bu$_3$Sn(*o* 2M4HBB)	57 11(57 27)	6 96(6 97)	22 2(21 80)
Pr$_3$Sn(*o* 2M4HBB)	55 09(54 90)	6 42(6 35)	23 78(23 62)
(*o*-2M4HBB)$_4$Sn	59 32(59 01)	3 67(3 86)	10 41(10 42)
Ph$_3$Sn(*o* 3M4HBB)	64 01(63 50)	4 42(4 30)	18 84(19 63)
Bu$_3$Sn(*o* 3M4HBB)	57 02(57 27)	6 98(6 97)	21 79(21 80)
Ph$_3$Sn(*o* 2M4HBB)	62 83(63 50)	4 52(4 30)	20 06(19 63)
Cy$_3$Sn(*o* 2M4HBB) [b]	60 79(61 66)	7 09(7 06)	19 17(19 06)
Ph$_3$Sn(*o*-2ANB)	65 33(65 66)	4 33(4 22)	17 66(18 55)
Ph$_3$Sn(*o* 4HNB)	66 18(65 55)	4 24(4 06)	18 32(18 53)
Bu$_3$Sn(*o*-4HNB)	59 71(59 81)	6 48(6 54)	20 23(20 44)
Cy$_3$Sn(*o* 4HNB)	63 78(63 76)	6 81(6 68)	17 66(18 02)
[Cy$_2$Sn(*o*-4HNB)]$_2$O	59 24(59 65)	6 00(5 66)	20 00(20 30)
Ph$_3$Sn(*o*-2HNB)	66 25(66 55)	4 17(4 06)	18 30(18 53)
Bu$_3$Sn(*o*-2HNB)	59 41(59 92)	6 71(6 54)	19 98(20 44)
Ph$_3$Sn(*p* 3M4HBB)	64 12(63 50)	4 42(4 30)	20 08(19 63)
Ph$_3$Sn(*p*-2H5MBB)	63 89(63 50)	4 37(4 30)	19 67(19 63)
Bu$_3$Sn(*o* 4DABB)	58 54(58 09)	6 98(7 35)	20 21(21 28)
[Bu$_2$Sn(*o*-4DABB)]$_2$O	53 85(54 20)	6 26(6 29)	22.40(23 30)
Ph$_3$Sn(*o*-4DABB)	63 80(64 10)	4 66(4 69)	18 76(19 21)
Cy$_3$Sn(*o*-4DABB)	62.89(62 69)	7 36(7 39)	17 68(18 67)
Pr$_3$Sn(*o*-4DABB)	55 88(53 84)	6 78(6 98)	23 18(23.42)

[a] Cy, cyclohexyl.

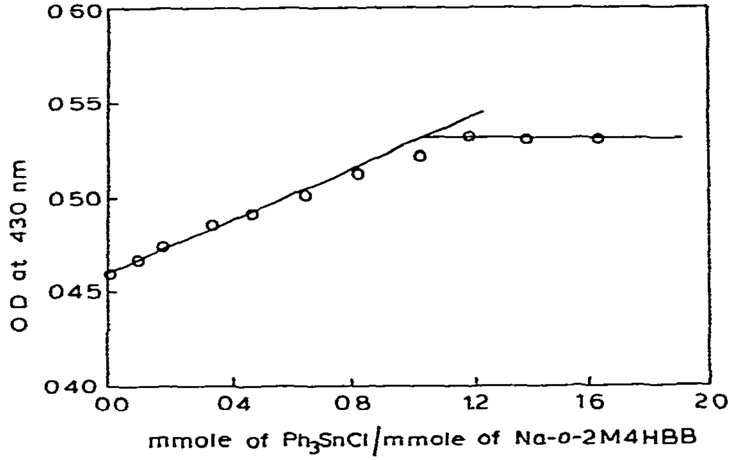


Fig. 1. Spectrophotometric titration of methanolic Ph$_3$SnCl with Na-o 2M4HBB in methanol

$$R_3SnOCOR + OH^- \rightarrow R_3SnOH + RCOO^- \qquad (2)$$

A typical curve is shown in Fig. 2. Compounds containing a OH group at 2-position, e g , R$_3$Sn(*o*-2H5MBB) and R$_3$Sn(*o*-2HNB), are significantly more resistant to cleavage by a hydroxyl ion than those without any such group. This

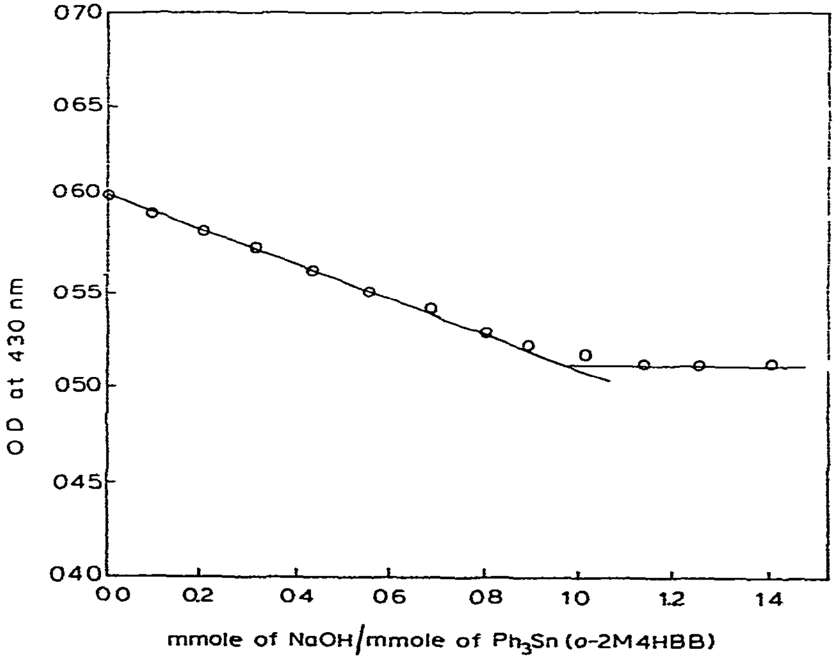
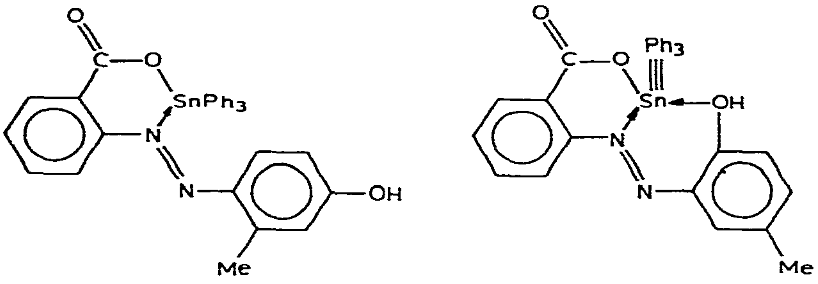


Fig. 2. Spectrophotometric titration of methanolic Ph$_3$Sn(o-2M4HBB) with methanolic NaOH'



(IV) (V)

Fig. 3 Probable structures of Ph_3Sn(o 2M4HBB) (IV) and Ph_3Sn(o 2H5MBB) (V)

suggests that the former involves hexa-coordinated tin, whereas the latter contains penta-coordinated tin, as shown in Fig. 3.

Because tin expands its coordination number beyond six only under comparatively drastic conditions compound V is cleaved by a hydroxyl ion only when the latter is present in large excess, while IV is cleaved readily by a facile nucleophilic attack at the penta-coordinated tin Methanolic solution of V may however be titrated spectrophotometrically with aqueous Cu^{2+} or Ni^{2+} solutions, since the transition metal complexes are so stable that the organotin group is completely replaced by these ions. A typical titration curve is shown in Fig 4.

Titration of the tetracarboxy derivative, (o-2M4HBB)$_4$Sn, with methanolic NaOH reveals another interesting feature The titration curve in this case shows two breaks, the first occurring at 2 moles and the second at 4 moles of NaOH per mole of the tin compound This indicates that the compound contains two

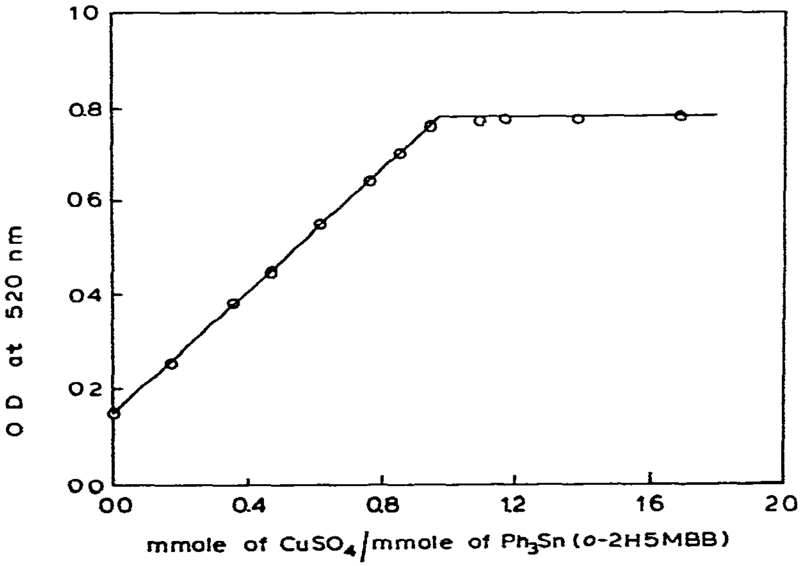


Fig. 4. Spectrophotometric titration of methanolic Ph_3Sn(o-2H5MBB) with aqueous $CuSO_4$.

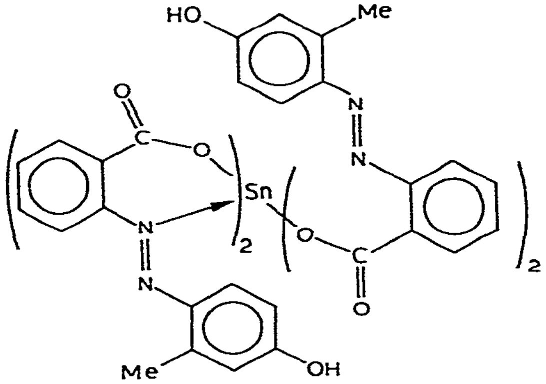


Fig 5 Probable structure of $(o\text{-}2M4HBB)_4Sn$.

chelated and two non-chelated, ester-like, carboxy groups, the compound being a hexa-coordinated tin derivative (Fig. 5). Convincing evidence for this is provided by the IR spectra, in which two $\nu_{as}(OCO)$ bands are found, one at 1700 cm^{-1} (ester like) and the other at 1620 cm^{-1} (chelated)

TABLE 4

FREQUENCIES OF SOME IMPORTANT VIBRATIONS IN THE ORGANOTIN (ARYLAZO)BENZOATES

Compound	$\nu_{as}(OCO)$ (cm^{-1})	$\nu(Sn{-}O)$ (cm^{-1})	Miscellaneous [a]
Pr_3Sn(*o* 2M4HBB)	1630	502	
Bu_3Sn(*o* 2M4HBB)	1632	504	
Ph_3Sn(*o* 2M4HBB)	1632	510	
Pr_3Sn(*o* 3M4HBB)	1626	512	ν(OH) 3150 w(sh)
Bu_3Sn(o 3M4HBB)	1626	512	ν(OH) 3150 w(sh)
Ph_3Sn(o 3M4HBB)	1632	520	ν(OH) 3200
Cy_3Sn(*o*-2M4HBB)	1635	525	ν(OH) 3200 w(sh)
Ph_3Sn(*o* 2M4HBB)	1626	520	ν(OH) 3200 w(sh)
Bu_3Sn(o 4HNB)	1626	498	ν(OH) 3130 (br)(sh)
Cy_3Sn(*o*-4HNB)	1635	505	ν(OH) 3100(br) s
Ph_3Sn(o 3HNB)	1626		ν(OH) 3140(br)(sh)
Ph_3Sn(*o* 2HNB)	1620	500	
Ph_3Sn(*o* 2ANB)	1622	510	$\nu(NH_2)$ 3440 $\delta(NH_2)$ 1610
Pr_3Sn(*o* 4DABB)	1600		
Bu_3Sn(*o* 4DABB)	1600		
Cy_3Sn(*o*-4DABB)	1670		
Ph_3Sn(o 4DABB)	1620		
Ph_3Sn(*p*-2M4HBB)	1627	515	
Ph_3Sn(*p*-3M4HBB)	1620	520	ν(OH) 3150(br)
Ph_3Sn(*p*-2H5MBB)	1628	510	
Cy_2Sn(OH)(*o* 2H5MBB)	1605	520	ν(OH) 3430
$[Cy_2Sn$(*o* 4HNB)$]_2O$	1638	485	
$[Bu_2Sn$(*o*-4DABB)$]_2O$	1635	486	$\nu_{as}(Sn{-}O{-}Sn)$ 632
(*o*-2M4HBB)$_4$Sn	1615, 1700		ν(OH) 3180
(*o*-2HNB)$_4$Sn	1620, 1710	502	

[a] w, weak, s strong, (sh) shoulder, (br) broad.

(C) Infrared spectra

The IR spectra of the organotin (arylazo)benzoates are very complex and complete assignment of the bands is not possible. The frequencies of important vibrational modes that could be assigned are listed in Table 4

Like triorganotin benzoates and substituted benzoates [7], the (arylazo)benzoates, whether *ortho*- or *para*-substituted, show an asymmetric carboxylate stretch, usually in the 1610—1640 cm^{-1} region. The IR spectra of a few typical compounds, e.g , $Ph_3Sn(o\text{-}2M4HBB)$, $Ph_3Sn(o\text{-}4DABB)$ in chloroform show no raising of $\nu_{as}(OCO)$, indicating the absence of any intermolecular bridging through the carboxy group The low value of $\nu_{as}(OCO)$ in these compounds must therefore be attributed to appreciable ionic character in the Sn—OCO bond

Tetracarboxy derivatives, viz , $(o\text{-}2M4HBB)_4Sn$ and $(o\text{-}2HNB)_4Sn$ show two $\nu_{as}(OCO)$ absorptions of nearly the same intensity at about 1700 and 1620 cm^{-1}. The 1700 cm^{-1} band obviously corresponds to a pure ester-like Sn—OCO bond, while the 1620 cm^{-1} band is similar to those given by triorganotin derivatives, indicating the presence of two chelated and two ester-like carboxy groups The tin atoms in the tetracarboxy derivatives are thus hexa-coordinated

Experimental

(A) Preparation of (arylazo)benzoic acids

A typical preparation is described below.

o-(2-Methyl-4-hydroxybenzeneazo)benzoic acid 10 g of anthranilic acid was diazotised [8]. *m*-Cresol (8 g) was dissolved in 100 ml of 10% NaOH solution and the solution was cooled to 5°C in an ice bath then added to the cold diazonium salt solution with vigorous stirring A reddish yellow colour developed The mixture was kept in an ice bath for 1/2 h and then acidified with acetic acid, when the azo derivative separated. It was filtered off, washed with water, air dried, and finally crystallized from methanol to give *o*-2M4HBB, m p 199—200°C,

Other azo derivatives were prepared analogously, the diazo component being diazotised anthranilic acid for the *o*-derivatives and *p*-aminobenzoic acid for the *p*-derivatives. The coupling components employed for the various derivatives are as follows: 3M4HBB: *o*-cresol; 2H5MBB, *p*-cresol, 2ANB. β-naphthylamine; 4NHB α-naphthol, and 2HNB β-naphthol.

(B) Preparation of the organotin derivatives

A typical preparation is described below

Triphenyltin o-(2-methyl-4-hydroxybenzeneazo)benzoate, $Ph_3Sn(o\text{-}2M4HBB)$ A mixture of triphenyltin chloride (1.61 g) and Na-*o*-2M4HBB (1 3 g) in 75 ml methanol was stirred for 6 h at room temperature, A red compound separated, and filtration gave 1.6 g of red solid, m p. 178°C. The filtrate on concentration gave a further crop of 0.8 g, m p. 176°C. The crops were combined and dissolved in benzene, and the solution was filtered, then concentrated to give red crystals of $Ph_3Sn(o\text{-}2M4HBB)$, m p 180°C.

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