ORGANOTIN DERIVATIVES OF ARYLAZOBENZOIC ACIDS

II. ABSORPTION SPECTRA AND STRUCTURE

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Summary

On the basis of their electronic spectra triorganotin (arylazo)benzoates are classified into three types. The derivatives of *p*-(arylazo)benzoic acids have spectra almost identical with those of the carboxylic acids. The spectra do not show any marked solvent dependence. On the other hand, triorganotin *o*-(arylazo)-benzoates show a considerable bathochromic shift of the first $\pi—\pi^*$ transition indicating chelation through the azo-N atom. The pentacoordinated compounds having only one chelate ring have low stability towards donor solvents, e.g., ether, methanol. DMSO and the N→Sn bond is easily broken. However, the presence of a OH or NH_2 group at the *o'*-position makes the azobenzoic acids terdentate. The resulting hexacoordinated tin compounds with two annelated chelate rings have marked stability towards donor solvents as indicated by the near absence of solvent effects on the absorption spectra.

Introduction

Though much work has been done on the electronic spectra of azobenzene and related compounds [1—12], there has been surprisingly little work done on their metal complexes [2,13—16]. According to MO descriptions [1,2,9], the upper MO for the longest wave length $\pi—\pi^*$ transition is the perturbed orbital originating from the antibonding π-orbital of the azo group, while the lower one is the orbital arising from the perturbation of the highest bonding π-orbital of the aryl residue. Coordination by the azo-N atom would thus be expected to cause a bathochromic shift of the longest wavelength band in metal complexes because of the lowering of the π^* orbital due to the partial electron withdrawing from the N atoms to the metal. In view of this, a detailed electronic spectral study of the organotin (arylazo)benzoates has been carried out in order to determine the role of the azo group in the tin complexes reported earlier.

Results and discussion

The (arylazo)benzoic acids along with the abbreviations used are listed in Table 1.

The absorption maxima and molar extinctions of the (arylazo)carboxylic acids and their organotin derivatives in different solvents are given in Table 2.

TABLE 1

LIGANDS AND THE ABBREVIATIONS USED FOR THEM

	Name	Abbreviation used [a]
	o-(2-Methyl-4-hydroxy-benzeneazo)benzoic acid	o-2M4HBB
	o-(3-Methyl-4-hydroxy-benzeneazo)benzoic acid	o-3M4HBB
	o-(2-Hydroxy-5-methyl-benzeneazo)benzoic acid	o-2H5MBB
	o-(4-Dimethylamino-benzeneazo)benzoic acid	o-4DABB
	p-(2-Methyl-4-hydroxy-benzeneazo)benzoic acid	p-2M4HBB
	p-(3-Methyl-4-hydroxy-benzeneazo)benzoic acid	p-3M4HBB
	p-(2-Hydroxy-5-methyl-benzeneazo)benzoic acid	p-2H5MBB
	o-(2-Aminonaphthyl-azo)benzoic acid	o-2ANB
	o-(2-Hydroxynaphthyl-azo)benzoic acid	o-2HNB
	o-(4-Hydroxynaphthyl-azo)benzoic acid	o-4HNB

[a] o, ortho; p, para; M, methyl; H, hydroxy; A, amino, DA, dimethylamino; BB, benzeneazobenzoic acid; NB, naphthylazobenzoic acid. The numbers in the abbreviation indicate the position of the group.

TABLE 2

ABSORPTION MAXIMA IN AZOCARBOXYLIC ACIDS AND THEIR ORGANOTIN DERIVATIVES

Compound		Solvent	λ_{max} (nm(log ϵ))		
I	o-2M4HBB	Methanol	259(3.93)	358(4.27)	460(3.62)
		Benzene		385(4.48)	
II	Ph$_3$Sn(o-2M4HBB)	Methanol	255(4.12)	358(4.24)	460(3.76)
		Benzene			450(4.34)
III	Bu$_3$Sn(o-2M4HBB)	Methanol	251(4.15)	355(4.22)	450(3.75)
		Benzene			440(4.27)
IV	Pr$_3$Sn(o-2M4HBB)	Methanol	250(4.16)	355(4.24)	458(3.80)
		Benzene			444(4.40)
V	o-3M4HBB	Methanol	255(4.03)	355(4.22)	460(3.68)
		Benzene		385(4.58)	
VI	Ph$_3$Sn(o-3M4HBB)	Methanol	252(4.10)	355(4.25)	456(3.72)
		Benzene		357(3.94)	449(4.36)
VII	Bu$_3$Sn(o-3M4HBB)	Methanol	251(4.15)	355(4.28)	460(3.68)
		Benzene			450(4.35)
VIII	Pr$_3$Sn(o-3M4HBB)	Methanol	251(4.13)	355(4.31)	454(3.66)
		Benzene			447(4.46)
IX	Ph$_3$Sn(o-2H5MBB)	Methanol	250(4.27)	320(4.23)	395(3.88)
		Benzene		330(4.20)	410(3.88)
X	Cy$_3$Sn(o-2H5MBB) [a]	Methanol	249(4.12)	325(4.28)	390(3.92)
		Benzene		325(4.24)	408(3.89)
XI	Ph$_3$Sn(o-4HNB)	Methanol	287(4.24)	326(4.02)	480(4.62)
		CCl$_4$		340	458
XII	Bu$_3$Sn(o-4HNB)	Methanol	288(3.91)	327(3.67)	490(4.35)
		CCl$_4$		334(3.88)	460(4.57)
XIII	Cy$_3$Sn(o-4HNB)	Methanol	288	325	487
		CCl$_4$		323(3.92)	465(4.53)
XIV	Ph$_3$Sn(o-2HNB)	Methanol	252(4.17)	310(4.06)	486(4.39)
		Benzene		475(4.30)	
		DMSO		485	
XV	Ph$_3$Sn(o-2ANB)	Methanol	249(3.55)	344(3.98)	454(4.15)
		Benzene		355(3.90)	472(4.14)
		Cyclohexane	276(4.31)	350(3.90)	463(4.07)
XVI	p-2M4HBB	Methanol	248(4.03)	330(4.44)	
		Benzene		338(4.39)	
XVII	Ph$_3$Sn(p-2M4HBB)	Methanol		330(4.64)	385(4.02)
		Benzene		336(4.44)	
XVIII	p-3M4HBB	Methanol	256(4.03)	355(4.39)	
		Benzene		361	
XIX	Ph$_3$Sn(p-3M4HBB)	Methanol	255(4.21)	360(4.39)	
XX	Ph$_3$Sn(p-2H5MBB)	Methanol	247(3.99)	325(4.34)	395(3.96)
		Benzene		335	

[a] Cy = cyclohexyl.

All the absorption bands have high molar extinctions and are presumably of π—π^* origin. The relatively weak n—π^* transitions which usually occur at 430—460 nm ($a_{max} \approx$ 600—1300) [1,7,9] are probably masked by the high intensity π—π^* transitions.

In non-polar solvents the first π—π^* transition of the organotin derivatives of o-carboxylic acids occurs at considerably longer wavelength than the corresponding acids, while the position remains nearly constant in the p-carboxylic acids and their tin derivatives (Table 3). The large bathochromic shift accompanying the stannylation of the o-azocarboxylic acids (Fig. 1) should thus be ascribed to coordination of the azo-N atom to tin as shown in I. A similar batho-

TABLE 3

THE FIRST π—π^* TRANSITION IN AZOCARBOXYLIC ACIDS AND THEIR ORGANOTIN DERIVATIVES IN BENZENE

Acid	λ_{max} (nm)	Organotin derivative	λ_{max} (nm)
o-2M4HBB	385	Ph$_3$Sn(o-2M4HBB)	450
		Bu$_3$Sn(o-2M4HBB)	440
o-3M4HBB	385	Ph$_3$Sn(o-3M4HBB)	449
		Bu$_3$Sn(o-3M4HBB)	450
p-2M4HBB	338	Ph$_3$Sn(p-2M4HBB)	336
p-3M4HBB	361	Ph$_3$Sn(p-3M4HBB)	362

chromic shift of the first π—π^* band has been observed in cyclopentadienyl-[o-(phenylazo)phenyl]nickel, where the N → Ni bond is believed to be present [18]. Such a bathochromic shift of the first π—π^* band due to N → Sn coordination is to be expected also from MO considerations [1,2,9].
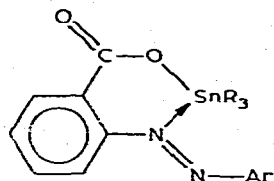
(I)

The electronic spectra of the azo compounds do not show any strong solvent dependence apart from a small redshift of both the π—π^* and n—π^* bands [1,19], but the organotin derivatives of the o-carboxyl compounds show strong solvent dependence indicating specific solvent—solute interaction. On the basis of the
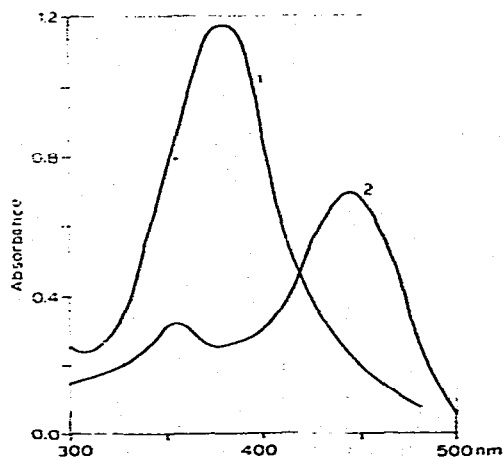

Fig. 1. Absorption spectra in benzene of (1) o-3M4HBB (2.8 × 10^{-5} M), (2) Ph$_3$Sn(o-3M4HBB) (1.45 × 10^{-5} M).

solvent effects the organotin derivatives may be classified into three types.

(i) Type I: organotin derivatives of p-(arylazo)carboxylic acids. In this case no intramolecular coordination of the azo-N atom to the tin is possible, and consequently the spectra are characterised by their similarity to those of the free ligands and the absence of significant solvent effect.

(ii) Type II: organotin derivatives of o-(arylazo)benzoic acids. As shown earlier these compounds are pentacoordinated. The absorption spectra show strong solvent dependence. The results for a typical compound, presented in Table 5, show that solvents containing donor atoms decrease the intensity of the longest wavelength band near 460 nm while increasing the intensity around 350—360 nm. Since only donor solvents induce the changes, solvent dependent azohydrazone tautomeric equilibrium 1, observed in some azo compounds [3,6,8,20,21] may be ruled out.

$$R_3SnOCOC_6H_4N=NC_6H_4OH \rightleftharpoons R_3SnOCOC_6H_4NHNC_6H_4=O \tag{1}$$

In order to determine the nature of the equilibria, a quantitative study was carried out by use of eq. 3 which applies to the 1/1 equilibrium 2 [17,23].

$$S + A \rightleftharpoons SA \tag{2}$$

$$D = E_{AS}C_A + Q\,(D_A - D)/C_S \tag{3}$$

In eq. 2 D_A is the optical density of the organotin compound (A) of concentration C_A in an inert solvent (e.g., carbon tetrachloride), D is the optical density in presence of donor solvent (S) of concentration C_S, and Q is the equilibrium quotient. The presence of an 1/1 equilibrium involving the pentacoordinated organotin derivative and the donor solvent is demonstrated by the excellent linearity of the plots of D vs. $(D_A - D)/C_S$ shown in Fig. 2 and 3. The deviation
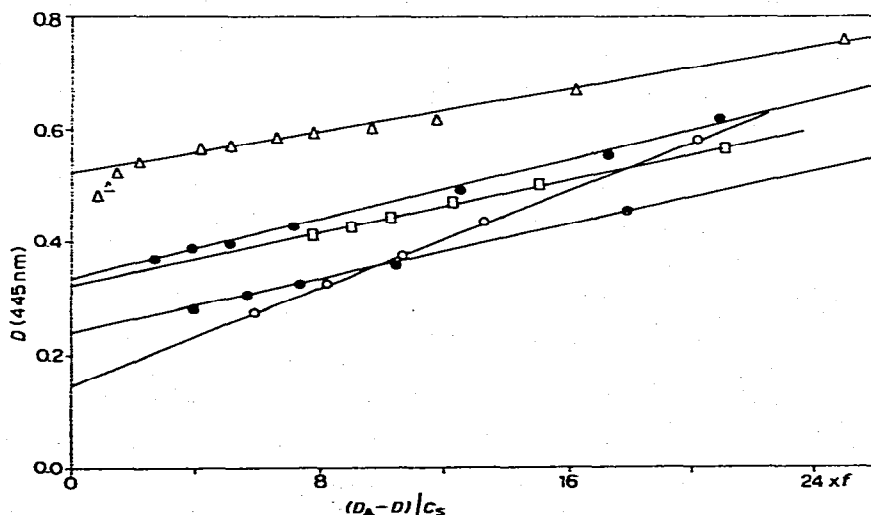

Fig. 2. Plot of D vs. $(D_A - D)/C_S$ for the equilibrium between Ph$_3$Sn(o-2M4HBB) and diethyl ether (1,-o-o-, f 0.05), acetone (2, -●-●-, f 0.05), methanol (3, -△-△-, f 0.1), pyridine (4, -□-□-, f 0.5), DMSO (5, -●-●-, f 1).
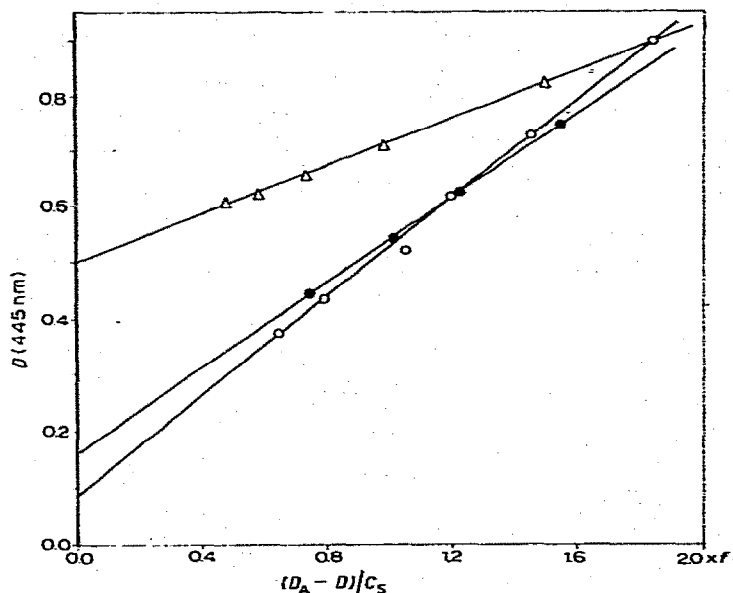
Fig. 3. Plot of D vs. $(D_A - D)/C_S$ for the equilibrium between $Pr_3Sn(o\text{-}2M4HBB)$ and diethyl ether (1, -○-○-, f 1/3), $Pr_3Sn(o\text{-}2M4HBB)$ and methanol (2, -△-△-, f 1), $Pr_3Sn(o\text{-}3M4HBB)$ and acetone (3, -●-●-, f 1/3).

TABLE 4

EQUILIBRIUM QUOTIENTS FOR TRIORGANOTIN(o-ARYLAZO)BENZOATE DONOR SYSTEMS (in l mol^{-1})

Organotin compound	Donor				
	Ether	Acetone	Methanol	Pyridine	DMSO
Ph$_3$Sn(o-2M4HBB)	2.3	4.2	10.5	37	82
Pr$_3$Sn(o-2M4HBB)	0.8	1.1	4.7	—	—
Pr$_3$Sn(o-3M4HBB)		0.9			

TABLE 5

ABSORPTION MAXIMA OF Ph$_3$Sn(o-2M4HBB) IN DIFFERENT SOLVENTS

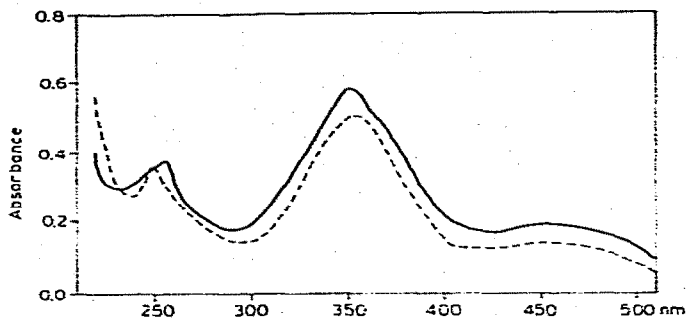| Solvent	λ_{max} (nm(log ϵ))		
Diethyl ether	252(4.15)	357(4.28)	—
Acetone		363(4.27)	—
Methanol	255(4.12)	358(4.24)	460(4.76)
Pyridine		356(4.09)	475(4.30)
DMSO		357(4.18)	490(4.04)
Carbon tetrachloride		355(3.85)	447(4.36)
Benzene			450(4.32)

Fig. 4. Absorption spectra in methanol of 1 o-3M4HBB (4.03 × 10⁻⁵ M), solid line and of 2 Ph₃Sn-(o-3M4HBB) (2.85 × 10⁻⁵ M) broken line.

from linearity at higher concentrations of the donor in some cases suggests the presence of more complicated equilibria at higher donor concentrations.

The equilibrium quotients, calculated from the plots of D vs. $(D_A - D)/C_S$, are given in Table 4. The large effect of the organotin group on the equilibrium quotient suggests direct interaction between the tin atom and the donor. Since the equilibrium quotient with a given donor is consistently higher for the tri-phenyltin compound than for the tripropyltin compound (the former having greater Lewis acid strength than the latter), it seems most likely that an S → Sn bond is formed at the expense of the rather weak N → Sn bond (eq. 4), presumably because of the steric crowding resulting from solvation.
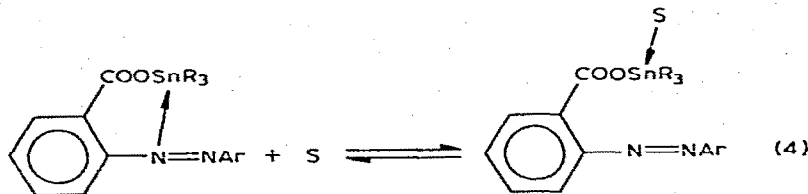

The close similarity between the absorption spectra of the organotin derivative and the free ligand in donor solvents (Fig. 4) also supports the breaking of the N → Sn coordination on solvation. Further evidence supporting the formation of a S → Sn bond, rather than the hydrogen bond formation between the donor solvent and the phenolic OH group present in the ligand, comes from a comparison of the equilibrium quotients of Pr₃Sn(o-2M4HBB) (II) and Pr₃Sn(o-3M4HBB) (III) with a given donor. For hydrogen bond formation, the equilibrium quotient for II would be expected to be considerably greater than that for III because of the presence of a methyl group *ortho* to the hydroxyl group. The situation is comparable to that in phenol and o-cresol, where the latter shows much less intermolecular hydrogen bonding than the former [24]. On the other hand, equi-librium quotients would be nearly equal if S → Sn coordinate bond formation were responsible, because both involve the tripropyltin group. In fact, the equilibrium quotients for II and III with the same donor are nearly equal (1.1 and 0.9 respectively with acetone in carbon tetrachloride).

(II)   (III)
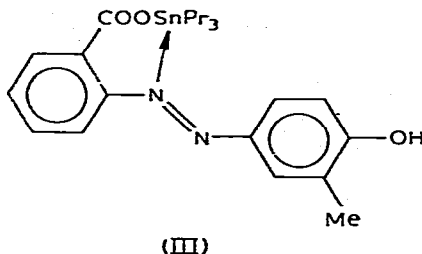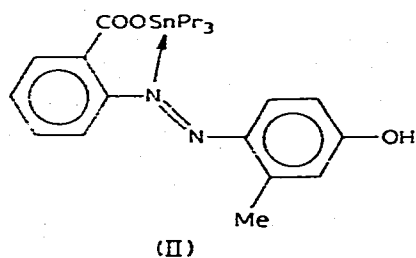
Since the equilibrium quotients between a given organotin compound and different solvents would be directly related to the S → Sn bond strength, which in turn is proportional to the donor strength or nucleophilicity of the solvent towards the tin atom, the sensitivity of the pentacoordinated azocarboxylates towards donor solvents may be used to determine the relative donor strengths. On the basis of the present results the donor strength towards the organotin group increases in the sequence: diethyl ether < acetone < methanol < pyridine < DMSO.

In o-4HNB derivatives the first π—π^* transition is shifted to longer wavelength in the order: carbon tetrachloride $\approx$ benzene < MeOH < DMSO (Table 6). Though this trend is consistent with the formation of a hydrogen bond, the absence of any isobestic point in the absorption curves in different solvents indicates a more complex equilibrium. This is not surprising since azohydrozone tautomerism is well known in the naphthyl series [3,6,8,20]. Thus o-4HNB derivatives are likely to exist as tautomers:

(Azo form)   (Hydrozone form)
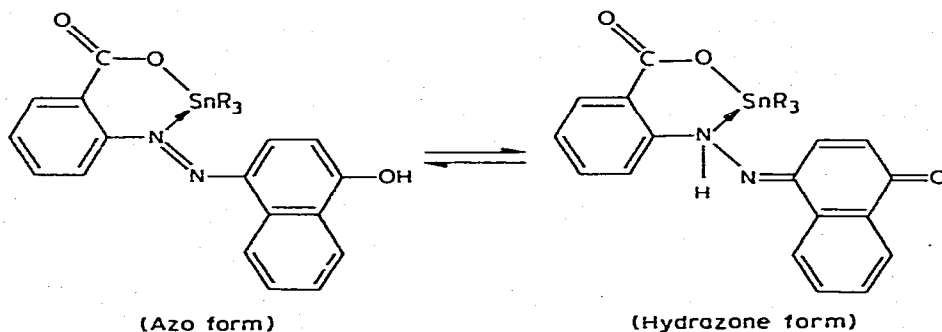
(iii) Type III: organotin derivatives of o-(arylazo)benzoic acids with a donor group at o'-position. These are characterized by the near absence of solvent effect on the absorption spectra (Table 7). This is consistent with the hexacoordinated structure IV proposed on the basis of spectrophotometric titration and IR data.

TABLE 6

ABSORPTION MAXIMA OF Ph₃Sn(o-4HNB) IN DIFFERENT SOLVENTS (λ_{max} (nm))

MeOH	DMSO	CCl₄	C₆H₆
287, 326, 480	504	340, 458	335, 460

TABLE 7

ABSORPTION MAXIMA OF Ph$_3$Sn(o-2H5MBB) IN DIFFERENT SOLVENTS (λ_{max}(nm)(log ϵ))

Et$_2$O	MeOH	DMSO	CCl$_4$	C$_6$H$_6$
252(4.13)	250(4.27)			
325(4.26)	325(4.23)	325	326	327(4.21)
400(3.86)	390(3.88)	389	409	400(3.87)

The increased stability expected for complexes of terdentate ligands compared to those of bidentate ligands (I) [3,22] greatly reduces the possibility of cleavage

X = —OH , NH$_2$

(IV)
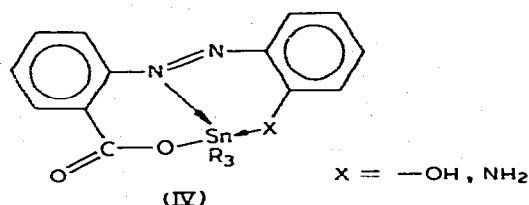
of N → Sn and X → Sn bonds by solvation. As a result, this class of compounds does not show any significant solvent effect. The small hypsochromic shift in ether, methanol, DMSO etc., may be due to solvation at the tin atom, which would raise the π^* orbital by decreasing the N → Sn bond polarity.

Experimental

All solvents were of Uvasol (E. Merck) grade. The optical densities were measured with a Beckman DU-2 spectrophotometer.

For equilibrium quotients a stock solution of the organotin compound (~10^{-4} M) was prepared in carbon tetrachloride. To a given amount of the stock solution varying amounts of the donor were added keeping the total volume constant. Optical densities were measured at 445 nm. Concentration ranges of the donors used were: diethyl ether, 0—3.8 M; acetone, 0—4 M; methanol, 0—1.3 M; pyridine, 0—0.07 M; and DMSO, 0—0.2 M.

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