

## ORGANOTIN COMPOUNDS

### I. THE ELECTRIC DIPOLE MOMENTS OF SOME TRIMETHYLPHENYLTIN DERIVATIVES

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Although  $d_{\pi}$ - $p_{\pi}$  bonding in certain organosilicon compounds is now fairly well established<sup>1</sup>, there has been little evidence for a corresponding effect in organotin compounds. Theoretical calculations<sup>2</sup> have shown that the amount of overlap in  $d_{\pi}$ - $p_{\pi}$  bonding is not critically dependent on the size of the  $d$ -orbitals involved. Thus in spite of its larger size, as compared with silicon, it seems probable that under favourable conditions, the  $d$ -orbitals of tin may engage in bonding with the  $p$ -orbitals of carbon, to perhaps the same degree as in organosilicon compounds. We have now measured the electric dipole moments of a number of organotin compounds in which  $d_{\pi}$ - $p_{\pi}$  bonding might be expected to occur, to see whether there is any dielectric evidence to support such a view. A preliminary account of our results has already been published elsewhere<sup>3</sup>.

#### EXPERIMENTAL

##### *Preparation and purification of materials*

Benzene of "crystallisable" grade was frozen twice, rejecting the unfrozen liquid each time and then boiled under reflux over  $P_2O_5$  and finally distilled.

*Trimethylphenyltin*. This was prepared from phenylmagnesium bromide and trimethyltin bromide (*cf.* ref. 4), b.p.  $205-6^{\circ}/760$  mm,  $d_{25}^{25}$  1.333,  $n_D^{25}$  1.5325. (Found: C, 44.81; H, 5.98.  $C_9H_{14}Sn$  calcd.: C, 44.87; H, 5.85%.)

*Trimethylbenzyltin*. Similarly, trimethylbenzyltin was prepared from benzyl chloride, magnesium and trimethyltin bromide, b.p.  $90-2^{\circ}/9$  mm,  $d_{25}^{25}$  1.300;  $n_D^{25}$  1.5426 (Found: C, 47.44; H, 6.57.  $C_{10}H_{16}Sn$  calcd.: C, 47.11; H, 6.32%.)

*(p-Chlorophenyl)trimethyltin*. The Grignard process employing *p*-bromochlorobenzene, magnesium and trimethyltin bromide in ether gave *(p*-chlorophenyl)trimethyltin<sup>4</sup>, b.p.  $82-5^{\circ}/ca. 2$  mm (lit.<sup>4</sup> b.p.  $80^{\circ}/2.3$  mm),  $n_D^{25}$  1.5487. (Found: C, 39.21; H, 4.84.  $C_9H_{13}ClSn$  calcd.: C, 39.23; H, 4.76%.)

*(p-Fluorophenyl)trimethyltin*. Prepared from trimethyltin bromide (61 g) and the Grignard reagent from *p*-fluorobromobenzene (44 g), magnesium (6 g) and ether, the product (40 g) had b.p.  $88^{\circ}/10$  mm,  $n_D^{25}$  1.5176. (Found: C, 42.07; H, 5.08; F, 6.44.  $C_9H_{13}FSn$  calcd.: C, 41.75; H, 5.06; F, 7.34%.)

*(p-Bromophenyl)trimethyltin*. The Grignard reagent from *p*-dibromobenzene and magnesium in ether on reacting with trimethyltin bromide gave the required com-

pound, b.p. 89–90°/1 mm (lit.<sup>5</sup> b.p. 124°/15 mm),  $d_{25}^{25}$  1.634,  $n_D^{25}$  1.5682. (Found: C, 33.86; H, 4.18.  $C_9H_{13}BrSn$  calcd.: C, 33.79; H, 4.06%.)

*(p-N,N-Dimethylaminophenyl)trimethyltin*

Four g (0.56 g-atom) of lithium (small pieces) were allowed to fall into anhydrous ether in a three-necked flask fitted with a dropping funnel, a reflux condenser and a mercury sealed stirrer. About 3 g of *p*-bromodimethylaniline in ether was added with vigorous stirring and the mixture was heated for about ten minutes to start the reaction. The remainder of a total of 52 g (0.26 mole) of *p*-bromodimethylaniline dissolved in ether was added at such a rate as to maintain gentle reflux. After addition was completed, the mixture was refluxed for about half an hour. Trimethyltin bromide (63 g, 0.26 mole), in ether was then added at a rate sufficient to keep the ether refluxing gently. After all the trimethyltin bromide had been added, the reaction mixture was refluxed for about three hours. The excess lithium was filtered off and the filtrate hydrolysed with ammonium chloride. The ethereal layer was separated, washed and dried ( $Na_2SO_4$ ) and the ether removed. The residue was fractionated to yield about 25 g of (*p*-*N,N*-dimethylaminophenyl)trimethyltin, b.p. 102–104°/6 mm, m.p. 40–41°. (Found: C, 46.37; H, 6.85; N, 4.81.  $C_{11}H_{19}NSn$  calcd.: C, 46.52; H, 6.74; N, 4.93%.)

*(p-Methoxyphenyl)trimethyltin*. This was prepared from *p*-bromoanisole, lithium and trimethyltin chloride as described by Buchman *et al.*<sup>6</sup>, b.p. 100–2°/10–12 mm (lit.<sup>6</sup> b.p. 125–7°/15 mm),  $n_D^{25}$  1.5414. (Found: C, 44.45; H, 6.16.  $C_{10}H_{16}OSn$  calcd.: C, 44.32; H, 5.91%.)

*p-Tolyltrimethyltin*. When prepared from *p*-bromotoluene, lithium and trimethyltin chloride<sup>6</sup>, the product had b.p. 100°/6 mm,  $n_D^{20}$  1.5330 (lit.<sup>6</sup> b.p. 64–7°/0.6 mm,  $n_D^{20}$  1.5330).

*(p-Chlorophenyl)triphenyltin*. This compound was prepared according to the method of Zasosov and Kocheshkov<sup>7</sup> from *p*- $ClC_6H_4MgBr$  and triphenyltin chloride in ether, m.p. 139–139.5° (lit.<sup>7</sup> m.p. 141°). (Found: C, 62.88; H, 4.20.  $C_{24}H_{19}ClSn$  calcd.: C, 62.43; H, 4.15%.)

*Physical measurements*

Electric dipole moments were determined by measuring the dielectric constants and densities of benzene solutions at 25°. A heterodyne beat capacitance apparatus was used, fabricated essentially from a design due to Dr. E. P. A. Sullivan. This consisted of a Franklin type variable frequency oscillator incorporating a variable precision condenser and dielectric cell, which could be "tuned" to a crystal-controlled Pierce-Miller oscillator radiating at a frequency of 2.6125 mc/s. Detection of beat notes was achieved aurally by an Eddystone communications receiver set at this frequency.

Dielectric constants of the solutions then were determined by tuning for "zero-beat" with the variable precision condenser, assuming the value 2.2727 for the dielectric constant of benzene at 25°. Density measurements were made with a Sprengel type pycnometer which was calibrated with air-free distilled water. Refractive indices for  $N_D$  light and densities of some liquids were measured and the molar refraction  $R_D$  calculated therefrom. In the other cases,  $R_D$  was calculated from bond refraction data. No allowance was made for atom polarisation when the measured moment exceeded 1 D; for smaller moments, the distortion polarisation was taken to be 1.05  $R_D$ .

The computation of moments follow the pattern of Le Fevre and Vine<sup>8</sup>. Within experimental errors, plots of dielectric constants *versus* weight fraction were found to be linear from the slopes of which  $\alpha$ 's were calculated. The results are given in Table I.

TABLE I

PHYSICAL CONSTANTS OF TRIMETHYLPHENYLTIN DERIVATIVES

$10^4 w_2$	$\epsilon_{12}$	$d_{12}$
<i>Trimethylphenyltin</i>		
866	2.2744	0.87630
2709	2.2781	0.88163
4346	2.2819	0.88708
4446	2.2822	0.88706
4962	2.2833	0.88870
$\alpha\epsilon_1 = 0.22$	$\beta d_1 = 0.30$	
$TP = 63.7$ c.c.	$1.05 R_D = 58.4$ c.c.	$\mu = 0.51$ D
<i>Trimethylbenzyltin</i>		
1136	2.2767	0.87673
1705	2.2798	0.87837
3181	2.2861	0.88263
3538	2.2901	0.88377
4534	2.2941	0.88663
5341	2.2976	0.88899
$\alpha\epsilon_1 = 0.48$	$\beta d_1 = 0.28$	
$TP = 81.9$ c.c.	$1.05 R_D = 64.9$ c.c.	$\mu = 0.91$ D
<i>(p-Chlorophenyl)trimethyltin</i>		
735	2.2871	0.87602
1326	2.2976	0.87836
1895	2.3090	0.88006
2504	2.3201	0.88224
3230	2.3335	0.88506
3879	2.3466	0.88704
$\alpha\epsilon_1 = 1.91$	$\beta d_1 = 0.34$	
$TP = 156.0$ c.c.	$R_D = 60.8$ c.c.	$\mu = 2.16$ D
<i>(p-Bromophenyl)trimethyltin</i>		
743	2.2852	0.87665
1468	2.2976	0.87950
2171	2.3082	0.88245
2263	2.3101	0.88287
2964	2.3224	0.88579
4275	2.3254	0.89110
$\alpha\epsilon_1 = 1.67$	$\beta d_1 = 0.41$	
$TP = 58.3$ c.c.	$R_D = 64$ c.c.; (63.8 c.c. calcd.)	$\mu = 2.15$ D
<i>(p-N,N-Di(methylaminophenyl)trimethyltin</i>		
663	2.2813	0.87547
1272	2.2891	0.87717
1724	2.2952	0.87849
2816	2.3108	0.88159
4248	2.3297	0.88573
$\alpha\epsilon_1 = 1.33$	$\beta d_1 = 0.28$	
$TP = 137.2$ c.c.	$R_D = 69.0$ c.c. (calcd.)	$\mu = 1.83$ D

(continued on p. 507)

TABLE 1 (*continued*)

$10^5 w_2$	$\epsilon_{12}$	$d_{12}$
<i>(p-Methoxyphenyl)trimethyltin</i>		
696	2.2793	0.87580
1695	2.2874	0.87891
2901	2.2989	0.88273
3474	2.3040	0.88449
4436	2.3123	0.88755
$\alpha\epsilon_1 = 0.90$	$\beta d_1 = 0.31$	
$TP = 105.9$ c.c.	$R_D = 62.1$ c.c. (calcd.)	$\mu = 1.46$ D
<i>p-Tolyltrimethyltin</i>		
896	2.2744	0.87633
1634	2.2757	0.87833
2232	2.2768	0.88001
2820	2.2778	0.88166
4189		0.88557
$\alpha\epsilon_1 = 0.19$	$\beta d_1 = 0.28$	
$TP = 68.3$ c.c.	$1.05 R_D = 63.5$ c.c.	$\mu = 0.48$ D
<i>(p-Chlorophenyl)triphenyltin</i>		
506	2.2777	0.87552
1121	2.2849	0.87775
2030	2.2953	0.88082
2720	2.3095	0.88332
$\alpha\epsilon_1 = 1.13$	$\beta d_1 = 0.35$	
$TP = 192.6$ c.c.	$R_D = 119.2$ c.c. (calcd.)	$\mu = 1.89$ D
<i>(p-Fluorophenyl)trimethyltin</i>		
1009	2.2981	0.87698
1764	2.3031	0.87952
2381	2.3144	0.88155
3508	2.3339	0.88532
3690	2.3374	0.88590
$\alpha\epsilon_1 = 1.75$	$\beta d_1 = 0.37$	
$TP = 136.3$ c.c.	$R_D = 55.7$ c.c.	$\mu = 1.98$ D

## DISCUSSION

The theories of interaction between a substituent group and the aryl radical to which it is attached have been reviewed by Everard and Sutton<sup>9</sup>. Two distinct effects have been recognised: (a) the inductive (*I*) effect, caused by the polarisation of the radical by the electric field of the substituent, which may itself be visualised as resulting from (i) the "classical" electrostatic process affecting both  $\sigma$  and  $\pi$  electrons, and (ii) the "non-classical" component in which the field of the substituent causes changes of  $\pi$  bond order; and (b) the mesomeric (*M*) effect due to the formation of a  $\pi$  bond between the substituent and the carbon atom to which it is attached, and thus modifying the bond characteristics of the rest of the molecule.

In the light of these theories, the approach we have adopted in the interpretation of our results is to estimate the contribution of the classical inductive effect for the organotin compounds concerned (with analogous organosilicon compounds<sup>10,11</sup> included for comparison wherever possible). A correction for the maximum induced

moment to be expected from the mutual classical electrostatic effects of the primary moments is applied to the moments of these compounds, calculated by adding vectorially the separate moments of the appropriate monosubstituted benzene molecules, on the assumption that no interaction of any sort exists between the polar groups. This gives  $\mu$  (calculated). Any residual interaction moment, defined as  $\mu$  (observed) —  $\mu$  (calculated), can then be attributed to the operation of either the non-classical inductive effect or an enhanced mesomeric effect, the latter of which must be closely associated with any  $d_\pi$ — $p_\pi$  bonding between the group IVB element and aromatic carbon. This separation of the two residual effects seems both possible and reasonable because all the substituents *para* to the Sn or Si group (except methyl) exert  $-I$  and  $\div M$  effects, *i.e.* the non-classical inductive effect which acts in the same sense as the classical one, is opposed to the mesomeric effect.

According to the electrostatic theory of the classical inductive effect as developed by Smallwood and Herzfeld<sup>12</sup> and by Frank<sup>13</sup>, the components of the induced moment  $\mu_x$  and  $\mu_y$ , respectively parallel and at right angles to the inducing moment  $\mu$ , are given by:

$$\mu_x = \mu \alpha \frac{\epsilon_a + 2}{3\epsilon_b r^3} (3 \cos^2 \Theta - 1) \quad (1)$$

$$\mu_y = \mu \alpha \frac{\epsilon_a + 2}{3\epsilon_b r^3} 3 \sin \Theta \cos \Theta \quad (2)$$

where  $\alpha$  is the polarisability of the polarisable system,  $\epsilon_a$  and  $\epsilon_b$  are the dielectric constants of the polarisable system and of the medium between this and the primary dipole respectively,  $r$  is the distance between the dipole and the polarisable centre, and  $\Theta$  is the angle between  $\mu$  and  $r$ . There is some uncertainty as to the correct values of  $\epsilon_a$  and  $\epsilon_b$ , but these can surely be taken without much error as 2.27, the dielectric constant of benzene.

Brown<sup>14</sup> has pointed out that the total dipole moment of a monosubstituted benzene compound may be regarded as the resultant of three components, namely (a) the group moment, (b) the moment induced in the phenyl ring by the substituent (the induced moment), and (c) the mesomeric moment. Thus, the moment induced in the  $(\text{CH}_3)_2\text{Sn}$  or  $(\text{CH}_3)_2\text{Si}$  group by the dipole of the *para* substituent can be calculated by vector summation of the moments induced by each of these three components. To do this it is necessary to know the mesomeric moments of the appropriate substituted benzene compounds together with the magnitudes and angles of the dipole moments of these compounds and of the corresponding substituted alkanes. Table 3 gives a summary of the required information with data for halogens taken from the work of Groves and Sugden<sup>15</sup> and for electron-releasing groups  $[\text{CH}_3, \text{CH}_3\text{O}$  and  $(\text{CH}_3)_2\text{N}]$  taken from similar tables set up by Katritzky, Randall and Sutton<sup>16</sup>. The mesomeric moment of an aromatic compound was originally defined by Sutton<sup>17</sup> as the vector difference between its dipole moment and that of its aliphatic analogue. It provides a measure of the interaction between the  $\pi$ -electron system of the aromatic ring and its substituent. Rather more accurate estimates of the mesomeric moments of some common aromatic compounds have been obtained by Groves and Sugden<sup>15</sup> by evaluating bond moments for polar groups from dielectric data for aliphatic compounds, after allowing for polarisability effects in non-polar parts of a

TABLE 2

DIPOLE MOMENTS OF DERIVATIVES OF TRIMETHYLPHENYLTIN AND TRIMETHYLPHENYLSILANE

 $\Delta\mu = \mu_{\text{obs}} - \mu_{\text{calcd}}$ . Errors  $< \pm 0.03$  D. Atomic polarisation neglected for moment  $> 1$  D, taken as 5% of molar refraction if  $< 1$  D.

X	$\mu_{\text{obs}}$ (D)	$\mu_{\text{calcd}}$ (D)	$\Delta\mu$ (D)
<i>p</i> -XC <sub>6</sub> H <sub>4</sub> Sn(CH <sub>3</sub> ) <sub>3</sub>			
H	0.51		
N(CH <sub>3</sub> ) <sub>2</sub>	1.83	1.54	+0.29
OCH <sub>3</sub>	1.46	1.31	+0.15
CH <sub>3</sub>	0.48	0.03	+0.45
Cl	2.16	2.01	+0.15
Br	2.15	2.01	+0.14
F	1.98	1.87	+0.11
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Sn(CH <sub>3</sub> ) <sub>3</sub>			
	0.91		
<i>p</i> -XC <sub>6</sub> H <sub>4</sub> Si(CH <sub>3</sub> ) <sub>3</sub>			
H	0.44		
N(CH <sub>3</sub> ) <sub>2</sub>	1.84	1.58	+0.26
OCH <sub>3</sub>			
CH <sub>3</sub>	0.46	0.03	+0.43
Cl	1.70	1.93	-0.23
Br	1.79	1.91	-0.12
F	1.69	1.79	-0.10
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Si(CH <sub>3</sub> ) <sub>3</sub>			
	0.71		

molecule. When these bond moments are used to compute the moments of aromatic compounds, additional moments are revealed which are identified as mesomeric moments. The gross and the mesomeric moment angles in Table 3 are defined such that if the moment acts along the X-C bond (where X is the substituent group), and X is at the positive end of the dipole, then it has angle 0°.



For axially symmetrical substituents, the group plus induced moment (taken as the difference between the mesomeric moment and the observed moment of the monosubstituted benzene compound) is considered as a single dipole acting at a distance  $r$  (equal to 5.74 or 5.51 Å), taken from the centre of the tin or silicon atom respectively to the points of contact between the halogen atoms or CH<sub>3</sub> group and the aromatic carbon. In the case of axially unsymmetrical substituents, the group plus induced moment is assumed to be equal to the moment of the corresponding substituted alkane, the distance  $r$  being taken from the centre of the tin or silicon atom to the centre of the nitrogen or oxygen atom.

The mesomeric moment is assumed to act at the centre of the phenyl ring so that the distances to the (CH<sub>3</sub>)<sub>3</sub>Sn and (CH<sub>3</sub>)<sub>3</sub>Si groups are 3.57 and 3.34 Å respectively. The internuclear distances or covalent radii used have been C-C (aromatic), 1.40; C-N, 1.45; Sn, 1.40; Si, 1.17; O, 0.74; C, 0.77 Å. The polarisabilities of the groups have been evaluated from bond refractivities and using the formula  $\alpha_X = 3[R]_X/(4\pi N)$

TABLE 3

GROSS AND MESOMERIC MOMENTS AND ANGLES

Substances	Moment magnitudes		Moment angles		Mesomeric moment	Angle of mesomeric moment in substituted benzene
	Subst. benzene	Subst. alkane	Subst. benzene	Subst. alkane		
Me	0.35	0	0°		0.35	0°
Cl	1.60		0	0°	0.97	0
Br	1.51 <sup>a</sup>		0	0	0.89	0
F	1.48 <sup>a</sup>		0	0	1.00	0
(CH <sub>3</sub> ) <sub>2</sub> N	1.61	0.86	30	109	1.66	0
CH <sub>3</sub> O	1.28	1.28	80	124	0.96	12

<sup>a</sup> The moments of bromo and fluorobenzene have been selected from ref. 31.

where  $\alpha_X$  is the polarisability of the group X with molar refraction  $[R]_X$ . Hence calculation gives  $\alpha[(CH_3)_3Sn] = 115.5 \times 10^{-25}$ ,  $\alpha[(CH_3)_3Si] = 91.7 \times 10^{-25}$  c.c. Application of eqns. (1) and (2) then allows a correction to be made for the classical inductive effect.

The calculations involving the angular substituents require further comment. The arguments are illustrated by considering *p*-(CH<sub>3</sub>)<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>Sn(CH<sub>3</sub>)<sub>3</sub> as an example. Marsden and Sutton<sup>18</sup> have calculated the angle of inclination ( $\theta$ ) of the dipole axis to the C<sub>ar</sub>-N bond in dimethylaniline from the relationship:

$$\mu^2[(CH_3)_2NC_6H_4CH_3] = \mu^2[(CH_3)_2NC_6H_5] + \mu^2[C_6H_5CH_3] - 2\mu[(CH_3)_2C_6H_5]\mu[C_6H_5CH_3] \cos \theta \quad (3)$$

and the latest value for  $\theta$  which Sutton and his co-workers<sup>13</sup> have obtained from the moments of dimethylaniline, dimethyl-*p*-toluidine and toluene, is 30°. To calculate the mesomeric moment of dimethylaniline, triethylamine is used as the aliphatic standard for comparison in which the 3 C-N bonds are assumed to be mutually inclined at the tetrahedral angle. For this group therefore,  $\mu$ (aliphatic) is 0.86 D with its axis at 109° to the C-N bond; to make this compatible with the value of  $\mu$ (aromatic) of 1.61 D inclined at 30° to the N-C<sub>ar</sub> bond, it is necessary to assume a mesomeric moment along the N-C<sub>ar</sub> bond of 1.66 D. The moments induced in the (CH<sub>3</sub>)<sub>3</sub>Sn group by  $\mu$ (aliphatic) and  $\mu$ (mesomeric) as a result of the classical electrostatic polarisation are then estimated by applying eqns. (1) and (2). The moment induced in the (CH<sub>3</sub>)<sub>2</sub>N group by the Sn group acting as a single dipole may likewise be computed\*. These are then compounded vectorially with the moments of dimethylaniline and trimethylphenyltin to give a (corrected) calculated moment for *p*-(CH<sub>3</sub>)<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>Sn(CH<sub>3</sub>)<sub>3</sub> by means of an equation analogous to (3):

$$\mu^2[(CH_3)_2NC_6H_4Sn(CH_3)_3] = \mu^2[(CH_3)_2NC_6H_5] + \mu^2[C_6H_5Sn(CH_3)_3] - 2\mu[(CH_3)_2NC_6H_5]\mu[C_6H_5Sn(CH_3)_3] \cos 30^\circ \quad (4)$$

Since the observed moment of *p*-(CH<sub>3</sub>)<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>Sn(CH<sub>3</sub>)<sub>3</sub> is 1.83 D, compared

\* In general, the moments induced by the Sn or Si group, acting as single dipoles, in the para substituents are negligible, being less than 0.02 D.

with the calculated value of 1.54 D, it is interesting to determine the moment ( $x$ ) along the N-C...C-Sn axis which will produce the observed value of 1.83 D when combined with the moment of dimethylaniline. This is easily obtained from the equation:

$$\mu^2[(\text{CH}_3)_2\text{NC}_6\text{H}_4\text{Sn}(\text{CH}_3)_3] = \mu^2[(\text{CH}_3)_2\text{NC}_6\text{H}_5] + x^2 + 2x\mu[(\text{CH}_3)_2\text{NC}_6\text{H}_5] \cos 30^\circ \quad (5)$$

Solution of the quadratic equation gives  $x = 0.28$  or  $-3.02$  D. The negative value does not seem reasonable as it implies a large moment vector pointed towards the dimethylamino group with its positive end near the Sn atom. It seems more probable from the known chemical properties of the dimethylamino group that there is a donation of electrons from the group towards the benzene ring. It follows therefore that there is an effective moment along the N-C...C-Sn axis of  $0.51 + 0.28 = 0.79$  D, opposing the moment of the Sn group (0.51 D) which is electron-releasing with respect to the benzene ring, as shown clearly by the moments of the halogen-substituted compounds. The calculations for the methoxy group may likewise be carried out from the data given in Table 3. The results for this group reported in Table 2 are based partly on a mesomeric moment angle of  $12^\circ$ . This is an approximation implicit in the treatment of the data for 4-substituted pyridines and pyridine 1-oxides by Katritzky, Randall and Sutton<sup>16</sup>. (An exact treatment would result in a mesomeric moment angle equal to zero for anisole.) It may be more satisfactory therefore to compute the moment of  $p\text{-CH}_3\text{OC}_6\text{H}_4\text{Sn}(\text{CH}_3)_3$  from the earlier data of Marsden and Sutton<sup>18</sup> with the mesomeric moment angle taken as zero:  $\mu(\text{CH}_3)_2\text{O} = 1.32$ , aliphatic moment angle =  $124^\circ$ ,  $\mu(\text{C}_6\text{H}_5\text{OCH}_3) = 1.23$  and  $\mu(p\text{-CH}_3\text{C}_6\text{H}_4\text{OCH}_3) = 1.20$  whence  $\Theta$ , the angle of inclination of the dipole axis to the C<sub>ar</sub>-O bond in anisole, equals  $76^\circ$ . Thus, the calculated moment of  $p\text{-CH}_2\text{OC}_6\text{H}_4\text{Sn}(\text{CH}_3)_3$  is now 1.18 D after allowing for classical polarisability effects. Hence  $\Delta\mu$ , the interaction moment, is  $+0.28$  D.

The methyl group in toluene is probably associated with a mixture of  $+M$  and  $+I$  effects arising from hyperconjugation and the difference in electronegativity between  $sp^2$  and  $sp^3$  hybridised carbon atoms\*. Because the moments of toluene and trimethylphenyltin are small, the correction for the classical electrostatic induction is small if the moment of toluene is ascribed to hyperconjugation, and negligible if it is regarded as a purely inductive effect. For the purpose of this discussion therefore, it is immaterial how the moment of toluene is interpreted. We have performed calculations on the basis of a mesomeric moment of 0.35 (see Table 3) as this leads to the greater correction\*\*. According to convention, a  $-I$  (inductive) or  $-M$  (mesomeric) effect associated with a substituent implies a moment vector pointing away from the benzene ring while a  $+I$  or  $+M$  effect has the moment vector pointed towards the ring. In other words, the minus sign indicates a drift of electrons from the ring towards the substituent and the plus sign the reverse. Given the direction of these effects, the resultant molecular moments, and the signs of the interaction moments, it becomes possible to examine the extent to which the results may be interpreted on the basis of  $d_\pi\text{-}p_\pi$  bonding.

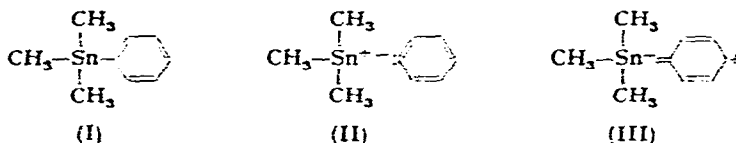
\* NMR evidence<sup>19</sup> suggests that the polar structures corresponding to hyperconjugation are unimportant.

\*\* The mesomeric moment effect as calculated here, is essentially a classical electrostatic effect and should be distinguished from the mesomeric effect of the substituent which causes a flow of electronic charge into the  $d$  orbitals of the tin or silicon atom.



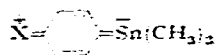
Tin, like silicon and other Group IVB elements, has vacant  $d$ -orbitals in its valence shell available for dative bonding with suitable electron donors. It is clear from the moments of the halogen-substituted compounds that the  $(\text{CH}_3)_3\text{Sn}$  group is electron-releasing with respect to the ring. Furthermore, our results indicate that dative  $\pi$ -bonding occurs, by donation of electrons from a molecular orbital of the aromatic system into a vacant  $5d$ -orbital of tin, when strongly electron-releasing substituents are attached *para* to the  $(\text{CH}_3)_3\text{Sn}$  group and probably even in trimethylphenyltin itself.

The following resonance structures may be postulated for trimethylphenyltin:



Structure (II) reflects the difference in electronegativity between carbon and tin. Just as the moment of  $(\text{CH}_3)_3\text{SnCl}^{20}$  (3.50 D) is greater than that of  $(\text{CH}_3)_3\text{CCl}^{21}$  (2.13 D), presumably because tin is more electropositive than carbon, we should expect the moment of trimethylphenyltin to be greater than that of tert-butylbenzene, but the moments of these two compounds are about the same, 0.51 and 0.53 D respectively<sup>22</sup> suggesting that  $\pi$ -bonding effects may be present in the former compound. Further support for the existence of some double bond character in the  $\text{Sn}-\text{C}_{ar}$  bond is provided by the group moment of  $(\text{CH}_3)_3\text{Sn}$  in trimethylbenzyltin (0.69 D), in which conjugation between the  $(\text{CH}_3)_3\text{Sn}$  group and the aromatic ring is eliminated, as compared with the somewhat smaller value in trimethylphenyltin itself (0.51 D).

If our approach is valid, the interaction moments of  $p\text{-XC}_6\text{H}_4\text{Sn}(\text{CH}_3)_3$  [ $\text{X} = (\text{CH}_3)_3\text{N}, \text{CH}_3\text{O}, \text{CH}_3$ ] would imply the existence of a drift of electrons towards the  $(\text{CH}_3)_3\text{Sn}$  group which cannot be accounted for in terms of classical electrostatic inductive effects. However, rationalization of these results is possible if one assumes that  $d_\pi-p_\pi$  bonding occurs between aromatic carbon and tin, as well as silicon. It seems probable therefore that structures such as



make significant contributions to the ground state of the tin molecule, as in the case of the silicon compounds.

When the substituent is a halogen atom, the direction and magnitude of the interaction moment indicate a net shift of electrons from the  $(\text{CH}_3)_3\text{Sn}$  group towards the halogen atom, over and above that implied by the moment of  $\text{C}_6\text{H}_5\text{Sn}(\text{CH}_3)_3$ . The negative inductive effect of the halogen atom thus outweighs the positive mesomeric, i.e.  $d_\pi-p_\pi$  bonding is not indicated in the halogen substituted tin compounds. In direct contrast to the tin compounds, however, appreciable interaction moments in the opposite sense have been found for the halogen-substituted silicon compounds, in which back-donation is thus presumably of relatively greater importance. This

contrasting and somewhat anomalous behaviour of the halogen atoms in the two series may be attributed to their dual ability of attracting electrons or releasing them according to circumstances, an effect which has been observed particularly clearly in the pyridine N-oxide system<sup>23</sup>. In the present work, since the controlling factors are the tin and silicon groups, it may be inferred that silicon in the  $(\text{CH}_3)_3\text{Si}$  group is more effective in delocalizing aromatic  $\pi$ -electrons than tin, *i.e.* the amount of  $d_\pi-p_\pi$  bonding between the elements silicon and tin on the one hand and the aromatic system on the other, is not quite the same in the halogen substituted compounds.

In this connection, it is interesting to note that according to recent electron spin resonance spectra of phenyltrimethylsilane and -germane radical anions, silicon in the  $(\text{CH}_3)_3\text{Si}$  group is more efficient than germanium in delocalizing aromatic  $\pi$  electrons<sup>24</sup>. Furthermore, studies on hydrogen bond formation of the compounds  $(\text{C}_6\text{H}_5)_3\text{MOH}$  (where  $\text{M} = \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$ ) with ether and phenol, suggest that  $\pi$ -bonding from oxygen to  $\text{M}$  decreases markedly in the order  $\text{Si} > \text{Ge} > \text{Sn}, \text{Pb}$ , being negligible for  $\text{Sn}$  and  $\text{Pb}$ . Since there is considerable disagreement concerning the exact sequence of electronegativity values of Group IVB elements in the quadri-positive state<sup>25-29</sup>, our dielectric results on the balance, may be cited as additional evidence in favour of the usually accepted sequence  $\text{Si} > \text{Sn}$ . This is in contrast to the proposal of Allred and Rochow<sup>26</sup> that  $(\text{M} =) \text{Pb} > \text{Ge} > \text{Sn} > \text{Si}$ , based on an analysis of measurements on proton shifts in  $(\text{CH}_3)_4\text{M}$ .

The moment of  $p\text{-ClC}_6\text{H}_4\text{Sn}(\text{C}_6\text{H}_5)_3$  was measured to discover the effect on  $(d_\pi-p_\pi)$  bonding when the methyl groups attached to  $\text{Sn}$  are replaced by phenyl groups. The replacement of methyl by phenyl groups introduces two opposing electronic effects which would influence the moment of the compound. The phenyl group, being more electronegative than methyl, should cause a decrease in moment ( $-I$  effect). On the other hand, electron release from the phenyl group into the  $d$ -orbitals of tin resulting in  $d_\pi-p_\pi$  bond formation should enhance the moment ( $+M$  effect). The moment of  $p\text{-ClC}_6\text{H}_4\text{Sn}(\text{C}_6\text{H}_5)_3$  was found to be 1.89 D which is somewhat lower than that of  $p\text{-ClC}_6\text{H}_4\text{Sn}(\text{CH}_3)_3$  (2.16 D), suggesting that the influence of the  $-I$  slightly outweighs the  $+M$  effect. This is in accord with similar conclusions drawn by Chatt and Williams<sup>30</sup> from the dissociation constants of  $p\text{-HOOC C}_6\text{H}_4\text{Sn}(\text{CH}_3)_3$  and  $p\text{-HOOC C}_6\text{H}_4\text{Si}(\text{C}_6\text{H}_5)_3$ .

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#### SUMMARY

The electric dipole moments of nine aryltin compounds containing the  $\text{SnR}_3$  group ( $\text{R} = \text{CH}_3$  or  $\text{C}_6\text{H}_5$ ) have been measured. The results are shown to be in accord with the view that  $d_\pi-p_\pi$  bonding occurs between  $\text{Sn}$  and aromatic carbon when strongly electron-releasing substituents are attached *para* to the  $\text{Sn}(\text{CH}_3)_3$  group.

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