1 A. A. Prokhorova und Ya. M. Paushkin, *Dokl. Akad. Nauk SSSR*, 135 (1960) 84.
2 R. Riemschneider und K. Heymons, *Monatsh. Chem.*, 92 (1961) 1080.
3 E. O. Fischer und S. Schreiner, *Chem. Ber.*, 93 (1960) 1417.

Eingegangen den 13. Mai 1964

J. Organometal. Chem., 2 (1964) 287–288

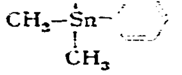
The electric dipole moments of some trimethylphenyltin derivatives

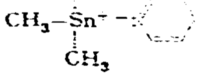
Although d_π–p_π bonding in certain organosilicon compounds is now fairly well established[1], the evidence for a similar effect in organotin compounds is meagre and also less conclusive. Theoretical calculations[2] have shown that the amount of overlap in d_π–p_π bonding is not critically dependent upon the size of the *d*-orbitals involved. Thus, in spite of its size, it is possible that the *d*-orbitals of tin may be capable of engaging in bonding with the *p*-orbitals of carbon. We have accordingly undertaken the measurement of the electric dipole moments of a number of suitable organotin compounds, in which d_π–p_π bonding might be expected to occur, in the hope that it may be illuminating.

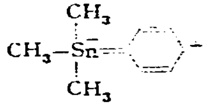
This report presents a preliminary account of the results obtained for some trimethylphenyltin derivatives measured in benzene solution at 25°. The results are given in the table, and as an additional point of interest, the moments of analogous silicon compounds[3,4] are included for comparison (wherever possible). Also listed in the table are the calculated interaction moments[5] for both series, after correction has been made by Frank's method[6] for the maximum induced moment to be expected from the mutual electrostatic effects of the primary moments. Where appropriate, the moments of the polar groups *para* to $Si(CH_3)_3$ or $Sn(CH_3)_3$, are regarded as separable[7] * into "mesomeric moments" and "group plus induced moments" whose combined effects may be obtained by summation. Account has also been taken of the fact that the OCH_3 and $N(CH_3)_2$ groups are axially non-symmetric with respect to the ring.

Tin, like silicon and other Group IV B 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 $Sn(CH_3)_3$ group is electron-releasing with respect to the ring. Furthermore, our results furnish evidence in support of the view that dative π-bonding occurs, by donation of electrons from a molecular orbital of the aromatic system into a vacant 5-*d*-orbital of tin, when strongly electron-releasing substituents are attached *para* to the $Sn(CH_3)_3$ group, and probably even in trimethylphenyltin itself.

The following resonance structures may be postulated for trimethylphenyltin:


(I)


(II)


(III)

Structure (II) reflects the difference in electronegativity between carbon and tin.

---

* We are indebted to a referee for this reference.

J. Organometal. Chem., 2 (1964) 288–290

TABLE 1

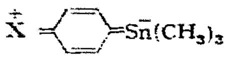
DIPOLE MOMENTS OF DERIVATIVES OF TRIMETHYLPHENYLTIN AND TRIMETHYLPHENYLSILANE

X	$\mu_{obs.}$ (D)	$\mu_{calc.}$ (D)	$\Delta\mu$ (D)
	p-$XC_6H_4Sn(CH_3)_3$		
H	0.51	—	—
$N(CH_3)_3$	1.83	1.54	+0.29
OCH_3	1.46	1.31	+0.15
CH_3	0.48	0.03	+0.45
Cl	2.16	2.01	+0.15
Br	2.15	2.01	+0.14
$C_6H_5CH_2Sn(CH_3)_3$	0.91	—	—
	p-$XC_6H_4Si(CH_3)_3$		
H	0.44	—	—
$N(CH_3)_2$	1.84	1.58	+0.26
OCH_3	—	—	—
CH_3	0.46	0.03	+0.43
Cl	1.70	1.93	−0.23
Br	1.79	1.91	−0.12
$C_6H_5CH_2Si(CH_3)_3$	0.71	—	—

(*a*) $\Delta\mu = \mu_{obs.} - \mu_{calc.}$. (*b*) Errors $< \pm 0.03$ D. (*c*) Atomic polarisation neglected for moment $>$ 1 D, taken as 5% of molar refraction if $<$ 1 D.

Since 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[8] suggesting that π-bonding effects may be present in the former compound. Further support for the existence of some double bond character in the Sn–C_{ar} bond is provided by the group moment of $Sn(CH_3)_3$ in trimethylbenzyltin (0.69 D), in which conjugation between the $Sn(CH_3)_3$ group and the aromatic ring is eliminated, as compared with the somewhat smaller value in trimethylphenyltin itself (0.51 D).

The interaction moments of p-$XC_6H_4Sn(CH_3)_3$ [$X = N(CH_3)_2$, OCH_3, CH_3] imply the existence of a drift of electrons towards the $Sn(CH_3)_3$ group which cannot be accounted for in terms of electrostatic inductive effects. These results, however, can be rationalized if one assumes that d_π–p_π bonding is possible 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 Cl of Br, the direction and magnitude of the interaction moment indicate a net shift of electrons from the $Sn(CH_3)_3$ group towards the halogen atom, over and above that implied by the moment of $C_6H_5Sn(CH_3)_3$. The negative inductive effect of the halogen atom thus outweighs the positive mesomeric, *i.e.* d_π–p_π 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[9]. In the present work, since the controlling factors are the tin and silicon groups, it may be inferred that silicon in the $Si(CH_3)_3$ group is more effective in delocalizing aromatic π-electrons than tin, *i.e.* the amount of d_π–p_π 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 anions, silicon in the $Si(CH_3)_3$ group is more efficient than germanium in delocalizing aromatic π-electrons[10]. Furthermore, studies on hydrogen bond formation of the compounds $(C_6H_5)_3MOH$ (where M = Si, Ge, Sn, Pb) with ether and phenol, suggest that π-bonding from oxygen to M decreases markedly in the order Si > Ge > Sn, Pb, being negligible[11] for Sn and Pb. Since there is considerable disagreement concerning the exact sequence of electronegativity values of Group IV B elements in the quadripositive state[12], our dielectric results, which, on the balance, support the usually accepted sequence Si > Sn [in contrast to that proposed by Allred and Rochow[12] on the basis of measurements on proton shifts in $(CH_3)_4M$, (M=)Pb > Ge > Sn > Si], should be of general interest. Further work on saturated and unsaturated organotin halides is in progress.

The organotin compounds were prepared by the Grignard method or using lithium. By the latter method, we prepared p-$(CH_3)_2NC_6H_4Sn(CH_3)_3$, m.p. 40–41°, which to our knowledge, has not been reported before. (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 %.)

We thank Mrs. H. K. Tong for microanalysis.

Chemistry Department, University of Singapore,
Singapore (Malaysia)
H. H. Huang
K. M. Hui

1 C. Eaborn, *Organosilicon Compounds*, Butterworth, London, 1960, chapter III.
2 D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel and L. E. Sutton, *J. Chem. Soc.*, (1954) 332.
3 J. D. Roberts, E. A. McElhill and R. Armstrong, *J. Am. Chem. Soc.*, 71 (1949) 2923.
4 H. Soffer and T. DeVries, *J. Am. Chem. Soc.*, 73 (1951) 5817.
5 R. J. B. Marsden and L. E. Sutton, *J. Chem. Soc.*, (1936) 599.
6 F. C. Frank, *Proc. Roy. Soc.*, London, Ser. A, 152 (1936) 171.
7 T. L. Brown, *J. Am. Chem. Soc.*, 81 (1959) 3232.
8 C. G. Le Fevre, R. J. W. Le Fevre and K. W. Robertson, *J. Chem. Soc.*, (1935) 480.
9 C. M. Bax, A. R. Katritzky and L. E. Sutton, *J. Chem. Soc.*, (1958) 1254.
10 J. A. Bedford, J. R. Bolton, A. Carrington and R. H. Prince, *Trans. Faraday Soc.*, 59 (1963) 53.
11 R. West, R. H. Baney and D. L. Powell, *J. Am. Chem. Soc.*, 82 (1960) 6269.
12 A. L. Allred and E. G. Rochow, *J. Inorg. Nucl. Chem.*, 5 (1958) 264, 269; R. S. Drago, *J. Inorg. Nucl. Chem.*, 15 (1960) 237; A. L. Allred, *J. Inorg. Nucl. Chem.*, 17 (1961) 215; H. O. Pritchard and H. A. Skinner, *Chem. Rev.*, 55 (1955) 745.

Received March 2nd, 1964