

ORGANOTIN COMPOUNDS II. π -BONDING AND THE ELECTRIC DIPOLE MOMENTS OF SOME ORGANOTIN CHLORIDES

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(Received July 24th, 1967)

SUMMARY

The electric dipole moments of 14 organotin compounds containing the methyl, ethyl, butyl, phenyl and vinyl groups, have been measured. The results are discussed in terms of d_{π} - p_{π} bonding and the relative importance of structures of the type $H^+C=\bar{S}n-Cl$ and $\bar{S}n=Cl^+$.

INTRODUCTION

In our recent work on organotin compounds^{1,2}, dielectric evidence was presented which showed that d_{π} - p_{π} bonding between aromatic carbon and tin probably occurs in *para*-substituted trimethylphenyltin derivatives containing electron-releasing groups. A similar effect may be expected when a SnX_3 group (where X is a strongly electronegative atom such as Cl) is linked to an unsaturated radical such as phenyl or vinyl. We have now extended our study of d_{π} - p_{π} bonding to such unsaturated organotin chlorides, including three series of aliphatic organotin chlorides for comparison and to investigate the relative importance of structures of the type $H^+C=\bar{S}n-Cl$ and $\bar{S}n=Cl^+$. During the course of the work described in this paper, Lorberth and Nöth³ reported on the electric moments of some of the compounds studied by us. Nevertheless, because of several discrepancies in the published moment values of organotin chlorides in the literature⁴, and the different scope and emphasis in previous work, it seems desirable to record our results in their entirety in this paper.

EXPERIMENTAL

Experimental methods and apparatus employed have been described before². All physical measurements were made at 25° in benzene solution.

The vinyltin chlorides were prepared according to the method of Rosenberg and Gibbons⁵; triethyltin chloride, diethyltin dichloride, tributyltin chloride and dibutyltin dichloride were prepared as described by Luijten and van der Kerk⁶. Trimethyltin chloride, dimethyltin dichloride, triphenyltin chloride, diphenyltin dichloride, phenyltin trichloride and n-butyltin trichloride were commercial samples freshly purified before use.

Di-tert-butyltin dichloride

This compound was obtained as a byproduct from an attempted preparation of tert-butyltin trichloride (*cf.* Luijten and van der Kerk, *loc. cit.*). tert-Butylmagnesium chloride was prepared in the usual manner from 24.3 g (1 g-atom) of magnesium and 92.5 g (1 mole) of tert-butyl chloride in 250 ml of anhydrous ether. The Grignard preparation was added slowly to a solution of 260.5 g (1 mole) of stannic chloride in 125 ml of dry benzene. The reaction mixture was immediately decomposed by 600 ml of water followed by filtration of the organic layer and subsequent removal of volatile solvents by distillation. A fraction boiling at 88–92°/5.5 mm and consisting mainly of tri-tert-butyltin chloride was collected. (Found: C, 44.68; H, 7.68; Cl, 16.55. $C_{12}H_{27}ClSn$ calcd.: C, 44.28; H, 8.30; Cl, 10.92 %). A second fraction b.p. 92–93.5°/5.5 mm was collected which later proved to be di-tert-butyltin dichloride, m.p. 42.5–43.5° (lit.⁷ not stated). (Found: C, 31.64; H, 6.09; Cl, 22.86. $C_8H_{18}Cl_2Sn$ calcd.: C, 31.61; H, 5.93; Cl, 23.38 %.)

Although the solid dichloride was easily purified by recrystallisation, the monochloride could not be obtained in a sufficiently pure state for physical measurements, being contaminated by the closely boiling dichloride. The reaction failed to give the desired product, tert-butyltin trichloride, presumably because the compound is easily hydrolysed and must have decomposed in the last step of the Grignard reaction. An attempt to prepare the trichloride by reacting tert-butyllithium in pentane with excess stannic chloride at 0° was also unsuccessful.

DISCUSSION

The detailed results are listed in Table 1. A comparison of the moments found in this work with previous measurements is given in Table 2. The largest discrepancies with earlier work occur in the compounds $(C_6H_5)_2SnCl_2$ (ref. 10) and $(C_2H_5)_2SnCl_2$ (ref. 9). On the whole, our results agree rather well with the values reported by Lorberth and Nöth. The moments of the vinyltin chlorides and of di-tert-butyltin dichloride are recorded here for the first time.

One of the main points of interest in this paper is the extent to which the dielectric data assembled here afford positive evidence for $d_{\pi}-p_{\pi}$ bonding in the organotin compounds concerned, particularly the vinyl and phenyl trichlorides where the opportunities for π -electron delocalization are more favourable. A useful general approach, originally proposed by Sutton^{1,2} for detecting mesomeric effects in a mono-substituted aromatic system, is to determine the mesomeric moment of the aromatic compound, defined as the vector difference between its dipole moment and that of its aliphatic analogue, since this provides a measure of the interaction between the π -electron system of the aromatic ring and its substituent. To allow for induction, the aliphatic standard for comparison should be the tert-butyl compound although the methyl compound is often used when the higher homologue is not available^{1,3}. These mesomeric moments associated with various groups were regarded as $+\mu$ or $-\mu$ according as their positive or negative ends, respectively, were towards the substituent group. Thus Sutton was able to show that *ortho-para* directing groups were invariably associated with positive, and *meta* directing with negative mesomeric moments. Applying the same arguments, it follows from the moments of $C_6H_5SnCl_3$ (4.23 D) and CH_3SnCl_3 (3.62 D) that a mesomeric moment of -0.61 D could be assigned to the

TABLE I

DIELECTRIC CONSTANTS AND DENSITIES OF SOLUTIONS AT 25°

$10^5 \cdot w_2$	d_{12}	ϵ_{12}
<i>Trimethyltin chloride</i>		
2471	0.88349	2.4389
2691	0.88431	2.4513
2924	0.88534	2.4681
3389	0.88701	2.4997
$\alpha \cdot \epsilon_1 = 6.71$	$\beta \cdot d_1 = 0.39$	
$\tau P = 289.0$ cc	$R_D = 36.1$ cc (calcd.)	$\mu = 3.52$ D
<i>Dimethyltin dichloride</i>		
679	0.87686	2.3334
1514	0.88092	2.4047
2006	0.88326	2.4480
3545	0.89083	
$\alpha \cdot \epsilon_1 = 8.80$	$\beta \cdot d_1 = 0.48$	
$\tau P = 397.6$ cc	$R_D = 35.8$ cc (calcd.)	$\mu = 4.21$ D
<i>Triethyltin chloride</i>		
743	0.87615	2.3191
1288	0.87797	2.3553
1790	0.87973	2.3893
2607	0.88254	2.4397
3495	0.88551	2.5003
$\alpha \cdot \epsilon_1 = 6.48$	$\beta \cdot d_1 = 0.33$	
$\tau P = 345.1$ cc	$R_D = 49.9$ cc (calcd.)	$\mu = 3.80$ D
<i>Diethyltin dichloride</i>		
546	0.87603	2.3201
1491	0.88004	2.3999
1854	0.88160	2.4310
2437	0.88411	2.4862
2913	0.88615	2.5338
$\alpha \cdot \epsilon_1 = 8.80$	$\beta \cdot d_1 = 0.43$	
$\tau P = 453.4$ cc	$R_D = 45.0$ cc (calcd.)	$\mu = 4.47$ D
<i>Tri-n-butyltin chloride</i>		
658	0.87545	2.2953
1790	0.87766	2.3411
3146	0.88059	2.3958
4106	0.88246	2.4378
4890	0.88425	2.4706
$\alpha \cdot \epsilon_1 = 3.96$	$\beta \cdot d_1 = 0.22$	
$\tau P = 325.9$ cc	$R_D = 77.6$ cc (calcd.)	$\mu = 3.48$ D
<i>Di-n-butyltin dichloride</i>		
943	0.87723	2.3371
2006	0.88055	2.4122
3104	0.88424	2.4903
3903	0.88727	2.5553
5408	0.89248	2.6603
$\alpha \cdot \epsilon_1 = 7.11$	$\beta \cdot d_1 = 0.34$	
$\tau P = 468.9$ cc	$R_D = 63.5$ cc (calcd.)	$\mu = 4.45$ D

(continued on next page)

TABLE 1 (continued)

$10^3 \cdot w_2$	d_{12}	ϵ_{12}
<i>n</i> -Butyltin trichloride		
930	0.87704	2.3484
1752	0.88069	2.4090
2442	0.88371	2.4708
3198	0.88727	2.5270
3698	0.88885	2.5703
4758	0.89315	2.6505
5108	0.89489	2.6853
$\alpha \cdot \epsilon_1 = 7.89$	$\beta \cdot d_1 = 0.69$	
$\tau P = 439.0$ cc	$R_D = 50.3$ cc	$\mu = 4.32$ D
<i>Di</i> - <i>tert</i> -butyltin dichloride		
498	0.87527	2.3052
752	0.87614	2.3229
1529	0.87865	2.3812
2008	0.88001	2.4069
2535	0.88170	2.4417
$\alpha \cdot \epsilon_1 = 6.68$	$\beta \cdot d_1 = 0.31$	
$\tau P = 448.0$ cc	$R_D = 63.5$ cc (calcd.)	$\mu = 4.34$ D
<i>Tri</i> vinyltin chloride		
966	0.87700	2.3108
1559	0.87910	2.3373
1614	0.87928	2.3387
1849	0.88021	2.3487
2994	0.88411	
$\alpha \cdot \epsilon_1 = 4.15$	$\beta \cdot d_1 = 0.34$	
$\tau P = 232.1$ cc	$R_D = 48.6$ cc (calcd.)	$\mu = 3.00$ D
<i>Di</i> vinyltin dichloride		
634	0.87649	2.3150
1958	0.88211	2.4178
2422	0.88417	2.4539
2965	0.88662	2.4937
3850	0.89056	2.5659
$\alpha \cdot \epsilon_1 = 7.40$	$\beta \cdot d_1 = 0.44$	
$\tau P = 381.3$ cc	$R_D = 44.1$ cc (calcd.)	$\mu = 4.06$ D
<i>Vinyltin trichloride</i>		
324	0.87529	2.2929
888	0.87796	2.3254
1207	0.87958	2.3451
2013	0.88352	2.3957
$\alpha \cdot \epsilon_1 = 6.15$	$\beta \cdot d_1 = 0.48$	
$\tau P = 330.4$ cc	$R_D = 39.7$ cc (calcd.)	$\mu = 3.77$ D
<i>Triphenyltin chloride</i>		
668	0.87628	
1314	0.87874	2.3160
1535	0.87975	2.3250
2554	0.88320	2.3597
3260	0.88614	2.3859
$\alpha \cdot \epsilon_1 = 3.43$	$\beta \cdot d_1 = 0.38$	
$\tau P = 323.3$ cc	$R_D = 94.5$ cc (calcd.)	$\mu = 3.44$ D

(continued on next page)

TABLE I (continued)

$10^5 \cdot w_2$	d_{12}	ϵ_{12}
<i>Diphenyltin dichloride</i>		
634	0.87623	2.3087
1771	0.88090	2.3812
2567	0.88435	2.4274
2930	0.88577	2.4500
3650	0.88890	2.4980
$\alpha \cdot \epsilon_1 = 6.08$	$\beta \cdot d_1 = 0.41$	
$\gamma P = 455.5$ cc	$R_D = 74.8$ cc	$\mu = 4.31$ D
<i>Phenyltin trichloride</i>		
488	0.87595	2.3024
1105	0.87885	2.3426
1815	0.88235	2.3902
2728	0.88657	2.4492
2992	0.88787	
4461	0.89500	
$\alpha \cdot \epsilon_1 = 6.58$	$\beta \cdot d_1 = 0.48$	
$\gamma P = 420.0$ cc	$R_D = 55.0$ cc (calcd.)	$\mu = 4.23$ D

SnCl_3 group, *i.e.* it should be *meta*-directing. Unfortunately, the ease with which the *Sn-C* (aromatic) bond is cleaved by electrophilic reagents may make this prediction difficult to test experimentally. The existence of a negative mesomeric moment can also be taken to confirm the incidence of $d_\pi-p_\pi$ bonding between aromatic carbon and tin in $\text{C}_6\text{H}_5\text{SnCl}_3$.

A difficulty arises, however, when $\text{C}_6\text{H}_5\text{SnCl}_3$ (4.23 D) is compared with $n\text{-C}_4\text{H}_9\text{SnCl}_3$ (4.32 D) since the mesomeric moment is now +0.09 D, in contrast to the value determined with CH_3SnCl_3 as standard. [Although *tert*- $\text{C}_4\text{H}_9\text{SnCl}_3$ is the more appropriate compound to use for comparison, we were not successful in preparing it; however, the near identity of the moments of (*tert*- C_4H_9) $_2\text{SnCl}_2$ (4.34 D) and ($n\text{-C}_4\text{H}_9$) $_2\text{SnCl}_2$ (4.45 D) indicates that $n\text{-C}_4\text{H}_9\text{SnCl}_3$ should be an adequate substitute]. The apparent inconsistency between the mesomeric moments calculated for the SnCl_3 group using CH_3SnCl_3 and $n\text{-C}_4\text{H}_9\text{SnCl}_3$ as standards of comparison, can be partly resolved by an alternative interpretation of the dipole moment data. Brown¹⁴ has shown that the series of organic radicals obtained by arranging the chloro-derivatives of these radicals, R-Cl , in order of increasing values of their carbon-chlorine bond moments, parallels the electronegativity scale of organic radicals established by the study of the selective hydrolytic splitting of organomercurials¹⁵. Provided that this correlation between the electronegativity series of organic radicals and dipole moments is generally applicable, then because the electronegativity scale is phenyl > methyl > ethyl > *n*-butyl > *tert*-butyl, it may be predicted that the moments of the compounds RSnCl_3 should lie in the order $n\text{-C}_4\text{H}_9\text{SnCl}_3 > \text{C}_2\text{H}_5\text{SnCl}_3 > \text{CH}_3\text{SnCl}_3 > \text{C}_6\text{H}_5\text{SnCl}_3$. The observed moments lie in the order $n\text{-C}_4\text{H}_9\text{SnCl}_3 > \text{C}_6\text{H}_5\text{SnCl}_3 > \text{C}_2\text{H}_5\text{SnCl}_3 > \text{CH}_3\text{SnCl}_3$, revealing the anomalous position of $\text{C}_6\text{H}_5\text{SnCl}_3$ in this context. This anomaly, however, is explicable in terms of $d_\pi-p_\pi$ bonding in $\text{C}_6\text{H}_5\text{SnCl}_3$, an effect which would cause a mesomeric moment to act in the molecule with its negative end towards the SnCl_3 group. Since this is in the same sense as the

TABLE 2

DIPOLE MOMENTS OF ORGANOTIN CHLORIDES IN BENZENE SOLUTION

Solute	μ (D)	References
Trimethyltin chloride	3.52	Present work
	3.50	Claeys <i>et al.</i> ⁸
	3.46	Lorberth and Nöth ³
Dimethyltin dichloride	4.21	Present work
	4.22	Claeys <i>et al.</i> ⁸
	4.14	Lorberth and Nöth ³
Methyltin trichloride	3.62	Claeys <i>et al.</i> ⁸
	3.74	Lorberth and Nöth ³
Triethyltin chloride	3.80	Present work
	3.44	Spaght <i>et al.</i> ⁹
	3.56	Lorberth and Nöth ³
Diethyltin dichloride	4.47	Present work
	3.85	Spaght <i>et al.</i> ⁹
	4.32	Lorberth and Nöth ³
	4.08	Lorberth and Nöth ³
Ethyltin trichloride	4.08	Lorberth and Nöth ³
Trivinyltin chloride	3.00	Present work
Divinyltin dichloride	4.06	Present work
Vinyltin trichloride	3.77	Present work
Tri-n-butyltin chloride	3.48	Present work
	3.29	Lorberth and Nöth ³
	3.64	Goldshtein <i>et al.</i> ¹⁰
	4.45	Present work
Di-n-butyltin dichloride	4.38	Lorberth and Nöth ³
	4.72	Goldshtein <i>et al.</i> ¹⁰
	4.32	Present work
n-Butyltin trichloride	4.27	Lorberth and Nöth ³
Di-tert-butyltin dichloride	4.34	Present work
Triphenyltin chloride	3.34	Present work
	3.31	Goldshtein <i>et al.</i> ¹⁰
	3.30	Smyth ¹¹
	3.44	Lorberth and Nöth ³
Diphenyltin dichloride	4.31	Present work
	3.59	Goldshtein <i>et al.</i> ¹⁰
	4.23	Lorberth and Nöth ³
Phenyltin trichloride	4.23	Present work
	4.24	Goldshtein <i>et al.</i> ¹⁰
	4.26	Lorberth and Nöth ³

group moment of SnCl_3 , the gross moment of the molecule would be increased beyond the value compatible with the position of C_6H_5 in the electronegativity scale.

Similar arguments may be used in the case of $\text{CH}_2=\text{CHSnCl}_3$. Although there is some uncertainty as to whether the phenyl or vinyl radical is more electronegative, there is little doubt that the trigonal character of the carbon atoms in vinyl would make its electron-attracting power comparable to that of phenyl and certainly greater than that of methyl. The $\text{p}K_a$ values of substituted acetic acids¹⁶ XCH_2COOH (X = phenyl, 4.31; vinyl, 4.35; and methyl, 4.82) confirm this expectation. Similarly, the ease of cleavage of unsymmetrical organotin compounds by halogens and acids¹⁷ suggests that the relative scale of electron-withdrawing power is phenyl > vinyl > ethyl, although a study of the cleavage of symmetrical organomercury compounds by HCl ¹⁸

suggests that it is vinyl > phenyl > ethyl, in agreement with Brown's dipole moment analysis (*loc. cit.*). In any case, it is certain that the difference in electronegativity between the phenyl and vinyl groups will be quite small and we should expect the moments of phenyltin chlorides and vinyltin chlorides to be practically the same, in the absence of complications due to steric effects. The observed moments of the phenyltin chlorides are all larger than those of the corresponding vinyltin chlorides, particularly in the case of the trichloride. Since steric effects are unlikely to intervene in the trichlorides, as shown by an examination of scale models, it seems reasonable to infer that there is more double bond character in the C(aryl)-Sn than in the C(vinyl)-Sn bond. Furthermore, although vinyl is more electronegative than either methyl or ethyl, the observed moment of vinyltin trichloride lies between those of methyltin trichloride and ethyltin trichloride. This suggests that even though $d_{\pi}-p_{\pi}$ bonding in vinyltin trichloride is not as fully developed as it is in the phenyl analogue, the effect is by no means insignificant in the former compound.

An alternative way of using the dipole moment data is to consider the ratios $\mu(\text{R}_3\text{SnCl}_3)/\mu(\text{R}_3\text{SnCl}) = m$ and $\mu(\text{R}_2\text{SnCl}_2)/\mu(\text{R}_3\text{SnCl}) = n$. In the absence of mutual induction between the polar groups and assuming tetrahedral bond angles in the organotin compounds, the values of m and n should be 1 and 1.16 respectively¹⁹. On the basis of the experimental dipole moments for the monochlorides, it is possible to

TABLE 3

CALCULATED AND EXPERIMENTAL DIPOLE MOMENTS^a

Compound	μ_{obs} (D)	μ_{calc} (D)	$\Delta\mu$ (D)
(CH ₃) ₃ SnCl	3.52	3.52	0
(CH ₃) ₂ SnCl ₂	4.21	4.08	0.13
(CH ₃)SnCl ₃	3.62 ^b	3.52	0.10
(C ₂ H ₅) ₃ SnCl	3.80	3.80	0
(C ₂ H ₅) ₂ SnCl ₂	4.47	4.40	0.07
(C ₂ H ₅)SnCl ₃	4.08 ^b	3.80	0.28
(CH ₂ =CH) ₃ SnCl	3.00	3.00	0
(CH ₂ =CH) ₂ SnCl ₂	4.06	3.48	0.58
(CH ₂ =CH)SnCl ₃	3.77	3.00	0.77
(C ₄ H ₉) ₃ SnCl	3.48	3.48	0
(C ₄ H ₉) ₂ SnCl ₂	4.45	4.04	0.41
(C ₄ H ₉)SnCl ₃	4.32	3.48	0.84
(C ₆ H ₅) ₃ SnCl	3.34	3.34	0
(C ₆ H ₅) ₂ SnCl ₂	4.31	3.88	0.43
(C ₆ H ₅)SnCl ₃	4.23	3.34	0.89

^a No allowance for atomic polarisation was made other than that implicit in taking the distortion polarisation (ρP) equal to the molar refraction (R_D). ^b The experimental dipole moments in the first column were chosen from the present work except the ones with the superscript which were taken from references 3 and 8.

calculate theoretical moment values for the R_2SnCl_2 and RSnCl_3 compounds expected from the above ratios. The results of such calculations are listed in Table 3.

The following features emerge from the table:

- there is a general increase in the deviations from the calculated values in a given series from the mono- to the trichloride;
- this increase is particularly marked in the vinyl, butyl and phenyl series.

In the methyl series, electron diffraction studies have shown that the bond angles are tetrahedral²⁰ and examination of the relevant space models indicates that it is likely these are retained even in the more bulky aliphatic homologues and the phenyl compounds, because of the size of the tin atom. Thus, with the possible exceptions of the vinyl mono- and dichloride where steric effects may complicate the situation owing to the geometry of the vinyl group, the deviations observed may be attributed to changes in the partial moments $\text{Sn} \rightarrow \text{C}$ and $\text{Sn} \rightarrow \text{Cl}$ in these molecules*. (a) can be explained if it is assumed that progressive chlorine substitution leads to an increase in the effective $\text{Sn}-\text{Cl}$ moment, either through a corresponding increase in ionic character of the $\text{Sn}-\text{Cl}$ bond, or because the structure $\text{Sn}=\overset{+}{\text{Cl}}$ (involving π -bonding between the p -orbitals of chlorine and the vacant d -orbitals of tin) is effectively more important in the monochloride than in the trichloride, or both. These assumptions are consistent with the existence of appreciable and increasing π -bond character in the $\text{Sn}-\text{Cl}$ bond in tin tetrachloride upon progressive organic group substitution, but not with the concurrent increase in $\text{Sn}-\text{Cl}$ ionic bond character postulated by Swiger and Graybeal²¹ to explain the trends observed in the nuclear quadrupole coupling constants of some phenyl- and *n*-butyltin chlorides and related group IV chlorides. It seems unlikely, however, that $\text{Sn}=\overset{+}{\text{Cl}}$ π -bonding would be the dominant factor responsible for (a) because such a structure, which requires the removal of an electron from an electronegative atom and its addition to an electropositive one, appears to be energetically unfavourable; whereas the assumption of increasing ionic character in the $\text{Sn}-\text{Cl}$ bond with successive chlorine substitution, due to greater withdrawal of electronic charge from the tin atom, and thus leaving a greater positive charge on it, involves the more facile reverse process of the electropositive tin atom donating electronic charge to the much more electronegative chlorine atom. Moreover, electron diffraction measurements²⁰ have indicated a decrease in the $\text{Sn}-\text{Cl}$ bond length in the methyltin chloride series with each additional $\text{Sn}-\text{Cl}$ bond added, in disagreement with the corresponding decrease in π -bond character postulated²¹. Smyth²³, from earlier dipole moment studies of aliphatic group IV B halides, has also concluded that except in the case of silicon compounds and to a lesser extent the germanium compounds, the lowering of the $Z-\text{Cl}$ ($Z = \text{Si}, \text{Ge}, \text{Sn}, \text{Pb}$) bond moment by contribution from doubly-bonded forms is small. In any case, the present analysis of the dipole moment data suggests that the conclusion that the $\text{Sn}-\text{Cl}$ bond polarity increases with progressive chlorine substitution, seems inescapable. (b) is explicable in terms of the relative importance of structures corresponding to $\text{H}^+ \text{C}=\overset{-}{\text{Sn}}-\text{Cl}$ (the hyperconjugation effect**) and $d_\pi-p_\pi$ bonding***. Thus the hyperconjugation effect, which can be expected to decrease in the order methyl > ethyl > butyl, is apparently stronger in $(\text{CH}_3)_3-$

* It may be pointed out that possible deviations from tetrahedral geometry arising from steric or other effects, would generally be in the direction of wider bond angles and this would result in smaller moments for the trichlorides and larger moments for the monochlorides, in disagreement with the experimental facts.

** A recent NMR study²² of the τ values of the protons bound directly to the tin atom in dialkyltin halide hydrides provides physical evidence of a different kind in support of hyperconjugation between the methyl group and the tin atom.

*** Since the double bond in the $\text{Sn}-\text{CH}_3$ link in hyperconjugation is not a conventional π -bond, arising as it does from the pairing of a tetrahedral orbital directed towards one of the hydrogen atoms with a π -orbital on tin, it is convenient to distinguish this from the double bond formed by $d_\pi-p_\pi$ overlap between the vacant d -orbitals of tin and a $2p$ π atomic orbital of trigonal carbon.

SnCl where there are three methyl groups, compared with CH_3SnCl_3 , where there is only one. This would compensate for the smaller effective Sn-Cl bond moment in the former compound with the result that the moments of the two compounds are now comparable in magnitude.

In the butyl series, the hyperconjugation effect is expected to be much less important and the relative moments of the compounds are now largely controlled by the number of chlorine atoms attached to tin. Hence, the moment of the trichloride is appreciably greater than that of the monochloride.

In the phenyl series, the deviations observed are undoubtedly due in part at least, to the increase in polarity of the Sn-Cl σ -bond accompanying an increase in the number of chlorine atoms in the molecule. Comparison with the methyl series shows that d_π - p_π bonding in $\text{C}_6\text{H}_5\text{SnCl}_3$ is more important than the hyperconjugation effect in CH_3SnCl_3 since the moment of the former compound is greater. On the other hand, the smaller moment of triphenyltin chloride compared with that of trimethyltin chloride suggests that the reverse is true in the monochloride. In butyltin trichloride and phenyltin trichloride, the moment deviations from the monochloride values are comparable in magnitude. This further implies that in triphenyltin chloride, d_π - p_π bonding, although predictably less important than it is in phenyltin trichloride, cannot be negligible, for if it were so, the difference in moment between the mono- and the trichloride would then be greater than the corresponding difference in the butyl compounds. A credible explanation of the varying degree of d_π - p_π bonding in the different members of the phenyl series, is that when electronegative ligands like chlorine are bonded to tin, they tend to withdraw electronic charge from the metal atom leaving behind a partial positive charge. As the number of chlorine atoms attached to tin increases, the increased polar character of the bonds will confer extra stability by improving the d_π - p_π overlap through contraction of the diffuse 5 d -orbitals and hence d_π - p_π bonding should decrease in the order $\text{C}_6\text{H}_5\text{SnCl}_3 > (\text{C}_6\text{H}_5)_2\text{SnCl}_2 > (\text{C}_6\text{H}_5)_3\text{SnCl}$. Furthermore, the spatial requirements in the case of the monochloride may force the phenyl rings into planes unfavourable for maximum overlap of carbon and tin π -orbitals, whereas in the trichloride, steric restrictions are absent and the π -bond can be formed equally well in all positions as the SnCl_3 group is rotated about the tin-phenyl bond²⁴.

It is noteworthy that in the vinyl series, $(\text{CH}_2=\text{CH})_3\text{SnCl}$ has the smallest moment of all the compounds listed in Table 2. A plausible reason for this observation is that in this compound, electronegativity (and steric) considerations are of greater relevance, d_π - p_π bonding being of minor importance. Steric effects, if operative, must act by reducing the C-Sn-C angles and thus increasing the resultant of the three Sn-C bond moments, but it is difficult to make a reasonable assessment of their importance. The relatively large difference between the moments of the monochloride and the trichloride is almost as striking as the corresponding differences in the phenyl and butyl series, and by analogy with the phenyl compounds, must be attributed to the increase in Sn-Cl σ -bond polarity and increasing importance of d_π - p_π bonding attending successive chlorine substitution.

ACKNOWLEDGEMENT

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

REFERENCES

- 1 H. H. HUANG AND K. M. HUI, *J. Organometal. Chem.*, 2 (1964) 288.
 - 2 H. H. HUANG AND K. M. HUI, *J. Organometal. Chem.*, 6 (1966) 504.
 - 3 J. LORBERTH AND H. NÖTH, *Chem. Ber.*, (1965) 969.
 - 4 A. L. MCCLELLAN, *Tables of Experimental Dipole Moments*, Freeman, San Francisco, 1963.
 - 5 S. D. ROSENBERG AND A. J. GIBBONS, JR., *J. Amer. Chem. Soc.*, 79 (1957) 2138.
 - 6 J. G. A. LUITEN AND G. J. M. VAN DER KERK, *Investigations in the Field of Organotin Chemistry*, Tin Research Institute, London, 1955.
 - 7 R. H. PRINCE, *J. Chem. Soc.*, (1959) 1783.
 - 8 E. G. CLAEYS, G. P. VAN DER KELEN AND Z. EECKHAUT, *Bull. Soc. Chim. Belges*, 70 (1961) 462.
 - 9 M. E. SPAGHT, F. HEIN AND H. PAULING, *Physik. Z.*, 34 (1933) 212.
 - 10 I. P. GOLDSHTEIN, E. N. GURYANOVA, E. D. DELINSKAYA AND K. A. KOCHESHKOV, *Dokl. Akad. Nauk. SSSR*, 136 (1961) 1079.
 - 11 C. P. SMYTH, *J. Amer. Chem. Soc.*, 63 (1941) 57.
 - 12 L. E. SUTTON, *Proc. Roy. Soc., Ser. A*, 133 (1931) 668.
 - 13 C. K. INGOLD, *Structure and Mechanism in Organic Chemistry*, Cornell University Press, New York, 1953, p. 103.
 - 14 H. C. BROWN, *J. Amer. Chem. Soc.*, 61 (1939) 1483.
 - 15 M. S. KHARASCH AND A. L. FLENNER, *J. Amer. Chem. Soc.*, 54 (1932) 674.
 - 16 J. F. J. DIPPY, *Chem. Rev.*, 25 (1939) 151.
 - 17 D. SEYFERTH, *J. Amer. Chem. Soc.*, 79 (1957) 2133.
 - 18 R. E. DESSY, G. F. REYNOLDS AND J. Y. KIM, *J. Amer. Chem. Soc.*, 81 (1959) 2683.
 - 19 C. P. SMYTH, A. J. GROSSMAN AND S. R. GINSBERG, *J. Amer. Chem. Soc.*, 62 (1940) 192.
 - 20 H. A. SKINNER AND L. E. SUTTON, *Trans. Faraday Soc.*, 40 (1944) 164.
 - 21 E. D. SWIGER AND J. D. GRAYBEAL, *J. Amer. Chem. Soc.*, 87 (1965) 1464.
 - 22 K. KAWAKAMI, T. SAITO AND R. OKAWARA, *J. Organometal. Chem.*, 8 (1967) 377.
 - 23 C. P. SMYTH, *J. Amer. Chem. Soc.*, 63 (1941) 57.
 - 24 D. P. CRAIG, A. MACCOLL, R. S. NYHOLM, L. E. ORGEL AND L. E. SUTTON, *J. Chem. Soc.*, (1954) 332.
- J. Organometal. Chem.*, 11 (1968) 515-524