STUDIES ON ORGANOTIN COMPOUNDS USING THE DEL RE METHOD II. DIPOLE MOMENTS OF ORGANOTIN COMPOUNDS AND VARIATION IN THE TIN–CHLORINE AND TIN–CARBON BOND POLARITY

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(Received May 20th, 1971)

SUMMARY

The electric dipole moments of 20 organotin compounds containing methyl, ethyl, tert-butyl, n-butyl, phenyl and vinyl groups have been calculated using an approximate quantum mechanical procedure. The σ-charge distributions have been calculated using the Del Re method and the π-charges by the Hückel LCAO MO method using the perturbation technique. Agreement with the experimental values is generally good. The calculated bond polarity of the tin–chlorine bond decreases in the order $R_3SnCl > R_2SnCl_2 > RSnCl_3 > SnCl_4$ in accordance with the variation in the nuclear quadrupole coupling constant of chlorine in these molecules. The tin–carbon bond polarity in R_nSnCl_{4-n} type compounds follow the order vinyl > phenyl > methyl > ethyl > n-butyl > tert-butyl as would be expected from the relative electronegativities of the R groups.

In the previous communication[1] it was shown that the heat of atomisation of organotin compounds may be calculated with remarkable accuracy by the Del Re method. As a further test for the applicability of the Del Re method we have used the theoretical σ-charge distributions obtained by this procedure to calculate the electric dipole moments of the organotin compounds. The agreement with the experimental values is remarkably good.

PROCEDURE

Calculation of σ-moments

In the present calculations the σ-charge distributions have been calculated by using the Del Re parameters given in our previous communication[1]. The Del Re parameters for the Sn–H bond, given in Table 1, have been determined from the dipole

TABLE 1

DEL RE PARAMETERS

Bond	$v_{A(B)}$	$v_{B(A)}$	ε_{AB}	$\delta_A{}^0$	$\delta_B{}^0$
Sn–H	0.50	−0.40	0.40	−0.10	0.00

moment of CH_3SnH_3 along with NMR and IR data for organotin hydrides. In our calculation the lengths of Sn–C, C–C, C=C (vinyl), C=C (phenyl), C–H, Sn–Cl and Sn–H bonds are taken to be 2.18 Å, 1.54 Å, 1.35 Å, 1.40 Å, 1.09 Å, 2.37 Å, and 1.70 Å, respectively[2–4], for all the compounds except methyltin chlorides, for which the electron diffraction data[2] have been used. For the tin atom a tetrahedral geometry has been assumed which is consistent with the X-ray and electron diffraction data[2,5,6] where these are available. In the ethyl- and vinyltin compounds, when more than one geometry is possible, the sterically most favoured one has been assumed in the dipole moment calculation. However, the dipole moments of the various configurations are found to differ by less than ± 0.06 D, which is much less than the variation in the reported data.

B. Calculation of π-moments

In the phenyl- and vinyltin compounds it is necessary to calculate the contribution of the π-charge distribution to the dipole moment. In Part I we showed that in the organotin compounds the Coulomb integral of the carbon atom attached to the tin atom is primarily altered, and a general method for calculating the Coulomb integral of this carbon atom was developed[1]. Since the Coulomb parameter "h" for the attached carbon atom has been found to be rather small for all the compounds discussed here, the π-charges may be obtained with very good accuracy by the perturbation technique[7] which gives

$$\Delta q_s = \pi_{s,r} \cdot \Delta \alpha_r$$

where Δq_s is the change in the π-charge at the sth atom due to a change in the Coulomb integral at the rth atom by an amount $\Delta \alpha_r$, and $\pi_{s,r}$ is the atom–atom polarizability, values which have been taken from Coulson and Streitwieser[7]. However, in the case of vinyl compounds the π-charges at the carbon atoms have been calculated directly by solving the appropriate 2×2 secular equation.

RESULTS

The calculated values of the dipole moments of a number of organotin compounds along with the experimental dipole moments are given in Table 2. Allowing for the large variations in the reported dipole moments the agreement between the calculated and the observed values is generally very good.

A very significant feature of the present calculation is the change in the Sn–Cl bond polarity in going from Me_3SnCl to $SnCl_4$. In order to account for the variations in the dipole moment in the series R_3SnCl, R_2SnCl_2, and $RSnCl_3$, Lorberth and Noth[8] and Huang et al.[9] have argued in favour of increase in the Sn–Cl bond polarity with progressive chlorine substitution, although the nuclear quadrupole coupling constants of organotin chlorides[10] indicate a reverse order of the Sn–Cl bond polarity. These apparently contradictory conclusions have been reconciled in our calculations. An examination of the variation in the bond polarities of the various bonds of methyltin chlorides given in Table 3 shows that the Sn–Cl bond polarity decreases from Me_3SnCl to $MeSnCl_3$ as would be expected from the nuclear quadrupole coupling constant data. However, the Sn–C bond polarity also decreases concurrently and, indeed, is reversed in $MeSnCl_3$. Thus, although the Sn–Cl bond moment decreases in the series,

TABLE 2

CALCULATED AND EXPERIMENTAL DIPOLE MOMENTS OF ORGANOTIN COMPOUNDS IN DEBYE UNITS

Compound	Dipole moment		Refs.
	Calcd.	Found	
Me_3SnCl	3.46	3.46–3.52	8, 9, 13
Me_2SnCl_2	4.04	4.14–4.21	8, 9, 13
$MeSnCl_3$	3.63	3.62–3.77	8, 13
Et_3SnCl	3.55	3.44–3.80	9, 14, 15
Et_2SnCl_2	4.14	3.85–4.47	9, 14, 15
$EtSnCl_3$	3.73	4.08	8
Me_3SnH	0.67		
Me_2SnH_2	0.78		
$MeSnH_3$	0.65	0.68	16
Me_3PhSn	0.54	0.51	17
Et_3PhSn	0.50	0.50	18
$EtPh_3Sn$	0.51	0.73	18
Me_3ViSn	0.52	0.45	19
$t-Bu_2SnCl_2$	4.14	4.34	9
Vi_3SnCl	3.05	3.00	9
Vi_2SnCl_2	3.65	4.06	9
$ViSnCl_3$	3.34	3.77	9
Ph_3SnCl	3.01	3.30–3.46	8, 9, 12, 14
Ph_2SnCl_2	3.64	3.59–4.31	8, 9, 12
$PhSnCl_3$	3.39	3.99–4.30	8, 9, 12

TABLE 3

POLARITY (PERCENT) OF DIFFERENT BONDS IN METHYLTIN CHLORIDES

Compound	Sn–Cl	Sn–C	H–C
Me_3SnCl	38.68	10.66	3.30
Me_2SnCl_2	33.79	4.48	3.64
$MeSnCl_3$	28.07	-2.77^a	4.05

^{a} Negative sign indicates reversal of polarity.

TABLE 4

COMPARISON OF CHARGE ON THE CHLORINE ATOM WITH ITS NUCLEAR QUADRUPOLE COUPLING CONSTANT

Compound	Charge on Cl	Coupling const. (MHz)
Bu_2SnCl_2	−0.338	34.6
$BuSnCl_3$	−0.281	43.2
$SnCl_4$	−0.212	48.2

the decrease in the Sn–C bond moment, which acts in the opposite direction, leads to an overall higher dipole moment.

That the calculated bond polarities are essentially correct is also indicated by the data given in Table 4, in which nuclear quadrupole coupling constants of chlorine

in Bu_2SnCl_2, $BuSnCl_3$ and $SnCl_4$ are compared with the calculated charge on the chlorine atom.

A feature which strongly indicates the validity of the Del Re calculations in the study of organotin compounds is the calculated variation in the Sn—C bond polarity in R_nSnCl_{4-n} compounds. Because the electronegativity sequence is phenyl > methyl > ethyl > n-butyl > tert-butyl, it is expected that the Sn—C bond polarity would follow the same order. This is clearly demonstrated by the data given in Table 5.

TABLE 5

VARIATION IN THE TIN—CARBON BOND POLARITY (PERCENT) OF R_nSnCl_{4-n} COMPOUNDS

R	R_3SnCl	R_2SnCl_2	$RSnCl_3$[a]
Vi	13.97	7.95	0.82
Ph	13.82	7.70	0.45
Me	10.66	4.48	−2.77
Et	10.61	4.29	−3.14
Bu	10.58	4.25	−3.19
t-Bu	10.55	4.05	−3.64

[a] Negative sign indicates reversal of polarity.

The Sn—C bond polarities in vinyltin compounds indicates the vinyl group is more electronegative than the phenyl group, which is consistent with the results of cleavage of symmetrical organomercury compounds by HCl[11].

Although the present calculations account for the dipole moments as well as the variation in the bond polarities satisfactorily, in two cases, namely, $PhSnCl_3$ and $ViSnCl_3$, the calculated moments are somewhat low. The high dipole moment of these compounds have been attributed to $d_\pi–p_\pi$ bonding between tin and carbon by Huang et al.[9]. However, the dipole moments of organotin chlorides, particularly those of R_2SnCl_2 and $RSnCl_3$ type compounds, show a strong solvent dependence. For example, the dipole moment of $PhSnCl_3$ varies from 3.99 to 5.81 D depending on the solvent[12], indicating a strong solvent–solute interaction in this case. Because of such large interactions it is not possible to obtain the dipole moment of the free molecule to which our calculation applies. In any case, the dipole moment of phenyltin trichloride in the absence of any interaction would be certainly lower than 3.99 D, which is the value in hexane, since the observed dipole moment increases in solvents like dioxane for which the interaction with the solvent is expected to be greater. It may be noted that comparatively large deviations from the calculated values occur only in such cases. Thus, it appears that the discrepancy between the calculated and the observed dipole moments in such cases is more likely to be due to error in the experimental values rather than to $d_\pi–p_\pi$ bonding. This view is supported by the fact that our calculations satisfactorily account for such diverse properties as heat of atomisation, bond polarities and nuclear quadrupole coupling constants without the need to invoke $d_\pi–p_\pi$ bonding. Further, it will be shown in the subsequent papers that even the chemical shifts, tin—chlorine stretching frequencies, and tin—chlorine distances in organotin chlorides can be accounted for without invoking $d_\pi–p_\pi$ bonding.

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