EVIDENCE FOR σ-π INTERACTION IN SOME ALLYLTIN COMPOUNDS. UV PHOTOELECTRON SPECTROSCOPY AND LCBO CALCULATIONS

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Summary

A series of allyltin compounds, $R_{3-n}Cl_nSnCH_2CH=CH_2$ (R = Me, n-Bu; $n = 0–2$) and $Ph_3SnCH_2CH=CH_2$, have been studied by gas-phase UV photoelectron spectroscopy, in order to determine the extent, if any, of σ-π conjugation (hyperconjugation) between the $\sigma(Sn-CH_2)$ bond and the $\pi(C=C)$ orbital of the allyl group. Analysis of the spectra, supported by a fragment analysis based on LCBO (Linear Combination of Bond Orbitals) calculations, indicated that the hyperconjugation operates for all the members of the series, the extent decreasing on passing from R = Me to R = n-Bu and, within each series, with increasing n.

Introduction

The question of presence and extent of conjugative interaction between $\sigma(Sn-C)$ orbitals and π systems of unsaturated carbon atoms can be effectively studied by means of gas-phase UV photoelectron spectroscopy (UPS), as proved by several investigations of alkyltin derivatives of benzene [1], alkenes [2–4] and alkynes [5]. In allyltin derivatives, where Sn is directly attached to the allyl group, hyperconjugation may occur between the π-type orbital of the allyl moiety and the $\sigma(Sn-C)$ bond responsible for the allyltin linkage:
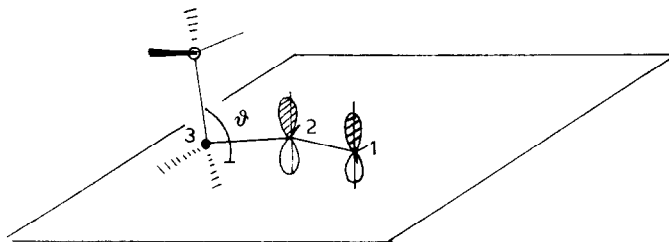
In such molecules the conformation plays a fundamental role in determining the extent of the σ–π interaction, which is related to the value of the dihedral angle between the C(1)–C(2)–C(3) plane and the C(3)–Sn bond. This angle can vary because of the (in principle) free rotation around the C(2)–C(3) bond, and any σ–π conjugation will be at a maximum for ϑ 90° and absent for ϑ 0°. The conformation of the free molecule will therefore be the result of the energy balance between electron repulsion due to the steric hindrance of the substituents on the tin atom and the stabilization due to the σ–π conjugation.

We discuss in this paper the results of a UPS study on the following compounds:

$Me_3SnCH_2CH=CH_2$ (**1**) trimethylallyltin

$Me_2ClSnCH_2CH=CH_2$ (**2**) dimethylchloroallyltin

$MeCl_2SnCH_2CH=CH_2$ (**3**) methyldichloroallyltin

$Bu_3SnCH_2CH=CH_2$ (**4**) tributylallyltin

$Bu_2ClSnCH_2CH=CH_2$ (**5**) dibutylchloroallyltin

$BuCl_2SnCH_2CH=CH_2$ (**6**) butyldichloroallyltin

$Ph_3SnCH_2CH=CH_2$ (**7**) triphenylallyltin

We recorded the He I (21.22 eV) spectra of all the compounds and the He II (40.81 eV) spectra whenever allowed by the low intensity of this radiation. The He I spectra of **1** [3] and **4** [4] were already known, but were redetermined.

The analysis of the spectra of the chlorosubstituted derivatives of these compounds allows us to discuss the influence of the presence of one or two chlorine atoms on the hyperconjugation. From the spectrum of **7** we expected indication of the presence or absence of further interactions with the aromatic π systems. The assignment of the photoelectron spectra and the study of the σ–π interaction were made by fragment analysis supported by LCBO (Linear Combination of Bond Orbitals) calculations [6].

Results and discussion

Methyl derivatives (1–3)

The UP spectra of these compounds, reproduced in Fig. 1, show a series of well-resolved bands in the region between 8 and 13 eV, which are assumed to arise from the ionization of the orbital originally localized on the π system of the allyl group, of the highest σ(Sn–C) orbitals, and of the chlorine atoms (lone pairs, l.p.).

$Me_3SnCH_2CH=CH_2$ (**1**). The fragment analysis for this compound starts form the parent molecules $CH_2=CH_2$ and Me_4Sn, as shown in the correlation diagram of Fig. 2. The details of the building of this diagram on the basis of the results of LCBO calculations are given in Appendix A. The π orbital of the double bond is destabilized relative to that of ethylene owing to the inductive effect of Me_3Sn-CH_2 moiety. We evaluated the shift as ca. 0.8 eV, i.e. an amount similar to that observed on passing from ethylene (IE of $\pi(C=C)^{-1}$ 10.51 eV [7]), to propene (IE 9.69 eV [8]). This implies an evaluation of the inductive effect of a R_3SnCH_2 group of the same order of magnitude as that of Me, as already proposed [1]. The σ(Sn–C) levels, with which the $\pi(C=C)$ orbital may interact, undergo a removal of orbital degeneracy on passing from Me_4Sn to Me_3SnCH_2 fragment $(t_2 \rightarrow a' + a' + a'')$, owing to the
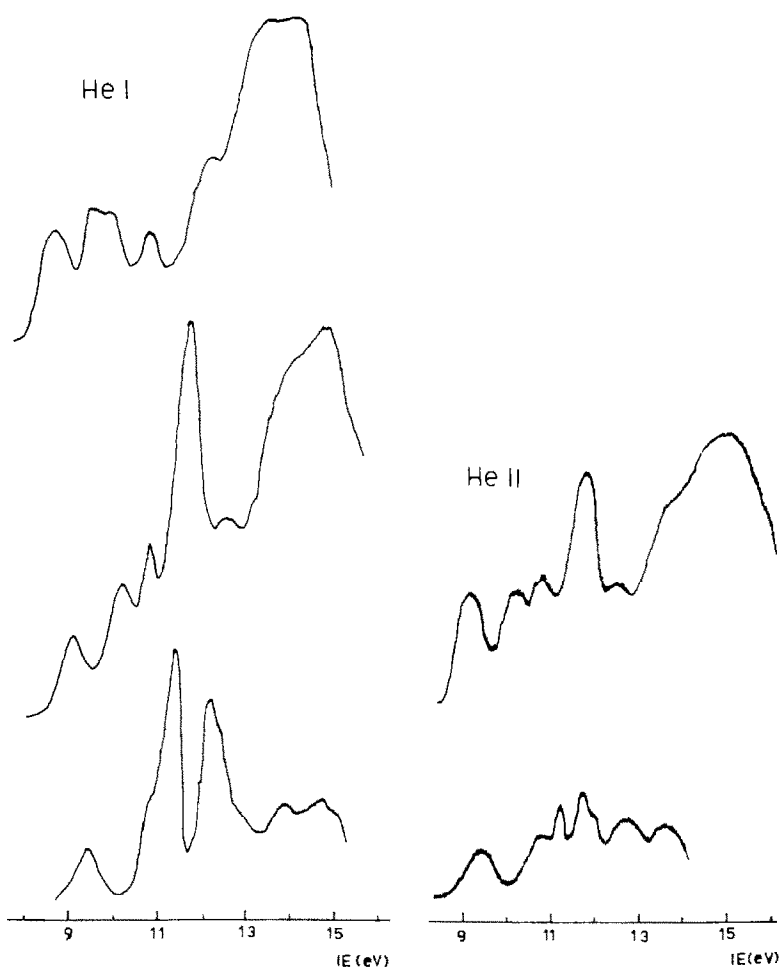
Fig. 1. Gas-phase photoelectron spectra of $Me_{3-n}Cl_nSnCH_2CH=CH_2$ ($n = 0, 1, 2$) (1-3).

symmetry lowering from T_d to C_s point group, followed by a removal of energetic degeneracy, destabilizing the a' orbital which is responsible for the bonding between Sn and the $CH_2CH=CH_2$ group, and is therefore much more sensitive to the electron-donor effect of the $CH=CH_2$ fragment. We estimated this effect at about 0.25 eV, a value suggested by the analysis of the ionization energies of π orbitals in butadiene [9], which may be formally regarded as the product of the fusion of two ethylenic fragments.

The occurrence of conjugation of this a' orbital with the $\pi(C=C)$ level, quite close in energy, would lead to two MOs, one antibonding and one bonding, of mixed character, whose energy separation is calculated by the LCBO method as

$$\Delta E = \left((\Delta E^\circ)^2 + 4\beta^2\right)^{1/2} \tag{1}$$

where ΔE° is the energy difference between the two interacting level and $\beta(\sigma-\pi)$ is the resonance integral. It follows that:

$$\beta(\sigma-\pi) = \left((\Delta E)^2 - (\Delta E^\circ)^2\right)^{1/2}/2 \tag{2}$$
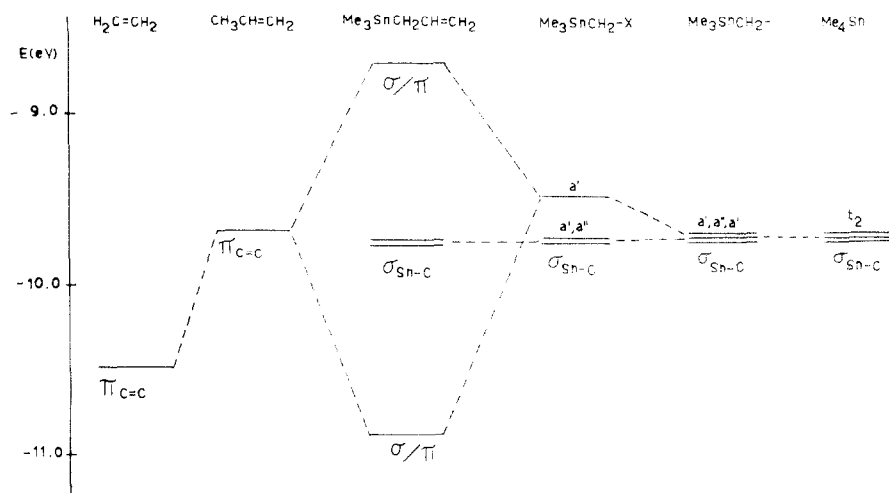
Fig. 2. Correlation diagram for $Me_3SnCH_2CH=CH_2$ (For details of the construction of this diagram see Appendix A).

If such an interaction does occur, and $\beta(\sigma-\pi)$ has a significantly high value, we must expect a sequence of three well-separated energy levels, i.e., in the order of increasing energy, the antibonding $\sigma-\pi$ MO, the two accidentally degenerate $\sigma(Sn-C)$ orbitals $(a' + a'')$, and the bonding $\sigma-\pi$ MO.

The analysis of the UP spectrum of **1** (see Fig. 1) indicates that the value of $\beta(\sigma-\pi)$ is quite large, leading to the appearance of three well-resolved bands, the first and third, at 8.70 and 10.87 eV, respectively, being single and attributable to ionization of the antibonding and bonding $\sigma-\pi$ MOs, and the second one, with a peak at 9.76 eV, broad and clearly double, to the two unperturbed $\sigma(Sn-C)(a' + a'')$ orbitals. From the observed ionization energies, listed in Table 1 along with those for other compounds, use of eq. 2 yields a value for $\beta(\sigma-\pi)$ of 1.08 eV (see Table 2). This value, very close to that found for allyl and benzyl compounds of elements of Group IVA [4], indicates a quite strong hyperconjugative interaction (cf. 1.22 eV for the $\sigma-\pi$ interaction in butadiene [9]).

Me$_2$ClSnCH$_2$CH=CH$_2$ (2). The correlation diagram for this molecule, shown in Fig. 3, was constructed in the same way as that for **1** starting from $CH_2=CH_2$ and

TABLE 1

IONIZATION ENERGIES (eV) IN THE SERIES R$_{3-n}$Cl$_n$SnCH$_2$CH=CH$_2$ (R = Me, n-Bu; $n = 0, 1, 2$ – R = Ph; $n = 0$) [a]

Compound	(σ/π)	$\pi(Ph)$	$\sigma(Sn-C)$	(σ/π)'	i.p. (Cl)
Me$_3$SnCH$_2$CH=CH$_2$ (**1**)	8.70		9.76	10.87	
Me$_2$ClSnCH$_2$CH=CH$_2$ (**2**)	8.95		10.06	10.65	11.46
MeCl$_2$SnCH$_2$CH=CH$_2$ (**3**)	9.33			10.69(s)	11.34 12.11
Bu$_3$SnCH$_2$CH=CH$_2$ (**4**)	8.40		8.95	10.30(s)	
Bu$_2$ClSnCH$_2$CH=CH$_2$ (**5**)	8.63		8.95	10.25	
BuCl$_2$SnCH$_2$CH=CH$_2$ (**6**)	9.24			10.42	
Ph$_3$SnCH$_2$CH=CH$_2$ (**7**)	8.33(s)	8.97	9.53(s)	10.63	

[a] (s): shoulders.

TABLE 2

RESONANCE INTEGRALS FOR σ/π INTERACTION ($\beta(\sigma/\pi)$) IN THE SERIES $R_{3-n}Cl_nSnCH_2$-$CH=CH_2$ (R = Me, n-Bu; $n = 0, 1, 2$)

Compound	E° of interacting levels (eV)		ΔE° (eV)	E (eV)		ΔE (eV)	β (eV)
	σ(Sn–C)	π(C=C)		$(\sigma/\pi)^+$	$(\sigma/\pi)^-$		
$Me_3SnCH_2CH=CH_2$ (1)	– 9.50	– 9.70	0.2	– 10.87	– 8.70	2.17	1.08
$Me_2ClSnCH_2CH=CH_2$ (2)	– 9.83	– 9.70	0.13	– 10.65	– 8.95	1.70	0.85
$MeCl_2SnCH_2CH=CH_2$ (3)	– 10.30	– 9.70	0.60	– 10.69	– 9.33	1.36	0.61
$Bu_3SnCH_2CH=CH_2$ (4)	– 8.95	– 9.70	0.75	– 10.30	– 8.40	1.90	0.87
$Bu_2ClSnCH_2CH=CH_2$ (5)	– 8.95 [a]	– 9.70	0.75	– 10.25	– 8.63	1.62	0.72
$BuCl_2SnCH_2CH=CH_2$ (6)	– 9.53 [b]	– 9.70	0.17	– 10.42	– 9.24	1.18	0.58

[a] From the IE of unperturbed σ(Sn–C) orbital (see text). [b] From the IE of σ(Sn–C) (a'') orbital in Bu_2SnCl_2 [18] (see text).

Me_3ClSn, whose UP spectrum was already known [10]. For the sake of simplicity, we assumed that no significant mixing of σ(Sn–C) and σ(Sn–Cl) orbitals occurs. Again we judged the inductive effect of the $Me_2ClSnCH_2$ group on the π(C=C) orbital to be similar to that of a methyl group — the electron-withdrawing Cl may be regarded, to a first approximation, as having no influence on such a distant orbital. (The details of the construction of the correlation diagram are given in Appendix A.) In this case the low IE region of the UP spectrum shows three bands of roughly the same intensity which are related to the MOs of the allyltin moiety, i.e. the two σ–π orbitals (IE 8.95 and 10.65 eV) and the unperturbed σ(Sn–C) (IE 10.06 eV, see Fig. 1 and Table 1). Thus in this case, again, the phenomenon of the σ–π conjugation is observed.

The $\beta(\sigma$–$\pi)$ value obtained from the experimental data is 0.85 eV (see Table 2), lower than that in 1. The fourth band, at 11.46 eV, refers to the ionization of the
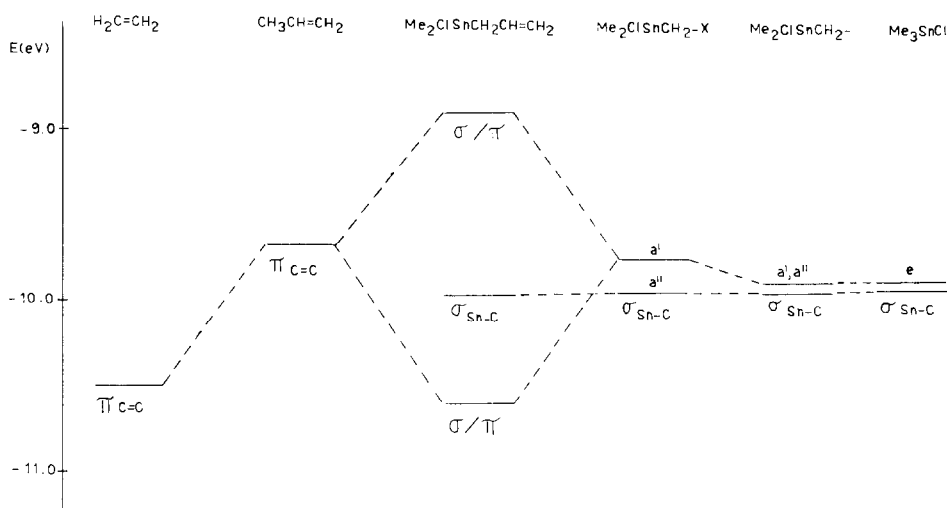

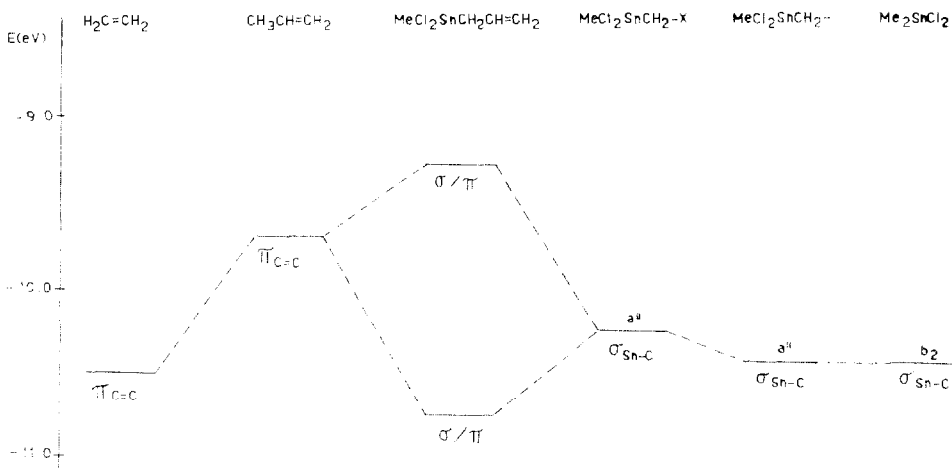Fig. 3. Correlation diagram for $Me_2ClSnCH_2CH=CH_2$ (For details of the construction of this diagram see Appendix A).

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Fig. 4. Correlation diagram for $MeCl_2SnCH_2CH=CH_2$ (For details of the construction of this diagram see Appendix A).

two chlorine lone pairs (IE in Me_3SnCl 11.31 eV [10]), as confirmed by the dramatic decrease in relative intensity on going from He I to He II ionizing radiation.

MeCl₂SnCH₂CH=CH₂ (3). Hyperconjugation also operates in this molecule, for which the correlation diagram, constructed by starting from Me_3SnCl_2 and $CH_2=CH_2$, is shown in Fig. 4. (For details see Appendix A). In this case, only one $\sigma(Sn-C)$ orbital falls in the low ionization energy region, so we expect the photoelectron spectrum to show two bands, arising from the antibonding and bonding linear combination respectively of this orbital with the $\pi(C=C)$ orbital. The experimental IE values, 9.33 and 10.69 eV (see Fig. 1 and Table 1) allow us to assign a value of 0.61 eV to the $\beta(\sigma-\pi)$ integral (see Table 2). The chlorine lone pairs ionization gives rise to two bands, at 11.34 and 12.11 eV.

In general for this series of molecules, the extent of hyperconjugation, which always operates, is not much smaller than that of a pure $\pi-\pi$ conjugation, and decreases regularly on passing from the trimethyl to the monomethyl derivative.

Butyl derivatives (4–6)

The spectra of these compounds are shown in Fig. 5, and the ionization energies are listed in Table 1.

The substitution of methyl by butyl groups leads to a destabilization of the $\sigma(Sn-C)$ levels (see the accidentally degenerate a'', a', a' orbitals in Bu_4Sn ionizing at 8.7 eV [2] compared with the t_{2g} orbital in Me_4Sn ionizing at 9.70 eV [11]), whilst the $\pi(C=C)$ orbital remains almost unchanged because the alkyl groups are so remote. As a consequence, the energy difference between the levels involved in $\sigma-\pi$ conjugation is greater in the butyl than in the methyl derivatives, and thus a smaller perturbation in terms of energy position is to be expected.

Bu₃SnCH₂CH=CH₂ (4). Comparative analysis of the spectra of this molecule (see Fig. 5 and Table 1) and its methyl analogue (**1**) clearly indicates that hyperconjugation is less important in **4** than in **1**. The experimental IEs yield a value for $\beta(\sigma-\pi)$ of 0.87 eV (see Table 2), smaller than that for **1** (1.08 eV). This, along with a
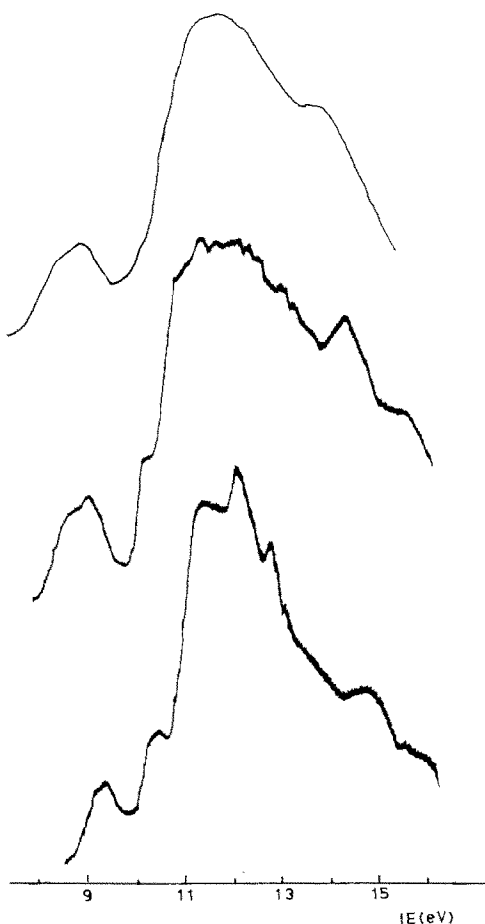
Fig. 5. Gas-phase photoelectron spectra of $Bu_{3-n}Cl_nSnCH_2CH{=}CH_2$ $(n = 0, 1, 2)$ (4–6).

ΔE° larger in **4** and with the absence of further inductive destabilization of the $\sigma(Sn\text{–}CH_2)$ bond by introduction of a $CH{=}CH_2$ in place of a n-propyl group, leads to a smaller splitting between the unperturbed $\sigma(Sn\text{–}C)$ orbitals and the antibonding $\sigma\text{–}\pi$ MO. The corresponding photoelectron bands are not clearly resolved.

Bu$_2$ClSnCH$_2$CH=CH$_2$ (5). The photoelectron spectrum of this compound (see Fig. 5) is analogous to that for **2** showing a set of three single bands between 8 and 10.5 eV, the only difference being the partial overlap of the first two bands. This triplet reflects a sequence of MOs resulting from $\sigma\text{–}\pi$ conjugation, which is weaker for **5** than for **2** ($\beta(\sigma\text{–}\pi)$ 0.72 eV, see Table 2). The chlorine lone pairs and $\sigma(Sn\text{–}Cl)$ ionizations contribute to the subsequent envelope of unresolved bands.

BuCl$_2$SnCH$_2$CH=CH$_2$ (6). The two bands displayed by the spectrum of this molecule (see Fig. 5 and Table 1) correspond to the antibonding and bonding $\sigma\text{–}\pi$ MOs, whose IEs suggest a value of 0.58 eV for $\beta(\sigma\text{–}\pi)$ (see Table 2).

The analysis of the results for the two series of allyltin compounds reveals the following features:
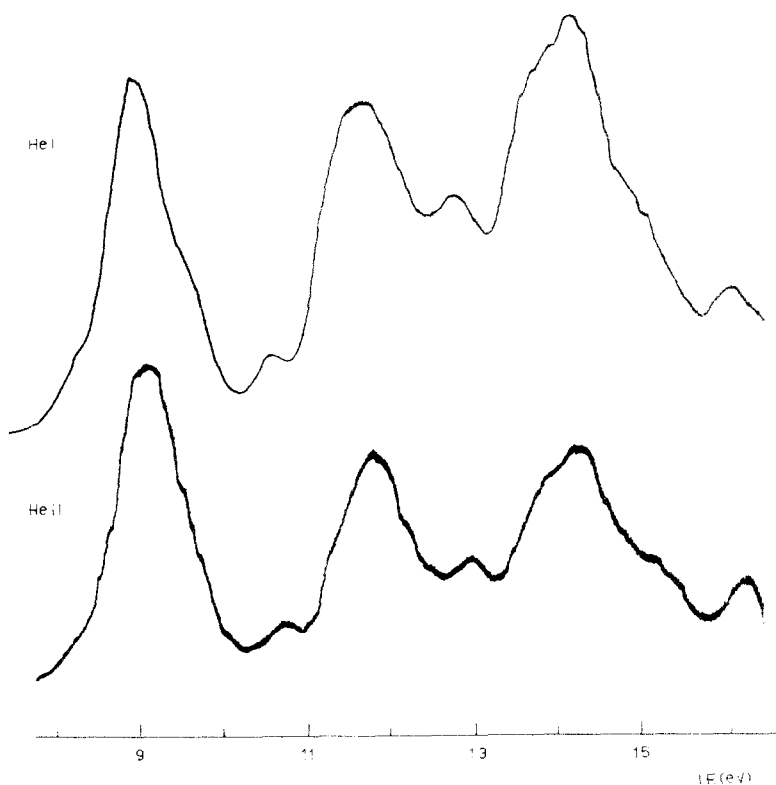
Fig. 6. Gas-phase photoelectron spectra of $Ph_3SnCH_2CH=CH_2$ (7).

i . In all the compounds of both series there is significant conjugation between the $\pi(C=C)$ orbital and the $\sigma(Sn-CH_2)$ bond.

ii . On going from the methyl derivatives to the butyl analogues, the extent of the conjugation decreases, the decrease being marked from **1** to **4** ($\Delta\beta(\sigma-\pi)$ 0.21 eV) and smaller from **2** to **5** ($\Delta\beta(\sigma-\pi)$ 0.13 eV) and from **3** to **6** ($\Delta\beta(\sigma-\pi)$ 0.03 eV). The hyperconjugation is probably less important in the butyl derivatives because of a deviation of the angle ϑ from 90°, owing to the greater bulk of the butyl groups.

iii. Within each series the extent of $\sigma-\pi$ conjugation falls, upon substitution of the alkyl groups by chlorine atoms. This can be attributed to a decrease in the $\beta(\sigma-\pi)$ value as a result of mixing of p atomic orbitals of chlorine with the function involved in the hyperconjugation.

The phenyl derivative

$Ph_3SnCH_2CH=CH_2$ (7). The photoelectron spectrum of this molecule (see Fig. 6 and Table 1) is more complex than that of the other compounds owing to the presence of ionizations of phenyl-based orbitals. The intense band centered at 8.97 eV mainly arises from the ionization of the highest π orbitals of the phenyl rings (e_{1g} in benzene, IE 9.25 eV [12]). The shift of this band to lower IE with respect to benzene is due to inductive effects. The fact that no splitting is observed indicates that there is no appreciable interaction of the phenyl rings, either with each other, or

with the allyltin moiety. (It has previously been shown that there is no significant interaction between the aromatic systems in the compounds Ph_2MH (M = Si, Ge, Sn) [13].) The two shoulders on both sides of the main band, at 8.33 and 9.53 eV, along with the single band at 10.63 eV, resemble the system of three bands in the spectrum of 1, reflecting significant $\sigma-\pi$ interaction. The detailed assignment is given in Table 1.

This interpretation of the electronic structure of 7 is consistent with the crystal structure of this compound determined by Ganis et al. [14], which indicated a paddle-wheel conformation for the system of the three phenyl groups, preventing any interaction of the orbital both with each other and with the $\sigma(Sn-CH_2)$ bond. The authors suggested the presence of significant hyperconjugation both in this compound and in the butyl derivatives [14] on the basis of the structural and IR [15–18] data.

Experimental

$Me_3SnCH_2CH=CH_2$ (1) was prepared as described by Petrov et al. [22].

$Me_2ClSnCH_2CH=CH_2$ (2) was prepared by exchange between $Me_2Sn(CH_2-CH=CH_2)_2$ [23] and Me_2SnCl_2. Thus a mixture of 15 g of $Me_2Sn(CH_2CH=CH_2)_2$ and 14.3 g of Me_2Cl_2Sn was stirred at room temperature for 24 h, then distilled under vacuum to give 25 g of pure $Me_2ClSnCH_2CH=CH_2$ (yield 85%), b.p. 84–85°C/21 mmHg.

$MeCl_2SnCH_2CH=CH_2$ (3) was prepared by an exchange reaction between $MeSn(CH_2CH=CH_2)_3$ [24] and $MeSnCl_3$.

$Bu_3SnCH_2CH=CH_2$ (4) was prepared by a published method [25–27], as were $Bu_2ClSnCH_2CH=CH_2$ (5) [28–29], $BuCl_2SnCH_2CH=CH_2$ (6) [30], and $Ph_3SnCH_2CH=CH_2$ (7) [31].

The gas-phase photoelectron spectra were recorded with a Perkin–Elmer PS 18 spectrometer equipped with a dual He I/He II lamp (Helectros Development). The spectra of the liquid samples were recorded at room temperature, and those of the solid at temperatures of 27–103°C.

Appendix A

Building of the correlation diagrams

$Me_3SnCH_2CH=CH_2$ (1). In Me_4Sn the four $\sigma(Sn-C)$ MOs may be regarded as the result of the interaction of four localized degenerate orbitals, transforming on T_d symmetry as $t_2 + a_1$. The energy value α of these orbitals can be readily evaluated from the photoelectron spectrum [16] as -11.19 eV in the framework of Koopmans' theorem [17]. The resonance integral β between these orthonormalized functions (φ_i) is calculated as -1.44 eV from the expression

$$E(a_1) = \alpha + 3\beta \quad (E(a_1) = -15.5 \text{ eV } [16])$$

where

$$\psi(a_1) = 1/2(\varphi_1 + \varphi_2 + \varphi_3 + \varphi_4)$$

On passing from Me_4Sn to the Me_3SnCH_2 fragment the symmetry lowering ($T_d \rightarrow C_s$) does not remove the energetic degeneracy of the t_2 orbitals, if we assume,

at the first stage of the perturbation, that α and β do not change. From a simple treatment it follows that

$$E_1(a') = E_2(a') = E_3(a'') = \alpha - \beta$$

$$E_4(a') = \alpha + 3\beta$$

The MOs of Me_3SnCH_2X (before hyperconjugation) were obtained by interaction of three localized functions of energy α and one of energy $\alpha + \delta$, where δ is the shift due to the inductive effect of the $CH=CH_2$ groups (δ was evaluated as $+0.25$ eV, see text). The resonance integral β was assumed to be unchanged. The resulting orbital energies were:

$$E_1^\circ(a') = \alpha + \delta - \beta = -9.50 \text{ eV}$$

$$E_2^\circ(a') = E_3^\circ(a'') = \alpha - \beta = -9.75 \text{ eV}$$

$$E_4^\circ(a') = \alpha + 3\beta = -15.5 \text{ eV}$$

$Me_3ClSnCH_2CH=CH_2$ (2). The photoelectron spectrum of Me_3SnCl [10] allows us to evaluate the α and β values of the three localized $\sigma(Sn-C)$ orbitals, transforming as $a' + e$ in C_{3v} symmetry: α -11.75 eV and β -1.75 eV.

On going from Me_3SnCl to $Me_2ClSnCH_2$ (C_s point group) the e orbital loses its degeneracy, although it is not split into two energy levels. In fact, the solution of simple secular determinant gives the following energy values:

$$E_1(a') = \alpha + 2\beta$$

$$E_2(a') = E_3(a'') = \alpha - \beta$$

By interaction of two localized functions of energy α and one of energy $\alpha + \delta$ we obtained the MOs' sequence for $Me_2ClSnCH_2X$ before hyperconjugation

$$E_1^\circ(a') = \alpha + \delta - \beta = -9.83 \text{ eV}$$

$$E_2^\circ(a'') = \alpha - \beta = -10.0 \text{ eV}$$

$$E_3^\circ(a') = \alpha + 2\beta = -15.17 \text{ eV}$$

$MeCl_2SnCH_2CH=CH_2$ (3). In Me_2Cl_2Sn (C_{2v}) the two localized $\sigma(Sn-C)$ orbitals give rise to the MOs ionizing at 10.43 (b_2) and 14.30 (a_1) eV [10,18]. From these IEs one can calculate for the $\sigma(Sn-C)$ functions in this molecule the values: α -12.36 eV and β -1.93 eV.

The MOs of $MeCl_2SnCH_2X$ before hyperconjugation were the result of the interaction between the unperturbed $\sigma(Sn-C)$ function ($E = \alpha$) and the $\sigma(Sn-C)$ orbital affected by the inductive effect of the $CH=CH_2$ moiety ($E = \alpha + \beta$). The two obtained levels had the energies:

$$E_1^\circ(a'') = \left(2\alpha + \delta + (\delta^2 + 4\beta^2)^{1/2}\right)/2 = -10.30 \text{ eV}$$

$$E_2^\circ(a') = \left(2\alpha + \delta - (\delta^2 + 4\beta^2)^{1/2}\right)/2 = -14.16 \text{ eV}$$

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