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THE ELECTRONIC STRUCTURE OF SOME ALKYL—TIN DERIVATIVES WITH SULPHUR-CONTAINING LIGANDS STUDIED BY UV PHOTOELECTRON SPECTROSCOPY

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Summary

HeI and HeII photoelectron spectra (UPS) of the following compounds are reported and discussed: $R_3Sn(S_2CNR'_2)$ (R, R' = CH_3, C_2H_5) (trialkyltin *N*,*N*-dialkyldithiocarbamates), $R_2Sn(S_2CNR'_2)_2$ (R = CH_3, n-C_4H_9, R' = CH_3) (dialkyltin bis-*N*,*N*-dimethyldithiocarbamates), R_2PS_2R (R = C_2H_5) (ethyldiethyldithiophosphinate), $R_3Sn(S_2PR'_2)$ (R, R' = CH_3) (trimethyltin dimethyldithiophosphinate), $R_2Sn(S_2PR'_2)_2$ (R = CH_3, n-C_4H_9, R' = C_2H_5) (dialkyltin bis-diethyldithiophosphinates).

The assignments are made by comparison with UP spectra of related molecules and the results of CNDO/2 calculations. A scheme for the energy levels of the valence shells is proposed.

Introduction

In extension of our earlier studies on alkyl—tin derivatives [1] and on transition-metal complexes with sulphur-containing ligands [2—5], by gas-phase UV photoelectron spectroscopy (UPS), we have investigated by the same technique some dialkyl- and trialkyl-tin *N*,*N*-dialkyldithiocarbamates and some dialkyl- and trialkyl-tin dialkyldithiophosphinates. These compounds have been extensively studied by other spectroscopic techniques [6—14]; the analysis of the photoelectron spectra may give further information about their electronic structures and bonding, and possibly help to clarify the structures of some of these compounds.

Both HeI (21.22 eV) and HeII (40.81 eV) ionizing radiations were used, since the relative intensity variations of the bands observed in the spectra induced by these sources can be used as instrumental aids.

To aid in the interpretation of the spectra of the compounds mentioned, we looked also at the UP spectra of simple molecules related to the free ligands, namely the corresponding alkyl esters; data for the dimethyldithiocarbamates were reported by Guimon et al [15], the spectrum and the ethyldiethyldithiophosphinate was determined in the present work.

The assignments were made by comparison with the UP spectra of related compounds and by correlation with CNDO/2 calculations performed on the free anions.

Results and discussion

The spectra are shown in the Figs. 2 and 3 and the measured ionization energies are reported in Tables 1 and 2.

Trialkyltin dialkyldithiocarbamates

The following compounds studied were $(CH_3)_3SnS_2CN(CH_3)_2$ (trimethyltin *N,N*-dimethyldithiocarbamate) (I) and $(C_2H_5)_3SnS_2CN(C_2H_5)_2$ (triethyltin *N,N*-diethyldithiocarbamate) (II).

The structure of I has been studied in the solid state and in solution [9,10] by X-ray diffraction, NMR and by Mössbauer spectroscopy, but the results are slightly ambiguous, and do not definitively establish whether the ligand is present in a mono- or a bidentate form; the structure determined by X-ray diffraction [9] shows short but different distances between the tin and the two sulphur atoms, which are halfway between tetra- and a pentacoordination to the central metal. The vapour-phase structure is unknown.

For the interpretation of the spectrum of I we started from the analysis of the UP spectrum of the methyl-*N,N*-dimethyldithiocarbamate by Guimon et al [15], which in the I.E. region, 8—9.5 eV, shows bands arising from (in order of increasing I.E.), (a) the in-plane non-bonding orbital centered on the thionic sulphur (sulphur lone pair); (b) a π-type orbital mainly centered on the C=S group; (c) a π-type orbital mainly centered on the $C—S—CH_3$ group, with contributions from the nitrogen atom. This assignment is supported by CNDO-type calculations, which however exaggerate the difference between the second and third highest energy levels.

Assuming, as a first approximation, that in I the ligand is bidentate, we would expect that in the complex the ligand-based energy levels would be of a different composition and order than in the ester, and might be correlated with those in the free anion $[S_2CN(CH_3)_2]^-$. We therefore performed CNDO/2 calculations both on the ester and on the anion, obtaining results for the former which are in agreement with those given in ref. 15.

A semiquantitative representation of the computed composition of the highest orbitals of the free anion is given in Fig. 1, the orbital energy ordering being: $n_- > \pi_3 > n_+ > \pi_2$. The n_- and n_+ levels are expected to be lowered in energy by coordination much more than π_3 and π_2, so that the relative energy ordering is probably changed in the complexes.

The UP spectrum of I (Fig. 2 and Table 1) shows a group of four well resolved bands between ca. 7.5 and 12 eV, followed by a broad unresolved envelope centered at ca. 13.5 eV. In the first region the spectral patterns are due to ionizations of the previously mentioned ligand-based orbitals and of

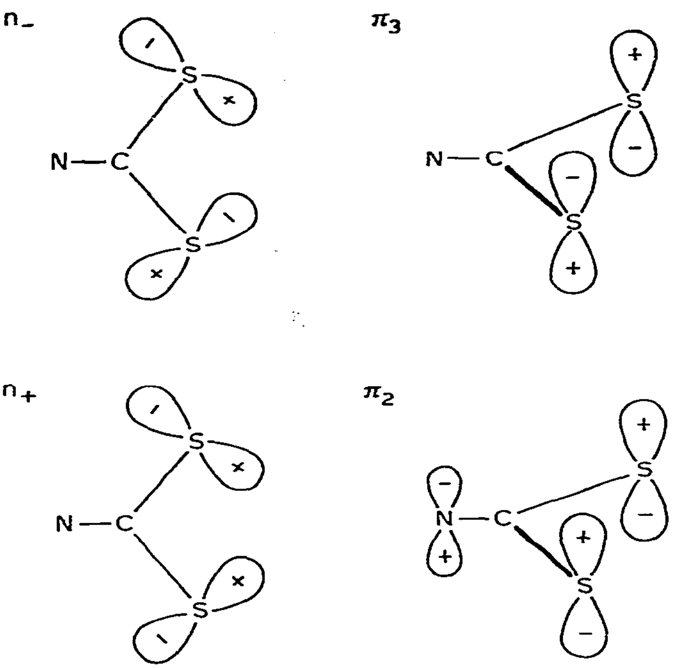

Fig. 1. MOs' predominant composition for highest levels of $[S_2CN(CH_3)_2]^-$.

electrons mainly localised on σ-Sn—C bonds. All these ionizations are likely to be from single levels due to the low molecular symmetry. Compared with the HeI spectrum, the HeII spectrum shows a strong relative decrease in intensity of the first band at 8.10 eV (with a shoulder at 7.86 eV) compared with the second one, at 8.74 eV, while the third band, at 9.82 eV, becomes more intense than both the other two bands. It is known [16,17] that orbitals with a predominant sulphur 3*p* contribution have a relative ionization cross section much smaller for HeII than for HeI radiation with respect to carbon 2*p* orbitals, whilst the valence shell tin orbitals show similar behaviour, but to a much smaller extent [18].

We thus attribute the bands whose intensity decreases on passing from the HeI to the HeII spectrum to ionizations of orbitals mainly localised on sulphur atoms. More precisely, the first double band may be associated with both π_3 and π_2 orbitals, which are relatively little involved in bonding to the central

TABLE 1

VERTICAL IONIZATION ENERGIES FOR SOME DITHIOCARBAMATES

Compounds	Ionization energies (eV) [a]						
$(CH_3)_3SnS_2CN(CH_3)_2$	(7.86)	8.10	8.74	(9.54)		9.82	11.76
$(C_2H_5)_3SnS_2CN(C_2H_5)_2$	(7.46)	7.94	8.30	8.78	9.06	9.50	11.26
$(CH_3)_2Sn[S_2CN(CH_3)_2]_2$	(7.70)	7.97	8.53	9.37		9.92	11.76
$(C_4H_9)_2Sn[S_2CN(CH_3)_2]_2$	(8.01)		8.26	9.18		9.69	

[a] Shoulders in parentheses.

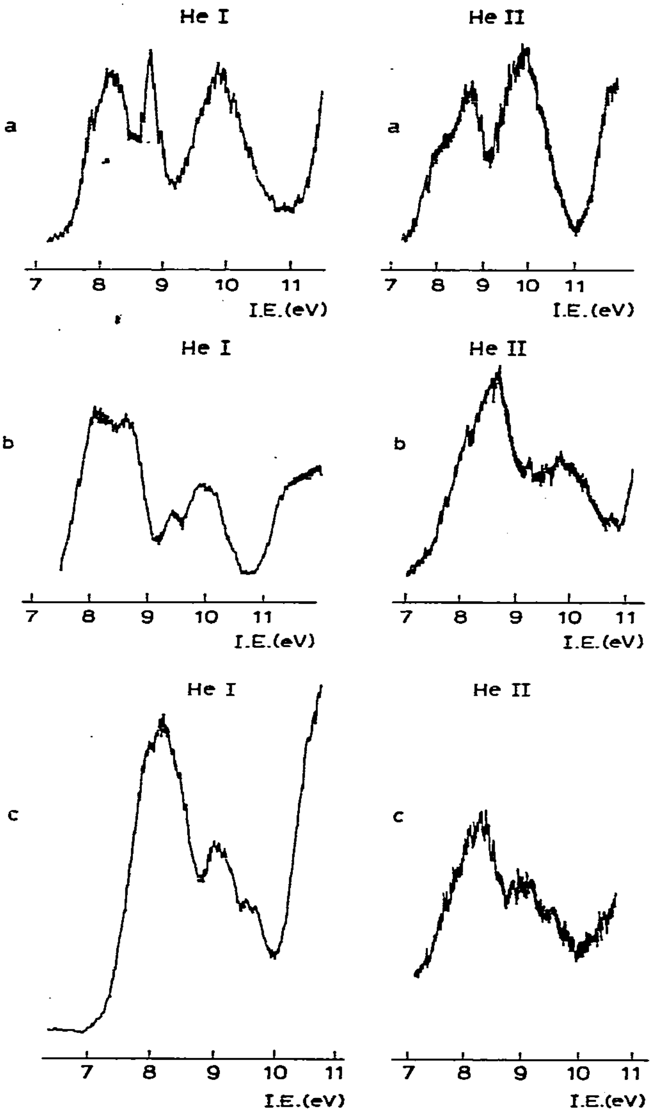

Fig. 2. HeI and HeII gas-phase UP spectra of: a) trimethyltin dimethyldithiocarbamate; b) dimethyltin bis(dimethyldithiocarbamate); c) di-n-butyltin bis(dimethyldithiocarbamate).

metal, and therefore keep their compositions substantially unchanged with respect to the free anion; the second, single band is likely to arise from ionization of the n_- orbital, now σ-bonding with the tin atom. The n_+ (σ Sn—S) ionization contributes probably to the third broad band, which accounts also for two nearly degenerate σ Sn—C orbitals. The intensity ratio between the first three bands in the HeI spectrum is satisfactorily consistent with the proposed assignments.

The assignment of the band at 9.82 eV to two σ Sn—C ionizations is supported also by comparison with data for other trialkyltin compounds, viz.

10.70 eV in $(CH_3)_3SnOCH_3$ and 10.72 eV in $(CH_3)_3Sn(acac)$ [1]; the shift to lower I.E. in I is then attributed to the presence of the less electronegative sulphur instead of the oxygen atom.

An alternative assignment must be made if the ligand is assumed to be monodentate in the complex. In this case the bonding of the two sulphur atoms would be similar to that in the methyl ester, and the UP spectrum would be interpreted by relating the band at 8.10 eV (sh 7.86 eV) to the band at 8.23 eV (sh 8.01 eV) of the ester [15] and assigning it to both n and π ionizations of the thionic sulphur, while the band at 8.74 eV (8.97 eV in the ester) would arise from a π-type orbital extending over the N—C—S skeleton, with the main contribution from the sulphur 3p orbital. The band at 9.82 eV, with no counterpart in the ester, would be then associated with the single σ Sn—S plus two σ Sn—C bonds. However, this interpretation scheme is less consistent with the HeII data than the former (Fig. 2), since it is difficult to account for large differences in intensity changes for HeII radiation such as those observed for the first two bands, if the ionizations are from orbitals with similar sulphur 3p contributions. Furthermore, the behaviour of the first two bands of the ester on passing from HeI to HeII radiation [19] is very different from that of the complex: thus in the former compound the relative intensities remain roughly unchanged, confirming a similar composition (mainly sulphur 3p) of the orbitals involved in the first two ionizations. In the complex, in contrast, the decrease in intensity of the first band with HeII suggests a contribution of tin orbitals to the second ionization in line with the first interpretation scheme, and so with a bidentate form of the ligand in the complex.

The band at 11.76 eV arises from a σ-type orbital of the S—C—S group. The broad envelope beyond 12 eV contains many overlapping bands related to other σ-type orbitals (included the third σ Sn—C) and to the third π-type orbital, with predominant contribution from the nitrogen atom.

The UP spectrum of II (Table 1) is very similar to 1, the main difference consisting in the shift of all bands to lower I.E. values due to the larger electron-releasing ability of the ethyl with respect to the methyl groups.

Dialkyltin bis-dialkyldithiocarbamates

The compounds examined were: $(CH_3)_2Sn[S_2CN(CH_3)_2]_2$ (dimethyltin bis-(*N,N*-dimethyldithiocarbamate)) (III) and $(C_4H_9)_2Sn[S_2CN(CH_3)_2]_2$ (di-n-butyltin bis(*N,N*-dimethyldithiocarbamate)) (IV).

There are ambiguities about the coordination form of the ligands for these compounds (8, 10—13). Two alternative assignments of the spectra can therefore be proposed as for in the cases above. The HeI spectrum of III (Fig. 2 and Table 1) in the I.E. region below 11 eV shows four bands, less separated than in I, consistent with the presence of two instead of one ligand groups and therefore of a double number of ligand-based ionized orbitals.

On the assumption of a distorted octahedral *trans*-configuration (implying the bidentate ligand form) the following assignment is proposed: the first band, with maximum at 7.97 eV and a shoulder at 7.70 eV, arises from ionization of the π_3 and π_2 orbitals of the dithiocarbamate groups, which seem to interact only weakly with each other, not generating separated components. The second band, at 8.53 eV, is associated with both n_- (σ Sn—S) orbitals, while the n_+

(σ Sn—S) ionizations fall in the fourth broad band centered at 9.92 eV. The third band, at 9.37 eV, with intensity about one half of the fourth, is probably related to the ionization of one of the two σ Sn—C bonds, the other lying beyond 11 eV and being masked by other ionizations. This assignment is supported by the HeII spectrum (Fig. 2), which shows a strong relative decrease in intensity of the first band, arising from orbitals mainly localised on the sulphur atoms, with respect to the second, related to orbitals with a contribution from the tin atom. Furthermore, the third band, assigned as σ Sn—C ionization, increases in intensity relatively to the fourth, which is consistent with the smaller decrease of ionization cross section for the tin than for the sulphur orbitals on passing from HeI to HeII radiation. Again, the HeII data support the hypothesis of a bidentate form of the ligand in the complex.

The 9.37 eV I.E. value assigned to the ionization of one σ Sn—C bond is the lowest so far found in UP spectra of alkyltin complexes [1,18]; this could be explained by the low electronegativity of the sulphur atoms, which induces a larger electron density in the Sn—C bonds. This value is also lower than the corresponding I.E. value for [I]: a similar difference was observed between dimethyltin bis(acetylacetonate) and trimethyltin acetylacetonate [1].

The HeI spectrum of IV (Fig. 2 and Table 1) shows some differences from that of III: the first two bands are closer than in III, and the intensity ratio between the third and the fourth band is reversed (ca. 2 : 1 in IV). Furthermore, all bands in IV are shifted to lower I.E. values, as an obvious consequence of the presence of two n-butyl groups in place of two methyl groups.

The behaviour on passing from HeI to HeII radiation is similar in the two compounds for the first two bands (7.97 and 8.53 eV in III, 8.01 and 8.26 eV in IV), whereas in IV the intensity ratio between the third (9.18 eV) and the fourth band (9.69 eV) remains substantially unchanged, in contrast with the situation for III.

The smaller separation between the first two bands in IV than in III can be explained by the larger influence of the different inductive effect of n-butyl and methyl groups on n_- (σ Sn—S) than on π_3 and π_2 orbitals.

The same effect may account for the different intensity ratio between the third and the fourth band in the two compounds (9.37 and 9.92 eV in III, 9.18 and 9.69 eV in IV); in the latter compound the third band proably arises from the ionization of one σ Sn—S and one σ Sn—C bond, while the fourth band arises from to the other σ Sn—S ionization.

Ethyldiethyldithiophosphinate

Compound V, $(C_2H_5)_2PS_2C_2H_5$ (ethyldiethyldithiophosphinate) has a pseudo-tetrahedral structure unlike the methyl-*N*,*N*-dimethyldithiocarbamate, which is planar. Despite this and the different chemical environment of the sulphur atoms in the two compounds (in the dithiocarbamate a more delocalised π system is present, with contribution from the nitrogen), the spectral patterns in the low I.E.s region are similar. This suggests an analogous composition of the highest MOs in the two esters, with predominant sulphur 3*p* contribution. We therefore assign the first band of V, at 8.68 eV, to the ionization of the π and n lone pairs of the unesterified sulphur and the second band, at 9.17 eV, to the π orbital of the esterified sulphur.

A more careful comparison of the spectra of these esters reveals some differences, however. The first band in the spectrum of V is narrower and more intense relative to the second than the corresponding band (8.01 (sh), 8.23 eV) in the spectrum of the dithiocarbamate, and both the first two bands are shifted in V to higher I.E.s.

These effects are satisfactorily reproduced by the CNDO/2 calculations on the methyl esters, and are not easily explained in chemical terms; on the other hand, the different structures of the two compounds precludes direct comparisons between all the orbital energy values. Furthermore, relaxation phenomena, probably stronger in the dithiocarbamate because of the presence of a largely delocalised π system, cannot be neglected.

Trimethyltin dimethyldithiophosphinate

The structure of $(CH_3)_3SnS_2P(CH_3)_2$ (trimethyltin dimethyldithiocarbamate) (VI) is likely to be a distorted trigonal bipyramid with both sulphur atoms

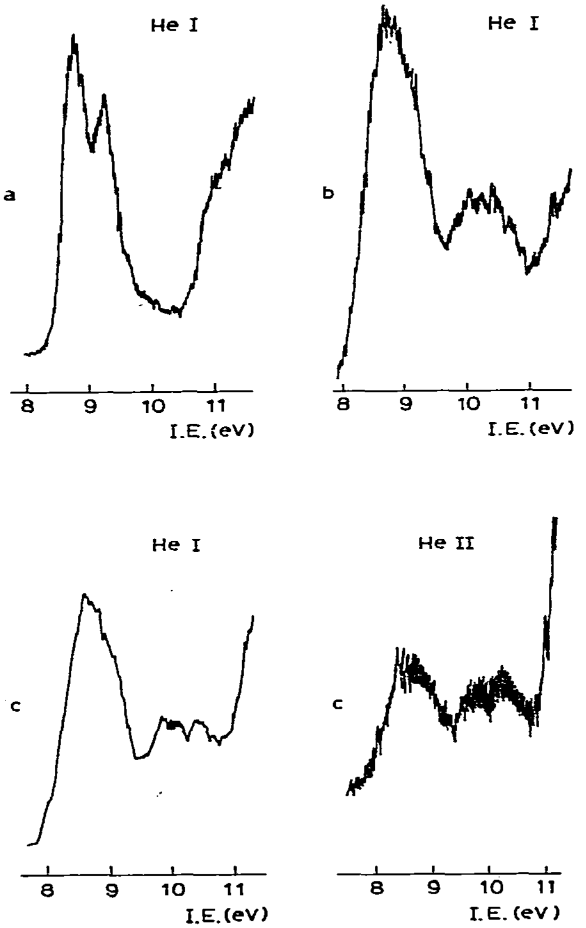

Fig. 3. HeI gas-phase UP spectra of: a) ethyldiethyldithiophosphinate; b) trimethyltin dimethyldithiophosphinate; HeI and HeII gas-phase UP spectra of c) dimethyltin bis(diethyldithiophosphinate).

TABLE 2

VERTICAL IONIZATION ENERGIES FOR SOME DITHIOPHOSPHINATES

Compounds	Ionization energies (Ev) [a]			
$C_2H_5S_2P(C_2H_5)_2$		8.68	9.17	10.98
$(CH_3)_3SnS_2P(CH_3)_2$		8.60	(9.09) 9.95	10.32
$(CH_3)_2Sn[S_2P(C_2H_5)_2]_2$	(8.34)	8.58 (8.79)	9.66	10.24
$(C_4H_9)_2Sn[S_2P(C_2H_5)_2]_2$		8.35		9.54

[a] shoulders in parenthesis.

bonded to tin, by analogy with other known dithiophosphinates [6].

The U.P. spectrum (Fig. 3 and Table 2) shows two broad bands in the low I.E. region, the first centered at 8.60 eV, and the second with two maxima at 9.92 and 10.32 eV, the first one being much more intense than the second. The CNDO/2 calculations performed on the free anion predict the following ordering of M.O. energy levels:

$$n_- > \pi_2 > n_+ > \pi_1$$

(for the approximate composition of these orbitals see Fig. 4). The energy of n_- and n_+ is certainly lowered by the coordination to tin and we relate all the ionizations from these four orbitals to the first unresolved band group, any more precise assignment within the sequence is necessarily arbitrary. The overall assignment is supported by comparison between the spectra of V and

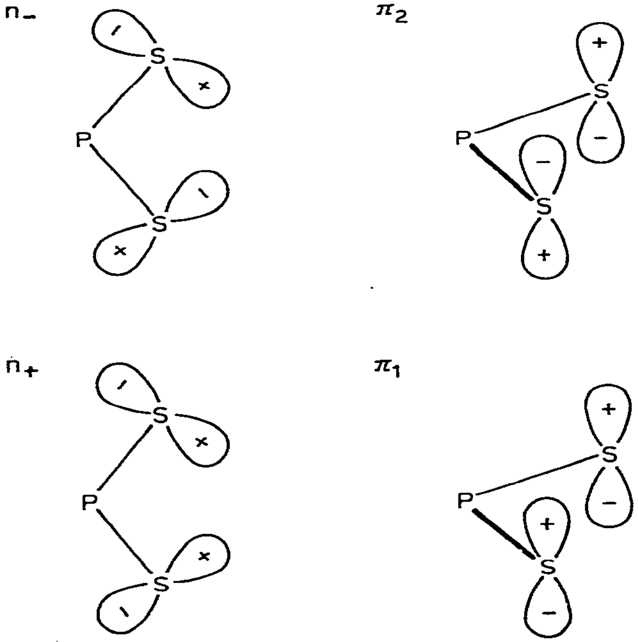

Fig. 4. MOs' predominant composition for highest levels of $[S_2P(CH_3)_2]^-$.

VI: in the 8.5—9.5 eV region the former shows two bands, arising from ionization of the in- and out-of-plane thionic sulphur lone pairs and the π-type thiolic sulphur lone pair, while the latter shows only one broad band. The lack of resolution in VI is due to the presence in this region of four in place of three ionizations, as a consequence of the fact that in the complex the two sulphur atoms are equivalent and their in-plane lone pairs give rise to two combinations (n_- and n_+, both bonding with the tin) of comparable energy.

The band with maxima at 9.95 and 10.32 eV, with no counterpart in the spectrum of V, is attributed to the ionization of two σ Sn—C bonds; this I.E. value is slightly higher than in the corresponding dithiocarbamate, following the same trend observed in the two series of compounds.

Dialkyltin bisdiethyldithiophosphinates

The U.P. spectra of the following compounds were determined: $(CH_3)_2Sn[S_2P(C_2H_5)_2]_2$ (dimethyltin bis(diethyldithiophosphinate (VII)) and $(n\text{-}C_4H_9)_2Sn[S_2P(C_2H_5)_2]_2$ (di-n-butyltin bis(diethyldithiophosphinate (VIII)). (Fig. 3 and Table 2).

The HeI spectrum of VII displays a broad band centered at 8.58 eV, similar to that from VI, followed by two much less intense overlapping bands at 9.66 and 10.24 eV. We assume that the first band contains the ionizations of two π_2, two π_1, two n_-(σ Sn—S) and one n_+(σ Sn—S) orbitals, while the second n_+ gives rise to one of the two next bands, together with one σ Sn—C bond. The other σ Sn—C ionization falls at a higher energy value and is masked by the broad envelope beyond 11 eV. The HeII spectrum (Fig. 3) confirms this assignment, showing a sharp decrease in the intensity of the first band compared with the others, which is consistent with the smaller ionization cross section of sulphur relative to tin orbitals under HeII radiation. The HeII spectrum suggests also that the band associated with the lower σ Sn—C ionization is the third one, at 10.24 eV, which increases slightly with respect to the second, as a consequence of the different composition of the orbitals involved in the ionization processes. (The 9.66 eV band is related to a σ orbital with large sulphur contribution.)

The spectrum of VIII (Table 2) is similar to that of VII, apart from the expected shift of all bands to lower I.E. values, due to the inductive effect of the butyl groups, and the poorer resolution in the region of the n_+(σ Sn—S) and σ Sn—C ionizations, which coalesce into a single broad band. The assignment is completely parallel to that one of VII.

An analysis of the results allows us to make some generalisations about the sequence of M.O.s in compounds in which alkyltin moieties are bonded to sulphur-containing ligands. The highest energy levels in dithiocarbamato and dithiophosphinato complexes are π-type orbitals mainly of sulphur 3*p* character; they are followed by bonding σ Sn—S and σ Sn—C orbitals. The I.E. values relating to the σ Sn—C bonds (between ca. 9 and 10.5 eV) are comparable to those found for other alkyltin compounds [1,18].

The analysis of the spectra of the dithiocarbamates suggests that both ligand sulphur atoms are involved in the coordinative bonding with the tin, supporting the view that the photoelectron spectroscopic technique can contribute to the resolution of structural problems.

Experimental

The compounds were prepared by published methods [6—8,10,14,20] and purified by crystallization or sublimation in vacuo.

HeI spectra were recorded on a Perkin-Elmer PS18 spectrometer; HeII spectra were recorded on two other PS16/18 spectrometers modified with a dual HeI/HeII source (Helectros development).

Spectra were run at temperatures between 26° C and 175° C.

Calibration was performed using Ar, Xe, N_2 and CH_3I as internal standards.

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