Inorganica Chimica Acta, 117 (1986) L37–L38

Gas-phase Conformation of Trimethylphenylthiostannane by UV Photoelectron Spectroscopy

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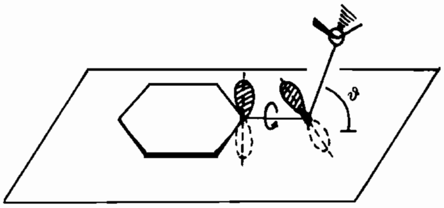
(Received February 22, 1986)

The structure of the title compound, Me_3SnSPh, which is a liquid at room temperature, is unknown. An investigation of the molecular conformation of this compound implies a detailed analysis of its electronic structure. In fact, the interactions between localized molecular orbitals (MO) critically depend on the molecular conformation. More precisely, the dihedral angle (ϑ) between the plane of the phenyl ring and the C–S–Sn plane determines the extent of the conjugation between the π system of the phenyl group, on one hand, and the sulfur lone pair and/or the σ_{Sn-S} bond, on the other one. The maximum interaction is with the sulfur lone pair in the extreme case of $\vartheta = 0°$ and with the σ_{Sn-S} orbital for $\vartheta = 90°$.



The gas phase UV photoelectron spectroscopy (UPS) proved a useful tool for the solution of similar conformational problems [1]. We measured the UP spectrum of Me_3SnSPh, assumed to be a monomer in the gas-phase, on the basis of mass spectrometric evidence [2]. The He(I) (21.22 eV) and He(II) (40.81 eV) spectra are reproduced in Fig. 1 and the ionization energies are reported in Table I. The first IE of this compound had already been measured by UPS along with C, Si, Ge and Pb analogues [3], but no attention had been devoted by the authors to the implications of the conformational aspects on the electronic molecular structure. The ionization energy value of the first band, clearly arising from ionization of an orbital with predominant sulfur 3p character (see the strong decrease in relative intensity on passing from He(I) to He(II) ionizing radiation) is very meaningful. It is in fact higher (8.39 eV) than that of the corresponding band in HSPh (8.28 eV [3]) and MeSPh (8.07 eV [4]), despite the greater electron-donor ability of Me_3Sn group relative to H and Me. This points out the different electronic situation of the trimethyltin derivative with respect to the other two thiophenyl compounds, where a significant interaction between the suflur lone pair and the π system of the phenyl ring is clearly present. On the contrary, in Me_3SnSPh the HOMO has essentially a sulfur 3p atomic character, with little, if any, admixture of σ-type orbitals of the Me_3Sn group (hyperconjugative interaction). The following system of three bands, at 8.63, 9.20 and 9.79 eV, is typical of conjugative interactions of a π orbital of the phenyl ring (e_{1g} in benzene) in monosubstituted benzenes. In this case the interaction involves the σ_{S-Sn} orbital. The first and third bands of the triplet represent the antibonding and bonding combinations, respectively, of the two fragment orbitals, while the second one is related to the unperturbated component of the phenyl π orbital with a node at the point of substitution. It is of interest that the $\sigma_{S-Sn}{}^{-1}$ ionization falls at 9.55 eV in the spectrum of Me_3SnSMe [5], where this orbital is not involved in conjugative interaction. This value is significantly higher than that of the

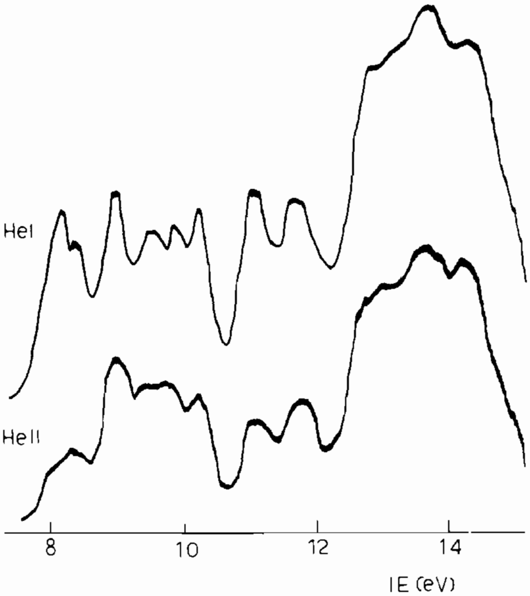


Fig. 1. He(I) and He(II) spectra of $(Me_3Sn)SPh$.

TABLE I. Ionization Energies (eV) for $(Me_3Sn)SPh$

8.39	8.63	9.20	9.79	10.10	10.48	11.34	13.85

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0020-1693/86/$3.50

first band of the triplet and quite close to that of the e_{1g}^{-1} ionization of benzene (9.25 eV [6]). It suggests a favourable energy matching of the localized σ_{S-Sn} and phenyl π orbitals in Me_3SnSPh, and consequently a large interaction, leading to a splitting of 1.16 eV between the resulting antibonding and bonding MOs. Such an interaction is in any case allowed by a proper molecular conformation, *i.e.*, with ϑ around 90°.

This conclusion is consistent with the conformational analysis carried out by some authors [8, 9] on the series C_6H_5-S-R (R = H, Me, Et, t-Bu), where a twisting of the S–R bond out of the planar conformation with increasing size of the alkyl group was found.

An analogous interaction was pointed out in a UPS study of $C_6H_5-CH_2-SnMe_3$ [10], where the only possible conjugation is that between the π phenyl system and the σCH_2-Sn bond.

This investigation is a nice example of a case in which the UP photoelectron spectroscopy proved successful in indicating the most stable conformation of a molecule in the vapor phase.

Experimental

The title compound was prepared following literature methods [11, 12].

The gas-phase photoelectron spectra were run on a Perkin-Elmer PS 18 spectrometer equipped with a He(I)/He(II) lamp (Helectros Development). Calibration was performed by N_2 and self-ionizing He as internal standards.

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