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UV Photoelectron Spectra and Pseudopotential *ab initio* Calculations of $(CH_3)_3PbC{\equiv}CCH_3$

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Abstract

Gas-phase UV photoelectron spectroscopy (UPS) and pseudopotential *ab initio* calculations were used to analyse the electronic structure of $(CH_3)_3PbC{\equiv}CCH_3$, with particular interest in the possible σ–π interaction between the π(C≡C) system and the σ(Pb–C) bonds. The results obtained, compared with the UPS data already known for the tin analogue, and with the pseudopotential calculations performed during the present work for both compounds, showed that the bonding is similar in the two molecules. In particular the σ–π interaction is quite weak and the HOMO has mainly π(C≡C) character. The present interpretation is supported by the analysis of the NMR results.

Introduction

The problem of σ–π interactions in acetylenic derivatives containing XIV group elements has been extensively investigated including the use of gas-phase UV photoelectron spectroscopy (UPS) [1–7]. In particular, a series of alkynyltin(IV) compounds has been studied by our groups [7], the UP spectra being analysed on the ground of pseudopotential *ab initio* calculations [7] and compared with the results of NMR investigations. The results evidenced a good agreement between the experimental ionization energies (IEs) and the computed orbital energies (in the framework of Koopmans' theorem [8]) and provided a reliable picture of the electronic structure of the studied molecules, in particular of the σ–π interaction between the σ(Sn–C) orbitals and the π(C≡C) system.

In the present study we extended the investigation to an analogous compound, namely $(CH_3)_3PbC{\equiv}CCH_3$. The aim was to verify whether the substitution of tin by lead implies a significant variation in the bonding, i.e. a change in the extent of the σ–π mixing. The analysis of the UP spectrum of $(CH_3)_3SnC{\equiv}CCH_3$ [7] suggested a substantial localization of the Highest Occupied Molecular Orbital (HOMO) on the π(C≡C) level and of the following two MOs on the σ(Sn–C) bonds, i.e. a weak σ–π conjugation. For the comparison of the electronic structure of the tin and lead derivatives, we performed pseudopotential *ab initio* calculations for both molecules. Both HeI (21.22 eV) and HeII (40.81 eV) spectra were run in order to observe also the ionization of the 5d electrons of lead, which falls usually around 25–30 eV. The analysis of the bonding in the two compounds was also supported by NMR measurements.

Experimental

Preparation

$(CH_3)_3PbC{\equiv}CCH_3$ was prepared according to a literature procedure [9] and redistilled twice before measurements.

UP Spectra

The UP Spectra of the liquid sample were recorded on a Perkin-Elmer PS18 spectrometer modified with HeI/HeII lamps (Helectros Developments) at room temperature. Calibration was performed by N_2 and self-ionizing He as internal standards.

Calculations

The *ab initio* LCAO-MO-SCF calculations were performed with the introduction of pseudopotentials to deal with all core electrons using the formalism proposed by Durand and co-workers [10], where for a given atom c and l value the purely local operator is described by the equation

$$W_{l,c}(r) = \Sigma_i a_i r^{n_i} \exp(-\alpha r^2)$$

The α, n_i and a_i parameters adopted for Pb, Sn and C atoms are reported in Table 1, while in Table 2 are reported those including the major relativistic corrections (mass and Darwin corrections [10, 11]) for Pb and Sn. The 3-1 G split Gaussian basis sets,

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TABLE 1. Non-relativistic pseudopotential parameters for C, Sn and Pb atoms

Atom	l	α	n_i	a_i
C	0	5.330459	−1	1.369252
			0	21.035110
	1	14.061160	0	−6.052015
Sn	0	1.357580	0	27.792300
			2	−9.754050
	1	0.604208	0	6.215820
			2	−1.265690
	2	0.441197	0	5.483580
			2	−0.711756
Pb	0	1.052570	0	23.234900
			2	−7.265510
	1	0.492487	0	5.480550
			2	−0.945042
	2	0.134520	−2	5.012530
			0	−0.362830

TABLE 2. Relativistic pseudopotential parameters for Sn and Pb atoms

Atom	l	α	n_i	a_i
Sn	0	1.448025	0	30.189200
			2	−12.333380
	1	0.620580	0	6.264130
			2	−1.343072
	2	0.441197	0	5.483580
			2	−0.711756
Pb	0	1.230006	0	28.246330
			2	−12.939920
	1	0.548523	0	5.912760
			2	−1.228280
	2	0.134520	−2	5.012530
			0	−0.362830

optimized for each valence shell of Pb, Sn and C atoms by a pseudopotential version of the ATOM program [12], are listed in Table 3 and the relativistic ones for Pb and Sn in Table 4. For H atom the standard Huzinaga Gaussian basis set [13] has been 3+1 contracted. All the molecular calculations were performed by using the PSHONDO program [14]*.

The C_{3v} symmetry molecular structure adopted in the calculations for $(CH_3)_3SnC{\equiv}CCH_3$ was derived from both the gas phase electron diffraction study of $(CH_3)_3SnC{\equiv}CH$ [15] and the geometrical parameters of propyne [16] (C≡C, C–C and C–H bond distances and C–C–H bond angle). The molecular structure of $(CH_3)_3PbC{\equiv}CCH_3$ is not known and is assumed of C_{3v} symmetry by analogy. The geometrical parameters adopted in the calculations were derived as follows: C≡C, C–C, C–H bond distances and C–C–H bond angle are those of propyne [16]; C–H bond distance (of the three methyl

TABLE 3. Orbital exponents and coefficients of the 3-1 G split Gaussian valence basis sets[a]

Atom	Orbital	Exponent	Coefficient
C	s	2.382013	−0.242140
		1.443065	0.185265
		0.405847	0.591283
		0.138427	1.0
	p	8.609570	0.043653
		1.943550	0.209497
		0.542798	0.502761
		0.152496	1.0
Sn	s	1.740366	0.252610
		1.074617	−0.603338
		0.187352	0.692616
		0.072331	1.0
	p	1.511702	0.068980
		1.073103	−0.119589
		0.180223	0.589895
		0.061094	1.0
Pb	s	1.575921	0.197080
		0.836893	−0.607325
		0.185218	0.677286
		0.070746	1.0
	p	1.263903	0.072611
		0.877903	−0.128384
		0.154578	0.625805
		0.054111	1.0

[a] Optimized with the pseudopotential parameters of Table 1.

TABLE 4. Orbital exponents and coefficients of the 3-1 G split Gaussian valence basis sets[a]

Atom	Orbital	Exponent	Coefficient
Sn	s	2.075900	0.168277
		1.098474	−0.527856
		0.204695	0.717337
		0.076663	1.0
	p	2.703705	0.023568
		0.960078	−0.074007
		0.188406	0.575838
		0.062796	1.0
Pb	s	1.562395	0.900398
		1.267078	−1.317915
		0.234808	0.743313
		0.086473	1.0
	p	1.687656	0.031691
		0.866422	−0.091532
		0.180201	0.572854
		0.060274	1.0

[a] Optimized with the pseudopotential parameters of Table 2.

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*PSHONDO is a modified version of HONDO program (M. Dupuis, J. Rys and H. F. King, *QCPE 336*) including pseudopotentials, developed by J. P. Daudey.

TABLE 5. Optimized geometrical parameters for $(CH_3)_3PbC{\equiv}CCH_3$

Bond distance (Å)		Bond angle (°)	
Pb–C≡	2.217	Pb–C–H	110.5
Pb–$\overset{|}{\underset{|}{C}}$–	2.272	C–Pb–C	108.5

groups) is that of $(CH_3)_4Pb$ [17]; Pb–C bond distances, C–Pb–C and Pb–C–H bond angles were optimized starting from bond distance values derived by extrapolation of the X–C bond lengths (X = C, Si, Ge, Sn) of structural related compounds [15], and C–Pb–C and Pb–C–H bond angles assumed equal to the C–Sn–C and Sn–C–H angles of $(CH_3)_3SnC{\equiv}CH$ [15]. The results are reported in Table 5.

Results and Discussion

The HeI and HeII spectra of the title compound are reported in Fig. 1. They look very similar to those of the tin analogue, showing in the *IE* region 8.5–11 eV a series of three bands with intensity ratio approximatively 2:2:1. They are shifted by *c.* 0.3 eV to lower *IE* values with respect to $(CH_3)_3SnC{\equiv}CCH_3$ [7], consistently with the higher metal character of lead.

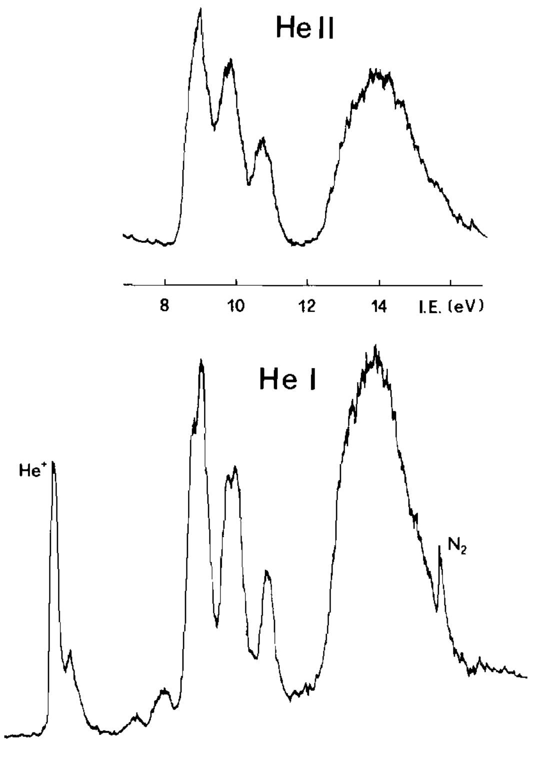
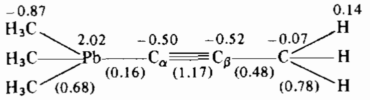


Fig. 1. HeI and HeII spectra.

In the HeI spectrum of the lead compound three extra bands of low intensity appear at apparent *IE* values of 5.40, 7.15 and 8.00 eV, not present in the spectrum of the tin analogue. The band of very low intensity at 7.15 eV is associated with the ionization of the HOMO by the HeI-β radiation (23.09 eV). The two bands at 5.40 and 8.00 eV arise from the HeII ionizing radiation and correspond to the true *IE* values of 24.99 and 27.59 eV. They are related to the two spin–orbit components $^2D_{5/2}$ and $^2D_{3/2}$ of the pseudo-valence Pb 5d electrons. The observed spin–orbit splitting (2.60 eV) is approximately the same found both in atomic lead and in lead compounds. As for the *IE* values, (24.99 eV for $^2D_{5/2}$, 27.59 eV for $^2D_{3/2}$), they are significantly lower than in compounds in which lead is bonded to highly electronegative elements, i.e. PbF_2 (*IE* 27.63 and 30.34 eV) [18], $PbCl_2$ (*IE* 27.34 and 29.92 eV) [19], $PbBr_2$ (*IE* 27.02 and 29.58 eV) [19], PbI_2 (*IE* 26.48 and 29.20 eV) [19], whilst being higher than in $(C_2H_5)_4Pb$, (*c.* 24.2 and 26.8 eV) [20], where the four ethyl groups exert a strong electron-donor effect on lead. In $(CH_3)_3PbC{\equiv}CCH_3$ the *IE* values of the d ionizations are found at intermediate values due to the presence of three electron-donor groups ($-CH_3$) and one electron-withdrawing group ($-C{\equiv}C-CH_3$).

For the assignment of the first three bands a reliable criterium is the comparison with the spectrum, already measured [7], of $(CH_3)_3SnC{\equiv}CCH_3$. To better understand the bonding situation in both molecules and to study possible variations induced by the presence of a different metal atom, we analysed the spectra also on the grounds of the result of the pseudopotential calculations, which are reported in Tables 6 and 7, along with the experimental *IE* values. Clearly, there is a good agreement between calculated and experimental data, mainly as far as the MO sequence is concerned. The absolute orbital energy values are systematically higher than the ionization energies. This difference decreases for the Pb compound when the relativistic calculation is performed, whilst remaining almost unchanged for the Sn derivative. Also the total electronic energy decreases on passing from non-relativistic calculations to relativistic calculations, the variation being much more pronounced for the lead than for the tin compound (0.31 versus 0.09 a.u.). Following the calculation, in $(CH_3)_3PbC{\equiv}CCH_3$ (see Table 6), the HOMO (6e), corresponding to the first UPS band at 8.99 eV, is mainly localized on the $\pi(C{\equiv}C)$ bond with a small contribution of the $\sigma(Pb-C)$ bonds. The second occupied MO (5e), related to the second UPS band at 9.91 eV, has the

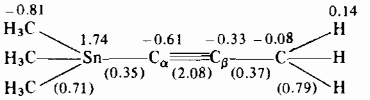
TABLE 6. UPS ionization energies and pseudopotential *ab initio* results for $(CH_3)_3PbC{\equiv}CCH_3$[a]



MO	Eigenvalue[c] (eV)	Eigenvalue[b] (eV)	Population[c] (%)					Dominant character	*IE* (eV)
			Pb	C_α	C_β	$3CH_3$	CH_3		
6e (HOMO)	−9.82	−9.54	3	33	31	27	6	$\pi(C{\equiv}C)$	8.99
5e	−10.78	−10.53	13	16	10	58	3	$\sigma(Pb{-}CH_3)$	9.91
$7a_1$	−12.40	−12.15	17	32	10	39	2	$\sigma(Pb{-}C)$	10.71

[a]Net atomic charges and overlap populations (in parentheses) are in electrons. [b]Eigenvalues of the relativistic calculation. [c]Eigenvalues and Mulliken population analysis of the non-relativistic calculation.

TABLE 7. UPS ionization energies and pseudopotential *ab initio* results for $(CH_3)_3SnC{\equiv}CCH_3$[a]



MO	Eigenvalue[c] (eV)	Eigenvalue[b] (eV)	Population[c] (%)					Dominant character	*IE* (eV)
			Sn	C_α	C_β	$3CH_3$	CH_3		
6e (HOMO)	−9.86	−9.81	3	36	34	21	6	$\pi(C{\equiv}C)$	9.23
5e	−11.05	−10.99	16	13	8	61	2	$\sigma(Sn{-}CH_3)$	10.12
$7a_1$	−12.61	−12.61	18	32	6	43	1	$\sigma(Sn{-}C)$	11.05

[a]Net atomic charges and overlap populations (in parentheses) are in electrons. [b]Eigenvalues of the relativistic calculation. [c]Eigenvalues and Mulliken population analysis of the non-relativistic calculation.

TABLE 8. ^{13}C, ^{119}Sn and ^{207}Pb NMR parameters[a] of $(CH_3)_3MC{\equiv}CCH_3$ (M = Sn, Pb)

$(CH_3)_3MC_\alpha{\equiv}C_\beta CH_3$	$\delta^{13}C_\alpha$	$\delta^{13}C_\beta$	$\delta^{13}C$		δM
			CH_3M	CH_3M	
M = Sn	81.1 (502.9)	105.7 (107.4)	−8.2 (404.1)	4.8 (11.0)	−73.8
M = Pb	84.7 (59.0)	103.9 (10.0)	0.5 (373.0)	4.7 (7.0)	−142.1

[a]Data from ref. 21; solutions in C_6D_6; $\delta^{13}C$ relative to $\delta^{13}C(C_6D_6) = 128.0$; $\delta^{119}Sn$ and $\delta^{207}Pb$ relative to external $(CH_3)_4M$; $^nJ(M^{13}C)$ values are given in parentheses.

main contribution from $\sigma(Pb{-}CH_3)$ orbitals with a small participation of the $\pi(C{\equiv}C)$ bond. The following MO ($7a_1$, third UPS band at 10.71 eV) is a σ delocalized orbital, with contributions from Pb, $-CH_3$ and $-C{\equiv}C-$ groups. This assignment suggests a weak interaction between the $\pi(C{\equiv}C)$ and the $\sigma(Pb{-}CH_3)$ orbitals. The situation is very similar for the tin analogue (see Table 7), this result being in agreement with the previous assignment of the UP spectrum of this molecule [7]. The calculated overlap populations are similar to those obtained for $(C_2H_5)_3SnC{\equiv}CH$ [7]. On the contrary, a significant difference is observed in the overlap populations of $(CH_3)_3PbC{\equiv}CCH_3$. For instance, the overlap population of the triple bond is 1.17 in the lead derivative, versus 2.08 in the tin derivative (see Tables 6 and 7). However this result is very sensitive to the computational scheme, since the difference practically vanishes in the relativistic calculation (2.11 in the Pb and 2.08 in the Sn compound).

The similar bonding in the tin and lead compounds is also reflected by the NMR parameters [21] (see Table 8), in particular by the $\delta^{13}C$ values. In the coupling constants $^1J(M^{13}C{\equiv})$ there is a major difference since the $^1J(^{207}\mathrm{Pb}^{13}\mathrm{C}\equiv)$ value is close to zero whereas the $^1J(^{119}\mathrm{Sn}^{13}\mathrm{C}\equiv)$ value is still large. This suggests a small s overlap integral for the M–C≡ bond if M = Pb and a fairly large one for M = Sn. The increasing polarity of the Pb–C≡ versus the Sn–C≡ bond as well as the reduction of the C≡C bond strength is also evident from the rather small $^1J(^{13}\mathrm{C}\equiv^{13}\mathrm{C})$ values in the tin (127.6 Hz) and the lead (120.0 Hz) compounds [22].

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