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PHOTOELECTRON SPECTROSCOPY STUDY OF THE TRIPHENYL DERIVATIVES OF THE GROUP IV ELEMENTS

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Summary

The photoelectron He(I) spectra of several phenyl derivatives of the Group IV elements are reported, and the first few bands are assigned to the corresponding MO's. A sizable interaction among the π orbitals of the rings has been found for the carbon derivatives $HCPh_3$, HC(mesityl)$_3$ and H_2CPh_2, but not for the Si, Ge and Sn triphenyl derivatives. The exceptional behaviour of the carbon compounds has been attributed to the short central atom—ring distance, by analogy with findings for the Group V triphenyl derivatives.

The charge transfer from the rings towards the Si atom is substantially reduced compared with that in H_3SiPh.

Introduction

The gas phase structure of triphenylmethane indicates [1] that the central carbon atom is nearly tetrahedral and that all the rings have the same sense and angle of twist so that the molecule belong to the C_3 symmetry class. The structures of $HSiPh_3$, $HGePh_3$ and $HSnPh_3$ have not been reported. However, given that all the $XZAr_3$ molecules studied to date have a propeller-like conformation [2], it is reasonable to assume that all the triphenylderivatives of the Group IV elements have C_3 symmetry. The propeller-like conformation allows through space interaction among the rings.

TABLE 1

IE's, (eV) FOR PHENYL DERIVATIVES OF THE GROUP IV ELEMENTS

	Ring π orbitals				XC_3	X—H								
HCPh$_3$	8.40	8.89	9.17	9.3	11.0		11.8		13.0	13.9	14.5	15.1	16.2	16.5
HSiPh$_3$			9.13		10.35	11.2	11.8	12.7	13.2	13.9	14.5		15.7	16.5
HGePh$_3$			9.15		10.11	10.9	11.8	12.6	13.1	13.9	14.6		15.7	16.4
HSnPh$_3$			9.11		9.6	10.3	11.8	12.6	13.0	13.9	14.5		15.7	16.4
BrGePh$_3$			9.17		9.81	{10.8 [a] 11.1	11.9	12.7	13.3	14.0	14.6		15.9	16.6
ClSnPh$_3$			9.29		9.71	11.1 [a]	12.0	12.7	13.2	14.1	14.6			16.5
H_2CPh_2	8.67		9.12	9.3										
H_2SiPh_2			9.23											
HC(mesityl)$_3$	7.68		8.12	8.3										

[a] Halogen lone pairs.

In this paper we present the UV photoelectron spectra of the title compounds. The aim of the work was to obtain information on the ring—ring interaction, to analyze the influence of changing the central atom and of groups attached to it, and to see if evidence could be obtained for the withdrawing ability of the SiR_3, GeR_3 and SnR_3 groups in these compounds.

Experimental

The samples of $HCPh_3$, H_2CPh_2, $HSiPh_3$, $BrGePh_3$ and $ClSnPh_3$ were obtained commercially. The samples of H_2SiPh_2 [3], $HGePh_3$ [4] and $HSnPh_3$ [5] were prepared by reduction of their halogen derivatives with $LiAlH_4$ in ether.

The sample of HC(mesityl)$_3$ was supplied by Dr. P. Finocchiaro, University of Catania.

The photoelectron spectra were recorded on a Perkin—Elmer PS 18 spectrometer and calibrated against Ar and Xe lines. The estimated error in the IE values is ±0.05 or ±0.1 eV depending upon the number of decimal quoted.

Results and discussion

The photoelectron spectra of relevant compounds are presented in Figs. 1-3 and the IE data in Table 1. The spectra of triphenyl derivatives of silicon, germanium and tin are very similar in terms of the number, the shape and the EI value of the bands. They differ, however, in some respects from that of the carbon analog. In particular, the first band in the spectra of the Si, Ge and Sn compounds is broad (FWHM about 0.75 eV), intense and its IE value is constant at 9.13 ± 0.02 eV (see Fig. 1). This indicates that the ionization occurs from the almost unperturbed π orbitals of the phenyl rings and that the effect of the H—Z group on them does not vary appreciably along the series.

In the corresponding region of the spectrum of the carbon derivative (see Fig. 2) there are three distinct maxima at 8.40, 8.89 and 9.17 eV, and one shoulder at about 9.3 eV. This structure indicates the presence of interaction among the rings. There is little doubt that the most intense peak centered at 9.17 eV corresponds to the ionization from the triple degenerate MO's arising from the unperturbed π_a* orbital of the rings; the other bands are described to the MO's deriving from the interaction of the π_s ring orbitals**.

A similar effect is evident in the spectrum of trimesitylmethane (see Fig. 2) where a stronger steric hindrance is present. However, the total splitting of the π ring orbitals decreases from about 0.9 eV in triphenylmethane to about 0.6 eV in trimesitylmethane. The presence of *ortho* substituents on the rings results in an increase of the angle at the central carbon arom and a reduction of the angle of twisting of the rings [1,6]. Both the effects are expected to reduce the trough space interaction. However, the distance

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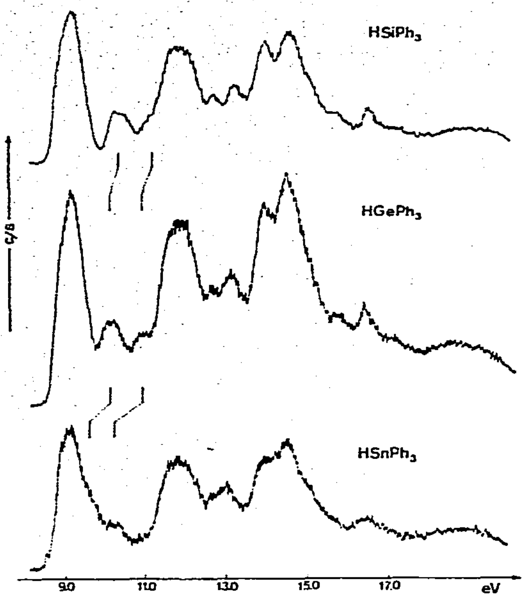
* a = antisymmetric, s = symmetric with respect to a plane perpendicular to the ring plane and passing through the substituted carbon atom and that in the *para* position.

** Due to the conformation of these molecules, extensive interaction within the various MO's are present so that the classification of the MO's as σ or π is no more strictly correct. However for the sake of simplicity this classification will be retained.



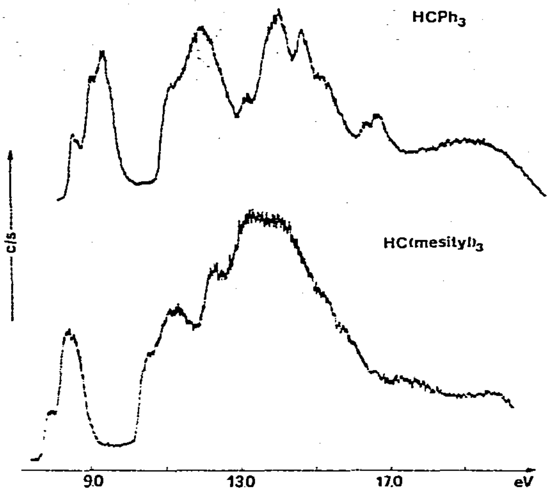


Fig. 1. Photoelectron He(I) spectra of $HXPh_3$ (X = Si, Ge and Sn).

Fig. 2. Photoelectron He(I) spectra of $HCPh_3$ and $HC(mesityl)_3$.

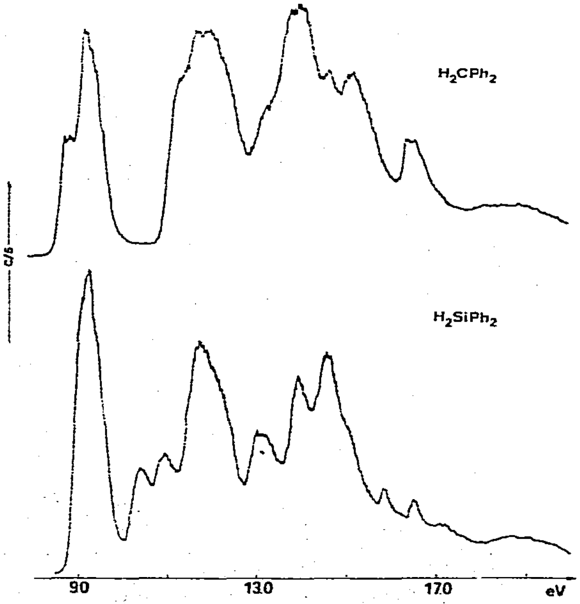


Fig. 3. Photoelectron He(I) spectra of H_2CPh_2 and H_2SiPh_2.

between the central carbon atom and the rings is not much influenced by this substitution [1,6].

Other factors can effect the interaction of the ring orbitals. These were discussed in a previous paper [7] dealing with triphenylderivatives of the Group V elements. In the present case also, the Z—ring bond distance (which increases with the atomic number of Z [8]) seems to be the predominent factor in determining through space interaction in $HZPh_3$.

Since the IE value of the π_a MO's from $HCPh_3$ is very close to the first IE of the other $HZPh_3$ ($Z \neq C$), it can be concluded that there is very slight through space interaction in the latter molecules.

The next band in the spectra of the triphenyl derivatives can be assigned to the Z—C orbitals belonging to the e symmetry species of a local C_{3v} symmetry. The decreasing value of the IE's (11.0, 10.35, 10.11 and 9.57 eV on going from the carbon to the tin derivative) is in accordance with the expected bond weakening along the series. Furthermore, these IE's are very close to those of the degenerated Z—C orbitals of t_2 symmetry of the corresponding tetramethyl derivatives: 10.96, 10.57, 10.23 and 9.70 eV respectively [9]. However, while the Z—C IE values from the Si, Ge and Sn triphenyl derivatives are lower than the corresponding values for the tetramethyl compounds, the carbon derivatives have very similar IE's.

This variation could be attributed to a symmetry allowed interaction with the appropriate combination of the π_s rings orbitals. This interaction *(i)* is largest in the carbon derivatives, in which the shortest bond length leads to better π_s ring orbital combinations, *(ii)* stabilizes the Z—C orbitals, and *(iii)* is likely to contribute to the observed π orbitals splitting in the carbon derivative.

The IE of the next band decreases progressively in the order $HSiPh_3 >$ $HGePh_3 > HSnPh_3$*, indicating again that the ejected electron is localized near the central atom. The assignment to the H—Z MO is supported by the fact that in the spectrum of $ClSnPh_3$ the band at 10.3 eV, assigned to the H—Sn MO in $HSnPh_3$, disappears and a new band, centered at 11.1 eV, is visible. The shape and energy of the latter allow it to be assigned to the chlorine lone pair. Similar, although less clear, evidence for the assignment of this band can be drawn from the comparison of the $HGePh_3$ and $BrGePh_3$ spectra.

The remaining bands in the photoelectron spectra are very similar in terms of their shapes, relative intensities and IE's, indicating a very small influence of the central atom on them.

The conclusion that geometrical factors are responsible for the lack of effective through space interaction when $Z \neq C$ is confirmed by the analysis of the π bands of the spectra of H_2CPh_2 and H_2SiPh_2 (see Fig. 3). The spectrum of the latter compound shows only one peak (FWHM = 0.7_2 eV) at 9.23 eV while that of the former compound shows a peak at 9.12 eV and two shoulders at 8.67 and 9.3 eV. The maximum is assigned to ionization from the π_a ring orbitals and the shoulders to the out of phase and in phase combinations of the π_s ring orbitals respectively. These data are in agreement with the presence of a larger ring—ring interaction in the carbon derivative. Interaction between the rings in

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* This band in the spectrum of the carbon derivative is probably masked by the intense envelop centered at about 11.8 eV.

diphenylmethane has been proposed on the basis of calculations [10] and kinetics [11].

The increase of the IE related to the ring π orbitals on going from $C_6H_5CH_3$ to $C_6H_5SiH_3$ (π_s 8.80 and 9.18, π_a 9.35 and 9.43 eV respectively) has been ascribed to ring→SiH_3 charge transfer [12]. Since *(i)* there is no sizable splitting in $HSiPh_3$ between the MO's arising from the π_s and π_a ring orbitals and *(ii)* the corresponding IE value (9.13 eV) is very close to that for the π_a orbitals from $HCPh_3$ (9.17 eV) unperturbed by ring—ring interaction, we conclude that in the triphenylsilicon derivative the charge transfer from the rings towards the Si (Ge and Sn) atom(s) is reduced with respect to the monophenyl derivative(s). This reduction is probably attributable to the unfavorable geometrical disposition of the phenyl rings, which does not allow the formation of effective π_s orbitals combinations and thus extensive overlap with vacant orbitals mainly localized on Z [13].

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