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Ultraviolet photoelectron spectroscopy of diphenyltrimethylsilyl-amine, -phosphine, -arsine, and -stibine

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Abstract

The He^I photoelectron spectra of the Ph_2ESiMe_3 (E = N, P, As, and Sb) derivatives have been assigned with the aid of those of related simpler molecules. The substitution of a trimethylsilyl group for a hydrogen atom in Ph_2EH to give the title compounds results in a significant reduction of the lone pair ionization energy of the fifth group atom when E ≠ N. When E = N, a slight stabilization is observed. This behaviour is probably attributable to the fact that the structure around the nitrogen atom is much further from planarity in the silyl derivative than in Ph_2NH.

Introduction

In recent years we have studied the electronic properties of organic and organometallic compounds containing fourth and fifth group elements. In particular we have investigated the effects of heteroatoms on the energy of valence (filled and virtual) and core molecular orbitals (MOs) and their localization properties at specific molecular centers by means of ultraviolet and X-ray photoelectron and electron transmission spectroscopies, assisted in some cases by theoretical calculations [1–8].

We have also used electron spectroscopy to obtain information on molecular conformation of compounds containing nitrogen or silicon [9–12] from the comparison of MO energies of the studied compounds with those of appropriate reference systems of known conformation, and with those derived from theoretical calcula-

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tions. In fact, MO energies depend, other factors being constant, on overlap, which in turn depends on conformation.

As part of this work, we present here the results of a UV-photoelectron spectroscopy (UPS) analysis of the diphenyltrimethylsilyl derivatives of the fifth group elements Ph_2ESiMe_3 (E = N, P, As, and Sb) where a fourth and fifth group element are both present and directly linked.

Experimental

The He^I photoelectron spectra were recorded with a Perkin–Elmer PS-18 photoelectron spectrometer. The spectra were calibrated with noble gas lines. The error in the quoted IE values is ±0.05 eV if two decimal digits are given and ±0.1 eV in the other cases.

The Ph_2ESiMe_3 derivatives (E = P, As, Sb) were prepared by standard methods [13–16]. Trimethylsilyldiphenylamine was synthesized by the following reaction sequence.

$$(C_6H_5)_2NH + CH_3(CH_2)_3Li \xrightarrow[0\,^\circ C]{\text{pentane/TMED}} (C_6H_5)_2NLi + C_4H_{10}$$

$$(C_6H_5)_2NLi + ClSi(CH_3)_3 \xrightarrow[0\,^\circ C]{\text{pentane}} (C_6H_5)_2NSi(CH_3)_3 + LiCl$$

Purity was checked by ^1H NMR spectroscopy and GC.

Results and discussion

The He^I photoelectron spectra of the studied compounds are presented in Fig. 1. The experimental IE values obtained from the low IE region of the spectra are shown in Table 1 together with those of related group orbitals taken from the literature and used for the assignment.

At low energy, the spectra show a weak band at about 7.5 eV which can be ascribed to ionization from the lone pair orbital of the fifth group heteroatom on the basis of the assignment of the spectra of the diphenyl [17] (Ph_2EH) and triphenyl [1] (Ph_3E) derivatives. The second, more intense, band at about 9 eV is mainly derived from π-benzene ionization. Electron extraction from the orbital mainly localised at the E–Si bond (E = P, As, Sb) contribute to the same energy region [18], while ionization from the $\sigma(EC_2)$ framework (E = P, As, Sb) produces bands between 10 (E = Sb) and 10.9 (E = P) eV [1,17]. The corresponding ionization from the N–Si and NC_2 groups occurs at about 11.7 eV [17,18]. Finally, the first (Jahn–Teller split) band ascribed to the SiC_3 skeleton occurs at about 10.4–10.6 eV in all cases [4,18,19].

The reduction of corresponding IE values on going from nitrogen to antimony causes a crowding of bands towards the beginning part of the spectrum, which loses resolution in the region between 9 and 11 eV for the derivatives of the heavier elements (see Fig. 1).

An unexpected result of the analysis of the UPS spectra is that the IE_1 value of the nitrogen derivative is only 0.2–0.3 eV smaller than that of the other species, while, in the Ph_2EH [17] and Ph_3E [1] series this difference is about 1 eV (see Table 1).

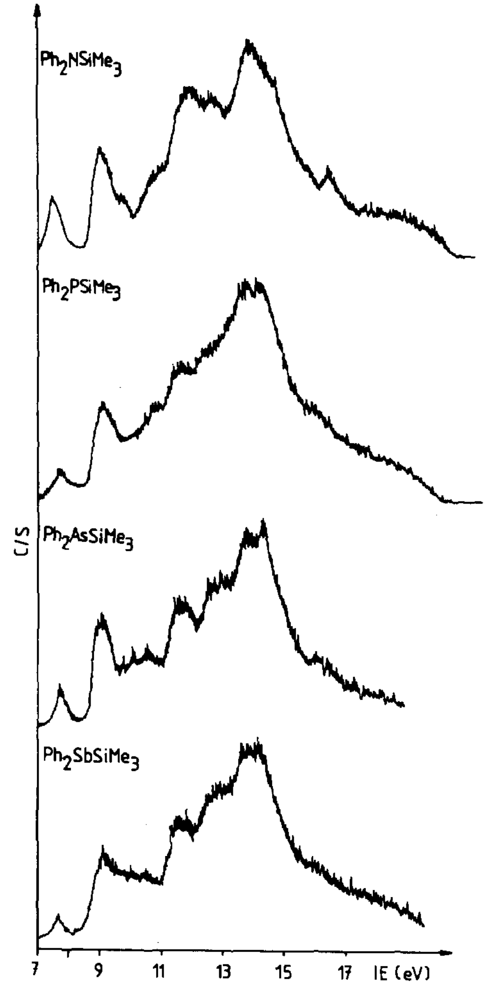

Fig. 1. He^I photoelectron spectra of diphenyltrimethylsilyl-amine, -phosphine- -arsine and -stibine, Ph$_2$ESiMe$_3$ (E = N, P, As and Sb).

Table 1

Ionization energy values (eV) for the compounds Ph$_2$ESiMe$_3$ (E = N, P, As, Sb) together with literature group orbital IE values used in the assignment procedure

E	IE$_1$	IE$_2$	IE$_3$	IE$_4$	IE$_1$ from	IE$_1$ from			
					Ph$_3$E [1]	Ph$_2$EH [17]	E–Si [18]	EC$_2$ [1,17]	SiMe$_3$ [4,18,19]
N	7.44	$\overline{9.05\ \ 9.2}$	9.73	10.9	7.00	7.35	11.65	11.7	10.5
P	7.74	$\overline{9.17\ \ 9.4}$	9.9	10.9	7.85	8.29	9.21	10.9	10.5
As	7.72	9.10	10.1	10.6	8.03	8.43	8.70–9.09	10.5	10.5
Sb	7.66	9.13	9.9	10.5	8.08		8.63	10.0	10.5

As mentioned above, molecular IE values change with the atomic IE values of E and with the conformation around the heteroatom. To the best of our knowledge, the conformation of the Ph_2ESiMe_3 derivatives has not been determined. The investigated compounds can be considered to be formed by the Ph_2E and $SiMe_3$ groups. If the conformation of the former group is assumed to be some as that it possesses in the Ph_2EH molecules, the UPS IE values [17] can be used to obtain the required information.

The ground state conformations of diaryl systems Ar_2ZXY (where X and Y are ligands or pseudo ligands) have been widely studied. X-ray structure determinations of diaryl compounds (diaryl sulphides, selenides, tellurides, ethers, methanes, ketones, and arsines) indicate that in the solid state these compounds assume a propeller-like comformation in which the two aromatic rings in a given molecule have the same sense of twist [20]. In solution, NMR and dipole moment measurements indicate that the helical conformation or that with the aromatic rings perpendicular to each other may be preferred, depending upon structural and electronic factors [20]. The same situation holds also in the gas phase for which the UPS measurements are carried out. In the perpendicular conformation the interaction between the lone pair orbital of E and the π-ring orbitals results in a MO splitting smaller than that present in the propeller conformation where π/π interaction is also present. If Ph_2NH was in the perpendicular conformation its uppermost IE values should be quite close to those of *N*-methylaniline, PhNHMe (IE_1 7.65, IE_2 9.05 and IE_3 10.20 eV [21]). The reported values (IE_1 7.35 IE_2 9.00 and IE_3 10.56 eV [17]) indicate that the n_N/π interaction, as measured from the IE_3–IE_1 splitting, is significantly larger in PH_2NH than in PhNHMe indicating for the former the helical conformation.

The extension of this conclusion to the other species in which $E \neq N$ is not straightforward because no photoelectron data are available for the relevant PhEHMe derivatives. The close similarity of the UP spectra of the Ph_2EH derivatives [17], however, indicates that the n/π interaction is of the same type, even though it decreases along the fifth group, suggesting a similar comformation for all the congeners. A similar n/π splitting decrease is also shown by the Ph_3E derivatives, which possess the same, propeller-like, conformation [11] with varying central angle.

As far as the structure of the C_2ESi skeleton is concerned, electron diffraction (ED) analyses indicate that trisilylamine and methyldisilylamine are planar [22], and that dimethylsilylamine is slightly non-planar (ED [23]) or planar (extended ab-initio calculations and UP spectra [24]). In contrast, trisilylphosphine and trisilylarsine are markedly pyramidal, the SiPSi and SiAsSi angles being 96.45 [25] and 93.79° [26], respectively. A decrease of the angle at the E atom on going down the group has been generally observed [27]. Even in the Ph_2ESiMe_3 series, therefore, the angle at the E atom should be significantly larger when E is N than when it is a heavier atom. The difference, however, is likely smaller than in other series. In fact, the substitution of a SiR_3 group for a hydrogen atom destabilises [28] the adjacent n_E orbital if conformation does not change. On going from Ph_2EH to Ph_2ESiMe_3 we observe the expected destabilization when $E = P$ (from 8.29 [17] to 7.74 eV) and As (from 8.43 [17] to 7.72 eV) and a small stabilization when $E = N$ (from 7.35 [17] to 7.44 eV). A likely explanation is that the introduction of the $SiMe_3$ group in the nitrogen derivative is accompanied by a structural change.

The decrease of the angle at the E atom causes the *np* lone pair orbital (more exactly the out of phase n-π combination) to mix in increasing amount of *s* character [19,24] and favors the charge-transfer interaction towards low-lying unoccupied MOs. Both effects increase the lone pair ionization energy. The greater pyramidalization around the nitrogen atom in Ph_2NSiMe_3 then around that in Ph_2NH also reduces the n-π interaction. This is confirmed by the sizeable destabilization (from 10.56 in Ph_2NH [17] to 9.73 eV in Ph_2NSiMe_3) of the band assigned to the in-phase (n-π) combination.

Ab-initio minimal basis set computations on Ph_2NSiMe_3 did not converge. However, available literature data on small related compounds confirm these conclusions. According to $X\alpha$ [29] and extended ab-initio [30] computations silicon *d* orbital effects have been found to be very similar in planar and pyramidal silylamine and trisilylamine. In addition, the MS $X\alpha$ one electron levels of $(H_3Si)_3N$ and $(H_3C)_3N$ are stabilized on going from planar to pyramidal structure because the decreased capability of the nitrogen lone pair to form π-bonding is outweighed by the stronger σ bonds in the pyramidal form [29]. Likely, therefore, a charge-transfer interaction from the Ph_2N group towards low-lying $\sigma^\star$ MOs highly localized at silicon stabilizes the pyramidal conformation. The corresponding interaction(s) in the planar Ph_2NSiMe_3 conformer and in Ph_2NH are weaker because of geometric and energetic reasons, respectively. In contrast with the hydrogen atom, the SiR_3 group possesses empty $\sigma^\star$ orbitals at low energy likely stabilized by mixing with silicon 3*d* orbitals [5,7].

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