Journal of Organometallic Chemistry, 280 (1985) 39–43
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

PHOTOELECTRON AND PENNING IONIZATION ELECTRON SPECTROSCOPIC INVESTIGATION OF SOME SILAZANES

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(Received July 24th, 1984)

Summary

Penning ionization electron spectroscopy and CNDO/S calculations have been successfully applied to the analyses of the UV photoelectron spectra of some silazanes. The relative intensities of the lone pair bands are enhanced in the Penning spectra compared with those in the UV photoelectron spectra. The intensity differences between the two spectra give useful informations for the investigation of the σ-electron systems.

Introduction

In recent papers we presented examples of the use of Penning ionization electron spectroscopy in the analyses of ultraviolet photoelectron spectra (UPS) of organosilicon compounds [1–3]. The most interesting difference between the UPS and Penning ionization electron spectra (PIES) is that the intensity of the π-bands in PIES are markedly enhanced relative to the σ-bands. Recently Ohno and coworkers have shown that orbitals on the outside of a molecule interact more effectively with metastable atoms and give stronger bands in PIES than inner orbitals [4]. This effect provides an approximate selection rule for PIES: outer orbitals are more active than inner orbitals. Further, when an MO is shielded from the impact of incoming metastable atoms by a bulky group of the investigated molecule, the corresponding band in PIES becomes weak, as was shown for substituted anilines [5]. The observation of this steric effect in PIES enables us to assign ionization bands to molecular orbitals.

In this paper we investigate the electronic structures of some silazanes which do not contain a π-electron system. With the help of the characteristics of the PIES stated above as well as semi-empirical (CNDO/S) quantum-chemical calculations,

0022-328X/85/$03.30

we arrive at assignment of the UPS bands for the following compounds: hexamethyldisilazane (**1**), hexamethylcyclodisilazane (**2**) and nonamethylcyclotrisilazane (**3**). In recent years these and related compounds have been investigated by X-ray diffraction and by UV, IR, Raman and NMR spectroscopy [6–11].

Experimental

The compounds were prepared by the usual methods [12] and purified by distillation.

The electron spectra were obtained at an ejection angle of 90° with respect to the metastable or photon beams by means of a hemispherical analyzer. The sample vapour was introduced into the collision chamber through a sample nozzle at ca. 25°C. Metastable neon atoms, Ne* ($^3P_2$ 16.62 eV) were produced by impact of 60 eV electrons; at this energy the contributions of Ne* ($^3P_0$ 16.72 eV) atoms and photons were negligible [13]. For the measurement of UPS, a discharge from pure neon gas was used to produce the Ne(I) (16.85 and 16.67 eV) radiations: the low energy component of the Ne(I) lines made little contribution to the spectra.

Results and discussion

Figure 1 shows the Ne(I) UPS and Ne* PIES of the compounds **1**, **2** and **3**. The spectra can be divided into three parts. The first part, between 8.0 to 8.7 eV in

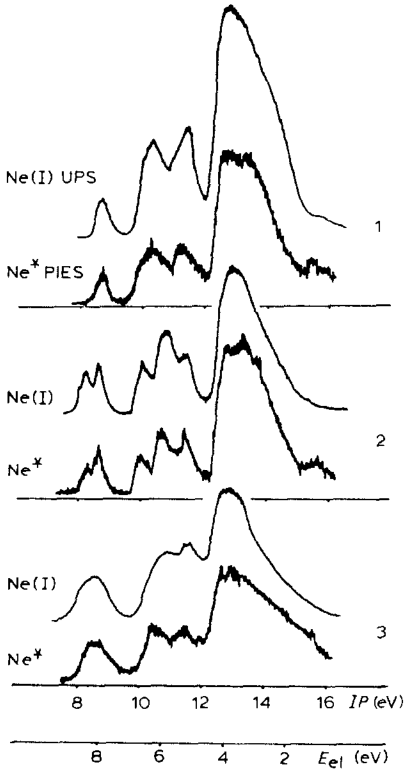


Fig. 1. Ne(I) photoelectron spectra and Ne* Penning ionization electron spectra of hexamethyldisilazane (**1**), hexamethylcyclodisilazane (**2**) and nonamethylcyclotrisilazane (**3**).

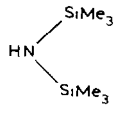
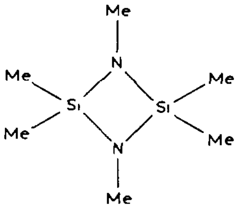
ionization potential (*IP*), can be unambiguously assigned to the lone pair orbitals of the nitrogen atoms. The sharp and nearly Gaussian-shaped band in the spectra of the compound **1** has only one peak, while in **2** there are two peaks with a splitting of about 0.33 eV. In **3** three or (in the case of D_{3h} symmetry) two peaks can be expected, but the UPS shows a structureless broad band which indicates, that there is a small splitting due to the non-rigid six-membered skeleton. Nevertheless, the positions of three peaks can be taken more or less precisely from the PIES. The first vertical *IP*'s in **2** and **3** are of almost the same value, 8.22 and 8.25 eV (the latter value from the Penning spectrum); thus if there is no significant difference in the energy of the LUMO levels, the similarity among the UV spectra in the long wavelength region for different silazane rings [9] can be explained. The first *IP* in **1** is at 8.68 eV. The reason for the shift in the *IP* compared to those in **2** and **3** is that in this compound the nitrogen atom is bonded to a hydrogen atom and not to a methyl group, which has an inductive effect.

The third broad bands in the spectra from 12 eV are very intense and may originate from the methyl groups.

The portion of the spectrum between 10 and 12 eV contains two (**1** and **3**) or three (**2**) peaks. Bock and coworkers have assigned the two peaks in **1** to orbitals having Si–C and the Si–N character, respectively [14]. However, it is difficult to give a qualitative interpretation of the three peaks in **2** and so we carried out quantum-chemical calculations by the CNDO/S method [15]. The calculated and observed *IP*'s are listed in Table 1. According to the calculations, compound **1** has four orbitals with the *IP* values between 10 and 12 eV. Three of them have Si–C character and the other Si–N character. It cannot be decided on the basis of the calculations which of these correspond to the first and second peaks, but probably the three orbitals having the Si–C character relate to the first peak at 10.35 eV and

TABLE 1

CALCULATED[a] AND OBSERVED IONIZATION POTENTIALS (eV)

Compound	$IP_{calc.}$		Assignment	$IP_{obs.}$
	CNDO/S*d*[b]	CNDO/S		
	9.60	8.80	$b_2(n)$	8.68
	10.19	9.95	b_1(Si–C)	10.35
	10.94	10.80	b_2(Si–C)	
	11.28	11.08	a_1(Si–C)	
	11.79	11.49	b_1(Si–N)	11.39
	12.10	12.04	$b_2(CH_3)$	12.2–15.0
	9.19	8.26	$b_{3u}(n)$	8.22
	9.34	8.91	$b_{2g}(n)$	8.55
	10.44	9.79	b_{2u}(Si–N)	10.10
	11.04	10.65	b_{3g}(Si–N)	10.70
	11.05	10.94	b_{1g}(Si–C)	11.42
	12.24	12.24	b_{3u}(Si–C)	12.5–14.0
	13.01	12.32	b_{1u}(Si–N)	

[a] Calculated values are corrected by use of the correlation line in Fig. 2. $IP^{i}_{corr} = -0.74\varepsilon_i + 1.7$ eV.

[b] Including *d* orbitals.

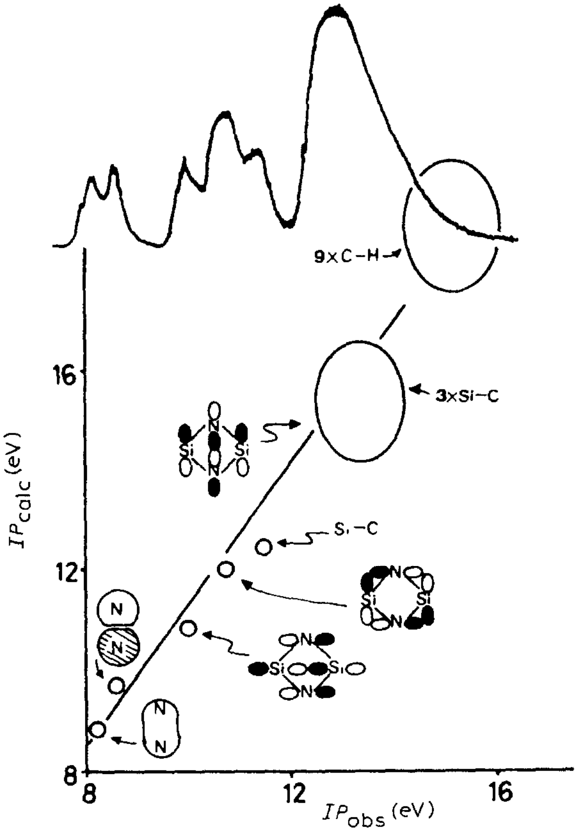


Fig. 2. Correlation between the calculated and observed ionization potentials.

the orbital having the Si–N character to the second peak at 11.39 eV. This assignment is confirmed by the Penning spectrum. Since the MO having the Si–N character is shielded from metastable atoms by the bulky $SiMe_3$ groups, its relative intensity in PIES should be lower compared with that in UPS. Applying the same interpretation to the spectra of **2**, we assign the peaks at 10.1 and 10.7 eV to the Si–N orbitals, because their relative intensities become weaker in PIES. Thus, the third peak at 11.42 eV is assigned to the Si–C orbitals. This assignment is supported by the calculations, as can be seen in Fig. 2, which shows a correlation between the calculated and the observed *IP*'s. Figure 2 also shows that the $b_{2g}(n)$ orbital lies more widely outside the molecule than the $b_{3u}(n)$ orbital. This is consistent with the fact that the second peak in the PIES of **2** is enhanced relative to the first band, and supports the present assignment of the two *n* bands.

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