

HeI and HeII photoelectron spectroscopic investigation of substituent effects in aminosilanes

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Abstract

The HeI and HeII ultraviolet photoelectron spectra of $\text{Ph}\Phi\text{NH}$, PhNHSiMe_3 , $\text{Ph}\Phi\text{NSiMe}_3$, $(\text{Ph}\Phi\text{N})_2\text{SiMe}_2$, $\text{Ph}_2\text{NSiMe}_2\Phi$, $\text{Ph}_2\text{NSiPh}_3$ and $\text{Ph}_2\text{NSi}\Phi_3$ ($\text{Me} = \text{CH}_3$; $\text{Ph} = \text{C}_6\text{H}_5$; $\Phi = \text{C}_6\text{F}_5$) are reported. Tentative assignment is given for the low-IE (ionization energy) region. HeI and HeII relative band intensities have been obtained from these spectra and also from the spectra of PhBr , ΦBr , PhNH_2 , ΦNH_2 , Ph_2NH and $\text{Ph}_2\text{NSiMe}_3$. In all cases, the HeII/HeI relative photoionization cross section ratio was determined for the highest occupied MO, localized on the aromatic amine fragment of the molecule. The cross section ratio values do not show any evidence of silicon *d*-orbital participation in the HOMO of the aromatic aminosilanes.

Introduction

The concept of $(p-d)\pi$ bonding in silicon compounds has been the subject of much controversy. Once widely accepted and extensively used, it seems to have lost much of its attraction recently. Alternative explanations have been found for a wide range of observations once held to be evidence for $p-d(\text{Si})$ interaction [1–4]. Such a great number of pro and contra arguments have been published on this subject that few of them seem to be really convincing now. The only almost certain thing is that if the interaction exists, it is rather small in energetic terms; it does not significantly affect the stability of molecules, and it has only secondary influence on bond lengths or most spectroscopic data [4–7]. In the few cases when its effect might be considerable (e.g. bond angles), the origins of the observed phenomena are strongly debated [1,8–10]. Therefore it is very difficult to obtain direct evidence for bonding with the involvement of empty silicon *d*-orbitals.

It is known from the practice of ultraviolet photoelectron spectroscopy (UPS) that the HeII/HeI intensity ratio ($R_{2/1}$) of a spectrum band—which, in turn, reflects the ratio of relative ionization cross sections at photon energies of 40.81 eV and 21.22 eV—is correlated with the character of the corresponding molecular orbital (MO) from which an electron is ionized [11]. There is a particularly marked

correlation in the spectra of transition metal complexes where ionization from MOs containing large contributions from the metal d -orbitals gives rise to bands with significantly higher HeII/HeI ratios than the others [12]. Our idea was that participation of silicon d -orbitals in one or several filled MOs of silicon compounds should lead to a similar effect in their photoelectron spectra.

We have chosen aminosilanes as the object of our investigations because most obviously anomalous molecular geometries, once explained with the help of $(p-d)\pi$ bonding, have been observed for this group of compounds [13–15]. Also it seemed a reasonable suggestion that $p(\text{N})-d(\text{Si})$ interaction is favoured by the relatively low ionization energy of the nitrogen lone pair. In the aromatic amines, the latter combines with the π -system of the phenyl rings in antibonding manner and thus its energy level is further “lifted up”. Aromatic derivatives also have another ad-

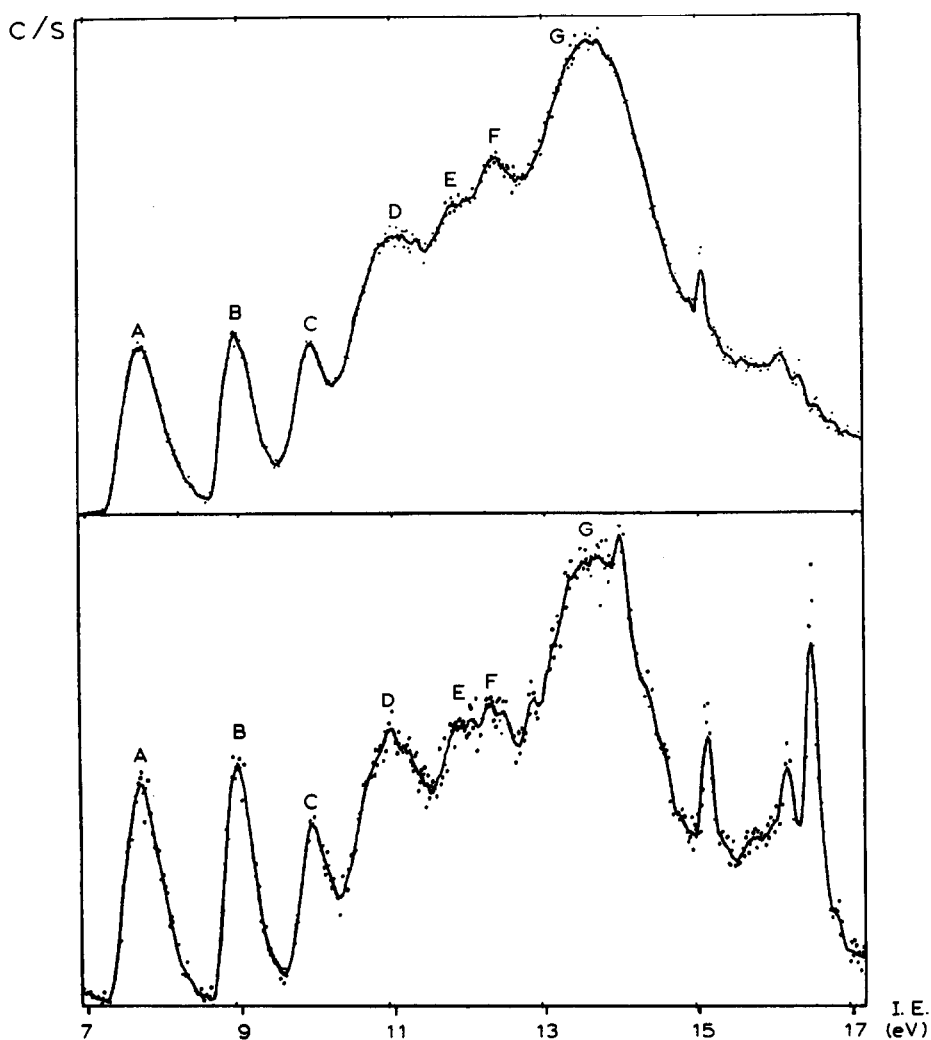


Fig. 1. HeI and HeII photoelectron spectra of $\text{C}_6\text{H}_5\text{NHSi}(\text{CH}_3)_3$.

vantage: their UP spectra contain ionizations from orbitals of pure π (phenyl) character which can serve as a kind of "internal standard" for intensity measurements. Therefore we have decided to investigate some aromatic amines and their silylated analogues by means of HeI and HeII ultraviolet photoelectron spectroscopy.

Results

The HeI and HeII photoelectron spectra of $\text{C}_6\text{H}_5\text{NHSi}(\text{CH}_3)_3$ (1,1,1-trimethyl-*N*-phenylsilanamine), $(\text{C}_6\text{H}_5)(\text{C}_6\text{F}_5)\text{NH}$ (2,3,4,5,6-pentafluoro-*N*-phenylbenzenamine), $(\text{C}_6\text{H}_5)(\text{C}_6\text{F}_5)\text{NSi}(\text{CH}_3)_3$ (1,1,1-trimethyl-*N*-pentafluorophenyl-*N*-phenylsilanamine), $[(\text{C}_6\text{H}_5)(\text{C}_6\text{F}_5)\text{N}]_2\text{Si}(\text{CH}_3)_2$ (1,1-dimethyl-*N,N'*-bis[pentafluorophen-

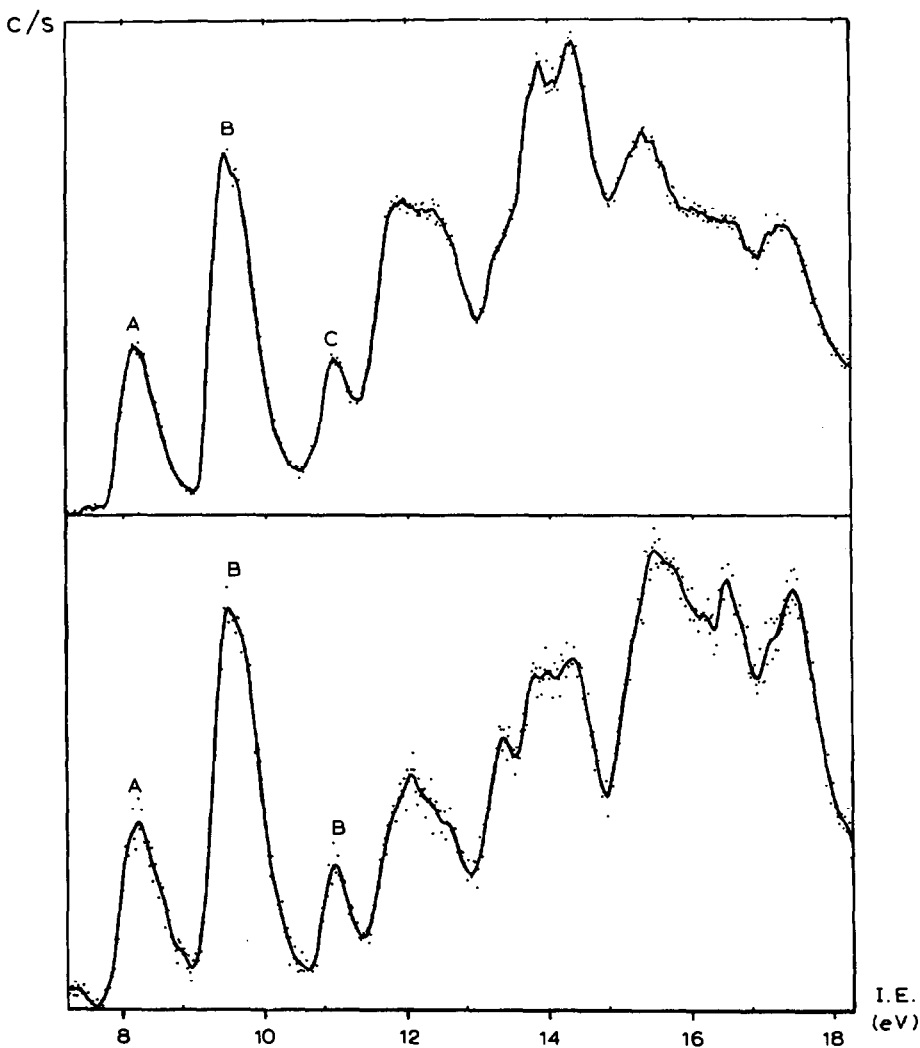


Fig. 2. HeI and HeII photoelectron spectra of $(\text{C}_6\text{H}_5)(\text{C}_6\text{F}_5)\text{NH}$.

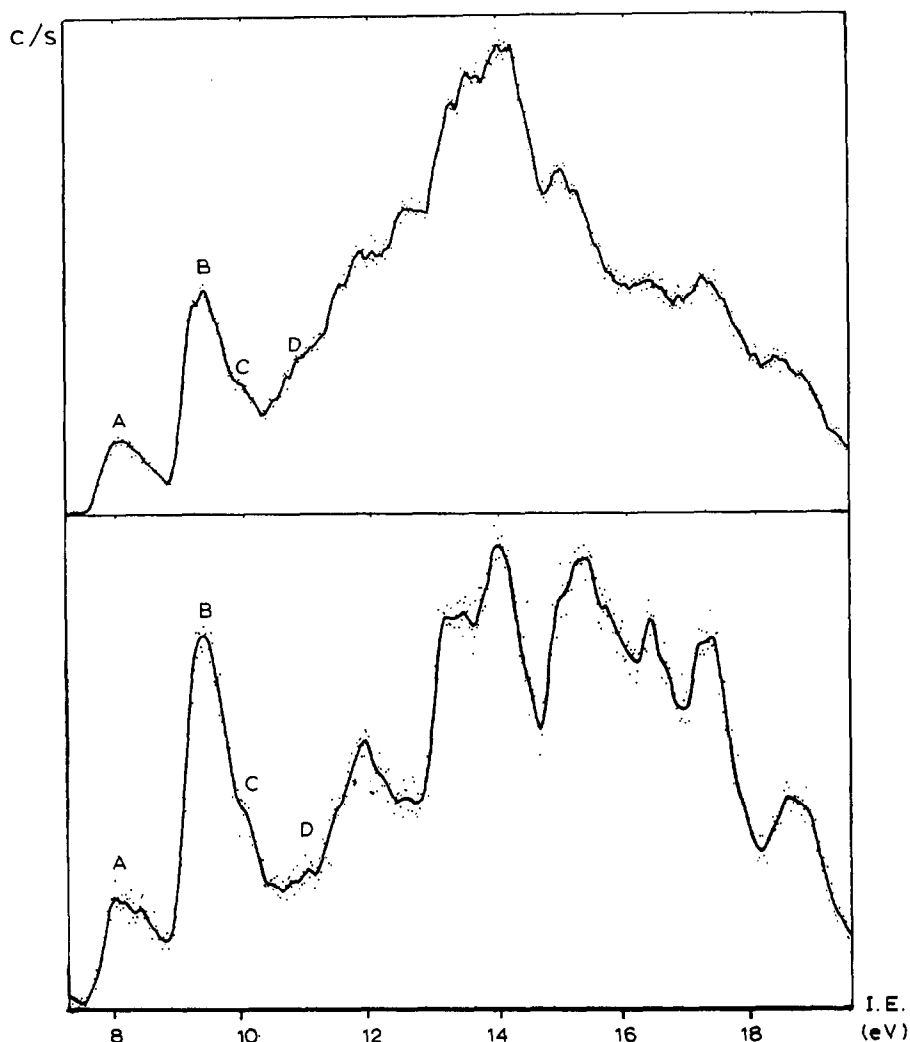


Fig. 3. HeI and HeII photoelectron spectra of $(\text{C}_6\text{H}_5)(\text{C}_6\text{F}_5)\text{NSi}(\text{CH}_3)_3$.

yl]-*N,N'*-diphenyl-silanediamine), $(\text{C}_6\text{H}_5)_2\text{NSi}(\text{CH}_3)_2(\text{C}_6\text{F}_5)$ (1,1-dimethyl-1-pentafluorophenyl-*N,N'*-diphenyl-silanimine), $(\text{C}_6\text{H}_5)_2\text{NSi}(\text{C}_6\text{H}_5)_3$ (pentaphenyl-silanimine) and $(\text{C}_6\text{H}_5)_2\text{NSi}(\text{C}_6\text{F}_5)_3$ (1,1,1-tris[pentafluorophenyl]-*N,N'*-diphenyl-silanimine) are given in Figs. 1–7. The points represent the experimental data and the continuous line is a least squares fit to these points. The vertical ionization energies are listed in Table 1. In the HeII spectra, the more or less intense sharp peak at ca. 17 eV IE is a He ($1s^{-1}$) ionization line generated by HeII β radiation. The sample of $\text{C}_6\text{H}_5\text{NHSi}(\text{CH}_3)_3$ was not totally free from N_2 ; bands from nitrogen ionization are present in the high-IE region of its spectra. No special effort was made to get rid of the nitrogen peaks since they do not interfere with the assignable region of the spectrum.

Although the HeI spectra of $\text{C}_6\text{H}_5\text{Br}$ [16], $\text{C}_6\text{F}_5\text{Br}$ [17], $\text{C}_6\text{H}_5\text{NH}_2$ [18], $\text{C}_6\text{F}_5\text{NH}_2$ [19,20], $(\text{C}_6\text{H}_5)_2\text{NH}$ [21] and $(\text{C}_6\text{H}_5)_2\text{NSi}(\text{CH}_3)_3$ [22] had already been recorded

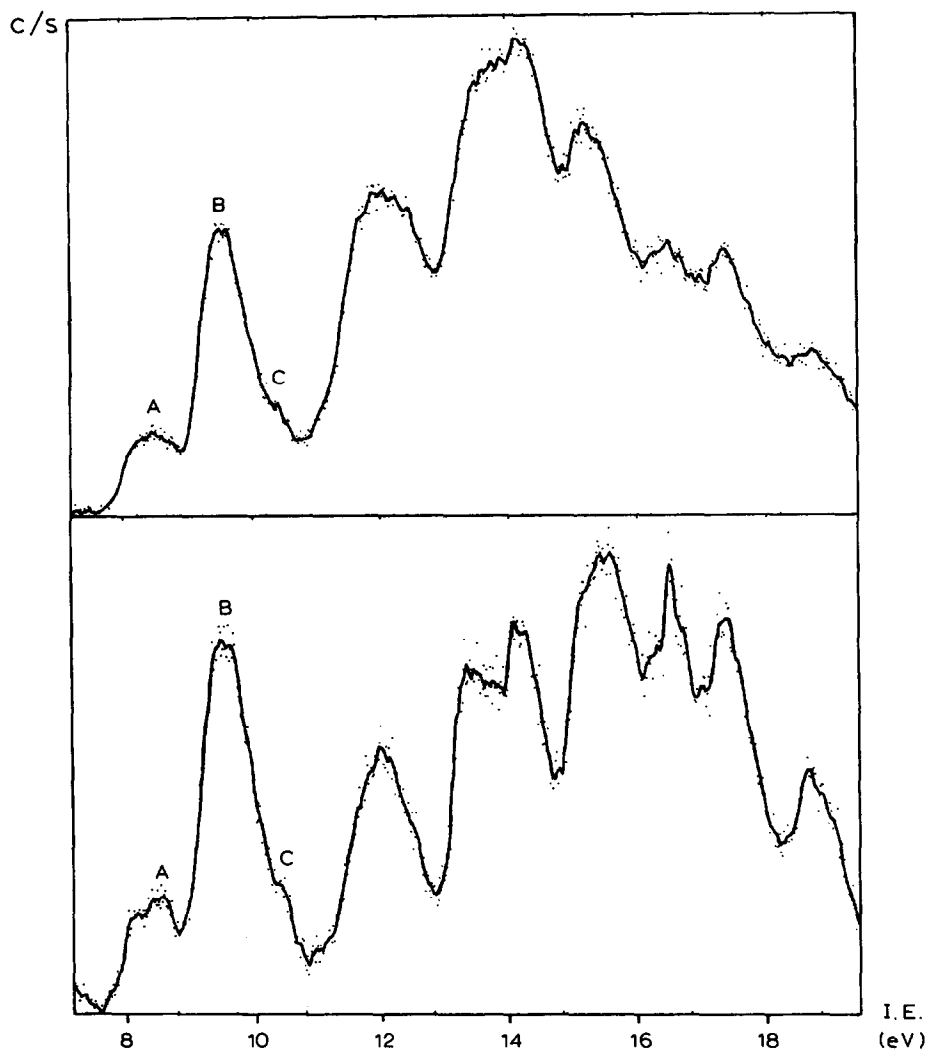


Fig. 4. Hel and HeI photoelectron spectra of $[(C_6H_5)(C_6F_5)N]_2Si(CH_3)_2$.

and assigned earlier, we have recorded both the Hel and HeI spectra of these compounds for the sake of intensity measurements. The vertical ionization energies measured by us in these spectra were in good agreement with the previously published values.

Table 2 contains the corrected relative band areas, proportional to relative partial ionization cross sections, for the low-IE bands of all spectra. They are normalized by dividing them by the area of the band with the lowest IE. The relative HeI/HeI area ratios of the bands are designated by $R_{2/1}$; obviously they are also normalized to $R_{2/1}$ of the band with the lowest ionization energy in each spectrum. For the compounds whose spectra are not presented in this communication, band assignments are given as published earlier.

Discussion

All compounds studied by us contain the aromatic amine fragment $C_6H_5N=$, and all but two—the $C_3SiN=$ moiety. Therefore it is not surprising that the structure of their PE spectra is largely analogous to that for the simpler compounds containing the trimethylsilyl group on one hand, and aniline and diphenylamine on the other hand.

Generally, the low-IE region of the PE spectra of monosubstituted aromatic amines can be divided into three parts; there are three distinct bands of approximately equal intensity in the case of aniline or pentafluoroaniline, and three bands with the intensity ratio of 1:3:1 in the case of diphenylamine. The reason for this structure is the splitting of the aromatic e_{1g} orbital [23,24]; its interaction with the

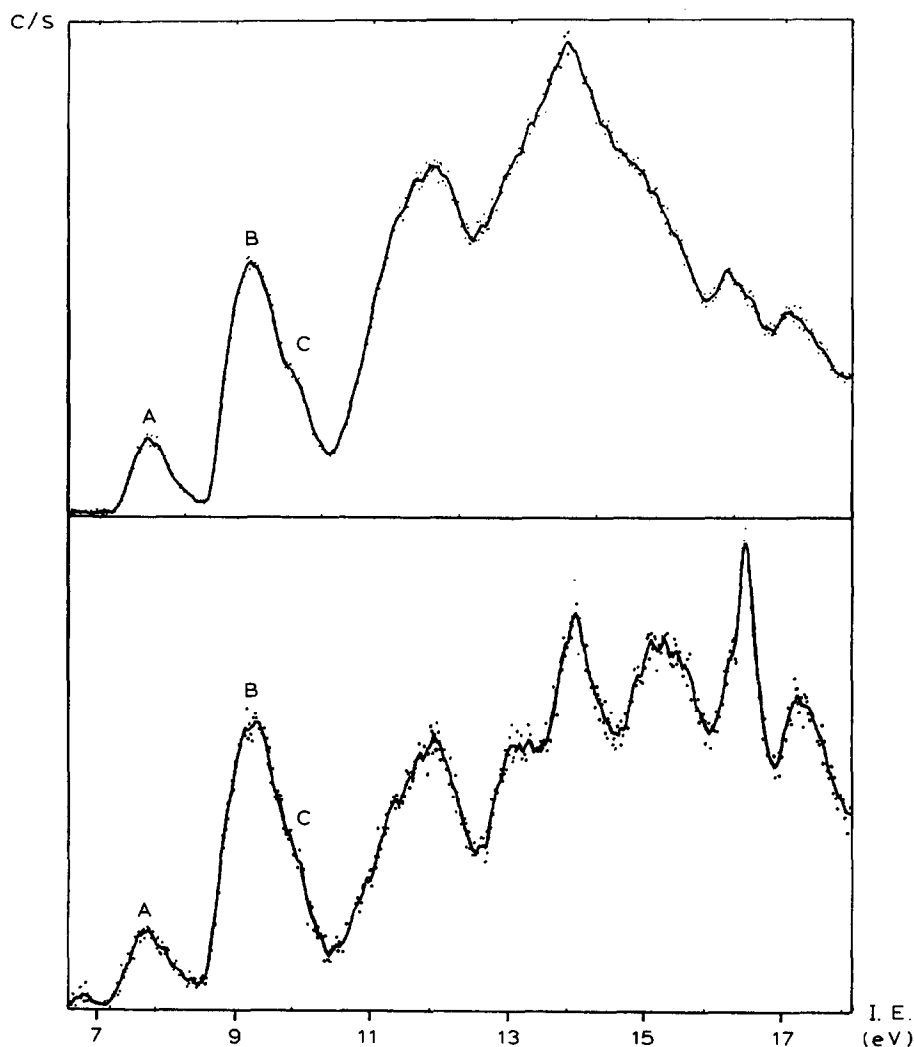


Fig. 5. HeI and HeII photoelectron spectra of $(C_6H_5)_2NSi(CH_3)_2(C_6F_5)$.

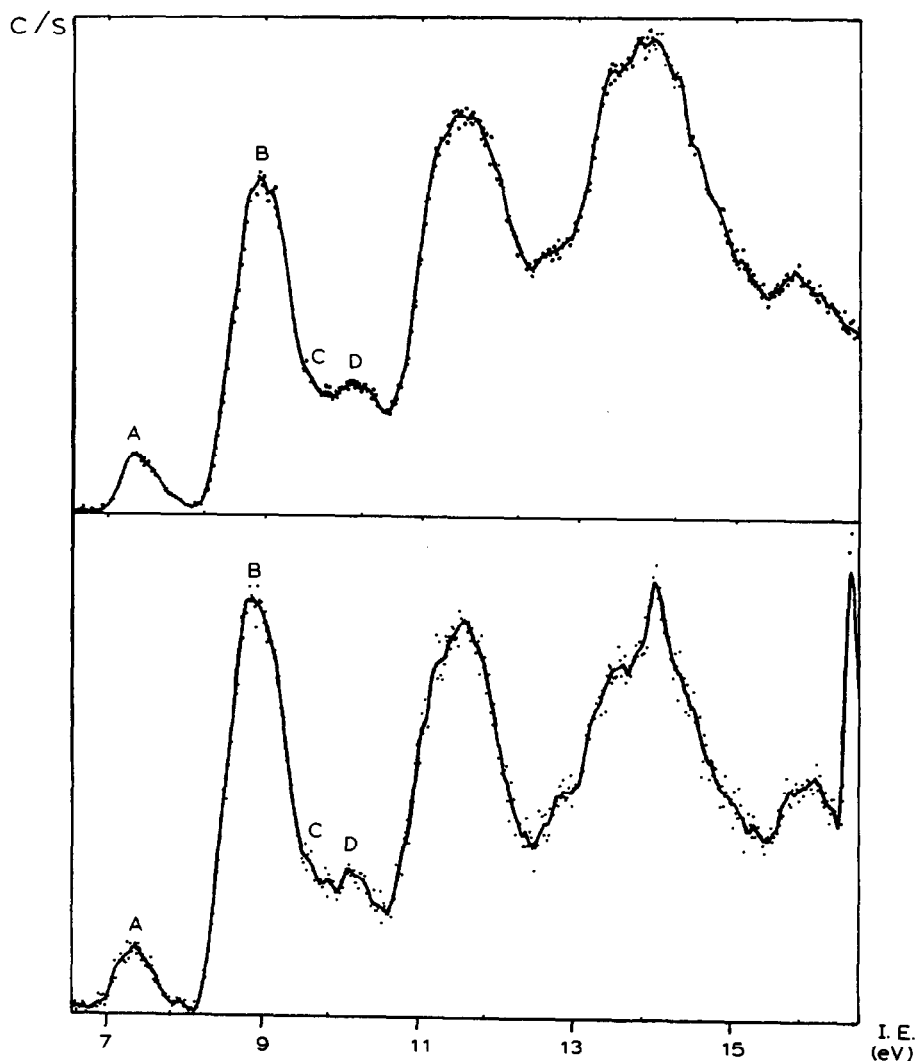


Fig. 6. HeI and HeII photoelectron spectra of $(\text{C}_6\text{H}_5)_2\text{NSi}(\text{C}_6\text{H}_5)_3$.

nitrogen lone pair leads to the formation of a bonding and an antibonding combination [25]. The energies of ionization from these two orbitals differ by 2–3 eV so they give rise to two distant bands; between these, a third band is located, corresponding to ionization from the component of e_{1g} which has a node at the place of substitution and is, consequently, undisturbed by it. Similar reasoning applies to the spectrum of diphenylamine [21]; here the π -orbitals of the two phenyl rings form three combinations that give zero overlap with the nitrogen lone pair orbital, which explains the triple intensity of the middle band. The low-IE region of the spectra of simpler aromatic aminosilanes contains three bands, just as in the case of the amines. This band system is in all cases more or less distinctly separated from the higher-IE part of the spectrum which usually does not contain individually distinguishable bands. The first three bands are, for all aminosilanes studied by us,

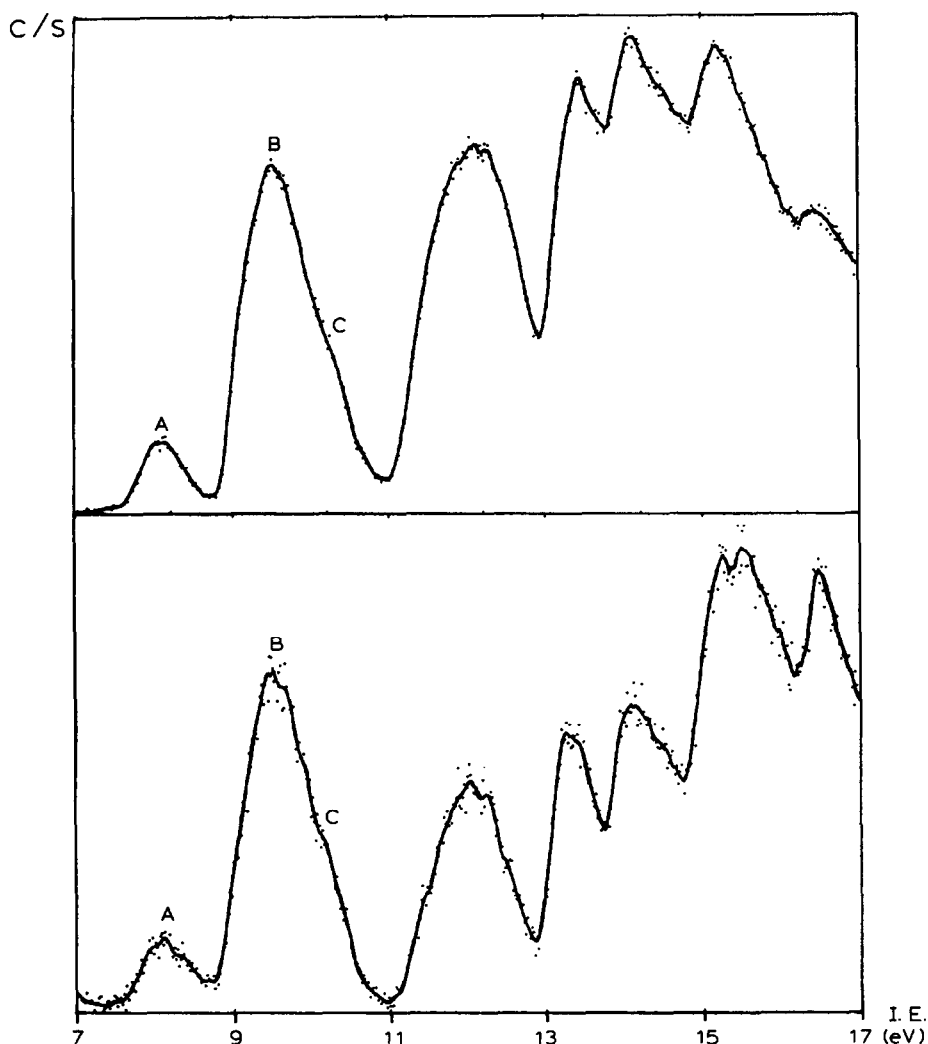


Fig. 7. HeI and HeII photoelectron spectra of $(\text{C}_6\text{H}_5)_2\text{NSi}(\text{C}_6\text{F}_5)_3$.

located at IE below 11 eV. These facts lead to the conclusion that the first three bands in the spectra of aminosilanes are originated from ionizations from the aromatic amine fragment in the same way as in the case of the amines. It can be concluded from the spectra of other trimethylsilyl compounds [22,26–30] that ionizations from orbitals localized on the Si–C bonds are to be found between 10–12 eV IE; for electrons localized on the C–H bonds of the methyl groups the IE is higher than 12 eV; finally, the IE of orbitals localized on Si–N σ -bonds in methylsilazanes [29] is 11–12 eV. There is no reason to expect a significant destabilization of any of these orbitals when the organosilicon group is connected to an aromatic amine fragment. For the aminosilanes studied by us, the valley separating the low-IE region from the rest of the spectrum is always centered at 10–11 eV; thus the low-IE region cannot contain ionizations from orbitals localized

Table 1

Vertical ionization energies and band assignments

Compound	Band	Vertical IE (eV)	Assignment
$C_6H_5NHSi(CH_3)_3$	A	7.70	$\pi_N - \pi_1$
	B	9.01	π_2
	C	10.09	$\pi_3 + n_N$
	D	11.26	$\sigma(ar)$ and Si-C
	E	12.04	π_1 and $\sigma(ar)$
	F	12.63	C-H
	G	13.93	C-H and $\sigma(ar)$
$(C_6H_5)(C_6F_5)NH$	A	8.17	$n - \pi$
	B	9.54, 9.66	π
	C	11.16	$\pi + n$
	Other	12.18; 12.68; 13.55; 14.24; 14.75; 15.82; 17.10; 17.87	
$(C_6H_5)(C_6F_5)NSi(CH_3)_3$	A	8.05	$n - \pi$
	B	9.29, 9.46	π
	C	10.08	$\pi + n$
	D	10.6-11.4	Si-C
	Other	12.13; 12.86; 13.91; 14.47; 15.45; 16.97 17.83	
$[(C_6H_5)(C_6F_5)N]_2Si(CH_3)_2$	A	8.36	$n - \pi$
	B	9.53	π
	C	10.46	$\pi + n$
	Other	12.21, 12.68; 13.92; 14.22; 14.61; 15.67; 17.03; 18.02	
$(C_6H_5)_2NSi(CH_3)_2(C_6F_5)$	A	7.69	$n - \pi$
	B	9.27	π
	C	9.93	$\pi + n?$
	Other	12.11; 14.16; 15.37; 16.64	
$(C_6H_5)_2NSi(C_6H_5)_3$	A	7.32	$n - \pi$
	B	9.02	π
	C	9.90	$\pi + n?$
	D	10.26	$\sigma(ar)$
	Other	11.79; 12.91; 13.79; 14.29; 16.28	
$(C_6H_5)_2NSi(C_6F_5)_3$	A	8.07	$n - \pi$
	B	9.50	π
	C	10.61	$\pi + n?$
	Other	12.00; 13.78; 14.46; 15.64; 16.98	

Table 2

Corrected relative band areas and HeII/HeI intensity ratios ($R_{2/1}$)

Compound	Band	Intensity		$R_{2/1}$
		HeI	HeII	
C_6H_5Br	A + B (π)	1.00	1.00	1.00
	C + D (n_{Br})	1.40	0.592	0.423
C_6F_5Br	A (π)	1.00	1.00	1.00
	B + C (n_{Br})	1.46	0.452	0.309
$C_6H_5NH_2$	A ($\pi - n$)	1.00	1.00	1.00
	B (π)	0.909	0.793	0.872
	C ($n + \pi$)	0.896	0.857	0.956
$C_6F_5NH_2$	A ($\pi - n$)	1.00	1.00	1.00
	B (π)	1.17	0.933	0.795
	C ($n + \pi$)	1.12	0.803	0.716
$(C_6H_5)_2NH$	A ($\pi - n$)	1.00	1.00	1.00
	B (π)	2.84	2.39	0.841
	C ($n + \pi$)	1.04	0.780	0.752
$(C_6H_5)_2NSi(CH_3)_3$	A ($\pi - n$)	1.00	1.00	1.00
	B (π)	2.70	2.62	0.970
	C ($n + \pi$)	1.12	0.826	0.734
$C_6H_5NHSi(CH_3)_3$	A	1.00	1.00	1.00
	B	1.00	0.947	0.947
	C	0.994	0.860	0.866
$(C_6H_5)(C_6F_5)NH$	A	1.00	1.00	1.00
	B	2.98	2.74	0.919
	C	1.19	0.856	0.717
$(C_6H_5)(C_6F_5)NSi(CH_3)_3$	A	1.00	1.00	1.00
	B + C	2.74	3.05	1.12
$[(C_6H_5)(C_6F_5)N]_2Si(CH_3)_2$	A	1.00	1.00	1.00
	B + C	4.26	4.69	1.10
$(C_6H_5)_2NSi(CH_3)_2(C_6F_5)$	A	1.00	1.00	1.00
	B + C	6.68	5.72	0.856
$(C_6H_5)_2NSi(C_6H_5)_3$	A	1.00	1.00	1.00
	B + C	9.39	10.06	1.07
$(C_6H_5)_2NSi(C_6F_5)_3$	A	1.00	1.00	1.00
	B + C	7.02	8.93	1.27

on the σ -skeleton of the molecules. On the other hand, when aromatic rings are attached to the silicon atom, the ionizations from their uppermost π -orbitals will also appear in the spectral region below 11 eV.

Thus, our assignment follows the obvious analogy between the spectra recorded by us and those of the simpler aromatic amines. In all the seven spectra listed in Table 1, band A is distinctly separated from the rest of the spectrum and it is always located at IE below 8.5 eV, significantly lower than the IE of undisturbed phenyl π -orbitals. In all cases, it corresponds to ionization from a single MO—the out-of-phase combination of the nitrogen lone-pair orbital and the appropriate component of the uppermost aromatic π -orbital(s). We shall designate this combination by “ $\pi - n$ ”. The remaining part of the low-IE spectral region (that consisting of bands B and C) is throughout assigned to ionizations from: 1.) the in-phase combination of the above orbitals (designated by “ $n + \pi$ ”); 2.) the aromatic π -orbital combinations which are unable to interact with the nitrogen lone pair; and 3.) the uppermost

π -orbitals of the aromatic ring(s) connected to the silicon atom. Silicon substitution does not lead to a major splitting between the components of e_{1g} [30,31]; consequently, 2.) and 3.) are energetically very close to each other. Never appearing separately in the spectra, they will be designated in common by " π ".

On the basis of the IE values, band B can be assigned in all cases to π -ionizations and band C to the $n + \pi$ -ionization. Although the spectra of smaller molecules show that the $n + \pi$ combination is significantly stabler than the pure aromatic π -orbitals, this assignment is very tentative in the cases where band C appears as a slight shoulder on the high-IE side of band B, particularly for the molecules containing pentafluorophenyl groups on the silicon atom. The vertical IE value of band C is obviously also very uncertain in these spectra.

An interesting feature is that, apart from the presence of $\pi - n$ and $n + \pi$ ionizations, the spectrum of pentaphenyl-silanamine is virtually identical to that of tetraphenylsilane (all IEs match within 0.1 eV). The latter, in turn, strongly resembles the spectrum of benzene. This similarity (i.e. the absence of splitting of the energy levels of benzene) was explained [32] by the suggestion that the interaction between the orbitals of different phenyl rings was very weak; in other words, the phenyl rings connected through a silicon atom were virtually isolated from each other. There is an intriguing parallel between this observation and the spectrum of *N*-pentafluorophenyl-aniline. The low-IE part of the latter is very similar to that for diphenylamine; the relative stabilization of the bands is roughly equal and even the second spectrum band, which arises from three π -ionizations, has exactly the same width in both cases. Bearing in mind that the highest π -level is by 0.9 eV stabler in hexafluorobenzene than in benzene, this is only possible if the orbitals of the two aromatic rings form an inseparable unified orbital system, i.e. the interaction between them is indeed very strong.

It has been noted earlier that the splitting between the $\pi - n$ and $n + \pi$ levels in 1,1,1-trimethyl-*N,N*-diphenyl-silanamine is significantly smaller than in diphenylamine. Then it was suggested that introduction of the trimethylsilyl substituent lead to a sharpening of valence angles around the nitrogen atom, and thus to poorer overlap between the aromatic π -orbitals and the nitrogen lone pair [22]. Our present observations are consistent with the earlier result; the splitting is about 3 eV for the aromatic amines, 2–2.4 eV for their *N*-trimethylsilyl derivatives and an intermediate value, ca. 2.6 eV, for the aminosilanes with aromatic substituents on the silicon atom. The latter value must be handled carefully since the exact position of the $n + \pi$ band is quite uncertain in the spectra of these compounds; it might indicate, however, a lesser degree of pyramidalization relative to 1,1,1-trimethyl-*N,N*-diphenyl-silanamine, in accord with the greater steric effect of the aromatic substituents relative to the methyl group. Finally it is worth noting that $(C_6H_5)(C_6F_5)NSi(CH_3)_3$ was assumed to have sharper bond angles at the nitrogen atom than $(C_6H_5)(C_6F_5)NH$, on the basis of shifts in the UV absorption spectra of these compounds [33].

As we have seen, ionization from the $\pi - n$ orbital gives rise to a well-separated band in the spectra of aromatic amines and aminosilanes. The area of this band can be reliably determined in both HeI and HeII spectra of these compounds. After correction for analyzer transmission and for the HeII β satellite spectrum, its relative ionization cross section (and HeII/HeI cross section ratio) may be compared with those of other bands in the same spectrum.

Our aim was to interrelate the HeII/HeI ratios measured for the $\pi - n$ bands in all investigated spectra. However, the comparison of relative cross sections of bands in two different spectra is clearly impossible without the exact knowledge of all experimental conditions that affect band intensities, unless some kind of "intensity standard" is found: a pair of bands, one in each spectrum, with a known ratio of ionization cross sections. In order to achieve this, we have made use of the (theoretically rather crude) approximation that if two different molecules contain the same functional group, and there are molecular orbitals characteristic for that functional group, i.e. largely localized on it without significant interaction with other parts of the molecule, then the ionization from such an orbital has the same probability for both compounds. Hence we have assumed equal photoionization cross sections, and particularly, equal HeII/HeI cross section ratios ($R_{2/1}$ values) for the corresponding UPS bands.

As the first step, $R_{2/1}$ of the uppermost π -orbital of the phenyl and pentafluorophenyl groups were compared with the help of the spectra of bromobenzene and bromopentafluorobenzene. Bands corresponding to the ionization of bromine lone pairs in both spectra were assumed to have the same $R_{2/1}$ value, defined as unity. Thus HeII/HeI cross section ratios of the π -orbitals were expressed in $R_{2/1}(n_{Br})$ units: $R_{2/1}(\pi_{C_6H_5}) = 2.37$ and $R_{2/1}(\pi_{C_6F_5}) = 3.24$ (cf. Table 2). These values were then applied to the spectra of aromatic amines and aminosilanes in the same way; e.g. in the case of aniline, $R_{2/1}(\pi) = 2.37$ was assigned to band B, identified as that of pure π (phenyl)-character, which gave $R_{2/1}(n + \pi) = 2.60$ and $R_{2/1}(\pi - n) = 2.71$. Following the assignments as given in Table 1, the $R_{2/1}$ values in Table 2 were all converted into $R_{2/1}(n_{Br})$ units in the same manner. For the bands containing several ionizations of different character, weighted averages were calculated. The resulting values are listed in Table 3.

The inspection of these data shows that despite all approximations used in the process of calculation, the $R_{2/1}$ values obtained for the $\pi - n$ bands of chemically similar compounds are remarkably close to each other: the difference is less than 4% for aniline and diphenylamine, and even less for their *N*-trimethylsilyl analogues. For the pair $(C_6H_5)(C_6F_5)NSi(CH_3)_3$ and $[(C_6H_5)(C_6F_5)N]_2Si(CH_3)_2$, with extremely similar chemical environment around the nitrogen atom, the $R_{2/1}$ s are

Table 3

Relative HeII/HeI ionization cross section ratios ($R_{2/1}$) for ionizations from the $(\pi - n)$ orbitals of the listed compounds, normalized to $R_{2/1}$ of bromine lone-pair ionization [$R_{2/1}(n_{Br}) = 1.000$]

Compound	$C_6H_5NH_2$	$(C_6H_5)_2NH$	$(C_6H_5)(C_6F_5)NH$
$R_{2/1}(\pi - n)$	2.71	2.81	3.05
Compound	$C_6H_5NHSi(CH_3)_3$	$(C_6H_5)_2NSi(CH_3)_3$	$C_6F_5NH_2$
$R_{2/1}(\pi - n)$	2.51	2.44	4.07
Compound	$(C_6H_5)(C_6F_5)NSi(CH_3)_3$	$[(C_6H_5)(C_6F_5)N]_2Si(CH_3)_2$	
$R_{2/1}(\pi - n)$	2.30	2.33	
Compound	$(C_6H_5)_2NSi(C_6H_5)_3$	$(C_6H_5)_2NSi(C_6F_5)_3$	
$R_{2/1}(\pi - n)$	2.16	2.23	
Compound	$(C_6H_5)_2NSi(CH_3)_2(C_6F_5)$		
$R_{2/1}(\pi - n)$	2.99		

virtually identical. These facts seem to justify the expectation that the errors caused by the approximations of our simple method of comparing bands in different spectra are small in relation to the variation of $R_{2/1}$ over the given range of compounds. Nevertheless, conclusions must be drawn with care, and the only obvious one probably is that substitution of a trimethylsilyl group for a hydrogen atom in aromatic amines has lead to a marked decrease of $R_{2/1}$ of the band assigned to the $\pi - n$ orbital in all cases investigated by us. The origins of this decrease are obviously rather complex. It cannot be explained with the help of one-centre factors such as change in the nitrogen character of the $\pi - n$ orbital; the decisive role must belong to multi-centre terms [11,34]. However, it may be noted that the direction of the observed change is contrary to that expected on the basis of the ($p-d$) π -interaction model. In the case of transition metal complexes, if a ligand orbital mixes to some extent (according to the calculations) with the d -orbitals of the central atom, this mixing invariably leads to a notable increase of its HeII ionization cross section relative to other ligand orbitals. This behaviour has been found characteristic for d -orbitals, regardless of their size or main quantum number [12,35,36]. Certainly there is no way of assessing the strength of this effect in the case of virtual silicon d -orbitals, but one at least would not expect lowering of the relative HeII cross section as a consequence of mixing with a d -type orbital. Thus our results do not supply any evidence of mixing between the uppermost $\pi - n$ -type orbital of the aromatic amine fragment and the empty silicon d -orbitals in the aminosilanes.

A similar conclusion is inferred from the very near $R_{2/1}(\pi - n)$ values of $(C_6H_5)_2NSi(C_6H_5)_3$ and $(C_6H_5)_2NSi(C_6F_5)_3$. The substitution of fifteen atoms of fluorine for hydrogen could be expected to exert strong influence on the supposed conjugated π -system of the molecule, and, in particular, the degree of ($p(N)-d(Si)$) interaction. This, in turn, should affect the HeII/HeI ionization cross section ratio of the orbitals taking part in this interaction, which is not the case.

We must once more emphasize that more exhaustive interpretation of our results would be a formidable theoretical task; for example, we are not able to give an explanation for the strikingly high $R_{2/1}(\pi - n)$ value measured for pentafluoroaniline, neither can we say why is this value higher for 1,1-dimethyl-1-pentafluorophenyl- N,N -diphenyl-silane than in the case of trimethylsilyl- and triphenylsilyl-amines. We can only state with some degree of certainty that the ionization cross section trends expected assuming a significant ($p(N)-d(Si)$) π -interaction are not present in our results.

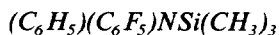
Experimental

C_6H_5Br , C_6F_5Br , $C_6H_5NH_2$, $C_6F_5NH_2$ and $(C_6H_5)_2NH$ were commercial products. The preparation of $(C_6H_5)(C_6F_5)NH$ [37], $C_6H_5NHSi(CH_3)_3$ and $(C_6H_5)_2NSi(C_6H_5)_3$ [38] was accomplished by literature methods. The remaining five aminosilanes were synthesized by the reaction of the corresponding chlorosilane with the lithium salt of the amine. The latter was prepared in tetrahydrofuran, under dry nitrogen atmosphere. The solution of diphenylamine was refluxed with a slight excess of lithium amide until the evolution of ammonia ceased; the solution of N -pentafluorophenyl-aniline was treated with the stoichiometric amount of 2.5 M

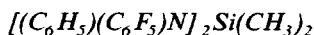
solution of butyllithium in hexane at 0 °C. The resulting THF or THF-hexane solutions were further used as follows (air and moisture were always excluded):



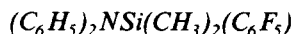
The solution of 37 mmol of lithium diphenylamide was slowly added to the solution of 4.1 g (38 mmol) of chlorotrimethylsilane in 25 cm³ of THF at room temperature. THF was then removed in vacuum and the residue was extracted with petroleum ether. The petroleum ether solution was cooled to -30 to -40 °C and filtered at the temperature readed in order to remove diphenylamine. Concentrating the filtrate and repeating the above procedure gave a satisfactorily pure product. Yield 7.2 g (81%). Purity was confirmed by ¹H NMR. The product of the literature synthesis [39,40] seems to be strongly contaminated with diphenylamine.



The solution of 32 mmol of lithium-(*N*-pentafluorophenyl-anilide) was added to a solution of 4.2 g (39 mmol) of chlorotrimethylsilane in 50 cm³ of THF at 0-10 °C. Solvents were removed in vacuum, the residue was extracted with petrol ether and the resulting solution was chromatographed on a silica column with petroleum ether as the eluant. The product was the first compound leaving the column. Yield 7.1 g (68%).



This was prepared in exactly the same way, from 64 mmol of lithium-(*N*-pentafluorophenyl-anilide) and a THF solution of 5 g (39 mmol) of dichlorodimethylsilane. Yield 14.0 g (76%).



A solution of 63 mmol of lithium diphenylamide in 60 cm³ of THF was very slowly filtered into a solution of 8.1 g (63 mmol) of dichlorodimethylsilane in 30 cm³ of THF, cooled with ice. A Grignard reagent was prepared [41] from 1.55 g of Mg turnings and 15.7 g (64 mmol) of bromopentafluorobenzene in 50 cm³ of THF and it was added at 0 °C to the solution obtained in the previous step. THF was removed in vacuum and the residue was extracted with 100 cm³ of warm petroleum ether. Concentration of this solution gave crystals of the product; they were recrystallized from petroleum ether several times. Yield 9.8 g (40%).



A solution of 12.4 mmol of lithium diphenylamide in 20 cm³ of THF was added to a solution of 2.11 g (12.4 mmol) of silicon tetrachloride in 20 cm³ of THF, cooled with ice. Consequently a Grignard solution prepared [41] from 1.1 g of Mg turnings and 9.4 g (38 mmol) of bromopentafluorobenzene in 30 cm³ of THF was dropped to the mixture. After removing THF in vacuum and extracting the residue with petroleum ether, the resulting solution was chromatographed on a silica column with petroleum ether as the eluant. The first fraction was concentrated and the remaining solid was recrystallized from petroleum ether, followed by two fractional vacuum sublimations. The less volatile fraction was collected since the main impurity was volatile (C₆F₅)₄Si. Yield 0.5 g (6%).

The compounds whose syntheses are described above gave satisfactory elemental analyses and ^1H NMR spectra consistent with their structural formulas.

HeI and HeII photoelectron spectra were recorded on a PES Laboratories 0078 spectrometer. The vapour of liquids and pentafluoroaniline was introduced into the ionization chamber through a gas inlet equipped with a needle valve; the less volatile solids were vapourized in the chamber by the heat from the helium lamp. The resolution was 0.05 eV or better. The data from 20–60 scans were accumulated using a Research Machines 380Z microcomputer; the typical intensity of the highest peak reached 4000 counts in the HeI spectra and 1000 counts in the HeII spectra. The spectra were calibrated by using N_2 , Xe and the helium autoionization line. The calibration error was no greater than 0.02–0.03 eV.

The “shadow” spectrum caused by ionization by $\text{HeII}\beta$ radiation was numerically calculated and subtracted from the HeII spectra. The low ionization energy regions of the HeI and the corrected HeII spectra were fitted with asymmetric Gaussian curves. The band areas obtained were corrected for the analyser transmission factor by dividing by the electron kinetic energy. The error of area determination was less than 2%; somewhat greater error might result from the uncertainty of determination of the $\text{HeII}\beta$ “shadow spectrum” (whose total intensity was taken 9% of the original spectrum) and from overlapping bands.

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