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Geometry and electronic structure of silylated hydroxylamine and carbamic acid derivatives

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Abstract

The He(I) and He(II) photoelectron spectra of silylated nitrogen and oxygen compounds were recorded in order to study their electronic structure and geometry. The X-ray crystal structure of *N*-trimethylsilyl *O*-*tert*-butyl carbamate is given. Ab initio Hartree–Fock calculations were also carried out to obtain theoretical geometries of the compounds and to help the assignments of their photoelectron spectra by means of Koopmans' theorem. Our results show that the planar/pyramidal spatial arrangements around nitrogen in the investigated compounds can be rationalised by the negative hyperconjugative effect of silyl group(s), by electrostatic effects and by the lone-pair repulsion of the neighbouring nitrogen and oxygen atoms. The considerable distortions in geometry cause only small variations in the electronic structure, and there are relatively small energy differences (about 15–20 kJ mol^{-1}) between the planar and the pyramidal conformers. These conclusions can also be applied for silylated oxygen compounds. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Ultraviolet photoelectron spectroscopy; X-ray diffraction; Conformation; Silylamines; Silylhydroxylamines; Silylcarbamates

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1. Introduction

The coordination geometry of compounds containing Si–N bond(s) has been of considerable interest. Mono-, di- and trisilyl amines, with very few exceptions, possess a planar arrangement around the nitrogen. The planar structure is associated with low basicity and with poor donor properties of the silylated amines [1,2]. For a long period of time, it was argued that the special bonding characteristics are due to p_π–d_π interactions [3], but more sophisticated theoretical treatments showed that negative hyperconjugative effect of the silyl-group [4,5], or an electrostatic repulsion model [6] can also be used to rationalise most of the unique features of silylamines. Systematic investigations of *N*-silylated carbamic acids and their derivatives show that in these compounds the nitrogen atom has also a planar conformation due to the above effects and the conjugation between the nitrogen lone-pair and the C=O double bond (amide-like structure) [7–13].

Recent studies have revealed that silylhydroxylamines even with two attached silyl groups possess a

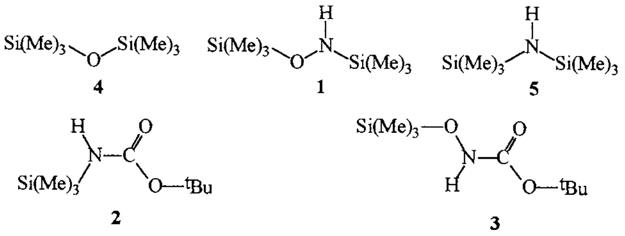

Fig. 1. The formulae of the investigated compounds.

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Table 1
Selected experimental and calculated geometric parameters of **4** ($Me_3Si–O–SiMe_3$)

	Electron diffraction [29]	HF/dzp	HF/dz(2)p	HF/tz2p
Number of basis functions		241	256	401
Calculated energy (a.u.)		−890.551281	−890.576915	−890.742295
r(Si–O)[a]	1.63 Å	1.67 Å	1.63 Å	1.62 Å
r(Si–C)[a]	1.87 Å	1.89 Å	1.87 Å	1.88 Å
∠(Si–O–Si)	148°	134.7°	162.9°	177.9°

[a] Average values.

Table 2
Selected experimental and calculated geometric parameters of **5** ($Me_3Si–NH–SiMe_3$)

	Electron diffraction [30]	HF/dzp	HF/dz(2)p	HF/tz2p
Number of basis functions		246	261	410
Calculated energy (a.u.)		−870.632452	−870.691847	−870.852647
r(Si–N)[a]	1.74 Å	1.72 Å	1.73 Å	1.73 Å
r(Si–C)[a]	1.88 Å	1.83 Å	1.88 Å	1.88 Å
r(N–H)	0.98 Å (fixed)	0.99 Å	1.00 Å	1.00 Å
Sum of bond angles around N	360.0° (fixed)	360.0°	360.0°	360.0°

[a] Average values.

pyramidal arrangement around the nitrogen [14,15]. This can also be explained by an electrostatic interaction between the oxygen and the silicon atoms [14] or a lone-pair repulsion of the neighbouring nitrogen and oxygen atoms [16]. The calculated energy differences between the planar and the pyramidal conformers of silylamines and silylhidroxylamines are small, in the case of *N*,*N*-disilyl hydroxylamine ($(SiH_3)_2NOH$) it is about 8 kJ mol^{-1} [16].

Ultraviolet photoelectron spectroscopy is a useful method for studying the electronic structure and geometry of molecules. One can expect that the higher localisation of the nitrogen lone pair in a pyramidal conformer results in the change of the corresponding ionisation energy compared to the photoelectron (PE) spectrum of a planar conformer. Furthermore, d-orbital participation in a molecular orbital increases the relative intensity of the corresponding peaks in He(II) PE spectra compared to He(I) ones. These spectral features can help the structure elucidation of the molecules [17].

In conjunction with these problems we have studied three compounds, namely, *N*,*O*-bis(trimethylsilyl) hydroxylamine (**1**), *N*-trimethylsilyl *O*-*tert*-butyl carbamate (**2**) and *N*-trimethylsiloxy *O*-*tert*-butyl carbamate (**3**) (Fig. 1). Ultraviolet photoelectron spectra of the compounds were recorded with He(I) and He(II) photon sources. The X-ray crystal structure of **2** was determined too. We have also carried out ab initio Hartree–Fock computations in order to gain calculated geometries for the compounds and to help the assignment of their PE spectra.

2. Experimental

Compounds **1**, **2**, **3** were prepared by known methods [18]. The purity of the compounds was checked by gas chromatography.

The PE spectra were recorded on an ATOMKI ESA 32 photoelectron spectrometer [19]. The spectrometer consists of a hemispherical analyser, a gas and direct inlet system. The spectra were calibrated against the Ar $^2P_{1/2}$ and $^2P_{3/2}$ peaks. By evaluating the spectra Shirley background and pseudo-Voigt peak shape were applied, the positions of the fitted pseudo-Voigt peaks were used to determine the vertical ionisation energies. The accuracy of the ionisation energies is estimated to be ± 0.05 eV, the energy resolution was better than 25 meV in He(I) and about 35 meV in He(II) spectra as measured on Ar ionisation.

In the course of the X-ray diffraction study of *N*-trimethylsilyl *O*-*tert*-butyl carbamate (**2**) data collection was performed on a Rigaku RAXIS-II imaging plate detector using graphite-monochromated Mo–K$_\alpha$ radiation at 293 K. Data processing was carried out using the software supplied with the diffractometer. Structure solution with direct methods was carried out with the teXsan package [20]. The refinement was carried out using the SHELXL-93 program [21] with full matrix least squares method on F^2. The crystal data were as follows: $C_8H_{19}NO_2Si$; M = 189.33; monoclinic, space group $P2_1/a$; $a = 11.405(5)$ Å, $b = 12.231(6)$ Å, $c = 9.442(3)$ Å, $\beta = 106.58(2)°$; $V = 1262.4(9)$ Å^3; $Z = 4$; $D_c = 1.059$ g cm^{-3}; μ(Mo–K$_\alpha$) = 0.158 cm^{-1}; λ(Mo) = 1.5418 Å.

Intensities of 5999 reflections (2018 unique; $R_{\mathrm{sym}} = 10.44\%$) were measured to 24.84°. Corrections for Lorenz polarisation effects were applied. Anisotropic thermal motion parameters were refined for the non-hydrogen atoms and isotropic thermal motion parameters for the hydrogen atoms. The positions of the hydrogen atoms were refined by the riding model. The refinement converged at $R = 0.0639$ for 1352 ($I > 2\sigma$) reflections.

The Hartree–Fock calculations were done using the Turbomole 2.35 program package [22] with no symmetry constraints. We employed the dzp [23], tz2p [23] and the dz(2)p [24] basis sets for the calculations. The dz(2)p basis set is equivalent to the original dzp basis set for the carbon and hydrogen atom, while for the nitrogen, oxygen and silicon atoms dz(2)p set means the dz basis set [23] augmented with two sets of polarisation functions taken from the tz2p basis set. This basis set is proved to provide accurate geometries at ab initio HF and MP2 levels with a moderate computational cost [24]. The geometry optimisations were carried out in natural internal coordinates [25] defined automatically by Turbomole.

The spectra were interpreted by means of Koopmans' theorem [26].

Table 3
Selected calculated geometric parameters of **1** (Me_3Si–O–NH–$SiMe_3$)

	HF/dzp	HF/dz(2)p	HF/tz2p
Number of basis functions	261	281	435
Calculated energy (a.u.)	−945.475023	−945.501107	−945.687540
r(Si–N)	1.80 Å	1.76 Å	1.76 Å
r(Si–O)	1.83 Å	1.66 Å	1.66 Å
r(Si(N)–C)[a]	1.84 Å	1.87 Å	1.88 Å
r(Si(O)–C)[b]	1.81 Å	1.87 Å	1.88 Å
r(N–O)	1.32 Å	1.42 Å	1.42 Å
r(N–H)	1.03 Å	1.00 Å	1.00 Å
∠(Si–O–N)	119.5°	113.6°	114.1°
Sum of bond angles around N	339.2°	330.3°	331.3°

[a] Average values in the case of the silicon atom attached to the nitrogen atom.

[b] Average values in the case of the silicon atom attached to the oxygen atom.

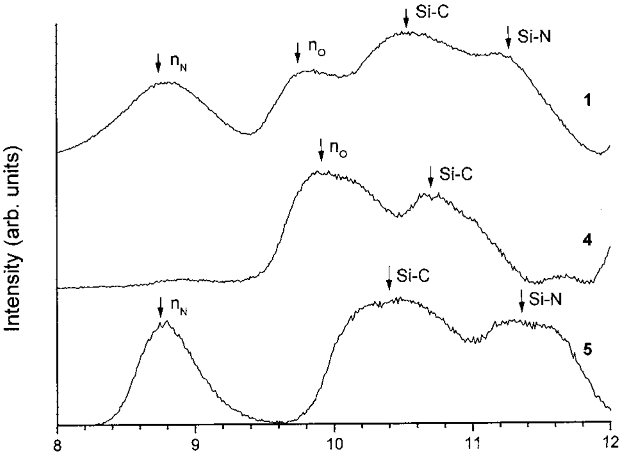

Fig. 2. He(I) photoelectron spectra of **1** (Me_3Si–O–NH–$SiMe_3$), **4** (Me_3Si–O–$SiMe_3$) and **5** (Me_3Si–NH–$SiMe_3$) (the MOs corresponding to the peaks denoted by n_N and n_O have some Si–C participation too, see text and Table 4).

3. Results and discussion

As far as the PE spectra are concerned we discuss only those of obtained by He(I) source because no difference can be found between the corresponding He(I) and He(II) measurements. This experimental finding indicates a negligible d-orbital participation in the bonding.

In order to put **1** into a consistent, chemically related series of compounds we also have studied hexamethyl disiloxane (**4**) and hexamethyl disilazane (**5**) (Fig. 1). Their photoelectron spectra [27,28] and gas phase geometries [29,30] are well known.

As the calculated geometries of **4** and **5** agree well with their electron diffraction structures [29,30] (Tables 1 and 2), the calculated geometric parameters of **1** (Table 3) are considered to represent correctly its gas phase geometry (although the good agreement between the calculated and experimental geometry of **4** and **5** may be only fortunate, our idea is also supported by the good correlation between the calculated and experimental geometries of **2** and **3**—see later in text and Table 5). The geometric parameters calculated with dz(2)p basis set are almost the same as in the case of the tz2p basis set (the only exception is the Si–O–Si bond angle in the case of **4**, where the computed angle varies heavily with the employed basis set).

The calculated parameters of the compounds show the aforementioned variations: the conformation around nitrogen is planar in the case of **5** (amine) and pyramidal in the case of **1** (hydroxylamine). The Si–N bond length is slightly longer in compound **1** than in **5**, while the Si–C bond lengths are almost the same. It is also interesting to point out that the Si–O–X bond angle also has a smaller value in the case in **1** than in **4**, similar to the case of bis(trimethylsilyl) peroxide [31]. In addition, the Si–O bond length in **1** is slightly longer than that of **4**.

The low-energy region of the He(I) photoelectron spectra of the compounds **1**, **4** and **5** are shown in Fig. 2. Their measured and calculated ionisation energies are collected in Table 4. As usual, the calculated ionisation energies are higher than the experimental ones and the

Table 4
Experimental and calculated ionisation energies and orbital characters of **1** ($Me_3Si–O–NH–SiMe_3$), **4** ($Me_3Si–O–SiMe_3$) and **5** ($Me_3Si–NH–SiMe_3$)

1	Exp.	8.72	9.74	10.51	11.27
I.E. (eV)	HF/dzp	10.07 n_N+Si–C	11.16 n_O+Si–C	11.54, 11.71, 11.79 Si–C	12.61 Si–N
	HF/dz(2)p	10.24 n_N+Si–C	11.27 n_O+Si–C	11.60, 11.81, 11.89 Si–C	12.75 Si–N
	HF/tz2p	10.22 n_N+Si–C	11.22 n_O+Si–C	11.54, 11.77, 11.85 Si–C	12.76 Si–N
4	This work		9.90	10.70	
I.E. (eV)	Ref. [27]		9.88	10.73	
	HF/dzp		10.96, 10.96 n_O+Si–C	11.69, 11.69 Si–C	
	HF/dz(2)p		11.09, 11.11 n_O+Si–C	11.77, 11.78 Si–C	
	HF/tz2p		11.01, 11.01 n_O+Si–C	11.70, 11.70 Si–C	
5	This work	8.74		10.40	11.35
I.E. (eV)	Ref. [28]	8.68		10.35	11.39
	HF/dzp	9.91 n_N+Si–C		11.49, 11.50, 11.51 Si–C	12.46, 12.86 Si–N
	HF/dz(2)p	10.04 n_N+Si–C		11.58, 11.60, 11.60 Si–C	12.54, 13.00 Si–N
	HF/tz2p	9.99 n_N+Si–C		11.51, 11.54, 11.54 Si–C	12.50, 12.98 Si–N

Table 5
Selected experimental (after the additional refinement with anisotropic N–H, see text) and calculated geometric parameters of **2** ($Me_3Si–NH–CO–O^tBu$) and **3** ($Me_3Si–O–NH–CO–O^tBu$)

	2		**3**	
	X-ray (this work)	HF/dz(2)p	X-ray [18]	HF/dz(2)p
Number of basis functions		246		266
Calculated energy (a.u.)		−807.214226		−882.016563
r(Si–N)	1.73 Å	1.76 Å		
r(Si–O)			1.67 Å	1.67 Å
r(Si–C)[a]	1.87 Å	1.87 Å	1.84 Å	1.87 Å
r(N–O)			1.42 Å	1.38 Å
r(N–H)	0.80 Å	1.00 Å	0.87 Å	1.00 Å
r(N–C)	1.36 Å	1.36 Å	1.36 Å	1.38 Å
∠(Si–O–N)			111.9°	115.2°
Sum of bond angles around N	359.9°	360.0°	343.4°	336.7°

[a] Average value.

corresponding values increase in the dzp–tz2p–dz(2)p order of basis sets. However, the order of molecular orbitals does not change. The spectra of **4** and **5** agree well with the data found in the literature [27,28]. The first peak in their spectra can be related to molecular orbitals with substantial oxygen (9.90 eV in **4**) and nitrogen (8.74 eV in **5**) lone-pair character, with some admixing of the Si–C σ-bonds. The peaks at 10.70 eV in the spectrum of **4** and at 10.40 eV in the spectrum of **5** corresponds to ionizations from the Si–C σ-bonds, followed by a peak at 11.35 eV which can be related to the Si–N σ-bonds. It is clearly seen that the spectrum of **1** can be constructed by adding the corresponding spectral parts of **4** and **5** together. The third peak in the spectrum of **1** seems to be a bit out of line in the assignation. However, here it has to be taken into consideration that, similarly to the second peak in the spectrum of **5**, this peak is quite wide and according to the HF calculations it consists of several ionisations. Finally, it is interesting to note that the joint electronic and geometric effects do not alter significantly the ionisation energy of the nitrogen lone pair in **1** compared to **5**, indicating a negligible substituent/geometric effect.

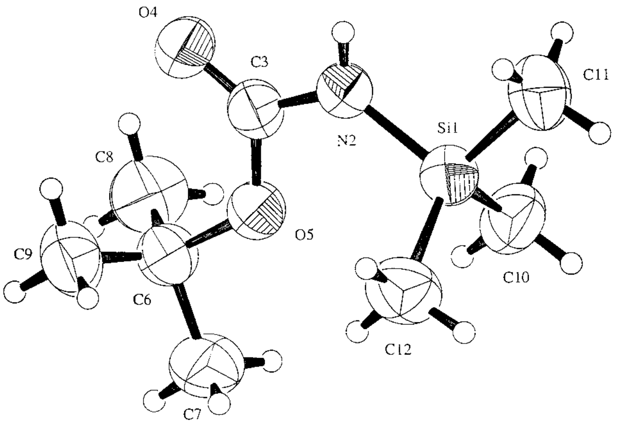

Fig. 3. The X-ray structure of *N*-trimethylsilyl *O*-*tert*-butyl carbamate (**2**).

Table 6
Fractional coordinates of **2** (Me$_3$Si–NH–CO–O^{t}Bu) with equivalent isotropic displacement parameters with estimated standard deviations in parentheses

Atom	x	y	z	B_{eq} (Å^2)
Si1	0.20910(9)	0.04112(8)	0.35713(11)	0.0966(5)
O4	0.1113(2)	−0.1019(2)	−0.0289(3)	0.1126(9)
O5	0.2875(2)	−0.1076(2)	0.1634(3)	0.1003(8)
N2	0.1303(3)	−0.0031(2)	0.1808(3)	0.0897(8)
C3	0.1698(3)	−0.0733(3)	0.0933(4)	0.0937(10)
C6	0.3534(3)	−0.1868(3)	0.0969(4)	0.1014(11)
C7	0.4788(3)	−0.1954(4)	0.2132(5)	0.139(2)
C8	0.3696(4)	−0.1438(4)	−0.0451(5)	0.144(2)
C9	0.2865(4)	−0.2955(3)	0.0783(5)	0.134(2)
C10	0.3526(4)	0.1163(3)	0.3566(5)	0.1273(14)
C11	0.0933(4)	0.1324(3)	0.4045(5)	0.138(2)
C12	0.2481(4)	−0.0751(3)	0.4856(5)	0.1343(15)

Table 7
Selected bond lengths from the X-ray structure of **2** (Me$_3$Si–NH–CO–O^{t}Bu) with estimated standard deviations in parentheses

Atom	Atom	Bond length (Å)
Si1	N2	1.737(3)
Si1	C12	1.839(4)
Si1	C11	1.878(4)
Si1	C10	1.879(4)
O4	C3	1.208(4)
O5	C3	1.381(4)
O5	C6	1.472(4)
N2	C3	1.355(4)
C6	C8	1.500(6)
C6	C9	1.517(5)
C6	C7	1.539(5)

It is also informative to compare the HF/dz(2)p calculated energies of the planar and pyramidal conformers of compounds **1** and **5**. The natural internal coordinate refering to the pyramidality was constrained in compound **5** to the same value as it is in the case of the minimum energy conformer of compound **1**. In parallel, the same coordinate of **1** was constrained to be planar. All the other natural internal coordinates were repeatedly optimized. The results show that the pyramidal conformer of compound **5** has a higher energy only by 15.15 kJ mol^{-1} than the minimum energy planar conformer. In contrast, in the case of compound **1** the planar conformer is at higher energy by 22.11 kJ mol^{-1} than the minimum energy pyramidal conformer. The δ_{NSi_2} Raman-frequency also indicates the flexibility of **5**; the corresponding value is 246 cm^{-1} [32].

Examining the same sort of problems in the case of carbamic acid derivatives it is resonable to consider first their X-ray structure. A previous X-ray diffraction study of *N*-trimethylsiloxy *O*-*tert*-butyl carbamate (**3**) [18] shows that the OHNCOO moiety of **3** is not planar in spite of the possibility of an amide-like structure. The OHNC and the NCOO planes form an angle of about 18°. An additional refinement calculation was also carried out with anisotropic N–H. As a result of this refinement the hydrogen atom moved out of the plane of the ONSi moiety. The r.m.s. height of N above the HOC plane is 0.2048 Å and the sum of bond angles around N is 343.4° (Table 5). These structural features can be attributed to the same effects as suggested in the case of hydroxylamines.

The X-ray structure of *N*-trimethylsilyl *O*-*tert*-butyl carbamate (**2**) was determined by single-crystal studies and is shown in Fig. 3. The fractional coordinates of non-hydrogen atoms are collected in Table 6, bond lengths, bond angles and selected torsion angles are shown in Tables 7–9. The main crystal building force is

Table 8
Selected bond angles from the X-ray structure of **2** (Me$_3$Si–NH–CO–O^{t}Bu) with estimated standard deviations in parentheses

(1)	(2)	(3)	Angle (°)
N2	Si1	C12	110.7(2)
N2	Si1	C11	101.9(2)
C12	Si1	C11	110.9(2)
N2	Si1	C10	111.3(2)
C12	Si1	C10	109.5(2)
C11	Si1	C10	112.5(2)
C3	O5	C6	122.7(3)
C3	N2	Si1	127.7(3)
O4	C3	N2	125.2(3)
O4	C3	O5	124.5(3)
N2	C3	O5	110.3(3)
O5	C6	C8	111.0(3)
O5	C6	C9	109.0(3)
C8	C6	C9	112.9(4)
O5	C6	C7	103.0(3)
C8	C6	C7	109.6(3)
C9	C6	C7	110.9(4)

Table 9
Selected torsion angles from the X-ray structure of **2** (Me$_3$Si–NH–CO–O^{t}Bu) with estimated standard deviations in parentheses[a]

(1)	(2)	(3)	(4)	Angle (°)
C12	Si1	N2	C3	−60.6(3)
C11	Si1	N2	C3	−178.6(3)
C10	Si1	N2	C3	61.3(3)
Si1	N2	C3	O4	179.8(3)
Si1	N2	C3	O5	−0.4(4)
C6	O5	C3	O4	−2.0(5)
C6	O5	C3	N2	178.2(3)
C3	O5	C6	C8	61.2(4)
C3	O5	C6	C9	−63.8(4)
C3	O5	C6	C7	178.4(3)

[a] The sign is positive if, when looking from atom (2) to atom (3) a clockwise motion would superimpose it on atom (4).

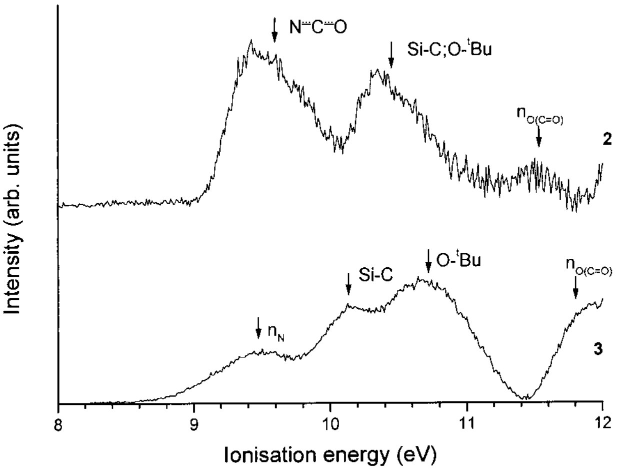

Fig. 4. He(I) photoelectron spectra of **2** (Me_3Si–NH–CO–O^{t}Bu) and **3** (Me_3Si–O–NH–CO–O^{t}Bu).

the intermolecular hydrogen bond formed between the carbonyl oxygen and the NH group (N2(1)...O4(2) 3.007Å, N2(1).H2(1).O4(2) 170.2°).

According to the X-ray diffraction study the Si1–O5 non-bonded distance is only 2.85 Å (the corresponding value calculated at the HF/dz(2)p level is 2.95 Å) while the sum of their van der Waals radii is 3.4 Å. This fact can be an indication of a non-bonded interaction between the oxygen and silicon atoms. The 'pseudo-pentacoordinate' environment of silicon atom is not uncommon in the case of silylated carbamates: this structural feature can be the reason for their high silylating reactivity [24].

As the employed structure refinement method (see Section 2) does not allow to determine the exact position of the H atom attached to the N atom, an additional refinement calculation was also carried out with anisotropic N–H. According to this refinement the geometry around the N atom is as follows: (Si1–N2) = 1.733(3) Å, (N2–C3) = 1.357(4) Å, (N2–H2) = 0.80(4) Å, (C3–N2–Si1) = 127.9(3)°, (H2–N2–Si1) = 122(3)°, (H2–N2–C3) = 110(3)°. In contrast to the case of **3**, the SiNHC group is close to planarity: the rms. height of N above the HSiC plane is 0.01563 Å and the sum of bond angles around N is 359.9° (Table 5).

The low-energy regions of the He(I) spectra of the carbamic acid esters **2** and **3** are shown in Fig. 4. The measured and calculated ionisation energies are collected in Table 10. The first peak in the photoelectron spectrum of **2** at 9.60 eV can be assigned to an ionisation from the conjugated π-system of the amide group having a substantial contribution from the nitrogen lone pair. The second peak at 10.45 eV corresponds to ionisations from the Si–C and O–^{t}Bu bonds and the third peak at 11.53 eV belongs to an oxygen lone pair of carbonyl oxygen. In the case of **3**, the first peak at 9.48 eV can be assigned to the nitrogen lone pair, successive ionizations can be related to the same orbitals as in the case of **2**. Similar to the case of **1** and **5**, the first ionisation energies of **3** and **2** do not differ significantly; the nitrogen lone pair of **3** has even a slightly lower ionisation energy than that of the conjugated π-system of **2**. This experimental finding supports our previous suggestion that pronounced geometric differences do not result in charasterestic ionisation energy changes.

4. Conclusions

Our photoelectron spectroscopic and quantum chemical studies show that the considerable changes in the geometry of silylated amines and hydroxilamines cause relatively small differences in their electronic structures. Furthermore, there are only slight energy differences (about 15–20 kJ mol^{-1}) between the planar and the pyramidal structures of these type of compounds. The silyloxy carbamates also have pyramidal arrangement around nitrogen similar to the silylhydroxilamines, in spite of the possibility of a conjugated and therefore planar amide-like structure. In the case of silylated oxygen compounds, the Si–O–X bond angle also shows great variations depending on the type of substituent X. The reasoning for these changes can be the same as for nitrogen compounds. In addition, we showed that the dz(2)p basis can be employed instead of the much larger tz2p basis set to obtain geometric parameters.

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Table 10
Experimental and calculated ionisation energies and orbital characters of **2** (Me_3Si–NH–CO–O^{t}Bu) and **3** (Me_3Si–O–NH–CO–O^{t}Bu)

2	Exp.	9.60	10.45	11.53	
I.E. (eV)	HF/dz(2)p	10.76 N⋯C⋯O	11.61, 11.99, 12.08, 12.33 Si–C; O–^{t}Bu	13.04 $n_{O(C=O)}$	
3	Exp.	9.48	10.12	10.72	11.8
I.E. (eV)	HF/dz(2)p	10.95 n_N	11.41, 11.75 Si–C	12.07, 12.25 O–^{t}Bu	13.27 $n_{O(C=O)}$

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