Photoelectron Spectroscopic Studies of the Electronic Structure of Some Silatranes†

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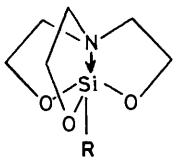
Ultraviolet photoelectron spectra of 17 substituted silatranes (silatrane = 2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]undecane), measured for gas-phase samples at convenient temperatures, are presented. The spectra are interpreted using both valence-electron molecular orbital calculations and a composite-molecule model. The first ionization band is, in most cases, assigned to the nitrogen lone-pair electrons which comprise the Si←N dative bond. This assignment is verified by the observed sensitivity of the location of this band towards substitution at the silicon atom. The σ_{SiN} ionization energies also correlate with the N 1*s* binding energies measured for these compounds.

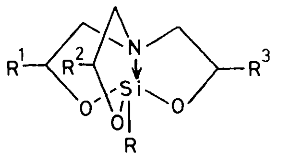
Silatranes (silatrane = 2,8,9-trioxa-5-aza-1-silabicyclo[3.3.3]-undecane) belong to a class of tricyclic compounds which are interesting from both theoretical and practical points of view. Their role in bio-organosilicon chemistry has been championed over many years by Voronkov.[1-3] With different substituents the silatranes show varying physiological activity. The more toxic aromatic substituted silatranes have been used as rodenticides.[4] The physiological action of aliphatic substituted silatranes includes the stimulation of growth in crops and the regeneration of tissue, such as the effect of the CH_2Cl group on hair growth and the regeneration of a burnt organism.[5] An anticancer agent has also been reported.[6]

The *X*-ray crystallographic study of methyl silatrane[7] (1-methyl-2,8,9-trioxa-5-aza-1-silatricyclo[3.3.3.0^{1,5}]undecane) (**1**) indicates that it is of C_3 symmetry and is characterised by a short Si–N distance of 2.175 Å. Structure theory suggests that a dative bond is involved similar to the short B←N bond in the analogous boratrans.[8] Studies by *X*-ray photoelectron spectroscopy (x.p.s.) on a series of silatranes have confirmed the existence of the Si←N dative bond and have examined the effect of substituents on its strength.[9] The ultraviolet photoelectron spectra (u.p.e.s.) of three silatranes have been reported[10] with the spectra being assigned by reference to the spectra of their precursor molecules.

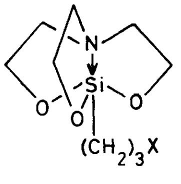
A total of 20 substituted silatranes were examined in the present study. The different substituents are generally at the Si atom, though some substitution at the bridging carbon atoms is included. The He I photoelectron (p.e.) spectra of the vapourized samples indicate considerable thermal decomposition in three cases, so their spectra are not included here. In three other cases there is partial decomposition, but this has not interfered with the spectral assignment. The 17 spectra illustrated are considered in four groups indicated by their general structural formulae, as shown. The thermally unstable compounds include the bromo- and iodo-analogues of (**3**), and the $(CH_2)_3Cl$ substituted variant of (**16**). Non-empirical valence-electron molecular orbital calculations have been performed for the smaller silatranes, (**1**)—(**5**), which comprise the first group.



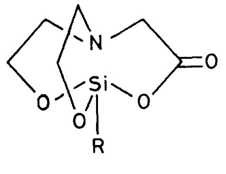
	R
(**1**)	Me
(**2**)	F
(**3**)	Cl
(**4**)	$CH{=}CH_2$
(**5**)	CH_2Cl



	R	R^1	R^2	R^3
(**9**)	Ph	H	H	H
(**10**)	C_6H_4Me	H	H	H
(**11**)	Ph	Me	Me	H
(**12**)	Ph	Me	Me	Me
(**13**)	CH_2NHPh	H	H	H
(**14**)	$(CH_2)_3NHPh$	H	H	H
(**15**)	CH_2NHPh	Me	Me	Me



	X
(**6**)	CN
(**7**)	SH
(**8**)	Cl



	R
(**16**)	CH_2Cl
(**17**)	Ph

Experimental

The synthesis and purification of the silatranes were reported earlier.[11-13] Their characterization was based on elemental analysis and mass spectrometry. The He I (21.22 eV) photoelectron spectra were measured on a double-chamber instrument[14] using a heated inlet system and temperatures up to 210 °C. Argon–methyl iodide mixtures were used for calibration of the ionization energy (i.e.) scale. The digitized spectra, time-averaged for *ca.* 1 h, are shown in Figures 1—4. The noise level in the spectra is such that none of the fine structure in any spectrum can be attributed to vibrationally resolved transitions. Some spectra include sharp peaks, indicated by asterisks, due to either argon calibrant or thermal decomposition products. The spectra exhibiting simple decomposition products include those of (**3**) and (**5**) which show small amounts of HCl, and of (**16**) which shows larger amounts of CH_3Cl.

Calculations

While all-electron *ab initio* calculations of the smaller silatranes are achievable using small basis sets, the other silatranes are

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† *Non-S.I. unit employed:* eV ≈ 1.60 × 10^{-19} J.

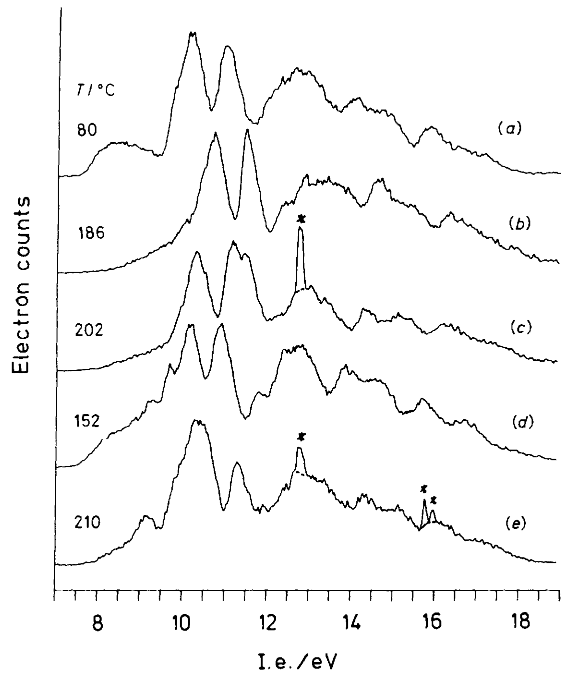

Figure 1. He I photoelectron spectra of the silatranes (**1**)—(**5**) [(*a*)—(*e*) respectively] measured at appropriate temperatures. Asterisked peaks include HCl decomposition product at 12.75 eV and Ar calibrant gas at 15.8 eV

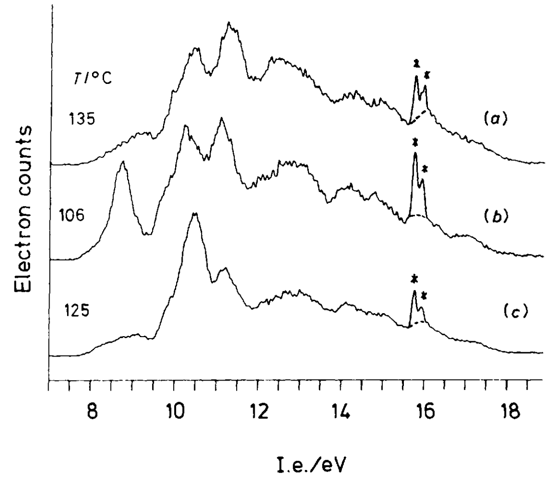

Figure 2. He I photoelectron spectra of the silatranes (**6**)—(**8**) [(*a*)—(*c*) respectively] measured at appropriate temperatures. Asterisked peaks are due to Ar calibrant gas

mostly outside the range of conventional molecular orbital (m.o.) programs. Accordingly a valence-electron-only model-potential (v.e.o.m.p.) m.o. method [15,16] was used in calculations on the smaller silatranes (**1**)—(**5**). This *ab initio* method, which was designed for calculations on molecules containing heavy atoms, is based on the GAUSSIAN 70 program [17] and uses an augmented valence STO-3G basis. It has recently been used in studying orbital interactions in some polycycloalkyl halides.[18]

The minimum STO-3G basis sets for electronegative atoms, such as O, F, and Cl in the present calculations, require the addition of polarization functions in order to bring their orbital energies into better correspondence with those of the lighter atoms and Si, when the Koopmans approximation is used with experimental i.e.s. An optimum value of $\zeta = 0.15$ for additional $2s$,$2p$ functions of O and F, and $3s$,$3p$ functions of Cl was found to provide an acceptable degree of stabilization for these orbitals. The theoretical i.e.s based on the Koopmans approximation ($I_{\text{theor.}} = -\varepsilon$) are compared with the experimental values (vertical i.e.s, I_v) for the silatranes (**1**)—(**5**) in Table 1. The data are confined to the lower i.e. range, below 15 eV.

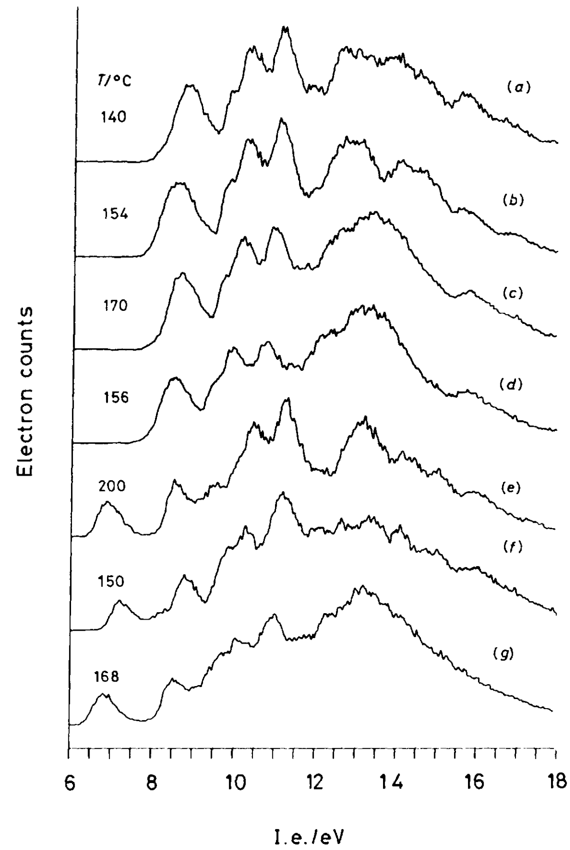

Figure 3. He I photoelectron spectra of the silatranes (**9**)—(**15**) [(*a*)—(*g*) respectively] measured at appropriate temperatures

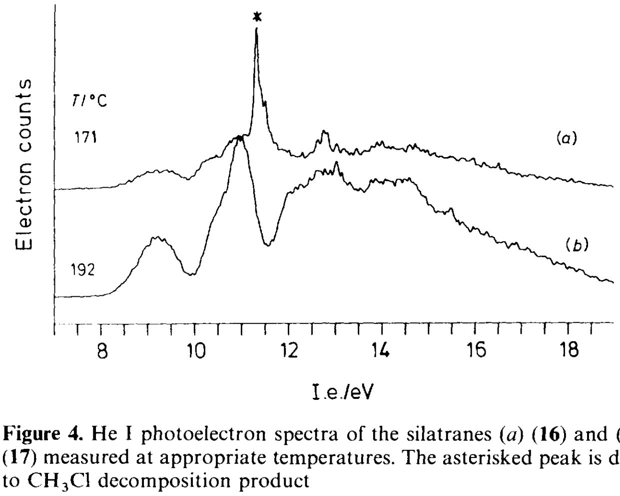

Figure 4. He I photoelectron spectra of the silatranes (*a*) (**16**) and (*b*) (**17**) measured at appropriate temperatures. The asterisked peak is due to CH_3Cl decomposition product

Table 1. Calculated ($-\varepsilon$) and experimental (I_v) ionization energies (in eV) and orbital assignments for the silatranes (**1**)—(**5**)

(**1**)			(**2**)			(**3**)			(**4**)			(**5**)		
$-\varepsilon^a$	I^b	m.o.	$-\varepsilon^a$	I^b	m.o.	$-\varepsilon^a$	I^b	m.o.	$-\varepsilon^a$	I^b	m.o.	$-\varepsilon^a$	I^b	m.o.
8.92	8.5	σ_{SiN}	10.12	9.7	σ_{SiN}	10.08	9.6	σ_{SiN}	8.13	8.5	σ_{SiN}	9.07	9.2	σ_{SiN}
9.61*	9.8	n_O	10.18*	10.0	n_O	10.18*	10.0	n_O	9.06	9.3	π_{CC}	9.96*	10.0	n_O
10.14	10.2		10.85	10.7		10.50*	10.3		9.70*	9.6	n_O	10.15*	10.3	n_{Cl}
10.82	11.0	$\bar{n}_O$	11.46*	11.4	$\bar{n}_O$	11.02	11.2	$\bar{n}_O$	10.22	10.2		10.69	10.5	n_O
10.92*			12.46	12.4		11.75*			10.84	10.9	$\bar{n}_O$	11.35*	11.3	$\bar{n}_O$
11.86	12.1		13.25*	12.9		11.87	11.5	n_{Cl}	11.02*			11.78	11.9	
12.82*	12.6		13.81*	13.4		12.66	13.0		11.89	11.8		12.31	12.4	
13.33*	12.9		14.10	14.6		13.69*			13.03*	12.4		12.91	12.8	
14.47*	14.0		15.37*			15.10*	14.3		13.22	12.8		13.34*	13.4	
14.65	14.7								14.35*	13.8		14.56	14.3	
									14.67	14.6				

[a] The doubly degenerate orbital eigenvalues are indicated by asterisks. [b] The vertical ionization energies (I_v), accurate to ±0.1 eV, are measured as band maxima or shoulder peaks.

Discussion

The major considerations in making assignments of the low i.e. bands of the silatranes concern the identification of ionizations associated with Si and N; specifically whether a Si←N dative bond is identifiable as a perturbed n_N lone pair, as well as the oxygen lone-pair orbitals, n_O, and the associated localized bonding orbitals, conveniently represented as $\bar{n}_O$. Additionally, low i.e. bands, where appropriate, of the substituent groups should be identifiable.

1. *Silatranes* (**1**)—(**5**).—The substituents Me, F, Cl, CH=CH$_2$, and CH$_2$Cl at the Si atom provide varying electrostatic influences on the Si and N atoms in particular, which is indicated by the good correlation between the calculated and experimental i.e.s given in Table 1. In the earlier work on methyl silatrane (**1**) the first band (I_v = 8.5 eV) was assigned as n_N, the nitrogen lone pair.[10] Our analysis essentially agrees with this result except that both our calculation and a He II (40.8 eV) p.e. spectrum measured for (**1**) indicate that the associated orbital includes some Si character and can be represented as the dative bond σ_{SiN}.

The He II measurement provides a sensitive indication of heavy-atom character in ionization bands because of the reduction in relative intensity which is generally observed.[19] It is particularly useful for molecules containing second-row atoms, as has been demonstrated for molecules containing P,[20] S,[21] and Cl.[20,22] Our He II spectra are characterized by low signal-to-noise ratios but are sufficient to indicate a relative loss of intensity of 50% for the first band of (**1**). The relative band areas under the maxima at 8.5, 10.2, and 11.0 eV are 1.0:2.3:1.7 in the He I spectrum, but 0.5:2.3:1.7 in the He II spectrum. These data also indicate the equivalence of the atomic contributions to the ionizations associated with the second and third band groups, and their assignment to the two groups of oxygen orbitals n_O and $\bar{n}_O$ is suggested by the v.e.o.m.p. calculation in agreement with the same assignment for the two intense band groups in the p.e. spectra of the boratrans.[23] This point appears to have been missed in the previous p.e. study of boratrans and silatranes.[10] Within C_3 symmetry the a + e combinations of the three lone-pair, n_O, orbitals of O show a slight separation of 0.4 eV in the spectrum of (**1**) while the v.e.o.m.p. calculation gives a splitting of 0.5 eV. However the three $\bar{n}_O$ orbitals involving O, which correspond to the second ionization band in ethanol (at 1.5 eV higher than n_O) also combine as a + e but with no discernible splitting to give the intense band group centred at 11.0 eV.

The substitution of F, in (**2**), and Cl, in (**3**), for the Me group in (**1**) provides the expected trends in inductive shifts of the σ_{SiN} and n_O, $\bar{n}_O$ bands illustrated in Figure 1. The n_O and $\bar{n}_O$ bands are moved uniformly to higher i.e. by *ca.* 0.4 eV for (**2**) and *ca.* 0.2 eV for (**3**). In both (**2**) and (**3**) the first band, σ_{SiN}, is considerably perturbed being both broadened and shifted toward the n_O bands. This observation verifies that the associated orbital includes Si character and indicates that the inductive influence of F and Cl on Si is strongly affecting the nitrogen lone pair which is the origin of the σ_{SiN} dative bond. These i.e.s also suggest that the Si–N bond varies in its strength, and hence its length, in these three silatranes. These variations are also reflected in the N 1s core ionization energies of 401.0, 402.8, and 402.5 eV measured, respectively, for (**1**), (**2**), and (**3**).[9]

While (**4**) and (**5**) are not strictly of C_3 symmetry because of the asymmetry introduced by the substituent groups CH=CH$_2$ and CH$_2$Cl, respectively, there are near degeneracies in the calculated i.e.s which are averaged, where appropriate, and entered accordingly in Table 1. In (**4**) the vinyl group shows no discernible shifts in comparison with the Me group in (**1**), as indicated by similar i.e.s. for the σ_{SiN}, n_O, and $\bar{n}_O$ bands, except for an increased a–e splitting of 0.6 eV for the n_O orbitals. The p.e. spectrum however differs from that of (**1**) around 9 eV and a maximum at 9.3 eV is assigned as the π_{CC} orbital of the substituent. This is reasonable since typical ethylenic π i.e.s occur in this region (*e.g.* 9.4 eV for the butenes[24]) and because the v.e.o.m.p. calculation on (**4**) indicates localized π_{CC} character in the outer orbitals.

For (**5**) the p.e. spectrum is expected to show n_{Cl} character in the vicinity of 11 eV. Because Cl and O are of similar electronegativity their valence p orbitals can mix strongly so that the usual sharp n_{Cl} bands are not seen in the p.e. spectrum. The spectrum of (**5**) shows a relatively intense group of bands with a maximum at 10.3 eV which are likely to include Cl 3p character. The v.e.o.m.p. calculation on (**5**) indicates that n_{Cl} mixes with the n_O rather than the $\bar{n}_O$ orbitals which correlates with the appearance of the $\bar{n}_O$ bands at 11.3 eV shifted by 0.3 eV from their location in (**1**). The calculation localizes the Cl character somewhat more in the second pair of degenerate m.o.s so this assignment is given in Table 1. The first band of (**5**), associated with σ_{SiN}, is increased by 0.7 eV above its i.e. in (**1**). This is a considerable inductive shift to ascribe to the Cl atom but it coincides with the lower than expected i.e. of 10.3 eV for the n_{Cl} orbitals and indicates a movement of electron density from Si to Cl and a strengthening of the Si–N bond. The N 1s core i.e. shows an increase of 0.8 eV between (**1**) and (**5**) which supports this description.[9]

2. *Silatranes* (**6**)—(**8**).—The terminally substituted n-propyl chain is expected to result in p.e. spectra which are similar to that of methyl silatrane (**1**) with the addition of ionization bands associated with the localized CN, SH, and Cl units respectively. A composite-molecule approach can be used by referring to the p.e. spectra of n-butyronitrile [$I_1(\pi_{CN})$ = 11.7 eV], propanethiol [$I_1(n_S)$ = 9.2 eV], and n-propyl chloride [$I_1(n_{Cl})$ = 10.9 eV].[24] Analysis of the spectra illustrated in Figure 2 indicates that the incorporation of the $(CH_2)_3X$ group into the silatrane moiety results in a uniform decrease of around 0.5 eV in the i.e. assigned to each of the localized X orbitals. So, as summarized in Table 2, π_{CN} of (**6**) overlaps the $\bar{n}_O$ orbitals at 11.3 eV, n_S of (**7**) overlaps the σ_{SiN} orbital at 8.7 eV, and n_{Cl} of (**8**) overlaps the n_O orbitals at 10.4 eV, each of these being observable by increased intensities relative to the spectrum of (**1**). The n_O and $\bar{n}_O$ ionizations show small inductive shifts relative to (**1**) which are consistent with the relative inductive strengths of the terminal X groups. Interestingly, the first n_O ionization is at the same i.e. in (**6**), (**7**), and (**8**), but the higher n_O and $\bar{n}_O$ i.e.s are increased, similarly for the CN and Cl substituents, but somewhat less for the SH substituent.

3. *Silatranes* (**9**)—(**15**).—The large substituents on Si are based on either a benzene ring or a *N*-methylaniline unit in these seven compounds. The composite-molecule model can be used in interpreting the spectra illustrated in Figure 3. This shows that in compounds (**9**)—(**12**) the lower ionization bands of benzene, π_B (9.3 eV) and σ_B (11.5 eV),[24] are shifted by an average of 0.6 eV to lower i.e.s, where they overlap strongly with the σ_{SiN} and n_O bands of the silatrane moiety. The assignments given in Table 3 also indicate that the n_O and $\bar{n}_O$ bands are easily visible in the spectra, and have i.e.s very close to their value in methyl silatrane (**1**).

The assignments for compounds (**13**)—(**15**) are based on the lower ionization bands of *N*-methylaniline, π_A (7.8 eV), π_A (9.1 eV), n_A (10.4 eV), and σ_A (11.6 eV), where the two π_A bands are singly degenerate orbitals derived from the doubly degenerate π_B orbitals of benzene, and n_A is effectively the nitrogen lone-pair orbital. In (**13**)—(**15**) these bands shift to lower i.e.s by an average of around 0.6 eV as indicated by the assignments in Table 3. The σ_{SiN} band is normally strongly overlapped, but does appear to be partly isolated in (**14**) where it is given a vertical i.e. of 8.3 eV, slightly lower than its value in (**1**). The n_O and $\bar{n}_O$ bands of the silatrane moiety are reasonably clearly visible around 10 and 11 eV but are increasingly crowded by other bands with increasing size of the substituents.

4. *Silatranes* (**16**) *and* (**17**).—The carbonyl substitution in one bridge of the silatrane unit replaces one of the three ether bridges with an ester bridge. As observed in the case of the boratrans,[23] this structural change is expected to cause a general increase in the lower i.e.s as well as increasing the relative intensity in the n_O and $\bar{n}_O$ regions. As illustrated in Figure 4, the spectrum of (**16**) is affected by considerable thermal decomposition, indicated by the intense CH_3Cl band at 11.3 eV. Though of poor quality this spectrum can be compared with that of (**5**) which also contains the CH_2Cl substituent on Si. Despite extensive overlapping, the lower i.e. bands of (**16**) are shifted to higher i.e. by *ca.* 0.2 eV, as shown by the assignments in Table 4. The spectrum of (**17**) can be compared with that of (**9**) which also has the phenyl substituent on Si, and shows a general increase in band positions of *ca.* 0.4 eV. The additional O atom causes a relative intensity increase around 11 eV and apparently also reduces the separation of the n_O and $\bar{n}_O$ groups of orbitals.

Conclusions

The He I photoelectron spectra of 17 substituted silatranes included in the present study have been interpreted on the basis of localized orbitals which are associated with the prominent bands observed at lower i.e.s. The ionization bands are influenced by the electronic properties of the substituent groups. For the smaller substituents valence-electron m.o. calculations simulate these observations with reasonable accuracy, but for the larger substituents a composite-molecule model is found to assign the spectra satisfactorily. The interesting feature of the

Table 2. Experimental ionization energies (I_v, in eV) and orbital assignments for the silatranes (**6**)—(**8**)

(**6**)		(**7**)		(**8**)	
I_v	m.o.	I_v	m.o.	I_v	m.o.
9.1	σ_{SiN}	8.7	$\sigma_{SiN} + n_S$	9.0	σ_{SiN}
9.9	n_O	9.9	n_O	9.9	n_O
10.4		10.2		10.4	$n_O + n_{Cl}$
11.3	$\bar{n}_O + \pi_{CN}$	11.1	$\bar{n}_O$	11.2	$\bar{n}_O$

* The vertical ionization energies, accurate to ±0.1 eV, are measured as band maxima or shoulder peaks.

Table 4. Experimental ionization energies (I_v, in eV) and orbital assignments for the silatranes (**16**) and (**17**)

(**16**)		(**17**)	
I_v[a]	m.o.	I_v[a]	m.o.[b]
9.3	σ_{SiN}	9.2	$\sigma_{SiN} + \pi_B$
10.3	n_O	10.4	n_O
11.0	$\bar{n}_O + n_{Cl}$	10.7	
11.5		11.0	$\bar{n}_O + \sigma_B$

[a] The vertical ionization energies, accurate to ±0.1 eV, are measured as band maxima or shoulder peaks. [b] Subscript B refers to orbitals localized in the benzene ring.

Table 3. Experimental ionization energies (I_v, in eV) and orbital assignments for the silatranes (**9**)—(**15**)

(**9**)		(**10**)		(**11**)		(**12**)		(**13**)		(**14**)		(**15**)	
I_v[a]	m.o.[b]	I_v[a]	m.o.[b]	I_v[a]	m.o.[b]	I_v[a]	m.o.[b]	I_v[a]	m.o.[b]	I_v[a]	m.o.[b]	I_v[a]	m.o.[b]
8.8	$\sigma_{SiN} + \pi_B$	8.5	$\sigma_{SiN} + \pi_B$	8.7	$\sigma_{SiN} + \pi_B$	8.5	$\sigma_{SiN} + \pi_B$	6.9	π_A	7.2	π_A	6.8	π_A
9.9	n_O	9.8	n_O	9.8	n_O	9.5	n_O	8.5	$\sigma_{SiN} + \pi_A$	8.3	σ_{SiN}	8.5	$\sigma_{SiN} + \pi_A$
10.4		10.2		10.2		10.0		9.5	n_A	8.8	π_A	9.4	n_A
11.2	$\bar{n}_O + \sigma_B$	11.0	$\bar{n}_O + \sigma_B$	11.0	$\bar{n}_O + \sigma_B$	10.8	$\bar{n}_O + \sigma_B$	10.1	n_O	9.8	$n_O + n_A$	9.7	n_O
								10.5		10.3	n_O	10.0	
								11.2	$\bar{n}_O + \sigma_A$	11.2	$\bar{n}_O + \sigma_A$	11.0	$\bar{n}_O + \sigma_A$

[a] The vertical ionization energies, accurate to ±0.1 eV, are measured as band maxima or shoulder peaks. [b] Subscripts A and B refer to orbitals localized in the aniline units and the benzene ring respectively.

bonding in silatranes, the dative bond σ_{SiN} formed from the lone-pair orbital on nitrogen, is shown to be associated with the first ionization band for all of the silatranes, except (**13**), (**14**), and (**15**) where the *N*-methylaniline substituent provides a lower i.e. band of benzene π origin. The σ_{SiN} ionization is sensitive to substitution at the Si atom, and its i.e.s correlate with the N 1*s* binding energies measured by *X*-ray photoelectron spectroscopy.

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