# THROUGH-BOND INTERACTION IN COMPOUNDS CONTAINING AN Si-O-C-C-N GROUP

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## Summary

Photoelectron, ultraviolet and infrared spectroscopy all prove that under certain conformations, through-bond interaction of the nitrogen and oxygen lone pairs is achieved in molecules of the silatranes $XSi(OCH_2CH_2)_3N$, 1,3-dioxa-6-aza-2-sila-cyclooctanes $R_2Si(OCH_2CH_2)_2NCH_3$ and 2-trimethylsiloxyalkylamines $(Me_3SiOCHRCH_2)_nNMe_{3-n}$ containing a common Si-O-C-C-N fragment. This coupling weakens the donor capacity of the nitrogen and increases that of the oxygen atoms. No interaction of this kind occurs in the system H-O-C-C-N owing to the existence of intramolecular hydrogen $O-H...N$ bonding.

## Introduction

In silatranes, 1,3-dioxa-6-aza-2-silacyclooctanes and 2-trimethylsiloxyalkylamines containing a common Si-O-C-C-N fragment, one can observe two types of electronic interaction between the heteroatoms Si, O and N. These are transannular interaction between the silicon and nitrogen atoms (Si ← N) [1] and 1,4-$n,n$-interaction of the nitrogen and oxygen atoms which are separated by two saturated carbon atoms (through bond or through space) [2–6].

The presence of a transannular Si ← N interaction in silatranes $XSi(OCHR-CH_2)_3N$ (Si-N distance 2.0–2.2 Å) was proved by numerous physico-chemical methods [1]. The $n-\sigma^*$ bands of solutions of these compounds are blue-shifted compared to the spectrum of triethylamine [7]. This is indicative of a lower electronic density on the nitrogen atom. The absence of bands below 9.5 eV in the photoelectron spectra of ethoxy- and 1-hydrosilatrane was also explained in terms of a bonding interaction of the nitrogen lone pair with vacant $3d_{z^2}$ orbitals on silicon [8]. The gas-phase molecule of 1-methylsilatrane exhibits very little interaction between silicon and nitrogen (Si-N 2.45(5) Å) in comparison with the solid-state

structure (Si–N 2.175(4) Å) [9]. The Si ← N transannular interaction of 1-hy-drosilatranes weakens with decreasing solvent polarity [10]. The transannular Si ← N coupling in molecules of 2,2,6-triorganyl-1,3-dioxa-6-aza-2-silacyclooctanes, $RR'Si(OCH_2CH_2)_2NR''$, in the crystalline state is weaker (Si–N 2.3-3.2 Å [11]). No interaction of this kind has been proved in the 2-trimethylsiloxyalkylamines, $(Me_3SiOCHRCH_2)_nNMe_{3-n}$ ($n = 1$–3).

The conformational requirements for efficient through-bond interaction between $n$-electron systems have been predicted by Hoffmann et al. [3]. Optimal through-bond interaction between two $n$-electron systems X separated by a saturated carbon–carbon bond can be expected when the orbitals of the lone pair are parallel to each other and to the C–C σ-bond [3–5]. The occurrence of this through-bond coupling is supported by the difference in ionization energy of the bands attributed to the lone pairs, as compared with these processes in the monofunctional compounds where these atoms are isolated [4,5]. Previous through-bond interactions have not focused on the coupling between unequivalent lone pairs [12].

A higher basicity of the oxygen atoms in the corresponding silatrane derivatives, compared to that in Si-substituted triethoxysilanes, $XSi(OCH_2CH_3)_3$, and the existence of an individual correlation line of the hydrogen bond energy vs. the entropy of phenol interaction with compounds containing a Si–O–C–C–N group, relative to a similar dependence involving acyclic and cyclic ethers and alkoxysilanes, seem to be due to a peculiar distribution of the electron density in the system Si–O–C–C–N [7,13]. The conclusion concerning the conjugation of oxygen and nitrogen in this fragment in molecules of 2-trimethylsiloxyalkylamines was arrived at using $^1H$ NMR spectroscopy [14].

In order to establish the nature of the interaction of heteroatoms in compounds containing the system Si–O–C–C–N, we have studied the infrared, ultraviolet and He-1 photoelectron spectra of the following types of compounds:

$(HOCHRCH_2)_nNMe_{3-n}$ ($n = 1$, R = H (I); $n = 2$, R = H (II); $n = 2$, R = Me (III); $n = 3$, R = H (IV))

$(Me_3SiOCHRCH_2)_nNMe_{3-n}$($n = 1$, R = H (V); $n = 2$, R = H (VI); $n = 2$, R = Me (VII); n = 3, R = H (VIII))

$MeRSi(OCH_2CH_2)_2NMe$ (R = Me (IX), R = Ph (X)).

The ionization energies of the molecule of 1-methylsilatrane, $MeSi(OCH_2CH_2)_3N$ (XI), were calculated using CNDO/S [15] and MNDO [16] semi-empirical SCF MO methods.

## Experimental

The He-1 photoelectron spectra of compounds I–XI in vapour were measured at room temperature on an ES 3201 spectrometer and calibrated with references to the 15.76 eV argon line. Ionization was effected by irradiation with 21.21 eV photons (λ 584 Å).

The IR and UV absorption spectra of the compounds studied in $CCl_4$ and $C_7H_{16}$, respectively, were recorded as described earlier [7].

All the compounds studied were obtained by previously described methods [1] and were purified by double-distillation or sublimation in vacuum. The purity of the compounds was verified by GC-MS on a Varian MAT-212 instrument.

## Results and discussion

The dependence of the frequency and intensity of a band maximum in the region 2805–2780 cm$^{-1}$ (stretching vibration of the :NCH$_3$ functional group [17,18]) on the change of solvent polarity has been studied to elucidate the coupling between the silicon and nitrogen atoms in acyclic molecules of the series (Me$_3$SiO-CHRCH$_2$)$_n$NMe$_{3-n}$. It has been established that the spectroscopic parameters do not depend on the solvent polarity in the spectra of compounds VI and VII (Fig. 1). This event indicates the absence of intramolecular Si ← N coordination in the above molecules. At the same time, in the spectra of 2,2,6-triorganyl-1,3-dioxa-6-aza-2-silacyclooctanes IX and X an increase in the solvent polarity leads to a higher frequency and a lower intensity of this band owing to the diminishing electron density on the nitrogen atom induced by strengthening of the transannular Si ← N interaction.

The $n \to \sigma^*$ bands of 2-trimethylsiloxyalkylamines V–VIII and 2,2,6-trimethyl-1,3-dioxa-6-aza-2-silacyclooctane IX are blue-shifted (195–196 nm) compared to the spectrum of triethylamine (204 nm). This may indicate a lower basicity of the nitrogen atom in these compounds.

The blue shift of the $n \to \sigma^*$ transition in the UV absorption spectra of solutions of mono-, bis- and tris-(2-hydroxyalkyl)amines I–IV is due to the presence of intramolecular hydrogen O–H...N bonding, which also lowers the nitrogen basicity [19]. So, independently of the similarity in the absorption spectra, the nature of the lower nitrogen atom basicity in 2-hydroxyalkylamines and in 2-trimethylsiloxyalkylamines is quite different. The blue shift in the absorption spectra of V–IX seems to be due to the nitrogen and oxygen lone-pair interaction rather than to transannular Si ← N coupling. In the spectra of solutions of silatranes, only an edge of this



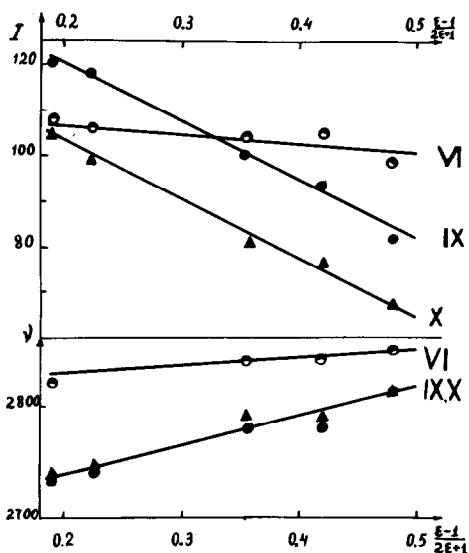Fig. 1. Dependence of the frequency ($\nu_{max}$, cm$^{-1}$) and intensity ($I_{max}$, l mol$^{-1}$ cm$^{-1}$) of the stretching vibration of the :NCH$_3$ functional group on the solvent polarity function $(\epsilon - 1)/(2\epsilon + 1)$ in the IR spectra of solutions of compounds VI, IX and X in C$_7$H$_{16}$, CCl$_4$, CHCl$_3$, CH$_3$CN and CH$_2$Cl$_2$.
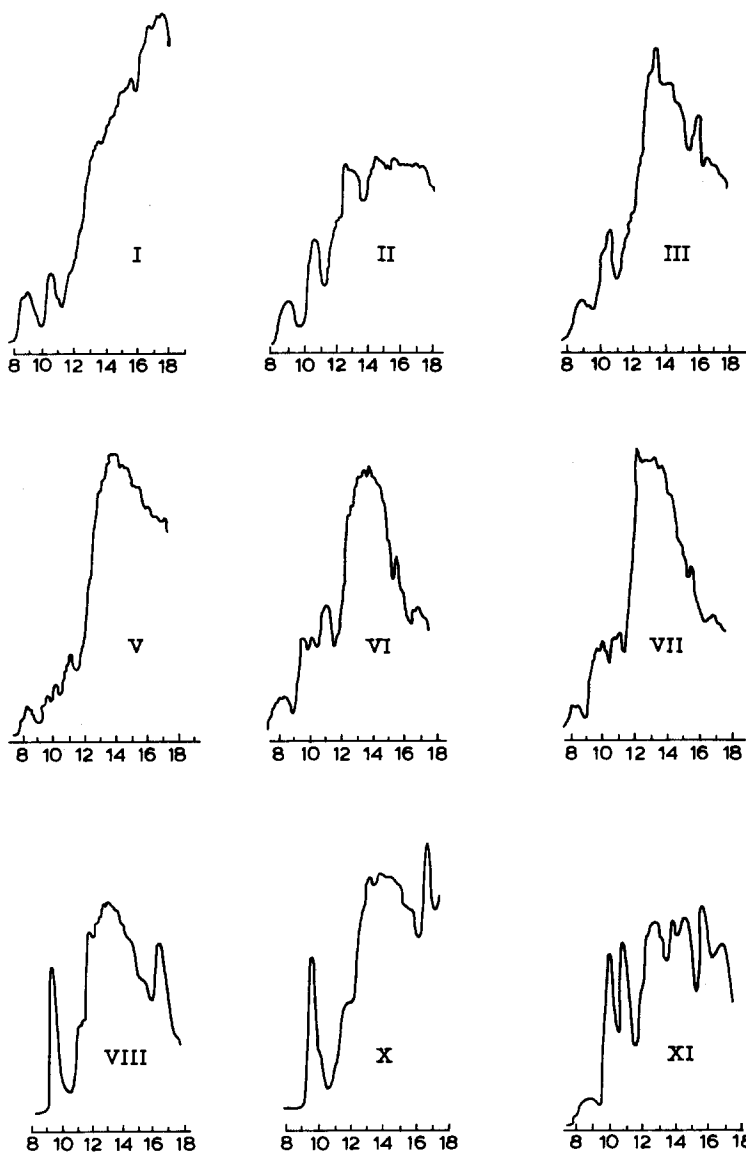
Fig. 2. He-I photoelectron spectra of compounds I–III, V–VIII and X–XI in counts/s vs. $Ip$ (eV).

band ($\lambda_{max} < 190$ nm) is observed owing to an even greater decrease of the nitrogen donor ability caused by both nitrogen and oxygen lone pairs and the transannular Si ← N interaction [7].

The presence of coupling between oxygen and nitrogen in the molecules of V–XI is confirmed by their photoelectron spectra (Fig. 2). Intramolecular hydrogen bonding in 2-hydroxyalkylamines [22] causes a marked increase in the ionization potential of the nitrogen lone pair (8.7–8.85 eV) with respect to its position in the spectra of trialkylamines (8.04 eV for tripropylamine [20] and 8.44 eV for trimethyl-

TABLE 1

CONTRIBUTIONS (%) OF ATOMS AND FRAGMENTS TO HOMOs OF 1-METHYLSILATRANE (XI)

| MO No. | Atom or group | | | | $E_{calc}$ | $E_{found}$ |
|---|---|---|---|---|---|---|
| | $CH_3$ | Si | N | $(OCH_2CH_2)_3$ | | |
| *CNDO/S* | | | | | | |
| 1 | 31.21 | 11.21 | 34.66 | 22.92 | −10.08 | −10.2 |
| 2 | 0.06 | 1.72 | 6.94 | 91.28 | −10.86 | −11.0 |
| 3 | 0.06 | 1.72 | 6.94 | 91.28 | −10.86 | −11.0 |
| 4 | − | − | − | 100.0 | −11.06 | −11.0 |
| *MNDO* | | | | | | |
| 1 | 41.40 | 17.20 | 7.30 | 34.10 | −10.93 | −10.2 |
| 2 | − | − | − | 100.0 | −11.04 | −11.0 |
| 3 | − | 0.45 | 0.50 | 99.05 | −10.81 | −11.0 |
| 4 | − | 0.45 | 0.50 | 99.05 | −10.81 | −11.0 |

amine [21]). The first ionization potential corresponding to the nitrogen lone pair is 8.31–8.34 eV in the photoelectron spectra of compounds V–VII and the second is 9.7–9.8 eV. On going from tris(2-hydroxyethyl)amine (IV) to tris(2-trimethyl-siloxyethyl)amine (VIII), the first ionization potential is increased from 8.7 to 9.64 eV, which shows that the nitrogen lone pair is considerably more tightly bound when the hydrogen atom in the system H–O–C–C–N is replaced by a trimethylsilyl group. The first ionization potential in the spectrum of 2,6-dimethyl-2-phenyl-1,3-dioxa-6-aza-2-silacyclooctane (X) is increased analogously (9.7 eV). In the photo-electron spectra of silatranes, the first ionization band is even more destabilized (10.2–10.6 eV) [8].

In order to establish the nature of the highest occupied molecular orbitals in compounds V–XI, the molecular orbital energies from CNDO/S and MNDO for the molecule of 1-methylsilatrane XI were calculated and are given in Table 1. The first MO (−10.08 eV) involves s, $p_x$ AOs of nitrogen, silicon, the carbon atoms of the methyl group and the $OCH_2CH_2$ fragment. Since the axis x is directed from silicon to nitrogen, the contribution from the latter (35%) is represented by its lone pair. The contribution from the O–C–C group (22.9%) to this MO may also provide evidence for through-bond interaction of the nitrogen and oxygen lone pairs in the silatrane molecule. The calculated HOMO energy (−10.08 eV) is fairly coincident with the observed peak (−10.2 eV). Furthermore, one can see three almost degen-erated MOs covering mainly the oxygen lone pair and the $CH_2–CH_2$ group. Their energies (−11.06, −10.86 and −10.86 eV) are consistent with the band position (−11.0 eV) in the photoelectron spectrum (Table 1). A negligible Wiberg index (0.0168) for the nitrogen–oxygen interaction indicates the absence of any through-space interaction of these atoms. Thus the first ionization potential in VIII, X and XI is mainly indicated by the MO formed from the nitrogen lone pair, lobe $OCH_2CH_2$ and silicon.

The Wiberg index for the through-space silicon–nitrogen interaction is 0.1091, which is 11.5% of the corresponding value for the covalent Si–$CH_3$ bond (0.9528). In the CNDO/2 calculation of the molecule of 1-methylsilatrane, the Wiberg index turned out to be 0.16 [23]. The low Wiberg index shows the Si ← N through-space

TABLE 2

INFRARED SPECTROSCOPIC BASICITY OF THE OXYGEN ATOM IN COMPLEXES OF PHE-
NOL ($\Delta\nu$(OH), cm$^{-1}$) AND DEUTEROMETHANOL ($\Delta\nu$(OD), cm$^{-1}$) WITH 2-TRIMETHYL-
SILOXYALKYLAMINES (V–VIII), 2,2,6-TRIMETHYL-1,3-DIOXA-6-AZA-2-SILACYCLOOC-
TANE (IX) AND 1-METHYLSILATRANE (XI) AND THE CORRESPONDING ETHOXYSILANE
DERIVATIVES [7]

| No. | $\Delta\nu$(OH) | $\Delta\nu$(OD) | Compound | $\Delta\nu$(OH) | $\Delta\nu$(OD) |
|---|---|---|---|---|---|
| V [a] | 293 | 110 | EtOSiMe$_3$ | 266 | 99 |
| VI [a] | 295 | 112 | | | |
| VII | 295 | 116 | | | |
| VIII | 297 | 114 | | | |
| IX | 286 | 106 | (EtO)$_2$SiMe$_2$ | 257 | 94 |
| XI | 276 | 98 | (EtO)$_3$SiMe | 246 | 85 |

[a] A low-frequency weak band in the region 2400–2440 cm$^{-1}$ is observed (Fig. 3).

interaction to be electrostatic. This conclusion is in agreement with a small charge transfer from nitrogen to silicon in the molecule of 1-methylsilatrane (0.1–0.3 e$^-$) [1] and in the SiF$_4$ · NH$_3$ complex [24,25]. This is also consistent with the positive charge on the silicon atom ($\sim$ 1.0 e$^-$) and the negative charge on the nitrogen and oxygen atoms in the molecule of 1-methylsilatrane (XI) ($-0.2$ and $-0.4$ e$^-$, respectively). Consequently, the appearance of the ionization band at 8.7 eV in the photoelectron spectrum of 1-methylsilatrane is apparently due to tris(2-hydroxy-ethyl)amine (IV) produced by hydrolysis of the sample.

At the same time, the oxygen atom has higher electron-donor properties in all the compounds V–XI containing a Si–O–C–C–N fragment (Table 2). Indeed, when the oxygen atoms are involved in hydrogen bonding with phenol or dueteromethanol, the stretching, $\Delta\nu$(OH) and $\Delta\nu$(OD), is higher than that in the complexes of the corresponding mono-, di- and tri-ethoxysilanes (Table 2). The difference between the $\Delta\nu$ values for these two classes of compounds is nearly independent of the extent of Si $\leftarrow$ N interaction, and approaches 29–31 and 12–15 cm$^{-1}$ for the



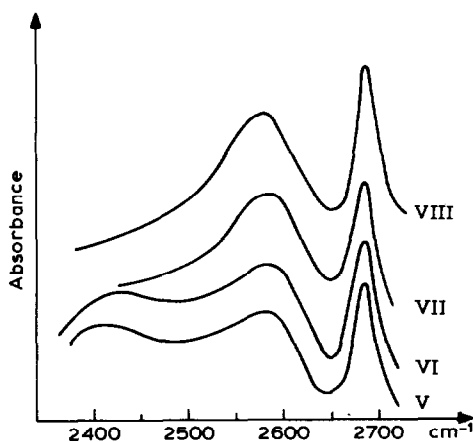Fig. 3. IR absorption spectra of solutions of compounds (Me$_3$SiOCHRCH$_2$)$_n$NMe$_{3-n}$ (V–VIII) ($c$ 0.1 mol/l) with CH$_3$OD ($c$ 0.05 mol/l) in CCl$_4$.
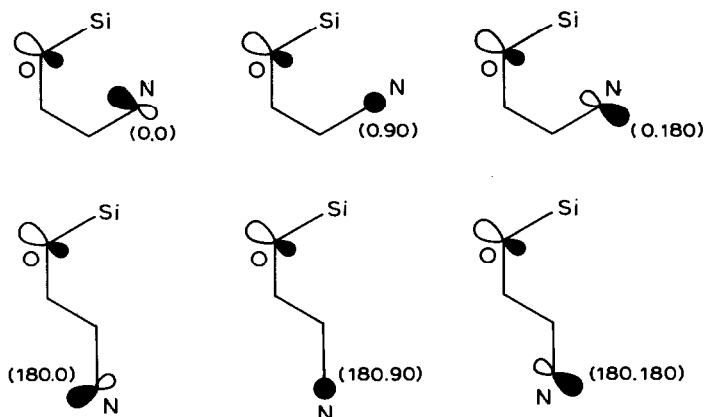
Fig. 4. Possible conformations of the Si–O–C–C–N fragment.

complexes with phenol and deuteromethanol, respectively. Only the infrared spectra (Fig. 3) of the hydrogen-bonded complexes of V and VI with deuteromethanol contain a weak additive low-frequency associated band in the 2400-2440 cm$^{-1}$ region, corresponding to hydrogen bonding of the type O–D...N [26]. This suggests that independently of the Si ← N interaction it is the 1,4-$n,n$-coupling of the nitrogen and oxygen lone pairs through the bond that is responsible for the higher donor properties of the oxygen and the lower basicity of the nitrogen atoms. The presence of intramolecular hydrogen O–H...N bonding in the molecules of 2-hydroxyalkylamines rules out the interaction between the nitrogen and oxygen lone pairs.

Thus the molecules of silatranes are able to exhibit two types of interaction, i.e. Si ← N through space and through bond of the nitrogen and oxygen atoms. In compounds VIII–X (VII in solution), only the conformations involving through-bond interaction of oxygen and nitrogen are achieved. In compounds V and VI (VII in the gas phase), different conformations which depend on the angles $\varphi$ (rotation about the C(1)–C(2) bond), $\theta$ (rotation about the C(2)–N bond) and $\psi$ (rotation about the C(1)–O bond) can be achieved. Structures with $\varphi$, $\theta$ and $\psi = 0, 180°$ are favourable for the through-bond nitrogen and oxygen lone-pair interaction ($Ip$ 9.7-9.8 eV) whereas this type of interaction cannot be achieved in structures with one of the angles equal to 90° ($Ip$ 8.3 eV) (Fig. 4 shows changes in only the $\varphi$ and $\theta$ angles).

The existence of conformations with a lower electron-donor ability of the nitrogen atom and higher base properties of the oxygen atoms is conditioned by the presence of bulky trimethylsilyl groups, branching of hydroxyalkyl groups and fixation of the conformations in a cyclic structure. Unsuccessful attempts to obtain tris(2-trimethylsiloxypropyl)amine under conditions analogous to those employed for the preparation of compounds V–VIII can be explained in terms of the steric factors prevailing in conformations in which the nitrogen and oxygen lone-pair through-bond interaction is achieved.

Thus, the data of infrared, ultraviolet and photoelectron spectroscopy allow a conclusion to be drawn that under certain steric factors in compounds containing a common Si–O–C–C–N fragment a through-bond interaction is mainly achieved

independently of the extent of transannular Si ← N coupling, which lowers the electron-donor properties of the nitrogen and increases those of the oxygen atoms. At the same time, no interaction of this type occurs in the system H–O–C–C–N owing to the existence of intramolecular hydrogen O–H...N bonding.

In accordance with ref. 27, the interaction of the nitrogen and oxygen atoms in compounds containing the Si–O–C–C–N system is best reproduced in terms of hyperconjugation, i.e. overlapping of a suitably oriented $\sigma$-bond with N and O lone pairs, rather than by the inductive effect.

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