Stereoelectronic effects and the problem of the choice of model compounds for organic derivatives of a pentacoordinated silicon atom (taking silatranes as an example)

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Anomeric effects at the silicon atom in silatranes $XSi(OCH_2CH_2)_3N$ and model trimethoxysilanes $XSi(OMe)_3$ (X = H, Me, SiH_3, F, Cl) containing a tetracoordinated silicon atom were studied by the MNDO and AM1 methods. Unlike silatranes, the nature of substituent X pronouncedly affects the type and degree of stereoelectronic effects on the values of X—Si—O—C dihedral angles, X—Si bond lengths, and proton affinities of trimethoxysilanes. The results obtained indicate the necessity of modifying the set of spectral and structural indications of pentacoordination of the anomeric silicon atom established previously and observing the principle of conformational similarity for compared compounds. Bicyclic organosilicon ethers $XSi(OCH_2)_3CH$ were proposed to be used as models of corresponding silatranes.

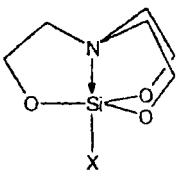
Key words: silatranes, trimethoxysilanes, pentacoordination, anomeric effect, conformation, proton affinity, quantum-chemical calculations.

To elucidate how pentacoordination of the silicon atom affects the structure and reactivity of its mono-, bi-, and tricyclic derivatives, tetracoordinated silicon derivatives are used as model compounds.[1—5]

The latter are usually chosen taking into account close values of the total electronegativity of the nearest environment of the central Si atom in compared compounds. However, such a simple criterion for selection of model compounds can appear to be inadequate. If the atoms adjacent to the silicon atom have the lone electron pairs (LEP), the Si atom becomes an anomeric center and an additional requirement arises of conformational similarity of the molecules of compared compounds. Only if this condition is met, can a possible effect of stereoelectronic contributions to analyzed properties of compounds compared be compensated, whereas differences will be mostly due to the effect of changing the coordination number of the silicon atom. No particular significance has been attached to this factor so far, though the problem of conformational factors when choosing model compounds for chelate derivatives of pentacoordinated silicon seems to be of great importance.

In this connection we studied how the anomeric effect at the silicon atom affects geometric characteristics and proton affinities of silatranes (**1**) and trimethoxysilanes $XSi(OCH_3)_3$ (**2**) (X = H, Me, SiH_3, F, Cl) by the semiempirical quantum-chemical MNDO and AM1 methods.

The choice of tricyclic molecules **1** as a subject of investigation is not accidental. They are the most extensively studied representatives of organic derivatives of pentacoordinates silicon.[1,2] Despite the fact that calculations of trisilanols $XSi(OH)_3$ are more simple than those of trimethoxysilanes **2**, it is more preferable to use the latter as model compounds, because the low stability and effective intermolecular H-bonding in trisilanols hamper obtaining necessary experimental information. On the structural level, we studied the influence of the anomeric effect by the MNDO method[6] since on the qualitative level this method reproduces the major results of *ab initio* studies of $H_nM(OH)_{4-n}$ (M = C, Si) molecules fairly well.[7] Investigation of the proton affinity of the oxygen atom in molecules **1** and **2** (X = Me, F) was performed by the AM1 method[8,9] using the MOPAC program package[10] (version 6.0).



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X = H, Me, SiH_3, F, Cl

Results and Discussion

According to the X-ray analysis[5] and electron diffraction data,[11,12] in the majority of silatranes **1** the positions of the O—C bonds in each of the atrane

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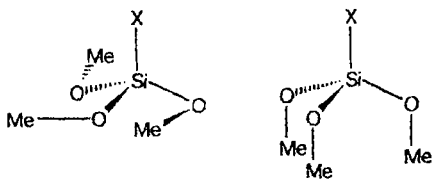
semirings with respect to the X—Si bond are independent of the nature of substituent X and the state of aggregation and are close to antiperiplanar (*ap*). Corresponding X—Si—O—C dihedral angles (φ) lie in the range 165° to 180°. According to the results of our MNDO calculations performed with full geometry optimization, the φ angles in silatranes are slightly dependent on the nature of substituent X. However, the calculated values of these angles are appreciably smaller than those observed experimentally (Table 1). Previous studies of silatranes by semiempirical[13—15] and *ab initio*[16,17] methods have led to analogous results.

An exhaustive set of possible conformations of trimethoxysilanes **2** can be obtained by rotating methyl groups about the Si—O bonds. Among them, only a symmetrical *ap,ap,ap*-rotamer is an adequate spatial model of silatranes (from the viewpoint of the manifestation of an anomeric effect). However, the fraction of this conformation can be negligibly small for some reasons. One of the reasons is the stereoelectronic effect of substituent X.*

In fact, on the orbital level the predominant conformation of molecules **2** should be determined by the balance of the interaction between the LEP of the oxygen atom and antibonding orbitals of the Si—X (n_O,σ^*_{SiX}) and Si—O (n_O,σ^*_{SiO}) bonds. It is obvious that the synclinal (*sc*) positions of the X—Si and O—C bonds (φ = 90°) and their *ap*-orientation is the most favorable for the first and the second type of interaction to occur, respectively. The contribution of a particular orbital interaction will depend on the ratio of acceptor properties of antibonding orbitals of the Si—X and Si—O bonds. Based on the general theory of stereoelectronic effects,[18] it can be expected that if the electronegativity (EN) of substituent X will be higher than that of the oxygen atom, the predominant conformation of **2** will be close to the *sc,sc,sc*-conformation; otherwise to the *ap,ap,ap*-conformation.



2 (*sc,sc,sc*) **2** (*ap,ap,ap*)

Taking into account all said above, we studied the structure of only two conformers of molecules **2**, *viz.*, the *ap,ap,ap*-conformer, simulating molecules **1**, and the most stable conformer. Calculations of the former were performed with optimization of all geometric parameters of molecules **2** except for the X—Si—O—C dihedral angles (at φ = 180°), whereas the search for the second conformer was carried out with full geometry optimization of molecules **2**.

Table 1. Torsion X—Si—O—C (φ) angles and X—Si (d_1) and Si—O (d_2) bond lengths in silatranes calculated by the MNDO method

X	φ/deg	d_1/Å	d_2/Å
H	157.2	1.383	1.665
Me	154.8 [147.3]	1.810 [1.862]	1.666 [1.651]
SiH_3	154.2 [148.2]	2.208 [2.344]	1.667 [1.653]
F	161.8 [150.6]	1.590 [1.587]	1.664 [1.638]
Cl	159.3 [150.3]	2.116 [2.063]	1.655 [1.639]

Note. The results of *ab initio* (HF/6-31G(d)) calculations[17] are given in brackets.

The results of calculations (Table 2) indicate a low stability (a virtually zero fraction) of the *ap,ap,ap*-conformation for all studied compounds **2**. The calculated values of the energy differences between the most stable and the *ap,ap,ap*-conformers seem to be quite admissible, except for the case of trimethoxychlorosilane.

The dependence of the structure of the most stable conformers of molecules **2** on the nature of substituent X is close to the expected one. *sc,sc,sc*-Rotamers with C_3 symmetry with torsion angles close to the optimum value (90°) for effective stereoelectronic n_O,σ^*_{SiX}-interaction to occur appeared to be the most stable among compounds with X = F, Cl, and H. In the case of halo derivatives this is due to the high EN of substituent X, whereas for X = H this is due to the high polarizability of the Si—H bond. The φ angles in the most stable conformers of molecules **2** with less electronegative substituents X (Me and SiH_3, C_3 symmetry in both cases) are much larger than 90°. This indicates an increase in the stabilizing role of n_O,σ^*_{SiO}-conjugation in this type of molecules. This is particularly clearly seen in the silyl derivative of **2**. The dihedral angles formed by the n_O-orbitals of its oxygen atoms with the vicinal Si—O bonds they mostly eclipse and with the X—Si bond are 14° and 46°, respectively. The results of the HF/6-31G(d) calculations[17] show an analogous stereoelectronic effect of substituent X also for the derivatives of trisilanols $XSi(OH)_3$ (see Table 2). The values of the X—Si—O—H torsion angles calculated for trisilanols are in fairly good agreement with the values of the X—Si—O—C angles we calculated for molecules **2**. The fact that virtually no experimental data on the geometry of trimethoxysilanes in the gas phase is available gives no way of estimating the reliability of these quantum-chemical calculations. Only methyltrimethoxysilane was studied by electron diffraction[19]; however, its geometry was not determined with adequate accuracy. It is believed that the optimum values of the φ angle lie in the range 25—80°; however, a conformer with a φ angle of 148° is also possible.

Discordance between the type and extent of stereoelectronic effects in the most stable conformation and the *ap,ap,ap*-conformations of trimethoxysilanes we

* No less an important factor, *viz.*, the medium effect on the conformational composition of trimethoxysilanes, requires special investigation.

Table 2. Torsion X—Si—O—C angles (φ), Si—O—C (θ_1) and X—Si—O (θ_2) bond angles, X—Si (d_1) and Si—O (d_2) bond lengths, and relative energies (ΔE) of trimethoxysilane conformers calculated by the MNDO method

X	Conformation	φ	θ_1	θ_2	d_1	d_2	ΔE
		deg			Å		/kcal mol^{-1}
H	The most stable	105.1	136.8	111.7	1.382	1.653	0
	ap,ap,ap	180.0	143.6	110.5	1.380	1.649	2.4
Me	The most stable	111.2 (25—80) [121.9]	136.4 (123.7)	112.0 (109.5)	1.807 (1.845) [1.858]	1.653 (1.632) [1.648]	0
	ap,ap,ap	180.0	142.9	110.8	1.806	1.650	2.5
SiH_3	The most stable	135.9 [120.5]	137.6	112.7	2.206 [2.343]	1.660 [1.650]	0
	ap,ap,ap	180.0	141.7	111.7	2.206	1.656	1.1
F	The most stable	77.7 [66.2]	137.0	108.3	1.594 [1.592]	1.644 [1.623]	0
	ap,ap,ap	180.0	142.0	107.6	1.586	1.642	2.6
Cl	The most stable	84.2 [61.2]	136.1	109.5	2.117 [2.071]	1.637 [1.621]	0
	ap,ap,ap	180.0	144.4	108.5	2.106	1.632	5.3

Note. Data of electron diffraction study[19] are listed in parentheses and the results of *ab initio* (HF/6-31G(d)) calculations[17] of trisilanols $XSi(OH)_3$ are listed in brackets.

found is the cause of differences in their structural parameters (see Table 2). The largest differences between the X—Si bond lengths in compared conformers are characteristic of halo derivatives of **2** (X = F, Cl). An apparent reason for lengthening (weakening) of the X—Si bond in *sc,sc,sc*-rotamers of their molecules is n_O,σ^*_{SiX}-interaction. The Si—X bond length therein exceeds even that calculated for corresponding silatranes,* which is in agreement with the data reported previously[17] (see Tables 1 and 2).

At first glance, the results of semiempirical and *ab initio* calculations indicate that the model of three-center four-electron (3c—4e) hypervalent bonding of the silicon atom is inapplicable to silatranes. According to this model, an appreciable weakening of the X—Si bond compared to the conventional two-center bond in tetracoordinated silicon derivatives should occur in the axial X—Si←N fragments of molecules **1**.[20] However, inadequacy of the model of 3c—4e-bonding is apparent. In fact, the ratio of the X—Si bond lengths in silatranes and in *ap,ap,ap*-rotamers of **2** with X = F and Cl that simulate their conformation more accurately is in complete agreement with the model of 3c—4e-bonding of the silicon atom in the former.

A weaker stereoelectronic effect of substituent X on the Si—O bond lengths in the conformers **2** considered (see Table 2) is not surprising: the strengthening of this bond is characteristic of each type of conjugation (n_O,σ^*_{SiX} and n_O,σ^*_{SiO}). A detailed analysis of such differences is difficult, since multilateral n_O,σ^*_{SiO}-interactions simultaneously stabilize and destabilize the Si—O bond.

Consideration of stereoelectronic effects is also important when comparing basic properties of silatranes and model compounds **2**.** Judging by the values of the frequency shifts of the stretching vibrations of the phenolic O—H bond in the IR spectra of solutions of **1** and **2**[21] and by changes in their ^{1}H NMR spectra induced by a paramagnetic shift reagent,[22] the basicity of the oxygen atoms in silatranes is higher than in trialkoxysilanes. This can be due to either the effect of the Si←N bond[21] or the interaction between the LEP of the N and O atoms in chelate SiOCCN fragments of silatranes.[22]

The results of AM1 calculations of the true basicity, *i.e.*, the proton affinity (*PA*), of oxygen atoms of methylsilatrane, fluorosilatrane, and corresponding trimethoxysilanes in the optimum and *ap,ap,ap*-conformations are listed in Table 3. The *PA* values were estimated using the standard equation:

$$PA = \Delta H(M) + 355.7 - \Delta H(MH^+),$$

where $\Delta H(M)$ and $\Delta H(MH^+)$ are the enthalpies of formation of the neutral and protonated molecule, respectively. Calculations of *PA* were performed with full geometry optimization of neutral and protonated forms,

* It is likely that this is a reason for the relatively low reactivity of 1-halosilatranes (except for **1** with X = I).[4]

** Consideration of other previously established spectroscopic indications of pentacoordination of the Si atom in silatranes (PES, IR, NMR, *etc.*) in the context of stereoelectronic effects seems to be no less important.

Table 3. Proton affinity (*PA*/kcal mol^{-1}), charges on oxygen atoms (q_O), average orbital energies (ε_{av}/eV) of the lone electron pairs, and reorganization energies (ΔE_r/eV) of Si—O bonds of silatrane and trimethoxysilane molecules calculated by the AM1 method

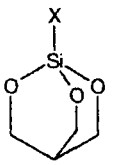
Molecule	Conformation	*PA*	q_O	ε_{av}	ΔE_r
$MeSi(OMe)_3$	The most stable	200.1	−0.589	10.4	3.8
	ap,ap,ap	230.2	−0.604	10.7	4.2
$MeSi(OCH_2Me)_3N$		203.7	−0.572	10.9	3.9
$FSi(OMe)_3$	The most stable	187.3	−0.612	11.2	3.6
	ap,ap,ap	216.7	−0.644	11.0	4.1
$FSi(OCH_2CH_2)_3N$		197.8	−0.593	10.5	3.7

except for the X—Si—O—C torsion angle in the *ap,ap,ap*-conformation.* It should be noted that the change in the geometry of the silatrane skeleton on going from the neutral form to the protonated one (the lengthening of the Si—O bond of the protonated oxygen atom and the shortening of the other equatorial Si—O bonds and axial Si—N bond) is in agreement with the known experimental data for triazasilatranes.[23]

According to spectroscopic data,[21,22] the calculated *PA* values of silatranes appeared to be higher than those of the most stable rotamers of model trimethoxysilanes (see Table 3). At the same time, the calculations indicate an unexpected decrease in the *PA* values of molecules **1** as compared to those predicted for the *ap,ap,ap*-conformers of molecules **2**. Hence, it is more correct to discuss the reasons for decreased *PA* values of silatranes rather than those for increased ones[21,22] as compared to correctly chosen model compounds.

As follows from the data in Table 3, changes in the *PA* values of the molecules listed therein can not be explained by the difference in the values of effective charges (q_O) and average (ε_{av}) orbital energies of the LEP of oxygen atoms $\varepsilon_{av} = (\varepsilon_{a_1(O)} + \varepsilon_{e(O)})/3$, where $\varepsilon_{a_1(O)}$ and $\varepsilon_{e(O)}$ are the orbital energies of the symmetric and doubly degenerate level, respectively. Only the quantity $\Delta E_r = \sum_{SiO}[E_{SiO}(M) - E_{SiO}(MM^+)]$ that characterizes the degree of reorganization of the electronic system of the SiO_3 fragment of the MH^+ cation relative to the neutral molecule M (E_{SiO} are corresponding two-center components of the total energy) is changed in parallel with *PA* changes. It is likely the ΔE_r value that is best to reflect the total effect of different factors on the *PA* values of silatranes and trimethoxysilanes.

The conclusions drawn when comparing the geometric parameters and *PA* values of silatranes and trimethoxysilanes are qualitative. At the same time, they demonstrate the fundamental importance of conformational similarity between the compared model and pentacoordinated compounds containing an anomeric silicon atom. From this point of view the conformationally rigid bicyclic organosilicon ethers **3** seem to be more convenient structural models of silatranes. In fact, the results of MNDO and AM1 calculations of derivatives **3** with substituents X = Me and F that strongly differ in electronegativity have shown that the values of the φ angles in these compounds (like those in silatranes) are almost independent of X and are close to 170°. The similarity of stereoelectronic effects in molecules **1** and **3** makes it possible to clearly distinguish their properties due to the changing coordination number of the Si atom. The calculated X—Si bond lengths in silatranes are longer than those in model compounds **3** (1.790 and 1.575 Å for X = Me and F, respectively) and are in complete agreement with the model of 3c—4e-bonding. According to AM1 calculations, the *PA* values of model compounds **3** (208.0 and 201.1 kcal mol^{-1} for X = Me and F, respectively) are higher than those of corresponding silatranes.



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X = Me, F

The conclusions drawn seem also to be valid for compounds of pentacoordinated germanium and tin. The point is how different are the magnitudes of the anomeric effects at the Si, Ge, and Sn atoms. Judging from the heats of isodesmic reactions (ΔH):

$$FM(OMe)_3 + MF_4 \longrightarrow F_2M(OMe)_2 + F_3M(OMe),$$

M = Si, Ge, Sn

we calculated by the MNDO method the magnitudes of the anomeric effect decrease in the sequence (with consideration of the sign of the ΔH/kcal mol^{-1} values): Si(5.02) > Ge(0.12) > Sn(−4.09).

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* The energetics and geometric parameters of molecules **1** and **2** calculated in the framework of the AM1 method are, on the whole, in agreement with the results of MNDO calculations.

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