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Geometry of intramolecular silicon complexes: an *ab initio* estimation of the sensitivity to the effect of medium. (Aroyloxymethyl)trifluorosilanes

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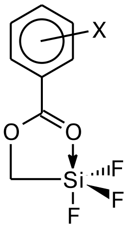
The effect of medium on the geometry of the (benzoyloxymethyl)trifluorosilane (**1**) molecule was studied by the HF and MP2 methods with the 6-31G(d), 6-311G(d), and 6-311+G(d,p) basis sets, as well as using the Onsager SCRF model, the PCM approach, and the data of X-ray diffraction study. Molecule **1** has a low complexation energy (5.4 kcal mol^{-1} according to MP2(Full)/6-31G(d)+ZPE calculations and ~6.8 kcal mol^{-1} according to IR spectroscopy data), while its geometric parameters are the least sensitive to the effects of medium among all hypervalent silicon compounds studied to date. Nevertheless, the results obtained revealed a pronounced deformation of the Si←O coordination bond in **1** on going from the gas phase to the polar solution and crystal. This serves as a theoretical substantiation of the hypothesis that substantial changes in the IR and NMR spectral characteristics of the (O—Si)-chelate (aroyloxymethyl)trifluorosilanes upon variation of external factors are due to geometric reasons. Analysis of the electron density distribution according to Bader indicates that the Si←O bond in molecule **1** can be treated as a covalent bond of high polarity.

Key words: (benzoyloxymethyl)trifluorosilane, trigonal-bipyramidal complexes of silicon, effect of medium, *ab initio* quantum-chemical calculations.

A wide range of intramolecular trigonal-bipyramidal silicon complexes (TBPSC) including (aroyloxymethyl)trifluorosilanes $XC_6H_4C(O)OCH_2SiF_3$ (**1**; X = H, Me, F, Cl, MeO, NO_2) is characterized by remarkably large changes in the IR and NMR spectral characteristics of their coordination sites upon varying the phase state, solvent polarity, and temperature.[1—5] It was hypothesized that the effects observed are primarily due to a strong dependence of the lengths of the axial bonds formed by the central atom on the external factors.[1,3,5,6] However, severe experimental difficulties allowed one to obtain rigorous proofs of this hypothesis only for two highly symmetric silatrane molecules $XSi(OCH_2CH_2)_3N$ (**2a**,**b**).[7,8]



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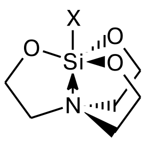
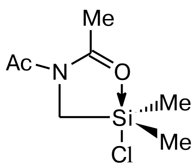


2a: X = Me
2b: X = F



3

Therefore, quantum-chemical substantiation of this hypothesis becomes of crucial importance. To date, *ab initio* quantum-chemical investigations of the effect of medium on the structure of TBPSC were carried out only for 1-fluorosilatrane (**2b**) [9] and some (O—Si)-chelate and zwitterionic complexes with the $ClSiC_3O$ coordination site (*e.g.*, **3** [10]). In this work we report on the results obtained for the simplest representative of the TBPSC **1**, (benzoyloxymethyl)trifluorosilane (**1a**).

Calculation Procedure

The solvent effect on the structure of the simplest TBPCS **1** was analyzed by calculations with full geometry optimization by the HF and MP2 methods (GAMESS program package[11]) with the 6-31G(d), 6-311G(d), and 6-311+G(d,p) basis sets using the polarizable continuum model[12] (PCM) and the Onsager self-consistent reaction field[13] (SCRF) model. For all versions of calculations the correspondence between the structures obtained and the minimum on the potential energy surface was proved by the positive sign of the corresponding Hessian eigenvalues. The topological analysis of the electron density distribution according to Bader was carried out using the Ext94b program incorporated into the AIMPAC program package.[14]

Results and Discussion

The molecule of (benzoyloxymethyl)trifluorosilane can exist in two forms, an (O—Si)-chelate form with the Si←O bond (**1a**) and an acyclic form **1a**´.

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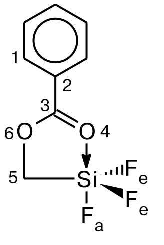
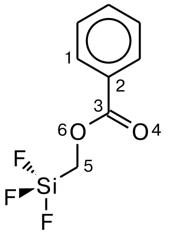


1a



1a′

The results of the X-ray diffraction[15] and NMR[16] and IR spectroscopic studies[2,17] revealed the chelate structure of this molecule not only in the crystals and solutions but also in the gas phase at moderate temperatures ($T < 420$ K). According to IR specstoscopy data,[17] the energy of intramolecular complexation (E_c) for complex **1a** in the gas phase is ~6.8 kcal mol^{-1} (*cf.* ~6.0 kcal mol^{-1} according to MP2(FC)/6-31G(d)//HF/6-31G(d) calculations[18]). Our MP2(Full)/6-31G(d)//MP2(Full)/6-31G(d) + ZPE calculations with inclusion of zero-point vibrational energy correction carried out in this work gave E_c = 5.4 kcal mol^{-1}.

Thus, there are strong grounds to disregard the equilibrium of complex **1a** with the acyclic form **1a′** in the subsequent text.

Both HF and MP2 calculations of molecules **2a**,[19] **2b**,[9,19,20] and **3**[10] revealed an very smooth dependence of the total energies of TBPSC with the $XSiO_3N$ and $ClSiC_3O$ coordination sites on the Si—N and Si—O internuclear distances, respectively.[9,10,19,20] According to our calculations (Fig. 1), this is also characteristic of molecule **1a**. However, a few *ab initio* studies of the equilibrium geometry of TBPSC reported to date[9,10,18—21] were carried out ignoring this fact. Indeed, calculations using the GAMESS program package are, as a rule, performed with the standard convergence criterion value (energy gradient, q) of 10^{-4} hartree Bohr^{-1}, while calculations using the GAUSSIAN program suite are carried out without using the "Tight (Very Tight)" optimization mode. As a consequence, the necessary accuracy of calculations of the coordination bond lengths (10^{-3} Å) is not achieved.

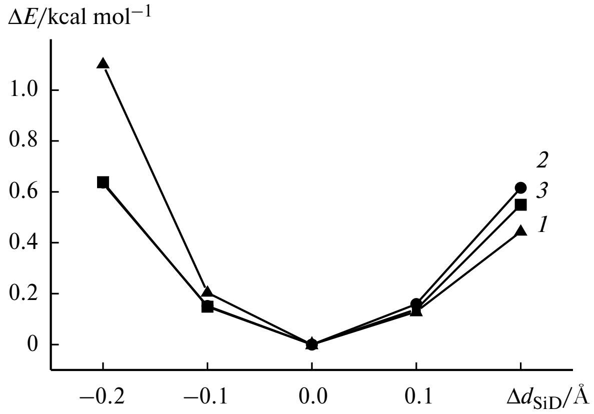


Fig. 1. Potential functions of molecules **1a** (*1*), **2b**[3] (*2*), **3**[10] (*3*) obtained from HF/6-31G(d)//HF/6-31G(d) calculations. The total energies and the lengths of the Si←D (D = O, N) coordination bonds at the corresponding minima were taken as zeroes.

The aforesaid can be illustrated most clearly taking calculations of complex **1a** with not only coplanar (**A**), like in Ref. 18, but also orthogonal (**B**) starting mutual arrangement of the phenyl ring and the Si—C(5)—O(6)—C(3)—O(4) chelate ring as an example. As can be seen in Table 1, the molecular geometry of **1a** optimized by the HF and MP2(FC) methods with the standard q value (case **B**) is appreciably different from that reported earlier[18] in lengths of the Si—F$_a$ and Si—O axial bonds (provided that the total energies of the system differ by at most $2 \cdot 10^{-3}$ kcal mol^{-1}). What is more, the results obtained in version **A** of the calculations[18] allowed a quite surprising, as applied to TBPSC, conclusion that the length of the coordination bond in complex **1a** is insensitive to the inclusion of correlation energy. In contrast to this, the lengths of the Si←O coordination bond (d_{SiO}) obtained from the "equal-in-rights" HF/6-31G(d) and MP2/6-31G(d) calculations with another molecular geometry (version **B**) become different. The apparent dependence of the lengths of the axial bonds formed by the silicon atom in **1a** on the initial value of the C(1)—C(2)—C(3)—O(6) dihedral angle disappears as the q value is decreased down to 10^{-5} hartree Bohr^{-1}.

Unlike other structural parameters (Table 2), the $d_{SiO}{}^{gas}$ value for free molecule **1a** calculated using the standard HF/6-31G(d) method is appreciably different from the corresponding value determined by X-ray diffraction analysis ($d_{SiO}{}^{solid}$), being 0.134 Å longer. The possible reasons are both the effect of the medium and an inadequate level of calculations due to neglect of electron correlation effects and incompleteness of the basis set. Indeed, HF calculations with the 6-311G(d) basis set lead to substantial reduction of the $d_{SiO}{}^{gas} - d_{SiO}{}^{solid}$ ($\Delta d_{SiO}{}^{gas-solid}$) difference down to 0.083 Å. However, further augmentation of the basis set with diffusion functions on the heavy atoms and with polarization functions has virtually no effect on the $\Delta d_{SiO}{}^{gas-solid}$ value.

The $\Delta d_{SiO}{}^{gas-solid}$ differences found from MP2(FC)/6-31G(d) and MP2(Full)/6-31G(d) calculations with inclusion of electron correlation are respectively slightly larger (by 0.003 Å) or 0.015 Å smaller than the value obtained in the Hartree—Fock calculations (0.134 Å). In contrast to this, as we go beyond the one-electron approxination the $\Delta d_{SiO}{}^{gas-solid}$ value calculated by the HF/6-311G(d) method (0.083 Å) dramatically increases to 0.130 (MP2(FC)/6-311G(d)) and 0.152 Å (MP2(Full)/6-311G(d)).

Methodologically, the following should be emphasized. Up to now, the studies of TBPSC have been carried out using the simplest version of the MP2 method, MP2(FC)/6-31G(d). However, the change in the d_{SiO}

Table 1. The bond lengths (*d*), bond angles (ω), and torsion angles (α) in molecule **1a** obtained from HF/6-31G(d) and MP2(FC)/6-31G(d) calculations

Parameter	$q = 10^{-4}$ hartree Bohr^{-1}				$q = 10^{-5}$ hartree Bohr^{-1}	
	HF/6-31G(d)		MP2/6-31G(d)		HF/6-31G(d)	MP2/6-31G(d)
	A*	**B**	**A***	**B**		
Bond			*d*/Å			
Si—O(4)	2.140	2.133	2.140	2.145	2.140	2.143
Si—F$_a$	1.608	1.608	1.627	1.633	1.608	1.633
Si—F$_e$	1.583	1.583	1.606	1.611	1.583	1.611
Si—C(5)	1.891	1.892	1.891	1.893	1.892	1.893
C(3)=O	1.213	1.213	1.242	1.242	1.213	1.242
Angle			ω/deg			
C(5)—Si—F$_a$	95.3	95.2	94.5	94.5	95.3	94.5
F$_a$—Si—F$_e$	100.1	100.0	100.4	100.4	100.1	100.4
C(5)—Si—F$_e$	119.6	119.7	119.7	119.8	119.7	119.7
			α/deg			
C(1)—C(2)—C(3)—O(6)	0.0	0.2	0.0	−2.3	0.0	0.0
C(3)—O(4)—Si—C(5)	0.0	0.4	0.0	−0.7	0.0	0.0
C(3)—O(6)—C(5)—Si	0.0	0.3	0.0	−0.7	0.0	0.0

* According to Ref. 18.

Table 2. The effect of medium on the bond lengths (*d*) and bond angles (ω) in molecule **1a** according to the results of quantum-chemical calculations and the data of X-ray diffraction study

Method	*d*/Å				ω/deg		
	Si—O(4)	Si—F$_a$	Si—F$_e$	C(3)=O	C(5)—Si—F$_a$	F$_a$—Si—F$_e$	C(5)—Si—F$_e$
				Gas phase			
HF/6-31G(d)^a	2.140	1.608	1.583	1.213	95.3	100.1	119.7
HF/6-311G(d)^a	2.089	1.611	1.585	1.210	95.1	99.2	120.1
HF/6-311+G(d)^a	2.088	1.615	1.586	1.210	95.3	99.0	120.2
HF/6-311+G(d,p)^a	2.090	1.615	1.586	1.210	95.3	99.0	120.1
MP2(FC)/6-31G(d)^a	2.143	1.633	1.611	1.242	94.5	100.4	119.7
MP2(Full)/6-31G(d)^a	2.125	1.631	1.609	1.242	94.4	100.2	119.9
MP2(FC)/6-311G(d)^a	2.136	1.631	1.605	1.232	94.8	100.1	119.9
MP2(Full)/6-311G(d)^a	2.158	1.622	1.599	1.230	95.1	100.5	119.7
				DMSO solution (ε = 45)			
SCRF HF/6-31G(d)^a	1.998^b	1.627	1.592	1.228	93.9	97.1	121.4
	2.068^c	1.616	1.587	1.219	94.6	98.7	120.5
PCM HF/6-31G(d)^d	1.969	1.632	1.600	1.233	94.8	96.0	121.4
				Crystal			
PCA^e	2.006^f	1.610	1.577 1.580	1.243	95.4	97.4 96.4	121.3 122.6

[a] The C(1)—C(2)—C(3)—O(6), C(3)—O(4)—Si—C(5), and C(3)—O(6)—C(5)—Si torsion angles are equal to 0°.

[b] The cavity radius, *a*, was determined using a quantum-chemical method.[22]

[c] Determined using the van der Waals radius of the molecule as the cavity radius.

[d] The C(1)—C(2)—C(3)—O(6), C(3)—O(4)—Si—C(5), and C(3)—O(6)—C(5)—Si torsion angles are 0.1°, 0.1°, and 0.2°, respectively.

[e] The C(1)—C(2)—C(3)—O(6), C(3)—O(4)—Si—C(5), and C(3)—O(6)—C(5)—Si torsion angles are 5.91°, 2.5°, and 2.6°, respectively.

[f] According to Ref. 15.

distance (0.003 Å) obtained for molecule **1a** with this method for inclusion of electron correlation is an order of magnitude smaller than the changes in the lengths of the "normal" bonds (*e.g.*, the Si—F and C=O bonds, see Table 2), which differs from the situation for molecules **2a**, **2b**, and **3**. A reasonable relation, namely, $|d_{\text{SiO}}{}^{\text{MP2(Full)}} - d_{\text{SiO}}{}^{\text{HF}}| > |d_{\text{CO(SiF)}}{}^{\text{MP2(Full)}} - d_{\text{CO(SiF)}}{}^{\text{HF}}|$, is restored only when using the MP2(Full)/6-311G(d) approximation. Based on the available data, it is impossible to predict with certainty how further extension of the basis set and a better inclusion of electron correlation effects will affect the $\Delta d_{\text{SiO}}{}^{\text{gas—solid}}$ difference for molecule **1a**. Nevertheless, it seems to be beyond reason to hope for substantial (by an order of magnitude) decrease in the $\Delta d_{\text{SiO}}{}^{\text{gas—solid}}$ value.

The possibility of deformation of the Si←O coordination bond due to the effect of the medium is clearly demonstrated in Fig. 1. As can be seen, the change in the Si...O internuclear distance over a rather wide range (~0.2 Å) requires a small expenditure of energy (~1.5 kcal mol^{-1}), which is comparable in magnitude with the energy of non-specific intermolecular interactions.

The feasibility of essential structural rearrangement in molecule **1a** upon changing the state of aggregation can also be illustrated using two solvation models, namely, the polarizable continuum model (PCM)[12] and the Onsager self-consistent reaction field (SCRF) model.[13] The results listed in Table 2 allow one to follow the changes in the Si—O bond length ($\Delta d_{\text{SiO}}{}^{\text{gas—liquid}}$) calculated by the HF/6-31G(d) method on going from the gas phase to the polar solution (DMSO). Irrespective of the method employed for determining the liquid-phase geometry of complex **1a**, the $\Delta d_{\text{SiO}}{}^{\text{gas—solid}}$ value exceeds the corresponding values for the "normal" bonds by more than an order of magnitude.

Physically reasonable shortening of the Si—O bond in the order $d_{\text{SiO}}{}^{\text{gas}} > d_{\text{SiO}}{}^{\text{liquid}} > d_{\text{SiO}}{}^{\text{solid}}$ obtained in the HF/6-31G(d) and MP2(FC)/6-31G(d) calculations using the SCRF model and the van der Waals radius of the molecule as the cavity radius corresponds to the increase in the molecular dipole moment (μ) along this direction ($\partial\mu/\partial d_{\text{SiO}} < 0$). Analogous behavior of the parameters d_{SiN} and d_{SiO} was also reported in the HF/6-31G(d) studies of intramolecular complexes of silicon with the F(O)$_3$Si←N [9] and Cl(C)$_3$Si←O [10] coordination sites carried out using the SCRF model. However, the data in Table 2 point that our calculations of complex **1a** failed to exactly reproduce the trend of changes in the length of the "covalent" axial Si—F$_a$ bond ($d_{\text{SiF}}{}^{\text{gas}} < d_{\text{SiF}}{}^{\text{liquid}} < d_{\text{SiF}}{}^{\text{solid}}$) expected from the results of both theoretical and experimental studies on the structure of TBPSC.[6—10]

It should be emphasized that all structural parameters of molecule **1a** found using the SCRF and PCM models for a high-polarity DMSO solution and those determined by X-ray diffraction analysis are close (see Table 2). This situation has also been reported for intermolecular complexes; it corresponds to the dipole mechanism of changes in their geometries upon crystallization.[23]

The spatial arrangement of the bonds formed by the silicon atom in molecule **1a** (both experimentally determined in the crystal and calculated using all the methods employed) corresponds to a distorted trigonal bipyramid with virtually planar Si—C(5)—O(6)—C(5)—O(4) chelate ring (see Table 2). The formation of such a ring is indicated by location of two critical points, (3, 1) and (3, −1), corresponding to the chelate ring and the Si—O bond, respectively, when analyzing the electron density distribution according to Bader by the MP2(Full)/6-31G(d) method. The properties of the (3, −1) critical point, that is, the electron density value (ρ = 0.312 e Å^{-3}), the Laplacian ($\nabla^2\rho$ = 1.351 e Å^{-5}), and the density of the electron energy (E = −0.111 hartree Å^{-3}) indicate that the Si←O coordination bond in molecule **1a** can be treated as a covalent bond of high polarity.

Of crucial importance is the problem of interrelation between the sensitivity of the TBPSC geometry to the effects of medium and their complexation energies (E_c) or, for simplicity, the parameters characterizing the strength of the coordination bonds (bond length, bond energy, degree of charge transfer, *etc.*). At first glance the smaller the E_c value, the higher the degree of structural rearrangement of the complex, initiated by the change in the state of aggregation. However, in the general case this is contrary to facts. According to the available data and results of our HF and MP2 calculations, molecule **1a** is characterized by the lowest sensitivity to the effect of the medium among the TBPSC. For instance, the $\Delta d_{\text{SiO}}{}^{\text{gas—solid}}$ difference for the coordination bonds in molecules **1a**, **3**,[10] **2b**,[9,20] and **2a** [21] obtained from HF/6-31G(d) calculations are 0.134, 0.321, 0.414, and 0.570 Å, respectively. This suggests that the complexation energies, E_c, of silatranes **2** are much lower than that of **1a** (5.4—6.8 kcal mol^{-1}, see above). Nevertheless, the estimates obtained exceed 12 kcal mol^{-1}.[5,24] A dome-shaped dependence of $\Delta d_{\text{SiO}}{}^{\text{gas—liquid (solid)}}$ on the strength of the Si←O coordination bond, which was found in HF/6-31G(d) calculations of the (O—Si)-chelate and zwitterionic compounds with the ClSiC$_3$O coordination site,[10] was confirmed by ^{29}Si NMR spectroscopy.[4]

Intermolecular complexes can also provide some impressive examples.[23,25] According to experimental data, the energy of the B←N bond in complex BH$_3$•NH$_3$ is much higher than in complex BF$_3$•NH$_3$ (~31 *vs.* ~19 kcal mol^{-1}, respectively). However, the $\Delta d_{\text{BN}}{}^{\text{gas—solid}}$ value for the former complex (about 0.1 Å) is an order of magnitude larger than for the latter (~0.01 Å). Hypersensitivity of the geometry of the complexes to the effects of medium, which is one—two orders of magnitude higher than that typical of the normal compounds,[23] is governed by not only the E_c value but also other characteristics and first of all the dipole moment and its gradients.[6,23]

The results obtained show that (aroyloxymethyl)trifluorosilanes **1** are inappropriate for detailed studies of hypersensitivity of the geometry of TBPSC to the effects of the medium. At the same time these results point to the possibility of appreciable shortening of the Si←O coordination bond in molecule **1a** on going from the gas phase to the polar solution and crystal. Thus calculations confirm the hypothesis that the changes in the spectral characteristics of (aroyloxymethyl)trifluorosilanes **1** depending on the medium conditions are due to geometric reasons.

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