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Structure of (O→Si)-(Acetoxymethyl)trifluorosilane in Three Phase States and in Solutions

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Abstract—According to the IR spectroscopy data, the molecules of (O→Si)-(acetoxymethyl)trifluorosilane having in the liquid state and in polar media the intramolecular bond C=O→Si, exist in the gas phase in the temperature range 438–538 K in the equilibrium with the molecules with tetracoordinate silicon atom. This allowed to determine experimentally the enthalpy of formation of the intramolecular bond C=O→Si for the gas phase to be $\Delta H = 2.2\pm0.1$ kcal mol^{-1}. In the solid state at 110 K and in the CS_2 solution, along with molecule with the C=O→Si bond, the dimers exist, which include both tetra- and pentacoordinate silicon atom. The data of quantum-chemical calculations (B3LYP/6-311G**) show that the shortest intermolecular bond Si–F→Si is realized in the associate formed by the molecules in the *ap,sp*- and *sp,sp*-forms, and the longest one, when both components are in the *sp,sp*-forms.

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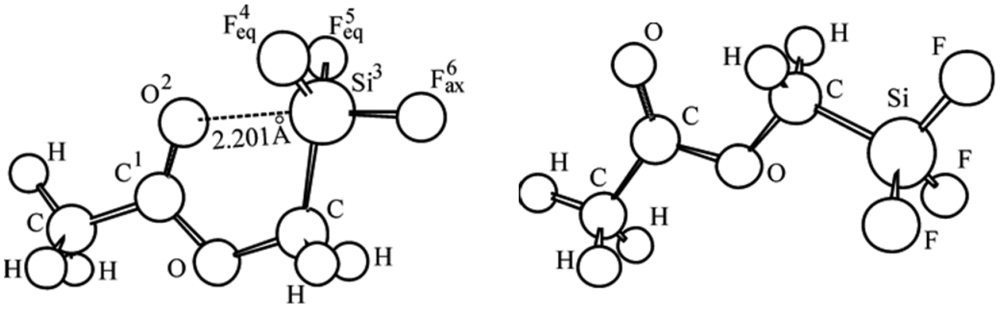
Organylsilanes with a substituent having a heteroatom are capable of formation of intra- and intermolecular bonds with the participation of the silicon atom [1–3]. In the alkyl- and phenylfluorosilanes the intermolecular coordination is realized by means of the Si–F→Si bonds [4, 5]. The most comprehensive experimental study of the ability to homo- and heteroassociation is that of tetrafluorosilane [1, 6–12]. Among the compounds of the general formula $SiH_{4-n}F_n{\cdot}B$ (B = NH_3, H_2O, n = 1–4) the complexes of tetrafluorosilane are the most stable ones [4]. With decrease in the number of electronegative substituents at silicon the energy of coordination with respect to that of tetrafluorosilane decreases. For example, the energy of complex formation of trifluorosilane $SiHF_3$ with the nitrogen- and oxygen-containing ligands is by ~3 kcal mol^{-1} lower than that of tetrafluorosilane [4]. The introduction of an organic substituent into the molecule further decreases the ability of the silicon atom to intermolecular interactions [1, 5, 6].

Compounds of pentacoordinate silicon with the intramolecular bond O→Si called dragonoids [13] are well studied in crystal, in solution, and as isolated molecules [13–18]. Their specific feature is a high sensitivity to solvent effects of stereoelectronic parameters of the C=O→Si–F fragment, which is common to most dragonoids [13, 15, 19–22]. (Aroyloxymethyl)trifluorosilanes $ArC(O)OCH_2SiF_3$ are a striking example of the sensitivity of compounds of pentacoordinate silicon with the intra-molecular bond C=O→Si to solvent effects. They are characterized by the experimentally found [13, 15, 23] and theoretically interpreted [24–26] uniquely high sensitivity to external factors of the geometry characteristics of the coordination node of the hypervalent silicon. These compounds are capable of formation of stable complexes with rather strong nitrogen-containing ligands. With pyridine, depending on the nature of the solvent, they form either the complex with one intermolecular N→Si bond (with the retention of the intramolecular fragment C=O→Si–F) or the complex with two intermolecular N→Si bonds (with breaking the C=O→Si bond) [27]. The hexacoordination of the silicon atom with bidentate electronodonors like 2,2'-dipyridyl, 1,2-bis(dimethyl-amino)ethane, and 1,10-phenanthroline is realized only with the formation of the chelate ring with two N→Si bonds [28]. Specific interaction of these intracomplex compounds with

Scheme 1.



I (*sp,sp*) **I** (*ap,sp*)

weaker bases is also possible. Thus, (benzoyloxymethyl)trifluorosilane and 4-nitro(aroyloxymethyl)trifluorosilane in protophilic media form solvate complexes in which the molecule of the solvent acts as an electron pair donor and the silicon atom expands its coordination number to six [29].

Therefore, the silicon atom of dragonoids is capable to expand its coordination number not only due to intramolecular but also due to intermolecular coordination. Therewith, to form the supramolecular structure, the silicon atom participates in the formation of both hetero- and self-associates. Thus, (phenacetoxymethyl)trifluorosilane $PhCH_2C(O)OCH_2SiF_3$ in the crystal contains the intramolecular bond C=O→Si, whereas in nonpolar inert media it can form self-associates with the intermolecular bond C=O→Si [30]. The molecules of (acylthiomethyl)trifluorosilanes $MeCOSCH_2SiF_3$ and $PhCOSCH_2SiF_3$ existing in the solid state and in solutions as an equilibrium mixture with the tetra- and pentacoordinate silicon atom also form both the intra- and intermolecular bonds C=O→Si [31]. In the gas phase, the conformation without the C=O→Si bond predominates in these compounds. Intermolecular bonds Si–F→Si were found in the crystals of 3-(trifluorosilyl)-2-cyanoethylpropionate containing the pentacoordinate silicon atom with the intramolecular bond C=O→Si [32].

The goal of the present work was to investigate the nature of the coordination bond C=O→Si in (acetoxymethyl)trifluorosilane $CH_3C(O)OCH_2SiF_3$ **I** and the ability of its molecules to form self-associates depending on the phase state of the compound (liquid, solid, gaseous) and on the nature of an inert solvent. The methods of investigation were IR spectroscopy and quantum-chemical calculations at the B3LYP/6-311G** level of theory. The conclusion about the presence of an intramolecular bond C=O→Si in compound **I** in the liquid state at 297 K has been earlier made based on the comparison of the IR spectrum of the compound in thin layer with the data of nonempirical calculations [33]. Therewith, for the isolated molecules **I** four minima corresponding to different conformers were located on the potential energy surface (PES). The most stable are the *syn-peri*-planar (*sp,sp*) conformer with the C=O→Si bond and the *anti-syn*-planar (*ap,sp*) conformer with the tetrahedral silicon atom. (Hereinafter, the adopted designations characterize the orientation of atoms in the fragments Si–C–O–C and C–O–C=O respectively). The difference between the total energies of these conformers determines the energy of intramolecular coordination (E_c) being 2.39 (RHF/6-31G*) and 4.94 kcal mol^{-1} (MP2/6-31G*) [33]. According to our calculations (B3LYP/6-311G**), the value of E_c for compound **I** is 3.66 kcal mol^{-1} for the O→Si bond length equal to 2.201 Å (Scheme 1), which is practically identical with the coordination energy of (phenacetoxymethyl)trifluorosilane **II** having an alkyl substituent in the ester group (3.69 kcal mol^{-1}).

This value exceeds the calculated coordination energy of di-$PhC(O)OCH_2SiF_2Me$ [2.06 kcal mol^{-1}, *d*(O→Si) 2.403 Å] and monofluoro $PhC(O)O·CH_2SiFMe_2$ [1.01 kcal mol^{-1}, *d*(O→Si) 2.553 Å] derivatives of benzoyloxymethylsilanes, which exist in solution in equilibrium with forms containing a tetrahedral silicon atom and free C=O group. However, this value is lower than the coordination energy of (benzoyloxymethyl)trifluorosilane $PhC(O)OCH_2SiF_3$ **III** [4.20 kcal mol^{-1}, *d*(O→Si) 2.151 Å], whose molecules with the C=O→Si bond are retained in the gas phase at temperatures higher than 420 K and exist in equilibrium with the molecules of tetracoordinate silicon having the free C=O group.

The values of the stretching vibrations of the C=O and Si–F bonds in the IR spectra of (acetoxymethyl)trifluorosilane **I** (Table 1) are the main criteria of the formation of the intramolecular bond C=O→Si by the silicon atom, as it is the case in the (aroyloxymethyl)-trifluorosilanes [13, 15]. Using the method of IR spectroscopy we have determined the enthalpy of formation of the intramolecular coordination bond C=O→Si (ΔH_c) of compound **I** in the gas phase. In its IR spectrum at temperatures higher than 373 K, along with a wide band ν(C=O) at 1653 cm^{-1} corresponding to the stretching vibrations of the carbonyl group in the spectrum of the liquid sample new bands ν(C=O) appear at 1721 and 1774 cm^{-1}, corresponding to the vibrations of its C=O group in the gaseous state. In the temperature range of 438–538 K only the latter two bands remain in the spectrum, which belong to the monomer molecules of **I** in the *sp,sp*- and *ap,sp*-forms, respectively. The value of ΔH_c was determined from the temperature dependence of the ratio of optical densities of the bands of the C=O group stretching vibrations of these conformers ($D_{sp,sp}$ and $D_{ap,sp}$) using the van't Hoff equation, as it was done earlier when studying the (aroyloxymethyl)fluorosilanes [34, 35].

T, K	383	404	421	447	474
$\ln (D_{sp,sp}/D_{ap,sp})$	0.843	0.620	0.531	0.374	0.203
T, K	478	494	517	538	
$\ln (D_{sp,sp}/D_{ap,sp})$	0.223	0.073	0.043	–0.022	

The following equation of linear regression was obtained.

$$\ln (D_{sp,sp}/D_{ap,sp}) = (-2146\pm112) + (1125\pm51)(1/T),$$
$$r\ 0.993,\ sd\ 37,\ n\ 9.$$

The value of ΔH_c of compound **I** is lower than the calculated coordination energy ΔE_c (3.66 kcal mol^{-1}) being equal to 2.2±0.1 kcal mol^{-1}. This is indicative of an overestimation of the stabilizing effect of nonvalent interactions by computational methods. The experimentally determined strength of the intramolecular coordination bond of compound **I** is substantially lower than that of (benzoyloxymethyl)trifluorosilane **III** (ΔH_c 6.8 kcal mol^{-1} [34]). At the same time, this value is close to the experimental ΔH_c in the gas phase for the di- and monofluorinated methyl(benzoyloxymethyl)fluorosilanes (2.8 and 1.3 kcal mol^{-1}, respectively) [35]. This is responsible for the fact that molecules of **I** are apt to change the conformation from *sp,sp*- to *ap,sp*-, the latter being able to participate in the formation of self-associates.

A wide band of the stretching vibrations of the C=O bond in the IR spectrum of thin film of liquid sample of compound **I** (298 K) with the maximum at 1653 cm^{-1} [33] has a fine structure on the high-frequency slope. Its complex shape can be due to frequency-amplitude modulation of high-frequency vibrations by the lower

Table 1. Frequencies of stretching vibrations (ν, cm^{-1}) of the C=O and Si–F bonds in the IR spectra of (acetoxymethyl)-trifluorosilane (**I**)

State/solvent	Liquid	Solid	n-C_4H_9Br	C_6H_6	n-C_6H_{14}	CS_2			Gas	
T, K	298	110	298	298	298	298		193	438	504
c, M	–	–	0.1	0.1, 0.01	0.1, 0.02	0.1	0.01	0.1	–	–
ν(C=O)	1653 s.w	1640 s.w	1662 v.s	1662 v.s	1698 sh, 1693 c, 1680 sh	1745 w, 1738 w, 1710 s, 1682 s, 1655 s, 1651 sh	1745 sh, 1731 sh, 1689 s, 1673 s, 1660 sh, 1650 sh	1737 m, 1709 c, 1640 w, 1635 w	1774 m, 1721 v.s	1768 s, 1730 s
$\nu_{as}(SiF_{eq})$	938 s	926 s, 915 s	957 v.s	951 v.s		985 v.s, 973 sh, 940 w, 916 w	972 v.s, 920 w		988 v.s, 983 sh	986 s, 983 sh
$\nu_s(SiF_{eq})$	861 s	881 m, 872 s, 853 m	867 s	866 s		893 v.s	898 w, 875s		885 m	881 m
$\nu(SiF_{ax})$	796 s.w, 780 s.w	794 sh, 756 v.s.w	804 v.s.w	801 s.w		835 v.s.w, 812 sh	815 v.s.w		842 c	842 w

frequency ones, in particular, by pseudorotational vibrations in the ring [36]. With lowering the temperature, the fine structure of the band becomes better resolved due to a decrease of the half-width of its vibration-rotational components. At 110 K, the film is solidified and a wide band ν(C=O) is shifted to lower frequencies by 10–20 cm^{-1} showing no global maximum. Therewith, the Si–F stretching vibration bands also suffer low-frequency shift. The band $\nu_{as}(\mathrm{SiF}_{eq})$ 938 cm^{-1} single at room temperature is split in two components (926 and 915 cm^{-1}), and the single and symmetric band $\nu_s(\mathrm{SiF}_{eq})$ (861 cm^{-1}), in three components (881, 872, 853 cm^{-1}). The band $\nu(\mathrm{SiF}_{ax})$ suffers the largest low-frequency shift from 780 to 756 cm^{-1}. Such a shift of the C=O and Si–F_{ax} stretching vibration bands in the spectrum (Table 1) with respect to the corresponding bands of the liquid film is indicative, first of all, of strengthening of the coordination bond C=O→Si in molecule **I**. However, their multiplicity can be considered as pointing to the presence of not only monomeric but also dimeric structures of this compound.

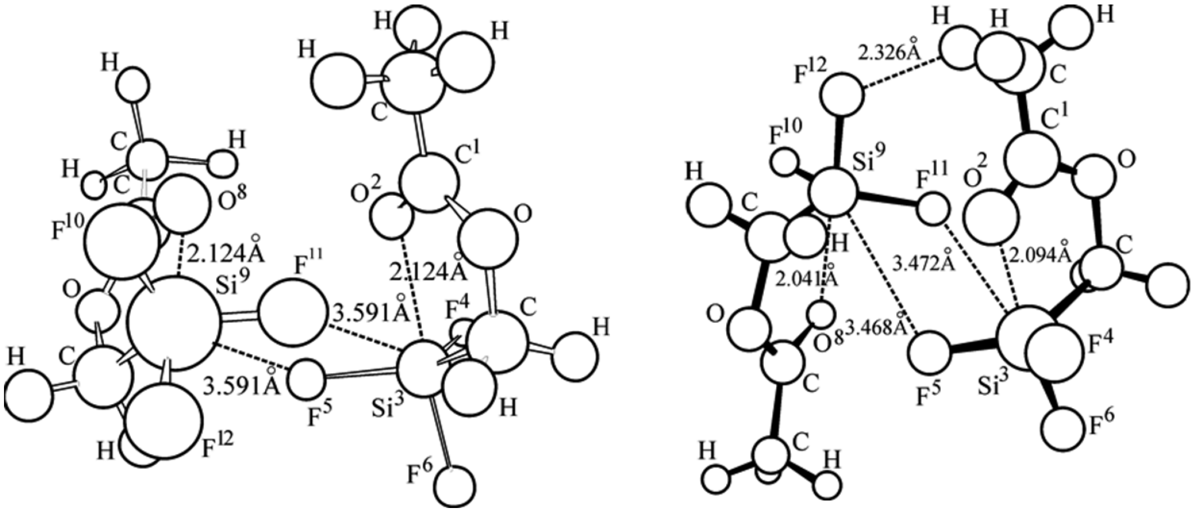
The frequency value at the maximum of the wide band ν(C=O) (1630–1640 cm^{-1}) in the spectrum of compound **I** at low temperature is close to that earlier observed [30] in the spectrum of solid compound **II** (1630 cm^{-1}) and is also highly sensitive to the medium effects (Table 1). In the heptane solution with very low Kamlet–Taft parameter (π* –0.02) quantitatively characterizing the polarity/polarizability of the solvent [37], the maximum of asymmetric band ν(C=O) is shifted to 1693 cm^{-1}. On going to butyl bromide (π* 0.48) or benzene (π* 0.59) the value of ν(C=O) is reduced with respect to heptane by 30 cm^{-1}. The position of the maximum of the ν(C=O) band in these solvents does not depend on concentration and, hence, corresponds to one molecular form. The dipole moment (μ) of compound **I** measured in benzene at 298 K is equal to 5.10 D and is also independent of concentration. Along with the calculated value of μ of the *sp,sp*-conformer of **I** (5.72 D) this is indicative of predominance of monomeric molecules **I** with the C=O→Si bond in this solution.

Another situation is realized in the solution of compound **I** in carbon disulfide, a nonpolar solvent with a high refractive index (n_D 1.619), which is responsible for its high disperging properties and, as a result, an enhanced role of the van der Waals interactions between the easily polarizable molecules of the solute and solvent [38]. In the IR spectrum of compound **I** in CS_2 at 298 K and concentration of the compound of 0.01 M the band ν(C=O) is very wide with several intense maxima. One of them at 1689 cm^{-1} characterizes the intramolecular bond C=O→Si and is only slightly different in the frequency from that in the spectrum of the heptane solution. A similar behavior is observed for the ν(C=O) band in the spectra of solutions of compound **II**: 1680 (decane) and 1676 cm^{-1} (CS_2) [30]. Also on the ν(C=O) band in the spectrum of solution of **I** in CS_2 there are low-frequency (1673, 1660, and 1650 cm^{-1}) and high-frequency (1745 and 1731 cm^{-1}) maxima with the ratio of relative intensities depending on the concentration of the compound and the temperature of the solution (Table 1). With the increase of concentration of **I** to 0.1 M the high-frequency components retain their position, whereas the global maximum of the low-frequency components appears at 1655 cm^{-1}. The lowering of the temperature of the solution to 193 K results in a decrease in the relative intensity of the low-frequency component of the ν(C=O) band and increase in the intensity of the high-frequency components. Hence, the presence of the latter is not related to the appearance of the less stable *ap,sp*-conformer of **I** in the solution. Besides, the free C=O group in the spectrum of the solution of the model compound $\mathrm{CH_3COOCH_2Si(OMe)_3}$ (**IV**) in pentane is characterized by a doublet band with substantially smaller splitting (1754, 1740 cm^{-1}) and a larger peak frequency caused by the existence of two conformers. This points to the presence of complex dynamic equilibrium in the carbon disulfide solution between the molecules of compound **I** in the *sp,sp*-form and its self-associates containing both the components with free C=O groups and those with the intramolecular bond C=O→Si. The bands in the region of the stretching vibrations of Si–F bond in this solvent are also multiplet and the relative intensity of their components changes with concentration (Table 1).

Theoretical analysis of the structure of self-associates of compound **I** represented by various combinations of the monomer components in the *sp,sp*- and *ap,sp*-conformations and of the energetics of their formation was performed with full optimization of geometry of the conformers and dimers. The energy of intermolecular coordination (ΔE_c) in self-associates (Table 2) was determined as a difference between the total energy of the dimer and the sum of total energies of the constituting molecules in the corresponding forms.

Dimers of **I** formed in the isolated state by its most stable *sp,sp*-conformer have been earlier analyzed by

Scheme 2.



Ia **Ib**

us theoretically at the B3LYP/6-311G** level of theory [39]. Two minima on the PES correspond to the configurational isomers **Ia, Ib** of the dimer with different mutual orientation of the monomeric *sp,sp*-subunits (Scheme 2).

The bridging atom of the intermolecular bonds Si–F→Si is the equatorial fluorine atom. The dihedral angle $Si^3O^2O^8Si^9$ is equal to 38° (**Ia**) and 163° (**Ib**), and the energy of formation of these dimers is 9.8 and 11.2 kcal mol^{-1} (B3LYP/6-311G**), respectively. The intramolecular bonds C=O→Si in the dimers are strengthened as compared to the monomers, which is the main stabilizing effect.

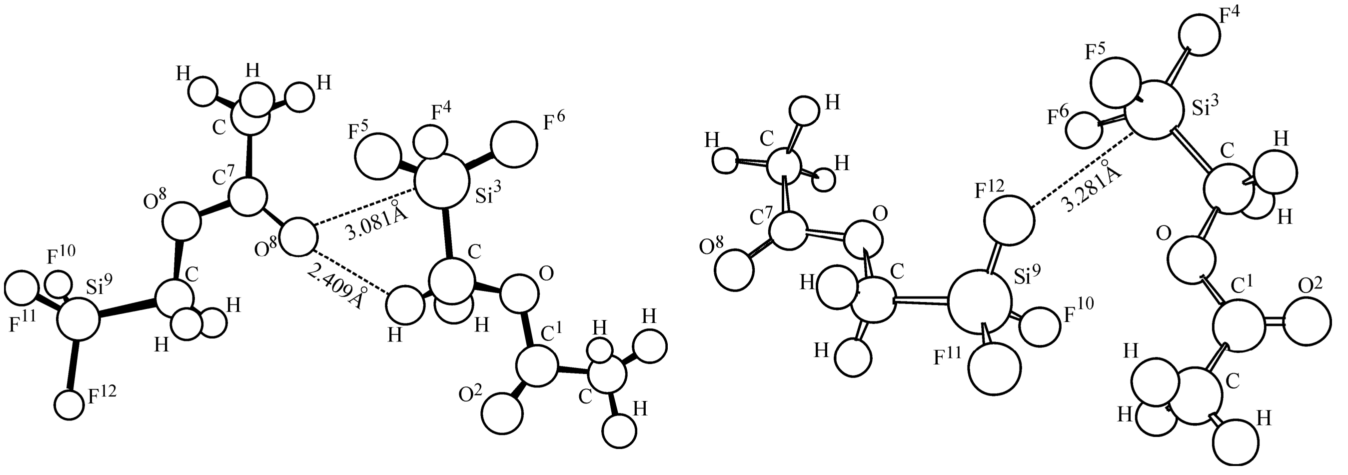
Self-associates of **I** formed by the two molecules in the *ap,sp*-conformation form intermolecular bonds of the two types: C=O→Si (**Ic**) and Si–F→Si (**Id**) (Scheme 3).

The dimers with the bridging fluorine atoms also consist of the *ap,sp*- and *sp,sp*-conformers. The Si–F→Si bond is formed with participation of the tetrahedral silicon atom of the *ap,sp*-form and the fluorine atom of the *sp,sp*-forms: the axial one in dimer **Ie** and the equatorial one in dimer **If** (Scheme 4).

The energy of formation of the intermolecular coordination bonds in the dimers under consideration varies within 2–11 kcal mol^{-1}. The largest value was found in the dimers **Ia, Ib** with two intermolecular bonds Si–F→Si consisting of two *sp,sp*-conformers, the smallest, in the dimer **Id** (2.6 kcal mol^{-1}) with one bond Si–F→Si, whose components exist in the *ap,sp*-forms. It should be mentioned, however, that only dimer **Id** has no additional nonvalent bonds F···H or O···H with the distances shorter than the sum of the van der Waals radii, and the energy of its formation exactly corresponds to the coordination bonding via the fluorine bridging atom. In all other cases nonvalent interactions (Schemes 3, 4) can notably contribute to the calculated values of E_c. Therefore, the calculated values of E_c hardly can be used for constructing the order of stability of dimers **Ia–If**.

The intermolecular distance O^8→Si^3 in dimer **Ic** (Scheme 3) is by 0.5 Å shorter than the sum of the van der Waals radii of the oxygen and silicon atoms, and by ~0.9 Å exceeds the length of the intramolecular bond C=O→Si in the *sp,sp*-form of the monomer. The elongation of the $C^7=O^8$ bond due to the intermolecular coordination is only 0.007 Å as compared to its elongation by 0.022 Å upon the formation of the chelate ring in the monomer. The bond angle $C^7O^8Si^3$ in dimer **Ic** is equal to 122°, which is substantially larger than in the chelate ring of the *sp,sp*-conformer (110°). At the same time, the $OSiF_{ax}$ bond angles in both cases are equal to 174 and 175°, respectively, proving the linearity of the formed three-center bond. The aforementioned geometric parameters of dimer **Ic** are close to those observed in the X-ray spectra of the silylacetate, the compound having the intra- and intermolecular bonds C=O→Si [40]. All three Si–F bond distances at the silicon atom, which

Scheme 3.



Ie **If**

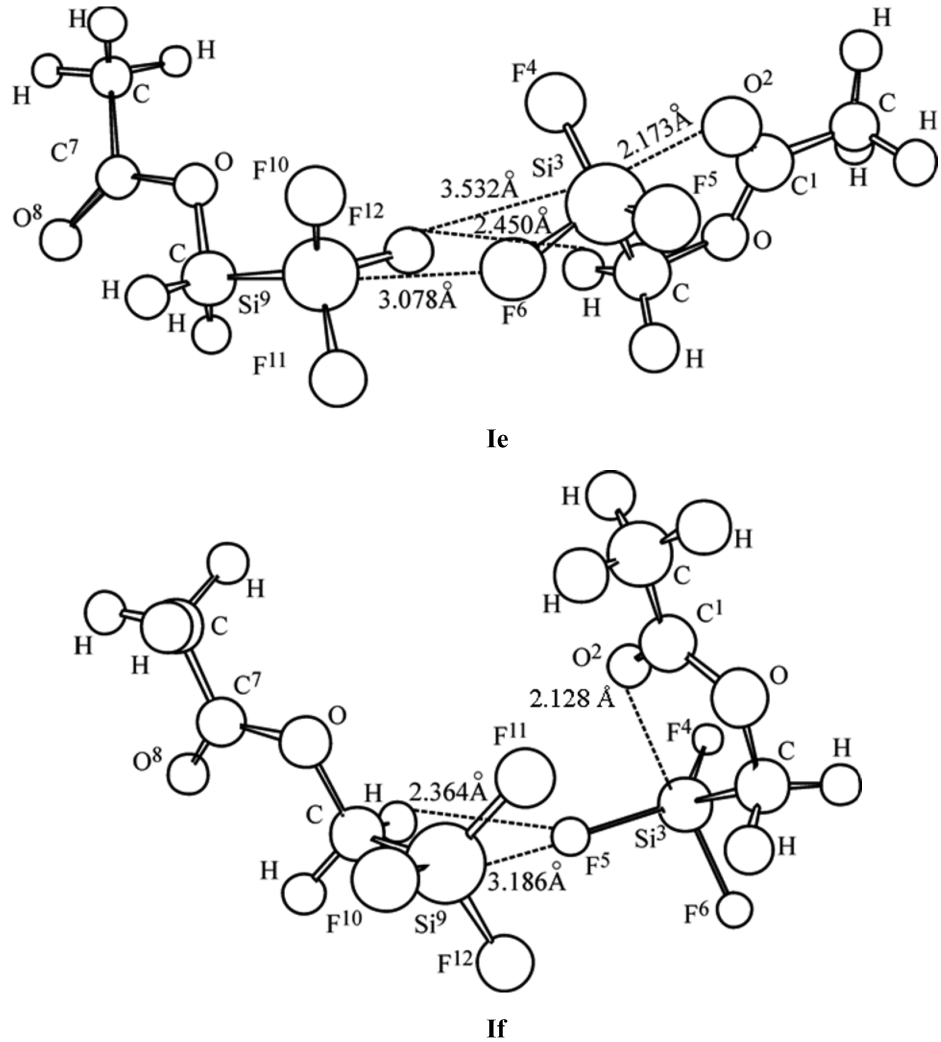
expands its coordination number in the dimer to five, are only slightly longer (by 0.005 Å) than the Si–F bonds at the tetrahedral silicon atom (1.595, 1.597 Å). Similar elongation is observed for the equatorial bonds (Si–F$_{eq}$) of the *sp,sp*-conformer **I** as compared to the *ap,sp*-conformer, while for the axial bonds (Si–F$_{ax}$) of the *sp,sp*-conformer it reaches 0.030 Å. Some contribution to the geometry parameters of dimer **Ic** with

Table 2. Calculated (B3LYP/6-311G**) coordination energies (ΔE_c), dipole moments (μ), and geometry parameters of (acetoxymethyl)trifluorosilane **I** and its dimers **Ic**–**If**

Compound	**I** (*sp,sp*)[a]	**Ic**	**Id**	**Ie**	**If**	Compound	**I** (*sp,sp*)[a]	**Ic**	**Id**	**Ie**	**If**
ΔE_c, kcal mol^{-1}	3.7	5.6	2.6	3.1	5.9	μ, D	5.72	1.27	1.59	5.33	6.11
Bond lengths, Å											
C^1–O^2	1.223	1.201	1.201	1.201	1.229	Si^9–F^{10}		1.595	1.595	1.604	1.599
C^7–O^8		1.208	1.201	1.226	1.200	Si^9–F^{11}		1.595	1.596	1.605	1.608
O^2–Si^3	2.201				2.128	Si^9–F^{12}		1.597	1.602	1.636	1.596
O^8–Si^9				2.173		Si^3–F^{12}			3.281	3.078	
O^8–Si^3		3.081				Si^9–F^5				3.532	3.186
Si^3–F^4	1.604	1.601	1.594	1.591	1.606	Si^3–F^{11}					
Si^3–F^5	1.604	1.601	1.597	1.604	1.620	O^8–H		2.409			
Si^3–F^6	1.627	1.602	1.601	1.596	1.628	F–H				2.450	2.364
Bond angles, deg											
$C^1O^2Si^3$	110				112	$O^8Si^9F^{12}$				174	
$C^7O^8Si^9$				111		$Si^3F^5Si^9$					127
$C^7O^8Si^3$		122				$Si^3F^{12}Si^9$			128	127	
$O^2Si^3F^6$	174				175	$F^5Si^9F^{10}$					177
$O^8Si^3F^6$		175				$F^{12}Si^3F^4$			160		

[a] Bond leghts C=O and Si–F in (**I** *ap,sp*) are 1.201 and 1.596, 1.596, 1.598 Å.

Scheme 4.



respect to the monomer and to the energy of its formation comes from a shortened contact (2.409 Å) between the oxygen O^8 and hydrogen atoms.

The F^{11}→Si^3 distance (3.281 Å) between the monomeric components in the *ap,sp*-form of dimer **Id** (Scheme 3) is by 0.32 A less than the sum of the van der Waals radii of the fluorine and silicon atoms. The angles $Si^9F^{12}Si^3$ and $F^{12}Si^3F^4$ in dimer **Id** are equal to 128° and 160°, respectively, and the Si–F bond lengths for the two silicon atoms, as in the case of dimer **Ic**, lie in the range 1.594–1.602 Å.

The intermolecular distances between the silicon and the fluorine atoms in dimers **Ie** (3.078 Å) and **If** (3.186 Å) (Scheme 4) are less than the sum of the van der Waals radii of these atoms by 0.5 and 0.4 Å, respectively. The participation of the axial fluorine atom of the *sp,sp*-component in coordination of dimer **Ie** leads to the elongation of the Si^9–F^{12}_{ax} bond to 1.636 Å and shortening (strengthening) of the intramolecular bond C=O→Si to 2.173 Å as compared to their values in the monomer *sp,sp*-conformer (1.627 and 2.201 Å, respectively). The lengths of other Si–F bonds remain unchanged. The intermolecular coordination via the equatorial fluorine atom in dimer **If** results in the elongation of the Si^3–F^5_{eq} bond to 1.620 Å without changing the Si^3–F^6_{ax} bond length (1.628 Å), and a more substantial shortening than in dimer **Ie** of the intramolecular bond O^2→Si^3 to 2.128 Å. The C=O bond in the monomeric components of the *sp,sp*-form is elongated in dimers **Ie** and **If** by 0.003 and 0.006 Å, respectively. The F_{ax}SiF and F_{eq}SiF bond angles are also substantially different. Thus, the angle formed by the equatorial fluorine atom F^5_{eq} and Si^9, F^{10} atoms of the molecule in the *ap*-form of dimer **If** is equal to 177°, whereas in dimer **Ie** the angle $F_{ax}^{12}Si^{3}F$ including any fluorine atom in the *ap,sp*-form is close to 70°. At the same time, the bond angles COSi (112°), OSiF (175°), and SiFSi (127°) characterizing the intra- and intermolecular three-centered bonds are practically identical for the two dimers (Table 2). The energy of formation of dimers **Ie** and **If** is 3.1 and 5.9 kcal mol^{-1}, respectively. Short contacts (2.4 Å) between the bridging fluorine atom and the hydrogen atom of the methylene group, contributing to these values, exist in both dimers. Besides, the distance between the silicon atom of the molecule in the *sp,sp*-form and the fluorine atom of the *ap,sp*-form in dimer **Ie** is rather short and close to the sum of their van der Waals radii (3.532 Å). This short contact may also contribute to the changes in the geometry parameters of the surrounding of the silicon atom, which becomes close to hexacoordinate, and to increase in the energy of stabilization of the dimer. However, more energetically stable is dimer **If**, which, as compared to dimer **Ie**, has less strong intermolecular bond SiF→Si. Apparently, this is caused by substantial strengthening of the intramolecular bond C=O→Si of the monomer component of **If** in the *sp,sp*-form due to the linearity of the intermolecular bond with the bridging fluorine atom.

Thus, according to calculations, (acetoxymethyl)trifluorosilane **I** is capable of formation of dimers with the bridging fluorine atom, the components of the dimers existing in the *ap,sp*- and *sp,sp*- or two *ap,sp*(*sp,sp*)-forms. Their coordination energy (ΔE_c) cannot be used for assessment of the strength of the intermolecular bonds since some contribution comes also from short intermolecular contacts F···H. We have compared the studied self-associates by analyzing the values of intermolecular distances F→Si. According to these data, the strongest bond Si–F→Si is realized in the self-associate having the molecules in the *ap,sp*- and *sp,sp*-forms and the least strong one, when both components are in the *sp,sp*-form. In both cases, the dimerization results in strengthening of the C=O→Si intramolecular bonds of the monomeric components. This strengthening is larger for the intermolecular bond Si–F→Si with the participation of the equatorial fluorine atom at the pentacoordinate silicon atom. The axial fluorine atom forms stronger intermolecular bond Si–F→Si, the intramolecular bond being strengthened to a lesser extent. The self-associate of (acetoxymethyl)trifluorosilane **I** with the intermolecular bond C=O→Si is formed only from the two molecules in the *ap,sp*-form.

The calculated dipole moment (μ) of dimer **Ic** of 1.27 D is the lowest with respect to other dimers (Table 2), which is consistent with its stabilization in the nonpolar solvent CS_2. The second self-associate which can be suggested to exist in the equilibrium mixture is dimer **Id** with the dipole moment 1.59 D. The presence of dimers **Ia, Ib, Ie, If** with large dipole moments (3–6 D) in solution is less probable. The two high-frequency components of the ν(C=O) band in the IR spectrum of solution of **I** in CS_2, apparently, belong to dimers **Ic**, **Id** with free C=O groups of the components, whereas the low-frequency ones may correspond to the superposition of the bands of the dimers containing the C=O→Si bond. Consequently, the self-association of compound **I** occurs, most probably, when its molecules are in the *ap,sp*-form without intermolecular bond C=O→Si. Transition of the molecule from the *sp,sp*- to the *ap,sp*-form is apparently due to the low strength of the intramolecular coordination bond C=O→Si of (acetoxymethyl)-trifluorosilane and a higher stability of dimer **Ic** relative to the molecule in the *sp,sp*-form.

EXPERIMENTAL

IR spectra of (acetoxymethyl)trifluorosilane **I** in solutions and at various phase states at 110–538 K were recorded on a Specord 75 IR spectrophotometer using a temperature-controlled cell. Dielectric permeability of the solutions was measured on a Sh2-5 instrument (Angarsk, AO OKBA) at working frequency of 1 MHz. Dipole moments were calculated according to the Higashi formula [41]. Quantum-chemical calculations were performed at the B3LYP/6-311G** level with the GAUSSIAN-98 software [42].

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