AM1 studies of photoelectron spectra
10.* (Acetylthiomethyl)- and (benzoylthiomethyl)trifluorosilanes

V. K. Turchaninov, N. N. Chipanina, T. N. Aksamentova, M. S. Sorokin, and V. A. Pestunovich*

Irkutsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences, 1 ul. Favorskogo, 664033 Irkutsk, Russian Federation. Fax: +7 (395 2) 35 0046. E-mail: root@irioch.irkutsk.su

Five ionization potentials for the *sp,ac* and *sp,sp* conformers of (acetylthiomethyl)trifluorosilane $MeC(O)SCH_2SiF_3$ and six ionization potentials for the same conformers of (benzoylthiomethyl)trifluorosilane $PhC(O)CH_2SiF_3$ were calculated by the semiempirical AM1 method. The resulting values are in good agreement with the data of photoelectron spectroscopy only for the *sp,ac* conformers. The structure of the preferred conformer of (acetylthiomethyl)trifluorosilane was confirmed by measurement of its dipole moment in the gas phase. The influence of the long-range inductive effect (field effect) on the energy of nonbonding electrons of the carbonyl oxygen atom in the series of acetic acid derivatives was observed.

Key words: photoelectron spectra, semiempirical quantum-chemical calculations, *S*-esters of thioacetic and thiobenzoic acids.

According to IR spectroscopy, molecules of (acetylthiomethyl)- and (benzoylthiomethyl)trifluorosilane $RC(O)SCH_2SiF_3$ (R = Me (**1**), Ph (**2**)) exist in the condensed media as equilibrium mixtures of isomers with tetra- and pentacoordinated silicon atoms.[2] This involves formation of both intra- and intermolecular coordination bonds (O→Si). In the gas phase (at 420—500 K), these compounds exist as sets of two rotational isomers.[2] High frequencies of the C=O stretching vibrations (ν(CO) 1670—1730 cm^{-1}) indicate that they contain no O→Si coordination bond. The difference between the heats of formation of the rotational isomers in the gas phase amounts to 3—5 kcal mol^{-1}. These values are in satisfactory agreement with the energy differences characterizing the rotational isomerism in methyl formate HC(O)OMe, *O*-methyl thioformate HC(S)OMe, and *S*-methyl thioformate HC(O)SMe (4—8 kcal mol^{-1}) in which synperiplanar (*sp*) conformers are the most stable.[2]

The existence of two conformers has also been proved experimentally for gaseous ethyl formate.[3] However, its synperiplanar, antiperiplanar (*sp,ap*) and synperiplanar, synclinal (*sp,sc*) rotational isomers, unlike those of methyl formate, result from the internal rotation around the $O-C(sp^3)$ bond. In the case of ethyl formate, the lowest energy corresponds to the *sp,ap* conformer. Similar data have been obtained for ethyl fluoroformate FC(O)OEt and ethyl cyanoformate NCC(O)OEt.[3] However, the energy differences between their *sp,ap* and *sp,sc* conformers, unlike those of (acetylthiomethyl)trifluorosilane **1**, are small. For example, in the case of ethyl formate, it is as low as 0.19 kcal mol^{-1}.

To elucidate more precisely the structure of the preferred conformer of **1**, in this work, we analyzed its dipole moments in the gas phase and in solution and studied the photoelectron spectra (PES) of this compound and some related compounds. First, it should be noted that in the analysis of PES, we found no reliable evidence for the occurrence of rotational isomerism in compounds of this class. Therefore, the experimental results outlined below refer to the PES of the most stable conformer.

Experimental

The photoelectron spectra of compounds **1** and **2** were recorded on an ES-3201 electron spectrometer. The excitation was accomplished by the resonance emission of HeI (21.21 eV). The energy scale was calibrated against the first ionization potentials of Ar (15.76 eV) and chlorobenzene (9.06 eV). The error in the determination of the positions of allowed bands was 0.05 eV.

The quantum-chemical calculations of the ionization potentials of the compounds studied were carried out by the AM1 method[4] using the configuration interaction (CI) scheme formalism. First, optimization of all the geometric parameters of the neutral molecule was carried out. Then characteristics of the ground and excited states of the radical cation were calculated by the CI method. To observe verticality of the transition, the geometry of the ion was taken to be identical to that of the molecule. The first ionization potential was found as the difference between the heats of formation of the molecule and the radical cation, and the subsequent ionization

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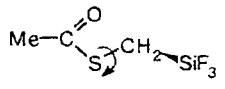
potentials were calculated as the sums of the first potential and the relative energies of excited (mostly Koopmans) states of the radical cation.

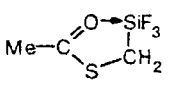
Dipole moments were calculated using the Hedestrand formula. The dielectric constants (ε) and densities of the benzene solutions were measured using a Sh2-8 instrument operating at a frequency of 1 MHz at 298 K. The dielectric constants of polar gases at pressures of up to 5 kPa and at 293 K were determined using the setup described previously.[5] Based on the ε′ values measured at a frequency of 9 GHz, the full polarizability and the dipole moment of the molecule were calculated (by the Debye first method).

Results and Discussion

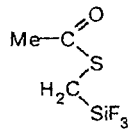
The dipole moment of (acetylthiomethyl)trifluorosilane. The dipole moments of this compound measured in the gas phase (293 K) and in solution (benzene, 298 K) (μ_{exp}) and those calculated in terms of the semiempirical AM1 approximation for its three most stable conformers (μ_{theor}) are presented in Table 1. The large difference between the μ_{theor} values found for the conformers of **1** permits fairly unambiguous interpretation of the experimental results. The *sp,ac* form is the preferred conformation of molecule **1** in the gas phase.



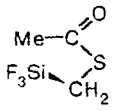
sp,ac



sp,sp



ap,ap



ap,sc

The aprotic solvent mostly stabilizes the form characterized by the largest μ_{exp} value, *i.e.*, the *sp,sp* conformer. The larger disagreement with the experimental results for the third rotational isomer is due most likely to the difference between the geometries of the free and solvated molecules.

The value μ_{theor} = 4.18 D is matched by an equilibrium O→Si distance of 2.44 Å. On going to the non-equilibrium (within the framework of the approximation used) structure of the *sp,sp* conformer of **1** with a shorter O→Si distance, the μ value increases. For example, μ_{theor} = 4.9 D corresponds to $l_{O\rightarrow Si}$ = 2.2 Å. The dipole moments for the two most stable conformers of **1** were also calculated by the vector-additivity procedure and in the CNDO/S approximation. This was done using the geometric parameters found in terms of the AM1 method. The μ_{theor} values thus found were in good agreement with the experimental results; the best agreement was attained by using the vector-additivity scheme (see Table 1).

Table 1. Dipole moments and relative heats of formation of the isomers of **1**

Conformer	Δ(Δ$_f H°$) /kcal mol^{-1}	μ/D			
		AM1	CNDO/S	Vector scheme	Experiment (medium)
sp,ac	0	2.4	2.9	2.0	2.70 (gas)
sp,sp	0.5	4.2	5.0	4.7	4.68 (benzene)
ap,ap	5.5	3.6	—	—	—

Empirical analysis of PES was carried out by two methods. The first of them is based on the correlation between the ionization energies of π- and σ-type molecular orbitals (MO). The second method is based on a comparison of the relative intensities and energies of the bands caused by ionization of the levels in the CH_2SiF_3 moiety.

In the region of energies lower than 10.5 eV, the PES of derivative **1** exhibits only one intense band (Fig. 1, spectrum *1*). However, this raises the suggestion that this band could be a superimposition of two neighboring bands. In fact, the low-energy region of the PES of related compounds, esters of acetic acid, exhibit two bands, which are normally well-resolved and correspond to the n_O(C=O) and the π_O(OCO) molecular orbitals. In carboxylic acid esters, the n_O MO is always the highest occupied orbital. However, in the series of formamides and acetamides, the order of arrangement of the highest occupied MO of the π- and σ-types varies ($n_O < \pi_N$, $n_O > \pi_N$); compounds with a quasi-degenerate set of frontier orbitals can also be found.[6–9]

The low-energy regions in the PES of organosilicon *S*-esters of thioacetic acid $MeC(O)SCH_2SiMeF_2$ and $MeC(O)SCH_2SiMeCl_2$ (Fig. 2) also contain two bands, the first of which has a lower relative intensity. The same profile is characteristic of the first group of bands

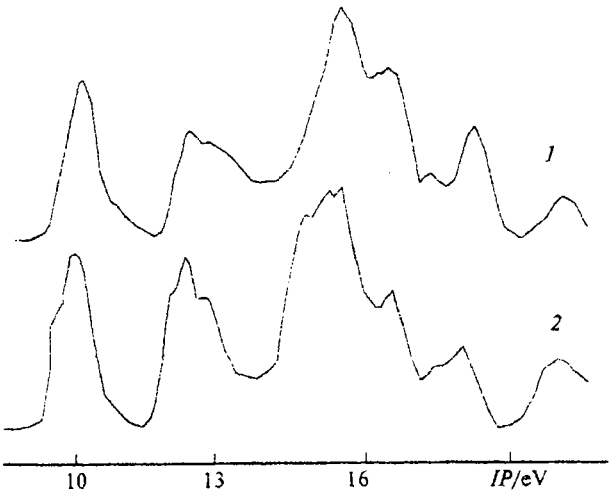


Fig. 1. PES of (acetylthiomethyl)trifluorosilane (*1*) and (benzoylthiomethyl)trifluorosilane (*2*).

in the PES of compound **2** (see Fig. 1, spectrum *2*). Since the π-system of organosilicon thioacetates contains an atomic group, whose ionization potential is at least not larger than that of the carbonyl O atom, it can be assumed that the first band in their PES corresponds to the π_S MO (it is assumed to contain the major contribution of the p_z AO of the S atom). To confirm this assumption, we used the following fact. The position of the π_X MO energy level in phthalic anhydride and its heavier chalcogen analogs varies in parallel with the known position of the n_X MO in model nonconjugated systems, namely, saturated five-membered heterocyclic compounds $CH_2CH_2CH_2XCH_2$.[10] Thus, the corresponding alcohols, ethers, or sulfides can be taken as model nonconjugated compounds for acyclic aliphatic acids and their derivatives (Table 2). Processing of the experimental data listed in Table 2 led to the following correlation:

$$IP(\pi_X) = (1.239\pm0.041)IP(n_X) - (1.045\pm0.041), \quad (1)$$
$$n = 12,\ r = 0.988,\ s = 0.096.$$

The sulfur compound fits this correlation.

Thus, the lowest-energy band in the PES of the thiocarboxylates in question is due to the ionization of the π_S energy level. The next band is associated with the MO of the nonbonding electron pair of the carbonyl O atom. Its energy position differs only slightly from that of the amide band (Table 3). In the PES of compound **1**, these two bands overlap. Therefore, in the series of halo-containing esters of thioacetic acid, the SiF_3 group exerts a more substantial effect on the π_S MO than on the σ MO. This behavior can be explained by different sensitivities of π and σ MOs to the field effect of the SiF_3 group.

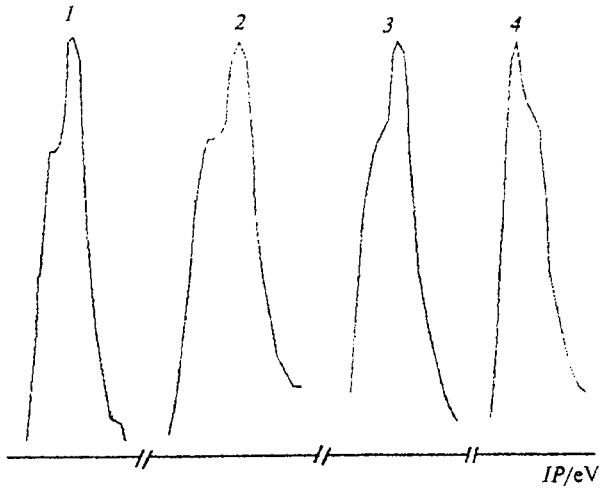


Fig. 2. PES of $MeC(O)SCH_2X$ (X = $(CH_2)_2Me$ (*1*), Cl_2SiMe (*2*), F_2SiMe (*3*), OMe (*4*)) in the energy region of <10.5 eV. The ionization potentials are given in Table 3.

Table 2. Vertical ionization potentials (*IP*) of carboxylic acids, their derivatives, and "nonconjugated" analogs[a]

Compound	$IP(\pi_X)^b$ /eV	Compound	$IP(n_X)^b$ /eV
HC(O)OH	12.51	MeOH	10.95[c]
$H_2NCH_2C(O)OH$	12.20	$H_2NCH_2CH_2OH$	10.71
$MeC(O)OH$	12.07[c]	$MeCH_2OH$	10.64
$MeCH_2C(O)OH$	12.04	$MeCH_2CH_2OH$	10.50[c]
$HC(O)OMe$	11.54[c]	MeOMe	10.04
$H_2NCH_2C(O)OMe$	11.20	$H_2NCH_2CH_2OMe$	10.00
$MeC(O)OMe$	11.16	$MeCH_2OMe$	9.86
$HC(O)OCH_2Me$	11.28	$MeOCH_2Me$	9.86
$CH_2CH_2CH_2OC(O)$	10.94	$CH_2CH_2CH_2OCH_2$	9.70[c]
$MeC(O)OCH_2Me$	10.99	$MeCH_2OCH_2Me$	9.61
$CH_2CH_2CH_2CH_2OC(O)$	10.63	$CH_2CH_2CH_2CH_2OCH_2$	9.50[c]
$MeC(O)S(CH_2)_3Me$	9.23	$MeCH_2S(CH_2)_3Me$	8.31[d]

[a] The PES were taken from published data.[6–13] [b] π_O or π_S, n_O or n_S. [c] The average value. [d] This work.

Table 3. Vertical ionization potentials (*IP*) of the highest occupied MOs (a′, a″) of acetates, thioacetates, and acetamides MeC(O)X

X	*IP*/eV	
	a″(π_X)	a′(n_O)
$S(CH_2)_3Me$ [a] (**1**)	9.23	9.55
SCH_2SiCl_2Me [a] (**2**)	9.41	9.81
SCH_2SiF_2Me [a] (**3**)	9.55	9.88
SCH_2OMe [a] (**4**)	9.75	9.75
		10.13[c]
SCH_2SiF_3 [a] (**5**)	10.03	10.03
NH_2 [b] (**6**)	10.32	9.96
	10.40[b]	10.0
NHMe (**7**)	9.68	9.85
	9.70[a]	9.70
NMe_2 [b] (**8**)	9.09	9.43
OH [b] (**9**)	12.05	10.87
OMe [b] (**10**)	11.16	10.48
OCH_2Me [b] (**11**)	10.99	10.39
$OCHMe_2$ [b] (**12**)	10.77	10.38
$OSiMe_3$ [a] (**13**)	10.67	10.27
OCH_2CF_3 [b] (**14**)	11.79	11.15

[a] This work. [b] The PES were taken from published data.[6,9]

The influence of the long-range inductive effect (field effect) on the energy of nonbonding electrons of the carbonyl O atom in the series of acetic acid derivatives can be estimated by analyzing relation (**1**). For compounds containing no halogen atom in the side chain, a linear correlation between the positions of π_X and n_O levels was found to hold over a fairly broad energy range (Fig. 3). The points corresponding to the fluorine-containing esters of acetic and thioacetic acids deviate from the line of regression toward larger $IP(n_O)$ values. This points to an additional stabilization of the n_O MOs in these compounds. The largest deviation was observed in the presence of the CF_3 group, whereas the smallest deviation is caused by the SiF_3 group. In general, the

Table 4. Characteristics of the field effect of atomic group in esters of acetic and thioacetic acids

Compound	Atomic group	μ_{MeR}/D	$\Delta IP(n_O)^a$/eV
$MeC(O)OCH_2CF_3$	CH_2CF_3	2.32[b]	0.40
$MeC(O)SCH_2SiF_2Me$	CH_2SiF_2Me	2.30[c]	0.20
$MeC(O)SCH_2SiF_3$	CH_2SiF_3	2.10[c]	0.15

[a] See the text. [b] From the Stark effect.[14] [c] From the following bond moments: SiF (3.3 D), SiC (1.2 D). The initial data were taken from a handbook.[14]

Table 5. Vertical ionization potentials (*IP*) of the MO[a] of the CH_2SiF_3 group

Compound	*IP*$_i$/eV				
	$1a_2$	3e	2e	$3a_1$	1e
CH_3SiF_3 [b]	15.55	16.25	16.84	17.53	18.30
$MeC(O)SCH_2SiF_3$	15.55	16.30 sh	16.57	17.40	18.28
$PhC(O)SCH_2SiF_3$	15.55	16.20 sh	16.63	17.40 sh	18.20

[a] The molecular orbitals of CH_3SiF_3. [b] The PES was taken from published data.[15]

additional stabilization of the n_O level is proportional to the μ values of the atomic groups (R) estimated either from the dipole moment of the molecule MeR or from the bond moments (Table 4).

The CH_2SiF_3 group in the *sp,ac* conformer of **1** should not differ markedly in its geometry and in the energies of its n_F and σ_{SiF} MOs from that incorporated in a molecule of trifluoromethylsilane $MeSiF_3$ (**3**), whose photoelectron spectrum has been studied previously.[14] Comparison of the profile of the PE bands located in the 15—19 eV range in the spectra of compounds **1**—**3**

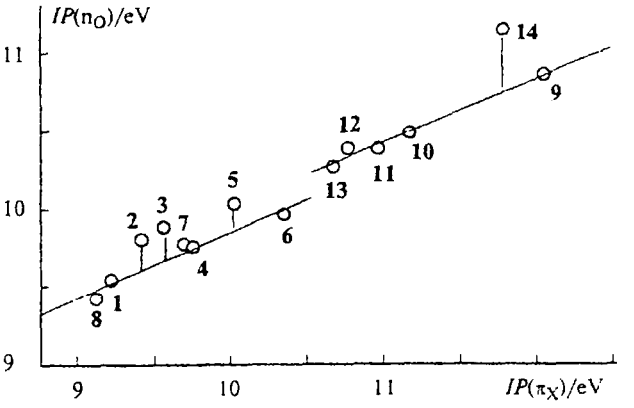


Fig. 3. The relationship of the ionization potentials of the π_X- and n_O-MO in acetic acid derivatives (**1**—**14**, see Table 3).

confirms this assumption (see Fig. 1; for the spectrum of the derivative, see Ref. 15). In fact, their relative intensities and the positions on the energy scale almost coincide (Table 5).

Empirical analysis of the PES of compound **1** permits some conclusions to be drawn. In rotamers of compounds of type **1** that contain no O→Si coordination bonds the MO of the nonbonding electron pair of the carbonyl O atom is stabilized by the field effect of the distant halo-containing group. For esters of thioacetic acid with a fluorinated substituent, this stabilization is proportional to the group moment. If the ionization potentials for the levels of the CH_2SiF_3 group in mol-

Table 6. Experimental and calculated ionization potentials (*IP*) of fluorine-containing derivatives of acrtic and benzoic acids

MO	Type of orbital[a]	*sp,ac*-Conformer			*sp,sp*-Conformer	
		IP/eV		Configurations	*IP*/eV,	Configurations
		PES	AM1		AM1	
				$MeC(O)SCH_2SiF_3$		
a″	π_S	10.03	9.24	$0.99\varphi_m$	9.44	$0.99\varphi_m$
a′	$\sigma_{OSC(n_O)}$	10.03	10.16	$0.92\varphi_{m-1}$	10.55	$0.87\varphi_{m-1}$; $0.31\varphi_{m-2}$
a′	σ_{CS}	12.58	12.74	$0.87\varphi_{m-2}$ [b]	11.90	$0.84\varphi_{m-2}$; $0.40\varphi_{m-1}$
a′	σ_{CS}	18.03	13.14	$0.59\varphi_{m-3}$; $0.58\varphi_{m-4}$	14.03	$0.35\varphi_{m-3}$; $0.59\varphi_{m-4}$; $0.39\varphi_{m-5}$
a′	σ_{CSi}	13.30 sh	13.24	$0.48\varphi_{m-4}$; $0.60\varphi_{m-3}$	14.16	$0.83\varphi_{m-3}$; $0.44\varphi_{m-5}$
				$PhC(O)SCH_2SiF_3$		
a″	π_S	9.50	9.00	$0.91\varphi_m$; $0.35\varphi_{m-2}$	9.16	$0.92\varphi_m$; $0.32\varphi_{m-2}$
a″	$\pi_{Ph(a_2)}$	9.90	9.91	$0.95\varphi_{m-1}$	10.00	$0.89\varphi_{m-1}$; $0.39\varphi_{m-2}$
a″	$\pi_{Ph(b_1)}$	9.90	9.98	$0.88\varphi_{m-2}$; $0.35\varphi_m$	10.13	$0.82\varphi_{m-2}$; $0.40\varphi_{m-1}$
a′	$\sigma_{OSC(n_O)}$	9.90	10.22	$0.87\varphi_{m-3}$	10.57	$0.91\varphi_{m-3}$; $0.33\varphi_{m-5}$
a′	σ_{Ph}	12.00 sh	12.16	$0.89\varphi_{m-4}$ [b]	11.82	$0.87\varphi_{m-5}$; $0.39\varphi_{m-3}$
a′	σ_{CS}	12.38	12.17	$0.60\varphi_{m-5}$ [b]	12.37	$0.95\varphi_{m-4}$
a′	σ_{CS}	12.60				
a′	σ_{Ph}	12.60				
a″	π_S	13.10 sh				
Other		13.30 sh; 14.80; 15.30				

[a] Classification in terms of symmetry (C_s) for the planar conformer. [b] Mixed with non-Koopmans configurations.

Table 7. Orbital energies (ε_i) and two-centered constituents of the energy (E/eV) of the O→Si interaction in the *sp,ac* conformer of silicon-containing *S*-esters of thioacetic acid

Compound	$-\varepsilon_i(n_O)$	$-E_E^{OSi}$	$-E_R^{OSi}$
$MeC(O)SCH_2SiH_3$	10.37	0.679	0.001
$MeC(O)SCH_2SiH_2F$	10.46	1.066	0.0
$MeC(O)SCH_2SiHF_2$	10.64	1.370	0.0
$MeC(O)SCH_2SiF_3$	10.79	1.643	0.001

Note. E_E^{OSi} is the electrostatic constituent; E_R^{OSi} is the resonance constituent.

ecules like **1** prove to be close to the values known for $MeSiF_3$, this can serve as an indication of the absence of the O→Si coordination bond.

Theoretical analysis of the ionic states and MO of (acetylthiomethyl)- and (benzoylthiomethyl)trifluorosilanes. The ionization potentials of these compounds were assigned based on the results of semiempirical AM1 calculations of the energies of the Koopmans states in the radical cations. From the data listed in Table 6, it follows that the calculated energies of the ionic states are in satisfactory agreement with the experimental values only in the case of the *sp,ac* conformer of derivatives **1** and **2**. For this conformer, the order of the MOs coincides with the order of the ionic states; in addition, the MO of the nonbonding electron pair of the carbonyl O atom corresponds to an ionic state not perturbed by configuration interactions.

It should be noted that in terms of the approximation used, the ionization potentials of the π_S MO level both in **1** and in **2** are underestimated by ~0.6 eV. In the *sp,sp* conformer of the thioester, a clear-cut tendency for the ionization potential of the n_O MO level to increase can be followed. It can be seen from the data presented in Table 6 that this finding is opposite to the tendency that would have been expected based on the assumed interaction of the ionized states. Therefore, the question of the mechanism of stabilization of the n_O-MO energy level in the *sp,sp* conformer could be tackled within the framework of the single-configuration (MO) theory.

In this connection, it was necessary to elucidate the role of those interactions that can influence the energy of nonbonding electrons of the carbonyl O atom in the *sp,ac* conformations of compounds related to **1**. This task was accomplished by using the procedure of partitioning the total energy[16] into bond constituents and by comparing them with the orbital energies found for the series of compounds that includes **1**, model acetylthiomethylsilane, and its monofluoro and difluoro derivatives (Table 7).

According to AM1 calculations, the orbital energies of the MO of the nonbonding electron pair of the carbonyl oxygen atom (ε_i) in the *sp,ac* conformers of these compounds are proportional to the total energy of the two-center electrostatic O→Si interaction (E_E^{OSi}) (see Table 7), while the resonance contribution (E_R^{AB}) is equal to zero. The SiF_3 group exerts a more substantial electrostatic effect on the n_O MO than the $SiHF_2$ group, although the latter is more polar [$\mu(H_2SiF_2)$ = 1.52 D, $\mu(HSiF_3)$ = 1.26 D, based on the Stark effect[14]]. Theoretically, this discrepancy could be due to the fact that in the former case, the C—S—C—Si torsion angle is smaller (for $MeC(O)SCH_2SiF_3$, θ_{theor} = 126°, while for $MeC(O)SCH_2SiHF_2$, θ_{theor} = 143°).

However, this explanation does not eliminate the contradiction between the calculated and experimental data (see Table 4) and casts doubt upon the validity of the application of the static model to the *sp,ac* conformers of silicon-containing thioacetates. In fact, according to quantum-chemical analysis, the potential curve for the internal rotation in compound **1** contains a gently sloping well in the region of the θ angles corresponding to the *sp,ac* conformation. At θ = 180°, the barrier is 0.8 kcal mol^{-1}, while that for (acetylthiomethyl)silane is 0.2 kcal mol^{-1}. Probably, in the case of (acetylthiomethyl)trifluorosilane and related compounds, complete agreement between the theoretical data for the *sp,ac* conformations and the experimental results can be achieved only using a dynamic model for rotational isomerism.

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