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Ab initio Calculations of the Geometry, Electronic Structure, and Vibrational Spectrum of (Acetoxymethyl)triflouorosilane

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Abstract — The geometries and electronic structures of various conformers of (acetoxymetyl)trifluorosilane, $CH_3C(O)OCH_2SiF_3$, and also the frequencies and intensities of its vibration bands were studied by *ab initio* [RHF(6-31G*)] calculations. According to the experimental spectra and calculation results, the most stable is the conformation in which the donor–acceptor interaction =O→Si is realized. Analysis of the geometry, atomic charges, and molecular orbital energies shows that this donor–acceptor bond is mainly due to interaction of the lone electron pairs of the carbonyl oxygen atom with the vacant Σδ* orbitals of the C–Si–F_a moiety.

Compounds of the general formula $MeC(O)XCH_2 \cdot SiF_3$ (X = NR, O, S), which are interesting objects for studying the role of the heteroatom X in formation of the O→Si donor–acceptor bond, have been studied poorly [1–4]. Fairly well studied (aroyloxymethyl)-trifluorosilanes contain an intramolecular donor–acceptor bond =O→Si, which is preserved in the gas phase [5–7]. In its formation, the geometry of the silicon surrounding changes substantially: from a tetrahedron to distorted trigonal bipyramid. The nature of this donor–acceptor bond was considered in [5–9] proceeding from the 3c–4e three-center four-electron model assuming that the electronic structures of the equatorial and axial bonds are mutually independent. The =O→Si interaction substantially affects the frequency of the C=O and Si–F_a stretching vibrations in the IR spectra, the ^{13}C and ^{19}F NMR chemical shifts, and the dipole moments (the degree of charge transfer is 0.1–0.2 e) [5]. Frolov *et al*. [6] analyzed by *ab initio* calculations how the geometry and energy of the (benzoyloxymethyl)trifluorosilane molecule are affected by formation of the =O→Si donor–acceptor bond. However, changes in the charge distribution in the nearest surrounding of silicon, nature and energy of the molecular orbitals involved in the interaction, and parameters of the vibrational spectra were not considered. For a simpler representative of this class of compounds, (acetoxymethyl)trifluorosilane, Gubanova [4] analyzed the IR stretching frequencies of the C=O and Si–F bonds and the ^1H, ^{19}F, and ^{29}Si chemical shifts; she revealed the =O→Si donor–acceptor interaction.

The goal of this work was to study the conformational behavior of the (acetoxymethyl)trifluorosilane molecule, $CH_2C(O)–O–CH_2SiF_3$ (**I**), and to reveal the differences between the steric and electronic structures and vibrational spectra of its stable conformers.

To this end, we calculated for this molecle by the RHF(6-31G*) method [10] the surface of the total energy as a function of the angle of rotation around the bonds involving the ester oxygen atom. When constructing the three-dimensional surface relfecting the dependence of the energy on the internal rotation coordinates, we varied the angles of rotation around the $C^2–O^7$ (θ_1) and $O^7–C^8$ (θ_2) bonds at a 10° step from 0° [cisoid (*c*) orientation of the $C^2–O^3$, $O^7–C^8$ and $O^7–C^2$, $C^8–Si^9$ bonds, respectively] to 180° (transoid (*t*) orientation of these bonds] (Fig. 1). The other geometric parameters in each point of the 19×19 surface matrix were optimized. At certain values of θ_1 and θ_2, we revealed on the three-dimensional surface the energy minima corresponding to various conformers (Fig. 2). In this points, we calculated the vibrational spectrum of the conformer with complete optimization of all the geometric parameters. In so doing, the starting geometry was chosen in the vicinity of the corresponding minimum.

The planar conformer (*c*,*c*, $\theta_1 = \theta_2 = 0°$) was found to be the most stable. Its energy was taken as zero. The other planar conformers (*c*,*t*, $\theta_1 = 0°$, $\theta_2 = 180°$; *t*,*t*, $\theta_1 = \theta_2 = 180°$) have higher energies, and the energy of the nonplanar conformer (*t*,*g*, $\theta_1 = 181.7°$, $\theta_2 = 96.2°$) is the highest. The difference between the energies of the *c*,*c* and *c*,*t* conformers and the barrier separating these states are relatively small (2.39 and 4.94 kcal mol^{-1} in the RHF/6-31G* and MP2/6-31G* approximations, respectively). The geometry of the *c*,*c* conformer appreciably differs from that of the other acyclic conformers (Table 2). The $C^2–O^3$, $Si^9–F^{12}$,

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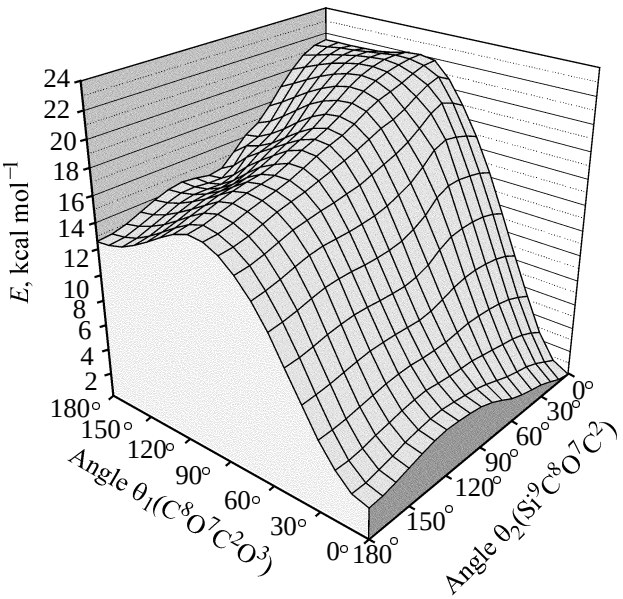

Fig. 1. Energy of the (acetoxymethyl)trifluorosilane molecule as a function of rotation angles θ_1 and θ_2.

and Si^9–C^8 bonds are longer by 0.02–0.03 Å, and the C^2–O^7 bond is shorter by 0.03–0.04 Å. The surrounding of the silicon atom in this conformer is close to trigonal bipyramidal {as in (aroyloxymethyl)trifluorosilanes [6]} and is also favorable for formation of the three-center four-electron bond =O→Si–F according to the 3c–4e hypervalent bonding model [8, 9, 12]. In this distorted trigonal bipyramid, the $F^{13}Si^9F^{14}$ angle is 114° (instead of 120°), and the $F^{12}Si^9F^{14}$ and $C^8Si^9F^{12}$ angles are 101° and 96°, respectively (instead of 90°).

The experimental geometry of the $C(O)OCH_2SiF_3$ fragment in the crystal of (benzoyloxymethyl)trifluorosilane [11] is in reasonable agreement with the calculation results for **I**. Significant shortening of the $Si^9\cdots O^3$ distance as compared to the calculated value (2.006 and 2.217 Å, respectively) is due to the effect of surrounding in the crystal. Similar shortening of the Si···N distance (by ~0.28 Å) in going from the gas phase to the crystal was observed in molecules of 1-substituted silatranes $XSi(OCH_2CH_2)_3N$ at X = Me, F [13, 14].

Table 1. Relative energies (E_{conf}) and rotation barriers (kcal mol^{-1}) for various conformers of (acetoxymethyl)trifluorosilane

Conformer	E_{conf}	Barrier height			
		c,*c*	*c*,*t*	*t*,*t*	*t*,*g*
c,*c*	0.00	–	3.68[a]	16.04[b]	16.04[b]
c,*t*	2.39	1.29[a]	–	13.65[b]	13.65[b]
t,*t*	12.61	3.43[b]	3.43[b]	–	1.64[c]
t,*g*	14.07	1.97[b]	1.97[b]	0.18[c]	–

Note: Barrier coordinates, θ_1, θ_2, deg: [a] 0, 120; [b] 110, 180; [c] 180, 130.

For the calculated conformations of **I**, we analyzed changes in the energy and nature of the highest occupied (E_1–E_5, E_{17}, E_{18}, E_{20}) and lowest unoccupied (E'_1–E'_5) molecular orbitals (Table 3). The heavy atoms are coplanar in all the planar conformations. The hydrogen and fluorine atoms that lie beyond the molecular plane are arranged symmetrically relative to this plane. This allows the σ and π orbitals to be clearly distinguished. In all the conformations, the highest occupied molecular orbital E_1 is mainly localized on the carbonyl (O^3) and ester (O^7) oxygen atoms and is oriented in the symmetry plane of the molecule, *xy* (*n* type). The E_3 orbital is similar to E_1 in the nature but involves also the C–O and C–Si bonds. The E_2 and E_4 π orbitals, antisymmetric relative to the *xy* plane, are mainly localized on the COO group but also involve the group orbitals of the CH_2 and CH_3 fragments of the corresponding symmetry. The E_5 (σ) orbital is mainly localized on the C–C, C–O, and C–Si bonds, and the E_{20}, E_{17}, and E_{18} orbitals, on the Si^9–F^{12} bond. The vacant π* orbitals E'_1 for the *c*,*c* and *c*,*t* conformers and E'_2 for the *tt* conformer are similar in the nature to the π orbitals E_2 and E_4. The lowest unoccupied σ* orbitals E'_2 and E'_3 for the *c*,*c* and *c*,*t* conformers, and E'_1 and E'_3 for the *t*,*t* conformer are localized on the C–Si–F^{12} fragment, and the σ* orbitals E'_4 (for the *c*,*c* and *c*,*t* conformers) and E'_5 also involve the C–O, C–C, and C–H bonds.

In the *c*,*c* conformer, the interaction of the C(O)O and SiF_3 groups results in a noticeable decrease in the energy of occupied molecular orbitals. The π orbital E_2 preserves its nature, and in the *n* orbital E_1 the contributions of the C^8, Si, and F^{12} atomic orbitals increase. Hence, in the *c*,*c* conformation the occupied molecular orbitals corresponding to the lone electron pair of the carbonyl oxygen interact with the vacant σ* orbitals of the CH_2SiF_3 fragment characterized by a large contribution of the C^8, Si, and F^{12} atomic orbitals. Correspondingly, the energy of the occupied molecular orbitals decreases, and that of the unoccupied orbitals increases (Fig. 3a). This means that, in **I**, the *n*,σ* interaction prevails, although the *n*,σ interaction also takes place. In contrast to these results, according to the 3c–4e hypervalent binding model [8, 9], the energy of the highest occupied molecular orbital increases at *n*,σ interaction of the lone electron

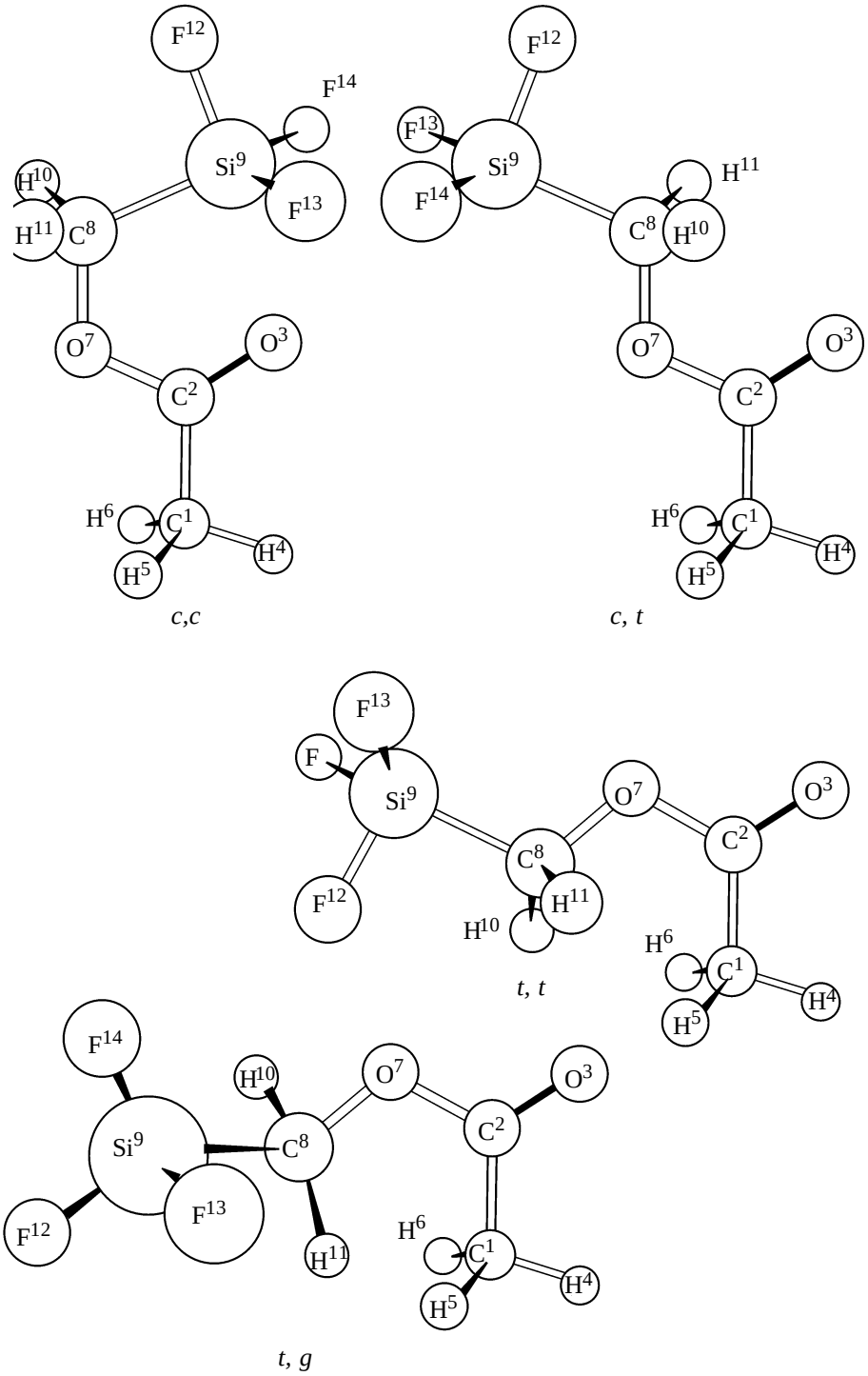

Fig. 2. Stable conformations of the (acetoxymethyl)trifluorosilane molecule.

pair of the carbonyl oxygen with the occupied σ orbital of the SiF^{12} bond (Fig. 3b).

Analysis of the charge distribution on the atoms of **I** allows also estimation of the interaction of the carbonyl and trifluorosilyl groups in the *c,c* conformation as compared to the other conformations (Table 4, *c,c* and *c,t* conformers). The charge on the axial F^{12} atom is noticeably higher (by 0.03 e) than that on the F^{13} and F^{14} atoms and on fluorine atoms in the other conformations. A similar increase in the negative charge on the C^8 (by 0.03 e) and carbonyl oxygen

Table 2. Calculated and experimental bond lengths (Å) and bond angles (deg) in the (acetoxymethyl)trifluorosilane molecule

Bond	Length					Angle	Angle value				
	s,s	*s,t*	*t,t*	*t,g*	experiment		*s,s*	*s,t*	*t,t*	*t,g*	experiment[a]
C^1–C^2	1.495	1.502	1.510	1.511	1.460(15)	$C^1C^2O^3$	124.5	126.0	123.3	123.0	123.9(9)
C^2–O^3	1.204	1.185	1.180	1.181	1.243(14)	$C^1C^2O^7$	114.3	111.3	117.9	118.6	116.9(0)
C^2–O^7	1.304	1.336	1.345	1.343	1.311(13)	$O^3C^2O^7$	121.2	122.8	118.8	118.5	119.8(9)
O^3–Si^9	2.217	4.456	4.784	4.521	2.006(8)	$O^3Si^9C^8$	76.7	9.3	37.1	46.1	81.2(4)
O^3–F^{12}	3.809	5.382	5.076	5.927	–	$O^3Si^9F^{12}$	173.0	118.3	91.6	149.2	176.3(4)
O^3–F^{13}	2.549	5.142	6.140	4.354	–	$O^3Si^9F^{13}$	82.6	107.1	145.1	73.9	84.9(4)
O^3–F^{14}	2.549	5.142	5.076	5.030	–	$O^3Si^9F^{14}$	82.6	107.1	91.6	99.8	85.4(4)
O^7–C^8	1.432	1.421	1.412	1.417	1.468(13)	$O^7C^8Si^9$	115.9	107.0	106.7	110.9	112.8(8)
C^8–Si^9	1.888	1.864	1.869	1.871	1.855(13)	$C^8O^7C^2$	115.6	116.9	123.1	124.6	112.9(8)
Si^9–F^{12}	1.598	1.572	1.567	1.572	1.610(7)	$C^8Si^9F^{12}$	96.3	109.0	111.9	109.2	95.1(5)
Si^9–F^{13}	1.576	1.569	1.573	1.571	1.577(9)	$C^8Si^9F^{13}$	119.0	111.9	107.9	110.6	122.6(5)
Si^9–F^{14}	1.576	1.569	1.567	1.567	1.580(9)	$C^8Si^9F^{14}$	119.0	111.9	111.9	112.4	121.3(5)
						$F^{12}Si^9F^{13}$	101.1	108.0	108.0	108.2	96.4(4)
						$F^{12}Si^9F^{14}$	101.1	108.0	108.8	108.1	97.4(4)
						$F^{13}Si^9F^{14}$	114.1	108.0	108.0	108.3	112.5(4)

[a] For the $PhC(O)OCH_2SiF_3$ molecule in a crystal [11].

Table 3. Energies of the occupied and unoccupied molecular orbitals (E_i, eV) in planar conformers of (acetoxymethyl)trifluorosilane[a]

E_i	*c,c*	*c,t*	*t,t*
E_{20}	–22.34 (σ)	–22.41 (σ)[b]	–22.55 (σ)[b]
E_{18}	–20.40 (σ)	–20.40 (σ)	–20.44 (σ)
E_5	–16.03 (σ)	–15.37 (σ)	–15.55 (σ)
E_4	–15.42 (π)	–14.75 (π)	–15.35 (π)
E_3	–14.06 (*n*)	–13.94 (*n*)	–14.08 (*n*)
E_2	–13.53 (π)	–13.06 (π)	–12.73 (π)
E_1	–13.13 (*n*)	–12.45 (*n*)	–12.18 (*n*)
E'_1	4.13 (π^*)	4.91 (π^*)	4.68 (σ^*)
E'_2	5.60 (σ^*)	5.07 (σ^*)	4.93 (π^*)
E'_3	6.16 (σ^*)	5.10 (σ^*)	4.98 (σ^*)
E'_4	6.42 (σ^*)	5.80 (σ^*)	5.64 (π^*)
E'_5	6.91 (σ^*)	6.30 (σ^*)	5.76 (σ^*)

[a] The type of the molecular orbital is given in parentheses.
[b] For the *c,t* and *t,t* conformers, E_{17}.

Table 4. Total charges (*q*, au) on atoms in various conformers of (acetoxymethyl)trifluorosilane

Atom	*c,c*	*c,t*	*t,t*	*t,g*
C^1	–0.573	–0.567	–0.621	–0.636
C^2	0.800	0.760	0.778	0.777
O^3	–0.625	–0.558	–0.513	–0.516
H^4	0.226	0.212	0.233	0.234
H^5	0.219	0.207	0.198	0.206
H^6	0.219	0.207	0.198	0.198
O^7	–0.580	–0.619	–0.614	–0.613
C^8	–0.335	–0.303	–0.299	–0.308
Si^9	1.665	1.644	1.661	1.644
H^{10}	0.219	0.216	0.197	0.228
H^{11}	0.219	0.216	0.197	0.200
F^{12}	–0.504	–0.477	–0.468	–0.473
F^{13}	–0.475	–0.473	–0.478	–0.478
F^{14}	–0.475	–0.473	–0.468	–0.465

(by 0.07 e) atoms is accompanied by an increase in the positive charge on the C^2 (by 0.04 e) and Si (by 0.02 e) atoms and by a decrease in the negative charge on O^7 (by 0.04 e). This pattern of charge variation is not fully consistent with the 3c–4e model, since this model suggests transfer of the electron density from the carbonyl oxygen atom to the axial fluorine atom (F^{12}) [8, 9]. Apparently, the calculated charge redistribution is due, to a greater extent, to the n,σ^* interaction. In this case, the occupied orbitals correspond to the lone electron pairs of the ester and carbonyl oxygen atoms, and the unoccupied orbitals are mainly localized on the C^8–Si and Si–F^{12} σ bonds. A certain effect on the electron density distribution is also exerted by interaction of the positively charged silicon atom and negatively charged carbonyl oxygen, and

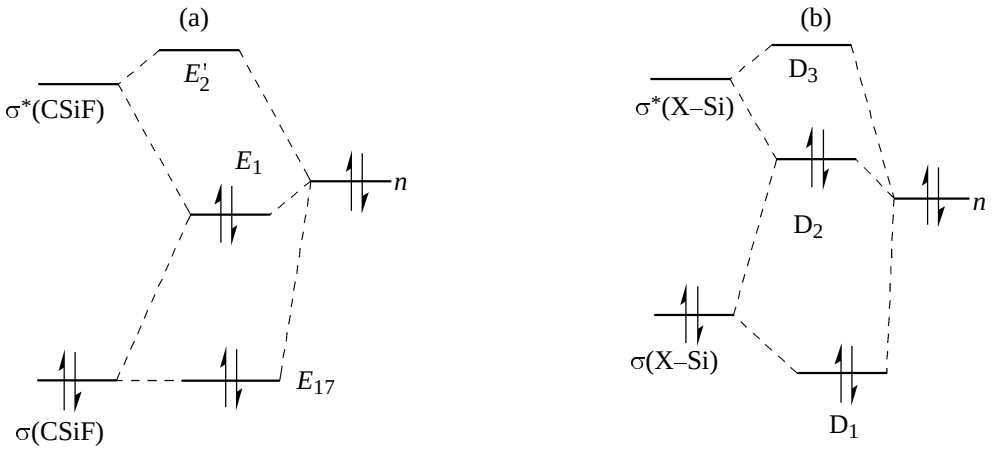

Fig. 3. Molecular orbital diagrams characteriziing energy changes in formation of the O→Si donor–acceptor bond in the *c,c* conformation: (a) our data and (b) data for the 3c–4e model [8].

also by the dipole–dipole interaction of the C–O, C=O, Si–F, and Si–C bonds. Thus, in formation of the O→Si donor–acceptor bond, changes in the C^8–Si and $Si–F^{12}$ bond lengths, charges on these atoms, energies of the occupied and unoccupied orbitals, and nature of these orbitals are mainly due to *n*,σ* interaction of the *n*-type molecular orbitals corresponding to the lone electron pairs of the carbonyl and ester oxygens with the unoccupied σ* orbitals of the $C–Si–F^{12}$ fragment. A noticeable difference between the state of the $Si–F_a$ and $Si–F_e$ bonds and the redistribution of the electron density on the Si and F atoms upon formation of the O→Si donor–acceptor bond in the compounds $4\text{-}XC_6H_4COOCH_2SiF_3$ are confirmed by their low-temperature ^{29}Si and ^{19}F NMR spectra. For example, the chemical shifts $\delta(^{19}F_a)$ –126.74 and $\delta(^{19}F_e)$ –140.94 ppm (X = OMe) appreciably differ, with the chemical shift of the equatorial fluorine atom being close to $\delta(^{19}F)$ –143.99 ppm in the spectrum of the model compound $ClCH_2SiF_3$ [15].

For each conformation of **I**, we calculated the parameters of the vibrational spectra (Table 5). As already shown, the *c,c* conformer is the most stable,

Table 5. Experimental and calculated (for different conformers) frequencies (ν, cm^{-1}) and integral intensities (*I*, km mol^{-1})[a] of bands in the IR spectra of (acetoxymethyl)trifluorosilane[b]

ν $(I)_{c,c}$	ν $(I)_{c,t}$	ν $(I)_{t,t}$	ν $(I)_{t,g}$	ν $(I)_{exp}$	Assignment[c]
47 (0.3)	33 (2)	27 (4)	30 (4)		$\tau(CH_3)$
62 (0.2)	40 (2)	42 (3)	50 (3)		$\tau(CH_3)$, $\tau(SiF_3)$, $\rho(CH_2)$
101 (41)	78 (3)	78 (3)	68 (5)		$\nu(SiO^3)$, $\delta(O^7C^8Si)$, $\delta(C^2O^7C^8)$
108 (0.1)	89 (0.1)	107 (2)	133 (2)		$\tau(SiF_3)$, $\tau(CH_3)$, $\tau(CH_2)$
172 (11)	152 (7)	159 (0.1)	166 (0.2)		$\rho(SiF_3)$
191 (5)	200 (2)	203 (0.2)	204 (0.2)		$\rho(CH_2)$, $\rho(CH_3)$
257 (4)	211 (1)	207 (8)	236 (2)		$\rho(CH_2)$, $\rho(SiF^{13}F^{14})$
280 (7)	216 (2)	219 (0.2)	298 (19)		$\delta(C^1C^2O^3)$, $\delta(C^1C^2O^7)$, $\delta(SiF_3)$
320 (58)	306 (23)	308 (24)	311 (23)		$\delta(F^{13}SiF^{14})$
326 (16)	313 (31)	321 (28)	331 (16)		$\rho(CH_2)$, $\delta_{as}(SiF_3)$
384 (74)	396 (145)	392 (102)	396 (125)	427 (90)	$\delta(C^1C^2O^3)$, $\delta(C^1C^2O^7)$, $\delta_s(SiF_3)$
505 (25)	417 (7)	472 (28)	454 (1)	539 (47)	$\nu(SiO^3)$, $\delta_s(SiF_3)$, $\delta(C^1C^2O^3)$, $\delta(O^3C^2O^7)$, $\delta(SiC^8O^7)$
605 (14)	592 (17)	556 (29)	561 (11)	625 (26)	$\gamma(C^1C^2O^3O^7)$
633 (41)	604 (15)	565 (16)	567 (20)	670 (74)	$\nu(C^8Si)$, $\delta(O_3C_2O_7)$

Table 5. (Contd.)

ν $(I)_{c,c}$	ν $(I)_{c,t}$	ν $(I)_{t,t}$	ν $(I)_{t,g}$	ν $(I)_{exp}$	Assignment[c]
667 (18)	695 (0.6)	693 (1)	657 (2)	698 (64)	$\nu(C^1C^2)$, $\delta(SiC^8O^7)$
736 (0.3)	775 (0.1)	790 (0.01)	749 (17)		$\rho(CH_2)$
813 (306)	853 (151)	789 (9)	788 (4)	789 (379)	$\nu(SiF^{12})$, $\nu(C^8Si)$, $\nu(C^8O^7)$
866 (118)	893 (35)	852 (275)	848 (1)	866 (186)	$\nu_{as}(SiF_3)$, $\nu(C^8Si)$, $\nu(O^7C^8)$, $\delta(CH_3)$
910 (12)	949 (165)	952 (198)	948 (193)	894 v.	$\nu(C^8Si)$, $\nu(C^8O^7)$, $\nu(C^2O^7)$
964 (217)	961 (217)	970 (217)	964 (233)	943 (186)	$\nu_{as}(SiF^{13}F^{14})$, $\rho(CH_2)$
984 (5)	976 (37)	1005 (40)	999 (27)	1005 (73)	$\rho(CH_3)$, $\nu(C^2O^7)$, $\nu(O^7C^8)$, $\nu(C^1C^2)$
1060 (15)	1056 (10)	1048 (11)	1050 (13)		$\rho(CH_3)$
1065 (80)	1074 (57)	1100 (68)	1093 (60)	1042 (172)	$\nu(O^7C^8)$, $\nu(C^2O^7)$, $\gamma(CH_3)$
1218 (13)	1216 (12)	1218 (14)	1204 (134)	1217 (68)	$\tau(CH_2)$
1271 (170)	1260 (431)	1247 (467)	1287 (275)	1250 (181)	$\nu(C^2O^7)$, $\nu(O^7C^8)$, $\omega(CH_2)$
1357 (101)	1327 (27)	1328 (4)	1324 (45)	1350 (171)	$\nu(C^2O^7)$, $\delta_s(CH_3)$, $\omega(CH_2)$
1413 (146)	1397 (86)	1394 (60)	1395 (80)	1386 (154)	$\delta_s(CH_3)$, $\delta(CH_2)$
1435 (28)	1440 (12)	1440 (7)	1440 (8)	1429 (93)	$\delta_{as}(CH_3)$, $\delta(CH_3)$
1443 (8)	1446 (7)	1457 (13)	1460 (12)	—	$\delta_{as}(CH_3)$
1460 (84)	1454 (10)	1459 (9)	1462 (5)	1458 (93)	$\delta(CH_2)$
1733 (357)	1812 (323)	1836 (450)	1831 (464)	1653 (291)	$\nu(C^2O^3)$, $\nu(C^1C^2)$
				(1658)[d]	$\delta(O^3C^2O^7)$, $\delta(C^1C^2O^7)$
2890 (1)	2886 (3)	2870 (10)	2883 (2)		$\nu_s(CH_3)$
2909 (14)	2894 (11)	2885 (11)	2903 (16)		$\nu_s(CH_2)$
2950 (3)	2937 (9)	2913 (15)	2943 (8)		$\nu_{as}(CH_3)$
2953 (9)	2945 (8)	2939 (16)	2944 (11)	2951 v.w	$\nu_{as}(CH_2)$
2993 (4)	2986 (10)	2990 (7)	2991 (6)	3005 v.w	$\nu_{as}(CH_3)$

[a] The integral intensity of the C=O stretching band was determined in a $CHCl_3$ solution (the spectrum was recorded on an IFS-25 spectrometer). The relative intensities of the other bands were determined similarly [15]. [b] Compound **I** prepared by us was 97.8% pure (GLC). Its constants, however, significantly differed from the published values: bp 147–148°C (726 mm) {132–133°C (730 mm) [4]}; n_D^{20} 1.3634 (1.3599 [4]). [c] The assignment was made for the *c,c* conformer; ν_s and ν_{as} are, respectively, the symmetric and antisymmetric stretching vibrations; δ_s and δ_{as}, symmetric and antisymmetric bending vibrations; ω, wagging, τ, torsion, ρ, rocking, and γ, out-of-plane bending vibrations; w, weak band. [d] In $CHCl_3$ solution.

with the energy of the *c,t* conformer being close. The experimental frequencies and intensities are better consistent with the characteristics of the *c,c* conformer. The differences between the spectra of these two conformers were the most significant for the bands originating from the C–O, Si–F, and C=O vibrations. The calculated and experimentally observed strong bands at 813 and 798 cm^{-1}, respectively, are mainly due to the $Si–F^{12}$ stretching vibrations, as suggested previously for (benzoyloxymethyl)trifluorosilane [16]. The intensity of the band in the range 1250–1270 cm^{-1}, originating from the stretching vibrations of the $Cu^2–O^7$ and $O^7–C^8$ bonds, is higher by a factor of 2.5 in the *c,t* and *t,t* conformers as compared to the *c,c* conformer and is close to the calculated (320–430) and experimental (356) values for the similar band in the spectrum of methyl acetate [17]. However, in the spectrum of the *c,c* conformer, the band at 1350 cm^{-1}, largely originating from the $C^2–O^7$ stretching vibrations and absent in the spectrum of methyl acetate, grows in intensity by a factor of 2.7. The experimental intensity ratio of these two bands is close to that calculated for the *c,c* conformer. In the vibrational spectrum of the *c,c* conformer, the calculated and experimental frequencies of the C=O stretching vibrations (1733 and 1653 cm^{-1}, respectively) are appreciably lower than the value calculated for the other conformers (~1820 cm^{-1}) and the experimental values for saturated esters (1740–1760 cm^{-1}) [18, 19]. Since the calculation is performed for the gas phase and the experimental values refer to the liquid phase, the low experimental value (1653 cm^{-1}) may be due to shortening of the =O···Si distance and hence to a decrease in the C=O stretching frequency in the liquid

phase, as compared to the gas phase. A similar trend (the frequency increased by 60 cm^{-1}) was observed with (4-fluorobenzoyloxymethyl)trifluorosilane in going from the solid to the gas phase [20]. The experimental intensities of the C=O stretching vibrations in the spectra of methyl acetate and the compound under consideration virtually coincide (281 [17] and 291 km mol^{-1}, respectively). The calculated value for the carbonyl group in (acetoxymethyl)trifluorosilane (257 km mol^{-1}) is somewhat higher than that for methyl acetate (236–312 km mol^{-1}) [21].

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