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(AROYLOXYMETHYL)TRIFLUOROSILANES: A NEW CLASS OF PENTACOORDINATE SILICON COMPOUNDS *

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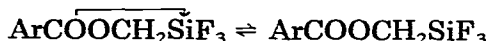
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Summary

A new class of organosilicon compounds containing a pentacoordinate silicon atom, (aroyloxymethyl)trifluorosilanes (AFS), has been prepared. The presence of an intramolecular coordinate $F_3Si \leftarrow O=C$ bond is supported by X-ray diffraction, IR spectroscopy and dipole moment data. $Si \leftarrow O$ coordination in AFS has been shown to remain intact in the gaseous and liquid states below 420 K as well as in solution in most organic solvents. The dielectric constant of the medium significantly affects the nature of the coordinate $Si \leftarrow O$ bond and that of the $Si-F$, $C=O$, $C-O-C$ bonds. In pyridine the intramolecular coordinate $Si \leftarrow O$ interaction is disturbed or greatly weakened.

At 420–500 K a reversible reaction takes place:



The changes in enthalpy and entropy are equal in this case:

$$-\Delta H = 8.1 \pm 0.7 \text{ kcal/mol}; -\Delta S = 15.3 \pm 0.8 \text{ e.u. } T = 450 \text{ K}$$

An assignment of bands in the IR spectra of AFS resulting from vibrations of atoms in the SiF_3 , $>C=O$ and $C-O-C$ groups is given. The electron impact-induced primary disintegration of the molecular ion $4\text{-XC}_6\text{H}_4\text{COOCH}_2\text{SiF}_3^+$ mainly involves abstraction of a fluorine atom.

Introduction

Silatrane remain until now the only systematically and comprehensively studied class of organosilicon derivatives containing a pentacoordinate silicon

* Dedicated to Prof. G.A. Razuvaev on the occasion of his 85th birthday on August 23rd, 1980.

TABLE 1
(AROXYLOXYMETHYL)TRIFLUOROSILANES $\text{XC}_6\text{H}_4\text{COOCH}_2\text{SiF}_3$

X	Yield (%)	M.p. (°C)	Found (Calcd. (%))				Empirical formula
			C	H	F	Si	
I H	95.2(2)	82–84	43.62 (43.63)	3.46 (3.20)	25.52 (25.88)	12.56 (12.75)	$\text{C}_8\text{H}_7\text{O}_2\text{SiF}_3$
II 4- CH_3	97.6(2)	90–91	47.12 (47.30)	3.65 (3.87)	24.40 (24.33)	12.01 (11.98)	$\text{C}_9\text{H}_9\text{O}_2\text{SiF}_3$
III 4-F	98(2)	102–104	40.46 (40.33)	2.61 (2.52)	31.93 (31.90)	11.13 (11.79)	$\text{C}_8\text{H}_6\text{O}_2\text{SiF}_4$
IV 4-Cl	94.5(2)	112–114	37.72 (37.37)	2.43 (2.37)	21.93 (22.38)	11.11 (11.02)	$\text{C}_8\text{H}_6\text{O}_2\text{SiF}_3\text{Cl}$
V 4-Br	98.5(2)	103	32.22 (32.12)	1.91 (2.02)	18.84 (19.05)	9.39 (9.38)	$\text{C}_8\text{H}_6\text{O}_2\text{SiF}_3\text{Br}$
VI 4- CH_3O	98(2)	148	43.45 (43.20)	3.54 (3.94)	22.55 (22.80)	11.12 (11.20)	$\text{C}_9\text{H}_9\text{O}_3\text{SiF}_3$
VII 2-Cl		75	37.61 (37.73)	2.40 (2.37)	21.76 (22.38)	11.01 (11.02)	$\text{C}_8\text{H}_6\text{O}_2\text{SiF}_3\text{Cl}$
VIII 4- NO_2	93(2)	102–103	36.70 (36.22)	2.24 (2.28)	10.45 (10.58)	20.95 (21.48)	$\text{C}_8\text{H}_7\text{O}_4\text{SiF}_3\text{N}$

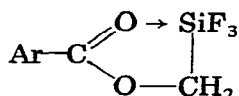
^a The number of the reaction is given in parentheses.

atom [1,2]. Nevertheless, the peculiarities of the silatrane structure do not allow one to settle finally the question of the energy of the Si $\leftarrow$ N transannular bond and the relationship of the factors which govern the existence of this bond. Other data on the synthesis and investigations of compounds having a pentacoordinate silicon atom are of a fragmentary nature [3–11]. Therefore organosilicon chemistry faces the problem of synthesizing new types of pentacoordinate silicon compounds and directly measuring the energy parameters of the intramolecular coordination.

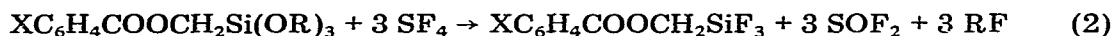
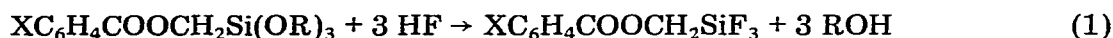
Results and discussion

Synthesis of (aryloxymethyl)trifluorosilanes

We were the first to prepare and study a new class of organosilicon compounds containing a pentacoordinate silicon atom, i.e., (aryloxymethyl)trifluorosilanes (AFS).



The synthesis was based on the reactions of (aryloxymethyl)trialkoxysilanes with hydrogen fluoride or sulfur tetrafluoride * according to the following reactions:



The yields of AFS prepared by reactions 1 and 2 were 80–85% and 97–99%, respectively. AFS are white crystalline odourless substances, distinguished from conventional organyltrifluorosilanes which are mobile fluids with an unpleasant odour. The physical constants of these compounds are listed in Table 1.

(3-Benzoyloxypropyl)trifluorosilane, $\text{C}_6\text{H}_5\text{COO(CH}_2)_3\text{SiF}_3$ (IX) prepared by us in this way is a fluid with a strong smell. The pentacoordinate character of silicon in the compounds obtained has been confirmed by X-ray diffraction [12]. In the molecule of (*para*-bromobenzoyloxymethyl)trifluorosilane (V) the Si $\leftarrow$ O bond length is 1.94 Å (Fig. 1) which is much lower than the sum of Van der Waals radii (3.4 Å) for the atoms of silicon and oxygen.

However, the X-ray diffraction data do not permit one to conclude whether the Si $\leftarrow$ O bond in AFS molecules in the gaseous, liquid and solution states remains intact and how the conditions outside the molecule influence this bond. This inspired us to carry out an extensive physico-chemical study of the structure and properties of AFS compounds I–VIII and to compare (3-benzoyloxypropyl)trifluorosilane (IX) and (benzoyloxymethyl)triethoxysilane (X).

* The synthesis from SF_4 was carried out together with L.N. Markovski and N.I. Liptuga, Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev.

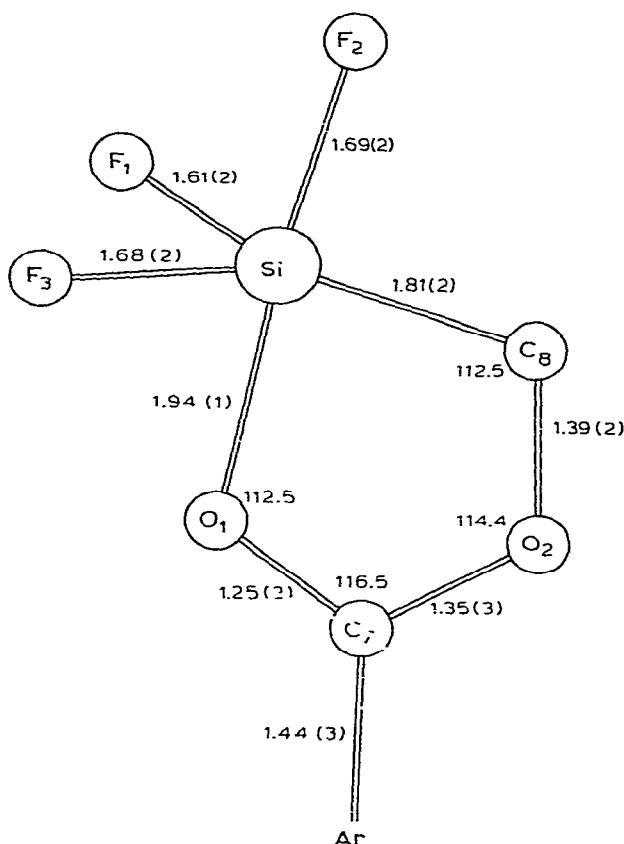


Fig. 1. The structure of the heterocyclic fragment of 4-BrC₆H₄COOCH₂SiF₃.

Dipole moments

The dipole moment values (μ) for AFS in benzene given in Table 2 are within the 5–7 D range. Such high values are common for coordinate compounds. By contrast, the μ value for compound X is only 2.52 D. Since the lengthening of the carbon chain between the silicon atom and etheric oxygen in AFS should not affect the μ value much, the significant difference in the dipole moments for AFS and compound IX (3–5 D) may be assumed to be caused by their different steric configuration due to the presence of intramolecular Si $\leftarrow$ O coordination.

IR spectra

Fig. 2 shows absorption spectra in the 400–1800 cm⁻¹ region taken under various conditions for compounds III. The IR spectra for compounds I, II, IV–VII do not differ much. Most sensitive to the presence of the coordinate Si $\leftarrow$ O bond should be the –SiF₃ and >C=O groups. The assignment of ν (C=O) stretching vibration in the spectra of AFS is beyond any doubt. In the spectra with KBr pellets this vibration appears as an intense absorption band with a

TABLE 2

DIPOLE MOMENTS (μ , D) IN BENZENE AT 25°C AND IR SPECTRA IN NUJOL AND CCl₄ FOR XC₆H₄COOCH₂SiF₃

X	n	μ (D)	$\nu(\text{C=O})$ (cm ⁻¹)	
			Nujol	CCl ₄
H	1	6.26	1626	1660
4-CH ₃	1	6.56	1627	1555
4-F	1	5.05	1641	1661
4-Cl	1	4.96	1646	1666
4-Br	1	5.00		
4-OCH ₃	1	7.07	1619	1651
2-Cl	1	7.61	1642	1680
H	3	2.52	1720 ^a	—

^a Liquid state.

maximum at 1620–1640 cm⁻¹ (Table 2). At the same time, in the spectra of compounds IX and X the $\nu(\text{C=O})$ maxima are at 1720 cm⁻¹. This difference by 80–100 cm⁻¹ is consistent with the absence of a coordinate Si ← O bond in molecules IX and X. The absence of coordination in IX seems to be due to difficulty confronted in building up a seven-membered ring required for the

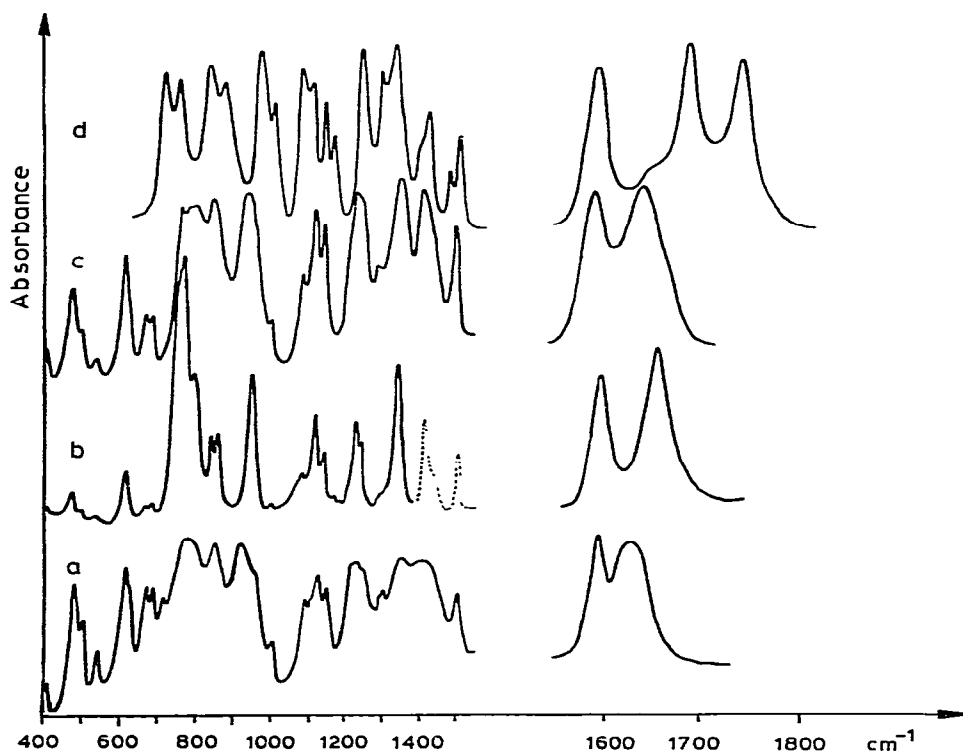


Fig. 2. IR spectra of 4-FC₆H₄COOCH₂SiF₃: a) KBr pellets; b) solid line, solution in CS₂; dotted line, solution in CCl₄; c) melt at 390 K; d) gas at 420 K.

formation of the Si $\leftarrow$ O bond. In the case of molecule X this may be caused by the electronegativity of ethoxy groups being lower than that of fluorine atoms as well as by the steric hindrance created by the ethoxy groups. In the IR spectra of AFS in non-polar solvents the $\nu(\text{C}=\text{O})$ band is displaced to the high-frequency region at 1650–1665 cm^{-1} . The $\nu(\text{C}=\text{O})$ absorption in the spectra of compounds IX and X, on the contrary, is not affected much by the solvents.

The spectra of AFS melts contain the $\nu(\text{C}=\text{O})$ maximum at 1630–1645 cm^{-1} . These spectra as well as the dipole moment measurements show that the coordinate Si $\leftarrow$ O bond is not affected in AFS in both the liquid state and solutions in CS_2 and CCl_4 .

An alternative hypothesis involving Si $\leftarrow$ O intermolecular coordination in AFS fails to be confirmed due to the absence of any concentration dependence of $\nu(\text{C}=\text{O})$ frequency and intensity in CCl_4 solution. In our opinion, no intermolecular coordination can occur owing to strong steric hindrances.

The nature of the substituents in the *para* position of the benzene ring in AFS I–VI does not greatly influence the $\nu(\text{C}=\text{O})$ frequency (Table 2). The latter increases in the following order with change of substituent X:



From the X-ray diffraction data, the torsional angle between the planes of the carboxyl group and the benzene ring is less than 10° . The chlorine atom in the *ortho* position should cause a considerable increase in this angle. Judging from the $\nu(\text{C}=\text{O})$ value for compound VII, *ortho*-substituted AFS VII retains its coordination interaction.

Measurements of the $\nu(\text{C}=\text{O})$ band parameters of AFS III in the gaseous state gave the following results. Above 420 K the 1640 cm^{-1} band (characteristic of the melt) disappears giving way to a band with a maximum at 1700 cm^{-1} . Upon further heating this peak also disappears, and a third one appears in the 1750 cm^{-1} region. After cooling of the sample the spectrum assumes its initial appearance. It is natural to suggest that the second band corresponds to stretching vibrations of the carbonyl group coordinated with a silicon atom of AFS in the gaseous state and the third band belongs to the $\nu(\text{C}=\text{O})$ of AFS molecules without Si $\leftarrow$ O coordination. This suggestion is supported by variations observed in other regions of the spectrum with an increase in temperature and by the existence of a strong functional dependence (discussed below) of $\nu(\text{C}=\text{O})$ on the dielectric constant of the medium (ϵ).

The $\nu(\text{Si}-\text{F})$ stretching vibrations are usually found in the 800–1000 cm^{-1} region. For compound IX, two intense bands at 890 cm^{-1} and 990 cm^{-1} are observed in this region. The bands may be assigned to the symmetrical $\nu_s(\text{Si}-\text{F})$ and antisymmetrical $\nu_{as}(\text{Si}-\text{F})$ vibrations, respectively. A narrow and rather intense band having its maximum at 845 cm^{-1} is likely to belong to out-of-plane deformational C–H vibrations of the benzene ring.

In AFS molecules with pentacoordinate Si the axis bond stretching vibrations ($\text{Si}-\text{F}_{ax}$) should not interfere with those of equatorial bonds ($\text{Si}-\text{F}_e$, $\text{Si}-\text{C}$). At the same time, the Si–F and Si–C vibrations may well be mixed.

As an extension of the coordination number of the central atom slightly decreases the strength of its bonds [13], the average $\nu(\text{Si}-\text{F})$ value should be assumed to be also lowered. The absorption of compound III in the 700–1000

cm^{-1} region is characterized by intense bands having maxima at 775, 862 and 947 cm^{-1} (KBr pellets). There are also weak bands in this range, the intense peaks displaying a shoulder-like structure. This makes a unique assignment of $\nu(\text{Si}-\text{F})$ vibrations difficult. In the IR spectrum of a solution of compound III in CS_2 the relative intensity of the 775 cm^{-1} band is greatly enhanced; the 862 cm^{-1} band is split into a triplet: 832 mw , 857 m(sh) and 874 sw cm^{-1} . The 947 cm^{-1} band is displaced towards the high-frequency region at 970 cm^{-1} .

In the spectrum of gaseous III further changes are observed at 500 K. The relative intensity of the 775, 874 and 970 cm^{-1} bands is lowered and new peaks appear at 733, 890 and 990 cm^{-1} . The $\nu_s(\text{Si}-\text{F}_e, \text{Si}-\text{C})$ and $\nu(\text{Si}-\text{F}_{ax})$ frequencies are assumed to be lower than $\nu_{as}(\text{Si}-\text{F}_e)$. The $947\text{--}970\text{ cm}^{-1}$ band is probably due to $\nu_{as}(\text{Si}-\text{F}_e)$. The 775 and 874 cm^{-1} bands may be assigned to the $\nu(\text{Si}-\text{F}_{ax})$ and $\nu_s(\text{Si}-\text{F}_e, \text{Si}-\text{C})$ vibrations, but this is less reliable. The peak at 855 cm^{-1} is likely to be related, as in the case of compound IX, to in-plane deformational C—H vibrations of the benzene ring.

The changes in the spectra of compound III in going from the gaseous to the liquid state facilitates the assignment of ν_s and ν_{as} vibrations of the C—O—C group. Usually the vibrations of this type give intense absorption bands in the $1000\text{--}1100$ and $1200\text{--}1300\text{ cm}^{-1}$ regions. These vibrations should be also sensitive to a breakage of the silicon atom—carbonyl oxygen coordination. In the $1000\text{--}1400\text{ cm}^{-1}$ region the spectrum of compound III displays a group of bands, however only two intense bands begin to disappear when the temperature rises to 500 K. These are the peaks at 1135 and 1360 cm^{-1} . At the same time, bands having maxima at 1100 and 1310 cm^{-1} appear. These bands have been assigned by us to the $\nu_s(\text{C}-\text{O}-\text{C})$ and $\nu_{as}(\text{C}-\text{O}-\text{C})$ frequencies, respectively. The higher frequency value of these bands is likely to be explained by strengthening of the p, π -conjugation between the ether oxygen and the carbonyl group resulting from the formation of the coordinate $\text{Si} \leftarrow \text{O}$ bond.

The Effect of Solvents on Intramolecular Coordination

The change in parameters of a number of AFS bands with the change in the AFS aggregate state and upon dissolving shows a considerable influence of the medium on the coordinate $\text{Si} \leftarrow \text{O}$ bond strength. Therefore we have measured the position of the $\nu(\text{C}=\text{O})$ band in the spectrum of compound III in various solvents (Fig. 3). In so doing we have found considerable changes in $\nu(\text{C}=\text{O})$ depending on the ϵ value. An increase in the ϵ value conforms with a lowering of the $\nu(\text{C}=\text{O})$ frequency. This means that the $\text{Si} \leftarrow \text{O}$ bond strength, as in the case of silatranes [14], depends on the dielectric constant of the medium. Weakening of the $\text{Si} \leftarrow \text{O}$ bond enhances the electron density on the carbonyl oxygen. This, in turn, decreases the charge transfer through p, π -conjugation and increases the C=O bond order. In this case, the $\nu_{as}(\text{C}-\text{O}-\text{C})$ frequency diminishes, ($\Delta\nu \sim 10\text{ cm}^{-1}$), and the $\nu(\text{Si}-\text{F})$ frequencies increase. The strongest intramolecular coordination is observed in crystalline AFS, the weakest one in AFS in the gaseous state. The increase in $\nu(\text{C}=\text{O})$ when compound III goes from the crystalline to the gaseous state is 60 cm^{-1} . Unlike in the case of silatranes [14], the function $\nu(\text{C}=\text{O}) = f(\epsilon - 1)/(2\epsilon + 1)$ is poorly approximated by linear dependence. The steric availability of the carbonyl oxy-

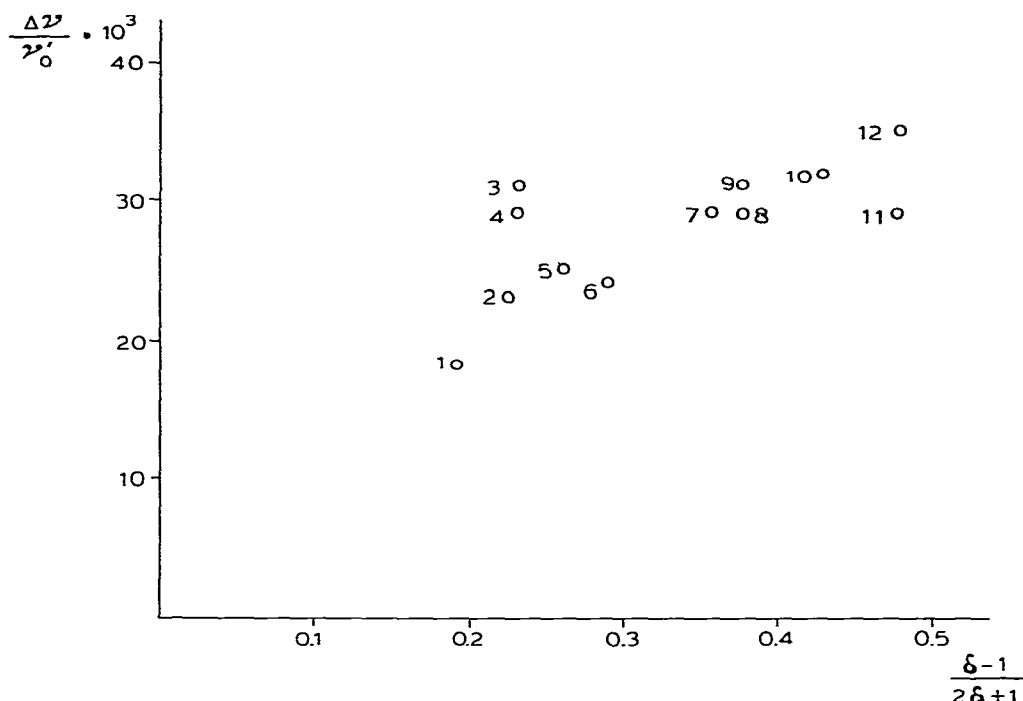


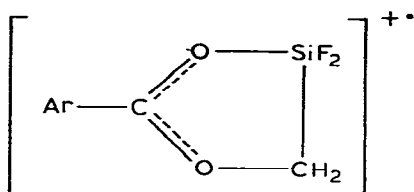
Fig. 3. The dependence of $\nu(\text{C}=\text{O})$ of $4\text{-FC}_6\text{H}_4\text{COOCH}_2\text{SiF}_3$ on the dielectric constant of the solvent (ϵ), for 1, n-heptane; 2, CCl_4 ; 3, dioxane; 4, C_6H_6 ; 5, CS_2 ; 6, $(\text{C}_6\text{H}_9)_2\text{O}$; 7, CHCl_3 ; 8, THF; 9, $\text{C}_6\text{H}_5\text{Cl}$; 10, 1,2-dichloroethane; 11, CH_3OH ; 12, CH_3CH . $\Delta\nu = \nu_0 - \nu$; ν_0 = value in the gaseous state.

gen and the SiF_3 group in AFS molecules makes the role of specific molecular interactions more important. Particularly significant deviations from the linear dependence are observed for AFS solutions in alcohols and strong organic bases. In a pyridine medium a leap of $\nu(\text{C}=\text{O})$ to 1709 cm^{-1} takes place, pointing to a breakage or a considerable weakening of the $\text{Si} \leftarrow \text{O}$ bond.

No change in the torsional angle between the planes of the carboxyl group and the benzene ring seems to occur with variation of the solvent ϵ value as evidenced from the agreement in the UV absorption spectra in the 200–300 nm region for solutions of compound III in n-heptane and acetonitrile. In both cases the peak is at 251 nm, the molecular extinction of the bands being nearly identical (1.95×10^4 and 1.99×10^4).

Mass spectra

Electron-impact fragmentation of AFS was studied for compounds I–IV and VI. The mass spectra display a rather high intensity of the peak assigned to the molecular ion ($W_M = 6\text{--}14$). Most intense is the peak from the ArCO^+ ion. The main route of initial disintegration of the molecular ion involving abstraction of a fluorine atom is typical for the compounds studied. The ion formed may be assumed to have the following structure:



In this case, abstraction of the substituent from the silicon atom and possible strengthening of the Si $\leftarrow$ O bond resemble the first step of silatrane fragmentation [15] where elimination of the axial substituent was associated with the presence of the transannular Si $\leftarrow$ N bond. Parallel routes of dissociative ionization of the molecular ions are 1) elimination of the hydrogen atom, 2) abstraction of the CH₂O, 3) loss of the substituent from the benzene ring.

Enthalpy and entropy of AFS intramolecular coordination

Determination of the thermodynamic parameters of the reaction



is most important for the understanding of the nature of the bonding of penta-coordinate silicon. Thermochemical measurements of enthalpy of trimethylamine-SiF₄ and -CH₃SiF₃ complexing have given the values of 13.2 and 8.1 kcal/mol, respectively [16]. These values may also be used for other cases of silicon pentacoordination.

We have measured the optical density of the $\nu(\text{C}=\text{O})$ bands for compound III in the gaseous state within the temperature range of 420–500 K, assigned to molecules with and without Si $\leftarrow$ O coordination. A calculation using Van 't Hoff equations led to the following results:

$$-\Delta H = 8.1 \pm 0.7 \text{ kcal/mol}; \quad -\Delta S = 15.3 \pm 0.8 \text{ e.u.}; \quad T = 450 \text{ K}$$

Thus, the energy of intramolecular Si $\leftarrow$ O coordination in compound III has been measured by a direct method. We believe that the enthalpy changes in the case of AFS are mainly determined by factors including, along with the Si $\leftarrow$ O bond formation, variations in the lengths of bonds and valence angles at the silicon atom. An entropy-increasing breakage of the Si $\leftarrow$ O bond is, to a large extent, due to an increase in the number of inner rotations with respect to the C–O and C–Si bonds.

The formation of the intramolecular coordinate Si $\leftarrow$ O bond in AFS molecules as well as the Si $\leftarrow$ N bond in silatranes [17] are interpreted by us in terms of the hypervalence theory developed for the Main Group V–VII elements by Musher [18]. For molecules of silatranes and AFS the bond nature differs from the cases discussed by Musher. On formation of the four-electron three-centre bond, one of the ligands serves as the donor of a lone electron-pair in molecules of AFS and silatranes. The bonding scheme resembles p, π -conjugation.

The results of NMR studies of AFS will be discussed in a separate communication.

TABLE 3
(AROYLOXYMETHYL)TRIALKOXYSILANES $\text{XC}_6\text{H}_4\text{COOCH}_2\text{Si}(\text{OR})_3$

X	R	Yield (%)	B.p. (°C/mmHg)	d_4^{20}	n_D^{20}	Found (calcd. (%))			Empirical formula
						C	H	Si	
H	CH_3	52.3	119/2	1.1545	1.4800	51.44 (51.55)	6.35 (6.29)	10.64 (10.95)	$\text{C}_{11}\text{H}_{16}\text{O}_5\text{Si}$
4- CH_3	CH_3	60	120-122/2	1.1177	1.4860	53.55 (53.31)	6.68 (6.71)	10.37 (10.38)	$\text{C}_{12}\text{H}_{18}\text{O}_5\text{Si}$
	C_2H_5	56	154/2	1.0651	1.5710	63.73 (63.80)	7.13 (7.02)	10.11 (9.94)	$\text{C}_{15}\text{H}_{24}\text{O}_5\text{Si}$
4-F	C_2H_5	58	120/2	1.1430	1.4530	53.16 (53.14)	6.71 (6.64)	8.56 (8.87)	$\text{C}_{14}\text{H}_{21}\text{O}_5\text{SiF}$
4-Cl	CH_3	58	140-141/2	1.2311	1.4955	45.55 (45.43)	5.02 (5.19)	9.60 (9.65)	$\text{C}_{11}\text{H}_{15}\text{O}_5\text{SiCl}$
	C_2H_5	58.5	150/2	1.1371	1.4851	50.52 (50.52)	5.39 (6.31)	8.19 (8.42)	$\text{C}_{14}\text{H}_{21}\text{O}_5\text{SiCl}$
4-Br	C_2H_5	50	158/2	1.2801	1.4940	44.39 (44.56)	5.53 (5.57)	7.32 (7.42)	$\text{C}_{14}\text{H}_{21}\text{O}_5\text{SiBr}$
4- CH_3O	CH_3	54	166/2	1.1796	1.4970	50.41 (50.33)	6.29 (6.33)	9.71 (9.80)	$\text{C}_{12}\text{H}_{18}\text{O}_6\text{Si}$
	C_2H_5	49	177/2	1.0947	1.4845	54.88 (54.87)	7.30 (7.31)	8.52 (8.53)	$\text{C}_{15}\text{H}_{24}\text{O}_6\text{Si}$
4- NO_2	C_2H_5	53.5	164-165/2	1.1641	1.4865	48.9 (48.62)	6.12 (6.04)	8.16 (8.29)	$\text{C}_{14}\text{H}_{21}\text{O}_7\text{SiN}$
2-Cl	CH_3	56	130-132/2	1.2331	1.4955	45.21 (45.43)	5.14 (5.19)	9.36 (9.65)	$\text{C}_{11}\text{H}_{15}\text{O}_5\text{SiCl}$

Experimental

The dielectric permeability of AFS solutions in benzene was measured on an Epsilon dielkometer at 1 MHz and 298 K. The density of solutions was determined using hydrostatic weighing methods directly in the measuring cell. The molecular polarization was calculated by the Hedestrand method [19]. Mass spectra were recorded on a MX-1303 mass spectrometer using a direct insertion probe, the temperature varying within the 333–473 K range depending on the volatility of the sample; accelerating voltage 2 kV, cathode emission current 150 mA, ionizing electron energy 50 eV.

Absorption IR spectra were recorded on a Specord 75 IR spectrometer. Crystalline AFS were taken in KBr pellets and Nujol mulls. Liquid AFS were taken as melts (microlayer) and 0.1–0.1 M solutions in CCl₄ and CS₂. In this case 0.01–0.025 cm cells with KBr windows were used. Spectra of gaseous AFS were recorded in the 400–500 K range ($\pm 1^\circ$) using 1 and 5 cm cells, filled under dry argon.

The heat of reaction 4 was calculated using the $\nu(\text{C}=\text{O})$ optical density values in the 400–500 K range. The calculation was carried out by the following equations:

$$\Delta H = k \frac{T_1 T_2}{T_1 - T_2} \ln \frac{D_1^{T_1} D_2^{T_2}}{D_2^{T_1} D_1^{T_2}} ;$$

$$\Delta S = \frac{\Delta H}{T} + R \ln \frac{D_1^T}{D_2^T} ;$$

where: D_1^T , D_2^T represent the $\nu(\text{C}=\text{O})$ optical densities for both free and bound C=O groups at temperature T , respectively.

The UV absorption spectra of AFS as 0.01–0.005 M solutions in n-heptane and CH₃CN were recorded on a Specord UV VIS.

The synthesis of (aroyloxymethyl)trifluorosilanes was carried out by two methods according to reactions 1 and 2. Two typical examples, common for all the compounds prepared (I–VII), are given in Table 1.

(4-Chlorobenzoyloxymethyl)trifluorosilane(IV) (reaction 1)

In a three-necked flask, equipped with a stirrer, reflux condenser and a dropping funnel, was placed a solution of 7.5 g (0.02 mol) of (4-chlorobenzoyloxymethyl)triethoxysilane in 20 ml of ether. Then 8 ml of 40% hydrofluoric acid (two-fold excess) was added with stirring. The reaction mixture was allowed to stir for 30 min, and then 50 ml of ether and 15 g of anhydrous CaCl₂ were added. After filtration, most of the ether was distilled from the reaction mixture. The deposited crystals of IV were removed, dried under vacuum and sublimed at a 82–85°C and 2 mm Hg. IV: Yield 5.3 g (85%); m.p. 112–114°C.

(4-Toluoyloxymethyl)trifluorosilane (II) (reaction 2)

In a 250 ml steel autoclave, was placed 5.0 g (0.02 mol) of (4-toluoyloxymethyl)trimethoxysilane and on cooling in liquid nitrogen, 7.1 g of sulfur tetra-

fluoride was added. The reaction mixture was allowed to stand in the autoclave for 20 h at 20°C. The crystalline mass formed (4.3 g, raw yield 100%) was recrystallized from acetonitrile. II: Yield 2.4 g (97.6%); m.p. 90°C.

The initial (aryloxy)methyl)trialkoxysilanes [20] were prepared by the reaction of potassium salts of the corresponding benzoic acids with (chloromethyl)-trialkoxysilanes in DMFA. A typical example is given. Physical constants, analytical data and yields are listed in Table 3.

(4-Chlorobenzoyloxymethyl)triethoxysilane

In a three-necked flask, equipped with a stirrer, reflux condenser and a dropping funnel, a solution of 12.4 g (0.06 mol) of potassium 4-chlorobenzoate in 150 ml of DMFA was placed, then 15 g (0.07 mol) of chloromethyltriethoxysilane was added dropwise with stirring. The reaction mixture was heated under reflux for 20 min. After filtration of the KCl precipitate and distillation of the solvent, the residue was distilled under vacuum. Yield 15.5 g (58.5%; b.p. 150°C/2 mm Hg, $d_4^{20} = 1.1371$, $n_D^{20} = 1.4851$).

(3-Benzoyloxypropyl)triethoxysilane was prepared in a similar manner. Yield 58.9%, b.p. 138°C/2 mm Hg, $d_4^{20} = 1.1071$, $n_D^{20} = 1.4800$. Found: C, 54.3; H, 6.9; Si, 9.93, $C_{13}H_{20}O_5Si$ calcd.: C, 54.9; H, 7.08; Si, 9.87%.

(3-Benzoyloxypropyl)trifluorosilane (IX)

In a three-necked flask, equipped with a stirrer, reflux condenser and a dropping funnel, containing a solution of 6.7 g (0.02 mol) (3-benzoyloxypropyl)-trimethoxysilane in 15 ml of ether was poured, with stirring, 10 ml of hydrofluoric acid. The reaction mixture was kept at 20°C for 30 min. Then 60 ml of ether and 10 g of anhydrous $CaCl_2$ were added. After filtration and distillation of the solvent, the residue was distilled under vacuum. IX: Yield 3.0 g (51%); b.p. 90°C/2 mm Hg. Found: C, 48.36; H, 4.69; Si, 11.10; F, 23.04, $C_8H_7O_2SiF_3$ calcd.: C, 48.37; H, 4.05; Si, 11.31; F, 22.95%.

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