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Solvatochromism of Heteroaromatic Compounds: XXIV.[1] Solvation Complexes of (=O→Si)(4-Nitrobenzoyloxymethyl)trifluorosilane in Protophilic Solvents

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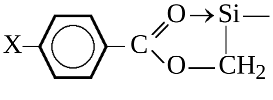
Abstract—(4-Nitrobenzoyloxymethyl)trifluorosilane containing a five-coordinate silicon atom (=O→Si) is specifically solvated in a protophilic medium to form a complex in which the solvent molecule donates an electron pair and the coordination number of the silicon atom increases to six. Formation of such solvation complexes gives rise to a pronounced positive specific solvatochromic effect in the UV spectra. According to dielectrometric, ^{19}F NMR, and IR data, and also to *ab initio* calculations (HF/6-31G*), the solvent molecule occupies an equatorial position.

One of the previous communications of this series [2] concerns the UV spectra of (aroyloxymethyl)trifluorosilanes (draconoids [3]) methyl(aroyloxymethyl)fluorosilanes $4\text{-}XC_6H_4COOCH_2SiMe_{3-n}F_n$ (n = 3–1) in an aprotic inert medium. These spectra show that formation of an intramolecular coordination bond =O→Si in these molecules causes stabilization of their second excited $\pi\pi^*$ state by 5–6 kcal mol^{-1} relative to the ground electronic state, due to strengthening of this bond. The silicon atom in such compounds under certain conditions tends to increase its coordination number from five to six [3]. Therefore, it can be expected that, in an aprotic protophilic solvent, the energy gap between the ground and excited states of (aroyloxymethyl)trifluorosilanes will be influenced by specific solvation with formation of solvation complexes containing a six-coordinate silicon atom (S is a protophilic solvent molecule):



Formation of such complexes was observed previously in the systems (aroyloxymethyl)trifluorosilane–donor molecule [pyridine, 2,2'-bipyridine, 1,2-bis(dimethylamino)ethane, 1,10-phenanthroline] [4, 5].

To check this hypothesis, we chose (4-nitrobenzoyloxymethyl)trifluorosilane **I** whose absorption band in the UV spectrum is fairly highly sensitive to the medium. The site of specific interaction in **I** is the silicon atom, which has a trigonal bipyramidal surrounding and is not directly involved in the π system. Hence, the effect of specific interactions on the UV spectrum of **I** should not be so pronounced as, e.g., in nitroanilines or nitrophenols [6–9]. Therefore, using a series of compounds **II**–**VIII**, we preliminarily determined the range of variation of the peripheral specific solvation effect:

$4\text{-}O_2NC_6H_4Y$,
I–VIII

Y = $C(O)OCH_2SiF_3$ (**I**), C(O)H (**II**), C(O)Me (**III**), $C(O)CH_2Br$ (**IV**), COOH (**V**), $C(O)NH_2$ (**VI**), $C(O)NH\cdot NH_2$ (**VII**), C≡CH (**VIII**).

As a quantitative measure of the solvating power of solvents, we used the Kamlet–Taft solvatochromic parameters; to describe the solvent effect on the UV spectrum, we chose an empirical solvatochromism equation (1) [10, 11]:

$$\nu^{\pi\pi^*} = \nu_0 + s\pi^* + b\beta. \qquad (1)$$

Here ν_0, s, and b are constants specific for a chosen indicator; π^* is the parameter determining the capability of a solvent to stabilize dipolar molecules (nonspe-

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[1] For communication XXIII, see [1].

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Table 1. Solvatochromism of the long-wave absorption band (ν, cm^{-1}) in the UV spectra of nitroarenes $4\text{-}O_2NC_6H_4Y$ **I–VIII**

Solvent[a]	Parameter		**I**	**II**	**III**	**IV**	**V**	**VI**	**VII**	**VIII**
	π^*	β								
Dibutyl ether	0.24	0.46	39 000	38 300	38 450	–	38 850	38 700	38 600	35 350
Diethyl ether	0.27	0.47	39 000	38 400	38 400	38 000	38 900	38 650	38 500	35 350
Diisopropyl ether	0.27	0.49	39 000	38 350	38 500[b]	–	–	–	–	35 300
Butyl acetate	0.50	0.45	38 700	–	38 000	37 800	38 650	38 400	38 100	35 000
1,2-Dimethoxyethane	0.53	0.41	38 600	37 850[c]	37 950	37 650	38 550	38 350	38 100	35 400[b]
Ethyl acetate	0.55	0.45	38 650	37 950	38 050	37 750	38 600	38 350	38 050	34 950
Dioxane	0.55	0.37	38 650	37 850	38 000	37 700	38 650	38 450	38 050	34 900
THF	0.58	0.55	38 550	37 800	37 900	37 600	38 450	38 250	38 000	34 750
Acetonitrile	0.75	0.31	38 450	37 700	37 750	37 600	38 400	38 200	37 800	34 800
Propylene carbonate	0.83	0.40	38 250	37 550	37 650	37 450	38 250	38 000	37 550	34 450
Tetramethylurea	0.83	0.80	–	–	37 700	37 500	–	37 750	–	34 200
HMPA	0.87	1.05	38 500[d]	37 500[e]	37 500	37 450	38 000	37 350	37 350	33 950
N,*N*-Dimethylacetamide	0.88	0.76	–	37 350[f]	37 500	37 450[g]	38 050	37 700[e,h]	–	34 150[i]
1-Methyl-2-pyrrolidone	0.92	0.77	38 600[j]	37 400	37 450	37 400	37 950	37 600	–	34 100
DMSO	1.00	0.76	38 150[k]	37 300	37 450	37 250	37 850	37 550	37 300	34 000

[a] Solvatochromic parameters were taken from [10, 11]. [b] Data for triethylamine (π^* 0.14, β 0.71). [c] For trimethoxymethane (π^* 0.58). [d] For ethyl chloroacetate (π^* 0.70, β 0.35). [e] For DMF (π^* 0.88, β 0.69). [f] For sulfolane (π^* 0.98). [g] In DMF and ethyl chloroacetate, ν 37 500 cm^{-1}. [h] In ethyl formate (π^* 0.61, β 0.36), ν 38 300 cm^{-1}. [i] In DMF, ν 34 200 cm^{-1}; in ethyl chloroacetate, ν 34 700 cm^{-1}. [j] In ethyl formate. [k] In butyrolactone (π^* 0.87, β 0.49).

cific solvation); and β is the parameter describing the capability of a solvent molecule to act as a hydrogen bond acceptor in an H complex with a solute (specific solvation). In the broad sense, the quantity β should be considered as a group measure of the affinity for positive charge.

Data on the solvatochromism of the long-wave absorption band in the compounds under consideration are listed in Table 1. In the spectra of solvatochromic indicators containing COZ fragments, the absorption band occurs at a high frequency, which restricts the range of protophilic solvents suitable for these experiments. Nevertheless, we were able to choose two fairly representative solvent groups with the parameters π^* and β varying in relatively wide ranges (Table 1). This allows us to obtain under equal conditions the reliable data on the solvatochromism of all the compounds **I**–**VIII**.

The results of the quantitative description of the solvatochromism [Eq. (1)] are listed in Table 2. It is seen that the UV spectra of compounds **II**–**IV**, which cannot form in significant concentrations H complexes with protophilic solvent molecules, are influenced by nonspecific solvation only ($s \neq 0$, $b \approx 0$). In the spectra of the compounds with the OH (**V**), NH_2 (**VI**), and $NHNH_2$ (**VIII**) peripheral groups, the specific solvatochromic effect ($\Delta\nu = b\beta$) is pronounced and positive. This means that, upon complexation with a solvent, the Franck–Condon excited state of **V**–**VII** is stabilized to a greater extent than the ground electronic state. Such a solvatochromic behavior is typical of compounds interacting with a solvent by the mechanism of two-center hydrogen bonding [6–9, 12]. These compounds are characterized by a decrease in the specific solvatochromic effect with a decrease in the number of “solvation-active” bonds (passing from NH_2 to $NHNH_2$, Table 2) [9]. The specific solvation effect caused by solvation of the peripheral group is comparable in value with that observed with such a strong hydrogen bond donor as 4-nitrophenylacetylene **VIII** (Table 2). Thus, complexation with peripheral proton-donor fragments of molecules has a significant effect on the $\pi \rightarrow \pi^*$ transition energies in solvatochromic indicator molecules.

Table 2. Quantitative characteristics of the solvatochromism of the long-wave absorption band in the UV spectra of nitroarenes $4\text{-}O_2NC_6H_4Y$

Comp. no.	μ^a, D	ν_0, cm^{-1}	$-s$, cm^{-1}	$-b$, cm^{-1}	*R*	*sd*	*n*
I	3.40	39600±80	1350±50	530±150	0.985	30	13
II	2.58	38680±40	1380±60	–	0.991	50	13
III	3.43	38720±40	1330±60	–	0.989	60	15
IV	2.85	38190±60	870±80	–	0.955	60	15
V	4.02	39390±40	1180±70	410±80	0.980	50	13
VI	4.84	39400±30	1220±60	880±60	0.991	40	15
VII	3.95	39070±40	1640±60	240±70	0.991	40	11
VIII	3.65	36100±40	1580±50	730±60	0.992	40	17

[a] Measured in dioxane at 298 K.

Table 3. Dipole moments (D) of **I** and **IX**–**XV** in solutions and dipole moments of configurational isomers **A**–**C** of the complexes with 1,4-dioxane (or THF), calculated by the vector additive scheme

Comp. no.	Experiment (298 K)			Calculation			
	CCl_4	C_6H_6	$C_4H_8O_2$	molecule	**A**	**B**	**C**
I	2.87 (2.95)[a]	3.08	3.40 (3.21)[b]	3.1	4.6 (3.5)	4.5 (5.1)	0.2 (2.0)
IX	5.48	5.84	6.09	5.0	3.2 (3.9)	6.0 (7.1)	3.9 (4.4)
X	6.25 (6.70)[c]	6.46	6.63	5.3	3.2 (4.2)	6.2 (7.4)	4.3 (4.7)
XI	4.43	4.79	4.94	4.1	4.2	5.1	2.3
XII	4.14	4.17	4.70				
XIII	5.52	5.63	5.60				
XIV	5.40	5.60	5.73				
XV	5.12	5.22					

[a] Calculated for the molecule by the HF/6-31G* method. [b] The same for the dioxane complex, form **B**. [c] The dipole moment of the complex of **X** with THF was determined by dielectrometric titration in CCl_4 at 278 K.

The UV spectrum of (4-nitrobenzoyloxymethyl)trifluorosilane **I** is also sensitive to the protophilic properties of the medium. The specific solvatochromic effect observed with this compound is close to that observed with 4-nitrobenzoic acid **V** forming strong H complexes with protophilic solvents. This fact allows a number of conclusions: (a) molecules of **I** are specifically solvated in a protophilic medium; (b) the excited nonequilibrium state of (4-nitrobenzoyloxymethyl)trifluorosilane is stabilized by the medium to a greater extent than the equilibrium ground state (positive specific solvatochromic effect, Table 2); (c) similar trends are observed in the effects of specific solvation on the UV spectra of compounds forming solvation complexes via a two-center hydrogen bond and via a bond with a six-coordinate Si atom. However, the stereoelectronic structure of solvation complexes of compounds with an $=O\rightarrow Si\text{–}F$ three-center bond cannot be elucidated without understanding the nature of the ground electronic state. Therefore, we studied the interaction of (aroyloxymethyl)trifluorosilanes with protophilic solvents by dielectrometry and by ^{19}F NMR and IR spectroscopy.

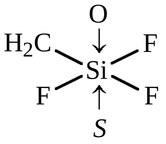
The occurrence of specific interaction between molecules of (aroyloxymethyl)trifluorosilanes $4\text{-}XC_6H_4\cdot C(O)OCH_2SiF_3$ [X = O_2N (**I**) H (**IX**), Me (**X**), Br (**XI**)] and an aprotic protophilic solvent can be judged from the solvent effect on the solute dipole moments, and also on the dipolarity of compounds with a four-coordinate Si atom: $4\text{-}O_2NC_6H_4OY$ [Y= CH_2SiMeF_2 (**XII**), $CH_2Si(OMe)_3$ (**XIII**), $CH_2Si(OMe)_2Me$ (**XIV**), $SiMe_3$ (**XV**) (Table 3)]. The mean dioxane effect ($\Delta\mu$) for **I** and **IX**–**XII** is 0.22 D relative to benzene and 0.52 D relative to CCl_4. These $\Delta\mu$ values considerably exceed the dioxane effect estimated from the experimental data for a wide range of nitrobenzene derivatives subject to nonspecific solvation only [13]. For example, the correlation between the dipole moments measured in benzene and 1,4-dioxane is described by

Eq. (2) [14], from which it follows that, under the conditions of nonspecific solvation, $\Delta\mu \approx 0.12$ D.

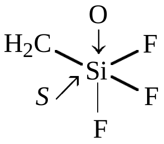
$$\mu(\text{dioxane}) = (0.12 \pm 0.05) + (1.00 \pm 0.01)\mu(\text{benzene}), \quad (2)$$

$$r\ 0.098,\ sd\ 0.11,\ n\ 33.$$

At the same time, apparently, correlation (2) should be valid for the molecules with a tetrahedral silicon atom whose surrounding, owing to the electronic effects and steric factor, prevents formation of solvation complexes. Indeed, the mean dioxane effect calculated for **XIII**–**XV** is 0.07 D relative to benzene and 0.20 D relative to CCl_4 (Table 3). Thus, higher values of $\Delta\mu$ for compounds with an intramolecular three-center bond =O→Si–F (**I**, **IX**–**XI**) suggest specific mechanism of their solvation with such a protophilic solvent as 1,4-dioxane. The composition of the solvation complex formed in a protophilic medium was determined by dielectrometric titration of solutions of (4-methylbenzoyloxymethyl)trifluorosilane **X** in CCl_4 with tetrahydrofuran (THF), which is a stronger donor of the lone electron pair than 1,4-dioxane. In CCl_4, molecules of **X** form with THF a 1 : 1 complex with a dipole moment of 6.70 D. This value exceeds by 0.45 D the dipole moment of the nonspecifically solvated molecule (Table 3). The dipole moments of this complex estimated in the vector additive approximation for the three possible configurational isomers (**A**–**C**, Table 3) suggest that form **B**, characterized by the preserved three-centered =O→Si–F bond and maximal dipole moment, is preferable (*S* is a solvent molecule):



A



B

Structure **A** could be rejected *a priori*, since the axial positions are usually occupied by the most electronegative atoms [15].

The dielectrometric data suggest that methyl(4-nitrophenoxymethyl)difluorosilane **XII**, although it does not form the =O→Si intramolecular bond in the solvents under consideration, is also specifically solvated by a protophilic solvent. This conclusion is consistent with the previously revealed capability of **XII** to form complexes with O- and N-donor molecules [4].

The thermochromism of the C=O stretching band in the IR spectra of **I** [Eqs. (3), (4)] is another indirect evidence of formation of solvation complexes of (aroyloxymethyl)trifluorosilanes in protophilic solvents.

1,2-Dichloroethane

$$\nu(\text{CO}) = (1640.4 \pm 0.1) + (0.46 \pm 0.003)T(^\circ\text{C}), \quad (3)$$

$$r\ 0.983,\ sd\ 0.3,\ n\ 9;$$

Anisole

$$\nu(\text{CO}) = (1639.8 \pm 0.1) + (0.067 \pm 0.004)T(^\circ\text{C}), \quad (4)$$

$$r\ 0.990,\ sd\ 0.5,\ n\ 9;$$

Equations (3) and (4) show that thermochromism is observed in both inert and protophilic solvents, being considerably more pronounced in the latter.

It is difficult to determine reliably from the UV spectra the actual configuration of a solvation complex in various solvents. We attempted to derive such information from the IR spectra. As investigation object we chose (benzoyloxymethyl)trifluorosilane **IX**, for which the solvatochromism of the C=O stretching band was studied in sufficient detail previously. Furthermore, the solvent effect on the IR characteristics of **IX** is stronger compared to **I**.

The general, for aprotic and amphiprotic solvents, equation for the solvatochromism of the C=O stretching band in the IR spectrum of **IX** has the form [16]

$$\nu(\text{C})) = 1666 - 31\pi^* - 0.2\alpha - 2.9\beta, \quad (5)$$

$$R\ 0.94,\ sd\ 2.1,\ n\ 24,$$

where α is the quantitative measure of the capability of a solvent molecule to act as a hydrogen bond donor in a complex with a solute.

It follows from Eq. (5) that the protophilicity of a solvent has a weak effect on the C=O stretching vibration frequency [ν(C=O)]. This, however, may be an artifact of the general description, since for some organic molecules the solvatochromism of IR bands should be analyzed separately even in different types of aprotic solvents [6]. Therefore, we obtained additional data on ν(C=O) in inert solvents (heptane, isooctane, 1,1,2,2-tetrachloroethane), refined the available ν(C=O) values (dichloroethane, dichloromethane, anisole), extended the data set on ν(C=O) in protophilic solvents (Table 4), and obtained separate equations for the solvatochromic behavior of **IX** in different types of solvents. Equations (6)–(8) only slightly differ from Eq. (5) in the values of the free term and regression coefficient.

Inert medium

$$\nu(\text{CO}) = (1667 \pm 1) - (32 \pm 2)\pi^*, \quad (6)$$

$$r\ 0.991,\ sd\ 2,\ n\ 9;$$

Table 4. Solvatochromism of the C=O and Si–F stretching bands in the IR spectra of (benzoyloxymethyl)trifluorosilane **IX** (cm^{-1})

Solvent[a]	π^*	β	ν(C=O)	$\nu_{as}(SiF_e)$	$\nu(SiF_a)$
Inert, δ 0:					
Heptane	–0.02	0	1668	972	817
Cyclohexane	0	0	1667		
Isooctane	0	0	1666		
Decane	0.03	0	1667	970	816
Inert, δ 0.5:					
Carbon tetrachloride	0.28	0	1660	965	816
Chloroform	0.58	0	1645		
1,2-Dichloroethane	0.81	0	1640	953	790
Dichloromethane	0.82	0	1641	951	790
1,1,2,2-Tetrachloroethane	0.95	0	1639	950	
Protophilic, δ 0:					
Dibutyl ether	0.24	0.46	1658	962	809
Diethyl ether	0.27	0.47	1655	961	807
Diisopropyl ether	0.27	0.49	1657		
Dioxane	0.55	0.37	1647	952	793
THF	0.58	0.55	1646	952	795
Ethyl formate	0.61	0.36	1644	950	791
Acetone	0.71	0.48	1643	948	793
Acetonitrile	0.75	0.31	1638	944	
Cyclohexanone	0.76	0.53	1644	948	792
Propylene carbonate	0.83	0.40	1638	939	
Nitromethane	0.85	0.25	1638	943	785
Butyrolactone	0.87	0.49	1637	942	780
DMSO	1.00	0.76	1633		
Protophilic, δ 1:					
Anisole	0.73	0.22	1641	948	793
Acetophenone	0.90	0.49	1639	947	790
Benzonitrile	0.90	0.37	1639	947	789
Benzaldehyde	0.92	0.44	1637	948	789
Nitrobenzene	1.01	0.30	1640	946	

[a] The solvatochromic parameters were taken from [10, 11].

Protophilic medium

$$\nu(CO) = (1664 \pm 1) - (30 \pm 2)\pi^*, \qquad (7)$$

r 0.977, sd 2, n 17;

Protophilic medium

$$\nu(CO) = (1663 \pm 2) - (30 \pm 2)\pi^* + (3 \pm 3)\beta, \qquad (8)$$

R 0.952, sd 2, n 17.

These solvatochromism equations also show that additional consideration of the electron-donor power of solvents [Eqs. (7) and (8) were obtained with exclusion of nitrobenzene] decreases the correlation coefficient and leads to a low and statistically insignificant regression coefficient at β [Eq. (8)].

Thus, the IR spectra show that the structure of the actually realized configurational isomer of the solvation complex of **IX** is characterized by weak influence of the capability of the solvent for specific solvation on the C=O vibration frequency. Hence, the solvent molecules are arranged in the equatorial plane of the complex (structure **B** or **C**). To characterize the structure of the solvation complexes with protophilic solvents more completely, it is necessary to reveal the presence of axial and equatorial Si–F bonds. This can be made by IR spectroscopy provided that the solvent effect on the ν(SiF) vibration frequencies is well understood. To gain insight into this effect, we calculated *ab initio* (HF/6-31G*) the normal mode frequencies of **I** and its 1 : 1 complex with dioxane. The oxygen atom of the solvent molecule was arranged between the C and F atoms, as suggested by dielectrometric data.

According to *ab initio* calculations, the 1 : 1 solvation complex of 1,4-dioxane with **I** is stable to dissociation into the components. At the length of the O→Si intermolecular coordination bond of 3.375 Å, which is 0.17 Å shorter than the sum of the van der Waals radii of the O and Si atoms, the energy of its formation $-\Delta E$ appeared to be 4.8 kcal mol^{-1}. The length of the O→Si intramolecular coordination bond increased from 2.290 to 2.380 Å upon complexation. Nevertheless, the C=O bond length in **I** (r 1.203 Å) changed only slightly upon complexation (r 1.200 Å). The Si–F bond lengths also change insignificantly upon complexation [r(Si–F$_e$) 1.573, 1.573 Å in the molecule and 1.573, 1.575 Å in the complex; r(Si–F$_a$) 1.594 Å in the molecule and 1.593 Å in the complex].

The order of the Si–F stretching frequencies in **I** and its solvation complex, calculated by the HF/6-31G* method, coincides with that found previously for (aroyloxymethyl)trifluorosilanes by normal mode calculation in the harmonic approximation [17]. The Si–F$_a$ stretching vibrations have the lowest frequency (815 cm^{-1} in both cases). In the IR spectra of solutions of (aroyloxymethyl)trifluorosilanes **I** and **IX**, e.g., in dibutyl ether, the bands of Si–F$_a$ stretching vibrations are observed at 824 and 809 cm^{-1}, respectively. The presence of Si–F$_a$ stretching bands in the IR spectra of solutions of these compounds in a protophilic solvent suggests that the equatorial configurational isomer of the solvation complex is energetically preferable. The symmetric stretching vibration of the Si–F$_e$ equatorial bonds, both in the molecule and in the complex, is strongly mixed with one of the bending modes of the ring involving the intramolecular coordination bond O→Si. According to the calculations made for **I** and its 1,4-dioxane complex, these mixed vibrations have close frequencies (887, 875 and 888, 874 cm^{-1}, respectively). In the IR spectra of solutions of **I** in dibutyl ether, these vibrations give bands with maxima at 875 and 848 cm^{-1}. The antisymmetric stretching vibration ν_{as}(SiF$_e$) is localized on the Si–F bonds to a greater extent. According to the calculation, upon complexation with 1,4-dioxane its frequency decreases from 969 to 958 cm^{-1}. In the experimental spectrum of a solution of **I** in dibutyl ether, the ν_{as}(SiF$_e$) band is located at 972 cm^{-1}.

The solvent effect on the Si–F vibration frequencies was studied empirically for **IX**. The solvatochromism of the corresponding IR bands was described by a three-parameter equation

$$\nu = \nu_0 + s\pi^* + b\beta + d\delta. \qquad (9)$$

To extend the sample, we included not only aliphatic but also aromatic protophilic solvents. Therefore, it became necessary to take into account their polarizability by introducing the group parameter δ. Unfortunately, experimental determination of ν(Si–F) in some solvents was impossible because of their absorption in the range 700–1000 cm^{-1} (Table 4). The ν(SiF$_a$) frequency, like the ν(CO) frequency, is independent of the affinity of solvent molecules for the positive charge. It is influenced only by the capability of aliphatic and aromatic solvents to stabilize dipolar species (π*, δ) [Eq. (10)].

$$\nu(\mathrm{SiF}_a) = (817 \pm 2) - (38 \pm 4)(\pi^* - 0.16\delta), \qquad (10)$$

$$r\ 0.954,\ sd\ 2,\ n\ 13.$$

The parameters of the equation for the solvatochromism of the Si–F$_a$ vibration band remain virtually unchanged on combining the sets of protophilic and inert solvents, which allows us to obtain a general relationship for all aprotic solvents:

$$\nu(\mathrm{SiF}_a) = (818 \pm 1) - (40 \pm 2)(\pi^* - 0.18\delta), \qquad (11)$$

$$r\ 0.976,\ sd\ 3,\ n\ 18.$$

The protophilic properties of solvents exert the most significant effect on the antisymmetric stretching vibrations of the Si–F$_e$ bonds in **I** [Eq. (12) was obtained with exclusion of propylene carbonate and nitrobenzene]:

$$\nu(\mathrm{SiF}_e) = (964 \pm 2) - (29 \pm 2)(\pi - 0.17\delta) + (11 \pm 3)\beta, \qquad (12)$$

$$R\ 0.966,\ sd\ 1,\ n\ 14.$$

Enhancement of the specific solvation, in contrast to nonspecific solvation, causes the frequency of this stretching vibration to increase. It is very important that the solvatochromism equation for an inert medium, i.e., under conditions of nonspecific solvation, has other parameters:

$$\nu(\mathrm{SiF}_e) = (971 \pm 1) - (23 \pm 1)(\pi^* - 0.02\delta), \qquad (13)$$

$$r\ 0.997,\ sd\ 1,\ n\ 6.$$

First, the free term (ν_0) in inert (971 cm^{-1}) and protophilic (964 cm^{-1}) solvents is different, suggesting that the trigonal bipyramidal surrounding of the Si atom in the molecule of **I** changes to the octahedral surrounding in the solvation complexes. Thus, the theoretical predictions (see above) for solvate **B** quantitatively agree with the experiment.

We also compared the parameters of the ^{19}F NMR spectra of (benzoyloxymethyl)trifluorosilane **IX** in various protophilic solvents.

Solvent	β	δ_F, ppm	$\nu_{1/2}$, Hz
Chloroform-*d*	0.00	–133.94	5.7
1,4-Dioxane	0.37	–133.95	5.7
Acetone-d_6	0.48	–133.99, –134.37	252
THF	0.55	–135.10, –135.30	162.3
DMSO-d_6	0.76	–121.10	406.7

In an inert medium ($CDCl_3$) at 298 K, the ^{19}F nuclei of this compound give a narrow singlet with the full width at half-maximum ($\nu_{1/2}$) not exceeding 6 Hz. The equivalence of the axial and equatorial F atoms was due to separate or combined effect of two fast (on the NMR time scale) processes: intramolecular exchange of fluorine atoms due to Berry pseudorotation; formation and cleavage of the =O→Si coordination bond [18]. In some protophilic solvents (acetone-d_6, THF), the signals are strongly broadened.

A similar effect on the ^{19}F NMR spectra of (aroyloxymethyl)trifluorosilanes is exerted by cooling to 173 K of their solutions in the mixed solvent $CCl_4 : CHCl_3 : CH_2Cl_2 = 13 : 27 : 60$ [19]. The ^{19}F NMR spectra of solutions of **IX** in moderately protophilic solvents (acetone, tetrahydrofuran) have an interesting feature. Even at 298 K, two ill-resolved signals are observed, suggesting magnetic nonequivalence of the fluorine atoms in (benzoyloxymethyl)trifluorosilane. Such a nonequivalence is possible only if the equatorial solvation complex of structure **B** or **C** is formed.

In the spectra of **IX** in DMSO, the ^{19}F signal is shifted downfield by 12.8 ppm relative to $CDCl_3$, and its $\nu_{1/2}$ increases to 407 Hz. This can be readily interpreted on the basis of the ^1H, ^{29}Si, and IR data [4, 18] suggesting that (aroyloxymethyl)trifluorosilanes form 1 : 1 and 1 : 2 complexes containing a six-coordinate Si atom with highly basic solvents such as DMSO, pyridine, and HMPA. The hexacoordination of the Si atom in highly protophilic solvents can be attained by formation of a complex with one base molecule (with preservation of the intramolecular O→Si bond) and/or with two base molecules (with cleavage of this bond).

The ^{19}F NMR spectra of a solution of **IX** in DMSO confirm the occurrence of an equilibrium between the 1 : 1 and 1 : 2 complexes. This is also indicated by the IR spectra of the solutions, containing two C=O stretching bands, one belonging to the C=O→Si group in the 1 : 1 complex ($1633\ cm^{-1}$), and the other, to the free carbonyl group in the 1 : 2 complex ($1720\ cm^{-1}$).

Thus, the whole set of data obtained by UV, NMR, and IR spectroscopy, dielectrometry, and quantum-chemical calculations shows that the specific solvation of (aroyloxymethyl)trifluorosilane molecules in protophilic solvents involves formation of solvation complexes in which the three-centered =O→Si–F bond is preserved. Formation of an intermolecular coordination bond with a solvent molecule is accompanied by a positive specific solvatochromic effect for the band corresponding to the π–π* electronic transition, enhancement of the dioxane effect, lengthening of one of the components of the three-centered =O→Si–F bond, decrease in the frequency of antisymmetric stretching vibrations of the $Si–F_e$ bond, and significant (even at 298 K) broadening of the ^{19}F resonance signal.

EXPERIMENTAL

The dielectric permittivity of solutions was measured on an Epsilon device (OKBA Joint-Stock Company, Angarsk, Russia) at 1 MHz. The dipole moments of molecules and complexes were calculated by the Higasi formula.

The IR spectra of solutions were recorded on a Specord IR-75 spectrophotometer, and the UV spectra, on a Specord UV-Vis spectrophotometer. The ^{19}F NMR spectra of **IX** were recorded on a Bruker DPX-400 spectrometer relative to external C_6F_6.

Compounds **I** [20] and **XII**–**XV** [21] were prepared by published procedures. Compounds **II**–**VIII** are commercial products.

Ab initio (HF/6-31G*) calculations of the isolated molecule of **IX** and its 1 : 1 complex with dioxane, and also of their vibration spectra were performed with complete geometry optimization using the GAUSSIAN 98 program package [22].

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