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NMR STUDY OF (AROYLOXYMETHYL)TRIFLUOROSILANES

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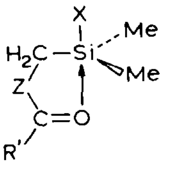
Summary

The effect of substituents at the silicon atom and in the side chain as well as those of the solvent and temperature on the strength of the intramolecular Si ← O bond in molecules of (aroyloxymethyl)trifluorosilanes and their analogs have been investigated by ^{1}H, ^{19}F and ^{29}Si NMR spectroscopy. The stereodynamic behavior and complexing ability of these molecules have also been studied.

Introduction

It has recently been reported that the silicon atom in some, at first view acyclic, compounds forms an intramolecular coordination bond with a nucleophilic oxygen or nitrogen in the δ-position of the side chain [1–11]. Thus organosilicon molecules of such a type tend, in fact, to form a five-membered ring structure. The main condition for the above intramolecular coordination is that the silicon should be bonded to at least one electronegative substituent. The silicon pentacoordination in these compounds was first characterized [1,2] in the dimethyl (trifluoroacetoxymethyl)acetoxysilane molecule (A) by ^{29}Si NMR spectroscopy.



(A) $X = OAc$; $Z = O$; $R' = CF_3$
(B) $X = Cl$; $Z = NR$; $R' = CH_3$

The intramolecular coordination has further been determined in the *N*,*N*-bis(chlorodimethylsilylmethyl)acetamide molecule (B) and its analogs by X-ray diffraction,

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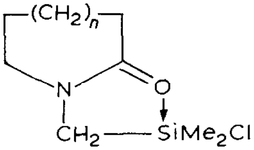
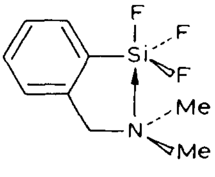
NMR and IR spectroscopy [3,4]. An analogous conclusion was drawn from a ^{29}Si NMR study of dimethyl(*N*-lactamomethyl)chlorosilanes (C) [5].



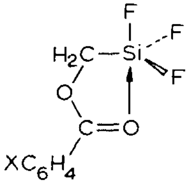
(C) $n = 1,2,3$

The existence of the intramolecular Si ← N bond in the 2-(*N,N*-dimethylaminomethyl)phenyltrifluorosilane (D) has been proved [6,7] by ^{1}H and ^{19}F NMR spectroscopy.

Among the compounds of the type under consideration, (aroyloxymethyl)trifluorosilanes (I) are being studied in more detail at present [8–11].



(D)



(I)

X-ray diffraction has shown that the length of the Si ← O coordinate bond in I depends on the nature of substituent X in the aromatic ring. Thus, the length of this bond increases in 4-halo-substituted compounds in the following order Br (1.94 Å) < F (2.04 Å) < Cl (2.08 Å). The IR data show that the intramolecular coordination in molecule I is present in not only the solution but even in the vapour state. The thermodynamic parameters of this coordination in the vapour phase at 400–500 K are estimated as being $\Delta H = -8.1$ kcal/mol and $\Delta S = -15.3$ e.u. The dipole moments of compounds in solutions are very large ($\mu = 5$–7 D).

We have studied the structure and stereodynamic behavior of (aroyloxymethyl)trifluorosilanes and their analogs in solution by NMR spectroscopy.

Results and discussion

^{29}Si NMR chemical shifts

The values of ^{29}Si chemical shifts as well as their variations in the series of (aroyloxymethyl)trifluorosilanes studied (Table 1) have two features. First, ^{29}Si screening in molecule I is 19–25 ppm higher than that of (chloromethyl)trifluorosilane (II) which is a model tetracoordinate silicon compound. But it is known [12–14] that in "normal" tetracoordinate silanes, the replacement of one α-carbofunctional silicon substituent by another with a similar electronegativity does not lead to such a significant change in the δ(Si) value. For example, ^{29}Si chemical shifts of (acetoxymethyl)triethoxysilane * and (chloromethyl)triethoxysilane differ by only 1.7 ppm (−58.2 and −59.9 ppm, respectively).

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* NMR data indicate that the silicon atom is a tetrahedral one in these compounds [15].

TABLE 1

NMR SPECTRAL PARAMETERS FOR (AROYLOXYMETHYL)TRIFLUOROSILANES AND THEIR ANALOGS IN CH_2Cl_2 AT ROOM TEMPERATURE

Compound	$\delta_{(Si)}$ (ppm)	$\delta_{(F)}$ (ppm)	$^1J_{(Si-F)}$ (Hz)	$\delta(^1H)$ (ppm)		$^3J_{(H-F)}$ (Hz)
				CH_2	aryl ring	
p-$CH_3OC_6H_4COOCH_2SiF_3$	−96.3	−136.43	225.5	3.83	8.06; 6.94	1.6
p-$CH_3C_6H_4COOCH_2SiF_3$	−95.8	−136.51	224.6	3.86	8.02; 7.25	2.1
$C_6H_5COOCH_2SiF_3$	−94.8	−136.56	225.0	3.91	8.09; 7.64	1.5
p-$FC_6H_4COOCH_2SiF_3$	−94.6	−136.62	229.4	3.82	8.20; 7.22	1.9
p-$ClC_6H_4COOCH_2SiF_3$	−93.6	−136.70	227.3	3.84	8.01; 7.48	1.7
p-$BrC_6H_4COOCH_2SiF_3$	−93.7	−136.66	227.5	3.94	7.95; 7.65	1.7
p-$O_2NC_6H_4COOCH_2SiF_3$	−90.9	−136.91	233.8	4.00	8.43; 8.36	1.8
o-$CH_3OC_6H_4COOCH_2SiF_3$	−96.3	−136.42	226.1	3.82	8.08; 6.96	1.5
o-$ClC_6H_4COOCH_2SiF_3$	−92.1	−136.83	231.0	3.94	8.09; 6.94	1.8
$ClCH_2SiF_3$	−71.3	−143.99	267.0	3.21	–	2.6
p-$CH_3OC_6H_4COOCH_2Si(OCH_2CH_3)_3$	−56.9	–	–	3.93	7.90; 6.81	–
p-$BrC_6H_4COOCH_2Si(OCH_2CH_3)_3$	−57.4	–	–	3.97	7.84; 7.49	–
p-$CH_3C_6H_4COOCH_2Si(OCH_3)_3$	−52.76	–	–	–	–	–
p-$FC_6H_4COOCH_2Si(OCH_3)_3$	−54.1	–	–	–	–	–
p-$ClC_6H_4COOCH_2Si(OCH_3)_3$	−53.3	–	–	–	–	–

Second, ^{29}Si chemical shifts of compounds I are essentially dependent on the nature of substituent X in the aromatic ring in spite of their distance from the indicator centre. An increase in the π- and σ-withdrawing power of substituent X increases ^{29}Si screening in I. A linear relation exists between ^{29}Si shifts of *p*-substituted compounds I and the Hammett parameter σ_p of the substituent X:

$$\delta_{Si} = -94.9 + (5.168 \pm 0.069)\sigma_p \quad r = 0.999 \quad s = 0.058 \quad n = 7 \qquad (1)$$

(r is the correlation coefficient, s is the dispersion and n is the number of points)

An analogous relationship for all compounds I studied, including the *ortho*-substituted ones, is reflected in the following equation:

$$\delta(Si) = -94.6 + (5.110 \pm 0.571)\sigma \quad r = 0.948 \quad s = 0.558 \quad n = 9 \qquad (2)$$

In contrast, the nature of substituent X does not much affect ^{29}Si chemical shifts of (aroyloxymethyl)trialkoxysilanes, $XC_6H_4COOCH_2Si(OR)_3$ (III), which are formal analogs of species I but contain a tetracoordinate silicon atom [9]. ^{29}Si screening of compounds II tends to increase with enhancement of the withdrawing ability of substituents X. The above tendency is similar to that [12–14] observed for molecules of the type $RSiY_3$ where Y is an electronegative substituent.

Both these features of the ^{29}Si screening in compounds I provide strong evidence [9] for their intramolecular Si ← O interaction remaining intact upon dissolution. Indeed, an extension of the silicon coordination number in derivatives of this element is always reflected in ^{29}Si NMR spectra as an upfield shift relative to that observed for the corresponding tetrahedral analogs [12–14]. The origin of this effect of substituent X on the ^{29}Si chemical shift for I is the influence of X on the degree of Si ← O coordination, i.e. an increase in the electron-withdrawing ability of substituent X raises the nucleophilicity of the carbonyl group and the Si ← O bond strength, thus increasing the ^{29}Si nuclei screening. Such an interpretation confirms the order of the change of Si ← O bond strength with variation of substituent X in (aroyloxymethyl)trifluorosilanes (I), based on the analysis of the carbonyl group stretching vibrations [9]. Strong evidence for the above conclusion is offered by the influence of substituent X on the stereodynamic mobility of I as will be discussed below.

^{19}F NMR parameters

In terms of the hypervalent bond model [16] the pentacoordination and trigonal-bipyramidal configuration of silicon in I are due to involvement of sp^2-hybrid silicon atomic orbitals in the formation of equatorial bonds (with two fluorine and α-carbon atoms) as well as utilization of the p_z-orbital for the axial hypervalent bonding (with one fluorine atom and the carbonyl oxygen). The distinction in the nature of axial and equatorial Si–F bonds should cause a significant difference between $^{19}F_a$ and $^{19}F_e$ chemical shifts as well as spin-spin coupling of these nuclei with ^{29}Si. However, only one signal with ^{29}Si satellite lines has been observed in ^{19}F NMR spectra of solutions of compounds I at room temperature. This means that under these conditions a rapid (on the NMR time scale) F_a–F_e intramolecular exchange occurs due to silicon pseudorotation and/or successive Si ← O cleavage and bonding. The only evidence for silicon pentacoordination in molecules I consists of strong downfield ^{19}F shifts with lower absolute values of $^1J(^{29}Si-^{19}F)$ of species I compared to those observed for the model compound (chloromethyl)trifluorosilane (Table 1).

Such a change in spectral parameters is rather typical of penta- and hexa-coordinate silicon derivatives [17,18]. As the temperature lowers to 173 K the F_a–F_e exchange rate in I decreases and the spectra undergo a transformation of the average ^{19}F signal into a triplet and a doublet with relative intensities 1 and 2. Similarly to other pentacoordinate silicon [17] and phosphorus [19] derivatives, the axial fluorine triplet is downfield and the equatorial fluorine doublet is upfield relative to the averaged signal, the value of the two-bond $^{19}F_a$–$^{19}F_e$ coupling being 45–50 Hz (Table 2). The value of $^1J(\text{Si–F}_a)$ for compounds I is higher than that of $^{19}F_e$–^{29}Si coupling (i.e. X = H, $^1J(\text{Si–F}_a)$ and $^1J(\text{Si–F}_e)$ are 239 and 211 Hz, respectively).

Independently of the fact whether the fluorine exchange mechanism involves trigonal-bipyramidal silicon pseudorotation or successive Si ← O cleavage and bonding, the values of activation free energies of this process (measured at the coalescence temperature) are indicative. They, undoubtedly, follow the same trend as the Si ← O bond strength in I. The observed results (Table 2) show that the stereodynamic stability of molecules I and intramolecular coordination strength increase with increasing electron donating ability of substituent X. However, the relationship between the ΔG^* values and the Hammett constants of substituent X is non-linear (Fig. 1). The comparison of the ΔG_c^* values for compounds I with those evaluated from Corriu's data [7] for 2-(*N*,*N*-dimethylaminomethyl)phenyltrifluorosilanes (9.9 kcal/mol) indicates a larger stereodynamic stability and, consequently, a stronger coordinate (Si ← N) bond in molecules of the latter.

^{19}F chemical shifts of the axial fluorine atom (Table 2) are linearly dependent on the Hammett substituent constants, σ_p^0:

$$\delta(F_a) = -127.43 - (2.23 \pm 0.24)\sigma_p^0; \quad r = 0.961 \quad s = 0.20 \quad n = 7 \qquad (3)$$

the $^{19}F_a$ resonance being shifted downfield by the electron-releasing effect of substituent X. These data also indicate that the Si ← O bond strength increases in the series I with an increase in the π- and σ-donating ability of substituent X. In contrast, ^{19}F chemical shifts of equatorial fluorine atoms are almost independent of the nature of substituent X. One may note only a slight tendency towards the

TABLE 2

^{19}F NMR CHEMICAL SHIFTS (δ, ppm) AND $^2J(F_a\text{–}F_e)$ COUPLING CONSTANTS (Hz) OF $XC_6H_4COOCH_2SiF_3$ (I)[a] AND FREE ENERGY OF ACTIVATION OF PSEUDOROTATION OF THE Si ATOM AT COALESCENCE TEMPERATURE

X	$\delta(F_e)$	$\delta(F_a)$	$^2J(F_a\text{–}F_e)$	T_c(K)	ΔG_c^* (±0.2) (kcal/mol)
p-CH_3O	−140.94	−126.74	47.0	213	9.0
p-CH_3	−140.89	−127.16	50.0	198	8.5
H	−140.69	−127.43	50.0	198	8.4
p-F	−140.72	−128.19	50.0	188	7.6
p-Cl	−140.55	−127.97	48.0	183	8.3
p-Br	−140.57	−127.91	47.0	183	8.3
p-O_2N	−140.39	−129.10	45.0	168	7.1
o-CH_3O	−140.74	−127.14	50.0	193	8.3
o-Cl	−140.40	−128.48	50.0	173	7.4

[a] In the solvent mixture $CCl_4 : CHCl_3 : CH_2Cl_2 = 13:27:60$ at $T \leqslant 150$ K.

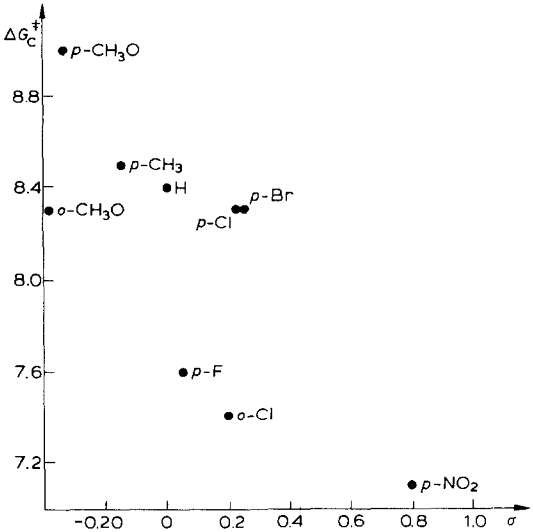


Fig. 1. Relationship between ΔG_c^* and Hammett constants σ of substituent X in $XC_6H_4COOCH_2SiF_3$.

increasing $^{19}F_e$ screening value in compounds I with electron-releasing substituents.

Thus the sensitivity of the axial fluorine chemical shifts to the nature of substituent X in compounds I is greater than that of the equatorial ones. This supports the predominant *trans* effect of the substituent attached to the pentacoordinate silicon atom, i.e. strengthening of one of the components ($Si \leftarrow O$) of the axial hypervalent $F\text{-}Si \leftarrow O$ bond upon variation in substituent X weakens the other component (F–Si) without any substantial change in the equatorial $Si{-}F_e$ bond state. The *trans* effect in silatranes has been reported previously [20] and appears to be a general feature of pentacoordinate silicon compounds.

Temperature and solvent effects

^{29}Si and ^{19}F chemical shifts as well as $^1J(Si{-}F)$ values of compounds I are linearly dependent on temperature. Table 3 shows the results of the least square root statistical treatment of the corresponding relationships

$$a_i = a_o + bT \text{ where } a_i = \delta \text{ or } J \qquad (4)$$

The signs of coefficients in these equations indicate $Si \leftarrow O$ bond weakening with increasing temperature. For compounds I in the same solvent, the sensitivity of any parameters a_i to temperature (the coefficient b value) increases with decreasing donating ability of substituent X. The replacement of a solvent of low polarity, C_6H_5Cl, by the more polar $C_6H_5NO_2$ reduces the values of coefficient b in the corresponding $\delta(Si) \sim f(T)$ relationships. In this case, NMR parameters of compounds I with $X = p\text{-}CH_3O$ or p-F display a smaller change than the corresponding NO_2 derivative does. These facts, along with the comparison of $\delta(Si)$ in different solvents at constant temperature show a stronger $Si \leftarrow O$ interaction in solvents of higher polarity. These data indicate also a decrease in the influence of external factors (solvent polarity and temperature) upon the $Si \leftarrow O$ bond as the latter is strengthening under the effect of substituent X. The linear $\delta(Si)\text{-}f(T)$ relationship is

TABLE 3

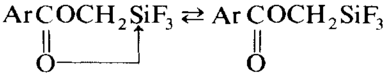
CORRELATION OF NMR SPECTRAL PARAMETERS FOR $XC_6H_4COOCH_2SiF_3$ WITH TEMPERATURE (see text, eq 4)

X	Parameter measured	Solvent	a_0	b [a]	r	s	Temperature range (K)	n
p-CH_3O	δ(Si)	C_6H_5Cl	−96.0	0.022	0.997	0.062	303–403	11
		$C_6H_5NO_2$	−96.0	0.018	0.995	0.063	303–403	11
p-F	δ(Si)	C_6H_6Cl	−94.3	0.030	0.997	0.074	303–403	11
		$C_6H_5NO_2$	−94.3	0.025	0.999	0.044	303–403	11
p-O_2N	δ(Si)	C_6H_5Cl	−91.4	0.043	0.997	0.094	303–393	10
		$C_6H_5NO_2$	−91.9	0.036	0.999	0.062	303–403	11
p-CH_3O	δ(F)	C_6H_5Cl	−135.37	−0.012	0.999	0.014	313–393	7
		$C_6H_5NO_2$	−134.42	−0.011	0.999	0.012	313–373	5
p-F	δ(F)	C_6H_5Cl	−135.23	−0.014	0.999	0.017	313–383	7
		$C_6H_5NO_2$	−134.81	−0.012	0.999	0.013	313–373	5
p-O_2N	δ(F)	C_6H_5Cl	−135.57	−0.015	0.997	0.025	313–373	6
		$C_6H_5NO_2$	−135.00	−0.014	0.999	0.019	313–403	6
p-CH_3O	^1J(Si–F)	$C_6H_5NO_2$	222	0.050	0.988	0.16	313–373	5
p-F	^1J(Si–F)	C_6H_5Cl	225	0.100	0.993	0.46	313–433	6
		$C_6H_5NO_2$	225	0.063	0.987	0.21	313–373	5

[a] Standard deviation of b is 0.002, 0.000 and 0.005 for δ(Si), δ(F) and J(Si–F), respectively.

valid in CH_2Cl_2 or in a mixture of solvents ($CH_2Cl_2 + CCl_4 + CHCl_3$) at temperature below 303 K. A deviation from the linear relationship is observed only in the temperature range near the freezing point of the solvents (below 183 K for a mixture of solvents and 203 K for CH_2Cl_2).

It is not certain whether the changes in NMR parameters and weakening of the coordinate Si ← O bond in I under external factors are caused by bond lengthening without breakage (as is the case in silatranes [21]) or a right-hand shift of the following equilibrium:



$$\mathrm{Ar\underset{\underset{O}{\|}}{C}OCH_2SiF_3} \rightleftarrows \mathrm{Ar\underset{\underset{O}{\|}}{C}OCH_2SiF_3}$$

The former is probable since appreciable (> 5%) amounts of uncoordinated forms of I were found by IR spectroscopy in only the vapour phase at $T \geqslant 420$ K [9]. Therefore we are prone to believe that the NMR temperature effects are due to only the change in the Si ← O bond length and the degree of electron transfer in compounds I.

Complexes of compounds I with organic base

As we have already shown the solvent polarity has a minor influence on ^{29}Si chemical shifts of compounds I (± 1.5 ppm). At the same time, ^{29}Si screening of this compound increases by 30–40 ppm at 293 K in solutions of strong organic bases such as DMSO or HMPTA (Table 4). Such a change in $\delta(Si)$ values, as well as the weakening of Si ← O coordination in these media observed recently by IR spectroscopy [9] confirms the complexing of (aroyloxymethyl)trifluorosilanes with the above organic bases. ^1H NMR titration of (benzoyloxymethyl)trifluorosilane with HMPTA in CH_2Cl_2 solution at 203 K could only be intepreted by assuming the formation of both 1 : 1 and 1 : 2 adducts (Fig. 2). This is in contrast to a model compound (chloromethyl)trifluorosilane (II) which exhibits a well-defined tendency towards 1 : 2 complexing with HMPTA. The almost constant values of ^{29}Si chemical shifts of compounds I (X = H) and II in HMPTA solution are consistent with a similar silicon coordination in their analogs under the above conditions. Hexacoordination of the silicon atom in I can be realized in two ways: (i) retention of intramolecular Si ← O coordination and complexing with only one molecule of a base or (ii) Si ← O bond breakage and the formation of an adduct with two molecules of an organic base. The stability of adducts of Lewis bases with compounds I and II in CH_2Cl_2 is low. At higher temperatures the spectroscopic titration curves become less informa-

TABLE 4

SOLVENT EFFECT ON ^{29}Si CHEMICAL SHIFT OF (BENZOYLOXYMETHYL)TRIFLUOROSILANE AT ROOM TEMPERATURE

Solvent	$\delta(Si)$ (ppm)
CCl_4	−92.0
C_6H_5Cl	−94.4
$CHCl_3$	−94.0
CH_3CN	−94.5
DMSO	−132.0
HMPTA	−126.9

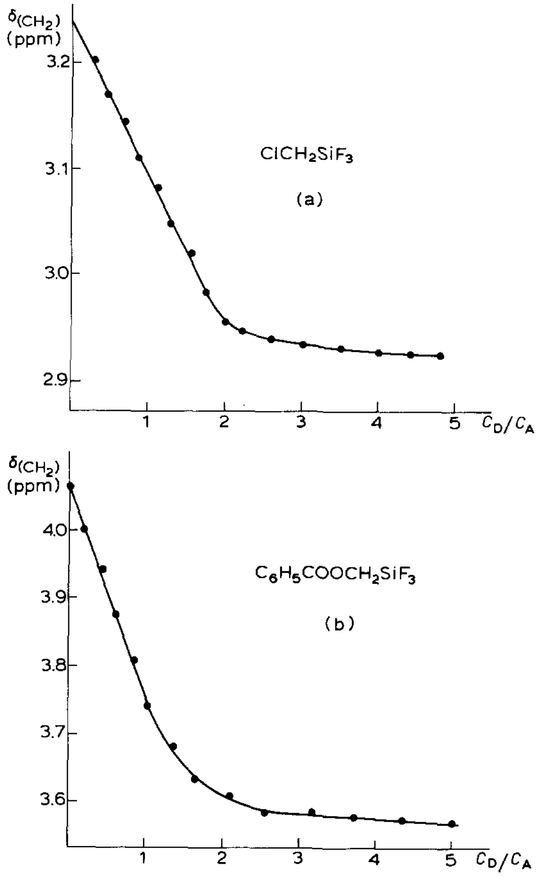


Fig. 2. ^{1}H NMR spectroscopic titration of $ClCH_2SiF_3$ (a) and $C_6H_5COOCH_2SiF_3$ (b) with HMPTA in CH_2Cl_2 solution at 203 K.

tive and do not allow one to distinguish the composition of the complexes at even 233 K.

The structure of (aroyloxymethyl)trifluorosilane analogs of the type $RCOO(CH_2)_m$-$SiF_n(CH_3)_{3-n}$ ($R = CH_3$, C_4H_3S, $C_6H_5CH{=}CH$, $m = 1$, $n = 3$; $R = Ar$, $m = 1$, $n = 1,2$; $R = C_6H_5$, $m = 3$, $n = 3$) and 1-(aroyloxymethyl)silatranes

The comparison of spectral parameters of compounds IV, V and VI (Table 5) with those of I reveals the pentacoordination of silicon in all these compounds. The replacement of the phenyl radical in I with a styrol, α-thienyl or methyl radical does not much affect ^{19}F and ^{29}Si NMR spectral parameters and, consequently, the coordinate Si ← O bond strength. This is also confirmed by a similar stereodynamic lability of molecules I and IV–VI (Table 5). In contrast, the replacement of one of fluorines attached to the silicon atom by a methyl group in (aroyloxymethyl)trifluorosilanes decreases the Si ← O bond strength. Indeed, non-equivalence between the axial and equatorial ^{19}F nuclei in methyl(aroyloxymethyl)difluorosilanes (VIII or IX) could not be observed even at 143 K. An analogous effect was observed earlier in going from $2\text{-}(CH_3)_2NCH_2C_6H_4SiF_3$ to $2\text{-}(CH_3)_2NCH_2C_6H_4Si(CH_3)_2F$ [7].

TABLE 5

NMR SPECTRAL PARAMETERS FOR SOME ANALOGS OF COMPOUNDS I AND THEIR MODEL COMPOUNDS IN CH_2Cl_2

Compound	Formula	δ(Si)	$\delta(CH_3)$	$\delta(CH_2)$	δ(F) (ppm) (aver.)	^1J(Si–F) (aver.) (Hz)	$\delta(F_e)$[a]	$\delta(F_a)$[a]	$^2J(F_a-F_e)$ (Hz)	T_c(K)	$\Delta G_c^{\neq}$ (kcal/mol)
IV	$C_6H_5CH{=}CHCOOCH_2SiF_3$	−96.3	–	3.74	−136.52	225.6	−140.84	−126.94	50.0	198	8.5
V	$C_4H_3SCOOCH_2SiF_3$	−94.1	–	3.86	−136.50	227.0	−140.60	−127.44	50.0	193	8.3
VI	$CH_3COOCH_2SiF_3$	−95.0	–	3.69	−136.73	224.0	−141.24	−127.63	50.0	198	8.5
VII	$C_6H_5COOCH_2CH_2CH_2SiF_3$	−58.1	–	1.09	–	295.0	–	–	–	–	–
VIII	p-$CH_3C_6H_4COOCH_2$-$SiCH_3F_2$	−29.8	0.54	3.76	−132.38	279.0	–	–	–	–	–
IX	$C_6H_5COOCH_2SiCH_3F_2$	−28.0	0.54	3.81	−133.00	274.0	–	–	–	–	–
X	$ClCH_2SiCH_3F_2$	−9.0	0.46	2.76	−138.54	300.0	–	–	–	–	–
XI	$C_6H_5COOCH_2Si(CH_3)_2F$	22.9	0.27	3.89	−158.17	282.0	–	–	–	–	–
XII	$ClCH_2Si(CH_3)_2F$	24.8	0.33	2.78	−161.56	287.0	–	–	–	–	–

[a] $T \leqslant 150$ K.

TABLE 6. ^1H AND ^{29}Si CHEMICAL SHIFTS OF 1-(AROYLOXYMETHYL)SILATRANES, $XC_6H_4COOCH_2\overline{Si(OCH_2CH_2)_3N}$ (XIII) IN $CDCl_3$ AT ROOM TEMPERATURE

X	δ(Si) (ppm)	δ(^{1}H) (ppm)				
		CH_2N	CH_2O	CH_2Si	aryl ring	CH_3
p-CH_3O	−79.2	2.89	3.83	3.81	8.03; 6.86	3.81
p-CH_3	−78.5	2.89	3.85	3.81	7.95; 7.15	2.35
H	−78.7	2.89	3.85	3.81	8.11; 7.28	–
p-F	−78.8	2.90	3.85	3.83	8.08; 7.01	–
p-Cl	−79.0	2.90	3.85	3.84	8.00; 7.31	–
p-Br	−79.1	2.90	3.85	3.84	7.94; 7.48	–
p-O_2N	−79.3	2.93	3.87	3.88	8.25; 8.18	–

Screening of the ^{29}Si and ^{19}F nuclei as well as ^{29}Si–^{19}F coupling constants of dimethyl(benzoyloxymethyl)fluorosilanes (XI) and dimethyl(chloromethyl)fluorosilane (XII) are almost the same which indicates a very weak, if any, coordinate Si ← O interaction in the former.

Insertion of a $-CH_2-CH_2-CH_2O$ bridge between silicon and the carbonyl group makes impossible the formation of intramolecular Si ← O coordination in the molecule (VII) because seven-membered rings are known to be sterically more strained than are five-membered species. The tetrahedral structure of the silicon atom in this molecule (VII) is demonstrated by the δ(Si) and *J*(Si–F) values (Table 5).

The typical values of the atrane ring proton chemical shifts [18] of (aroyloxymethyl)silatranes (XIII) (Table 6) as well as the similar δ(Si) values for these compounds and 1-(chloromethyl)silatrane (XIV) (−79.9) are consistent with the absence of any additional coordination between the silicon and carbonyl oxygen atoms in compound XIII. This fact has been recently established by X-ray diffraction for crystals of silatrane XIII with X = *p*-F [10]. ^{29}Si screening in molecules XIII is almost independent of the nature of substituent X. This also shows that silicon is not capable of hexacoordination in these molecules.

Experimental

Syntheses and physico-chemical constants of the compounds studied have been reported recently [8–11,22]. NMR and ^1H-(^{29}Si) INDOR spectra were obtained with a BS 487C Tesla spectrometer equipped with a heteronuclear double resonance device [23] and an Sigma accumulator. Spectra were recorded for 0.1 *M* solutions, TMS and C_6F_6 were used as internal standards for ^1H, ^{29}Si and ^{19}F NMR, respectively. The accuracy of chemical shift measurements is ±0.01 ppm for ^1H and ^{19}F and ±0.1 ppm for ^{29}Si. The ^{19}F–^{19}F and ^{29}Si–^{19}F coupling constants were measured with an accuracy of ±1 Hz. The $\Delta G_c^{\neq}$ values were estimated using an approximation method [24]. The values of the Hammett constants were taken from the literature [25–26].

Conclusion

The silicon atom of (aroyloxymethyl)trifluorosilanes, $XC_6H_4COOCH_2SiF_3$ (I), in solution is pentacoordinate due to intramolecular Si ← O bonding as demonstrated by ^{1}H, ^{19}F and ^{29}Si NMR spectroscopy. The strength of the Si ← O bond increases with increasing π- and σ-donating ability of substituent X and the polarity of the medium, but with decreasing temperature. The free energy of activation of pseudorotation of the trigonal-bipyramidal silicon atom in I is 7–9 kcal/mol at 170–200 K. Compounds I form unstable 1 : 1 and 1 : 2 adducts with DMSO and HMPTA. The replacement of one or two fluorine atoms in I by methyl groups substantially weakens the coordinate Si ← O bond. Such a bond is absent in molecules of (aroyloxymethyl)silatranes. The intramolecular Si ← O bond strength in molecules of $RCOOCH_2SiF_3$ with $R = CH_3$, $C_6H_5CH{=}CH$ and C_4H_3S is of the same order as that in molecules I.

References

1 M.F. Larin, Thesis of Candidate Dissertation, Irkutsk, 1977.
2 V.A. Pestunovich, M.F. Larin, A.I. Albanov, L.P. Ignatyeva and M.G. Voronkov, Dokl. Akad. Nauk SSSR, 247 (1979) 393.
3 K.D. Onan, A.T. Phail, C.H. Yoder and R.W. Hillyard, J. Chem. Soc. Chem. Commun., (1978) 209.
4 R.W. Hillyard, C.M. Ryan and C.H. Yoder, J. Organometal. Chem., 153 (1978) 369.
5 V.A. Pestunovich, A.I. Albanov, M.F. Larin, M.G. Voronkov, E.P. Kramarova and Yu. I. Baukov, Izv. Akad. Nauk SSSR, Ser. Khim., (1980) 2178.
6 R.J.P. Corriu, G. Royo and A.D. Saxcè, J. Chem. Soc. Chem. Commun., (1980) 892.
7 C. Brelière, F. Carré, R.J.P. Corriu, A.D. Saxcé, M. Poirier and G. Royo, J. Organometal. Chem., 205 (1981) C1.
8 M.G. Voronkov, A.A. Kashaev, E.A. Zel'bst, Yu. L. Frolov, V.M. Dyakov and L.I. Gubanova, Dokl. Akad. Nauk SSSR, 247 (1979) 1147.
9 M.G. Voronkov, Yu. L. Frolov, V.M. Dyakov, N.N. Chipanina, L.I. Gubanova, G.A. Gavrilova, L.V. Klyba and T.N. Aksamentova, J. Organometal. Chem., 201 (1980) 165.
10 E.A. Zel'bst, V.E. Shklover, Yu. T. Struchkov, Yu. L. Frolov, A.A. Kashaev, L.I. Gubanova, V.M. Dyakov and M.G. Voronkov, Zh. Strukt. Khim., 22 (1981) 82.
11 E.A. Zel'bst, V.E. Shklover, Yu.T. Struchkov, A.A. Kashaev, L.I. Gubanova, V.M. Dyakov, Yu.L. Frolov and M.G. Voronkov, Dokl. Akad. Nauk SSSR, 259 (1981) 1369.
12 J. Schraml and J.M. Bellama, Determination of Organic Structures by Physical Methods, Vol. 6 (1976) p. 203.
13 E.A. Williams and J.D. Cargioli, Annual Reports of NMR-Spectroscopy Chem. Soc., London. Vol. 9, 1979 p. 221.
14 H. Marsmann, in P. Dichl, E. Fluck, R. Kosfeld (Eds) NMR Basic Principles and Progress Springer Verlag, Berlin-Heidelberg-New York. Vol. 17, 1981 p. 65.
15 J. Schraml, Nguyen-Due-Chuy, P. Novak, V. Chvalovsky, M. Mägi and E. Lippmaa, Coll. Czech. Chem. Commun., 43 (1978) 3202.
16 J.I. Musher, Angew. Chem., Intern. Ed., 8 (1969) 54.
17 F. Klanberg and E.L. Muetterties, Inorg. Chem., 7 (1968) 155.
18 V.A. Pestunovich, S.N. Tandura, M.G. Voronkov, V.P. Baryshok, G.I. Zelchan, V.I. Glukhikh, G. Engelhardt and M. Witanovski, Spectroscop. Lett., 11 (1977) 333.
19 W. Mahler, R. Schmutzler and E.L. Muetterties, Inorg. Chem., 2 (1963) 613.
20 V.F. Sidorkin, V.A. Pestunovich and M.G. Voronkov, Dokl. Akad. Nauk SSSR, 235 (1979) 1363.
21 V.A. Pestunovich, B.Z. Sterenberg, E.T. Lippmaa, M. Mägi, M.A. Alla, S.N. Tandura, V.P. Baryshok, L.P. Petukhov and M.G. Voronkov, Dokl. Akad. Nauk SSSR, 258 (1981) 1410.
22 M.G. Voronkov, L.I. Gubanova and V.M. Dyakov, Zh. Obshch. Khim., 45 (1975) 1903.
23 M.F. Larin and B.Z. Sterenberg, Zavod. Lab., 45 (1979) 721.
24 G. Binsch, Topics in Stereochemistry, New York. Vol. 3, 1968 p. 97.
25 S. Ehrenson, R.T.C. Brownlee and R.W. Taft. Progress in Physical Organic Chemistry. Vol. 10, 1973 p.1.
26 C.D. Johnson, The Hammett Equation, Cambridge University Press, 1973.