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SYNTHESIS AND SOME CHEMICAL PROPERTIES OF 2,2-DIMETHYL-4-R-1-OXA-4-AZA-2-SILA-5-BENZOCYCLOHEPTANONES*

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One-pot synthesis of 2,2-dimethyl-4-R-1-oxa-4-aza-2-sila-5-benzocycloheptanones (R = Me, CH_2SiMe_2Cl) from the N-methylamide of salicylic acid and salicylamide, respectively, by treatment of these amides with a mixture of hexamethyldisilazane and dimethylchloromethylchlorosilane was developed. The hydrolysis and other nucleophilic substitution reactions of the resultant seven-membered silacyclanes were studied. In the case of the silacyclane with R = Me, hydrolysis leads to the corresponding disiloxane, while the silacyclane with R = CH_2SiMe_2Cl gives either 2,2,6,6-tetramethyl-4-(2-hydroxybenzoyl)-2,6-disilamorpholine or its hydrochloride, depending on the reaction conditions. The chlorine atom was replaced by fluorine in the silacyclane with R = CH_2SiMe_2Cl. The structures of 2,2,6,6-tetramethyl-4-(2-hydroxybenzoyl)-2,6-disilamorpholine and its hydrochloride as well as 2,2-dimethyl-4-R-1-oxa-4-aza-2-sila-5-benzocycloheptanones (R = CH_2SiMe_2Cl, CH_2SiMe_2F) were confirmed by X-ray diffraction.

Keywords: 1-oxa-4-aza-2-silacyclanes, hexamethyldisilazane–dimethylchloromethylchlorosilane system, pentacoordinated silicon compounds, intramolecular coordination.

We have already described the general strategy for the synthesis of 1-oxa-4-aza-2-silacyclanes including 2-sila-5-morpholinones and 4-acyl-2-silamorpholines [1-3], 4-acyl-2,6-disilamorpholines [1, 4], and 4-acyl-2,6-disilapiperazines [5] using unsaturated and functionally-substituted amides of carboxylic acids and dimethylchloromethylchlorosilane as the cyclosilylmethylating agent. The formation of the silacyclanes proceeds through pentacoordination silicon intermediates [1-5], which are highly reactive in nucleophilic substitution reactions relative to model compounds with tetrahedral silicon [6]. The scope of this reaction is not exhausted by the synthesis of six-membered silacyclanes and it may be employed to obtain seven-membered ring analogs, which hold interest in their conformational structure, chemical behavior, and biological activity. Thus, the cyclosilylmethylation of salicylamide derivatives gave 2,2-dimethyl-4-(2-trimethylsiloxyethyl)-1-oxa-4-aza-2-sila-5-benzocycloheptanone, which is a potential corrector of adaptational mechanisms [3], and

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* Dedicated to Academician M. G. Voronkov on the occasion of his eightieth birthday.

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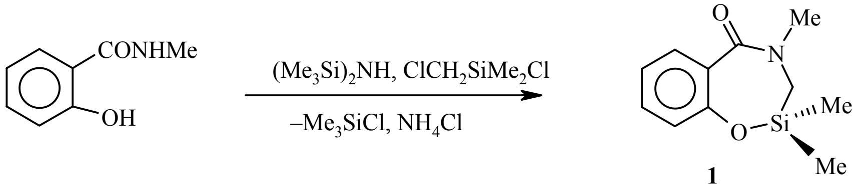
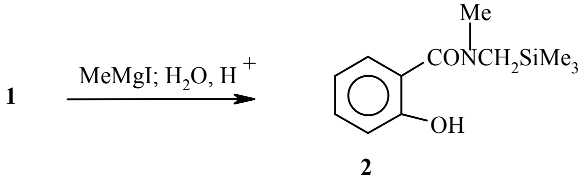
2,2,4-trimethyl-1-oxa-4-aza-2-sila-5-benzocycloheptanone [7]. We should note the recently reported synthesis of seven-membered silaheterocycles, namely, benzosilaoxaazaheptane and silaspirane, upon the action of Me_2SiCl_2 or $SiCl_4$ on the C,O-lithium derivative of N-methyl-N-phenylcolamine [8].

In a continuation of studies on silicon derivatives of salicylamide, we describe a one-step method for the N-chlorosilylmethylation and cyclization of the amide or N-methylamide of salicylic acid by the hexamethyldisilazane–dimethylchloromethylchlorosilane system.

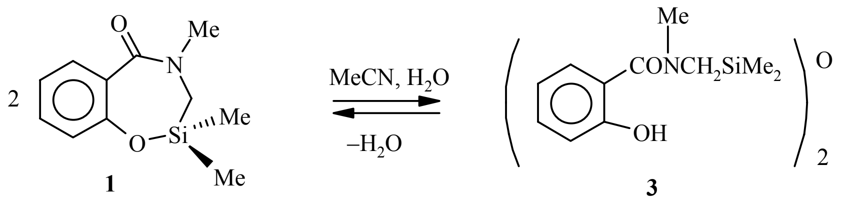
Use of the hexamethyldisilazane–dimethylchloromethylchlorosilane system, which we have already proposed for the N-chlorosilylmethylation of amides and lactams [9], in cyclosilylmethylation reactions simplifies the synthesis of 2-sila-5-morpholinones and 2-sila-4-acylmorpholines by the direct introduction of amides of α-hydroxycarboxylic acids and N-acylcolamides [1]. Analogously, heating N-methylsalicylamide with a mixture of hexamethyldisilazane and dimethylchloromethylchlorosilane gave 2,2,4-trimethyl-1-oxa-4-aza-2-sila-5-benzocycloheptanone (**1**) in a single step and high yield. This compound was obtained in our previous work in the reaction of N,O-bis(trimethylsilyl)-N-methylsalicylamide with dimethylchloromethylchlorosilane [7].



In contrast to other silacyclanes containing an O–Si bond [10], silacyclane **1** does not undergo oligomerization upon storage. Thus, samples of this compound stored for more than a year at room temperature do not show spectral evidence of oligomerization and the molecular mass determined cryoscopically is virtually identical to the calculated value (M_{exp} = 222.2, M_{calc} = 221.33). This compound proved unreactive relative to electrophilic reagents such as Me_3SiCl, acetyl chloride, benzoyl chloride, and acetic anhydride upon heating up to 120°C. However, silacyclane **1** readily reacts with methylmagnesium iodide to give N-trimethylsilylmethyl-N-salicylamide (**2**).



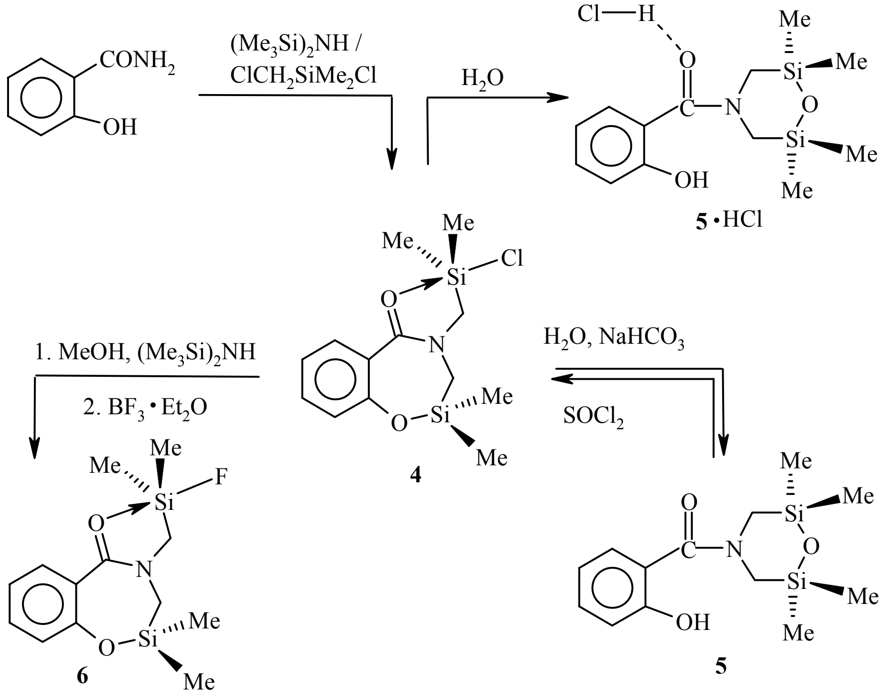
Hydrolysis of silacyclane **1** upon heating it in chloroform at reflux with excess of 10% aqueous sodium carbonate for 5 h is not observed. However, **1** readily dissolved in 10% aqueous KOH upon heating. Acidification of the resultant solution leads to the isolation of the corresponding disiloxane **3** as white crystals. Disiloxane **3** was also obtained upon heating a solution of silacyclane **1** in 1:1 acetonitrile–water at reflux.



A special feature of disiloxane **3** is its tendency to undergo dehydration upon heating to give starting silacyclane **1**. In particular, this transformation occurred in an attempt to fractionate disiloxane **3** in vacuum.

Treatment of salicylamide with an excess of the hexamethyldisilazane–dimethylchloromethylchlorosilane system gave 2,2-dimethyl-4-(dimethylchlorosilylmethyl)-1-oxa-4-aza-2-sila-5-benzocycloheptanone (**4**), which contains one tetracoordinated silicon atom and one pentacoordinated silicon atom (Scheme 1).

Scheme 1



Evidence for the existence of an intramolecular O→Si coordination bond in **4** was found in the IR bands at 1600 and 1523 cm^{-1} and the corresponding signals in the ^{1}H, ^{13}C, and ^{29}Si NMR spectra (Table 1, see the data of our previous work [11]) as well as in X-ray diffraction analysis.

In contrast to silacyclane **1**, the hydrolysis of chloride **4** readily proceeds upon its treatment in chloroform solution with aqueous sodium bicarbonate and leads to 2,2,6,6-tetramethyl-4-(2-hydroxybenzoyl)-2,6-disilamorpholine (**5**) by analogy to the hydrolysis or aminolysis of N,N-bis(dimethylchlorosilylmethyl)amides [2, 5].

Disilamorpholine **5** may also be obtained by a one-pot method from salicylamide upon heating it at reflux with an excess of the hexamethyldisilazane–dimethylchloromethylchlorosilane system and subsequent hydrolysis of resultant chloride **4** without its isolation. However, disilamorpholine **5** readily reconverts to chloride **4** upon treatment with thionyl chloride.

The signals of the $SiMe_2$ and NCH_2 groups in the ^{1}H NMR spectra of compound **5** in deuterochloroform at -60°C appear as two pairs of singlets with equal intensity (Table 1). Warming to room temperature leads to the consecutive broadening of these signals and coalescence into two singlets with averaged chemical shift. Lowering the temperature restores the original spectrum. The observed dynamic process is characteristic for hindered rotation about the amide bond. The barrier for this process established by a dynamic NMR method was 11.3 kcal/mole relative to NCH_2 and 11.6 kcal/mole relative to $SiMe_2$. In the case of $PhC(O)NMe_2$, this barrier

TABLE 1. ^{1}H, ^{13}C and ^{29}Si NMR Spectra of **4-6**

Compound	δ ^{1}H, ppm.		δ ^{13}C, ppm				δ ^{29}Si, ppm
	CH$_3$	CH$_2$	CH$_3$	CH$_2$	C(O)	Ar	
4	0.39	3.10	-2.46	39.74	170.58	152.62 C(O); 121.29 C(CO)	30.4
	0.68*	3.00*	7.24*	47.70*		121.78; 122.96; 130.72; 134.12	-36.3*
5	0.22	3.20	0.06	41.05	169.97	158.15 C(O); 117.98; 118.32; 118.40; 127.95; 131.83	9.7
6	0.39*	2.95	-2.58	39.97	169.48	152.01 C(O); 124.11 C(CO)	28.6
	0.38* (7.8)*^{2}	2.73*	1.63* (22.9)*^{2}	43.09* (40.0)*^{2}		121.38; 122.84; 130.57; 132.88	-17.0* (237.8)*^{2}

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* Group or atom attached to the pentacoordinated silicon atom or signal of the pentacoordinated silicon atom.

*^{2} Coupling constant with the fluorine atom.

is 15.3 kcal/mole [12]. The difference in the hindered rotation barrier by almost 4 kcal/mole is apparently related to several factors, one of which may be the difference in the acidity of the medium in solutions of **5**, which contains a phenolic hydroxyl group.

The hydrolysis of chloride **4** by atmospheric moisture upon its prolonged storage under conditions excluding an external acceptor of hydrogen chloride led to the formation of the 2,2,6,6-tetramethyl-4-(2-hydroxybenzoyl)-2,6-disilamorpholine hydrochloride (**5**·HCl). An X-ray diffraction of this hydrochloride indicated that the oxygen atom of the amide group undergoes protonation rather than the oxygen atom of disiloxane fragment. This behavior is analogous to that observed for adducts of 4-acyl-2,6-disilamorpholines with strong acids [13].

Replacement of the chlorine atom in **4** by a fluorine atom with retention of the silacyclane fragment was carried out by its consecutive treatment with a mixture of methanol and hexamethyldisilazane and then with $BF_3 \cdot Et_2O$ (see scheme 1). This reaction probably proceeds through the intermediate formation of the corresponding silylmethoxide, which, upon treatment with $BF_3 \cdot Et_2O$, is converted into the final product, 2,2-dimethyl-4-(dimethylfluorosilylmethyl)-1-oxa-4-aza-2-sila-5-benzocycloheptanone (**6**).

The existence of a pentacoordinated silicon atom in fluoride **6** was established using its spectral data (see Table 1) and an X-ray diffraction investigation.

Bicyclic derivatives **4** and **6** contain a pentacoordinated silicon atom in five-membered chelate ring $C(O)CH_2SiMe_2X$. The hypervalent X–Si(C$_3$)–O (X = Cl, F) in these compounds was studied in detail for lactams and amides of carboxylic acids [11]. A feature of compounds **4** and **6** is a seven-membered ring condensed at the N–C bond, which is considered a medium-sized ring with increased internal energy (strain). However, this addition does not introduce any significant changes in the nature of hypervalent bonding in this fragment. The NMR spectral parameters for **4** and **6** in low-polarity solvents at low concentration and room temperature indicate intramolecular C=O→Si coordination. Thus, two signals are seen in the ^{29}Si NMR spectrum of each compound. The downfield chemical shifts (30.4 ppm for **4** and 28.6 ppm for **6**) are characteristic for XCH_2SiMe_2OAr derivatives and correspond to a tetracoordinated silicon atom. The two other signals (-36.3 for **4** and -17.0 for **6**) are considerably shifted upfield relative to model tetracoordinated XCH_2SiMe_2Y compounds, for which shielding of the silicon atom is in the range 25±5 ppm, i.e., the second silicon atom in these compounds is pentacoordinated. Similar values for the pentacoordinated silicon atom

δ_{Si} = -39.0 ppm were observed in bis(N-dimethylchlorosilylmethyl)acetamide $CH_3C(O)N(CH_2SiMe_2Cl)_2$, while δ_{Si} = 26.8 ppm in $CDCl_3$ at 20°C for the second tetracoordinated silicon atom in an analogous environment [14].

The pentacoordinated silicon atom in compound **6** has δ_{Si} = -17.0 ppm, which is similar to the chemical shifts of the hypervalent silicon atom in bis(N-dimethylfluorosilylmethyl)acetamide $CH_3C(O)N(CH_2SiMe_2F)_2$, δ_{Si} = -23.5 ppm, while δ_{Si} = 29.0 ppm for the tetrahedral silicon in the same molecule [14]. The decrease in shielding of the ^{29}Si nucleus by 19.2 ppm in going from chloro derivative **4** (δ_{Si} = 36.3 ppm) to fluoro derivative **6** (δ_{Si} = -17.0 ppm) is analogous to that observed for N-(dimethylhalosilylmethyl)-N-(1-phenylethyl)acetamide in $CDCl_3$ at 20°C (δ_{Si} = 18.8 ppm) [15, 16]. Furthermore, the lower direct coupling constant $^1J_{SiF}$ = 237.8 Hz for **6** relative to values 270-290 Hz characteristic for tetracoordinated organosilicon compounds also suggests pentacoordination of the silicon atom.

Comparison of the ^{13}C NMR spectra for compounds **4** and **6** (see Table 1) shows that replacement of a chlorine atom by a fluorine atom leads to increased shielding of the carbon atoms in the $SiMe_2$, $SiCH_2$, and C=O groups by $\Delta\delta^{13}C$ = -5.61 (1.63 - 7.24), -4.61 (43.09 - 47.70), and -1.10 (169.48 - 170.58) ppm, respectively. Analogous behavior is found for O–Si-chelated N-(dimethylhalosilylmethyl)-N-(1-phenylethyl)acetamides: $\Delta\delta^{13}C$ = -5.44, -4.53, -1.58 ppm, respectively, in $CDCl_3$ at 20°C [16].

The ^{1}H NMR spectra correspond to the proposed structures **4-6** (see Table 1 and Experimental).

An X-ray diffraction of halides **4** and **6** showed that one of the two silicon atoms in these compounds is pentacoordinated ($Si_{(1)}$) while the other is tetracoordinated ($Si_{(2)}$). The analogs differ only in the halo substituent at the pentacoordinated silicon atom (Cl in **4** and F in **6**). Nevertheless, these molecules display somewhat different conformations in the crystal although the space groups are the same and the unit cell parameters are quite similar (Table 2).

TABLE 2. Major X-ray Diffraction Parameters for **4, 5, 5**·HCl, and **6**

Parameters	**4**	**5**	**5**·HCl	**6**
Empirical formula	$C_{13}H_{20}ClNO_2Si_2$	$C_{13}H_{21}NO_3Si_2$	$C_{13}H_{22}ClNO_3Si_2$	$C_{13}H_{20}FNO_2Si_2$
T, K	210	290	100	130
a, Å	12.390(4)	9.394(6)	8.036(4)	10.592(5)
b, Å	10.386(3)	12.843(7)	9.674(4)	14.075(5)
c, Å	12.524(4)	15.142(9)	22.00(1)	11.524(5)
α, deg.	90	109.37(4)	90	90
β, deg.	95.48(2)	98.89(5)	99.16(1)	114.50(3)
γ, deg.	90	105.28(5)	90	90
V, Å^3	1604.2(8)	1603(2)	1689(1)	1563(1)
d_{calc}, g·cm^{-3}	1.300	1.225	1.306	1.264
Space group, Z	$P2_1/c$, (4)	$P\bar{1}$, (4)	$P2_1/n$, (4)	$P2_1/c$, (4)
$2\theta_{max}$(°)	52	48	58	52
Scanning	ω/2θ	θ/2θ	ω/2θ	θ/2θ
Number of measured reflections	3247	5081	10338	3051
Number of reflections in least squares calculation	3101	4671	3941	2883
Number of parameters in least squares calculation	252	351	269	252
Absorption coefficient, cm^{-1}	3.85	2.25	3.74	2.35
$R_1(I > 2\sigma(I))$	0.036	0.080	0.078	0.040
wR_2 (all reflections)	0.096	0.258	0.121	0.106

Some difference in the conformations is attributed to the shape of the central seven-membered heterocycle. The torsion angles of the $C_{(10)}{-}O_{(2)}{-}Si_{(2)}{-}C_{(13)}$ differ by 16-26° in these analogs. However, the twist form of this heterocycle with an approximate two-fold axis traversing through $Si_{(2)}$ and the midpoint of the $C_{(4)}{-}C_{(5)}$ bond is the same in these molecules. These conformational differences presumably arise due to the high flexibility of the heterocycle fragment containing the oxygen atom.

On the other hand, the major differences in molecular packing in the crystals of **4** and **6** should be ascribed to the large difference in the Si–Cl and Si–F bond lengths (0.65 Å) and the difference in the van der Waals radii of the chlorine and fluorine atoms (0.4 Å), which leads to a considerable difference in the shape of these molecular analogs in the vicinity of the hypervalent fragment. Despite the difference in packing, a characteristic approximation of the halogen atoms and $Si_{(2)}$ of the adjacent molecule is observed. Specifically, the chlorine and fluorine atoms are found opposite to the $Si_{(2)}{-}O_{(2)}$ bond at distances of 3.86 and 3.31 Å from the silicon atom, which are similar to the corresponding sums of the van der Waals radii (3.8 Å for Cl and Si and 3.4 Å for F and Si) [17]. The crystal of chloride **4** consists of centrosymmetric "dimers" (see Fig. 1), while the analogously contacting molecules in the crystal of fluoride **6** form infinite chains (see Fig. 2). The electrostatic Si···halogen interaction is rather clearly evident here. The slight positive charge on $Si_{(2)}$ is due to the polarity of the Si–O bond. However, the slight lengthening of the $Si_{(2)}{-}O_{(2)}$ bond by 1.67 Å in the structures of **4** and **6** relative to the usual values 1.63-1.64 Å (for example, in the structures of **5** and **5**·HCl, see Tables 3 and 5) is evidently due to very weak intermolecular Hal→Si coordination interactions. The larger expansion of the coordination tetrahedron of $Si_{(2)}$ in **4** and **6** toward $O_{(2)}{-}Si_{(2)}$ ···Hal than in **5** and **5**·HCl also indicates such an interaction (the $Si_{(2)}{-}C_{(11)}{-}C_{(12)}{-}C_{(13)}$ torsion angle in **4** and **6** is 10-17° greater than in **5** and **5**·HCl).

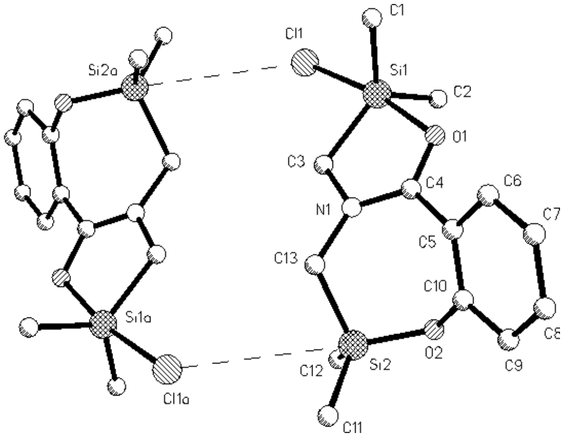

Fig. 1. Molecular structure of **4** in the crystal. Hydrogen atoms are not shown. The short Si···Cl contacts of adjacent molecules are shown by dashed lines.

TABLE 3. Main Bond Lengths (*l*) in **4** and **6**

Bond	*l*, Å		Bond	*l*, Å	
	4	**6**		**4**	**6**
$Cl_{(1)}{-}Si_{(1)}$	2.308(1)		$Si_{(2)}{-}O_{(2)}$	1.671(2)	1.673(2)
$F_{(1)}{-}Si_{(1)}$		1.672(2)	$O_{(1)}{-}C_{(4)}$	1.278(2)	1.259(2)
$Si_{(1)}{-}O_{(1)}$	1.961(1)	2.158(2)	$N_{(1)}{-}C_{(4)}$	1.316(2)	1.332(3)

TABLE 4. Main Bond Angles (ω) in **4** and **6**

Angle	ω, deg.		Angle	ω, deg.	
	4	**6**		**4**	**6**
$\mathrm{Cl(F)_{(1)}{-}Si_{(1)}{-}C_{(1)}}$	94.2(1)	98.5(1)	$\mathrm{C_{(2)}{-}Si_{(1)}{-}O_{(1)}}$	90.3(1)	87.6(1)
$\mathrm{Cl(F)_{(1)}{-}Si_{(1)}{-}C_{(2)}}$	93.7(1)	96.9(1)	$\mathrm{C_{(3)}{-}Si_{(1)}{-}O_{(1)}}$	82.9(1)	79.2(1)
$\mathrm{C_{(1)}{-}Si_{(1)}{-}C_{(2)}}$	118.5(1)	117.9(1)	$\mathrm{O_{(2)}{-}Si_{(2)}{-}C_{(12)}}$	106.6(1)	105.0(1)
$\mathrm{Cl(F)_{(1)}{-}Si_{(1)}{-}C_{(3)}}$	88.0(1)	92.0(1)	$\mathrm{O_{(2)}{-}Si_{(2)}{-}C_{(11)}}$	110.8(1)	110.2(1)
$\mathrm{C_{(1)}{-}Si_{(1)}{-}C_{(3)}}$	119.6(1)	120.6(1)	$\mathrm{C_{(12)}{-}Si_{(2)}{-}C_{(11)}}$	114.6(1)	113.9(1)
$\mathrm{C_{(2)}{-}Si_{(1)}{-}C_{(3)}}$	121.6(1)	118.5(1)	$\mathrm{O_{(2)}{-}Si_{(2)}{-}C_{(13)}}$	102.1(1)	102.0(1)
$\mathrm{Cl(F)_{(1)}{-}Si_{(1)}{-}O_{(1)}}$	170.81(5)	171.2(1)	$\mathrm{C_{(12)}{-}Si_{(2)}{-}C_{(13)}}$	113.4(1)	113.4(1)
$\mathrm{C_{(1)}{-}Si_{(1)}{-}O_{(1)}}$	91.1(1)	86.0(1)	$\mathrm{C_{(11)}{-}Si_{(2)}{-}C_{(13)}}$	108.6(1)	111.4(1)

TABLE 5. Main Bond Lengths in **5** and **5**·HCl

Bond	*l*, Å		Bond	*l*, Å	
	5	**5**·HCl		**5**	**5**·HCl
$\mathrm{Si_{(1)}{-}O_{(1)}}$	1.630(4)	1.636(3)	$\mathrm{Si_{(21)}{-}O_{(21)}}$	1.639(4)	
$\mathrm{Si_{(2)}{-}O_{(1)}}$	1.640(4)	1.637(3)	$\mathrm{O_{(22)}{-}C_{(27)}}$	1.240(7)	
$\mathrm{O_{(2)}{-}C_{(7)}}$	1.216(7)	1.292(5)	$\mathrm{O_{(23)}{-}C_{(29)}}$	1.356(7)	
$\mathrm{O_{(3)}{-}C_{(9)}}$	1.345(7)	1.362(5)	$\mathrm{N_{(21)}{-}C_{(27)}}$	1.355(7)	
$\mathrm{N_{(1)}{-}C_{(7)}}$	1.340(7)	1.297(5)			

The hypervalent fragments in **4** and **6** have the ordinary distorted trigonal bipyramidal configuration. The deviations of the silicon atoms from the plane of the equatorial substituents toward the halogen atom (Δ_{Si}) are 0.06 and 0.19 Å, respectively. Thus, the hypervalent O–Si–Hal bond in fluoride **6** is more asymmetric, which indicates a greater O→Si bond length. The ratios between the lengths of the components of the hypervalent bonds and parameters Δ_{Si} in these structures are in good accord with the relationships found in our previous work [18] for pentacoordinated silicon compounds.

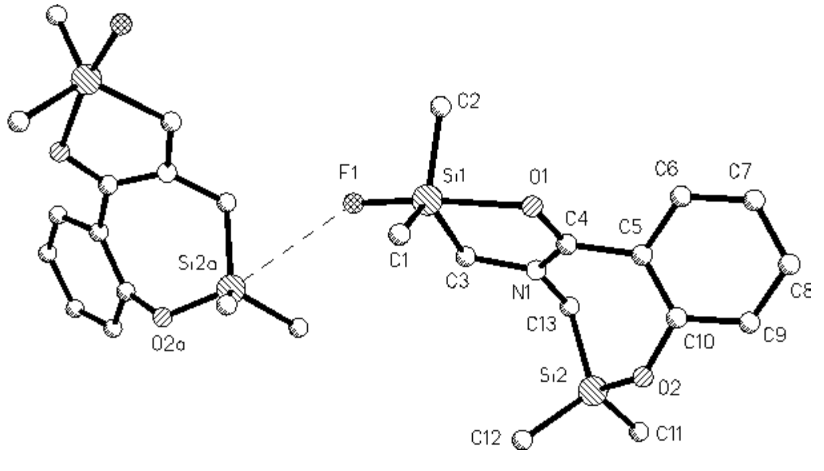

Fig. 2. Molecular structure of **6** in the crystal. Hydrogen atoms are not shown. The short Si···F contact with an adjacent molecule is shown by a dashed line.

TABLE 6. Main Bond Angles in **5** and **5**·HCl

Angle	ω, deg.		Angle	ω, deg.
	5	**5**·HCl		**5**
$O_{(1)}$–$Si_{(1)}$–$C_{(1)}$	110.1(3)	108.5(2)	$O_{(21)}$–$Si_{(21)}$–$C_{(22)}$	107.9(3)
$O_{(1)}$–$Si_{(1)}$–$C_{(2)}$	108.8(3)	112.2(2)	$O_{(21)}$–$Si_{(21)}$–$C_{(21)}$	111.0(3)
$C_{(1)}$–$Si_{(1)}$–$C_{(2)}$	110.7(4)	111.6(3)	$C_{(22)}$–$Si_{(21)}$–$C_{(21)}$	112.3(4)
$O_{(1)}$–$Si_{(1)}$–$C_{(5)}$	105.0(3)	105.7(2)	$O_{(21)}$–$Si_{(21)}$–$C_{(25)}$	105.6(3)
$C_{(1)}$–$Si_{(1)}$–$C_{(5)}$	109.9(4)	108.0(3)	$C_{(22)}$–$Si_{(21)}$–$C_{(25)}$	112.5(3)
$C_{(2)}$–$Si_{(1)}$–$C_{(5)}$	112.3(3)	110.6(2)	$C_{(21)}$–$Si_{(21)}$–$C_{(25)}$	107.4(3)
$O_{(1)}$–$Si_{(2)}$–$C_{(3)}$		112.6(2)	$O_{(21)}$–$Si_{(22)}$–$C_{(23)}$	108.2(3)
$O_{(1)}$–$Si_{(2)}$–$C_{(4)}$		108.1(2)	$O_{(21)}$–$Si_{(22)}$–$C_{(24)}$	109.6(3)
$O_{(1)}$–$Si_{(2)}$–$C_{(6)}$	105.4(3)	104.7(2)	$C_{(23)}$–$Si_{(22)}$–$C_{(24)}$	114.0(3)
$C_{(3)}$–$Si_{(2)}$–$C_{(6)}$	110.4(4)	107.7(2)	$O_{(21)}$–$Si_{(22)}$–$C_{(26)}$	104.0(3)
$C_{(4)}$–$Si_{(2)}$–$C_{(6)}$	110.0(3)	111.9(2)	$C_{(23)}$–$Si_{(22)}$–$C_{(26)}$	110.8(3)
$Si_{(1)}$–$O_{(1)}$–$Si_{(2)}$	129.3(3)	130.3(2)	$C_{(24)}$–$Si_{(22)}$–$C_{(26)}$	109.8(3)
			$Si_{(21)}$–$O_{(21)}$–$Si_{(22)}$	128.8(3)

Disilamorpholine **5** and its hydrochloride **5**·HCl (Figs. 3 and 4) contain six-membered disiloxane heterocycles featuring virtually the same chair conformation with a plane of symmetry traversing the oxygen and nitrogen atoms. The distortion of this symmetry may be evaluated by the difference in absolute values of the corresponding torsion angles over both sides of this plane and was found to be only 2° and 7° for two crystallographically independent molecules of **5** and 6° in hydrochloride **5**·HCl. The corresponding bond lengths and angles in the heterocycles of these compounds are very similar (see Tables 5 and 6).

The crystallographically independent molecules in the structure of **5** differ from each other in the orientation of the plane of the hydroxyphenyl group. Molecule A transforms into B upon rotation of this plane relative to the $C_{(7)}$–$C_{(8)}$ bond by 46°. This conformational difference probably provides for denser packing of the molecules in the crystals by permitting all the OH and C=O groups to participate in hydrogen bonding. The pairs of molecules A and B form centrosymmetric tetrameric hydrogen-bonded aggregates (Fig. 3). The hydrogen bond parameters are as follows: $O_{(3)}\cdots O_{(22)}$, 2.77 Å; $H_{(3)}\cdots O_{(22)}$, 1.93 Å; $O_{(3)}$–$H_{(3)}\cdots O_{(22)}$, 154° and $O_{(23)}\cdots O_{(2a)}$, 2.62 Å; $H_{(23)}\cdots O_{(2a)}$, 1.76 Å; $O_{(23)}$–$H_{(23)}\cdots O_{(2a)}$, 170°. These results indicate medium-strength hydrogen bonds.

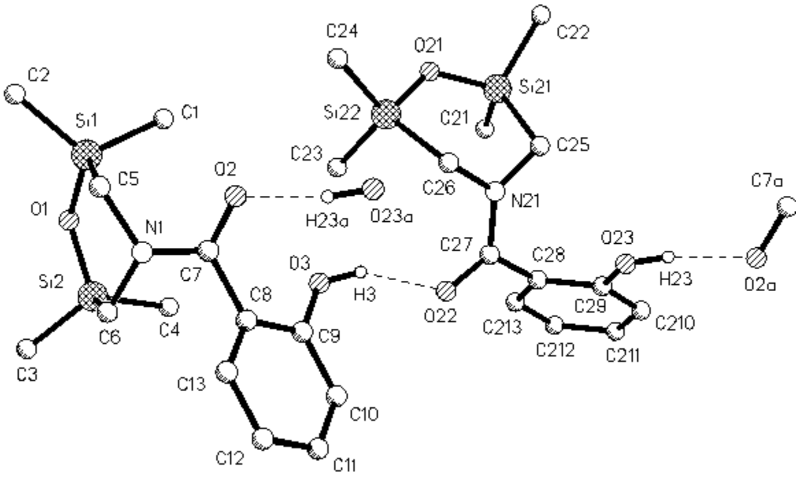

Fig. 3. Crystallographically independent part of the centrosymmetric tetrameric hydrogen-bonded aggregate in the structure of **5**. The hydrogen atoms of the OH groups and hydrogen bonds are shown. The atoms with subscript a belong to the molecules of the second half of the tetramer.

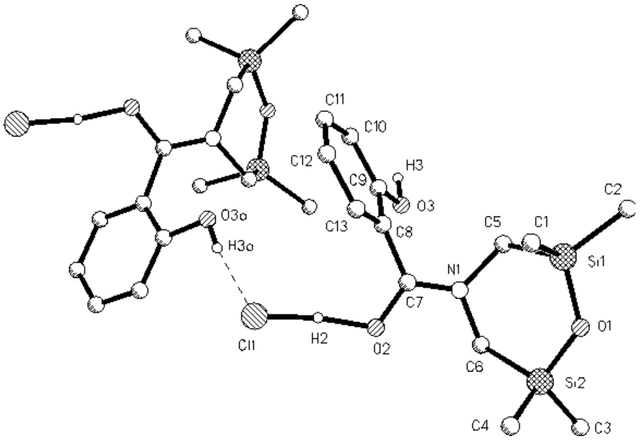

Fig. 4. Structure of hydrochloride **5**·HCl in the crystal.
The hydrogen atoms in the OH and HCl groups are shown. Cl···HO hydrogen bonds connect molecules related by a 0.5 – *x*, 0.5 + *y*, 0.5 – *z* screw axis into chains extending along the *b*-axis.

Only partial, protonation of the $C_{(7)}=O_{(2)}$ group is found in the structure **5**·HCl but it leads to lengthening of this bond by 0.05-0.07 Å relative to the corresponding bond in the structure **5** (see Tables 4 and 5). The lengths of bonds $Cl_{(1)}–H_{(2)}$ (1.49(3) Å) and $O_{(2)}–H_{(2)}$ (1.39(3) Å) are greater than the usual value in the HCl molecule and OH group by 0.2 and 0.4 Å, respectively, i.e., this compound should indeed be considered as an adduct **5**·HCl. In addition to this strong bond with a molecule **5**, the HCl group forms a hydrogen bond $Cl_{(1)}\cdots H_{(3a)}–O_{(3a)}$ with an adjacent molecule (see Fig. 3): $Cl_{(1)}\cdots O_{(3a)}$, 3.048(3) Å; $Cl_{(1)}\cdots H_{(3a)}$, 2.22(4) Å; $Cl_{(1)}\cdots H_{(3a)}–O_{(3a)}$, 170(4)°. These values indicate a medium-strength hydrogen bond. The hydrogen bonds unite the molecules in the crystal **5**·HCl into chains extending along the *b*-axis. The nature of the intermolecular contacts in hydrochloride **5**·HCl will be discussed in a separate communication.

EXPERIMENTAL

The IR spectra were taken neat or in solution in KBr cells on a two-beam Specord IR-75 spectrometer. The ^{1}H, ^{13}C, and ^{29}Si NMR spectra were taken for solutions of the sample compounds in $CDCl_3$ on a Varian XL-400 spectrometer at 400.0, 100.6, and 79.5 MHz, respectively, in a pulse mode with subsequent Fourier transformation and ^{2}H-stabilization of the resonance conditions using TMS as the internal standard.

2,2,4-Trimethyl-1-oxa-4-aza-2-sila-5-benzocycloheptanone (1). A. A sample of dimethylchloromethylchlorosilane (10.2 g, 0.072 mol) was added with stirring to a mixture of N-methylsalicylamide (10.9 g, 0.072 mol) and hexamethyldisilazane (11.6 g, 0.072 mol) in *o*-xylene (30 ml). After 5 h heating the reaction mixture was filtered and the filtrate was evaporated. Fractionation of the residue gave 13.1 g (82%) of compound **1**; bp 180-182°C (8 mm Hg). IR spectrum ($CHCl_3$), ν, cm^{-1}: 1624 (NCO). (Bp 178-180°C (7 mm Hg), IR spectrum ($CHCl_3$), ν, cm^{-1}: 1624 (NCO) [7]).

B. A sample of 1,1,2,2-tetramethyl-1,2-bis(N-methyl-2-hydroxybenzoylamino)methyl]-1,2-disiloxane (**3**) (2.4 g) was added to a distillation flask. Fractionation of this compound in vacuum gave 2.14 g (92%) of compound **1**; bp 179-183°C (8 mm Hg). IR spectrum ($CHCl_3$), ν, cm^{-1}: 1624 (NCO).

N-Methyl-N-trimethylsilylmethylsalicylamide (2). A sample of compound **1** (4.9 g, 0.022 mol) in ether (30 ml) was added with stirring to a solution of methylmagnesium iodide (3.6 g, 0.022 mol) in ether (50 ml). After decomposition of the reaction mixture by adding NH_4Cl/H_2O and distilling off the solvent, recrystallization of the crystalline precipitate from ether gave 4.01 g (77%) of compound **2**; mp 142-143°C (ether). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.05 (9H, s, $SiMe_3$); 2.99 (2H, s, NCH_2Si); 3.35 (3H, s, NMe); 6.40-7.33 (4H, m, C_6H_4); 9.28 (1H, s, OH). Found, %: C 60.65; H 7.90; N 5.97; Si 11.79. $C_{12}H_{19}NO_2Si$. Calculated, %: C 60.72; H 8.07; N 5.90; Si 11.83.

2,2-Dimethyl-4-(dimethylchlorosilylmethyl)-1-oxa-4-aza-2-sila-5-benzocycloheptanone (4). A. A mixture of salicylamide (6.8 g, 0.05 mol), hexamethyldisilazane (19.3 g, 0.12 mol), and dimethylchloromethylchlorosilane (35.5 g, 0.25 mol) in absolute *o*-xylene (50 ml) was heated at reflux with stirring for 10 h. The hot reaction mixture was filtered and the volatile compounds were distilled off. The residue was recrystallized by adding 20 ml *o*-xylene to give 17.7 g (76%) of chloride **4**; mp 118-121°C (*o*-xylene). IR spectrum ($CHCl_3$), ν, cm^{-1}: 1600 and 1523 (NCO), 1580 (Ar). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.39 (6H, s, $OSiMe_2$); 0.68 (6H, s, $SiMe_2Cl$); 3.00 (2H, s, CH_2SiCl); 3.10 (2H, s, NCH_2SiO); 7.12, 7.44, 6.95, 7.49 (4H, t, dt, ddd, C_6H_4). Found, %: C 49.70; H 6.31; Si 17.77. $C_{13}H_{20}ClNO_2Si_2$. Calculated, %: C 49.72; H 6.42; Si 17.89.

The crystals for the X-ray diffraction structural analysis were prepared by recrystallizing **4** from *p*-xylene.

B. A sample of thionyl chloride (1.2 g, 0.01 mol) was added dropwise with stirring to a mixture of compound **5** and *o*-xylene (10 ml). After 24 h, the precipitate formed was filtered off to give 3.0 g (95%) of compound **4**; mp 121-124°C (*p*-xylene). IR spectrum ($CHCl_3$), ν, cm^{-1}: 1600 and 1525 (NCO), 1580 (Ar).

Hydrolysis of 2,2,4-trimethyl-1-oxa-4-aza-2-sila-5-benzocycloheptanone (1). A. A solution of silacyclane **1** (5 g, 0.023 g) in chloroform (10 ml) with aqueous sodium bicarbonate (5 ml) was heated at reflux for 5 h. The organic layer was separated. Chloroform was removed and the residue was fractionated in vacuum to give 4.8 g (96%) of starting **1**; bp 180-182°C (8 mm Hg).

B. A sample of silacyclane **1** (2.5 g, 0.011 mol) was dissolved in 10% aq. KOH (15 ml) with moderate heating. The solution obtained was acidified by adding 0.01 mol/liter sulfuric acid to pH 6. The crystalline residue obtained after 24 h was filtered off to give 1.8 g (72%) of 1,1,2,2-tetramethyl-1,2-bis[(N-methyl-2-hydroxybenzoylamino)methyl]-1,2-disiloxane (**3**); mp 108-109°C. IR spectrum ($CHCl_3$), ν, cm^{-1}: 1597 (NCO). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.04 (6H, s, $2SiMe_2$); 3.15 (2H, s, NCH_2Si); 3.31 (6H, s, 2NMe); 6.42-7.34 (4H, m, C_6H_4); 9.16 (2H, s, 2OH). Found, %: C 58.30; H 7.43. $C_{22}H_{32}N_2O_5Si_2$. Calculated, %: C 57.36; H 7.00.

C. A sample of water (3 ml, 0.16 mol) was added to a solution of silacyclane **1** (2.5 g, 0.011 mol) in acetonitrile (8 ml). The reaction mixture was heated at reflux with vigorous stirring. The solution was cooled and the precipitate formed was filtered off and recrystallized from 1:1 acetonitrile–water to give 2.0 g (77%) of 1,1,2,2-tetramethyl-1,2-bis[(N-methyl-2-hydroxybenzoylamino)methyl]-1,2-disiloxane (**3**); mp 106-108°C. IR spectrum ($CHCl_3$), ν, cm^{-1}: 1597 (NCO).

2,2,6,6-Tetramethyl-4-(2-hydroxybenzoyl)-2,6-disilamorpholine (5). A. A solution of compound **4** (21 g, 0.067 mol) in chloroform (100 ml) was stirred for 2 h with a solution of $NaHCO_3$ (5.6 g) in water (50 ml). The organic layer was separated and the aqueous layer was extracted with chloroform (50 ml). The organic layers were combined and the solvent was removed. The residue was crystallized from toluene (40 ml). The crystalline precipitate formed was separated to give 17.8 g (90%) of compound **5**; mp 150-152°C (toluene). IR spectrum ($CHCl_3$), ν, cm^{-1}: 1637 (NCO), 1600, 1590 (Ar). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm, *J* (Hz): 0.22 (6H, s, $2SiMe_2$); 3.20 (4H, s, $2CH_2$); 6.99 (1H, d, $^3J_{HH}$ = 8.3); 6.83 (1H, t, $^1J_{HH}$ = 8.3); 7.27 (1H, t, $^3J_{HH}$ = 8.3); 7.31 (1H, t, $^3J_{HH}$ = 8.3, Ar); 9.38 (1H, s, OH). Found, %: C 52.79; H 7.14. $C_{13}H_{21}NO_3Si_2$. Calculated, %: C 52.84; H 7.16.

The crystals of **5** for the X-ray diffraction analysis were obtained from toluene.

B. A sample of dimethylchloromethylchlorosilane (35.5 g, 0.25 mol) was added with stirring to a mixture of salicylamide (6.85 g, 0.05 mol), hexamethyldisilazane (20.1 g, 0.125 mol), and toluene (50 ml) and heated at reflux for 8 h. The mixture was filtered and the solvent evaporated. The residue was dissolved in chloroform (50 ml) and stirred with a solution of $NaHCO_3$ (4.2 g) in water (30 ml) for 2 h. The organic layer was separated and the aqueous layer was extracted with chloroform (30 ml). The solvent was removed from the combined organic layers and the residue was crystallized from toluene (30 ml) to give 10.9 g (74%) of compound **5**; mp 150-152°C (toluene). IR spectrum ($CHCl_3$), ν, cm^{-1}: 1637 (NCO), 1600, 1590 (Ar).

2,2,6,6-Tetramethyl-4-(2-hydroxybenzoyl)-2,6-disilamorpholine Hydrochloride (5·HCl). A sample of chloride **4** was stored under conditions excluding atmospheric moisture for six months. The mp changed from 118-121°C (*p*-xylene) to 146-150°C. This product was **5**·HCl. IR spectrum taken on a Specord M82 spectrometer with CaF_2 plates in vaseline mull, ν, cm^{-1}: 1735, 1640 (NCO), 1606, 1573 (Ar). Found, %: C 47.02; H 6.68; N 4.22. $C_{13}H_{22}ClNO_3Si_2$. Calculated, % C 47.04; H 6.68; N 4.22.

The crystals of hydrochloride **5**·HCl for the X-ray diffraction analysis were obtained from benzene.

2,2-Dimethyl-4-(dimethylfluorosilylmethyl)-1-oxa-4-aza-2-sila-5-benzocycloheptanone (6). A mixture of hexamethyldisilazane (1.55 g, 9.6 mmol), methanol (0.31 g, 9.6 mmol), and benzene (10 ml) was added with stirring to a cooled mixture of chloride **4** (1.5 g, 4.8 mmol) and benzene (10 ml). After 24 h, the precipitate of NH_4Cl was filtered off and the reaction mixture was dissolved in benzene (10 ml). Then, $BF_3 \cdot Et_2O$ (0.23 g, 1.6 mmol) was added dropwise with cooling. After 24 h, the reaction mixture was evaporated and diethyl ether (10 ml) was added. The precipitate (0.25 g) was separated. Ether was removed and the residue was recrystallized by adding heptane (10 ml) to give 0.75 g (52%) of compound **6**; mp 102-105°C (ether). IR spectrum ($CHCl_3$), ν, cm^{-1}: 1620, 1578 (NCO), 1600 (Ar). ^1H NMR spectrum ($CDCl_3$), δ, ppm, *J* (Hz): 0.38 (6H, s, $SiMe_2$); 0.39 (6H, s, $SiMe_2$); 2.73 (2H, s, CH_2); 2.95 (2H, s, CH_2); 6.93 (1H, d, $^3J_{HH}$ = 8.3); 7.39 (1H, t, $^3J_{HH}$ = 8.3); 7.10 (1H, t, $^3J_{HH}$ = 8.3); 7.51 (1H, d, $^3J_{HH}$ = 8.3, Ar). Found, %: C 51.98; H 6.94; N 4.21. $C_{17}H_{20}FNO_2Si_2$. Calculated, %: C 52.49; H 6.78; N 4.71.

Crystals of **6** for the X-ray diffraction analysis were obtained from ether.

X-ray Crystallography. The crystal structure parameters and major features of the X-ray diffraction experiments for **4**, **5**, **5**·HCl, and **6** are given in Table 2. The experiments were carried out on Syntex $P2_1$ (**4** and **6**), Siemens P3/PC (**5**), and SMART CCD diffractometers (**5**·HCl) using λMoKα radiation and graphite monochromator. The structures were solved by the direct method and refined by the method of least squares relative to F^2 anisotropically for the nonhydrogen atoms. The hydrogen atoms in the structures of **4**, **5**·HCl, and **6** were revealed in the difference map and refined isotropically. The hydrogen atoms in the structure of **5** were placed in calculated positions and refined by the rider model with fixed temperature parameters U equal to $1.2U_c$ for the CH_2 group and $1.5U_c$ for the methyl groups (U_c is the equivalent temperature parameter of the corresponding carbon atom). A profile analysis was carried out for the reflection data obtained from a crystal of **6** using the PROFIT program [19]. All the calculations were carried out on an IBM PC using the SHELXTL PLUS program package (version 5.0) [20]. The atomic coordinates for these structures have been deposited in the Cambridge Structural Data Bank. The major bond lengths and angles are given in Tables 3-6.

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