Chemistry of Heterocyclic Compounds, Vol.35, No. 8, 1999

SYNTHESIS AND SOME CHEMICAL PROPERTIES OF 4-ACYL-2,6-DISILAPIPERAZINES. MOLECULAR AND CRYSTAL STRUCTURE OF 4-FORMYL-2,2,6,6-TETRAMETHYL-2,6-DISILAPIPERAZINE

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An one-pot synthesis of 4-acyl-2,6-disilapiperazines has been developed which consists of treatment of carboxamides with hexamethyldisilazane and dimethylchloromethylchlorosilane mixture with subsequent amination of the intermediate N,N-bis(dimethylchlorosilylmethyl)amides (which are derivatives of pentacoordinated silicon) with ammonia or primary amines. The hydrolytic stability of the 4-acyl-2,6-disilapiperazines and their reactions with benzenesulfonamide have been studied. The structure of 4-formyl-2,2,6,6-tetramethyl-2,6-disilapiperazine has been confirmed by X-ray diffraction analysis.

The increased activity of pentacoordinated silicon compounds relative to the corresponding tetrahedral analogs in nucleophilic substitution reactions is reflected in a review of the possibility of their wide use for synthetic purposes [1]. In particular we have previously synthesized the almost unstudied earlier heterocyclic systems – the 1-oxa-4-aza-2-silacyclanes from N-monodimethylchlorosilylmethyl derivatives of amides [2-4], and we have obtained 4-acyl-2,6-disilamorpholines for the first time from N,N-bis(dimethylchlorosilylmethyl)amides [2, 5].

In development of these investigations in the present work we have synthesized 4-acyl-2,6-disilapiperazines, studied some of their chemical reactions, and studied one of them by X-ray diffraction analysis method. It should be noted that silicon-containing derivatives of piperazine are of interest with respect to their specific reactivity, their biological activity, and the possibility of using them in practice (see, for example, the review [6] and references cited in it).

The proposed route for the synthesis of 4-acyl-2,6-disilapiperazines is based on the high disposition to cyclocondensation of pentacoordinated dimethyl(amidomethyl)chlorosilanes with an additional functional group at the amide nitrogen atom. We previously used this approach to obtain 4-acyl-2,6-disilamorpholines [2, 5]. Carboxamides, which were converted into the corresponding N,N-bisdimethylchlorosilylmethyl derivatives by reaction with dimethylchloromethylchlorosilane/hexamethyldisilazane, served as the starting materials. These intermediate derivatives were hydrolyzed to the required disilamorpholines without isolation from the reaction mixture.

Following the above strategy and one-pot technique but using ammonolysis reaction (with ammonia or primary amines) in place of hydrolysis, we have synthesized 4-acyl-2,2,6,6-tetramethyl-2,6-disilapiperazines Ia,b and IIa,b, which differ from those described in [6] by the presence of acyl group in position 4 of the piperazine ring.

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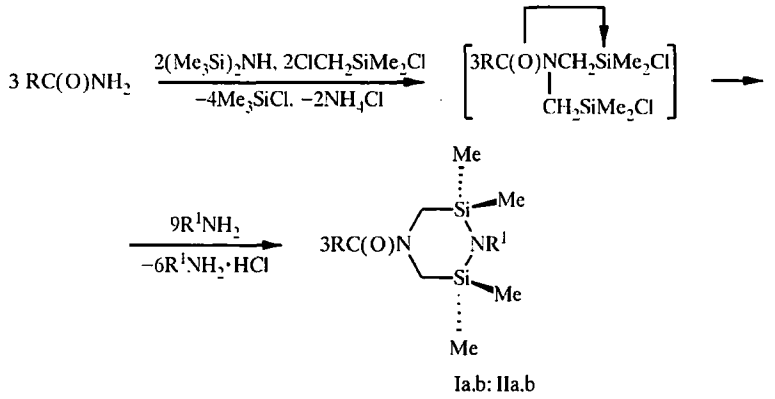
Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, 1077-1084, August 1999. Original article submitted May 18, 1999.

0009-3122/99/3508-0947$22.00©1999 KluwerAcademic/Plenum Publishers



I R = H; II R = Me; I, II a R^1 = H, b R^1 = Me

Note that the dimethylchloromethylchlorosilane/hexamethyldisilazane system [7] which was used to prepare the intermediate N,N-bis(dimethylchlorosilylmethyl)amides gave the best results from the preparative point of view in comparison with other known methods for the N-dimethylchlorosilylmethylation of amides – trans-silylation of trimethylsilyl derivatives of amides with dimethylchloromethylchlorosilane (the trans-silylation method) and amination of amides with this reagent in the presence of triethylamine [8, 9]. The sequence of stages leading to the N-dimethylchlorosilylmethylated product here is evidently analogous to a considerable extent to that established for the trans-silylation method by ^{1}H NMR spectroscopic monitoring (i.e., initial formation of N-dimethylchloromethylsilyl derivatives, followed by their isomerization to the products of O-silylmethylation, and finally rearrangement of the latter to the N-silylmethylated end products) [10]. However the more vigorous reaction conditions in our case preclude the ^{1}H NMR spectroscopic monitoring to establish the course of the reaction. The IR spectra of the disilapiperazines Ia,b and IIa,b contain a single amide group absorption band in the 1670-1670 cm^{-1} region.

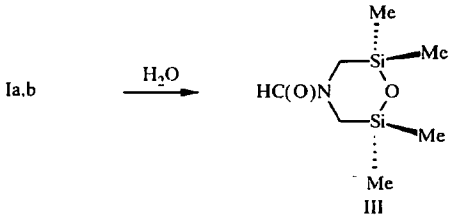
The NMR spectra are in complete agreement with the proposed structures. The spectra show pairs of sets of signals for the CH_2N and Me_2Si groups in the ^{1}H and ^{13}C spectra (Table 1) and two silicon signals in the ^{29}Si NMR spectra, which arise from steric hindrance to the amide group rotation in molecules of these compounds, together with singlet signals for all other groups of atoms. The absence of other sets of signals in the NMR spectra

TABLE 1. ^{1}H and ^{13}C NMR Spectroscopic Data for 2,6-Disilapiperazines Ia,b and IIa,b

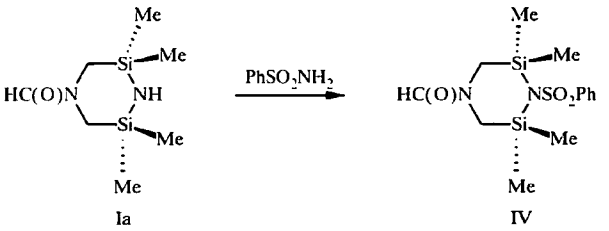
Compound	NMR spectrum	δ, ppm				
		$Si(CH_3)_2$	NCH_2	NH NCH_3	HC(O) $CH_3C(O)$	C=O
Ia	^{1}H	0.19 br. s	2.98 s 2.65 br. s	2.62 br. s	8.0 s	
	^{13}C	-0.27 -0.60	39.51 34.44			161.12
Ib	^{1}H	-0.09 br. s	2.78 s 2.58 s	2.23	7.80 s	
	^{13}C	-2.31 -2.62	39.16 33.82		28.01	160.79
IIa	^{1}H	0.12 s 0.15 s	2.87 s 3.10 s		2.10	
IIb	^{1}H	0.09 s 0.06 s	3.08 s 2.85 s	2.39	2.05 s	
	^{13}C	-2.30 -2.48	40.82 36.41		27.81	168.39

and the relatively low melting points indicate that the compounds are monomeric. We note that the structurally analogous 4-acyl-2,6-disilamorpholines have a marked tendency to oligomerize on storage [2]. The monomeric structure of the obtained disilapiperazines follows from the X-ray crystallographic data for Ia (see below).

The presence of the $RC(O)NCH_2SiNSi$ unit in the molecules of disilapiperazines Ia,b and IIa,b, analogous to the $RC(O)NCH_2SiOSi$ unit in 4-acyl-2,6-disilamorpholines for which an increased reactivity of the Si–O bond has been noted,* permits the prediction that possibly the Si–N bond in the SiNSi unit of the disilapiperazines has increased reactivity. In fact hydrolysis of compounds Ia,b with water at room temperature occurs without complications to give 2,6-disila-4-formylmorpholine (III)



NMR spectral data are in agreement with this result. When compound Ia was kept in $CDCl_3$ solution under conditions which did not exclude access to traces of moisture, a second set of signals appeared at 6.6 (s) and 9.3 (s) ppm in the ^{29}Si NMR spectrum and these increased in intensity with time. We assigned this set of signals to morpholine III. When a known sample of this substance was added to the NMR spectrometer ampule, the intensity of these signals increased. Morpholine III was also obtained by an independent method: the one-pot synthesis from formamide, hexamethyldisilazane, and dimethylchloromethylchlorosilane with subsequent hydrolysis of the formed N,N-bis(dimethylchlorosilylmethyl)formamide (see Experimental).



The reaction of disilapiperazine Ia with benzenesulfonamide also occurred without complications but under somewhat more vigorous conditions (the reagents were boiled for 3 h in *o*-xylene). The sulfonamide IV was isolated in a yield of 45%.

The molecule of disilapiperazine Ia (Fig. 1) has sufficiently rigid conformation which is determined by the hybridization of its atoms. Indeed, the 6-membered heterocycle has the sterically favorable chair conformation (the deviation of the SiNSi and CNC fragments from the mean plane of the ring is 27° and 59°, respectively) in which the bond lengths and angles (Tables 2 and 3) have almost standard values [11]. The torsion angle $O_{(1)}$–$C_{(7)}$–$N_{(2)}$–$C_{(5)}$ of 1.6° also corresponds to the most suitable (*cis*) conformation for these units. There are no data in the Cambridge Structural Data Bank [12] referring to compounds with a 6-membered SiNSiCNC ring, but it does contain structures with the CSiNSiC fragment [13-15], but only in 8- and 9-membered rings or in acyclic compounds. As is usual, in smaller rings of disilapiperazine Ia the Si–N bond lengths and the SiNSi angle are somewhat increased (by 0.02-0.03 Å and ~7° respectively) because of some steric strain. The siloxane analog of disilapiperazine Ia – disilamorpholine III,*[2] has the same conformation (deviations of the angles SiOSi and CNC from the planar central part of the heterocycle are 26° and 63°), but the delocalization degree of the unshared electron pair of the nitrogen atom is considerably less: the N–C(=O) bond length is 1.340(3) Å versus 1.307(6) Å in disilapiperazine Ia. This is

* This will be published in a separate paper.

*[2] The complete data from the X-ray diffraction study of disilamorpholine III will be published.

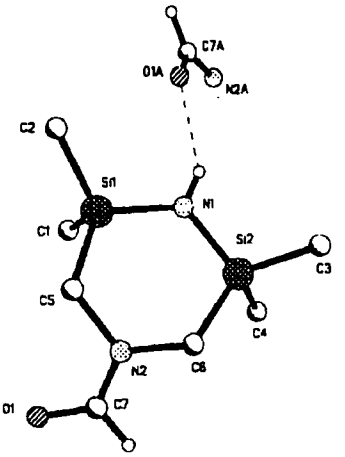


Fig. 1. Structure of molecule of compound Ia in the crystal. The hydrogen bond with neighboring molecule is shown.

possibly due to the different electronic effects of the SiOSi and SiN(H)Si units. The intermolecular hydrogen bond $N_{(1)}$–H:···$O_{(1)}$ (0.5 – x, 2 – y, -0.5 + z) is characterized by the geometric parameters N···O 3.14 Å, H···O 2.42 Å, and angle N–H···O 147°. Since the observed N–H distance of 0.82 Å is strongly understated because of the shift of the electron density from the hydrogen atom to nitrogen atom a more realistic parameter would be obtained if the hydrogen atom were placed at a distance of 1.1 Å from the nitrogen atom. In this case the H···O distance would equal to 2.19 Å and the angle N–H···O would be 143° which corresponds to a weak hydrogen bond. In the crystal of disilapiperazine Ia these bonds unite the molecules in chains along the crystallographic c axis.

TABLE 2. Bond Lengths in the Molecule of Compound Ia

Bond	Bond length (Å)	Bond	Bond length (Å)
$Si_{(1)}$–$N_{(1)}$	1,705(4)	$Si_{(2)}$–$C_{(4)}$	1,859(5)
$Si_{(1)}$–$C_{(2)}$	1,847(4)	$Si_{(2)}$–$C_{(6)}$	1,885(4)
$Si_{(1)}$–$C_{(1)}$	1,858(5)	$O_{(1)}$–$C_{(7)}$	1,217(6)
$Si_{(1)}$–$C_{(5)}$	1,875(4)	$N_{(2)}$–$C_{(7)}$	1,307(6)
$Si_{(2)}$–$N_{(1)}$	1,703(4)	$N_{(2)}$–$C_{(6)}$	1,460(5)
$Si_{(2)}$–$C_{(3)}$	1,851(4)	$N_{(2)}$–$C_{(5)}$	1,466(5)

TABLE 3. Bond Angles (deg) in the Molecule of Compound Ia

Angle	ω	Angle	ω
$N_{(1)}$–$Si_{(1)}$–$C_{(2)}$	110,3(2)	$C_{(3)}$–$Si_{(2)}$–$C_{(6)}$	109,4(2)
$N_{(1)}$–$Si_{(1)}$–$C_{(1)}$	111,9(2)	$C_{(4)}$–$Si_{(2)}$–$C_{(6)}$	107,9(2)
$C_{(2)}$–$Si_{(1)}$–$C_{(1)}$	111,3(2)	$Si_{(2)}$–$N_{(1)}$–$Si_{(1)}$	127,3(2)
$N_{(1)}$–$Si_{(1)}$–$C_{(5)}$	104,8(2)	$C_{(7)}$–$N_{(2)}$–$C_{(6)}$	122,9(4)
$C_{(2)}$–$Si_{(1)}$–$C_{(5)}$	110,1(3)	$C_{(7)}$–$N_{(2)}$–$C_{(5)}$	120,8(4)
$C_{(1)}$–$Si_{(1)}$–$C_{(5)}$	108,3(2)	$C_{(6)}$–$N_{(2)}$–$C_{(5)}$	116,2(3)
$N_{(1)}$–$Si_{(2)}$–$C_{(3)}$	111,7(2)	$N_{(2)}$–$C_{(5)}$–$Si_{(1)}$	112,8(3)
$N_{(1)}$–$Si_{(2)}$–$C_{(4)}$	112,3(2)	$N_{(2)}$–$C_{(6)}$–$Si_{(2)}$	113,7(3)
$C_{(3)}$–$Si_{(2)}$–$C_{(4)}$	110,5(2)	$O_{(1)}$–$C_{(7)}$–$N_{(2)}$	127,4(5)
$N_{(1)}$–$Si_{(2)}$–$C_{(6)}$	104,8(2)		

TABLE 4. Coordinates of the Atoms ($\times 10^4$ for Non-hydrogen Atoms, $\times 10^3$ for Hydrogen Atoms) in the Structure of Compound Ia

Atom	x	y	z
$Si_{(1)}$	2108(1)	9185(1)	4945(1)
$Si_{(2)}$	-327(1)	10621(1)	3689(1)
$O_{(1)}$	1613(5)	11773(3)	7261(3)
$N_{(1)}$	1012(4)	9524(3)	3812(3)
$N_{(2)}$	169(4)	10825(3)	5975(2)
$C_{(1)}$	3984(5)	10007(4)	4970(5)
$C_{(2)}$	2443(6)	7587(4)	5017(6)
$C_{(3)}$	-1987(5)	10187(4)	2796(3)
$C_{(4)}$	561(7)	12010(4)	3188(4)
$C_{(5)}$	895(6)	9675(4)	6150(3)
$C_{(6)}$	-1058(4)	10878(4)	5138(3)
$C_{(7)}$	600(8)	11734(5)	6556(4)
$H_{(1N)}$	131(5)	924(4)	323(2)
$H_{(1C)}$	377(1)	1083(1)	503(3)
$H_{(1A)}$	455(2)	986(3)	430(2)
$H_{(1B)}$	460(2)	976(3)	559(2)
$H_{(2C)}$	146(1)	719(1)	504(4)
$H_{(2A)}$	303(4)	740(1)	567(2)
$H_{(2B)}$	302(4)	734(1)	438(2)
$H_{(3B)}$	-248(3)	950(2)	310(2)
$H_{(3A)}$	-161(1)	1002(3)	207(1)
$H_{(3C)}$	-273(2)	1082(1)	2760(23)
$H_{(4C)}$	135(3)	1226(2)	370(2)
$H_{(4A)}$	-23(1)	1260(1)	313(3)
$H_{(4B)}$	102(4)	1188(1)	247(2)
$H_{(5A)}$	8(1)	910(1)	628(1)
$H_{(5B)}$	155(1)	971(1)	680(1)
$H_{(6A)}$	-155(1)	1164(1)	517(1)
$H_{(6B)}$	-185(1)	1030(1)	531(1)
$H_{(7)}$	2(5)	1242(4)	642(3)

EXPERIMENTAL

IR spectra of compounds were obtained in thin films, in solutions, and in KBr cuvettes with a Specord IR-75 double beam spectrometer. ^1H, ^{12}C, and ^{29}Si NMR spectra of $CDCl_3$ solutions of the compounds studied were recorded with a Varian XL-400 spectrometer at working frequencies of 400.0, 100.6, and 79.5 MHz respectively using a pulse sequence with Fourier transformation and ^2H stabilization of the resonance conditions. Tetramethylsilane was used as the internal standard.

The X-ray diffraction study of compound Ia was performed on Siemens P3/PC diffractometer ($MoK\alpha_1$ radiation, $\omega/2\theta$ scanning, $2\theta_{max} = 52°$, 1354 reflection intensities measured) at room temperature. Crystals of the compound Ia are rhombic, $a = 8.547(3)$; $b = 11.4505(5)$; $c = 12.111(7)$ Å; $V = 1180(1)$ Å^3; $d_{calc} = 1.139$ g/cm^3, $Z = 4$ ($C_7H_{18}N_2OSi_2$), space group $P2_12_12_1$ (one crystallographically independent molecule in the cell). The structure was solved by the direct method and refined by the least-squares method in the anisotropic approximation for non-hydrogen atoms (for 1339 reflections and 121 parameters). The hydrogen atoms were localized by difference synthesis and refined isotropically. Profile analysis was carried out for the mass of the reflections from the Ia crystal using the PROFIT program [16]. The final values of the divergence factors were $R_1 = 0.044$, $wR_2 = 0.094$, GooF = 1.064 from 1048 reflections with $I > 2\sigma(I)$. All calculations were carried out with an IBM PC/AT using the SHELXTL-93 programs [17]. The atomic coordinates are given in Table 4.

4-Formyl-2,2,6,6-tetramethyl-2,6-disilapiperazine (Ia). $ClCH_2SiMe_2Cl$ (85.2 g, 0.6 mol) was added with stirring to mixture of formamide (13.5 g, 0.3 mol) and $(Me_3Si)_2NH$ (38.64 g, 0.24 mol) in toluene (150 ml) and the resulting mixture was boiled for 1 h, then filtered and the solvent evaporated, and the residue dissolved in toluene (200 ml). Dry ammonia (15.3 g, 0.9 mol) was then bubbled through the obtained solution under cooling with water. The reaction mixture was filtered, the solvent evaporated, and the crystalline residue extracted with boiling hexane (2 × 50 ml), and the solution reduced to half. The crystals were filtered off to obtain compound Ia (23,7 g, 39%); mp 65-67° (hexane). IR spectrum ($CHCl_3$): 1637 cm^{-1} (NCO). ^{29}Si NMR spectrum: -1.0 (s); -1.8 ppm (s). Found, %: C 41.00; H 8.69; N 13.47. $C_7H_{18}N_2OSi_2$. Calculated, %: C 41.54; H 8.96; N 13.84. Crystals used for X-ray crystallography were recrystallized from hexane.

4-Formyl-1,2,2,6,6-pentamethyl-2,6-disilapiperazine (Ib). $ClCH_2SiMe_2Cl$ (85.2 g, 0.6 mol) was added with stirring to mixture of formamide (13.5 g, 0.3 mol) and $(Me_3Si)_2NH$ (38.64 g, 0.24 mol) in toluene (150 ml) and the mixture was boiled for 1 h, filtered, the solvent evaporated, the residue dissolved in toluene (200 ml) and dry methylamine (27.9 g, 0.9 mol) was passed through the water-cooled solution. The reaction mixture was filtered, the filtrate evaporated, and the residue fractionated to give compound Ib (23.2 g, 36%); bp 129-130°C/7 mm Hg, n_D^{20} 1.4835. IR spectrum (thin film): 1670 cm^{-1} (NCO). ^{29}Si NMR spectrum: -0.3 (s); 0.6 ppm (s). Found, %: C 44.22; H 9.35; Si 25.78. $C_8H_{20}N_2OSi_2$. Calculated, %: C 44.40; H 9.31; Si 25.95.

4-Acetyl-2,2,6,6-tetramethyl-2,6-disilapiperazine (IIa). $ClCH_2SiMe_2Cl$ (57.2 g, 0.4 mol) was added to mixture of acetamide (11.8 g, 0.2 mol) and $(Me_3Si)_2NH$ (25.8 g, 0.16 mol) in benzene (75 ml), the mixture was boiled for 1 h, after which it was filtered, the filtrate was evaporated and the residue was dissolved in benzene (100 ml). Dry ammonia (10.2 g, 0.6 mol) was bubbled through the obtained solution. The reaction mixture was filtered, the solvent evaporated, and the residue crystallized by the addition of hexane (40 ml) to give compound IIa (20.5 g, 47%); mp 64-67°C (hexane). IR spectrum ($CHCl_3$): 1630 cm^{-1} (NCO). ^{29}Si NMR spectrum: -1.38 ppm (br. s). Found, %: C 44.40; H 9.16; Si 25.61. $C_8H_{20}N_2OSi_2$. Calculated, %: C 44.39; H 9.31; Si 25.95.

4-Acetyl-1,2,2,6,6-pentamethyl-2,6-disilapiperazine (IIb). $ClCH_2SiMe_2Cl$ (85.2 g, 0.6 mol) was added with stirring to mixture of acetamide (17.7 g, 0.3 mol) and $(Me_3Si)_2NH$ (38.64 g, 0.24 mol) in toluene (150 ml) and the mixture was boiled for 1 h, after which the reaction mixture was filtered, the solvent was evaporated, and the residue was dissolved in toluene (200 ml). Dry methylamine (27.9 g, 0.9 mol) was then passed through the water-cooled solution. The reaction mixture was filtered, the solvent was evaporated, and the residue fractionated to give compound IIb (45.2 g, 65%); bp 130-131°C/7 mm Hg, n_D^{20} 1.4845. IR spectrum (thin film): 1655 cm^{-1} (NCO). ^{29}Si NMR spectrum ($CDCl_3$): -0.7 (s); 0.8 ppm (s). Found, % C 47.06; H 9.66; Si 24.11. $C_9H_{22}N_2OSi_2$. Calculated, %: C 46.91; H 9.62; Si 24.37.

4-Formyl-2,2,6,6-tetramethyl-2,6-disilamorpholine (III). A. Water (10 ml) was added to solution of 2,6-disilapiperazine Ia (2.1 g, 0.01 mol) in chloroform (15 ml) and the mixture was stirred for several hours. The organic layer was separated and the water layer was extracted with chloroform (10 ml). After the combined organic layers were evaporated the residue was recrystallized from hexane to give compound III (1.8 g, 89 %); mp 83-86°C (hexane). Mixed sample melting point showed no depression (mp 83-86°C). IR spectrum ($CHCl_3$): 1670 cm^{-1}.

B. Water (10 ml) was added to solution of 2,6-disilapiperazine Ib (2.3 g, 0.01 mol) in chloroform (15 ml) and the mixture was stirred for several hours. The organic layer was separated and the water layer was extracted with chloroform (10 ml). After evaporation of the combined organic layers crystallization of the residue from hexane gave compound III (1.5 g, 70%); mp 79-81°C (hexane).

C. Dimethylchloromethylchlorosilane (28.6 g) was added dropwise with stirring and cooling to mixture of formamide (4.5 g), hexamethyldisilazane (12.88 g), and benzene (50 ml), the mixture was boiled for 1 h, cooled and treated with aqueous solution of $NaHCO_3$ (16.8 g in 40 ml of water). The organic layer was separated, and the aqueous layer was extracted with chloroform (50 ml). Fractionation of the combined organic layers gave disilamorpholine III (10.05 g, 50%); bp 123-125°C/10 mm Hg; mp 83-85°C (hexane). IR spectrum ($CHCl_3$): 1670 cm^{-1} (C=O). ^1H NMR spectrum: 0.20 (3H, s, CH_3); 0.21 (3H, s, CH_3); 2.78 (2H, s, CH_2); 2.99 (2H, s, CH_2); 8.03 ppm (1H, s, CH). ^{13}C NMR spectrum: -0.42 (CH_3); -0.77 (CH_3); 34.27 (CH_2); 39.32 (CH_2); 160.93 ppm (C=O). ^{29}Si NMR spectrum: 6.6 (s); 9.3 ppm (s). Found, %: C 41.33; H 8.47. $C_7H_{17}NO_2Si_2$. Calculated, %: C 41.30; H 8.43.

4-Formyl-2,2,6,6-tetramethyl-1-phenylsulfonyl-2,6-disilapiperazine (IV). Mixture of disilapiperazine Ia (2 g, 0.01 mol), benzenesulfonamide (1.57 g, 0.01 mol), and *o*-xylene (20 ml) was boiled for 3 h until evolution of ammonia ceased. The solvent was distilled off and the residue poured over with heptane to give sulfonamide IV (2 g, 45%); mp 122-124°C (1:3 benzene-heptane). IR spectrum ($CHCl_3$): 1090, 1150, 1390 (SO_2), 1600 cm^{-1}. ^1H NMR spectrum: 0.09 (3H, s, CH_3); 0.21 (3H, s, CH_3); 2.93 (2H, s, CH_2); 3.15 (2H, s, CH_2); 7.87 (2H, d, $^3J_{HH}$ = 7.0 Hz, H-*ortho*); 7.47 (1H, t, $^3J_{HH}$ = 7.0 Hz, H-*para*); 7.44 (2H, t, $^3J_{HH}$ = 7.0 Hz, H-*meta*); 8.12 ppm (1H, s, CH). ^{13}C NMR spectrum: -0.73 (CH_3); -0.55 (CH_3); 39.75 (CH_2); 45.59 (CH_2); 126.00 (C-*meta*); 128.49 (C-*ortho*); 131.36 (C-*para*); 142.99 (C-*ipso*); 156.66 ppm (C=O). ^{29}Si NMR spectrum: 6.7 (s); 8.2 ppm (s).

The authors thank the Russian Fund for Fundamental Research (projects No. 96-07-89187 and 97-03-33783) and also GK RF at VO (MNTP "General and Technical Chemistry) P.T. 402.95, project No. 01.0204f) for financial support of this work.

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