NITROGEN-CONTAINING ORGANOSILICON COMPOUNDS.

150.* SYNTHESIS AND CHROMATOGRAPHIC AND ^{1}H, ^{13}C, ^{15}N, AND ^{29}Si NMR SPECTROSCOPIC INVESTIGATION OF SUBSTITUTED (PIPERIDINOALKYL)SILANES

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Substituted (piperidinoalkyl)silanes were synthesized and investigated by means of multinuclear NMR spectroscopy and GLC. The data obtained indicate an additional N—Si interaction in α-aminomethylsilanes that depends substantially on the properties of the substituents attached to the silicon atom. The effect of the $R^1R^2R^3Si$ substituent on the capacity of the nitrogen atom for intermolecular interactions is not restricted to steric effects but also has electronic character.

In a study of the organosilicon amines $R^1R^2R^3Si(CH_2)_mR^4$ (where R^4 is a substituent that contains a nitrogen atom) it was shown that a number of their properties are not in agreement with the concept of the inductive effect of $R^1R^2R^3Si(CH_2)_m$ groups, which is explainable by the possibility of the realization of an N→Si intramolecular interaction in them [2]. However, in the case of silylalkylamines of the $Me_{3-n}(OEt)_nSi(CH_2)_mNH_2$ type the changes in the ^{13}C, ^{15}N, and ^{29}Si chemical shifts (CS) were explained without calling upon the concept of the existence of long-range coupling between the silicon and nitrogen atoms in them [3]. At the same time, in investigations of pyrrolidinoalkylsilanes [4] and piperazinoalkylsilanes [5] by GLC and ^{1}H, ^{13}C, ^{15}N, and ^{29}Si NMR spectroscopy anomalous behavior of their chromatographic and NMR characteristics caused by electronic and steric effects, including also an α effect, was observed. For the further study of these phenomena we synthesized substituted (piperidinoalkyl)silanes with various radicals attached to the silicon atom (H, Ph, polymethylene) and a methyl group in various positions of the piperidine ring. The compounds were studied by GLC and ^{13}C, ^{15}N, and ^{29}Si NMR spectroscopy.

Trimethyl[(methylpiperidino)alkyl]silanes were obtained by a general method [5, 6]. The reaction with the amine is carried out with a twofold excess of the amine in hexane (m = 1) or benzene (m = 3). Compounds with phenyl substituents attached to the silicon atom (X-XV) and (piperidinoalkyl)silacyclanes XXXIV-XXXIX were similarly obtained. The physicochemical constants and the results of analysis are presented in Tables 1-3. The yields of the products obtained are the values obtained after twofold fractional distillation in vacuo. The starting compounds for the synthesis of the 1-methyl-1-(piperidinoalkyl)-substituted silacyclopentanes and -hexanes were obtained by means of the Grignard reaction [7, 8]. The constants of the synthesized compounds are in agreement with the data in [9]. Methyl(piperidinoalkyl)silanes $H_{3-n}Me_nSi(CH_2)_mNC_5H_{10}$ (n = 0-2 and m = 1, 3) were obtained by a somewhat modified method [10]:

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*See [1] for communication 149.

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TABLE 1. Physicochemical Constants of (Piperidinoalkyl)silanes $R^1R^2R^3Si(CH_2)_mNC_5H_{10}$

Compound	$R^1R^2R^3Si$	m	bp, °C (mm)	n_D^{20}	d_4^{20}	MR_D		Yield, %
						Found	Calc.	
I	H_3Si	1	125...128 (760)	1,4657	0,8464	42,19	41,91	41
II	H_3Si	3	73...74 (15)	1,4692	0,8543	51,29	51,17	31
III	H_2MeSi	1	70...72 (40)	1,4598	0,8433	46,45	46,31	62
IV	H_2MeSi	3	85...88	1,4641	0,8488	55,71	55,57	63
V	HMe_2Si	1	77...80 (35)	1,4542	0,8325	50,85	50,71	59
VI	HMe_2Si	3	99...102 (20)	1,4591	0,8448	60,04	59,97	71
XII	$PhMe_2Si$	3	145...148 (3,5)	1,5108	0,9390	83,42	83,98	74
XIII	Ph_2MeSi	1	170...172 (2)	1,5665	1,0237	94,23	94,33	55
XIV	Ph_2MeSi	2	173...175 (2,5)	1,5619	1,015	98,85	98,96	40
XV*	Ph_3Si	2						

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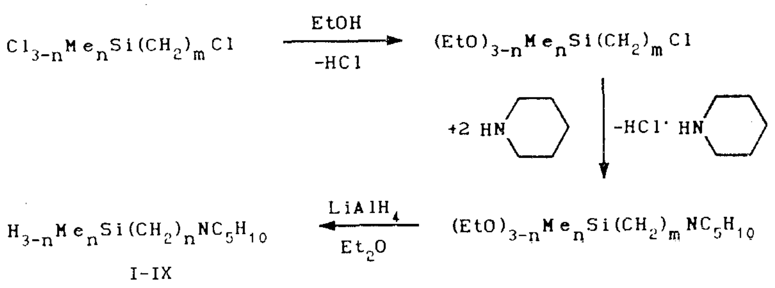
*bp 85-86°C.

TABLE 2. Physicochemical Constants of Substituted Piperidinosilanes $Me_3Si(CH_2)_mNC_5H_9X$

Compound	X	m	bp, °C (mm)	n_D^{20}	d_4^{20}	MR_D		Yield, %
						Found	Calc.	
XX	4-Me	1	86 (22)	1,4461	0,8259	59,86	59,74	78
XXI	4-Me	2	90...92 (15)	1,4501	0,8336	64,11	64,37	82
XXII	4-Me	3	92...94	1,4570	0,8429	68,84	69,00	69
XXIII	3-Me	1	78...79 (20)	1,4464	0,8256	59,86	59,74	83
XXIV	3-Me	2	87...89 (14)	1,4502	0,8345	64,21	64,37	79
XXV	3-Me	3	92...94 (6)	1,4515	0,8438	68,17	69,00	76
XXVI	2-Me	1	80 (22)	1,4536	0,8374	59,89	59,74	68
XXVII	2-Me	2	93...95 (15)	1,4552	0,8447	64,27	64,37	78
XXVIII	2-Me	3	121...122 (22)	1,4576	0,8452	68,27	69,00	68
XXIX	2,6-Me	1	101...102 (22)	1,4618	0,8551	64,11	64,37	63
XXX	2,6-Me	3	128...129 (23)	1,4578	0,8528	72,78	73,03	62



Urea was used to tie up the HCl in the alcoholysis reaction, and ethanol was used in a twofold excess with respect to the starting methyl(chloroalkyl)chlorosilane and was simultaneously the solvent.

TABLE 3. Physicochemical Constants of (Piperidinoalkyl)silacycloalkanes $R(CH_2)_mNC_5H_{10}$

Compound	R	m	bp, °C (mm)	n_D^{20}	d_4^{20}	MR_D		Yield, %
						Found	Calc.	
XXXIV	$(CH_2)_5SiMe$	1	120...122 (13)	1,4882	0,9101	66,92	66,88	68
XXXV	$(CH_2)_5SiMe$	2	144...145 (13)	1,4861	0,9054	71,49	71,50	66
XXXVI	$(CH_2)_5SiMe$	3	113...115 (2)	1,4868	0,9086	75,80	71,13	68
XXXVII	$(CH_2)_4SiMe$	1	112...114 (16)	1,4855	0,9099	62,39	62,24	65
XXXVIII	$(CH_2)_4SiMe$	2	135...137 (15)	1,4841	0,9003	67,05	66,88	45
XXXIX	$(CH_2)_4SiMe$	3	142...146 (16)	1,4861	0,9069	71,37	71,50	67

The ^{29}Si CS of the investigated piperidylalkylsilanes varied over a range of 84 ppm (Tables 4-6), depending on the properties of the substituents attached to the silicon atom. We did not find quantitative multiple correlations between the ^{29}Si CS and the inductive constants σ^* of the $R^1R^2R^3$ substituents. The presence of a $(CH_2)_mNC_5H_{10}$ group in the molecule has little effect on the overall character of the change in the ^{29}Si CS as the substituents attached to the silicon atom in organosilicon compounds is varied [11, 12]; one observes a weak-field shift of the ^{29}Si signal as the hydrogen atoms are gradually replaced by methyl groups and a strong-field shift as the number of phenyl substituents is increased.

The change in the bond angles at the silicon atom due to its inclusion in a ring changes the ^{29}Si CS substantially (see Table 6). The cyclization effect $\Delta^{29}Si = \delta^{29}Si[(CH_3)_nSi(Me)(CH_2)_mNC_5H_{10}] - \delta^{29}Si[Me_3Si(CH_2)_mNC_5H_{10}]$ is virtually the same for all m and amounts to -3.7 ppm ($n = 5$) and 16.8-17.4 ppm ($n = 4$); these values are comparable to the ΔSi values for alkylsilanes $Me_2Si(CH_2)_n$ and Me_4Si, respectively ($\Delta = -1.3$ ppm when $n = 5$ and 16.8 ppm when $n = 4$).

The formation of the hydrochloride gives rise to the expected deshielding effect on the location of the ^{29}Si signal. We calculated the shifts induced by a substituent $\Delta Si = \delta^{29}Si[Me_3Si(CH_2)_mR] - \delta^{29}Si[Me_3Si(CH_2)_mH]$, where R = piperidino (Table 7). For comparison, data for analogous classes of organosilicon compounds, where $R = OR^1$ [13], Ph [14], Me [15], and $NC_4H_8N{-}Me$ [5], are presented. When $m = 1$, ΔSi for the series of compounds is a negative value, which may constitute evidence for an additional α effect between substituent R and the silicon atom. A different explanation was also given in [13] for the negative values of the substitution increment. Varying the site of substitution in the piperidine ring has little effect on the ^{29}Si CS.

We compared the changes in the ^{29}Si CS as the number of methylene groups was varied from one to three. An increase in their number causes a gradual weak-field shift of the ^{29}Si resonance signal, which is expressed to a greater extent in the case of the transition $m = 1$-2, as one should have expected. The greatest changes are observed for compounds in which the substituent attached to the silicon atom is a hydrogen atom or a phenyl group; this can be explained in part by differences in steric interactions, as well as by the nonlinear dependence of the ^{29}Si CS on the charge on the silicon atom. In addition, the gradual decrease in the strong-field shift of the ^{29}Si signal on passing from $m = 1$ to $m = 3$ in the substituent order H_3Si (-6.9 ppm) > H_2SiMe (-6.3 ppm) > $HSiMe_2$ (-5.4 ppm) > Me_2SiPh (-3.8 ppm) > MeSi (-2.8 ppm) probably constitutes evidence for a decrease in the intramolecular $N \rightarrow Si$ interaction in the same order. The greatest contributions to changes in the ^{29}Si CS in the formation of an $N \rightarrow Si$ bond are made by the resulting distortion of the bond angles and the change in the coordination number of the silicon atom. The contribution due to steric factors and an increase in the electronegativity of the $(CH_2)_mNC_5H_{10}$ substituent does not exceed 2 ppm, as follows from an analysis of the ^{29}Si CS of salts XXXI-XXXIII (see Table 5).

The ^{15}N CS of the (piperidinoalkyl)silanes vary over a range of 13 ppm. The location of the ^{15}N resonance signal is determined primarily by the m value. The $m = 1$-2 transition gives rise to a weak-field shift of 11-13 ppm, while the $m = 2$-3 transition, on the other hand, causes a strong-field shift (2-4 ppm). These changes are in agreement with the previously [16] determined substitution increments in amines for solutions in cyclohexane, which amount to 11.7 and -2.2 ppm, respectively. It is apparent that the ^{15}N CS exceed this value somewhat in the case of XIII and XIV. Changing the substituent attached to the silicon atom has a small effect on the ^{15}N CS (see Tables 4-6). In the case of $N \rightarrow Si$ intramolecular complexing

TABLE 4. ^{13}C, ^{15}N, and ^{29}Si NMR Spectra of (Piperidinoalkyl)silanes $R^1R^2R^3Si(CH_2)_mNC_5H_{10}$

Compound	$R^1R^2R^3Si$	m	δ ^{29}Si, ppm	δ ^{15}N, ppm	δ ^{13}C $(CH_2)_m$, ppm			δ ^{13}C (NC_5H_{10}), ppm			δ ^{13}C $(R^1R^2R^3)$, ppm			δ ^{13}C (R=Me), ppm
					C—Si	CH_2	C—N	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	
I	H_3Si	1	—66,5	—338,5	42,13	—	—	58,18	26,79	24,39	—	—	—	—
II	H_3Si	3	—59,6	—330,5	7,10	28,81	64,42	57,53	28,81	26,40	—	—	—	—
III	H_2MeSi	1	—39,9	—338,2	46,42	—	—	58,57	26,86	24,45	—	—	—	—8,82
IV	H_2MeSi	3	—33,6	—329,3	11,26	28,87	65,00	57,47	28,87	25,43	—	—	—	—5,64
V	HMe_2Si	1	—18,4	—337,7	49,93	—	—	58,83	26,92	24,52	—	—	—	—4,40
VI	HMe_2Si	3	—13,0	—328,7	14,83	28,94	65,66	57,60	28,94	24,71	—	—	—	—1,61
VII	Me_3Si	1	—1,9	—337,0	52,20	—	—	59,09	26,86	24,45	—	—	—	—0,70
VIII	Me_3Si	2	0,4	—325,4	14,96	55,26	—	55,26	26,66	25,23	—	—	—	—1,15
IX	Me_3Si	3	0,9	—327,7	14,70	22,05	63,25	55,19	26,79	25,36	—	—	—	—1,15
X	Me_2PhSi	1	—6,7	—338,2	51,10	—	—	59,09	26,86	24,39	139,94	134,22	128,24; 129,35*	—2,19
XI	Me_2PhSi	2	—3,7	—326,6	14,25	55,06	—	54,51	26,60	25,23	139,74	134,09	128,24; 129,28*	—2,32
XII	Me_2PhSi	3	—2,9	—328,7	13,92	21,92	63,38	55,19	26,60	25,17	139,74	134,03	128,24; 129,28*	—2,52
XIII	$MePh_2Si$	1	—11,9	—339,0	49,86	—	—	59,09	26,86	24,39	137,86	135,20	128,31; 129,61*	—3,56
XIV	$MePh_2Si$	2	—7,3	—325,4	12,88	54,93	—	54,54	26,53	25,23	137,73	135,00	128,31; 129,61*	—3,49
XV	Ph_3Si	2	—10,4	—323,9	11,71	55,06	—	54,61	26,53	25,17	135,65	136,30	128,50; 130,06*	—
XVI	$(OEt_3)Si$	1	—	—	45,70	—	—	58,83	26,99	24,51	58,83	18,67	—	—
XVII	$(OEt_3)Si$	3	—	—	8,66	20,75	63,79	59,50	26,66	25,16	55,99	18,80	—	—
XVIII	$N(CH_2CH_2O)_3Si$	1	—	—	51,42	—	—	59,03	26,79	24,78	58,44	51,94	—	—
XIX	$N(CH_2CH_2O)_3Si$	3	—	—	14,25	22,50	64,03	55,13	26,60	25,17	58,51	51,94	—	—

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*$\delta^{13}C$ (C_p).

TABLE 5. ^{13}C, ^{15}N, and ^{29}SI NMR Spectra of Substituted (Piperidinoalkyl)silanes $Me_3Si(CH_2)_mNC_5H_9X$

Compound	X	m	δ ^{29}Si, ppm	δ ^{15}N, ppm	δ ^{13}C (Me), ppm	δ ^{13}C (X), ppm	δ ^{13}C $(CH_2)_m$, ppm			δ ^{13}C (NC_5H_9), ppm				
							C—Si	CH_2	C—N	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	$C_{(6)}$
XX	4-Me	1	−1,9	−337,4	−0,89	22,50	51,36	—	—	58,44	35,50	30,82	35,50	58,44
XXI	4-Me	2	0,2	−326,4	−0,83	22,50	15,29	54,80	—	54,15	35,24	31,73	35,24	54,15
XXII	4-Me	3	0,8	−329,0	−1,09	22,63	14,70	22,18	62,80	54,61	35,31	31,67	35,31	54,61
XXIII	3-Me	1	−1,9	—	−0,70	20,23	51,75	—	—	66,83	31,86	33,10	26,40	58,44
XXIV	3-Me	2	0,2	—	−0,83	20,29	15,16	54,15	—	62,47	31,67	34,00	26,14	54,93
XXV	3-Me	3	0,8	—	−1,09	20,29	14,70	22,11	62,93	62,93	31,67	34,01	26,21	54,67
XXVI	2-Me	1	−1,3	—	−0,50	20,23	46,42	—	—	60,46	35,11	24,65	27,05	56,75
XXVII	2-Me	2	0,8	—	−1,15	19,38	11,91	49,60	—	55,32	35,44	24,78	26,92	51,75
XXVIII	2-Me	3	1,3	—	−1,15	19,51	14,70	21,40	58,05	56,43	35,56	24,71	27,05	52,59
XXIX	2,6-Me_2	1	−1,7	—	0,02	22,96	42,91	—	—	60,00	35,37	24,32	35,37	60,00
XXX	2,6-Me_2	2	0,5	—	−1,15	22,24	14,64	19,84	53,44	56,30	35,96	25,30	35,96	56,30
XXXI	H*	1	−0,5	—	−0,05	—	49,99	—	—	57,34	23,41	22,83	23,41	57,34
XXXII	H*	2	1,0	—	−1,35	—	12,04	55,52	—	52,59	23,34	22,76	23,34	52,59
XXXIII	H*	3	1,7	—	−1,22	—	14,25	18,86	60,91	53,50	23,22	22,57	23,22	53,50

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*$Me_3Si(CH_2)_mNC_5H_{10}\cdot HCl$.

TABLE 6. ^{13}C, ^{15}N, and ^{29}Si NMR Spectra of (Piperidinoalkyl)silacyclanes $R(CH_2)_mNC_5H_{10}$

Compound	R	m	δ ^{29}Si, ppm	δ ^{15}N, ppm	δ ^{13}C (Me), ppm	δ ^{13}C $(-CH_2)_m$, ppm			δ ^{13}C (NC_5H_{10}), ppm			δ ^{13}C (R), ppm		
						C—Si	—CH_2—	C—N	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(1)}$	$C_{(2)}$	$C_{(3)}$
XXXIV	$(CH_2)_5SiMe$	1	−5,6	−337,4	−4,27	50,19	—	—	59,16	26,92	24,45	13,92	25,04	30,63
XXXV	$(CH_2)_5SiMe$	2	−3,3	−324,8	−4,27	12,49	55,00	—	54,61	26,66	25,30	13,17	25,04	30,76
XXXVI	$(CH_2)_5SiMe$	3	−2,7	−327,9	−4,40	12,30	21,79	63,58	55,26	26,66	25,23	13,40	25,04	30,76
XXXVII	$(CH_2)_4SiMe$	1	15,1	−336,6	−2,78	50,71	—	—	58,96	26,86	24,39	12,88	27,70	—
XXVIII	$(CH_2)_4SiMe$	2	17,2	−325,4	−2,65	13,66	55,32	—	54,61	26,60	25,23	12,30	27,77	—
XXXIX	$(CH_2)_4SiMe$	3	18,2	−329,3	−2,78	13,34	22,31	63,51	55,26	26,60	25,17	12,23	27,83	—

TABLE 7. Substituent Increments ΔSi = $\delta^{29}Si[Me_3Si(CH_2)_mR]$ − $\delta^{29}Si[Me_3Si(CH_2)_nH]$

R*	n	ΔSi
Piperidino	1	−1,9
Piperidino	2	−1,2
Piperidino	3	0,2
Me [15]	1	1,6
Me [15]	2	−0,9
Me [15]	3	−0,1
OMe [13]	1	−2,1
OMe [13]	2	−1,7
OMe [13]	3	−0,3
Ph [14]	1	0,4
Ph [14]	2	−0,5
Ph [14]	3	0,4
4-MP** [15]	1	−1,4
4-MP** [15]	2	−0,7
4-MP** [15]	3	0,8
4-MPD*** [15]	1	0,2
4-MPD*** [15]	2	0,3
4-MPD*** [15]	3	1,5

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*Citations to the literature source are given in square brackets.

**4-MP is 4-methyl-1-piperazinyl.

***4-MPD is 4-methyl-1-piperazinyl (dihydrochloride).

the ^{15}N resonance signal should experience the influence of two opposite effects: a weak-field shift caused by transfer of the electron density and a strong-field shift due to the development of additional steric interactions [17]. Steric effects evidently prevail in the series of compounds that we investigated.

The ^{13}C CS of Si—Me groups change little as m is varied. Compounds containing a hydrogen atom attached to the silicon atom, in which the strongest N→Si bond is expected, constitute an exception. In this case the m = 1-3 transition gives rise to weak-field shifts (~3 ppm), which is extremely unexpected and is possibly, in part, a consequence of N→Si charge transfer. When m = 1, we did not find linear correlations between the ^{13}C CS of the Si—CH_2 carbon nucleus and the inductive constants σ^* of the $R^1R^2R^3$ substituents attached to the silicon atom. However, one observes a quite definite tendency of a strong-field shift of the ^{13}C signal of the CH_2 groups as electronegative substituents attached to the silicon atom accumulate. On the other hand, the formation of the hydrochloride also causes strong-field ^{13}C shifts of the Si—$(CH_2)_m$ carbon atoms and the piperidine ring. This is in agreement with [18], in which the same changes were noted for (piperidinoalkyl)silanes with a different set of substituents attached to the silicon atom. Consequently, the ^{13}C CS for I-IX for the change m = 1-3 are in complete agreement with the certain degree of increase in the positive charge on the nitrogen atom when m = 1 as compared with m = 3.

To investigate the relative basicity of the nitrogen atom in the investigated compounds we used ^1H NMR spectroscopy to determine the parameters of their complexing with chloroform (Table 8). We used chloroform because the changes in its ^1H CS upon complexing are quite large, whereas self-association is insignificant. The CS of chloroform in the completely complexed state of the relatively pure monomer (σ_c) is proportional to the strength of the hydrogen bond, which in this case is determined by the basic properties of the nitrogen atom. The results obtained provide evidence that the electron-donor capacity of the nitrogen atom in compounds with m = 1 is markedly decreased as compared with compounds in which m = 2 or 3, which may attest to an N→Si interaction if there is only one methylene group between these atoms.

The synthesized compounds were also investigated by GLC with nonpolar and polar columns. The Kovacs retention indexes and ΔI values, which are presented in Table 9, make it possible to draw some conclusions regarding the effect of the structure of the sorbates on their polarities and nonspecific and specific intermolecular interactions.

Despite the fundamental possibility that the compounds exist in the form of cis and trans isomers, their separation was not detected in a single instance. In the investigated series one observes deviations from the Kovacs rules that attest to

TABLE 8. Parameters of the Complexing of Chloroform with Substituted Piperidines $Me_3Si(CH_2)_mNC_5H_9X$

Compound	X	m	K_c*	δ_c, ppm**
VII	H	1	1,30	−0,85
VIII	H	2	3,59	−1,35
IX	H	3	3,65	−1,24
XX	4-CH_3	1	0,99	−0,89
XXI	4-CH_3	2	1,71	−1,67
XXII	4-CH_3	3	1,58	−1,65
XXIII	3-CH_3	1	1,13	−0,83
XXIV	3-CH_3	2	2,95	−1,29
XXV	3-CH_3	3	3,36	−1,16
XXVI	2-CH_3	1	0,84	−1,22
XXVII	2-CH_3	2	2,60	−1,58
XXVIII	2-CH_3	3	1,88	−1,64
XXIX	2,6-CH_3	1	2,29	−1,21
XXX	2,6-CH_3	3	3,77	−1,40

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*K_c is the complexing constant for $CHCl_3 \cdots amine \rightarrow CHCl_3 + amine$.

**δ_c is the shift for the $CHCl_3 \cdots$amine complex.

TABLE 9. Retention Indexes of Piperidine Derivatives $XC_5H_9N(CH_2)_mR$*

Compound	X	R	m	I (Apiezon L)	I (Carbowax 20M)	ΔI
	H	H	0	772	1060	288
	H	Et	0	862	1019	157
VII	H	$SiMe_3$	1	1048	1119	171
VIII	H	$SiMe_3$	2	1182	1283	107
IX	H	$SiMe_3$	3	1265	1367	102
	2-Me	H	0	827	1070	243
	2-Me	Et	0	948	1086	138
XXVI	2-Me	$SiMe_3$	1	1121	1185	64
XXVII	2-Me	$SiMe_3$	2	1251	1347	94
XXVIII	2-Me	$SiMe_3$	3	1328	1420	92
	3-Me	H	0	851	1130	279
	3-Me	Et	0	921	1062	141
XXIII	3-Me	$SiMe_3$	1	1101	1144	43
XXIV	3-Me	$SiMe_3$	2	1225	1301	76
XXV	3-Me	$SiMe_3$	3	1310	1390	80
	4-Me	H	0	847	1127	280
	4-Me	Et	0	926	1068	142
XX	4-Me	$SiMe_3$	1	1106	1161	55
XXI	4-Me	$SiMe_3$	2	1232	1309	77
XXII	4-Me	$SiMe_3$	3	1323	1406	83
	2,6-Me	H	0	856	1054	198
	2,6-Me	Et	0	928	1052	124
XXIX	2,6-Me	$SiMe_3$	1	1231	1310	79
XXX	2,6-Me	$SiMe_3$	3	1388	1474	86

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*The column temperature was 100°C for the compounds with m = 0 and 180°C for the compounds with m = 1-3.

intramolecular interactions in the sorbates. Thus a nonlinear increase in I was noted as the chain becomes longer (m = 1-3): a pronounced jump on passing from m = 1 to m = 2 and a significantly smaller jump on passing to m = 3. This sort of phenomenon has already been noted in a series of piperazine derivatives [5].

The ΔI parameter serves as a measure of the effective chromatographic polarity of the sorbates. An analysis of the values obtained shows that the substances with m = 1, in which the $SiMe_3$ group is maximally close to the nitrogen atom, have the lowest polarities, while the ΔI values for the compounds with m = 2 and 3 are higher and are close to one another.

A comparison of the organosilicon derivatives with alkyl derivatives shows that the substances of the first group have a substantially lower capacity for interacting with stationary phases. It is well known that alkyl groups attached to α-carbon atoms substantially decrease the capacity of the heterocyclic nitrogen atom for such interactions. This leads to a decrease in the ΔI parameter. However, in the examined series this sort of effect is observed only for derivatives with R = H and Et, which indicates the dominating role of steric effects. On the other hand, an increase in the effective polarity in the order γ-substituted, α-substituted, α,α′-disubstituted is characteristic for the organosilicon derivatives.

EXPERIMENTAL

The NMR spectra of solutions of the compounds in $CDCl_3$ at a sample temperature of 40°C were obtained with a Bruker WH-90/DS spectrometer. In the case of the ^{13}C NMR spectra the operating frequency was 22.63 MHz, the pulse duration was 5 μsec, proton decoupling was complete, the internal standard was tetramethylsilane (TMS), and the accuracy in measuring the CS was ±0.07 ppm. In the case of the ^{29}Si NMR spectra the operating frequency was 17.88 MHz, the pulse duration was 5 μsec, proton decoupling was complete, the number of accumulations was 500-1000, the internal standard was TMS, and the accuracy in measuring the CS was ±0.1 ppm. In the case of the ^{15}N NMR spectra the operating frequency was 9.12 MHz, proton decoupling was complete, the pulse duration was 12 μsec, the average number of accumulations was 8000, the external standard was ^{15}N-nitromethane, and the accuracy in measuring the CS was ±0.2 ppm.

The retention indexes were measured with Hewlett—Packard 7620 and Khrom-4 chromatographs. Apiezon L and Carbowax 20M, applied in 5% amounts to Chromosorb W-HP, were used as the stationary phases. The column was 1.2-m long, and the temperatures used were 100°C and 180°C. The investigated substances were introduced in 1-μl amounts of 5% solutions in acetone. Alkanes with 8 to 14 carbon atoms were used as standards for measuring the retention indexes.

The parameters of the complexing of chloroform with substituted (piperidinoalkyl)silanes were determined by the method in [19].

Trimethyl[(4-methylpiperidino)methyl]silane (XX). A mixture of 32 g (0.32 mole) of 4-methylpiperidine and 20 g (0.16 mole) of trimethyl(chloromethyl)silane in 100 ml of dry hexane was refluxed for 15 h, after which the precipitate was removed by filtration, and the solvent was removed by distillation. Twofold fractional distillation in vacuo gave 18.9 g (63%) of XX with bp 86°C (22 mm) and n_D^{20} 1.4461.

A similar procedure was used to obtain VII [bp 67-68°C (19 mm), n_D^{20} 1.4500], IX [bp 68°C (mm), n_D^{20} 1.4535], and X [bp 145-148°C (17 mm), n_D^{20} 1.5174] [6, 8].

Trimethyl[2-(4-methylpiperidino)ethyl]silane (XXI). A 0.2-g (0.03 mole) sample of finely cut lithium was added in a nitrogen atmosphere to 7.2 g (0.07 mole) of 4-methylpiperidine in 15 ml of THF, the mixture was heated to 40°C, 9.9 g (0.1 mole) of trimethyl(vinyl)silane was added with stirring, and the resulting mixture was refluxed for 3 h. The precipitate was removed by filtration, and the THF was removed by distillation. The residue was fractionally distilled in vacuo to give 11.3 g (78%) of XXI with bp 90-92°C (15 mm) and n_D^{20} 1.4501.

A similar procedure was used to synthesize VIII [bp 81-82°C (14 mm), n_D^{20} 1.4530] and XI [bp 166-167°C (16 mm), n_D^{20} 1.5153] [6, 8].

Dimethyl(piperidinomethyl)silane (V). A 10.1-g (0.06 mole) sample of dimethyl(piperidinomethyl)ethoxysilane in 20 ml of ether was added with stirring to 1 g (0.03 mole) of $LiAlH_4$ in 70 ml of dry ether, and the mixture was stirred for 2 h and refluxed for 1 h. It was then allowed to stand for 15 h at 20°C, after which the ether layer was decanted. Benzene (20 ml) was added to the residue, and the mixture was stirred. After 1 h, the benzene solution was decanted, and the two solutions were combined. The solvents were removed by distillation, and the residue was fractionally distilled in vacuo to give 4.8 g (62%) of V.

Dimethyl(chloromethyl)ethoxysilane. A 100-g (0.7 mole) sample of dimethyl(chloromethyl)chlorosilane was added dropwise with stirring to a mixture of 32.2 g (0.7 mole) of dry ethanol and 42 g of urea, and the mixture was stirred for 2 h. The lower layer was separated, and the upper layer was neutralized with NaOH. The precipitate was removed by filtration, and the ethanol was removed by distillation. The residue was fractionally distilled in vacuo to give 88.2 g (80%) of dimethyl(chloromethyl)ethoxysilane with bp 136-138°C and n_D^{20} 1.4147.

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