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THE CONFORMATIONS OF N-SUBSTITUTED 2,2-DIARYL-1,3-DIOXA-6-AZA-2-SILACYCLOOCTANES IN SOLUTION *

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Summary

^1H , ^{13}C and ^{29}Si NMR data obtained for 2,2-diaryl-1,3-dioxa-6-aza-2-silacyclooctanes $\text{Ar}_2\text{Si}(\text{OCH}_2\text{CH}_2)_2\text{NR}$ indicate the occurrence in solution of an equilibrium between the conformations boat-boat \rightleftharpoons chair-chair which are determined by the presence or absence of a transannular $\text{N} \rightarrow \text{Si}$ bond. The equilibrium is greatly affected by the electronic and steric effects of the N- and Si-substituents.

Introduction

The molecules of silicon-containing diethanolamine esters $\text{R}^1\text{R}^2\text{Si}(\text{OCH}_2\text{CH}_2)_2\text{NR}$ (I) exist in the crystalline state in the boat-boat conformation, allowing the formation of a $\text{N} \rightarrow \text{Si}$ transannular bond, as revealed by recent X-ray studies [1–4]. ^{29}Si NMR spectra of *N*-methyl and *N*-unsubstituted derivatives of 2,2-diphenyl-1,3-dioxa-6-aza-2-silacyclooctane (I, $\text{R} = \text{H}, \text{CH}_3$; $\text{R}^1, \text{R}^2 = \text{C}_6\text{H}_5$) show a diamagnetic shift with respect to diphenyldiethoxysilane. In addition, ^1H resonances of the *N*-methyl protons are shifted to higher field values. These results were regarded as a possible indication of a donor-acceptor (DA) $\text{N} \rightarrow \text{Si}$ bond present in the solution [5–6]. However, no systematic NMR investigation of I has been reported so far.

Our objective was to study by NMR the conformations of *N*-substituted 2,2-diaryl-1,3-dioxa-6-aza-2-silacyclooctanes (I, $\text{R}^1, \text{R}^2 = \text{Ar}$) and to examine factors affecting DA $\text{N} \rightarrow \text{Si}$ bond formation in solution. ^1H , ^{13}C and ^{29}Si NMR spectra have been obtained for these compounds (Tables 1–4).

Two extreme conformations: chair-chair (CC, II) exhibiting no $\text{N} \rightarrow \text{Si}$ inter-

* Dedicated to Prof. G.A. Razuvaev on the occasion of his 85th birthday on August 23rd, 1980.

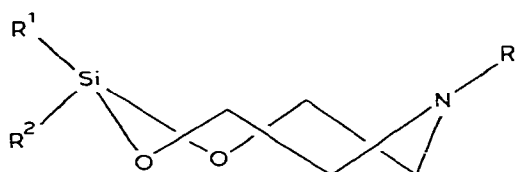
TABLE I
¹H CHEMICAL SHIFTS FOR DIETHANOLAMINES AND THEIR CYCLIC ORGANOSILICON ESTERS I AT 30°C (ppm)

Formula	OCH ₂	NCH ₂	α-CH ₂	β-CH ₂	γ-CH ₂	δ-CH ₂	SiR
(HOCH ₂ CH ₂) ₂ NH	3.69	2.75	—	—	—	—	—
(HOCH ₂ CH ₂) ₂ NCH ₃	3.65	2.57	2.29	—	—	—	—
(HOCH ₂ CH ₂) ₂ NC ₂ H ₅	3.60	2.63	2.61	1.03	—	—	—
(HOCH ₂ CH ₂) ₂ NC ₃ H ₇ n	3.60	2.63	2.49	1.47	1.88	—	—
(HOCH ₂ CH ₂) ₂ NC ₄ H ₉ n	3.60	2.64	2.53	1.60	1.80	0.91	—
(HOCH ₂ CH ₂) ₂ NC ₄ H ₉ t	3.46	2.69	—	1.08	—	—	—
(C ₆ H ₅) ₂ Si(OCH ₂ CH ₂) ₂ NH	3.92	2.83	—	—	—	—	7.20—7.60
(C ₆ H ₅) ₂ Si(OCH ₂ CH ₂) ₂ NCH ₃	3.98	2.58	1.65	—	—	—	7.20—7.60
(4-CH ₃ C ₆ H ₄) ₂ Si(OCH ₂ CH ₂) ₂ NCH ₃	3.94	2.59	1.77	—	—	—	7.08, 7.47 (C ₆ H ₄) 2.27 (CH ₃)
(4-ClC ₆ H ₄) ₂ Si(OCH ₂ CH ₂) ₂ NCH ₃	3.97	2.59	1.64	—	—	—	7.27, 7.47 (C ₆ H ₄)
(2-C ₄ H ₃ O) ₂ Si(OCH ₂ CH ₂) ₂ NCU ₃	3.87	2.67	1.85	—	—	—	6.61 (H ₃); 6.3 (H ₄) 7.53 (H ₅)
(C ₆ H ₅) ₂ Si(OCH ₂ CH ₂) ₂ NC ₂ H ₅	3.97	2.64	2.01	0.62	—	—	7.20—7.60
(C ₆ H ₅) ₂ Si(OCH ₂ CH ₂) ₂ NC ₃ H ₇ n	3.96	2.66	1.92	1.50	0.59	—	7.20—7.60
(C ₆ H ₅) ₂ Si(OCH ₂ CH ₂) ₂ NC ₄ H ₉ n	3.96	2.65	1.94	1.60	1.80	0.77	7.20—7.60
(C ₆ H ₅) ₂ Si(OCH ₂ CH ₂) ₂ NC ₄ H ₉ t	3.99	2.71	—	0.80	—	—	7.20—7.60

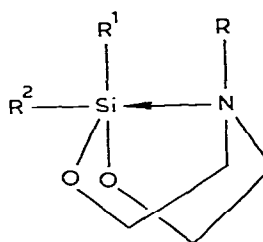
TABLE 2
 ^{13}C CHEMICAL SHIFTS FOR $(\text{HOCH}_2\text{CH}_2)_2\text{NR}$ AT 30°C (ppm)

R	OC	NC	C_R			
			α	β	γ	δ
H	61.0	51.9	—	—	—	—
CH_3	60.3	59.7	42.9	—	—	—
C_2H_5	60.2	56.4	49.0	11.9	—	—
$n\text{-C}_3\text{H}_7$	60.2	57.0	57.6	20.5	12.2	—
$n\text{-C}_4\text{H}_9$	60.2	56.9	55.3	29.5	21.1	14.5
$t\text{-C}_4\text{H}_9$	62.6	53.1	55.3	27.4	—	—

action and boat-boat (BB, III) with the transannular $\text{N} \rightarrow \text{Si}$ bond are conceivable for the title compounds.



(II)



(III)

Transannular $\text{N} \rightarrow \text{Si}$ bonding is supported by the fact that ^{15}N chemical shifts are correlated with the total sum of induction constants of the Si-substituents ($\Sigma\sigma^*$), a topic to be specifically treated elsewhere.

Results and discussion

In comparison with the model N-substituted diethanolamines, the ^1H and ^{13}C spectra of dioxazasilacyclooctanes fail to demonstrate such remarkable resonance shifts for the NCH_2 group on the ring (Tables 1–3) as, for example, in the case of silatranes [7]. This may be indicative either of insignificant charge transfer along the $\text{N} \rightarrow \text{Si}$ bond or of the existence of a conformational equilibrium ($\text{CC} \rightleftharpoons \text{BB}$) shifted to the CC form. Alternatively, the ^1H resonance of the NR substituent is displaced toward higher field with respect to the model amino alcohol (Table 1), implying close proximity of the NR and SiAr_2 groups and suggesting that the BB conformation constitutes a considerable portion in the solution. At lower temperatures the resonance absorption of NR-protons is displaced to higher field values as a result of still closer proximity of these two groups. Such temperature-dependent changes in the ^1H spectra provide direct evidence for the existence of a conformational equilibrium ($\text{CC} \rightleftharpoons \text{BB}$) for molecules of I in solution. Furthermore, considerable displacement of the resonance toward higher fields noted for SiAr_2 group *ortho*-protons at low temperatures also suggests increased share in the solution of the conformer

TABLE 3

 ^{13}C CHEMICAL SHIFTS FOR $(\text{Ar})_2\text{Si}(\text{OCH}_2\text{CH}_2)_2\text{NR}$ AND MODEL COMPOUNDS AT 30°C (ppm)

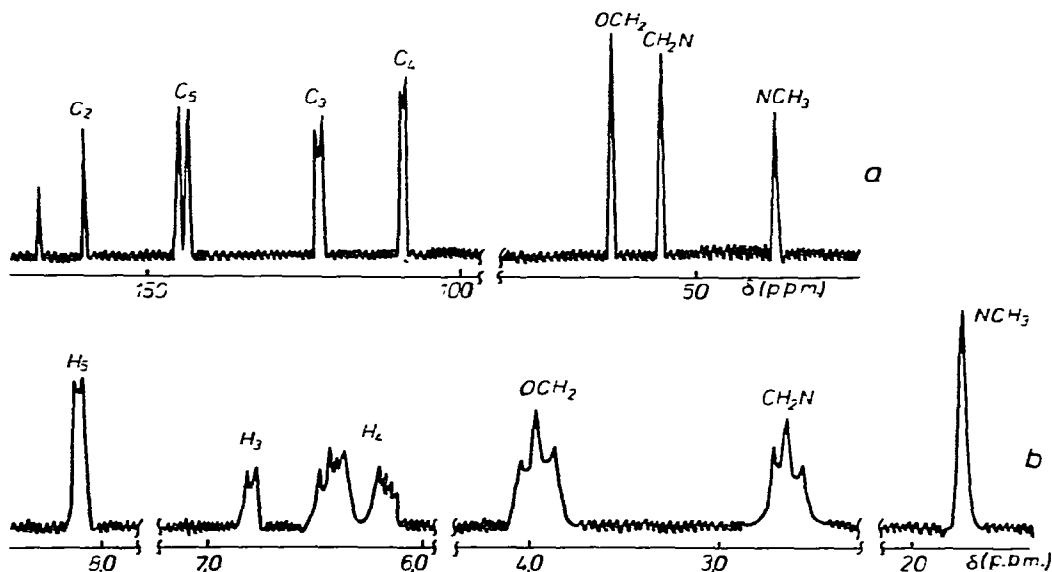
Ar	R	OC	NC	Cr		γ	δ	Ar		Remaining groups		
				α	β			C_α	C_m	C_o	C_p	
C_6H_5	H	63.8	49.0	—	—	—	—	136.1	128.3	134.7	129.7	
C_6H_5	CH_3	61.9	55.9	42.6	—	—	—	139.3	128.1	134.1	129.1	
$4\text{-CH}_3\text{C}_6\text{H}_4$	CH_3	62.2	56.7	43.1	—	—	—	138.8	128.9	134.4	135.2	21.9 (CH_3)
$4\text{-ClC}_6\text{H}_4$	CH_3	61.8	56.8	42.7	—	—	—	137.7	128.4	135.4	128.8	
$2\text{-C}_4\text{H}_3\text{O}$	CH_3	61.5	56.7	41.9	—	—	—	159.6 (C_2)	120.1 (C_3)	109.8 (C_4)	146.1 (C_5)	
C_6H_5	C_2H_5	63.1	43.5	48.8	9.8	—	—	138.3	128.2	134.5	129.5	
C_6H_5	$n\text{-C}_3\text{H}_7$	63.1	54.2	57.5	18.3	12.2	—	138.1	128.1	134.6	129.5	
C_6H_5	$n\text{-C}_4\text{H}_9$	63.1	54.3	55.5	27.4	21.1	14.4	138.1	128.2	134.6	129.5	
C_6H_5	$t\text{-C}_4\text{H}_9$	66.1	52.3	55.9	27.0	—	—	136.3	128.2	135.2	130.2	
$(\text{C}_6\text{H}_5)_2\text{Si}(\text{OC}_2\text{H}_5)_2$		59.4	—	—	—	—	—	134.0	128.4	135.5	130.8	18.8 (CH_3)
$(\text{C}_6\text{H}_5)_2\text{Si}(\text{OCH}_2\text{CH}_2\text{NMe}_2)_2$		62.2	61.9	—	—	—	—	133.6	128.4	135.6	130.8	46.6 (NCH_3)
$(2\text{-C}_4\text{H}_3\text{O})_2\text{Si}(\text{OC}_2\text{H}_5)_2$		59.9	—	—	—	—	—	153.0 (C_2)	124.0 (C_3)	109.8 (C_4)	147.9 (C_5)	18.6 (CH_3)
$(4\text{-ClC}_6\text{H}_4)_2\text{Si}(\text{OC}_2\text{H}_5)_2$		59.6	—	—	—	—	—	137.5	128.8	136.9	131.9	18.7 (CH_3)

TABLE 4

 ^{29}Si CHEMICAL SHIFTS FOR $(\text{Ar})_2\text{Si}(\text{OCH}_2\text{CH}_2)_2\text{NR}$ AT 30°C (ppm)

Ar	R	$\delta_{^{29}\text{Si}}$
C_6H_5	H	-44.7
C_6H_5	CH_3	-43.9
$4\text{-CH}_3\text{C}_6\text{H}_4$	CH_3	-41.5
$4\text{-ClC}_6\text{H}_4$	CH_3	-47.0
$2\text{-C}_4\text{H}_3\text{O}$	CH_3	-69.4
C_6H_5	C_2H_5	-40.0
C_6H_5	$n\text{-C}_3\text{H}_7$	-39.6
C_6H_5	$n\text{-C}_4\text{H}_9$	-39.6
C_6H_5	$t\text{-C}_4\text{H}_9$	-35.2
$(\text{C}_6\text{H}_5)_2\text{Si}(\text{OC}_2\text{H}_5)_2$		-32.4
$(\text{C}_6\text{H}_5)_2\text{Si}[\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2]_2$		-31.6
$(2\text{-C}_4\text{H}_3\text{O})_2\text{Si}(\text{OC}_2\text{H}_5)_2$		-50.6
$(4\text{-ClC}_6\text{H}_4)_2\text{Si}(\text{OC}_2\text{H}_5)_2$		-33.4

carrying the transannular $\text{N} \rightarrow \text{Si}$ bond. In the case of strong acceptors at the silicon atom ($\text{Ar} = 2\text{-furyl}$, 4-chlorophenyl) signals from both aryl groups located equatorially and axially in the trigonal bipyramid can be observed in ^1H and ^{13}C spectra at -60°C (Fig. 1), with no evidence, however, of the CC conformation. In ^{29}Si NMR spectra at -60°C a single signal is observed which is displaced by 6–7 ppm to higher field as compared with the corresponding signal obtained at room temperature. These results suggest a complete shift of the equilibrium to the BB conformation in the case of $\text{Ar} = 2\text{-furyl}$, 4-chlorophenyl at low temperature. The signals from two aryl groups present in ^1H and ^{13}C spectra demonstrate the occurrence of I in CDCl_3 solution predominantly in conforma-

Fig. 1. NMR spectra of 2,2-di(2'-furyl)-1,3-dioxo-6-aza-2-silacyclooctane at 215 K: ^{13}C (a), ^1H (b).

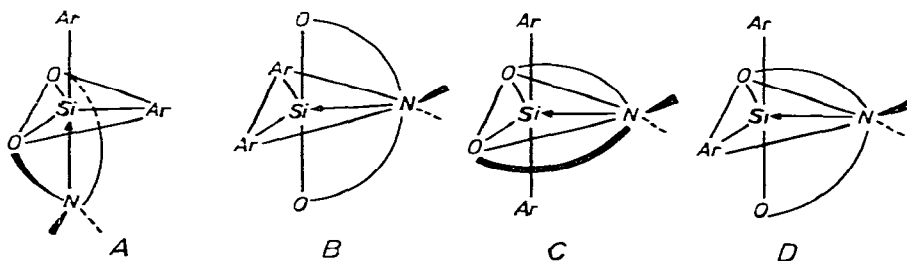


Fig. 2. Possible trigonal bipyramidal conformations of 2,2-diaryl-1,3-dioxo-6-aza-2-silacyclooctanes.

tion A, but not B or C. Conformation D is rejected on the basis of identity of ^1H and ^{13}C chemical shifts registered for the two $\text{OCH}_2\text{CH}_2\text{N}$ fragments at low temperatures (Fig. 2).

The free enthalpy of activation (ΔG_c^\ddagger) estimated at the temperature of signal coalescence of 2-furyl groups is 11.6 kcal/mol. This value is significantly lower than that obtained by the same process for $\text{R}_2\text{Sn}(\text{XCH}_2\text{CH}_2)_2\text{NCH}_3$ [8]. We have estimated the enthalpy and entropy changes upon transition from CC to BB conformation along with the conformational equilibrium constants at $+30^\circ\text{C}$ (Table 5) on the basis of the temperature-dependence of the ^1H resonance of *ortho*-protons in the SiAr_2 group. The values of equilibrium constants demonstrate that increased donor capacity of Si-substituents and greater size of N-substituents result in the shift of the equilibrium to CC conformation.

In the ^{13}C spectra the signal of the *para*-carbon in the phenyl cycle is considerably displaced to higher field values, as compared with the model compounds $\text{Ph}_2\text{Si}(\text{OEt})_2$ and $\text{Ph}_2\text{Si}(\text{OCH}_2\text{CH}_2\text{NMe}_2)_2$. This displacement being less pronounced in the N-H and N-*t*-butyl derivatives provides further evidence for a smaller proportion in solution of the coordinated form, in agreement with the data summarized in Table 5.

The more negative values of the chemical shifts observed for ^{29}Si NMR spectra (Table 4) of I in comparison with the model compounds $\text{Ph}_2\text{Si}(\text{OEt})_2$ and $\text{Ph}_2\text{Si}(\text{OCH}_2\text{CH}_2\text{NMe}_2)_2$ may be due to (1) the occurrence of $\text{CC} \rightleftharpoons \text{BB}$ equilibrium, (2) the altered total sum of charges at the silicon atom coordinated with nitrogen atom in the BB conformation, (3) the effects of the

TABLE 5

THERMODYNAMIC PARAMETERS OF $\text{CC} \rightleftharpoons \text{BB}$ CONFORMATIONAL EQUILIBRIUM FOR $(\text{Ar})_2\text{Si}(\text{OCH}_2\text{CH}_2)_2\text{NR}$

Ar	R	$-\Delta H$ (kcal/mol)	$-\Delta S$ (e.u.)	$k_{303^\circ\text{K}}$
C_6H_5	H	6.7 ± 1.6	24.6 ± 5.7	0.36
C_6H_5	CH_3	1.8 ± 0.1	6.1 ± 0.3	0.96
4- $\text{CH}_3\text{C}_6\text{H}_4$	CH_3	2.4 ± 0.2	10.4 ± 0.7	0.31
4- ClC_6H_4	CH_3	1.7 ± 0.2	4.2 ± 0.8	1.44
2- $\text{C}_4\text{H}_3\text{O}$	CH_3	2.6 ± 0.1	6.3 ± 1.5	3.20
C_6H_5	C_2H_5	2.2 ± 0.1	7.5 ± 0.5	0.83
C_6H_5	<i>n</i> - C_3H_7	2.7 ± 0.2	8.6 ± 0.6	1.11
C_6H_5	<i>n</i> - C_4H_9	2.4 ± 0.2	7.9 ± 0.6	1.06
C_6H_5	<i>t</i> - C_4H_9	6.9 ± 2.1	20.7 ± 8.0	0.54

geometry of the BB conformation. In as much as the substituents at silicon in the title compounds remain the same, variation in the silicon charge may be neglected. The CC \rightleftharpoons BB equilibrium was estimated using equilibrium constants determined from ^1H NMR spectra according to the formulas:

$$\Delta\delta_{\text{Si}}^0 = \frac{1+k}{k} \Delta\delta_{\text{Si}};$$

$$\Delta\delta_{\text{Si}}^0 = \delta_{\text{Si}}^c - \delta_{\text{Si}}^{\text{nc}};$$

$$\Delta\delta_{\text{Si}} = \delta_{\text{Si}}^{\text{ob}} - \delta_{\text{Si}}^{\text{nc}};$$

where $\delta_{\text{Si}}^{\text{nc}} = ^{29}\text{Si}$ chemical shift for a noncoordinated form (in this particular case model compound $\text{Ph}_2\text{Si}(\text{OCH}_2\text{CH}_3)_2$; $\delta_{\text{Si}}^{\text{ob}}$ = observed chemical shift for a compound; δ_{Si}^c = chemical shift for a compound in BB conformation, $k =$ equilibrium constant.

The values of $\Delta\delta_{\text{Si}}^0$ and the corresponding values for para-carbon $\Delta\delta_{\text{Cp}}^0$ calculated according to this method are summarized in Table 6. Reliability of $\Delta\delta_{\text{Si}}^0$ values can be verified using ^{29}Si NMR spectra at low temperature when the compound exists exclusively in the coordinated form. The experimentally found value of $\Delta\delta_{\text{Si}}^0$ for the di(2-furyl)-6-methyl derivative is -24.6 ppm, the calculated value being -24.7 ppm.

The data presented in Table 4 must be directly linked with changes in the silicon coordination number. As the obtained $\Delta\delta_{\text{Si}}^0$ values diminish in the N-substituent series from H to tert-butyl it can be surmised that in the complexed form, silicon hybridization, and consequently N \rightarrow Si bond length, would vary with different N-substituents. This assumption is supported by the fact that $\Delta\delta_{\text{Si}}^0$ is correlated with Δl and l , where Δl is a measure of silicon deviation from the equatorial plane formed by three atoms of the substituents (O, O, C) and l stands for N \rightarrow Si bond lengths.

$$\Delta\delta_{\text{Si}}^0 = -77.7 + 142.0 \Delta l \quad r = 0.999$$

$$S = 0.13$$

$$\Delta\delta_{\text{Si}}^0 = -134.0 + 40.2 l \quad r = 0.993$$

$$S = 1.5$$

X-ray analysis performed on crystals yielded the values of Δl and l for N-substituents H [1], CH_3 and $(\text{CH}_3)_3\text{C}$ [9]. Thus, the changes in silicon hybridiza-

TABLE 6
CALCULATED $\Delta\delta_{\text{Si}}^0$ AND $\Delta\delta_{\text{Cp}}^0$ VALUES FOR $(\text{Ar})_2\text{Si}(\text{OCH}_2\text{CH}_2)_2\text{NR}$ COORDINATE FORMS (ppm)

Ar	R	$\Delta\delta_{\text{Si}}^0$	$\Delta\delta_{\text{Cp}}^0$
C_6H_5	H	-42.1	-5.8
C_6H_5	CH_3	-23.9	-3.5
4-Cl C_6H_4	CH_3	-32.0	-5.3
C_6H_5	C_2H_5 1	-16.7	-2.7
C_6H_5	n- C_3H_7	-13.7	-2.5
C_6H_5	n- C_4H_9	-14.0	-2.4
C_6H_5	t- C_4H_9	-8.0	-1.7
2- $\text{C}_4\text{H}_3\text{O}$	CH_3	-24.7	

tion from sp^3 to sp^3d in these compounds is accompanied by the shift of ^{29}Si signal to higher field by ≈ 78 ppm.

Correlation is also noted between $\Delta\delta_{\text{C}_p}^0$ values for the *para*-carbon in the phenyl ring and the values of $\Delta\delta_{\text{Si}}^0$ and ΔI :

$$\Delta\delta_{\text{C}_p}^0 = -0.86 + 0.11 \Delta\delta_{\text{Si}}^0 \quad r = 0.995 \\ s = 0.06$$

$$\Delta\delta_{\text{C}_p}^0 = -10.1 + 17.3 \Delta I \quad r = 0.999 \\ s = 0.04$$

It is apparent that altered hybridization of the silicon atom (and formation of the donor-acceptor bond $\text{N} \rightarrow \text{Si}$) brings about a significant increase in donor capacity of the substituent $(\text{Ph})\text{Si}(\text{OCH}_2\text{CH}_2)_2\text{NR}$.

Consequently, changes in the geometry of the coordinated form of I upon transition from NH to *tert*-butyl substituents are largely determined by the nature of the N-substituents because of their different induction and steric effects.

Quantitation of these two parameters for the N-substituents is possible with the aid of two factors, i.e., correlation between $\Delta\delta_{\text{Si}}^0$ values, E_S and σ^* constants:

$$\Delta\delta_{\text{Si}}^0 = -18.6 + 2.6E_S - 61.0\sigma^* \quad r = 0.995 \\ s = 1.85$$

The latter equation may be used to predict the geometry of the coordinated form of I for various N-substituents.

Experimental

^1H , ^{13}C , ^{29}Si NMR spectra were recorded with a WH-90/DS spectrometer operating in the pulsed Fourier transform mode using proton decoupling (for ^{13}C and ^{29}Si). Tube diameter was 5 mm for ^1H and 10 mm for ^{13}C and ^{29}Si . The pulse length for ^1H was 1.5 μsec , for ^{13}C and ^{29}Si , 5 μsec . Delay time was 3 sec for ^{13}C and ^{29}Si . The compounds were used as 0.01 *M* (^1H) or 0.1 *M* (^{13}C and ^{29}Si) solutions in CDCl_3 . The accuracy of chemical shift measurements was ± 0.01 ppm. (^1H) and ± 0.1 pm. (^{13}C and ^{29}Si) with tetramethylsilane used as internal standard.

Enthalpy and entropy variation and equilibrium constants were estimated in the -50 to $+50^\circ\text{C}$ range, as outlined in ref. 10.

The title compounds I were synthesized by reacting diaryldiethoxysilanes with the appropriate dialkanolamines in the presence of sodium alcoholate. Purification of I was achieved through distillation in vacuo or by crystallization from *n*-hexane. The synthetic procedure and the properties of I will be described elsewhere.

Similarly, the model compound $(\text{C}_6\text{H}_5)_2\text{Si}[\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2]_2$ was synthesized from diphenyldimethoxysilane and dimethylaminoethanol (b.p. $210^\circ\text{C}/3$ mmHg, n_D^{20} 1.5185).

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