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THE CONFLICT BETWEEN THE CONFORMATIONAL PROPERTIES OF THE EIGHT-MEMBERED HETEROCYCLE AND TRIGONAL BIPYRAMID OF FIVE-COORDINATED SILICON IN 1,3-DIOXA-6-AZA-2-SILACYCLOOCTANES

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Summary

The ^1H, ^{13}C and ^{29}Si NMR spectra of 1,3-dioxa-6-aza-2-silacyclooctanes (I) containing a transannular N → Si bond have been studied at different temperatures in solution. The sterically less crowded equatorial location of the Si substituent at the trigonal bipyramid (TBP) corresponds to the energetically unfavourable axial position in the eight-membered heterocycle (C_8). For this reason, the preferred orientation of the Si substituent and the conformational equilibrium of C_8 strongly depend on the energy of the N → Si bond. The C_8 of I in solution has the boat-chair (BC) and/or chair-chair (CC) conformations. The weakening of the N → Si bond leads to an increase in dihedral angle φ_{ON} and shifts the conformational equilibrium of C_8 to the CC form. The exchange between the Si substituent positions at the TBP, observed at low temperatures proceeds through the inversion of C_8 and requires dissociation of the N → Si bond.

Introduction

There is strong experimental evidence in favour of the existence of a transannular N → Si bond in the molecules of 1,3-dioxa-6-aza-2-silacyclooctanes (I) both in the crystalline state and solution, as revealed by X-ray [1–4] and NMR [5–8] studies. It has been shown [1,2] that the geometry around the silicon atom is close to trigonal bipyramidal (D_{3h}) with two atoms of oxygen and one substituent in the equatorial plane. A rapid (on the NMR time scale) exchange between the axial and equatorial arrangement of substituents [5] is observed at room temperature is solution. At lower temperatures, this process becomes slow. A dissociative mechanism [9] for the exchange process and the existence of the conformational equilibrium boat-boat (BB) $\rightleftharpoons$ chair-chair (CC) for the eight-membered cycle in solution, have been proposed [5].

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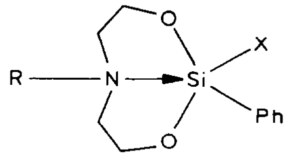


1. X = Ph
2. X = Me
3. X = Pr
4. X = OMe
5. X = H
6. X = Cl

(a) R = Me
(b) R = t-Bu
(c) R = Ph

(I)

This work is an extension of the study of the process of substituent position exchange in the trigonal bipyramid (TBP) of five-coordinated silicon with special emphasis on the conformational equilibrium of the eight-membered cycle (C_8) in solution. For this purposes, we examined ^1H, ^{13}C, ^{29}Si NMR spectra of compounds **1**–**6** in acetone-d_6 solution at temperatures ranging from +30°C to −90°C.

Results and discussion

The ^1H, ^{13}C and ^{29}Si chemical shifts for **1**–**6** at room temperature are given in Tables 1 and 2. There are characteristic upfield shifts of ^{29}Si resonances in **1**–**6** in comparison with the model compounds, diethoxysilanes $R_2Si(OEt)_2$ (II). These shift values are proportional to the strength of the N → Si bond as revealed for the deuteriochloroform solution [5,6,8]. The results presented in Tables 1 and 2 show that the strengthening of the N → Si bond is observed with increasing electron withdrawing ability of the silicon atom and its weakening in the series **a** > **b** > **c** [5,6].

In the crystalline state [1], however, the distance between N and Si in **1c** is somewhat shorter (3.08 Å) than in **1b** (3.16 Å, see also Table 6).

The low temperature spectra of **2a**, **2b**, **3a** and **4b** consist of two sets of signals with unequal intensities (Tables 3 and 4). This fact may be explained by the freezing out of the substituent position exchange process in the TBP of the five-coordinated silicone, as depicted in Fig. 1.

The N → Si bond is retained in both isomers. This is apparent from the ^{29}Si chemical shifts, which are significantly upfield for both isomers as compared to II [5,6]. The only slight difference in ^{29}Si shifts is indicative of the almost equal strengths of N → Si bonds in isomers E and A. The $\Delta G_c^{\neq}$ values (Table 5) tend to decrease in the order **a** > **b** > **c**, showing that the height of the energy barrier for the substituent position exchange process in TBP depends mainly on the strength of the N → Si bond. This agrees with the dissociative mechanism for the exchange process.

The equatorial SiPh group in TBP results in strong shielding effects experienced by ^1H (and ^{13}C) resonances of the N substituents (Table 4). This allowed us to perform a complete assignment of ^1H, ^{13}C, ^{29}Si signals to isomers A and E in the NMR spectra by employing their integral intensities. This is also suggestive of a total shift of the equilibrium towards one isomer (Table 5) for the compounds **4a**, **5a** and **6a** at low temperatures.

The obtained isomer ratios, on the whole, correspond to the general ideas revealed for TBP of the five-coordinated phosphorus [10,11] that has been studied in

(Continued on p. 136)

TABLE 1

^1H AND ^{29}Si NMR CHEMICAL SHIFTS FOR COMPOUNDS **1**–**6** ACETONE-d_6 AT 293 K

Compound	δ^1H (ppm)									$\delta^{29}Si$ (ppm)
	SiPh			X	R	1	2	3	4	
	o-	*m*-	*p*-							
1a	7.54		7.25	–	1.612	2.611		3.947		−45.75
1b	7.65		7.34	–	0.807	2.740		3.966		−36.44
1c	7.53	7.23	7.32	–	7.07(*o*) 6.64(*m*) 6.59(*p*)	3.675		4.151		−31.07
2a	7.53		7.28	0.151	2.074	2.552	2.616	3.781	3.799	−28.19
2b	7.60		7.32	0.340	1.018	2.554	2.853	3.832	3.807	−21.27
2c	7.55	7.27	7.33	0.032	6.747(*o*) 7.185(*m*) 6.674(*p*)	3.431	3.834	3.960	4.157	−20.98
3a	7.50		7.29	0.622(α) 1.295(β) 0.845(γ)	1.909	2.509	2.599	3.793	3.805	−28.83
4a	7.49		7.31	3.330	1.704	2.470	2.618	3.830	3.868	−66.30
4b	7.62		7.35	3.460	0.915	2.727	2.619	3.811	3.909	−58.51
5a	7.52		7.20	5.045	2.364	2.861	2.747	3.828	3.788	−57.23
5a [a]	7.52		7.14	5.062	2.285	2.643	2.594	3.797	3.777	–
5a [b]	7.60		7.29	5.104	2.383	2.835	2.731	3.915	3.862	–
5a [c]	7.44		7.20	4.917	2.332	2.869	2.726	3.788	3.730	–
5c [b]	7.59		7.36	4.862	6.727(*o*) 7.266(*m*) 6.802(*p*)	3.396	3.888	4.071	4.287	–
6a	7.49		7.33	–	1.699	2.730	2.978	4.013	4.013	−69.99

[a] In cyclohexane-d_{12}. [b] In $CDCl_3$, $^1J(Si–H) = -258.3$ Hz (**5a**), $^1J(Si–H) = -244.1$ Hz (**5c**). [c] In dimethylsulphoxide-d_6.

TABLE 2

^{13}C CHEMICAL SHIFTS FOR COMPOUNDS 1–6 IN ACETONE-d_6 AT 293 K (ppm)

Compound	OC	NC	SiPh				X	R
			α-	*o*-	*m*-	*p*-		
1a	61.67	55.65	140.36	134.01	128.09	128.91	–	42.25
1b	65.99	52.46	137.20	135.11	128.24	130.09	–	55.83(α) 26.60(β)
1c	63.04	55.27	134.42	135.27	128.33	130.55	–	148.90(α) 129.65(*m*) 113.03(*o*) 117.22(*p*)
2a	62.32	57.60	140.40	133.73	127.97	129.01	−0.91	43.22
2b	66.06	53.10	138.55	134.51	128.09	129.86	−2.08	55.90(α) 26.90(β)
2c	62.98	56.73	136.72	134.55	128.19	130.26	−5.48	148.59(α) 129.91(*m*) 112.73(*o*) 117.42(*p*)
3a	62.12	57.05	139.27	133.87	128.15	129.06	17.47(α) 19.62(β) 18.32(γ)	43.07
4a	61.82	55.74	136.55	133.56	128.04	128.99	50.02	42.79
4b	65.71	51.68	133.86	135.31	128.11	130.25	50.37	55.71(α) 26.79(β)
5a	59.97	55.10	145.66	134.03	127.57	128.37	–	41.35
6a [a]	60.50	54.58	139.07	130.82	128.80	129.58	–	43.86

[a] In $CDCl_3$.

TABLE 3

^1H AND ^{29}Si CHEMICAL SHIFTS FOR ISOMERS A AND E COMPOUNDS 1–6 IN ACETONE-d_6 AT 183 K

Compound	Isomer	δ^1H (ppm)									$\delta^{29}Si$ (ppm)	$\Delta^{29}Si$ [a] (ppm)
		SiPh			X	R	NCH_2		OCH_2			
		o-	*m*-	*p*-			ax	eq	ax	eq		
1a	A	7.56		7.40	–	1.434	2.52	2.72	3.96		−49.42	−3.67
	E	7.56		7.24	–							
1b	A	7.62		7.47	–	0.711	2.34	3.11	3.98		−38.34	−1.90
	E	7.74		7.34	–							
1c	A,E	7.50	7.31	7.40	–	6.69(*o*) 7.10(*m*) 6.59(*p*)	3.70		4.15		−35.50	−0.91
2a	A	7.44		7.29	−0.090	1.427	2.42	2.59	3.79		−31.27	−3.08
	E	7.61		7.29	0.297	2.460	2.64		3.79		−30.79	−2.60
2b	A	7.42		7.39	0.050	0.681	2.24	3.00	3.80		−22.39	−1.12
	E	7.62		7.39	0.503	1.125	2.29	3.15	3.77	3.82	−21.66	−0.39
2c	A,E	7.76	7.50	7.55	−0.028	6.97(*o*) 7.40(*m*) 6.87(*p*)	3.44	3.97	4.00	4.25	−21.91	−0.93
3a	A	7.31		7.10	0.35(α) 1.17(β) 0.77(γ)	1.359	2.38	2.56	3.73		−32.51	−3.68
	E	7.49		7.10	0.83(α) –	2.457	2.59		3.73		−30.40	−1.57
4a	A	7.42		7.35	3.274	1.378	2.44	2.67	3.89		−70.32	−4.02
4b	A	7.63		7.56	3.365	0.631	2.24	2.94	3.80	3.92	−57.53	+1.00
	E	–		–	3.472	1.139	2.28	3.09	–	–	−60.00	−1.47
5a	E	7.51		7.18	4.420	2.418	2.94	2.77	3.83		−64.25	−7.02
6a	A	7.49		7.38	–	1.725	2.84	3.09	4.02		−76.18	−6.17

[a] $\Delta^{29}Si = \delta^{29}Si_{183\ K} - \delta^{29}Si_{293\ K}$.

TABLE 4

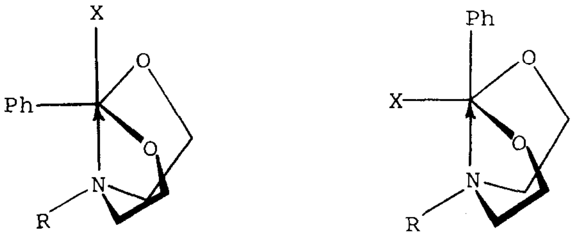
^{13}C CHEMICAL SHIFTS FOR ISOMERS A AND E OF COMPOUNDS 1–6 IN ACETONE-d_6 at 183 K (ppm)

Compound	Isomer	OC	NC	SiPh			
				α-	o-	m-	p-
1a	A	61.22	54.53	139.52	132.41	123.81	123.91
	E			143.32	135.06	128.07	129.06
1b	A	66.20	52.87	136.20	135.06	128.94	130.39
	E			139.15	135.15	128.54	130.59
1c	A,E	62.96	56.66	134.02	135.43	128.93	130.06
2a	A	61.14	54.90	140.12	132.33	128.62	128.89
	E	62.62	58.15	142.02	134.68	128.22	129.59
2b	A	65.59	52.43	137.20	136.69	128.54	130.79
	E	66.48	53.53	139.27	134.83	128.54	130.79
2c	A,E	63.29	58.16	136.58	134.91	128.66	130.86
3a	A	61.12	54.84	139.15	132.56	128.55	128.83
	E	62.65	57.96	140.71	135.11	128.18	129.65
4a	A	61.05	54.02	137.33	132.25	128.58	129.22
4b	A	64.95	50.00	133.05	134.74	128.30	130.45
	E	65.32	51.25	134.49	135.20	128.30	130.45
5a	E	58.75	53.54	148.49	134.09	127.83	128.40

^{a} $^{1}J_{(Si-C)} = -78.8$ Hz. ^{b} $^{1}J_{(Si-C)} = -76.7$ Hz.

greater detail. According to these findings, five-membered semicycles occupy less strained axial-equatorial positions. Axial orientation is preferable for electronegative and sterically non-demanding substituents ($X = Cl$, OCH_3). The preferred equatorial population of the most bulky SiPh group may be explained mainly by the more serious sterical constraints conferred on the axial position, as compared with the equatorial one. Compound **5a**, where the phenyl group assumes the axial orientation the TBP because of greater electronegativity, presents an exception.

It is necessary to note that the sterically less crowded equatorial position in the TBP corresponds to the unfavourable axial orientation of the substituent in the eight-membered heterocycle (C_8) (see Fig. 2). This discrepancy between the confor-



A (X - ax) E (X - eq)

Fig. 1. The substituent position exchange in the TBP of Si atom.

X			R			
α-	β-	γ-	α-	o-	m-	p-
	–		42.00			
	–					
	–		56.10	27.50(β)		
	–					
	–		148.14	112.69	131.24	117.04
2.88 [a]			42.27			
−2.14 [b]			43.27			
0.96			56.28	27.00(β)		
−2.23			56.28	27.00(β)		
−6.33			148.09	112.46	130.46	117.63
22.18	18.08	19.36	42.06			
16.83	18.96	19.36	43.01			
	49.96		42.31			
	49.84		56.80	27.00(β)		
	50.58		56.80	27.00(β)		
	–		41.26			

mational trends of TBP and C_8 essentially influences the equilibrium A ⇄ E. On the other hand, the ratios of isomers A and E are opposite for compounds **2a** and **2b** (Table 5). This points out the essential role of the steric requirement of the N substituent in establishing equilibrium conditions in the TBP of the Si atom. It appears likely that for the molecules possessing a strong N → Si bond the conformational trends of the TBP are prevalent, whereas the weakening of the donor-acceptor bond leads to an increase in the conformational role of C_8. This becomes particularly apparent when we compare **4a** and **4b**: purely equatorial orientation of the SiPh group in the TBP of **4a** (which corresponds to the axial orientation in C_8) becomes less preferable with weakening of the N → Si bond in the molecule of **4b**.

The high sensitivity of ^{13}C chemical shifts with respect to electronic effects allows a closer examination of the interaction between the Si atom and aromatic ring as a function of the Si configuration. For this purpose, we have used ^{13}C shifts determined at low temperatures. It is hoped that the TBP configuration in solution and in the crystalline state would show little variation under these conditions. Harris and

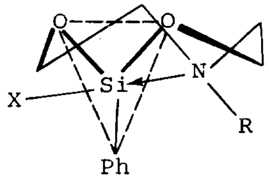


Fig. 2. Inconsistency of the axial-equatorial orientation of the Ph ring in the TBP and C_8 for isomer A.

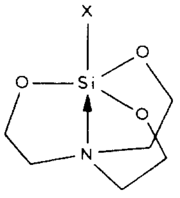
TABLE 5

THERMODYNAMIC PARAMETERS OF A ⇄ E EXCHANGE FOR COMPOUNDS **1–6**

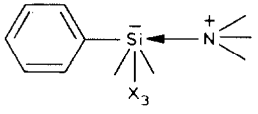
Compound	Isomer	Population at 183 K (%)	$k_{E/A}$	ΔG°_{183} (kcal/mol)	T_c [b] (K)	$\Delta G_c^* \pm 0.2$ (kcal/mol)
1a	A	50	1	0.00	223 [c]	10.1
	E	50				
1b	A	50	1	0.00	213 [d]	9.6
	E	50				
1c	A	50	1	0.00	<183 [d]	<9
	E	50				
2a	A	61	0.68	0.17	220	9.9
	E	39				9.7
2b	A	24	3.22	-0.43	204	9.2
	E	76				9.7
2c [a]	A	(21.5)	(3.65)	(-0.75)	<183	<9
3a	A	80	0.25	0.50	220	10.2
	E	20				9.6
4a	A	>98	<0.02	>1.42	–	–
4b	A	87	0.15	0.69	203	9.8
	E	13				9.1
5a	E	>98	>49	<-1.42	–	–
5c [a]	A	(12)	(5.67)	(-1.01)	–	–
6a	A	>98	<0.02	>1.42	–	–

[a] Calculated using eqs. 6–9 for room temperature. [b] Coalescence temperatures of NR protons resonance except for **1a**, **1b**, **1c**. [c] ^{13}C NMR signal coalescence temperatures for $SiPh_2$ *ortho* carbons. [d] ^{13}C NMR signal coalescence temperatures for $SiPh_2$ α-carbons.

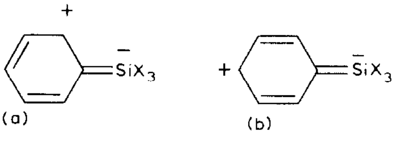
Kimber [12] have recently suggested that transannular N → Si bond formation may lead to a disturbance in $(d\text{–}p)_\pi$ conjugation between the silicon and phenyl ring due to the lengthening of the axial Si–C bond in the molecule of phenylsilatrane (III, X = Ph). This compound may be considered as a model for isomer E.



(III)



(IV)



(V)

Increase in the population of structure IV and the corresponding decrease in V leads to a downfield shift of the C_α-carbon resonance and upfield shift of the *ortho* and *para* resonances relative to the model compound $XSi(OEt)_3$ (VI, X = Ph). A quantitative analysis of the $(d\text{–}p)_\pi$ conjugation effect is possible by means of the $\Delta = \delta(c_p) - \delta(c_m)$ value that directly characterizes the contribution of resonance interactions to the alteration of π-electron density at the *para* carbon [13]. The configuration of the Si atom for the different N → Si bond strength may be characterized [14] from the value $90 + \Sigma\theta_{ax} - \Sigma\theta_{eq}$, where $\Sigma\theta_{ax}$ and $\Sigma\theta_{eq}$ are the sums of axial and equatorial angles, respectively, obtained from the results of X-ray analysis [1,2]. As expected, deviation of the Si atom configuration from the tetrahedron to the TBP with increasing strength of the N → Si bond, leads to a gradual decrease in $(d-p)_\pi$ conjugation between the silicon and the axially located phenyl ring (see Table 6). However, the decreased $(d-p)_\pi$ conjugation at the equatorial site is initially much more pronounced, as is revealed by the Δ values (Fig. 3).

The minimum conjugation for equatorial location is observed in the transition state which may be characterized as "monocapped tetrahedron" [14]. With the silicon configuration further approaching the TBP, the conjugation (Δ value) in the equatorial position increases, whereas in the axial position it is still decreasing. Thus, in the TBP the contribution of the resonance $(d-p)_\pi$ interactions to the equatorial substituent becomes more important than for the axial one, in agreement with the general rules [15]. Stronger $(d-p)_\pi$ conjugation in the axial position in comparison with the equatorial one in the monocapped tetrahedron can be explained by the symmetry of the *d* orbitals of the silicon atom, as demonstrated for the apical location in tetragonal pyramid [15].

With the silicon configuration moving towards the TBP state, the value of the coupling constant $^1J(^{29}\text{Si}-^1\text{H})$ for the equatorial proton decreases in the sequence II > **5c** > **5a** (−242.8; −244.1 and −258.3 Hz, respectively). On the other hand, an increase in the coupling constant has been observed for the axially located proton in III (X = H, ^1J(Si–H) = −278.1 Hz) in comparison with VI (X = H, ^1J(Si–H) = −288.2 Hz) [20]. So far, the absolute values of the ^1J(Si–H) coupling constants tend to vary in keeping with the observation that in the five-coordinated phosphorus TBP the corresponding ^1J(P–H) coupling constants are much larger for the equatorial protons [16-18] than for the axial ones [19]. In compound **2a**, the coupling constant

TABLE 6

PARAMETERS WHICH CHARACTERIZE CHANGES IN $(d-p)_\pi$-CONJUGATION BETWEEN Si ATOM AND PHENYL RING UPON CHARGE OF Si CONFIGURATION FROM TETRAHEDRAL TO TRIGONAL BIPYRAMID

Compound	Δ_{ax} (ppm)	Δ_{eq} (ppm)	$\Sigma\theta_{ax}$ (°)	$\Sigma\theta_{eq}$ (°)	$90 + \Sigma\theta_{ax} - \Sigma\theta_{eq}$ (°)	l(N → Si) (Å)	Ref.
(Tetrahedron)	2.36 [a]	2.36 [a]	328.5	328.5	90		
1c	2.27	2.27	319	338	71	3.08	1
1b	2.05	1.45	320	337	73	3.16	1
3a	1.47	0.28					
2a	1.37	0.27					
1a	0.99	0.10	309	345	54	2.68	1
4a	–	0.64					
5a	0.57	–					
6a [b]	–	0.78					
III [b]	0.40	–	291	357	24	2.19	12,17
(TBP)			270	360	0		

[a] II, R = Ph. [b] In $CDCl_3$ at 303 K.

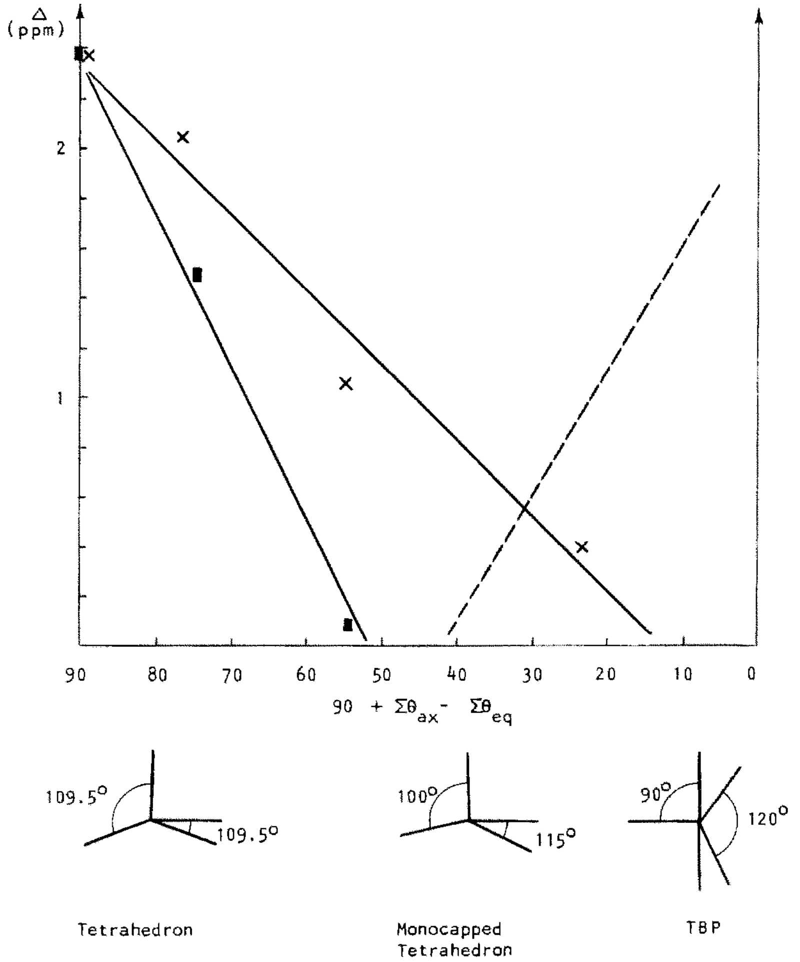


Fig. 3. The character of $(d-p)_\pi$ conjugation (Δ) changes between the silicon atom and the phenyl ring upon transition from the tetrahedral to TBP configuration at the axial and equatorial sites. Experimental points are taken from Table 6.

$^1J(^{29}Si-^{13}C)$ for the axial CH_3 group is smaller (−78.8 Hz) than for the equatorial one (−76.7 Hz). The latter value is close to that observed for compound II (−75.9 Hz). A decrease in the coupling constant $^1J(Si-C)$ was also found for the axially oriented CH_3 group in III ($X = CH_3$, $^1J(Si-C) = -106.9$ Hz), as compared to VI ($X = CH_3$, $^1J(Si-C) = -97.0$ Hz) [20].

The question of eight-membered heterocycle conformation is undoubtedly a most complicated one [21,22]. X-ray analysis has revealed that eight-membered heterocycles containing a 1,5-transannular bond can exist in boat-chair (BC) [1,2,14,23–27], chair-chair (CC) [2,28,29] and twisted boat (TB) conformations [1,30,31]. The question is further complicated in solution because of the possible existence of equilibria between different conformations. A characteristic feature of low temperature spectra of compounds in the **b** and **c** series is the large internal chemical shift

(0.7–0.9 ppm) for the NCH_2 protons. This is indicative of the fact that the CC is the predominant conformation [32,33]. This suggestion is confirmed by the shape of the multiplets, permitting the assignment of the axial ($J_{aa} = 11$ Hz, $J_{ae} = 3$ Hz) and equatorial ($J_{ee} + J_{ea} = 6$ Hz) protons in the heterocycle. This signifies that a conformational change occurs in compounds in the series **b** upon transition from the crystalline state (BC) [1] to solution (CC). As will be shown later, this is caused mainly by the weakening of the N → Si bond in solution. For the **a** series compounds, the NCH_2 proton signals in the 360 MHz ^1H NMR spectra are equivalent or nearly equivalent ($\Delta\delta \leqslant 0.2$ ppm). The shape of multiplets in this case does not allow one to distinguish between the axial and equatorial proton signals. This situation is characteristic of the BC conformation in these compounds [34].

The analysis of coupling constants in the $-OCH_2CH_2N$ fragment provides information about the conformation of the entire molecule. It is possible to obtain the value of the dihedral angle (φ_{ON}) between the planes OCC and CCN in solution by employing the "*R*-factor" method [35,36]:

$$\cos^2\varphi_{ON} = \frac{3}{4R + 2} \tag{1}$$

$$R = \frac{J_{trans}}{J_{cis}} = \frac{J_{1,4} + J_{2,3}}{J_{1,3} + J_{2,4}} \tag{2}$$

As can be demonstrated using the Dreiding stereomodels, φ_{ON} is directly linked to the distance between Si and N atoms. The same conclusion is reached on the basis of X-ray data analysis (see Table 7).

The obtained φ_{ON} values for **2**–**6** permitted us to compare quantitatively the distance $l(N \rightarrow Si)$ in various compounds. An increase in the values φ_{ON} (and $l(N \rightarrow Si)$) is observed in the series **a** < **b** < **c** and with the decrease in electron-acceptor ability of the Si atom. Besides, the extent of the temperature influence on the ^{29}Si chemical shifts changes in the same order, indicating that increased charge transfer is observed with the shortening of the $l(N \rightarrow Si)$ distance (compare values $\Delta^{29}Si$ and φ_{ON} in Table 3).

The geminal coupling constants for NCH_2 protons also depend on the $l(N \rightarrow Si)$ distance. There is almost linear correlation between the $^2J(NCH_2)$ and φ_{ON} for the compounds within the **a** series:

$$^2J(NCH_2) = -5.38 - 0.14\,\varphi_{ON} \quad r = 0.994 \tag{3}$$

Some deviation from this correlation for the points in the **b** and **c** series can be attributed to differences in the predominant conformation; however, the general trend persists (see Fig. 4). Such a correlation results from changes in electronegativity or orientation of the lone electron pair of the nitrogen atom [37,38]. The alteration of OCH_2 geminal coupling is not so characteristic (Table 7).

The vicinal coupling constants of the OCH_2CH_2N fragment permitted us to carry out a quantitative estimation of the conformational equilibrium in the eight-membered ring using the equation:

$$\langle J_{ij} \rangle = p^A J_{ij}^A + p^E J_{ij}^E \tag{4}$$

The following cases are possible.

TABLE 7

PROTON SPIN–SPIN COUPLING CONSTANTS IN FRAGMENT OCH_2CH_2N FOR COMPOUNDS **1–6** IN ACETONE-d_6 AT 293 K

Compound	J(H–H) (Hz)						ΣJ_{trans} = 1.4 + 2.3	ΣJ_{cis} = 1.3 + 2.4	RMS (Hz)	$\langle \varphi_{ON} \rangle$ (°)	Preferred conformation of C_8
	1.2	1.3	1.4	2.3	2.4	3.4					
1a										22.9[a]	BC
1b										46.0[a]	BC[a],CC
1c										59.0[a]	CC
2a	−13.29	3.55	7.37	5.87	3.42	−11.38	13.24	6.97	0.03	56.0	BC
2b	−14.43	2.83	7.39	5.86	2.95	−11.41	13.25	5.78	0.03	58.8	CC
2c	−15.36	2.63	9.30	3.84	2.04	−11.83	13.14	4.67	0.03	61.6	CC
3a	−13.27	3.69	6.90	6.34	3.48	−11.40	13.24	7.17	0.03	55.6	BC
4a	−12.92	4.21	6.69	6.45	3.92	−11.33	13.14	8.13	0.03	53.5	BC
4b	−14.25	3.34	6.86	6.48	3.06	−11.37	13.34	6.40	0.03	57.4	CC
5a	−12.56	4.79	6.97	5.98	4.82	−11.13	12.95	9.61	0.03	50.4	BC
5a[b]	−12.67	4.26	7.49	5.20	4.34	−11.16	12.69	8.60	0.04	52.0	BC
5a[c]	−12.51	4.65	7.05	5.92	4.79	−11.22	12.97	9.38	0.04	50.9	BC
5a[d]	−12.35	5.10	6.69	6.25	5.14	−11.08	12.94	10.24	0.04	49.3	BC
5c[c]	−15.33	2.75	9.92	3.26	2.06	−11.74	13.18	4.81	0.07	61.2	CC
6a[c]	−12.34	5.20	6.43	6.48	5.08	−11.35	12.91	10.28	0.03	49.2	BC

[a] In crystalline state. [b] In cyclohexane-d_{12}. [c] In $CDCl_3$. [d] In dimethylsulphoxide-d_6.

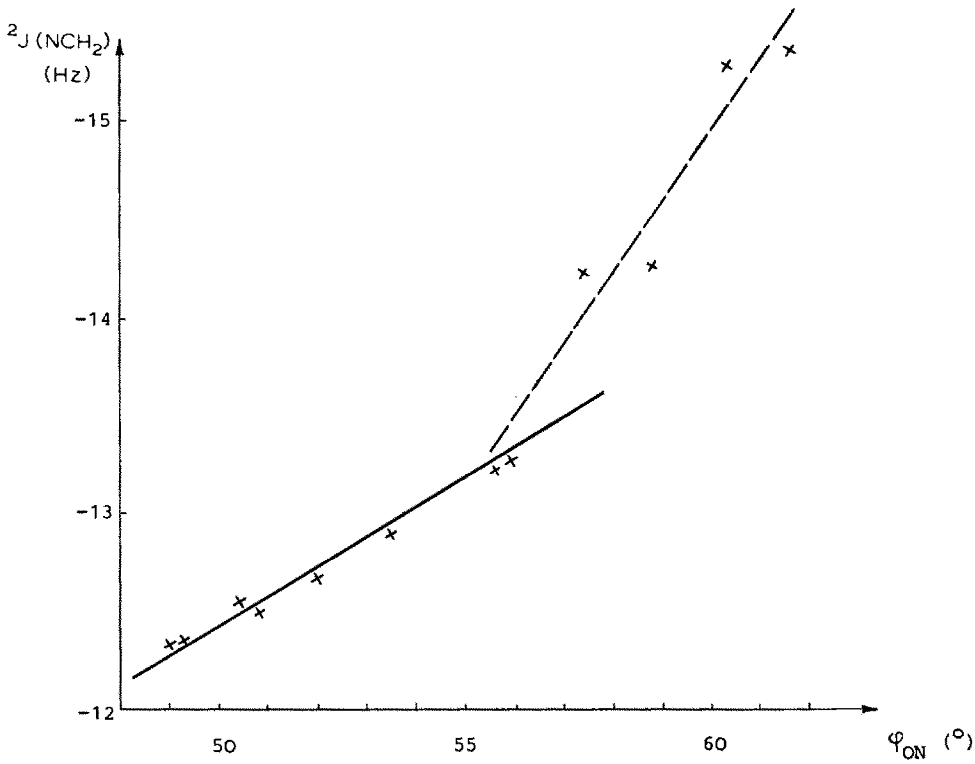


Fig. 4. Geminal coupling for NCH$_2$-protons vs. dihedral angle φ_{ON} for Ia (solid line) and Ib and Ic (dashed line). Experimental points are taken from Table 7.

(1) The population of the CC conformation $p_{CC} = 0$, $p_{BC} = 1$

As can be seen from Table 7, the CC conformation characterizes compounds with a weak N → Si bond. The strengthening of this bond leads to the shift of equilibrium towards the BC conformation. An exchange between the two enantiomeric conformations BC and CB (see Fig. 5) results in additional averaging of the vicinal couplings.

$$J_{ij}^{A(E)} = \tfrac{1}{2}\left(J_{ij}^{BC} + J_{ij}^{CB}\right) \qquad (5)$$

In the case when $\varphi_{ON}^{BC} = \varphi_{ON}^{CB}$, this averaging leads to the equality of couplings: $J_{2,3} = J_{1,4} = J_{trans}^{BC}$ and $J_{1,3} = J_{2,4} = J_{cis}^{BC}$. In fact, the values of the dihedral angles φ'_{ON} and φ''_{ON} in the crystalline state are somewhat different [2,43]. Since J_{cis} depends to a much greater extent on φ_{ON}, than does J_{trans} (see Table 7), the expression $|\Delta J_{cis}| \geqslant |\Delta J_{trans}|$ holds for the BC conformation, where $\Delta J_{cis} = J_{1,3} - J_{2,4}$ and $\Delta J_{trans} = J_{1,4} - J_{2,3}$. The best agreement with this suggestion is provided by compound **6a**. The small difference in the *cis* couplings indicates similarity of the φ'_{ON} and φ''_{ON} values in solution. It is necessary to point out that an exchange between the enantiomeric conformations BC and CB corresponds to the pseudorotation process in cyclooctanes [34,39] and does not lead to the exchange of substituent position on the silicon. This process in characterized by a low activation energy and therefore cannot be

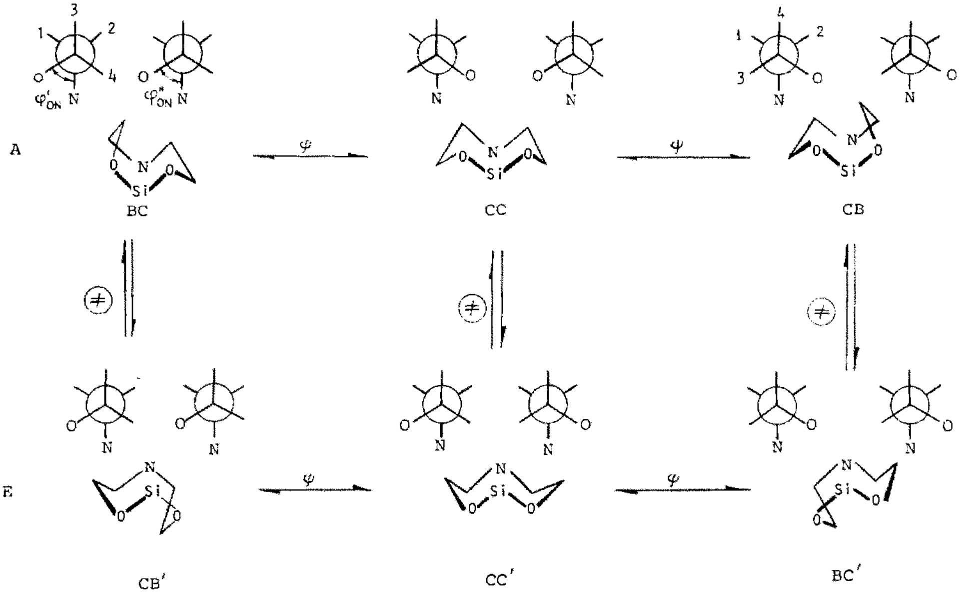


Fig. 5. Conformational equilibrium scheme for the eight-membered cycle of I in solution.

frozed out in ^{1}H, ^{13}C NMR spectra at the temperatures used in the present study. Thus, an exchange between isomers A and E is possibly due only to the C_8 ring inversion, which requires the dissociation of the N → Si bond.

(2) The population of the BC conformation $p_{BC} = 0$, $p_{CC} = 1$

This condition is observed for compounds in the series **c**, since conjugation between the lone electron pair of nitrogen and the phenyl ring weakens the N → Si bond and therefore leads predominantly to the CC conformation both in crystals and in solution (see Table 7). If we assume that the equilibrium in **2c** and **5c** is shifted towards isomer E (i.e. according to the C_8 rules), it is possible to calculate, taking into account equation 3, the population of isomers A and E by means of the following expressions:

$$J_{1,4} = p^{E}J_{aa} + p^{A}J_{ee} \quad (6)$$

$$J_{2,3} = p^{E}J_{ee} + p^{A}J_{aa} \quad (7)$$

$$J_{1,3} = p^{E}J_{ae} + p^{A}J_{ea} \quad (8)$$

$$J_{2,4} = p^{E}J_{ea} + p^{A}J_{ae} \quad (9)$$

We used as models the coupling constants obtained for the corresponding As derivative (X = lone pair) [40], where there is evidence for a complete shift in equilibrium towards isomer E. ($J_{aa} = 11.5$ Hz, $J_{ee} = 1.98$ Hz, $J_{ae} = 3.9$ Hz, $J_{ea} = 2.18$ Hz). The best agreement with experimental findings is reached when $p^{A} = 21.5\%$ for **2c** and $p^{A} = 12\%$ for **5c**. At the same time, it can be concluded from equations 6–9 that, if $p^{A}_{CC} = p^{E}_{CC} = 0.5$, it is practically impossible to distinguish between conformations BC and CC, and hence to determine their population on the basis of the OCH_2CH_2N coupling constant data, see, for example, **4a** and **4b** in Table 7. But intuitively, it may be suggested from the φ_{ON} values that the BC conformation in **4a** is more populated than in **4b**.

(3) The twisted boat (TB) or BB conformations

Several authors [1,5,27,30,31,41,42] have proposed the TB or BB conformations for heterocycle C_8. However, the order of dihedral angles ($++-+/--+-$ for BC vs. $++--/--++$ for BB [39]) shows that in all cases the given conformation must represent a very flattened form of BC [23,43]. Investigation of Dreiding's stereomodels has revealed that the $l(N \rightarrow Si)$ distance in the BB conformation cannot exceed 2.3 Å due to the strong increase in nonbonded interactions. Thus, the BB conformation is possible only for compounds with a very strong N → Si interaction. As in the case of CC, dissimilarity of the coupling constants for the BB conformation must be expected. In fact, this is not the case, even for **6a** which is believed to have the strongest N → Si bond. On these grounds, the BB conformation can be neglected for the compounds studied in solutions.

(4) $p_{CC}^{A} = 0$; $p_{CC}^{E} = 1$ ($p_{CC}^{A} = 1$, $p_{CC}^{E} = 0$)

In this case, it is easier to calculate the populations of the CC and BC conformations from the values of coupling constants (in principle, it can be done in other cases, too, if p_{CC}^{A} and p_{CC}^{E} are known). The equations 4–9 can be easily rewritten:

$$p_{CC} = p_{CC}^{E} = \frac{J_{1,4} - J_{2,3}}{J_{aa}^{CC} - J_{ee}^{CC}} = \frac{J_{1,4} - J_{2,3}}{9.58} \qquad (10)$$

We calculated the population of the CC conformation for compound **5a** in different solvents by inserting the experimental coupling constant data into eq. 10, since the initial conditions are fulfilled in this case. Furthermore, we measured the nuclear Overhauser effect (NOE) between the SiH and NCH_3 protons and calculated [44] the distance $l(CH_3,H)$. Although this distance differs from the length of the N → Si bond, these values are related. Therefore, one may derive from changes in $l(CH_3,H)$ the factors influencing the coordinative bond N → Si in the molecule of **5a**. The data in Table 8 show that an increase in solvent polarity results in a decreased distance $l(CH_3,H)$ ($l(N \rightarrow Si)$). In the same manner, the change of solvent affects both the population of the CC conformation and the dihedral angle φ_{ON}, and these changes are linearily related:

$$l(CH_3,H) = 2.775 + 2.236 \times 10^{-2} p_{CC} \quad r = 0.96 \qquad (11)$$

$$\varphi_{ON} = 49.0 + 13.2 \times 10^{-2} p_{CC} \quad r = 0.97 \qquad (12)$$

The value $\varphi_{ON} = 62.2°$ calculated from eq. 12 for the "pure" CC conformation actually characterizes compounds in the series **c**.

It has been suggested recently [7] that only one conformation exists in I both in solution and the crystalline state, on the grounds that a single Si–H absorption band is observed in the IR spectra of **5a**. Our IR results for the Si–H vibration in compounds **5a** (2102 cm^{-1} in solid) and **5c** (2148 cm^{-1}, Nujol), where the NMR data show different conformations of C_8 are indeed different. However, it can also be explained by inequality of the N → Si bond strength [7]. Nevertheless, in

TABLE 8

SOLVENT DEPENDENCE OF STRUCTURAL PARAMETERS FOR COMPOUND **5a**

Solvent	φ_{ON} (°)	p_{CC} (%)	NOE (%)	$l(CH_3,H)$ (Å)
Dimethylsulphoxide-d_6	49.3	5	19	2.82
Acetone-d_6	50.4	10	14	3.02
$CDCl_3$	50.9	12	12	3.10
Cyclohexane-d_{12}	52.0	24	8	3.28

cyclohexane solution of **5a**, the population of the CC conformation being the largest, the main Si–H absorption band (2127 cm^{-1}) corresponding to the BC conformation has a conspicuous shoulder at 2155 cm^{-1}, which can be attributed to the CC form. Therefore, we believe that the failure to find two Si–H stretching frequencies earlier is due to the small share of the CC conformation in the crystalline state and polar solutions, and also to the fact that the absorption bands coincide in solutions of medium polarity.

Thus, the conflict between the conformation properties of the eight-membered heterocycle and trigonal bipyramid of five-coordinated silicon in 1,3-dioxa-6-aza-2-silacyclooctanes consists in the dependence of the orientation of substituents at silicon and conformational equilibrium of the ring system on the energy of N → Si bond.

Experimental

^1H, ^{13}C and ^{29}Si NMR spectra were recorded using a Bruker WM-360 spectrometer. Proton spectra were obtained using 5 mm tubes for 0.01 *M* solutions with TMS as an internal standard. Solvents ($CDCl_3$, cyclohexane-d_{12}, acetone-d_6 and dimethylsulphoxide-d_6) were dried over 4 Å molecular sieves. For NOE experiments solutions were carefully degassed. Analysis of spin systems of the OCH_2CH_2N fragment were carried out using the iterative programme PANIC. Free energies of activation ($\Delta G_c^{\neq}$) at coalescence temperature were calculated as elsewhere (see, e.g. ref. 45).

^{13}C and ^{29}Si NMR spectra recorded using broad-band decoupling with protons. Delay time between 60° pulses was 3–10 sec. The ^{29}Si spectra were obtained without NOE in the inverse gated mode. Chemical shifts were determined with 0.1 ppm accuracy. Both, ^{13}C and ^{29}Si spectra were obtained using 10 mm tubes and 0.1 *M* solutions.

Compounds within the series I were prepared as described previously [46].

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