STUDY OF SEQUENCE OF N AND O ATOMS IN DIMETHYLSILAZAOXANES BY MEANS OF ^{1}H, ^{13}C, AND ^{29}Si NMR

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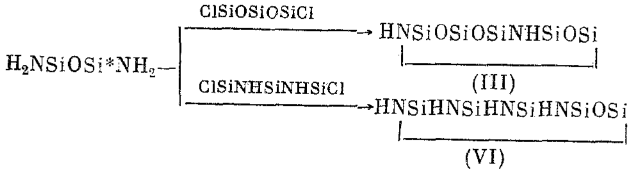
NMR spectroscopy of heavy nuclei is a highly informative method for investigating the microstructure of polysiloxane chains. In particular, ^{29}Si NMR has been used successfully in studying the structure of polysiloxanes with various substituents on the silicon atom [1, 2].

We were interested in studying the influence of the distribution of N and O atoms in the chain of polydimethylsilazaoxanes on the spectra of the various nuclei. To this end, we measured the ^{1}H, ^{13}C, and ^{29}Si spectra of model compounds: 10- and 12-membered dimethylcyclosilazaoxanes (DMCSAO) with various numbers of N atoms in the ring. The large rings were selected so that the size of the ring would have less influence, and the models would approximate linear chains.

Up to the present time, only simple DMCSAOs containing one or two NH groups have been prepared [3, 4]. We have accomplished the synthesis of more complex DMCSAOs containing from two to four NH groups in the ring, primarily by the reaction of heterofunctional condensation of linear diamino and dichloro derivatives of siloxanes and silazanes in the presence of Et_3N. Linear α,ω-dichloropolydimethylsiloxanes were obtained by the procedure of [5], dichlorotetramethyldisilazane was obtained according to [6], and the amino derivatives were obtained by ammonolysis with liquid ammonia, with only the diaminotetramethyldisiloxanes and the diaminotetramethyldisilazane being isolated in individual form. No diamines with three or more Si atoms were recovered from the reaction medium.

Decamethyl-1-aza-3,5,7,9-tetraoxapentasilacyclodecane (I) and dodecamethyl-1-aza-3,5,7,9,11-pentaoxahexasilacyclododecane (VII) were obtained previously [3, 4], and dodecamethyl-1,7-diaza-3,5,9,11-tetraoxahexasilacyclododecane (X) was obtained in [4]. Dodecamethyl-1,5-diaza-3,7,9-trioxapentasilacyclodecane (III) and decamethyl-1,5,7,9-tetraaza-3-oxapentasilacyclodecane (VI) were obtained in accordance with the scheme



The original 1,5-dichlorohexamethyltrisilazane was obtained by splitting hexamethylcyclotrisilazane under the influence of a solution of HCl in ether

$$[Me_3SiNH]_3 + 3HCl \xrightarrow[-NH_4Cl]{} ClSiNHSiNHSiCl$$

Decamethyl-1,3-diaza-5,7,9-trioxapentasilacyclodecane (II), decamethyl-1,3,5-triaza-7,9-dioxapentasilacyclodecane (IV), dodecamethyl-1,5-diaza-3,7,9,11-tetraoxahexasilacyclododecane (IX), dodecamethyl-1,3-diaza-5,7,9,11-tetraoxahexasilacyclododecane (VIII), dodecamethyl-1,3,5-triaza-7,9,11-trioxahexasilacyclododecane (XI), and dodecamethyl-1,3,5,7-tetraaza-9,11-dioxahexasilacyclododecane (XIII) were obtained in accordance with the scheme (see next page for scheme).

The synthesis of decamethyl-1,5,7-triaza-3,9-dioxapentasilacyclodecane (V) is possible only in the presence of 1,5-dichlorohexamethyltrisila-2-oxa-4-azane, which we were successful

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*In all of the formulas, there are two methyl groups on the Si atom.

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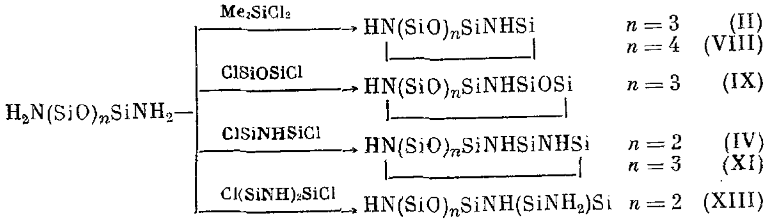
TABLE 1. Physicochemical Constants and Elemental Analysis of Dimethylcyclosilazaoxanes

Compound	Yield, %	bp, °C (p, mm Hg)	n_D^{20}	d_4^{20}	Found/calculated, %			
					Si	C	H	N
(II)	43	124–135(30)	1,4315	0,9776	38,00/38,13	32,74/32,62	8,61/8,69	7,41/7,61
(III)	48	113–115(12)	1,4320	0,9809	38,71/38,13	32,40/32,62	8,49/8,69	7,36/7,61
(IV)	27	130–135(20)	1,4442	0,9711	38,18/38,22	33,00/32,72	9,01/8,98	11,12/11,44
(V)	35	143–145(20)	1,4465	–	38,38/38,22	32,59/32,79	8,87/8,98	11,69/11,44
(VI)	31	140–143(20)	1,4607	0.9776	38.50/38,32	32,91/32,79	9,01/9,28	14.87/15,29
(VIII)	42	91–93(3)	1,4293	0.9677	38.01/38,10	32,68/32,59	8,71/8,59	6,30/6,32
(IX)	37	102–108(2)	1,4290	0.9685	38,12/38,10	32,60/32,59	8,67/8,59	6,28/6,32
(XI)	15	99–106(1)	1,4401	0.9705	37,99/38,18	32,83/32,66	8,64/8,84	9,70/9,52
(XII)	6	145–150(15)	1,4380	0.9744	38,20/38,18	32,61/32,66	8,78/9,64	9,58/9,52
(XIII)	12	137–140(13)	1,4470	0,9738	38,80/38,27	32,49/32,74	9,01/9,09	12,99/12,72

Scheme



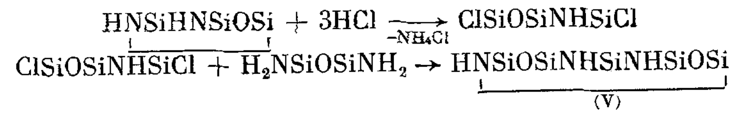
$$H_2N(SiO)_nSiNH_2 \xrightarrow{Me_2SiCl_2} \underbrace{HN(SiO)_nSiNHSi}\quad n=3\ (II),\ n=4\ (VIII)$$

$$H_2N(SiO)_nSiNH_2 \xrightarrow{ClSiOSiCl} \underbrace{HN(SiO)_nSiNHSiOSi}\quad n=3\ (IX)$$

$$H_2N(SiO)_nSiNH_2 \xrightarrow{ClSiNHSiCl} \underbrace{HN(SiO)_nSiNHSiNHSi}\quad n=2\ (IV),\ n=3\ (XI)$$

$$H_2N(SiO)_nSiNH_2 \xrightarrow{Cl(SiNH)_2SiCl} HN(SiO)_nSiNH(SiNH_2)Si\quad n=2\ (XIII)$$

in obtaining by splitting hexamethyl-1,3-diaza-5-oxatrisilacyclohexane under the influence of HCl



$$\underbrace{HNSiHNSiOSi} + 3HCl \xrightarrow[-NH_4Cl]{} ClSiOSiNHSiCl$$

$$ClSiOSiNHSiCl + H_2NSiOSiNH_2 \rightarrow \underbrace{HNSiOSiNHSiNHSiOSi}_{(V)}$$

(V)

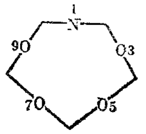
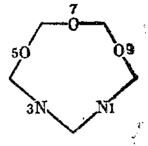
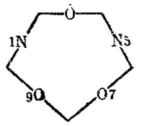
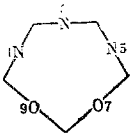
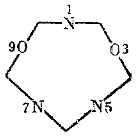
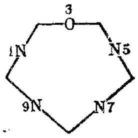
From the products of ammonolysis of 1,3-dichlorotetramethyldisiloxane, along with the basic 8-membered cyclosilazaoxane, we recovered a high-boiling cyclic product, dodecamethyl-1,5,9-triaza-3,7,11-trioxahexasilacyclododecane (XII)

$$ClSiOSiCl + NH_3 \xrightarrow[-NH_4Cl]{} (SiOSiNH)_n,\quad n=3\quad (XII)$$

Certain physicochemical characteristics of the DMCSAOs that were synthesized are listed in Table 1. The structures of these compounds were proved by means of NMR spectroscopy.

The parameters of the PMR spectra of the 10-membered DMCSAOs are listed in Table 2. For the majority of the signals of the methyl protons, the assignments are ambiguous. From the symmetry of these 10-membered rings, it follows that each of them contains three types of methyl groups in a 2:4:4 ratio. In compounds (I)-(VI), either all of the signals are separated, as in (IV) and (VI), or two of the three signals coincide (2 + 4 or 4 + 4). Therefore, in all cases, on the basis of the integral intensities, we have been able to assign the signals pertaining to two methyl groups lying the plane of symmetry of the 10-membered ring, perpendicular to the plane of the ring, i.e., 8,8-Me in (IV) and 2,2-Me in (I). The assignment of the signals of the other pairs of dimethyl fragments in the NMR spectra is not so definite, since the intensities of the signals coincide. These signals were identified by

TABLE 2. ^{1}H, ^{29}Si, and ^{13}C Chemical Shifts of 10-Membered Dimethylcyclosilazaoxanes*

Compound†	N atom numbers	PMR δNH, ppm	Si atom number	PMR (Me)	^{29}Si NMR	^{13}C (Me) NMR
				δ, ppm		
 (I)	1	0,87	6 2, 10 4, 8	0.050 0.081 0,050	−22,82 −12,46 −21,95	0,89 1,96 1.02
 (II)	1, 3	0,71	2 4, 10 6, 8	0,083 0.083 0,039	−8,23 −12,69 −22,89	3,20 2,16 1,00
 (III)	1, 5	0.83	8 2, 4 6, 10	0.031 0.067 0,067	−23,73 −13,22 (−12,63) −12,63 (−13,22)	0,98 1,93 (1,81) 1,81 (1,93)
 (IV)	1, 5 3	0.72 0,63	8 2, 4 6, 10	0,030 0.068 (0,080) 0,080 (0,068)	−23,79 −8,06 −12,75	1,16 3,42 2,16
 (V)	1 5, 7	0,84 0,71	6 2, 10 4, 8	0.078 0,066 0,066	−8,47 −13,46 −13,46	3,21 2,10 (2,31) 2,31 (2,10)
 (VI)	1, 5 7. 9	0,75 0,67	8 2, 4 6, 10	0.050 0,072 (0,058) 0,058 (0,072)	−7,72 −8,38 −13,81	3,93 3,37 2,28

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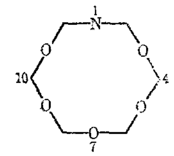
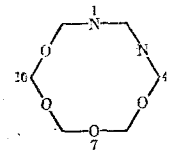
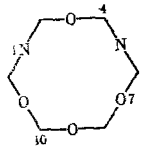
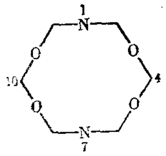
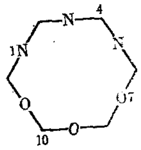
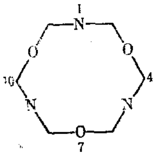
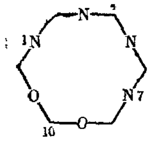
*Chemical shifts measured from TMS.

†Si atoms are at vertices.

comparison of the chemical shifts (CS). It can be seen from Table 2 that for the most precisely assigned signals of the $-OSiMe_2O-$ (those mentioned above), the smallest CS is characteristic. On this basis, we have assigned the signal with δ 0.05 ppm in (I) to the 4,8-Me_2Si, and the signal with 0.039 ppm in the spectrum of (II) to 6,8-Me_2Si. The range of CS of the methyl protons of the $-OSiMe_2O-$ is 0.03-0.05 ppm. The other signals in the spectra of (I) and (II) with δ 0.081 and 0.083 ppm are assigned to 2,10- and 4,10-Me_2Si, respectively ($NSi \cdot Me_2O$ fragments). When (III) and (V) are taken into account, the CS region of $NSiMe_2O$ is 0.066-0.083 ppm.

The reliably assigned signals of the $NSiMe_2N$ fragments are in the 0.050-0.083 ppm region. As can be seen, the two regions overlap to a great degree. It is not possible from these data to identify precisely the signals of the 2,4 and 6,10 Me_2Si in (IV), nor the 2,4 and 6,10 in (VI), that are listed in Table 2. For these methyl groups, the assignment may be reversed. The comparatively large scatter of the $NSiMe_2N$ CS is probably related to the influence of distant N atoms or to inconstancy of the effects of the near N atoms when there are changes in the structure of the molecule as a whole.

TABLE 3. Chemical Shifts in ^{1}H, ^{29}Si, and ^{13}C NMR Spectra of 12-Membered Dimethylcyclosilazaoxanes[*]

Compound[†]	N atom number	PMR δNH, ppm	Si atom number	PMR(Me)	^{29}Si NMR	^{13}C (Me) NMR
				δ, ppm		
 (VII)	1	0,89	2, 12 4, 10 6, 8	0,081 0,052 0,068	−11,60 −22,59 −22,59	2,24 1,08 (0,97) 0,97 (1,08)
 (VIII)	1, 3	0,95	2 4, 12 6, 10 8	0,077 0,077 0,057 0,077	−7,16 −11,21 −22,34 −22,42	3,67 2,24 1,08 1,00
 (IX)	1, 5	1,03	2, 4 6, 12 8, 10	0,089 0,071 0,058	−12,10 (−11,61) −11,61 (−12,10) −22,58	2,32 (2,21) 2,21 (2,32) 1,10
 (X)	1, 7	1,01	2, 6, 8, 12 4, 10	0,092 0,044	−11,89 −22,61	2,24 1,21
 (XI)	1, 5 3	0,92 0,84	2, 4 6, 12 8, 10	0,085 0,076 0,062	−7,33 −11,66 −22,52	3,67 2,08 1,10
 (XII)	1, 5, 9	1,07	2−12	0,078	−12,13	2,29
 (XIII)	1, 7	0,82	4 2, 6 8, 12 10	0,073 0,080 0,087 0,049	−7,62 −7,71 −11,90 −22,82	3,83 3,51 2,13 1,24

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[*] Chemical shifts measured from TMS.

[†] Si atoms are at vertices.

For the NH protons, stronger and more distinct effects are observed when the environment is changed than is the case for the methyl groups. The signals of the NH protons in the silazanes are broadened to 20-30 Hz as a result of spin-spin coupling with ^{14}N and fast relaxation of the N nuclei. Therefore, under the normal conditions for recording ^{1}H spectra, it is impossible to observe the fine structure of these signals. In order to narrow the NH signals, we made use of suppression on the frequency of ^{14}N nuclei.

TABLE 4. Chemical Shifts in ^{29}Si and ^{13}C NMR Spectra of Central Group in Heptads of Dimethylcyclosilazaoxanes*

Heptad	δ ^{29}Si, ppm	δ ^{13}C, ppm
	10-membered	
(11)	−21,95 (I)	0,89 (I)
(21)	−22,82 (I), −22,89 (II)	1,02 (I), 1,00 (II)
(31)	−23,73 (III), −23,79 (IV)	0,98 (III), 1,16 (IV)
(12)	−12,46 (I)	1,95 (I)
(22)	−12,69 (II), −12,75 (IV), −13,46 (V)	2,16 (II), 2,16 (IV)
(32)	−13,46 (V), −13,81 (VI)	2,28 (VI)
(13)	−8,23 (II), −8,47 (V)	3,20 (II), 3,21 (V)
(23)	−8,06 (IV), −8,38 (VI)	3,42 (V), 3,37 (VI)
(33)	−7,72 (VI)	3,93 (VI)
	12-membered	
(11)	−22,59 (VII), −22,42 (VIII)	1,00 (VIII)
(21)	−22,59 (VII), −22,58 (IX), −22,34 (VIII)	1,08 (VIII), 1,10 (IX), 1,10 (XI)
(31)	−22,61 (X), −22,82 (XIII)	1,21 (X), 1,24 (XIII)
(12)	−11,60 (VII)	2,24 (VII)
(22)	−11,90 (XIII), −12,13 (XII), −11,66 (XI)	2,24 (VIII), 2,08 (XI), 2,29 (XII)
(13)	−7,16 (VIII)	3,67 (VIII)
(23)	−7,33 (XI), −7,71 (XIII)	3,67 (XI), 3,51 (XIII)
(33)	−7,62 (XIII)	3,83 (XIII)

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*Compound numbers are shown in parentheses.

The following ranges of variation of the CS of the fragments are observed: OSiN$\underline{\mathrm{H}}$SiO 0.83-0.87; NSi$\underline{\mathrm{H}}$NSiO 0.71-0.75; NSiN$\underline{\mathrm{H}}$SiN 0.63-0.67 ppm.

In Table 3 we have listed the CS of the protons of the CH_3 and NH groups in the series of 12-membered DMCSAOs. From the ratio of integral intensities and the symmetry of the molecules, reliable assignments of the methyl-proton signals can be made only for (X) and (XII). In the other cases, the assignment of the methyl signals is arbitrary. Any pairs of signals of equal intensity can be reversed.

The farthest upfield signals are assigned to the fragments $OSiMe_2O$ by analogy with the 10-membered DMCSAOs and by comparison with the spectrum of (X). However, in contrast to the 10-membered rings, signals of the $OSiMe_2O$ protons are also observed for these compounds in the weaker field (0.044-0.081 ppm).

An analysis of the CSs showed that the ranges of the methyl protons of the OSiO, NSiO, and NSiN fragments overlap to a considerable degree. For example, for the assignments listed in Table 3, the ranges are 0.044-0.081, 0.071-0.092, and 0.073-0.087 ppm, respectively.

The assignment of the NH proton signals in this series of compounds does not give rise to any doubt. For the fragments OSiN$\underline{\mathrm{H}}$SiO, NSiN$\underline{\mathrm{H}}$SiO, and NSiN$\underline{\mathrm{H}}$SiN, the CSs of the NH protons lie in the respective regions 0.98-1.07, 0.82-0.95, and 0.69-0.84 ppm.

From an examination of the PMR spectra of the DMCSAOs, we can draw the following conclusions. The signals of the methyl protons for the chain sections $OSiMe_2O$, $NSiMe_2O$, and $NSiMe_2N$ overlap to a great degree, and hence are not characteristic. The signals of the NH protons for each series of compounds give certain ranges for the sequence of five atoms, but these ranges for the 10- and 12-membered DMCSAOs are shifted relative to each other.

The ^{29}Si and ^{13}C NMR spectra of the 10- and 12-membered DMCSAOs (see Tables 2 and 3) give different ranges of CS for the OSiO, NSiO, and NSiN units. In addition, differences are observed in the signals of the Si. The signals of the N–^{29}Si–O and N–^{29}Si–N are somewhat broadened (2 and 3 Hz, respectively), as a result of ^{14}N–^{29}Si spin–spin coupling and fast relaxation of ^{14}N. Owing to these circumstances, most of the signals in the ^{29}Si and ^{13}C spectra could be assigned reliably. Exceptions are the signals of the fragments of the molecules with identical close environment and identical content of the nuclei being investigated. For thse signals, other variants of the assignment are shown in parentheses.

It is of interest to examine the influence of the size of the ring and the distribution of N atoms in the chain on the ^{29}Si and ^{13}C CSs. The influence of the ring size can be evaluated from the mean values of the CS for each type of close environment of the Si atom: OSiO, OSiN, and NSiN. For the 10-membered rings, the shielding (upfield shift) of ^{29}Si and ^{13}C is higher (0.6-1.2 and 0.1-0.3 ppm, respectively) than for the 12-membered rings. This is a manifestation of the features of the ^{29}Si spectra of cyclosilazaoxanes in comparison with cyclosiloxanes. The Si nucleus in a 12-membered cyclosiloxane is shielded more than in the 10-membered cyclosiloxane [7].

The influence of the order of arrangement of the O and N atoms in the siloxazane ring on the CS of the nuclei under investigation can be conveniently regarded in triads (sequences of three atoms) and heptads (sequences of seven atoms). The triads OSiO (1), NSiO (2), and NSiN (3) correspond to different combinations of the close environment for the Si atom. Extension of the environment leads to the following heptads:

$$\mathrm{OSiO}\ (1)\begin{cases}\mathrm{OSiO\underline{Si}OSiO} & (11)\\ \mathrm{NSiO\underline{Si}OSiO} & (21)\\ \mathrm{NSiO\underline{Si}OSiN} & (31)\end{cases}\qquad \mathrm{NSiO}\ (2)\begin{cases}\mathrm{OSiN\underline{Si}OSiO} & (12)\\ \left.\begin{array}{l}\mathrm{NSiN\underline{Si}OSiO}\\ \mathrm{OSiN\underline{Si}OSiN}\end{array}\right\} & (22)\\ \mathrm{NSiN\underline{Si}OSiN} & (32)\end{cases}$$

$$\mathrm{NSiN}\ (3)\begin{cases}\mathrm{OSiN\underline{Si}NSiO} & (13)\\ \mathrm{NSiN\underline{Si}NSiO} & (23)\\ \mathrm{NSiN\underline{Si}NSiN} & (33)\end{cases}$$

The effect by replacing an adjacent O atom by N is determined from the difference in the ^{29}Si and ^{13}C CSs in the fragments where only the close environment is changed, with the remainder of the environment the same.

Replacement of the first atom leads to a downfield shift of the ^{29}Si signal by 9.9±0.5 ppm for the 10-membered DMCSAOs and by 10.6±0.1 ppm for the 12-membered compounds. The replacement of the second atom leads to a signal shift of 4.7±0.5 ppm for the 10-membered compounds and 4.1±0.25 ppm for the 12-membered compounds. The additivity of the CSs breaks down to a considerable degree. The analogous contributions of the methyl groups to the ^{13}C CS differ to a smaller degree. Upon replacement of the first atom, the change in the CS is 1.05±0.1 ppm for the 10-membered DMCSAOs and 1.1±0.1 ppm for the 12-membered compounds; upon replacement of the second, the respective shifts are 1.4±0.2 and 1.4±0.1 ppm, respectively. The variation of the ^{13}C shielding is symbatic with the variation of shielding of the ^{29}Si.

A calculation performed in a similar manner for the contributions to the CS from the more distant atoms does not yield any satisfactory results, because of the great scatter of the values. Therefore, it is advisable to analyze the ^{29}Si and ^{13}C CSs of the central element $-\mathrm{SiMe_2}-$ in the heptads mentioned above. Here we selected a suitable heptad, assuming insignificant influence of atoms distant from the central Si by five or more bonds. For example, in (I), the sequence of atoms 3, 4, 5, 6, 7, 8, and 9 constitutes the heptad (11) with the central atom Si^6; the sequence of atoms 1, 2, 3, 4, 5, 6, and 7 forms the heptad (21) with central atom Si^4; and the sequence of atoms 9, 10, 1, 2, 3, 4, and 5 forms the heptad (12) with central Si^2.

We have analyzed the shielding of ^{13}C and ^{29}Si in the heptads for the most reliably assigned signals (Table 4). In the ^{13}C spectra of the 10-membered DMCSAOs in the heptads with central triad (1), the CSs change as follows: (11) < (21) ⩽ (31); the transition from one sequence to the next leads to a 0.1 ppm change of the CS; in one case, the ^{13}C CS of heptad (31) coincides with the CS range of heptad (21). For heptads with central triads (2) and (3), an analogous order of CS change is observed: (12) < (22) < (32) and (13) < (23) < (33). The differences between the CSs of the heptads in this case amount to 0.2-0.5 ppm. For the 12-membered DMCSAOs, in the heptads with central triad (1), the relationships between the CSs are the same as between those of the analogous heptads of the 10-membered DMCSAOs: (11) < (21) < (31) with a step of approximately 0.1 ppm. The heptads (12) and (22) cannot be characterized by separate ranges of CS (2.24 and 2.08-2.29 ppm, respectively). For the heptads with central triad (3), the relationships between the CSs are as follows: (13) ≃ (23) < (33).

From an analysis of the ^{13}C NMR spectra it follows that, even though there are certain deviations, there is a definite relationship between the ^{13}C CS of the methyl groups and the order of location of the O and N atoms in the siloxazane chain: Replacement of the nearest O atom by N leads to a downfield shift of 1 ppm, and replacement of an O atom removed by three bonds by an N atom leads to a downfield shift of 0.1-0.2 ppm, or in some cases 0.5 ppm.

The ^{29}SI NMR spectra present a far more variegated picture. For the 10-membered DMCSAOs, the change to heptads with the central triad (1) is accompanied by a considerable change (~1 ppm) in the direction opposite to the influence of a change in the immediate environment? (11)> (21) > (31). In the heptads with the central triad (2), the relationships of the ^{29}Si CSs are expressed as follows: (12) > (22) ≥ (32). Reverse trends are observed for the heptads of the third type: (13) ≤ (23) < (33). For the 12-membered DMCSAOs, the CSs of type (1) heptads lie in a narrow interval from −22.34 to −22.82 ppm) and do not manifest any particular trends: (11) ≃ (21) and (31). The CSs of the other types of heptads are characterized by the following relationships: (12) ≥ (22) and (13) > (23) ≥ (33).

Thus, a change in shielding of ^{29}Si related to replacement of an O atom removed by three bonds by an N atom in most cases is opposite to the change in ^{13}C shielding and to the effects of the immediate environment in the ^{29}Si spectra. But this rule breaks down to a greater degree than is observed in the relationships in the ^{13}C NMR spectra.

The results of the present work lead to the following conclusions relative to the possibility of investigating the sequence of units in linear polydimethylsilazaoxanes: 1) The spectra of the methyl protons cannot be used for this purpose; 2) the CSs of the NH protons may be characteristic for the fragments —OSiNHSiO—, OSiNHSiN, and NSiNHSiN, since in the series of 10-membered and 12-membered DMCSAOs, definite relationships are observed, and there will be no influence of ring size in linear systems; 3) the ^{13}C NMR spectra of the methyl groups can be used to identify heptads in linear polymers if the signals are sufficiently narrow; 4) the ^{29}Si NMR signals are the most sensitive to changes in the environment, but the effects of the distant environment in the series that we have investigated are not stable, and any final conclusions will depend on the results from investigation of linear model compounds.

EXPERIMENTAL

The PMR spectra were taken in an RYa 2309 spectrometer (90 MHz). For narrowing of the NH signals, suppression on the frequency of the ^{14}N nuclei was used.

The ^{29}Si NMR spectra were taken in a Varian FT-80A spectrometer (15.801 MHz) with pulse suppression of ^{1}H nuclei, pulse period 30 sec, number of accumulations 1000-2000, sweep width 2000 Hz with 4096 points. The ^{13}C NMR spectra were taken in a Bruker HX-90 spectrometer (22.63 MHz) with noise suppression of ^{1}H nuclei, number of accumulations 500-1000, sweep width 2500 Hz with 4096 points. The measurements were performed on solutions of the samples in CCl_4, concentration 10% for the PMR spectra and 30-50% for the ^{13}C and ^{29}Si NMR spectra, internal standard TMS.

Decamethyl-1,5-diaza-3,7,9-trioxapentasilacyclodecane (III). To a solution of 13.8 g (0.137 mole) of Et_3N in 150 ml of dry ether at −60°C, solutions were added dropwise from two funnels: a solution of 10.3 g (0.063 mole) of 1,3-diaminotetramethyldisiloxane in 30 ml of ether, and 17.3 g (0.063 mole) of 1,5-dichlorohexamethyltrisiloxane in 50 ml of ether. Then the mixture was heated and boiled for 1 h. After filtration and driving off the solvent, the product was fractionated under vacuum two times. The fraction with bp 113-115°C (12 mm) was taken, yield 48%.

All of the reactions of condensation of diamino and dichloro derivatives were performed by analogous procedures.

1,5-Dichlorohexamethyltrisila-2-aza-4-oxane (XIV). To a solution of 50.0 g (0.227 mole) of hexamethyl-1,3-diaza-5-oxatrisilacyclohexane in 150 ml of ether at −60°C, 95 ml of a 7.2 N solution of HCl in ether was added dropwise. Then the mixture was warmed to approximately 20°C and stirred for 48 h. The NH_4Cl precipitate was filtered off, the solvent was driven off, and the residue was vacuum-fractionated. The fraction with bp 70-80°C (5 mm) was taken; according to GLC data, this contained 90% (XIV) yield 39%.

By ammonolysis by liquid NH_3 in ether at −60°C, from 1,3-dichlorotetramethyldisiloxane and 1,3-dichlorotetramethylsilazane we obtained (respectively) 1,3-diaminotetramethyldisiloxane, bp 34-40°C (10 mm), yield 63%, n_D^{20} 1.4130, and 1,3-diaminotetramethyldisilazane, bp 34-38°C (1-2 mm), yield 51%, n_D^{20} 1.4425.

CONCLUSIONS

1. A study has been made of the PMR spectra of 10- and 12-membered dimethylcyclosilazaoxanes. The spectra of the methyl-group protons are not characteristic.

2. From the PMR spectra of the NH protons, the sequence of five atoms with a central N atom can be identified.

3. From the ^{13}C NMR spectra, sequences of seven atoms with a central Si atom can be differentiated.

In the ^{29}Si NMR spectra, the influence of the immediate environment is the most clear-cut; the influence of the more distant atoms is complex in nature.

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STEREOCHEMISTRY OF SEVEN-MEMBERED HETEROCYCLES.

11. ISOENERGY CHAIR—TWIST CONFORMATION EQUILIBRIUM IN PHTHALYLFORMAL AND ITS 2-PHENYL DERIVATIVE

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It is known that a chair—twist (C—T) equilibrium is characteristic for 1,3-dioxacyclohept-5-enes and their benzene derivatives [1-6]. We have been able to obtain quantitative information on the influence of substituents at the C^2 on the position of the conformation equilibrium by means of IR spectroscopy [4]. A comparative conformation analysis shows that the enrichment of the conformation mixture in the chair form upon the introduction of a 2-methyl or 2-tert-butyl substituent should be explained by the unfavorable 1,3-syn-axial interaction of the substituent in the flexible form. On the basis of the data that were obtained, an approach was proposed for a quantitative description of the influence of substituents in this type of heterocycle [4]. Investigation of these compounds by means of dynamic ^{13}C NMR [5, 6] gave limited information. Only phthalylformal was described quantitatively; for the other compounds, it was concluded that there was an anancomeric equilibrium.

The maximum fraction of the cross form in the case of tert-butyl derivatives can be readily interpreted in terms of the bulk of the substituent. The less bulky methyl group has less effect.

The behavior of 2-phenyl derivatives is unusual, as indicated by data reported on dipole moments [1-3, 7] and also IR spectra [3, 4]. No shift of the conformation equilibrium toward the chair is observed for the 2-phenyl derivatives relative to the formal, and hence we can regard the effect of the 2-phenyl substituent as specific. In order to obtain additional evidence for the unusual behavior of the 2-aryl substituent in such systems, it becomes necessary to examine the comparative quantitative characteristics, using a procedure that will permit direct observation of the conformational forms.

We have investigated the dynamic ^{13}C NMR spectra of phthalylformal (I) and its 2-phenyl derivative (II) with the aim of determining the position of the conformation equilibrium by analyzing the integral intensities of the "frozen" forms C and T (solvent $CD_2Cl_2:C_2Br_2F_4 = 1:3$) (see next page for scheme).

From the data of [5] it follows that all of the singlet signals of the ^{13}C of the seven-membered ring in (I) undergo changes when the temperature is varied; and in CHF_2Cl at $-130°C$,

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