Translated from *Uspekhi Khimii*, 50, 2212-2249 (1981) U.D.C. 678.84.765 : 54.07.09(047)

The Structure and Properties of Organocyclodisilazanes

Yu.M.Varezhkin, D.Ya.Zhinkin (deceased), and M.M.Morgunova

A survey and a systematic account of data on monomeric, oligomeric, and polymeric four-membered cyclic silazane systems are given and the fundamentals of the theory of their structure and reactivity are described. The physical and chemical properties, the methods of analysis, and certain aspects of the practical applications of these compounds are examined in detail. The review contains an exhaustive bibliography on organocyclodisilazane compounds starting from the first available information about them and extending up to 1978 (polycyclic systems in which the four-membered rings are linked via a silicon spiro-atom are excluded).
The bibliography includes 164 references.

CONTENTS

I. Introduction 1158
II. The structure of organocyclodisilazanes 1158
III. Chemical reactions and properties of organocyclodisilazanes 1163
IV. Polymers containing cyclodisilazane units 1168
V. Applications of organocyclodisilazanes 1173

I. INTRODUCTION

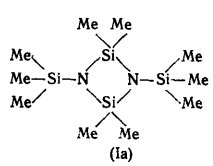
Continued progress in the modern chemistry of silicon- and nitrogen-containing compounds has led to the establishment and development of specific fields in this branch of chemistry such as the chemistry of four-membered cyclic silazane heterocycles—organocyclodisilazanes. This is associated both with the applied importance of compounds of this type, since they exhibit a high thermal stability, and with the interest in purely theoretical questions due to the somewhat unusual structure of these compounds.

A vigorous development of research not only into the synthesis of organocyclodisilazanes but also into the properties and structures of compounds of this class has taken place in recent years. In the study of these compounds almost the entire range of modern chemical methods has been used, including infrared Raman spectroscopy, ^{1}H NMR, mass spectrometry, and X-ray diffraction. Interesting data have been obtained but hitherto no attempts have been made to compile and survey all this information apart from a review published four years ago[1]. This review, which is devoted to the synthesis and applications of organocyclodisilazanes, covers a fairly wide range of problems and it is quite natural that many data concerning the structure and properties of these compounds have been omitted; furthermore, during the period which has elapsed since its publication, important new data have been obtained.

This review gives a systematic account and surveys the results of studies on the structures, properties, and reactivities of organocyclodisilazanes, and the possibilities of their practical applications are considered. Problems associated with the synthesis of monomers with the cyclodisilazane structure have already been described in detail[1-3].

II. THE STRUCTURE OF ORGANOCYCLODISILAZANES

Crystals of 1,3-Bis(trimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane (Ia)

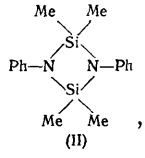


(Ia)

are monoclinic: $a = 6.75(2)$ Å, $b = 13.18(4)$ Å, $c = 11.22(3)$ Å, $\beta = 104°23' \pm 30'$, $V = 968.7$ Å^3, $D_m = 0.998$ (density determined by flotation in a diethylene glycol–methanol mixture), $Z = 2$, $D_c = 1.003$ (calculated density), space group $P2_1/n$ ($C_{2h}5$, No.14).[4]

Fig.1 shows that the silicon–nitrogen bonds in the cyclodisilazane ring are somewhat longer than exocyclic silicon–nitrogen bonds but shorter than the Si–N bonds in hexamethylcyclotrisilazane [1.78(3) Å].[5,6] The average length of the silicon–carbon bond (1.876 Å) corresponds to the usual values[7]. The distance between the opposite silicon atoms in the ring (2.476 Å) is somewhat greater than between the opposite nitrogen atoms (2.402 Å). The cyclodisilazane ring is highly strained compared with the hexamethylcyclotrisilazane (117° ± 4°) or octamethylcyclotetrasilazane (123° ± 4°) ring.[5,6] Compound (Ia) has a planar structure, which has been confirmed by ^{1}H NMR,[8] with the aid of which the unusually pronounced π-character of the exocyclic Si–N bond was observed in addition[9].

For 1,3-diphenyl-2,2,4,4-tetramethylcyclodisilazane (II)



(II)

the following parameters have been found: $a = 8.545(2)$ Å, $b = 16.820(3)$ Å, and $c = 11.622(2)$ Å; $V = 1670.38$ Å^3, $Z = 4$, $D_x = 1.187$, space group $Pbca$ (No.61).[10]

The molecule of compound (II) has a centre of symmetry; the cyclodisilazane ring is planar and the two benzene rings are parallel to one another. The length of the endocyclic Si–N bonds in compound (II) (see Fig.2) is greater than in compound (Ia); the length of the Si–N bonds is 1.728 Å in octamethylcyclotetrasilazane[11] and 1.732(2) Å in trisilylamine[12]. The distance between the opposite silicon atoms in the ring of compound (II) is 2.56 Å, which is somewhat greater than in compound (Ia), while the distance between the opposite nitrogen atoms (2.37 Å) is somewhat smaller.

The π-electron bond orders in compound (II) have been calculated by the Pariser–Parr–Pople (PPP) method: p(Si–N) = 0.346 and p(C–N) = 0.325. The latter agrees with the calculated value p(C–N) = 0.342, obtained[13] from

a modified Coulson formula. The results indicate a considerable contribution of the d_π–p_π interaction in the Si–N bond[10].

The structure of 1-methyldiphenylsilyl-3-(1,1,3-trimethyl-3,3-diphenylsilazanyl)-2,2,4,4-tetramethylcyclodisilazane (III) has been determined by X-ray diffraction[14,15]. The compound consists of colourless transparent monoclinic crystals: a = 15.790(10) Å, b = 8.443(5) Å, and c = 27.944(16) Å; β = 103.9(2)°, V = 3616.3 Å^3, D_m = 1.122 (determined by flotation), Z = 4, D_c = 1.124, space group $P2_1/c$ ($C_{2h}5$, No.14).[14]

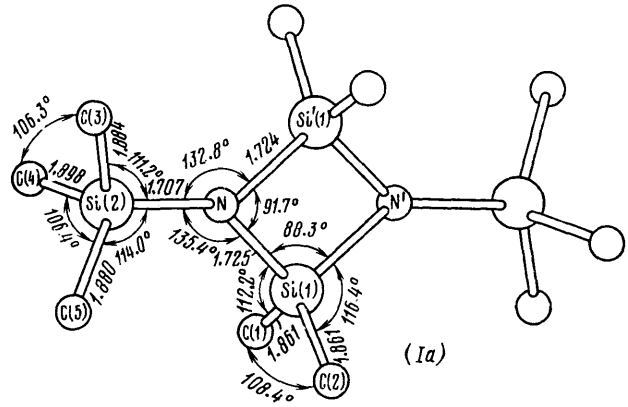


Figure 1. The bond lengths and angles in the 1,3-bis(trimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane (Ia) molecule[4].

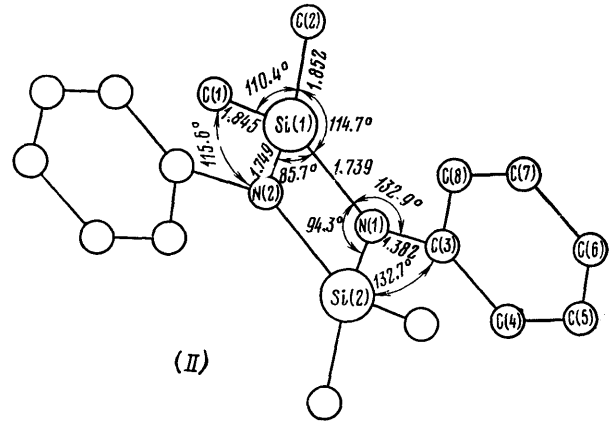


Figure 2. The bond lengths and angles in the 1,3-diphenyl-2,2,4,4-tetramethylcyclodisilazane (II) molecule[10].

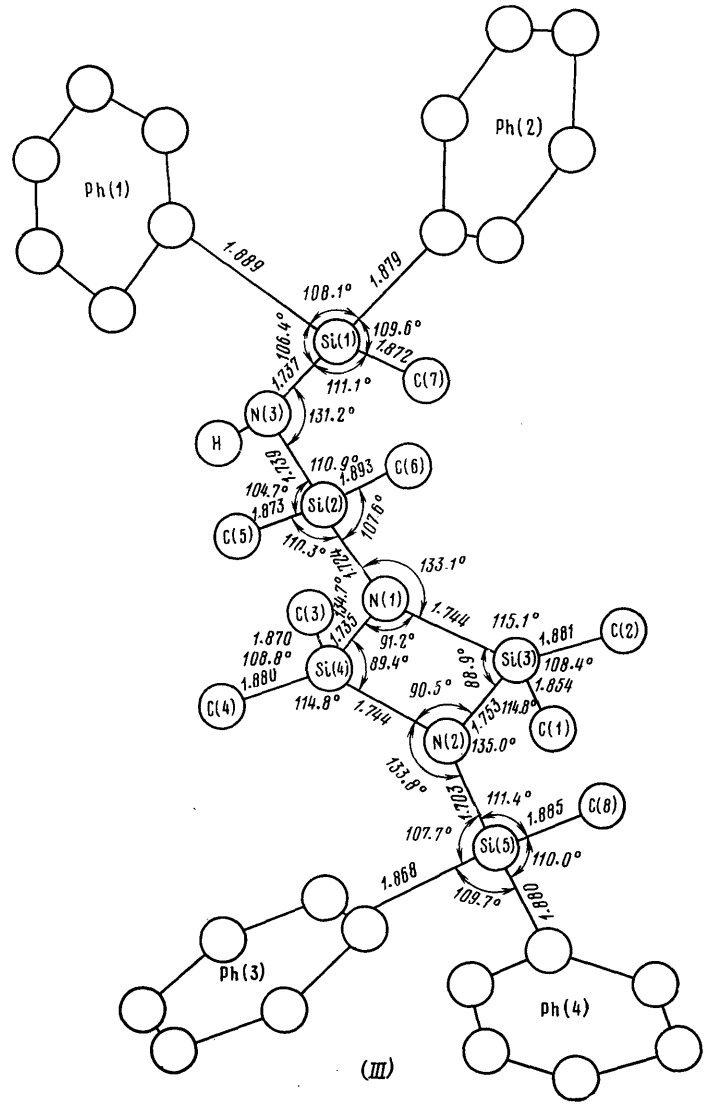


Figure 3. The bond lengths and angles in the 1-methyldiphenylsilyl-3-(1,1,3-trimethyl-3,3-diphenylsilazanyl)-2,2,4,4-tetramethylcyclodisilazane (III) molecule[14].

In compound (III) the average length of the Si–C(Me) bonds is the same as in compound (Ia) and corresponds to the usual value of 1.870 Å;[7] on the other hand, the Si–C(Ph) (1.879 Å) bond length is somewhat greater than the value usually adopted (1.843 Å).[7] The Si–N bonds in the ring are longer than the exocyclic bonds and than the Si–N bonds in the side chain (Fig.3). The distance between the opposite silicon atoms in the ring (2.484 Å) is greater, as in compound (Ia), than the distance between the opposite nitrogen atoms (2.448 Å). The torsional angles along the chain are Si(1)N(3)Si(2)N(1) = 80.19° and N(3)Si(2)N(1)Si(3) = 135.76°.[14]

The study of the crystal and molecular structures of 1,3-bis-(2,2,4,4,6-pentamethylcyclotrisiloxanyloxydimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane (IV) showed[16] that the colourless crystals of this compound are triclinic, belong to the space group $P1$, and have the following parameters: a = 8.316(5) Å, b = 10.528(5) Å, and c = 12.320(4) Å; α = 76.65(3)°, β = 77.55(4)°, γ = 71.95(4)°, and Z = 1. The structure has been elucidated by a direct method and

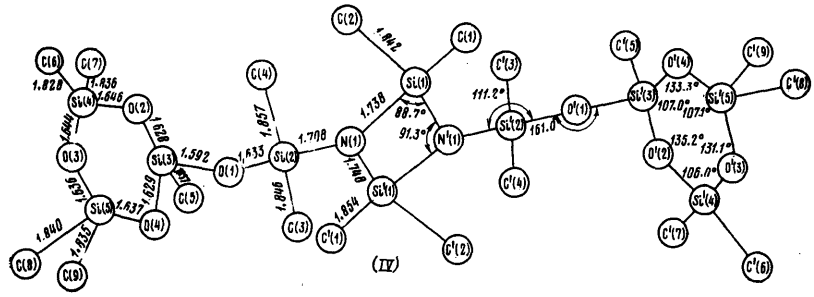


Figure 4. The molecular structure of 1,3-bis(2,2,4,4,6-pentamethylcyclotrisiloxanyloxydimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane (IV).[16] The bond lengths (Å) and the valence angles (in degrees) are given on the left- and right-hand sides respectively.

has been refined by the method of least squares in terms of the full matrix anisotropic approximation up to $R = 0.038$ on the basis of 2866 reflections with $F^2 > 1.96\sigma$.

The molecule of compound (IV) is located at the centre of symmetry. The dihedral angle between the planes of the trisiloxane and disilazane rings is 21°. The bond lengths and angles in the cyclodisilazane (IV) molecule are presented in Fig. 4.[16]

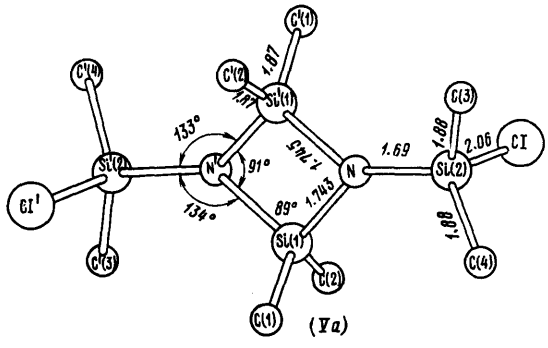


Figure 5. Stereochemistry of the 1,3-bis(chlorodimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane (Va) molecule, bond lengths, and valence angles[18].

X-Ray diffraction study[17,18] of 1,3-bis(chlorodimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane (Va) showed that crystals of this compound are monoclinic and have the lattice parameters $a = 6.653(3)$ Å, $b = 11.527(4)$ Å, and $c = 13.169(6)$ Å; $\gamma = 111.91(03)°$, space group $P2_{1/b}$, $Z = 2$. The structure has been elucidated by the direct method and has been refined by the method of least squares in terms of the anisotropic approximation up to an R factor of 6.9% using 1003 reflections. The four-membered disilazane ring is planar. No structural manifestations of the β-effect (the Cl → Si interaction) have been observed[18]. The bond lengths and valence angles are indicated in Fig. 5.

The amount of data available on the structure of phenylcyclodisilazanes is extremely small. Thus the crystal structure of 1,3-bis(chlorodiphenylsilyl)-2,2,4,4-tetraphenylcyclodisilazane (VI) has been determined[19] (Fig. 6). Crystals of compound (VI) are triclinic: $a = 11.192$ Å, $b = 12.016$ Å, $c = 9.707$ Å; $\alpha = 102.68°$, $\beta = 78.07°$, and $\gamma = 106.83°$. The structure has been refined up to an R factor of 10.6% on the basis of 1784 diffraction reflections with $I > 3\sigma$. It has been established that the crystals consist of a 1 : 1 solvate with benzene. The unit cell contains one formula unit, because both molecules are located at the centres of symmetry of the lattice (space group $P1$). The C(25), C(26), and C(27) atoms belong to the solvating benzene molecule located at the centre of symmetry (1/2; 1/2; 1/2).

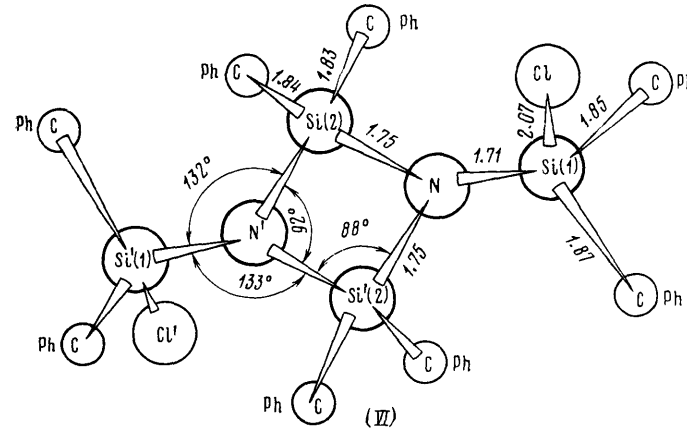


Figure 6. Stereochemistry of the 1,3-bis(chlorodiphenylsilyl)-2,2,4,4-tetraphenyldisilazane (VI) molecule, bond lengths and valence angles[19].

In conformity with symmetry requirements, the four-membered ring is planar. The Si–N bond lengths in the ring and the NSi(2)N′ and Si(2)NSi′(2) valence angles agree satisfactorily with other data[6,14]. The nitrogen atom has a nearly planar configuration (the sum of the valence angles is 357°), which indicates the delocalisation of its electron pair due to the d_π–p_π interaction with the Si(1), Si(2), and Si′(2) atoms. As in the previously investigated structures[6,14], the exocyclic Si(1)–N bond (1.713 Å) is shorter than the endocyclic Si(2)–N and Si′(2)–N bonds (1.746 and 1.750 Å respectively).

The observed Si(1)–Cl bond length, which is 2.072 Å, is appreciably greater than the normal value (2.01 Å);[20] nevertheless the compound exhibits an enhanced hydrolytic stability[17,19].

Thus the geometrical parameters of the molecules of the methyl- and phenyl-containing cyclodisilazanes (Va) and (VI) are in the main identical. The greatest differences were found on comparing the lengths of the exocyclic N–Si(R_2)Cl [1.690 Å for (Va) and 1.713 Å for (VI)] and Si–Cl [2.056 Å for (Va) and 2.072 Å for (VI)] bonds[18]. It is therefore impossible to observe a correlation between the differences in the reactivities and molecular geometries.

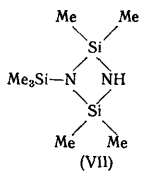
The infrared spectra of N-alkyl- or N-aryl-substituted cyclodisilazane have so far been inadequately investigated. It has been established that the nature of the substituents at the nitrogen atom affects the nature of the d_{π}–p_{π} bond and a corresponding shift of the region of asymmetric stretching vibrations of the Si–N bond in the Si(NSi) fragment of cyclodisilazane is observed[21–32].

The change in the nature of the organic group attached to the silicon atom[21] does not exert such an influence (Table 1).

Table 1. The influence of the nature of the organic group in the cyclodisilazane on the shift of the stretching vibration frequency ν_{as}[Si(NSi)] (cm^{-1}).[21]

Fragment	R					
	Me	Et	n-Pr	n-Bu	n-C_6H_{11}	Ph
$(Me_2Si—NR)_2$	912	955	—	923	953	963
$(RSiNHPh—NPh)_2$	—	917	917	919	—	—

As mentioned previously[4], *N*-substituted and particularly *N*-triorganosilyl-substituted organocyclodisilazanes are stable compounds. However, since the cyclodisilazane ring is highly strained, the replacement of one of the substituents at the nitrogen atom by hydrogen leads to the formation of chemically fairly reactive compounds[4,33], which is manifested by the anomalous disposition of the absorption bands due to stretching vibrations. Thus in the spectrum of 1-trimethylsilyl-2,2,4,4-tetramethylcyclodisilazane (VII)



(VII)

the nearest ν(NH) band shifts to 3510 cm^{-1} (which indicates an increased acidity of the proton attached to the N atom) and there is a corresponding shift of the central band to 1000 cm^{-1}. The ν(Si–N–Si) absorption band, corresponding to asymmetric stretching vibrations, which is believed[4,34] to characterise also the cyclodisilazane ring, is located in the region of 870 cm^{-1}.

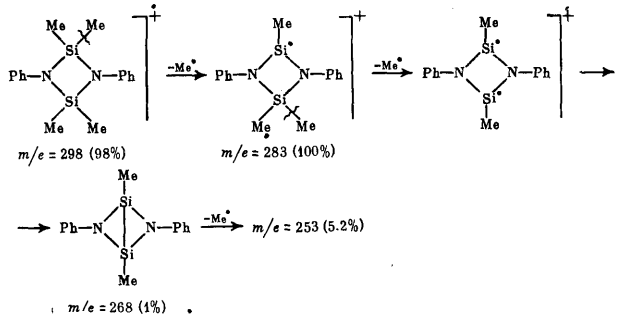
Analysis of the vibrational spectra of methylcyclodisilazanes showed[35] that vibrations due to individual Si–N bonds (endocyclic or exocyclic) cannot be isolated for the Si_4N_2 fragment (which can be treated to a first approximation independently of the vibrations of methyl groups and other functional groups attached to silicon atoms as a consequence of the so-called barrier effect of the silicon atom) and one must consider the vibrations of the fragment as a single whole. The wavenumbers 1050, 880, 770, 720, 460, and 430 cm^{-1} have been assigned to the stretching vibrations of the Si_4N_2 fragment. These wavenumbers do not in fact change as the functional groups at the silicon atom are varied. The bands in the region of 1050 cm^{-1}, which are intense in the infrared spectrum and are absent from the Raman spectrum, as well as the intense polarised bands in the region of 460 cm^{-1} in the Raman spectrum[35–37] can be specified as the most characteristic. It has been confirmed spectroscopically that the Si_4N_2 skeleton in 1,3-bis(chlorodimethylsilyl)-2,2,4,4-tetramethylcyclodisilazanes (Va) is planar, because the alternative prohibition rule holds for the stretching vibrations of the Si_4N_2 fragment, three of which (1050, 880, and 430 cm^{-1}) are active only in the infrared spectrum, while three others (770, 720, and 460 cm^{-1}) are active only in the Raman spectrum. This result agrees satisfactorily with X-ray diffraction data[17]. The deformation vibrations of the Si_4N_2 fragment are not considered, since they lie in the region of very low frequencies where their interpretation is difficult. Comparison of the spectra of liquids (melt at 100 °C) and crystals showed that significant changes are not observed in the transition from the liquid to the crystalline state[35].

The vibrational spectra of phenylcyclodisilazanes have been interpreted by comparison with the spectra of diphenylsilane. The majority of the vibrations of the benzene rings are characteristic either in terms of frequency or in terms of frequency and mode, which makes it possible to separate them from the vibrations of the Si_4N_2 fragment. In the Raman spectra the bands corresponding to the vibration of the benzene rings are much more intense than those due to the stretching vibrations of the Si_4N_2 fragment. The wavenumbers 1020, 800, 720, 610, 540, and 400 cm^{-1} have been assigned to the stretching vibrations of the Si_4N_2 fragment[38].

The intense infrared band in the region of 800 cm^{-1} can be specified as the analytical band for phenylcyclodisilazanes. The changes in the frequency of this band as a function of the functional groups attached to the exocyclic silicon atom are 798 cm^{-1} when H is replaced by OH, 800 cm^{-1} for Cl, 801 cm^{-1} for OEt, and 824 cm^{-1} for NH_2.[39]

The vibrational spectroscopic data are satisfactorily consistent with the planar structure of the four-membered silazane ring in 1,3-bis(chlorophenylsilyl)-2,2,4,4-tetraphenylcyclodisilazane (VI). The alternative prohibition rule holds for the ν(Si–N) stretching vibrations: the frequencies corresponding to vibrations of the B_{2u} and B_{3u} symmetry types (540, 800, and 1020 cm^{-1}) are active only in the infrared spectra, while the frequencies corresponding to the vibrations of the A_g and B_{1g} symmetry type (400, 610, and 720 cm^{-1}) are active only in the Raman spectra[38].

The mass spectra of *N*-alkyl- and *N*-aryl-cyclodisilazanes as well as the interpretation of the differences between the mass spectroscopic fragmentations of organocyclodisilazanes have been described[21,31,40,41]. A characteristic feature of the mass spectrum of compound (II) is the high (98%) intensity of the peak due to the molecular ion whose decomposition takes place via the consecutive loss of methyl groups[40]. The transitions $M^+ \rightarrow (M - Me)^+ \rightarrow (M - 2Me)$ have been confirmed by the presence of the corresponding metastable peaks.



The *m/e* 149 peak (Table 2) corresponds to the doubly charged molecular ion M^{2+} and not to the singly charged ion formed as a result of the decomposition involving the dissociation of two Si–N bonds. The dissociation of the bonds in the ring leads to rearranged ions with *m/e* 119 and 93:

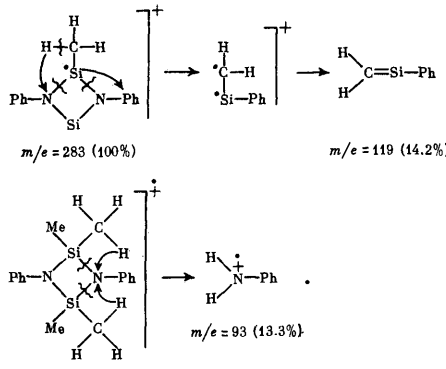
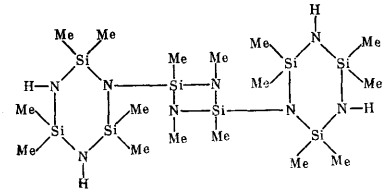


Table 2. Mass spectrometric data for 1,3-diphenyl-2,2,4,4-tetramethylcyclodisilazane (II).[40]

m/e	*I*, %	*m/e*	*I*, %	*m/e*	*I*, %	*m/e*	*I*, %
301	1.9	148	4.8	104	2.7	72	3.1
		147	4.1	101	3.8	71	5.2
300	13.4	137	7.7	100	13.4	70	9.9
299	36.7	127	5.8	99	1.9	69	7.4
298	98	126	7.6	96	2.5	60	3.8
297	2	125	5.7	95	5.7	59	21.1
286	1.7	124	4	94	3.8	58	15.4
285	12.9	123	7.2	93	13.3	57	7.2
284	25	122	5.8	92	3.7	56	7.6
283	100	121	5.6	91	9.1	55	7
268	1	120	7.5	86	4.4	54	5.7
254	1.2	119	14.2	85	5	52	1.9
253	5.2	118	3.8	84	12.5	51	4
225	3.3	111	3.6	83	5.8	45	12.8
194	1.1	110	3.4	82	2.9	44	3.8
193	1.7	109	3.5	78	3.7	43	48.1
192	1.6	108	2.3	77	9.6	42	3.7
191	1.7	107	3.7	75	5.4	41	7.7
150	3.8	106	3.8	74	7.7	40	19.2
149,5	3.9	105	3.9	73	23.1	39	7.7
149	21						

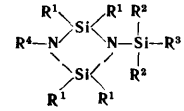
The mass spectrum of 1,3-dimethyl-2,4-bis(2,2,4,4,6,6-hexamethylcyclotrisilazanyl)-2,4-dimethylcyclodisilazane



is characterised by the following peaks: *m/e* 580 (6%) $[M]^+$; *m/e* 565 (49%) $[M - Me]^+$; *m/e* 548 (19%) $[M - Me, -NH_3]^+$; *m/e* 534 (100%) $[M - 2Me, -CH_2]^+$; *m/e* 519 (10%) $[M - 3Me, -CH_4]^+$; *m/e* 495 (9%), *m/e* 482 (15%), *m/e* 461 (14%), *m/e* 275 (12%).[41]

The principal ^1H NMR data for *N*-alkyl- and *N*-aryl-cyclodisilazanes have been published in a number of studies[2,22,26–28,41–53]. In the ^1H NMR spectra of cyclodisilazane derivatives of compound (Va) the chemical shift of the signals due to the protons in the methyl group linked to the silicon atom of the cyclodisilazane is $\tau = 9.76–9.79$; for the protons of the methyl groups linked to the exocyclic silicon atom, $\tau = 10.01–10.05$ (10% solution in CCl_4).[27,32] The following chemical shifts of the proton signals are characteristic of the ^1H NMR spectra of 1,3-dimethyl-2,4-bis(2,2,4,4,6,6-hexamethylcyclotrisilazanyl)-2,4-dimethylcyclodisilazane (solution in CH_2Cl_2, internal standard—$SiMe_4$):[41] $\tau = 9.96$ for the protons of the $SiMe_2$ group, $\tau = 9.89$ for the protons of $N(SiMe_2)_2$, $\tau = 9.83$ for the protons of SiMe, and $\tau = 7.43$ for the protons of NMe. The chemical shifts of the protons in the cyclodisilazane compounds with different organic groups are presented in Table 3.

Table 3. Chemical shifts of the proton signals of *N*-triorganosilyl-*N'*-organocyclodisilazanes (VIII)–(XI) [27,32]



Compound	R^1	R^2	R^3	R^4	$\tau_{(R^1)}$	$\tau_{(R^2)}$	$\tau^*_{(R^4)}$
(VIII)	Me	Me	Me	Me	9.85	10.04	7.55
(IX)	Me	Me	Me	Et	9.83	10.03	7.18 qu. 8.97 t.
(X)	Me	Me	Me	Ph	9.57	9.94	2.80—3.69 m.
(XI)	Me	Me	Ph	Me	9.87	9.72	7.53

*J = 7 Hz; notation: qu. = quartet, t. = triplet; m. = multiplet.

The chemical shift of the protons of the methyl groups linked to the endocyclic silicon atom is 9.85 for compound (VIII) and is intermediate between the values of τ for compound (Ia) (9.79) and 1,2,2,3,4,4-hexamethylcyclodisilazane (XII) (9.89), while the value for compound (XI) (9.57) is intermediate between 9.79 for compound (Ia) and 9.37 for compound (II).[26]

The photolysis of certain trialkylsilyl azides, such as trimethylsilyl azide or n-propyldimethylsilyl azide, results in the formation of cyclodisilazanes with different organic

groups[53]. Further photolysis of these cyclodisilazanes leads to the formation of high-molecular-weight alkylsilazanyl azides. The photolysis was carried out in a Rayonet reactor using Rayonet RPR-2737 lamps; the illumination periods ranged from 30 min to 65 h.[53]

There are no reports in the literature of systematic studies of organocyclodisilazanes by quantum-chemical methods. This is evidently because these methods have been introduced comparatively recently, but they permit a fairly correct analysis of the electronic structures of molecules. Quantum-mechanical methods have been used in terms of the approximation involving complete neglect of differential overlap and were not specially optimised for calculations on systems such as organocyclodisilazanes where the *d* atomic orbital of silicon plays a major role in the electronic structure and in which there is a marked charge separation in the Si–N bonds.

A version of the LCAO-MO SCF CNDO method[55] was used in one of the studies [54] and quantum-chemical calculations were made for cyclosilazanes. Compared with cyclosiloxanes, the quantum-chemical calculation for cyclosilazanes predicts a higher electron density at the silicon atom. As a result of the smaller charge separation in cyclosilazanes, the electrostatic component, which determines the dihedral angle involving the two silicon ring atoms, is smaller when the nitrogen atom is present at its vertex than in the compound with an oxygen atom. This is the cause of the formation of small SiNSi angles and relatively large SiOSi angles.

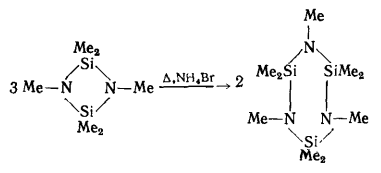
One of the factors which explains the cause of the stability of organocyclodisilazanes compared with organocyclodisiloxanes is the occurrence of strong additional endocyclic p_π–p_π interaction between opposite nitrogen atoms. The N...N bond index in cyclodisilazane is 0.478 a.u., which is approximately ten times greater than for the corresponding O...O interaction in cyclodisiloxane. In cyclosilazanes the extent of the N...N interaction diminishes rapidly with increasing ring size and in the eight-membered ring it already approaches the extent of the corresponding O...O interaction in cyclosiloxanes.

III. CHEMICAL REACTIONS AND PROPERTIES OF ORGANOCYCLODISILAZANES

1. *N*-Alkyl- and *N*-Aryl-Cyclodisilazanes

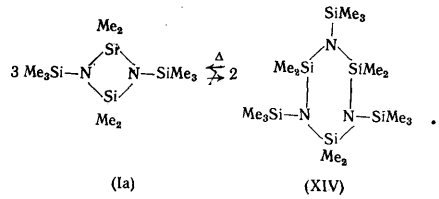
It has been shown by X-ray diffraction[4,14] that the angle between the bonds at the nitrogen atom in cyclodisilazanes is distorted and approaches the angle corresponding to pure *p* orbitals. This is manifested by a weakening of the endocyclic Si–N bond on passing from compound (XII) to compound (Ia).[8,24] However, although the reactivity of this bond should have increased in this direction, in reality it diminishes. Thus compound (XII) is readily solvolysed[56], while compound (Ia) is more stable in relation to water and alkalis[2]. The stability of cyclodisilazanes with methyl substituents at the silicon atom in relation to acids varies in the following sequence as a function of the substituents at the nitrogen atom: alkyl < trimethylsilyl < aryl.

Heating of compound (XII) or other *N*-methylated cyclodisilazanes in the presence of a catalyst leads to the irreversible formation of a six-membered silazane ring[24,57]:



(XII) (XIII) (1)

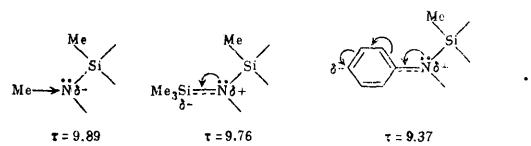
On the other hand, compound (Ia) and *N*-phenylcyclodisilazanes do not undergo a rearrangement under similar conditions[2]:



(Ia) (XIV) (2)

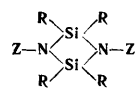
Compound (Ia) does not react with ammonium bromide [like compound (XII), which undergoes reaction (1)], while *N*-phenylcyclodisilazanes react only above 400 °C and very slowly, a mixture of products without a six-membered silazane ring being formed[2]. 1,3,5-Tris(trimethylsilyl)cyclotrisilazanes of type (XIV) are capable of being converted into cyclodisilazanes via reaction (2) at elevated temperatures (400–425 °C), but even at 450 °C the reaction does not go to completion[2].

The differences between the stabilities of cyclodisilazanes of different types can be accounted for by the different distributions of electron density in the molecule. Substituents at the nitrogen atom can increase or decrease the electron density as a result of the inductive influence. The reactions involving the Si–N bond, for example, hydrolysis, normally take place on protonation of the nitrogen atom and are facilitated by increasing nucleophilicity of the substituent. The electron density at the nitrogen atom and hence also the basicity decrease in the following sequence as a function of the substituent: Me > Me_3Si > Ph; the resistance of organocyclodisilazanes to electrophilic attack then increases. The d_π–p_π contribution to the Si–N bond in the ring decreases in the same sequence, which is confirmed by the changes in τ_{SiMe}:[2,8,24]



τ = 9.89 τ = 9.76 τ = 9.37

Table 4. Temperatures of the onset of decomposition of organocyclodisilazanes[58,59]



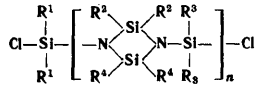
R	Z	*t*, °C	R	Z	*t*, °C	R	Z	*t*, °C
Ph	Me	392	Ph	Ph	455	Ph	*m*-C_6H_4F	418
Ph	Et	394	Me	*p*-$C_6H_5C_6H_4$	432	Ph	*m*-$(CF_3)_2C_6H_3$	384
Me	n-Bu	>223	Ph	*p*-$C_6H_5C_6H_4$	443	Me	$SiPh_2Me$	416
Me	C_6H_{11}	>317	Me	*m*-$C_6H_5OC_6H_4$	442	Me	$SiPh_3$	439
Me	Ph	481	Me	2,4,6-$(CH_3)_3C_6H_2$	365	Ph	$SiMe_3$	421

N-Phenyl- and *N*-trimethylsilyl-cyclodisilazanes exhibit a high thermal stability. An appreciable decomposition of the ring is not observed even at 450 °C.[58,59] Table 4 lists the temperature at which the test compounds lose 1% of their weight[58].

2. Reactions of α,ω-Diorganosilylcyclodisilazanes

The reactions of α,ω-diorganohalogenosilylcyclodisilazanes with electrophiles and nucleophiles, leading to different derivatives, are of great interest. In organocyclodisilazanes containing a chlorine atom in the side chain, for example, in compounds (Va)–(Vf), (VI), and (XV)–(XX) (Table 5), the latter is readily substituted by an organic group on treatment with an organometallic compound, for example, a Grignard reagent[27,34,60–63]. There is also a possibility of the replacement of only one Cl atom in compounds (XXII)–(XXIV) (Table 6) by selecting an appropriate reactant ratio[61,64]. The substitution of chlorine atoms by a triorganosiloxy-group can be achieved by allowing compounds of type (V) to react with the corresponding sodium triorganosilanoxides. The trimethylsiloxy- and methyldiphenylsiloxycyclodisilazanes (XXV) and (XXVI) obtained in this way are liquids; triphenylsiloxycyclodisilazanes (XXVII) are solids; oligomers with an odd number *n* are crystalline, while those with an even number *n* are waxy substances (Table 6).[61]

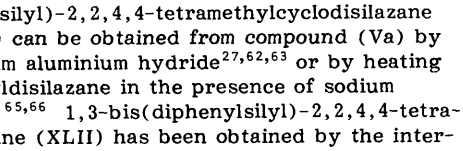
Table 5. Organocyclodisilazanes



Compound	*n*	R^1	R^2	R^3	R^4	B.p., °C/mmHg	M.p., °C	Refs.
(Va)	1	Me	Me	Me	Me	64/0.08	68–69	[27, 61–63]
(Vb)	2	Me	Me	Me	Me	118/0.05	43,5	[61, 64]
(Vc)	3	Me	Me	Me	Me	186/0.01	109–110	[61, 64]
(Vd)	4	Me	Me	Me	Me	248/0.01	93	[61, 64]
(Ve)	5	Me	Me	Me	Me	287/0.005	149–152	[61, 64]
(Vf)	6	Me	Me	Me	Me	315/0.005	147	[61, 64]
(VI)	1	Ph	Ph	Ph	Ph	—	260	[60]
(XV)	1	Ph	Ph	Me	Ph	282/0.05	283	[60]
(XVI)	1	Ph	Ph	Ph	Me	282/0.05	106	[60]
(XVII)	1	Ph	Me	Ph	Me	218/0.05	139	[60]
(XVIII)	1	Ph	Ph	Me	Me	218/0.05	*	[60]
(XIX)	1	Ph	Me	Me	Me	144/0.005	41	[60]
(XX)	1	Me	Ph	Me	Me	134/0.005	73	[60]

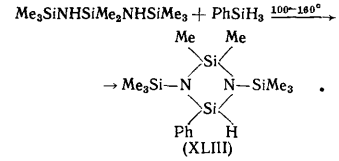
*n_D^{36} = 1.5863.

1,3-Bis(dimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane (XXVIII) (Table 6) can be obtained from compound (Va) by reaction with lithium aluminium hydride[27,62,63] or by heating 1,1,3,3-tetramethyldisilazane in the presence of sodium methoxide or KOH;[65,66] 1,3-bis(diphenylsilyl)-2,2,4,4-tetraphenylcyclodisilazane (XLII) has been obtained by the interaction of diaminodiphenylsilane with diphenylsilane via reaction (3) using molar reactant ratios ranging from 1 : 3 to 1 : 4 in the presence of potassium trimethylsilanoxide as the catalyst[67,68].



(XLII) (3)

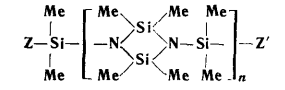
Dehydrocondensation can be used for the specific synthesis of organocyclodisilazanes containing a hydrogen atom at the endocyclic Si atom, for example[69]:



(XLIII)

The interaction of organocyclodisilazanes (V) with ammonia, amines, or amides leads to the formation of the corresponding nitrogen-containing cyclodisilazanes (XXIX)–(XXXV) (Table 6).[27,33,61–63,70,71] Other organocyclodisilazanes with the groups NH_2, NHR, or NR_2 (R = Me, Et, n-Bu, t-Bu, Ph, or $SiMe_3$) are obtained by the thermal condensation of organoaminosilanes $R_nSi(NHSiR'_3)_{4-n}$ (*n* = 0–2) or tetra-alkyl(aryl)-aminosilanes[72–76].

Table 6. Physical characteristics of organocyclodisilazanes

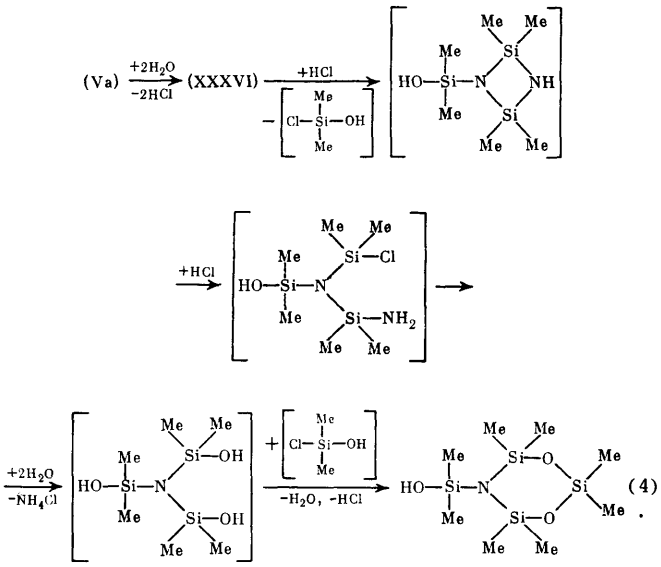


Compound	Z, Z'	*n*	B.p., °C/mmHg	M.p., °C	n_D^{20}	Refs.
(Ia)	Z=Z'=Me	1	85/7	39	1.4237*	[61]
(Ib)	Z=Z'=Me	2	104/0.005	20	1.4553	[61]
(Ic)	Z=Z'=Me	3	169/0.005	100	—	[61]
(XXIa)	Z=Z'=Ph	1	133/0.03	62	—	[61]
(XXIb)	Z=Z'=Ph	2	185/0.005	—	1.5093	[61]
(XXIc)	Z=Z'=Ph	3	275/0.02	—	1.535**	[61]
(XXIIa)	Z=Me; Z'=Cl	1	103/12	52	—	[61]
(XXIIb)	Z=Me; Z'=Cl	2	121/0.005	28	—	[61]
(XXIII)	Z=Ph; Z'=Cl	1	109/0.3	—	1.4892	[61]
(XXIV)	Z=p-$C_6H_5C_6H_4$; Z'=Cl	1	165/0.005	49	—	[61]
(XXVa)	Z=Z'=Me_3SiO	1	105/1	12	1.4227	[34, 61]
(XXVb)	Z=Z'=Me_3SiO	2	146/0.005	3	1.4425	[61]
(XXVc)	Z=Z'=Me_3SiO	3	205/0.01	18	1.4581	[61]
(XXVIa)	Z=Z'=$MePh_2SiO$	1	226/0.01	—	1.5338	[61]
(XXVIb)	Z=Z'=$MePh_2SiO$	2	274/0.001	39	1.5219	[61]
(XXVIIa)	Z=Z'=Ph_3SiO	1	—	189–191	—	[61]
(XXVIIb)	Z=Z'=Ph_3SiO	2	320–330/0.002	95***	—	[61]
(XXVIIc)	Z=Z'=Ph_3SiO	3	—	160	—	[61]
(XXVIII)	Z=Z'=H	1	73/10	—	1.4308	[27, 62, 63]
(XXIX)	Z=Z'=NH_2	1	108/12	36	—	[62, 63]
(XXX)	Z=Ph; Z'=NH_2	1	87/0.005	—	1.4880	[61]
(XXXI)	Z=Z'=NHMe	1	118/8	—	1.4518	[62, 63]
(XXXII)	Z=Z'=NMe_2	1	113–114/4	—	1.4530	[63]
(XXXIIIa)	Z=Z'=NEt_2	1	164/12	7–8	1.4584	[59, 63]
(XXXIIIb)	Z=Z'=NEt_2	2	152/0.01	−2	1.4675	[59]
(XXXIIIc)	Z=Z'=NEt_2	3	224/0.01	65	—	[59]
(XXXIIId)	Z=Z'=NEt_2	4	280/0.005	91	—	[59]
(XXXIV)	Z=Z'=NC_5H_{10}	1	142–144/0.1	42–43	—	[61]
(XXXV)	Z=Z'=NHPh	1	—	106–107	—	[63]
(XXXVI)	Z=Z'=OH	1	—	122–123	—	[27,62,63,80]
(XXXVII)	Z = Z' = OMe	1	104–106/6	—	1.4368	[26, 62, 63]
(XXXVIII)	Z = Z' = OEt	1	115–116/8	—	1.4342	[26, 62, 63]
(XXXIX)	Z = Z' = $OCH(CH_3)_2$	1	85/1	—	1.4298	[63]
(XL)	Z = Z' = OPh	1	147–149/0.02	44–45	—	[63]
(XLI)	Z = Z' = $OCOCH_3$	1	95–97/0.2	49–52	—	[63]

*At 45 °C.
**At 50 °C.
***Reduced softening temperature.

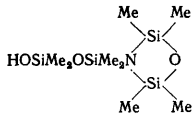
The hydroxycyclodisilazanes (XXXVI) (Table 6) and (XLIV) (Table 7) have been obtained by the hydrolysis of the organocyclodisilazanes (Va), (VI), (XV)–(XVIII), and (XXIX).[27,63,77–80].

The study of the hydrolysis of organocyclodisilazanes showed[77,78] that the composition of the final hydrolysis products of compounds (V) and (XXIX) is influenced not only by the acidity of the medium and the amount of hydrolysing agent, as in the hydrolysis of aminosilanes and silazanes, but also by the order of mixing of the initial components. The mechanism of the hydrolysis has been established:



The opening of the cyclodisilazane ring in the hydrolysis of compound (Va) can be apparently accounted for by the effect of the hydrogen chloride evolved in the first instant of the reaction, while the formation of the silazanesiloxane ring of 2,2,4,4,6,6-hexamethyl-5-hydroxydimethylsilyl-1,3-dioxa-5-aza-2,4,6-trisilacyclohexane can be explained by the intermolecular condensation of the intermediates in reaction (4) under the influence of water.

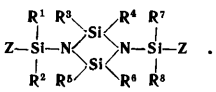
The initial and final compounds were analysed on the basis of mass spectrometric[81] and X-ray diffraction[79] data. The structure of the hydrolysis product of compound (XXXVI) was established on the basis of the observed behaviour[81]. The presence in the mass spectrum of this compound of the peak due to a molecular ion with *m/e* 295 and the peak of the ion $(M-Me)^+$ with *m/e* 280, which has the maximum intensity, indicates unambiguously the presence in the molecule of three oxygen atoms and one nitrogen atom. The high intensity (12%) of the peak of the $(M-MeOSiMe_2)^+$ ion with *m/e* 206 indicates the presence of the hydroxydimethylsilyl group at the nitrogen atom in the ring. The loss of the end group in decomposition following electron impact is not characteristic of linear siloxanes. This makes it possible to rule out the alternative structure with a four-membered ring



proposed by Fink[80] and to confirm the structure of the six-membered ring of 2,2,4,4,6,6-hexamethyl-5-hydroxydimethylsilyl-1,3-dioxa-5-aza-2,4,6-trisilacyclohexane. Crystals of this compound (Fig. 7) are monoclinic with the lattice parameters $a = 6.866(2)$ Å, $b = 19.161(6)$ Å, and $c = 13.423(5)$ Å; $\beta = 105.25(10)°$, space group $P2_1/C$, $Z = 4$.

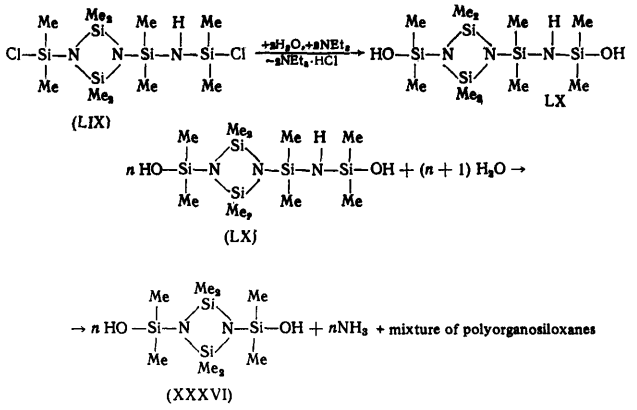
In the hydrolysis of 1-(3-chloro-1,1,3,3-tetramethyldisilazanyl)-3-chlorodimethylsilyl-2,2,4,4,-tetramethylcyclodisilazane (LIX) the reaction is influenced by the ratio of the amounts of the cyclodisilazane and the hydrolysing agent[82]; depending on the hydrolysis conditions, the product is either 1-(3-hydroxy-1,1,3,3-tetramethyldisilazanyl)-3-hydroxydimethylsilyl-2,2,4,4-tetramethylcyclodisilazane (LX) [reaction

Table 7. Physical characteristics of organocyclodisilazanes



Compound	Z	R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8	B.p., °C/mmHg	M.p., °C	n_D^{20}	References
(XLII)	H	Ph	Ph	Ph	Ph	Ph	Ph	Ph	Ph	—	224—225	—	[39, 67, 68]
(XLIV)	OH	Ph	Ph	Ph	Ph	Ph	Ph	Ph	Ph	—	158	—	[39, 60, 80]
(XLI)	NH_2	Ph	Ph	Ph	Ph	Ph	Ph	Ph	Ph	—	235—236	—	[39]
(XLVI)	OEt	Ph	Ph	Ph	Ph	Ph	Ph	Ph	Ph	—	—	1.5795	[39]
(XLVII)	Me	Me	Me	Me	Ph	Ph	Me	Me	Me	Me	120/0.03	51	—	[60]
(XLVIII)	Me	Ph	Ph	Me	Me	Me	Me	Me	Me	Me	124/0.005	—	1.5210	[60]
(XLIX)	Me	Ph	Ph	Ph	Ph	Me	Me	Me	Me	Me	—	97	—	[60]
(L)	Me	Ph	Ph	Me	Me	Me	Me	Ph	Ph	—	144	—	[40, 60]
(LI)	Me	Me	Me	Ph	Ph	Ph	Ph	Me	Me	—	260	—	[60]
(LII)	Me	Ph	Ph	Ph	Ph	Me	Me	Ph	Ph	—	150	—	[60]
(LIII)	Me	Ph	Ph	Ph	Ph	Ph	Ph	Me	Me	—	215		[60]
(LIV)	$NH(C_3H_7)$	Ph	Ph	Ph	Ph	Ph	Ph	Ph	Ph	—	248—251	—	[60]
(LV)	NMe_2	Me	C_3H_4F	Me	C_3H_4F	Me	C_3H_4F	Me	C_3H_4F	140—142/0.1	80—85	—	[70]
(LVI)	NMe_2	Me	Ph	Me	Ph	Me	Ph	Me	Ph	206—210/0.01	—	1.5728	[70]
(LVII)	NMe_2	Me	$CH_2=CH$	Me	$CH_2=CH$	Me	$CH_2=CH$	Me	$CH_2=CH$	104—106/0.2	—	1.4849	[70]
(LVIII)	NMe_2	Me	Et	Me	Et	Me	Et	Me	Et	138—140/0.2	—	1.4722	[70]

(5)] or the products of its further transformation into a mixture of polyorganosiloxanes[82] [reaction (6)]:



(5)

(6)

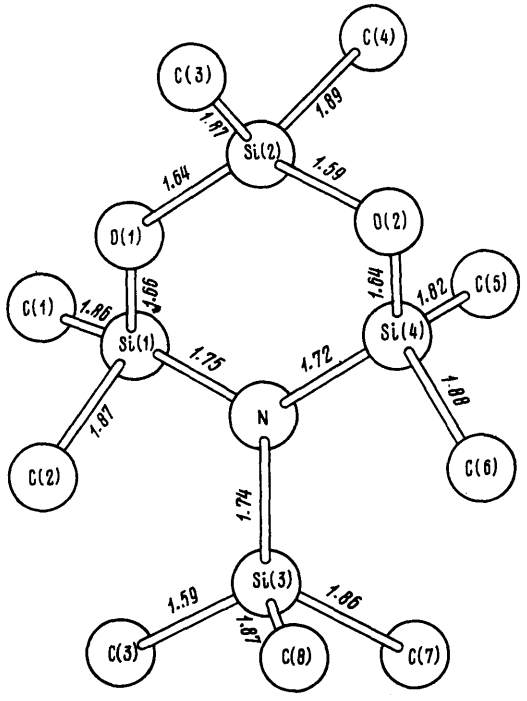
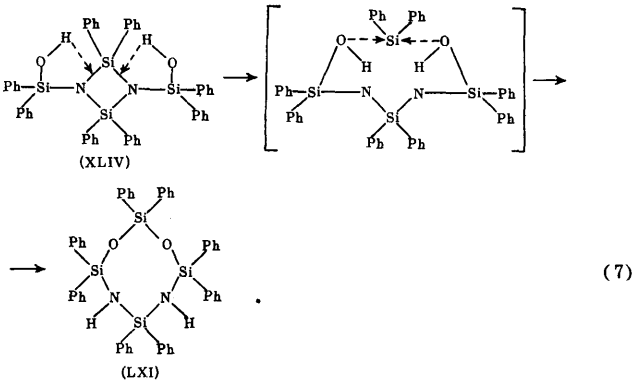


Figure 7. Stereochemistry of the 2,2,4,4,6,6-hexamethyl-5-hydroxydimethylsilyl-1,3-dioxa-5-aza-2,4,6-trisilacyclohexane molecule[81].

In contrast to methylcyclodisilazanes, the hydrolysis of 1,3-bis(diphenylsilyl)tetraphenylcyclodisilazanes proceeds with retention of the cyclodisilazane ring regardless of the conditions[39].

The study of the influence of the functional groups (Cl, H, OH, NH_2, OEt), linked to the exocyclic Si atom in phenylcyclodisilazanes (VI) (Table 5) and (XLII)–(XLVI) (Table 7), on their hydrolytic stability showed that the hydrolysis involving the functional groups Cl and NH_2 takes place over a period of time and the final product is a mixture of the initial compound and the hydrolysis product, which is difficult to separate. Phenylcyclodisilazanes with the OEt of H substituents are hydrolytically stable under the same conditions[39].

Approximately 2–3% of 2,2,4,4,6,6,8,8-octaphenyl-1,3-dioxa-5,7-diaza-2,4,6,8-tetrasilacyclo-octane (LXI) was isolated in the separation of the hydrolysis products of phenylcyclodisilazane. Thus the hydrolysis of phenylcyclodisilazanes at the Si–X bond (X = Cl or NH_2) is accompanied to a slight extent by hydrolytic cleavage at the Si–N bond [reaction (7)] regardless of the conditions under which it takes place. Reaction (7) leads to the expansion of the four-membered cyclodisilazane ring[83]:

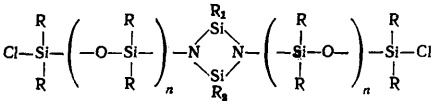


(7)

It is noteworthy that the separation of compounds (XLIV) and (LXI) presents considerable difficulties and can be achieved only by repeated recrystallisation from benzene. The presence of compound (LXI) decreases the melting point of compound (LXIV) from 157–158° to 141–150 °C.[83]

The structure of the product (LXI) was established by X-ray diffraction. The crystals of compound (LXI) are triclinic, belong to the space group $P\bar{1}$, and have the lattice parameters a = 14.912 Å, b = 13.258 Å, and c = 14.218 Å; α = 124.61°, β = 104.64°, and γ = 91.24°. The structure was elucidated on the basis of 2827 reflections and was refined up to an R factor of 11.6% (Fig.8).[83]

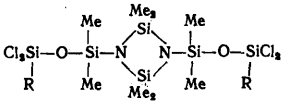
The hydrolysis of cyclodisilazane oligomers (LXII) yielded the corresponding α,ω-dihydroxy-derivatives[80,84,85], consisting of oily liquids:



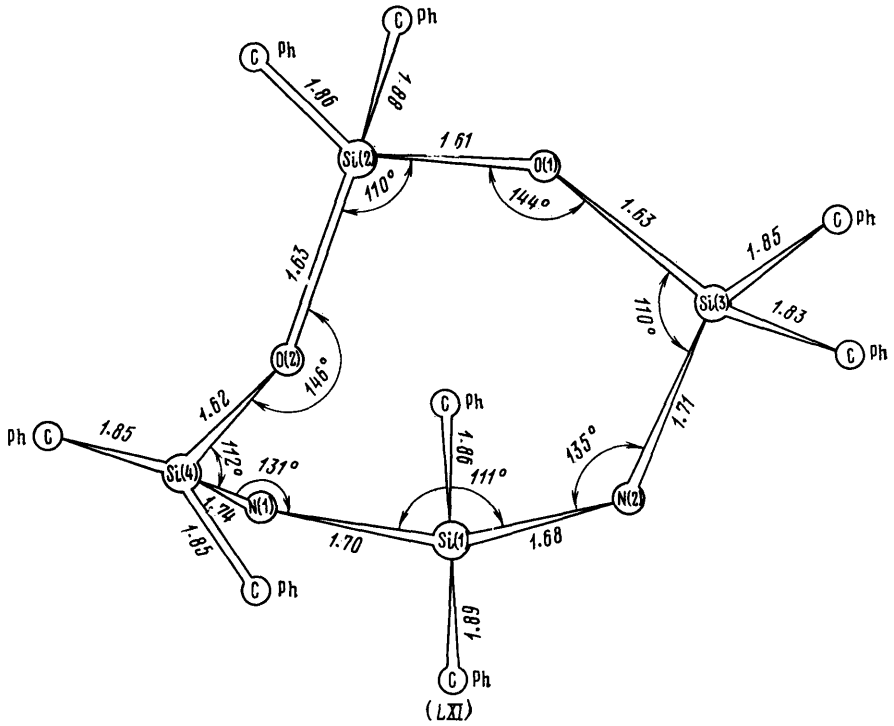
(LXII)

R = Me, Et, CH_2 = CH or Ph; n = 1 – 3 .

The interaction of hydroxy-derivatives with trichloromethylsilane or trichlorophenylsilane in the presence of a hydrogen chloride acceptor gave rise to the tetrachloroderivatives (LXIII):[86]



(LXIII)

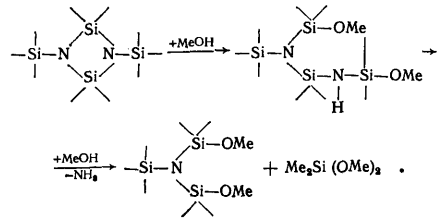


(LXI)

Figure 8. Stereochemistry of the 2,2,4,4,6,6,8,8-octaphenyl-1,3-dioxa-5,7-diaza-2,4,6,8-tetrasilacyclo-octane (LXI) molecule, bond lengths, and bond angles[72].

The interaction of organocyclodisilazanes with alcohols, phenol, and glacial acetic acid yielded the corresponding derivatives (XXXVII)–(XLI) (Table 6).[27,62,63]

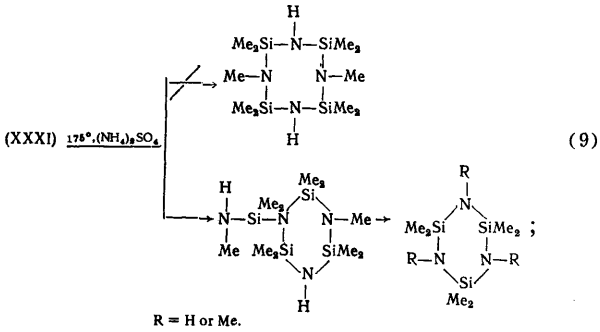
The alcoholysis of organocyclodisilazanes [reaction (8)] with a large (16-fold) excess of an alcohol, for example, methanol, cleaves the Si–N ring bond and symmetrical and asymmetrical silylamines are formed[26]:



(8)

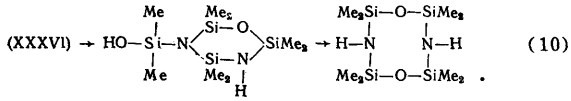
N,N'-Bis(diorganohalogenosilyl)cyclodisilazanes as well as the corresponding alkoxy- and phenoxy-derivatives (XXXVII)–(XL) (Table 6) remain unchanged on heating up to the boiling point in the presence of catalytic amounts of ammonium sulphate. Heating of 1,3-bis(dimethylaminosilyl)-2,2,4,4-tetramethylcyclodisilazane (XXIX) with ammonium sulphate (for 24 h at 200 °C) leads to a mixture of products, from which only hexamethylcyclotrisilazane was isolated (15%), although compound (XXIX) does not undergo any changes on refluxing (236 °C) without a catalyst[63].

It has been claimed[63] that, when 1,3-bis[dimethyl(methylamino)silyl]-2,2,4,4-tetramethylcyclodisilazane (XXXI) is heated to 175 °C with ammonium sulphate [reaction (9)], the ring expands and 1,2,2,4,4,5,6,6,8,8-decamethylcyclotetrasilazane is formed (38%). However, other workers[87] showed that this reaction results in the formation of a mixture of *N*-methylcyclotrisilazanes:



(9)

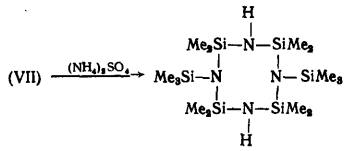
Andrianov et al.[88] showed that, on heating (1.5 h, 60 °C) in the presence of tetramethylammonium silanoxide (0.05%), compound (XXIX) undergoes reaction (10) and gives rise to octamethylcyclotetrasilazane (36%). A rearrangement with ring expansion is observed under the same conditions also for 1,3-bis(hydroxydimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane (XXXVI):[88]



(10)

1-Trimethylsilyl-2,2,4,4-tetramethylcyclodisilazane (VII) remains unchanged on heating, but in the presence of ammonium sulphate (1%) at 190 °C is converted via reaction

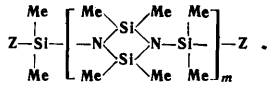
(11) into a dimer with an eight-membered ring[89]:



(11)

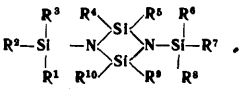
The characteristics of derivatives of oligomeric α,ω-diorganosilylcyclodisilazanes are presented in Table 6 and 7. Data for the thermal stabilities of certain organocyclodisilazanes[58] are given in Tables 8–10.

Table 8. Temperatures of the onset of decomposition of cyclodisilazanes[58]



m	Z			
	Me	Ph	$MePh_2SiO$	Ph_2SiO
1	503	>369	427	418
2	>340	422	419	419
3	462	426	—	418
5	459	—	—	—
7	395	—	—	—

Table 9. Temperatures of the onset of decomposition of cyclodisilazanes[58]



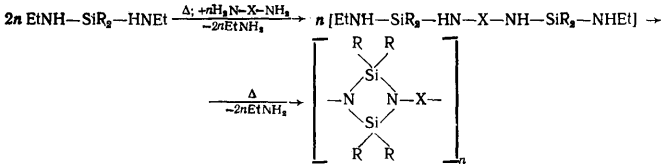
R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8	R^9	R^{10}	*t*, °C
Me	Me	Me	Ph	Ph	Me	Me	Me	Ph	Ph	421
Ph	Me	Ph	Me	Me	Ph	Me	Ph	Me	Me	416
Me	Me	Ph	Me	Ph	Me	Me	Ph	Me	Ph	417
Me	Me	Me	Ph	Ph	Ph	Me	Ph	Me	Me	414
Ph	Me	Ph	Ph	Ph	Ph	Me	Ph	Me	Me	411
Ph	Me	Me	Ph	Ph	Me	Me	Me	Ph	Ph	418
Ph	Ph	Ph	Me	Me	Ph	Ph	Ph	Me	Me	439

IV. POLYMERS CONTAINING CYCLODISILAZANE UNITS

The polymers (LXIV) (Table 11) are usually synthesised in two ways—by the polycondensation of aromatic diamines with diaminosilanes and by the catalytic silylation of aliphatic or aromatic diamines by the organosilanes R_nSiH_{4-n}, where $n = 1$ and 2.

1. Polycondensation of Aromatic Diamines with Diaminosilanes

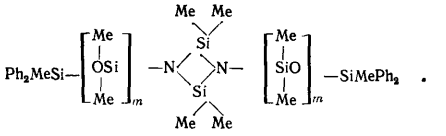
The polymers (LXIV, a–d) are formed via the following reaction with a reactant ratio of 2 : 1:[59,90]



(LXIV, a–d)

X=Ar; (Ia) — (Ib) : R=Me; (Id) : R=Ph; $n = 15 - 20$. (12)

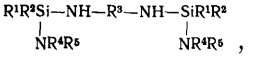
Table 10. Temperatures of the onset of decomposition of cyclodisilazanes[58]



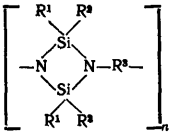
m	1	2	3	4
t, °C	427	417	413	411

N,N'-Alkylethyldiaminosilanes, whose amino-residue is readily split off, are used as the silyl component. Among aromatic diamines, derivatives with functional groups in the 1,4-, 3,3'-, and 4,4'-positions have been used. The formation of an intermediate via reaction (12) proceeds readily at 135–260 °C (depending on *R*); the cyclisation requires higher temperatures (~400 °C). The reaction can be carried out in the melt or in a high-boiling solvent, but neither method is altogether satisfactory, since the yield does not exceed 75%. Further reaction is prevented by the marked increase of viscosity or by the insolubility of the products as the degree of condensation increases. The degree of condensation obtained for compounds (LXIV, a–d) is therefore only 15–20.

By heating to a high temperature a compound

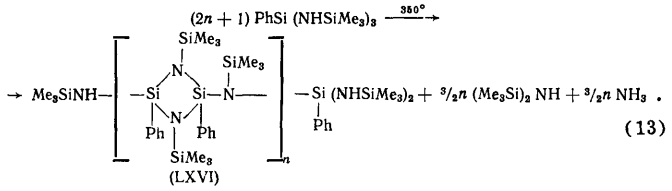


which is formed in its turn by heating a compound $R^4HNSiR^1.R^2NHR^4$ with a diamine $H_2NR^3NH_2$, one can obtain similarly the cyclodisilazane polymers (LXV), where R^1, R^2 = F, H, alkyl, alkenyl, alkynyl, cycloalkyl, or aryl [or R^1, R^2 = $-(CH_2)m-$] and R^3 = arylene or a bivalent polyarylene oxide, polyarylene sulphide, or polyarylene sulphone residue[90–95]:



Solid not unduly brittle polymers with a slightly yellowish colour have been obtained. They are insoluble in various organic solvents and in water even after prolonged boiling. Such polymers do not melt up to 600 °C.

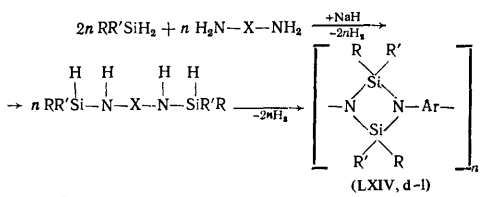
The thermal condensation of tris(trimethylsilylamino)phenylsilane leads to the formation of the oligomers (LXVI):[25]



(LXVI) (13)

2. Polycondensation of Aromatic and Aliphatic Diamines with Di- and Mono-organosilanes

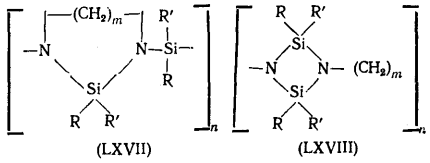
The polymers (LXIV, d–l) with a higher degree of polymerisation can be obtained by the catalytic silylation of primary aromatic diamines by di- and mono-organosilanes[59]:



(LXIV, d–l)

(LXIV, d–g); : R=R′=Ph; (LXIV, h–j); : R=H, R′=Ph;(LXIV, k and l): R= Me, R′=Ph . (14)

Reactions (14), catalysed by alkali metals or their hydrides, proceed very rapidly at 50–150 °C. Both polar (ether) and non-polar (benzene, xylene, etc.) solvents can be used. Only hydrogen is a side product of the reaction, the yield amounting to ~100%. The properties of the polymers (LXIV, d–l) are given in Table 11. α,ω-Polymethylenediamines condense with dihydro-organosilanes in the presence of catalysts (Na, K, NaH), forming polymers (LXVIII).[96] Fink[59] achieved the reactions of diphenylsilane with ethylenediamine, 1,3-diaminopropane, 1,4-diaminobutane, and 1,6-diaminohexane at 30° to 85 °C with quantitative conversions of the initial reactants. Whereas the rigidity of the benzene residue in aromatic 1,4-, 3,3′-, and 4,4′-diamines clearly determines the structure of the polymers (LXIV) formed by reaction (14), the flexibility of the methylene chain in aliphatic diamines permits in this instance the formation of two isomeric polymers:

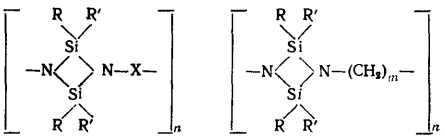


(LXVII) (LXVIII)

The polymethylene chain is either a component part of the ring as in formula (LXVII) or it links disilazane rings [see formula (LXVIII), Table 11].

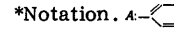
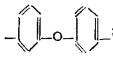
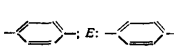
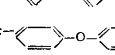
When the polymers (LXIV, a–l) are formed, they precipitate from the solution in the form of a light-coloured powder, which in most cases has a yellowish tint due to the charring of the amine. If the polycondensation is carried out in the melt, the polymers are obtained in a monolithic form with a very high viscosity. The polymers (LXVIII) are plastic and transparent. The solubility of the polymers (LXIV) in organic solvents is very low, with the exception of compounds (LXIVk) and (LXIVl); the polymers (LXVIII) readily dissolve in both aromatic and aliphatic solvents. The softening temperatures of some of the polymers (Table 11) lie above their decomposition temperatures, which can be explained by the reduced mobility and rigidity of the molecular chains[59].

Table 11. Cyclodisilazane polymers[59]



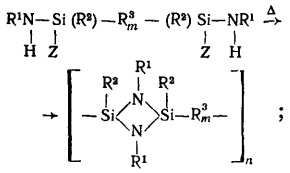
(LXIV, a–l), n=15–20 (LXVIII, a and b)

Compound	R	R′	X*	Softening temperature, °C	Structural unit
(LXIVa)	Me	Me	*A*	133	$C_{16}H_{20}N_2Si_2$
(LXIVb)	Me	Me	*B*	—	$C_{16}H_{20}N_2OSi_2$
(LXIVc)	Me	Me	*C*	—	$C_{22}H_{24}N_2O_2Si_2$
(LXIVd)	Ph	Ph	*A*	>315	$C_{36}H_{28}N_2Si_2$
(LXIVe)	Ph	Ph	*D*	>328	$C_{30}H_{24}N_2Si_2$
(LXIVf)	Ph	Ph	E	212	$C_{37}H_{30}N_2Si_2$
(LXIVg)	Ph	Ph	F	68	$C_{35}H_{28}N_2OSi_2$
(LXIVh)	H	Ph	D	>315	$C_{18}H_{16}N_2Si_2$
(LXIVi)	H	Ph	A	>315	$C_{24}H_{20}N_2Si_2$
(LXIVj)	H	Ph	E	>315	$C_{25}H_{22}N_2Si_2$
(LXIVk)	Me	Ph	A	117	$C_{26}H_{24}N_2Si_2$
(LXIVl)	Me	Ph	E	83	$C_{27}H_{26}N_2Si_2$
(LXVIIIa)	Ph	Ph	$-(CH_2)_4-$	61	$C_{28}H_{28}N_2Si_2$
(LXVIIIb)	Ph	Ph	$-(CH_2)_6-$	24	$C_{30}H_{32}N_2Si_2$

*Notation. *A*: ; *B*: ; *C*: ; *D*: ; *E*: ; *F*: .

The thermal stabilities of the polymers (LXIV) and (LXVIII) have been studied in very great detail[59]. The polymers (LXIV, d–g) decompose at 360–380 °C in an atmosphere of nitrogen. The aromatic residue linked to the ring nitrogen atom has only a very slight influence on the stability of the polymers. The decomposition temperature changes little also when the substituents at the silicon atom are varied [polymers (LXIV, a, d, i, and k)]. Whereas the temperature of the onset of the thermal decomposition of all the polymers investigated is independent of the nature of the organic framework around the silicon atom, the degree of weight loss depends markedly on the nature of the organic groups. Thus compounds (LXIV, f, i, and j) lose at 600 °C up to 30–35% of their initial mass and then do not decompose further. The thermal stability of compound (LXVIII) is low and depends markedly on the length of the methylene chain.

Thermostable cyclodisilazane polymers (LXIX) can be obtained by heating a tetrasubstituted aminodisilane:



(LXIX)

m = 0, 1, n > 10,

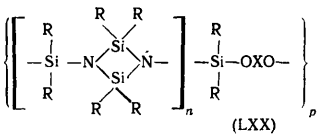
where *Z* is a primary amine residue, R^1 = alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, arylalkyl, alkylaryl, alkenylaryl, alkynylaryl, or aryl, R^2 represents the same

groups or OR^1, and R^3 = alkylene, alkenylene, alkynylene, arylalkynylene, biarylene, etc.[97-101]

Such polymers are pale-yellow resins, which melt at ~350 °C and are insoluble in the usual organic solvents and water.

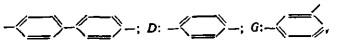
The polymers (LXX) ($p > 10$) (Table 12) are obtained by the polycondensation of cyclodisilazanes containing functional groups with bisphenols or bifunctional silanols. The α,ω-bis-(amino or chloro)silylcyclodisilazanes have been used as cyclodisilazanes with functional groups. The polycondensation is usually carried out in boiling xylene and the yield is 95–100% (calculated from the amount of amine evolved)[59,63,76,80,84-86,96-111].

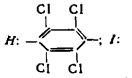
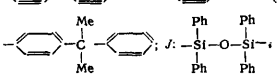
Table 12. Cyclodisilazane polymers[59]

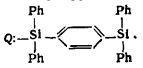


(LXX)

Compound	n	R	X*	Softening temperature, °C	Structural unit
(LXXa)	1	Me	*A*	330	$C_{20}H_{32}N_2O_2Si_4$
(LXXb)	2	Me	*A*	99	$C_{26}H_{50}N_4O_2Si_7$
(LXXc)	3	Me	*A*	127	$C_{32}H_{68}N_6O_2Si_4$
(LXXd)	4	Me	*A*	119	$C_{38}H_{86}N_8O_2Si_{13}$
(LXXe)	1	Me	*D*	90	$C_{14}H_{28}N_2O_2Si_4$
(LXXf)	1	Me	*G*	—	$C_{14}H_{28}N_2O_2Si_4$
(LXXg)	1	Me	*H*	238	$C_{14}H_{24}Cl_4N_2O_2Si_4$
(LXXh)	1	Me	*I*	145	$C_{23}H_{38}N_2O_2Si_4$
(LXXi)	1	Me	*J*	—	$C_{32}H_{44}N_2O_2Si_6$
(LXXj)	1	Ph	*A*	324	$C_{60}H_{48}N_2O_2Si_4$
(LXXk)	1	Ph	*Q*	101	$C_{78}H_{64}N_2O_2Si_6$

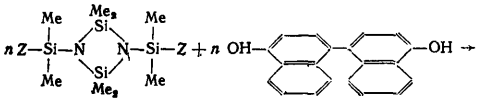
*Notation: *A*: ; *D*: ; *G*: ;

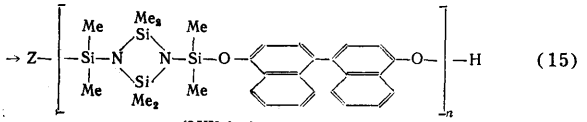
H: ; *I*: ; *J*: ;



The polymers (LXX, a–d) are white or yellowish elastic products; the softening temperatures of the polymers with an even number of cyclodisilazane units in the chain are lower than those of the polymers with an odd number of units. Their plasticity as well as their solubility in aromatic solvents increase with n. On passing from *p*-cresol and *m*-cresol to 2,2-bis(4-hydroxyphenyl)propane, the polymers (LXX, f–h) become more elastic. When the cyclodisilazanes are fully phenylated, the polymers (LXX, j and k) consist of white brittle compounds with an extremely low solubility in the usual organic solvents. The polymers (LXX, a, e, and f) are able to swell in hexane and benzene.

An interesting group of polymers (LXX, l–o) have been obtained by the low-temperature (up to 150 °C) and high-temperature (150–200 °C) condensation of cyclodisilazane monomers containing functional groups with 4,4'-dihydroxy-1,1'-binaphthyl:[112]





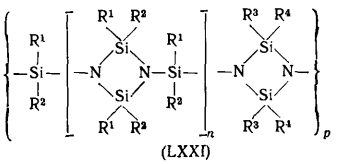
(15)

(LXX, l–o)

Z = Cl or NY; Y = H_2, Me_2, or HPh.

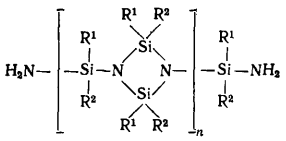
The polymers (LXX, l–o) have a molecular weight of the order of thousands, are thermally stable up to ~500 °C, are readily soluble in benzene or ethyl methyl ketone, and do not decompose on treatment with methanol, which indicates an increase of the stability of the cyclodisilazane ring in a macromolecular chain of this type[112].

Polymers containing the fully methylated cyclodisilazane are as a rule stable on heating to 430–440 °C in nitrogen. At this temperature the polymers begin to decompose slowly: rapid decomposition takes place at 510–560 °C. The stability of such polymers is not influenced either by the nature of the groups -OXO-, linking the silazane rings, or by the increase of the fraction of silazane rings in the polymers resulting from the incorporation of oligomeric cyclodisilazanes. In the case of the fully phenylated polymers (LXX, j and k) the decomposition does not begin until 500 °C, which is the absolute maximum for polymers with Si–N bonds.

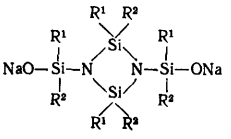


(LXXI)

The polymers (LXXI) are obtained by the interaction of α,ω-bisaminosilylated cyclodisilazanes



with the hydrosilanes $R^3R^4SiH_2$ (R^1, R^2, R^3, R^4 = H, F, a hydrocarbon group, or R^1R^2 and R^3R^4 = polymethylene group; n = 1–10) (molar ratio 2 : 1) in the presence of alkali and alkaline earth metals or their hydrides as catalysts[105,113-118], or by the condensation of the disodium or dilithium salts of 1,3-bis(diorganosilyl)cyclodisilazanes

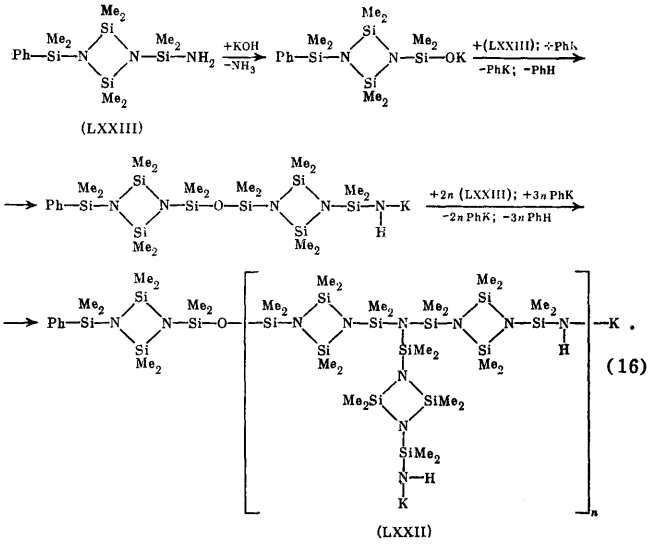


with dichlorodiorganosilanes $R^3R^4SiCl_2$ (with α,ω-dichlorodiorganosiloxanes) at 30–50 °C.[84,85,104,109,119,120]

The polymers (LXXI) are light-coloured brittle resins with softening temperatures in the range 80–100 °C. All the polymers (LXXI) obtained are thermally stable up to 450 °C.

The cyclodisilazane polymer (LXXII) with a branched structure has been obtained by the condensation of the monofunctional cyclodisilazane monomer (LXXIII) in the presence of KOH as the catalyst and without a solvent at 150–450 °C

in air or in an atmosphere of nitrogen at atmospheric pressure or *in vacuo*[112]:



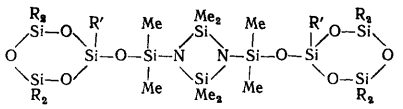
(LXXIII)

(LXXII)

(16)

The reaction is catalysed by potassium hydroxide introduced initially into the reaction and (as suggested by Deyak et al.[112]), by the phenylpotassium and potassium silanoxide formed in the reaction, each catalyst playing a specific role at different stages of reaction (16). A polymer of this type is readily soluble and exhibits a fairly high thermal stability (up to ~500 °C).

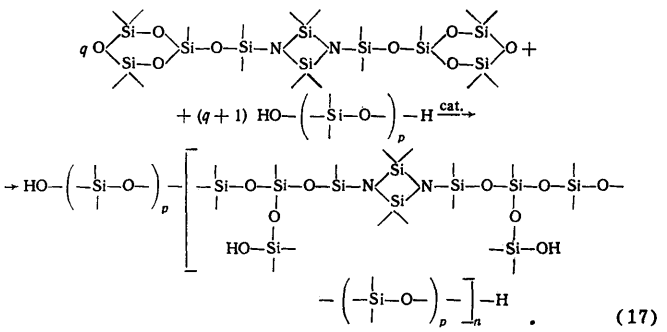
Anionic copolymerisation of cyclodisilazanes (LXXIV) [86]



(LXXIV)

R=R'=Me; R=Me, R'=Ph; R=Ph, R'=Me,

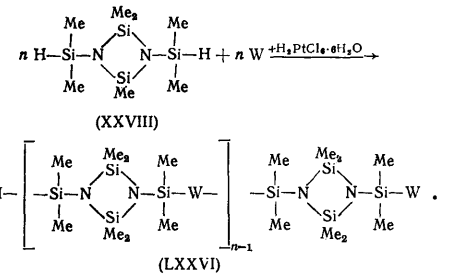
and α,ω-dihydroxypolydimethylsiloxanes also yielded branched cyclodisilazane polymers (LXXV).[121,122] The reaction is carried out in the presence of a catalytic amount of the diammonium or dipotassium salt of polydimethylsiloxanediol at 60–80 °C or at 140 °C respectively. The copolymerisation is based on the fact that the proton of the hydroxy-group exchanges for the catalyst cation, as a result of which the active centres are transferred from the catalyst to the organosilicon diol, which acquires the ability to interact with the cyclodisilazane (LXXIV), opening the siloxane rings in the latter and forming a polymer[121]:



(17)

A soluble polymer is formed in the initial stage of reaction (17) and then passes to a structured state (a three-dimensional network) with a high content of the insoluble product. Thermo-oxidative degradation of the polymers (LXXV) showed that the main decomposition reaction of these polymers proceeds in the range 400–450 °C.[121]

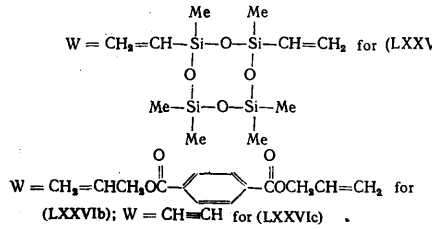
An interesting group of polymers (LXXVI) have been obtained by the reaction involving the polyaddition of 1,3-bis(dimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane to unsaturated organosilicon and organic compounds in the presence of chloroplatinic acid and rhodium compounds[123]:



(XXVIII)

(LXXVI)

The polymer (LXXVIa), with an intrinsic viscosity $\eta = 0.28$, is formed in the course of 3.5 h after the introduction of $H_2PtCl_2.6H_2O$ (1.5×10^{-5} M), in the form of a 0.1 M solution in tetrahydrofuran, into the equimolar mixture and on heating the reaction mixture to 170 °C. The reaction with diallyl isophthalate, leading to the formation of the polymeric product (LXXVIb), takes place under the same conditions in the course of 20–25 min up to a conversion of 98% when 1×10^{-4} M $H_2PtCl_6.H_2O$ is introduced into the equimolar mixture ($\eta = 0.41$ dl g^{-1}) or after 15–20 s up to a conversion of 100% in the presence of acetylacetonatorhodium dicarbonyl and rhodium carbonyl at concentrations of the rhodium compounds changing from 1×10^{-4} to 1×10^{-5} M, but under these conditions $\eta \leq 0.2$ dl g^{-1}. 1,3-Bis(dimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane (XXVIII) reacts with acetylene at the normal pressure in an acetylene atmosphere at 170 °C and an $H_2PtCl_6.6H_2O$ concentration of 5×10^{-4} M. This results in the formation after 6 h of a viscous product (LXXVIc) (after reprecipitation from toluene, its yield is 90%), which sets on cooling and has a glass point of 153 °C.



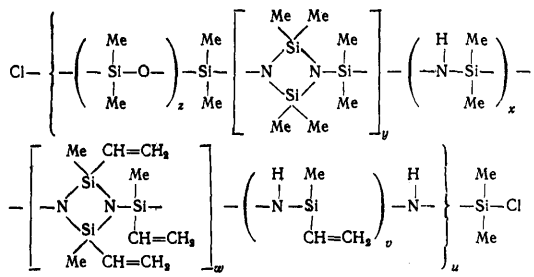
(LXXVIb); W = CH≡CH for (LXXVIc).

From the results obtained by Andrianov et al.[123], one may claim that 1,3-bis(dimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane is highly reactive, but apparently one of the most important conditions for the polyaddition reaction is the occurrence of the stage involving the formation of an intermediate in the presence of catalysts. This has been confirmed by the study of the dependence of the induction period on the reaction temperature and catalyst concentration[123]. A change in process conditions and of the catalyst concentration does not then influence significantly the rate of reaction.

The thermo-oxidative degradation of the synthetic polymers (LXXVI, a–c) has been investigated on a DO-102 derivatograph in air in the range from 20° to 800 °C at a heating rate

of 5 K min^{-1}. Comparison of the results of the thermogravimetric analysis (TGA) for the polymers (LXXVI, a–c) shows that the resistance of the carbo-organosilazane polymers (LXXVI, b and c) to degradation is lower than that of the polymer (LXXVIa) with alternating cyclodisilazane and cyclosiloxane fragments. Thus a weight loss of only 10% is observed at 350 °C for the polymers (LXXVI, b and c), while the same weight loss by the polymer (LXXVIa) is reached at 480 °C. The results of differential thermographic analysis (DTA) also indicate an increase of the resistance of the polymers to thermo-oxidative degradation after the introduction of cyclodisilazane fragments into the polymer chain. Thus the maximum rate of decomposition of polymer (LXXVIa) occurs at 570 °C.

The organosilazoxane polymers (LXXVII), containing cyclodisilazane and linear silazane fragments with terminal chlorosilyl groups, have been obtained by the thermal condensation of organocyclotrisilazanes with α,ω-dichlorodiorganosiloxanes [124,125]:

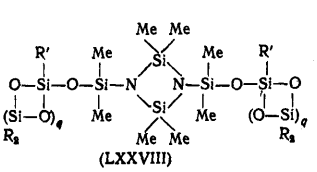


$z = 1-4$; $y = 1.8-2.5$; $x = 0.5-2.6$; $w = v = 0-0.2$; $u = 0-2$.

The authors[124,125] showed that the degree of reaction increases with increasing temperature and with enhancement of the electron-accepting properties of the substituents at the silicon atoms in the organocyclosilazane and also that the reactivity of α,ω-dichlorodiorganosiloxanes is almost independent of chain length. However, in the study of this reaction a complete transformation of the secondary nitrogen atoms in the cyclotrisilazane into the tertiary nitrogen atoms of the cyclodisilazane could not be achieved, so that the final reaction products contained the linear silazane fragments ≡Si–NH–Si≡. The course of the reaction was followed in all cases from the change in the content of the NH groups in the reaction mixture. The polymers obtained by the thermal condensation of 1,3,5-trimethyl-1,3,5-trivinylcyclotrisilazane with α,ω-dichlorodiorganosiloxanes became subsequently structured, which may be accounted for by the partial polymerisation of the vinyl groups and the formation of a branched structure.

In order to eliminate low-molecular-weight products, the compounds (LXXVII, a–h) synthesised were evacuated to 5 mmHg at 200 °C, after which the content of active hydrogen was determined. The polymers (LXXVII, a–h) were identified from ^{1}H NMR and infrared spectroscopic data.

Polymers have been obtained[126] by the anionic polymerisation of tricyclic compounds (LXXVIII), whose molecules consist of two siloxane and one disilazane rings:



(LXXVIII)

$R = R' = Me$, $q = 2.3$; $R = Me$, $R' = Ph$, $q = 2$; $R = Ph$, $R' = Me$, $q = 2$.

The reaction takes place in the presence of the diammonium or dipotassium salts of polydimethylsiloxanediols at different temperatures in solution, in bulk, or in the solid state. The ratio of the soluble and insoluble fractions of the product then depends on the molecular structure of the initial compound (LXXVIII) and on its concentration.

Polymers with a branched macromolecular structure have been obtained[127,128] by the analogous reaction of 1,3-bis-(hydroxydimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane (XXXVI) with hexamethylcyclotrisiloxane or octamethylcyclotetrasiloxane in the presence of tetramethylammonium siloxanedioxide with different initial reactant ratios. In both cases intramolecular rearrangements involving the expansion of both the disilazane and siloxane rings take place. This has been demonstrated by means of ^{1}H NMR spectra, in which a new peak due to methyl protons appears in a higher field than the peak of the methyl protons of the cyclodisilazane fragment; this new peak refers to the methyl protons in the trisilylamino-group of the expanded ring or the branched molecule[126]. The infrared spectra of such polymers were found to contain absorption bands in the range 930–950 cm^{-1}, characteristic of the Si–N bond and absent from the spectra of organocyclodisilazane compounds, as well as bands in the region of 1165, 1180, 3385, and 3420 cm^{-1}, characterising the deformation vibrations of the NH group and the stretching vibrations of the =N–H bond in the ≡Si–NH–Si≡ group[128].

The influence of the cyclodisilazane fragments on the hydrodynamic, conformational, and thermomechanical characteristics of polyorganosilazosiloxanes has been studied in relation to the products of the copolymerisation of 1,3-bis-(hydroxydimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane and hexamethylcyclotrisiloxane or octamethylcyclotetrasiloxane introduced into the reaction mixture in molar proportions of 1 : 25, 1 : 50, 1 : 75, and 1 : 100.[127,128] The authors expected that the introduction of the cyclodisilazane fragments into the polydimethylsiloxane chain should influence the flexibility of the macromolecular chain and ultimately the mechanical properties of the polyorganosilazosiloxanes.

In order to determine the hydrodynamic, conformational, and molecular parameters, all the polymers were fractionated in the benzene–dioxan system. The molecular weights were measured in CCl_4 on a Sofica photogoniodiffusometer (the refractive index increment $dn/dc = 0.05$; 25 °C; wavelength $\lambda = 5460$ Å). The intrinsic viscosities were measured in toluene at 25 °C and in ethyl methyl ketone at 20 °C. The Mark–Kuhn–Houwink equations for the first two polyorganosilazosiloxanes (molar ratios 1 : 25 and 1 : 50) $[\eta] = 2.04 \times 10^{-5} M^{0.86}$ and $[\eta] = 1.09 \times 10^{-5} M^{0.92}$ are close to the analogous equation for polydimethylsiloxane $[\eta] = 1.10 \times 10^{-5} M^{0.92}$ in toluene at 25 °C, while at 20 °C in ethyl methyl ketone the equation is $[\eta] = 9.99 \times 10^{-4} M^{0.49}$ for the second polyorganosilazosiloxane (1 : 50) and $[\eta] = 8.90 \times 10^{-4} M^{0.50}$ for polydimethylsiloxane.

Calculation of the unperturbed molecular sizes from the Fixman–Stockmayer equation (which makes it possible to eliminate the effect of long range action) yielded a value of K_θ for the second polyorganosilazosiloxane (1 : 50) in agreement with K_θ for polydimethylsiloxane[127]. The conformational parameters obtained indicate a virtually complete agreement between the flexibility parameters of polyorganosilazosiloxanes and polydimethylsiloxane. The authors[127] adopted the following geometrical parameters for the calculation of the conformational parameters: Si–N and Si–O bond lengths 1.73 and 1.65 Å respectively and 90° angles in the disilazane ring. Consequently the flexibility of the polyorganosilazosiloxanes obtained is close to that of polydimethylsiloxane and the chosen ratios of the cyclodisilazane and dimethylsiloxane

fragments do not have a significant influence on the properties of the polymers. An estimate of the hydrodynamic and conformational parameters of polydimethylsilazosiloxanes from data concerning their behaviour in dilute solution showed that their macromolecules have a predominantly linear structure[128]. For ratios of 1 : 25 and 1 : 50, a unimodal distribution was observed both on molecular weight distribution curves obtained by fractionation and on curves obtained by gel chromatography. This shows that the polymer specimens contained macromolecules of the same type. For ratios of 1 : 75 and 1 : 100, a bimodal distribution was observed on the molecular weight distribution curves, which is undoubtedly due to the formation of two types of macromolecule—with linear and branched structures.

V. APPLICATIONS OF ORGANOCYCLODISILAZANES

Comparative tests on the thermal stabilities of a series of cyclic and linear silazanes and silylamines showed that only four-membered cyclodisilazane compounds are stable at ~500 °C.[129] Furthermore, organocyclodisilazanes exhibit effective separating properties and a high solubility in organic solvents. The physical properties of cyclodisilazane polymers vary as a function of the nature of the substituents: certain polymers exhibit a high elasticity, others are elastic and rubber-like, those of a third kind are transparent, and polymers of the fourth kind are characterised by effective antiadhesion properties which facilitate the removal of castings from moulds. Cyclodisilazane polymers may find the same applications in many branches of industry as siloxanes and may prove to be actually more effective[109,130–134].

The vast majority of studies on organocyclodisilazane compounds have been published in the form of patents. A considerable proportion of the information contained in the latter is extremely indefinite although optimistic; a number of valuable properties characteristic of these compounds have been described.

The heat and frost resistance, effective dielectric properties, the absence of adhesion, and the exceptional resistance to atmospheric conditions made it possible to use organocyclodisilazanes in the manufacture of insulating materials for electric cables employed in important branches of industry such as aeroplane construction and automobile, electrotechnical, and chemical industries.

Materials based on organocyclodisilazanes possess a unique combination of properties such as flexibility at a low temperature, thermal stability, and resistance to hot engine oil. This results not only in an improvement of operating characteristics but also in an increased reliability of many components used in aeroplane, bus, and automobile engines (seals, cooling hose, washers, etc.).

The possibility of using organocyclodisilazanes as coatings for paper is of interest. A fairly large amount of such paper is necessary in the processing and packing of a wide variety of sticky materials such as untreated raw rubber or confectionery with a high sugar content; however, the most important application involves the preparation of backs of labels, decorative coatings, etc.

Further possible applications of organocyclodisilazanes should be noted: (1) as high-temperature liquid heat exchangers[64,135–143]; (2) as lubricants and as additives to lubricating oils[64,137,138]; (3) as thermostable film-forming coatings[99 101,105,115,116]; (4) as adhesion-improving coatings[117]; (5) as impregnating compounds for fabrics imparting thermal stability[99,105]; (6) as impregnating compounds imparting thermal stability to other materials[101,113,115,116]; (7) as components of fibre-forming materials imparting thermal stability to the latter[101,113,115,116]; (8) as reagents for the improvement of the properties of paper and mica[99,113]; (9) as auxiliary materials in the leather industry[113]; (10) as casting resins[90]; (11) as dyes resistant to heat and atmospheric conditions[99,101,105,113,115,116]; (12) in the manufacture of plastics[69,91,101,113,115,116].

In certain reports the use of organocyclodisilazanes as stabilising, structure-forming, and covulcanising agents has been mentioned. Apart from the possible applications of organocyclodisilazanes described above, isolated claims have been made in the patent literature concerning the good prospects for their application in other fields.

---o0o---

During the preparation of the review for the press, a number of studies on organocyclodisilazanes were published.

It has been shown[144] that 1,3,2,2,4,4-hexaphenylcyclodisilazane forms monoclinic crystals with the lattice parameters $a = 10.471(2)$ Å, $b = 15.487(3)$ Å, and $c = 19.996(6)$ Å; $\beta = 108.06°$, $V = 3082.9(2.6)$ Å^3, $D_x = 1.178$, $Z = 4$, space group $C2/c$. The crystallographic twofold axis passes through the centre of the cyclodisilazane ring. The four-membered cyclodisilazane ring is not entirely flat: the dihedral angle, whose axis passes between two endocyclic Si atoms, is 1.2°. The *N*-phenyl fragments are almost coplanar with the plane of the cyclodisilazane ring (the dihedral angle between one of the halves of the cyclodisilazane ring and the phenyl group is 3.5°), demonstrating in its turn a characteristic feature of *N*-phenylcyclodisilazane derivatives, which consists in a favourable partial overlap of the π-electron system of the phenyl group with the unshared pair of *p* electrons of the nitrogen atom.

The crystal and molecular structures of 1,3-bis(chlorodimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane have been examined in detail[145]. The principal structural parameters of the molecule agree satisfactorily with previous values.

The ^{1}H NMR, NMR, and infrared spectra of monomeric organocyclodisilazanes incorporating various groups (Me, Et, CH_2=CH, iso-Pr, F, Cl) have been published[146–150].

Reactions involving the hydride addition of 1,3-bis(dimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane to pentamethylvinylcyclotrisiloxane and heptamethylvinylcyclotetrasiloxane in the presence of chloroplatinic acid (0.1 M solution of $H_2PtCl_6 \cdot 6H_2O$ in tetrahydrofuran; 0.5×10^{-5} g-atom Pt per litre of mixture) have been investigated[151] and mono- and di-addition products have been isolated.

The α,ω-bis(chlorodimethylsilyl)cyclodisilazane oligomers containing between 2 and 5 cyclodisilazane fragments in the molecular chain have been formed by the reaction of equimolar amounts of hexamethylcyclotrisilazane and dichlorodimethylsilane and characterised[152]. The hydrolysis of these oligomers[153] and the hydrolysis of oligomers containing the cyclosiloxane ring in addition to the cyclodisilazane fragment[154] have been investigated.

Oligomers with different lengths of the molecular chain have been obtained by the thermal condensation of tetrakis(trimethylsilylamino)silane[155], or 1,3-bis(hydroxydimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane[156], or 1,3-bis(aminodimethylsilyl)-2,2,4,4-tetramethylcyclodisilazane[156], or α,ω-dichlorodiorganosiloxanes with organocyclodisilazanes[157]. An interesting group of oligomers have been obtained as a result of the anionic polymerisation of oligo-organocyclodisilazanes incorporating siloxane rings in the presence of the diammonium or dipotassium salts of polydimethylsiloxanediols[158] and also via the interaction of oligoamino-organocyclodisilazanes, dimethylsiloxane, diphenylsiloxane, and butadiene oligomers containing terminal hydroxy-groups[159].

The ammonolysis and aminolysis of chlorine-containing organocyclodisilazanes, which leads to monomeric and dimeric reaction products with amino-groups, have been studied in detail[160,161]. The composition and structure of the ammonolysis products are significantly influenced by the nature of the solvent employed and of the groups attached to the silicon atom.

It has been established that the interaction of methylcyclodisilazanes with anhydrous hydrogen chloride proceeds with dissociation of endocyclic Si–N bonds and the opening of the cyclodisilazane ring, while the interaction of phenylcyclodisilazanes takes place only via the functional groups with retention of the cyclodisilazane structure[162].

In the study of the alcoholysis and acidolysis of 1,3-bis(diorganosilyl)tetraorganocyclodisilazanes it was found that the mode and rate of these reactions are influenced significantly by the electronic nature of the organic and functional groups attached to the silicon atoms and also by the ratio of the initial reactants[163,164].

REFERENCES

1. Yu.M.Varezhkin, D.Ya.Zhinkin, and M.M.Morgunova, "Sintez i Primenenie Polimerov Tsiklodisilazanovoi Struktury" (The Synthesis and Applications of Polymers with the Cyclodisilazane Structure), Izd. NIITEKhIM, Moscow, 1977.
2. W.Fink, Angew.Chem., 1966, **78**, 803; Angew.Chem., Int.Ed., 1966, **5**, 760.
3. U.Wannagat, Pure Appl.Chem., 1966, **13**, 263.
4. P.J.Wheatley, J.Chem.Soc., 1962, 1721.
5. M.Yokoi and K.Yamasaki, J.Amer.Chem.Soc., 1953, **75**, 4139.
6. M.Yokoi, Bull.Chem.Soc.Japan, 1957, **30**, 100; Chem. Abs., 1957, **51**, 13 485.
7. L.E.Sutton, "Tables of Interatomic Distances and Configuration in Molecules and Ions", Chem.Soc.Special. Publ., 1958, No.11; Supplement, 1956–1959, Chem. Soc.Special.Publ., 1965, No.18.
8. H.Schmidbauer, J.Amer.Chem.Soc., 1963, **85**, 2336.
9. E.Murrill and L.E.Breed, Inorg.Chem., 1971, **10**, 641.
10. L.Parkanyi, G.Y.Argay, P.Hencsei, and J.Nagy, J.Organometal.Chem., 1976, **116**, 299.
11. G.S.Smith and L.E.Alexander, Acta Cryst., 1963, **16**, 1015.
12. A.G.Robiette, G.M.Sheldrick, and W.S.Sheldrick, J.Mol.Struct., 1970, **5**, 423.
13. A.M.Liquori and A.Vaciago, Gazzetta, 1956, **86**, 769.
14. G.Chioccola and J.J.Daly, J.Chem.Soc.A, 1968, 1658.
15. G.W.Adamson and J.J.Daly, J.Chem.Soc.A, 1970, 2724.
16. V.E.Shklover, P.Ad'yaasuren, Yu.T.Struchkov, E.A.Zhdanova, V.S.Svistunov, G.V.Kotrelev, and K.A.Andrianov, Dokl.Akad.Nauk SSSR, 1978, **241**, 377.
17. A.I.Gusev, S.N.Gurkova, N.V.Alekseev, Yu.M.Varezhkin, M.M.Morgunova, and D.Ya.Zhinkin, "I Vsesoyuznoe Simpozium 'Stroenie i Reaktsionnaya Sposobnost' Kremniiorganicheskikh Soedinenii'" (The Ist All-Union Symposium on the "Structure and Reactivity of Organosilicon Compounds"), Irkutsk, 1977, p.54.
18. A.I.Gusev, S.N.Gurkova, and N.V.Alekseev, "II Vsesoyuznoe Soveshchanie po Organicheskoi Kristallokhimii i Sessiya Sektsii kristallokhimii po Probleme 'Sovremennoe Sostoyanie Bioorganicheskoi Kristallokhimii'" (The IInd All-Union Conference on Organic Crystal Chemistry and Session of the Crystal Chemistry Section on the Problem of "The Present State of Bio-organic Crystal Chemistry"), Zvenigorod (Chernogolovka), 1978, p.81.
19. S.N.Gurkova, A.I.Gusev, N.V.Alekseev, Yu.M.Varezhkin, M.M.Morgunova, and D.Ya.Zhinkin, Zhur.Strukt.Khim., 1978, **19**, 182.
20. N.G.Bokii and Yu.T.Struchkov, Zhur.Strukt.Khim., 1968, **9**, 722.
21. G.Kannengiesser, F.Damm, A.Deluzarche, and A.Maillar, Bull.Soc.chim.France, 1969, 894.
22. W.Fink, Helv.Chim.Acta, 1969, **52**, 2261.
23. W.Wolfsberger and H.Schmidbaur, J.Organometal. Chem., 1971, **28**, 301.
24. K.Lienhard and E.G.Rochow, Z.anorg.Chem., 1964, **331**, 316.
25. K.A.Andrianov, G.V.Kotrelev, V.V.Kozakova, and I.E.Rogov, Izv.Akad.Nauk SSSR, Ser.Khim., 1975, 2600.
26. L.W.Breed and R.L.Elliott, J.Organometal.Chem., 1968, **11**, 447.
27. L.W.Breed, W.L.Budde, and R.L.Elliott, J.Organometal.Chem., 1966, **6**, 676.
28. L.W.Breed, R.L.Elliott, and J.C.Wiley, J.Organometal. Chem., 1971, **31**, 179.
29. P.Geymayer and E.G.Rochow, Sci.Foundation Grant NSF-GP-2007, 1965, 44.
30. H.Bürger, R.Mellies, and K.Wiegel, J.Organometal. Chem., 1977, **142**, 55.
31. U.Klingebiel, J.Neemann, and A.Meller, Z.anorg. Chem., 1977, **429**, 63.
32. M.Schlingmann and U.Wannagat, Z.anorg.Chem., 1977, **429**, 74.
33. K.A.Andrianov and N.V.Delazari, Izv.Akad.Nauk SSSR, Ser.Khim., 1972, 2748.
34. R.P.Bush, N.C.Lloyd, and C.A.Pearce, J.Chem.Soc. A, 1970, 1587.
35. V.P.Anosov, Yu.A.Pentin, L.V.Khristenko, Yu.M.Varezhkin, D.Ya.Zhinkin, and M.M.Morgunova, "I Vsesoyuznoe Simpozium 'Stroenie i Reaktsionnaya Sposobnost' Kremniiorganicheskikh Soedinenii'" (The Ist All-Union Symposium on the "Structure and Reactivity of Organosilicon Compounds"), Irkutsk, 1977, p.26.
36. V.P.Anosov, Vestnik Moskov.Gos.Univ., 1978, Ser.2, Khim., **19**, 614.
37. V.P.Anosov, Yu.A.Pentin, L.V.Khristenko, M.M.Morgunova, Yu.M.Varezhkin, and D.Ya.Zhinkin, Vestnik Moskov.Gos.Univ., 1978, **19**, 668.
38. V.P.Anosov, Yu.A.Pentin, L.V.Khristenko, Yu.M.Varezhkin, M.M.Morgunova, and D.Ya.Zhinkin, "I Vsesoyuznoe Simpozium 'Stroenie i Reaktsionnaya Sposobnost' Kremniiorganicheskikh Soedinenii'" (The Ist All-Union Symposium on the "Structure and Reactivity of Organosilicon Compounds"), Irkutsk, 1977, p.24.
39. Yu.M.Varezhkin, D.Ya.Zhinkin, M.M.Morgunova, and V.P.Anosov, Zhur.Obshch.Khim., 1977, **47**, 2089.
40. C.Lageot and J.C.Maire, J.Organometal.Chem., 1972, **37**, 239.
41. D.Enterling, U.Klingebiel, and A.Meller, Z.Naturforsch., 1978, **33b**, 527.
42. H.Roesky, M.Diehl, and M.Banek, Chem.Ber., 1978, **111**, 1503.

43. U.Klingebiel and A.Meller, Z.Naturforsch., 1977, **32b**, 537.
44. T.Kitazume and J.M.Shreeve, Inorg.Chem., 1977, **16**, 2040.
45. U.Klingebiel and H.Hluchy, and A.Meller, Chem.Ber., 1978, **111**, 906.
46. U.Klingebiel and A.Meller, Z.anorg.Chem., 1977, **428**, 27.
47. U.Klingebiel, J.Organometal.Chem., 1978, **152**, 33.
48. W.Wolfsberger. Z.Naturforsch., 1977, **32b**, 961.
49. U.Klingebiel, Chem.Ber., 1978, **111**, 2735.
50. G.W.Smith, J.Chem.Phys., 1971, **54**, 174.
51. K.A.Andrianov, V.M.Kopylov, A.I.Chernyshev, M.I.Shkol'nik, D.Ya.Zhinkin, V.V.Yastrebov, and Zh.S.Syrtsova, "I Vsesoyuznoe Simpozium 'Stroenie i Reaktsionnaya Sposobnost' Kremniiorganicheskikh Soedinenii'" (The Ist All-Union Symposium on the "Structure and Reactivity of Organosilicon Compounds"), Irkutsk, 1977, p.19.
52. K.A.Andrianov, A.I.Chernyshev, D.Ya.Zhinkin, V.V.Yastrebov, V.M.Kopylov, M.I.Shkol'nik, and Zh.S.Syrtsova, Zhur.Obshch.Khim., 1977, **47**, 2060.
53. D.W.Klein and J.W.Connolly, J.Organometal.Chem., 1971, **33**, 311.
54. E.A.Kirichenko, A.I.Ermakov, and I.N.Samsonova, Zhur.Fiz.Khim., 1977, **51**, 2506 [Russ.J.Phys.Chem., 1977(10)].
55. E.A.Kirichenko and A.I.Ermakov, Zhur.Fiz.Khim., 1976, **50**, 2381 [Russ.J.Phys.Chem., 1976(9)].
56. BRD P.1 291 338 (1969); Auszüge Patentanmeld., 1969, **15**(13), 885.
57. K.Lienhard and E.G.Rochow, Angew.Chem., 1965, **75**, 638.
58. W.Fink, Helv.Chim.Acta, 1969, **52**, 1841.
59. W.Fink, Helv.Chim.Acta, 1968, **51**, 954.
60. W.Fink, Helv.Chim.Acta, 1968, **51**, 1743.
61. W.Fink, Helv.Chim.Acta, 1968, **51**, 1011.
62. U.Wannagat, E.Bogusch, and P.Geymayer, Monatsh., 1971, **102**, 1825.
63. L.W.Breed, R.L.Elliott, and J.C.Wiley, J.Organometal. Chem., 1970, **24**, 315.
64. B.P.1 203 621 (1970); Chem.Abs., 1970, **71**, 50 203.
65. K.A.Andrianov, V.M.Kopylov, L.M.Khananashvili, and T.V.Nesterova, Dokl.Akad.Nauk SSSR, 1967, **176**, 85.
66. K.A.Andrianov, M.I.Shkol'nik, V.M.Kopylov, and P.L.Prikhod'ko, Dokl.Akad.Nauk SSSR, 1976, **227**, 352.
67. K.A.Andrianov, Zh.S.Syrtsova, V.M.Kopylov, and T.Augustiniene, Khim.Geterotsikl.Soed., 1972, 751.
68. K.A.Andrianov, Zh.S.Syrtsova, V.M.Kopylov, and T.Augustiniene, Symposium, "Khimiya i Khimicheskaya Tekhnologiya" (Chemistry and Chemical Engineering), Izd.MITKhT im.Lomonosova, Moscow, 1972, p.234.
69. K.A.Andrianov, M.I.Shkol'nik, Zh.S.Syrtsova, K.I.Petrov, V.M.Kopylov, M.G.Zaitseva, and E.N.Koroleva, Dokl.Akad.Nauk SSSR, 1975, **223**, 347.
70. L.W.Breed and J.C.Wiley, Inorg.Chem., 1972, 11, 1634.
71. W.Fink, Angew.Chem., 1969, **81**, 499.
72. B.P.1 265 001 (1972); Chem.Abs., 1972, **76**, 141 013.
73. US P.3 518 290 (1970); Chem.Abs., 1970, **73**, 67 339.
74. US P.3 575 922 (1971); Chem.Abs., 1971, **75**, 64 645.
75. US P.3 580 941 (1971); Chem.Abs., 1971, **75**, 140 370.
76. BRD P.1 955 906 (1971); Chem.Abs., 1971, **75**, 64 633.
77. Yu.M.Varezhkin, D.Ya.Zhinkin, M.M.Morgunova, and V.N.Bocharev, Zhur.Obshch.Khim., 1975, **45**, 2455.
78. Yu.M.Varezhkin, D.Ya.Zhinkin, M.M.Morgunova, and V.N.Bochkarev, "IV Mezhdunarodnyi Simpozium po Khimii Kremniiorganicheskikh Soedinenii" (The IVth International Symposium on the Chemistry of Organosilicon Compounds), Moscow, 1975, Vol.1, Part 2, No.144, p.28.
79. A.I.Gusev, M.G.Los', Yu.M.Varezhkin, M.M.Morgunova, and D.Ya.Zhinkin, Zhur.Strukt.Khim., 1976, **17**, 378.
80. W.Fink, Helv.Chim.Acta, 1969, **52**, 1833.
81. V.N.Bochkarev, A.A.Bernadskii, Yu.M.Varezhkin, M.M.Morgunova, and D.Ya.Zhinkin, Symposium, "Khimiya Elementorganicheskikh Soedinenii" (The Chemistry of Organoelemental Compounds), Izd.Nauka, Leningrad, 1976, p.31.
82. Yu.M.Varezhkin, M.M.Morgunova, and D.Ya.Zhinkin, Zhur.Obshch.Khim., 1971, **47**, 1536.
83. M.G.Voronkov, Yu.M.Varezhkin, D.Ya.Zhinkin, M.M.Morgunova, S.N.Gurkova, A.I.Gusev, and N.V.Alekseev, Dokl.Akad.Nauk SSSR, 1977, **237**, 102.
84. BRD P.1 813 553 (1969); Chem.Abs., 1969, **71**, 124 642.
85. BRD P.1 813 171 (1969); Chem.Abs., 1969, **71**, 102 005.
86. K.A.Andrianov, G.V.Kotrelev, E.A.Zhdanova, T.V.Strelkova, and N.I.Pankov, Dokl.Akad.Nauk SSSR, 1977, **233**, 349.
87. U.Wannagat, R.Braun, and L.Gerschler, Z.anorg. Chem., 1971, **381**, 168.
88. K.A.Andrianov, G.V.Kotrelev, V.V.Kozakova, and M.A.Teveneva, Dokl.Akad.Nauk SSSR, 1977, **233**, 353.
89. R.P.Bush, N.C.Lloyd, and C.A.Pearce, Chem.Comm., 1967, 1269.
90. French P.1 425 306 (1965); Bulletin officiel de la Propriété industrielle, 1966, No.4.
91. B.P.1 085 012 (1967); Brit.Pat.Abstrs., 1967, **7**, No.42, 1.5.
92. Japanese P.13 760/68 (1968); Derwent Japanese, 1968, **7**, No.23, part 1.8.
93. BRD Appl.1 570 907 (1969); Auszüge Offenlegungsschr., 1969, **2**, 2766.
94. B.P.1 130 375 (1968); Brit.Pat.Abstra., 1968, **8**, No.45, 1.2.
95. US P.3 414 585 (1968); Chem.Abs., 1969, **70**, 87 947.
96. US P.3 431 222 (1969); Chem.Abs., 1969, **70**, 88 453.
97. Swiss Appl.12 731/63 (1963); Industrial Property 1963.
98. French P.1 418 315 (1965); Bulletin officiel de la Propriété industrielle, 1965, No.47.
99. B.P.1 085 703 (1967); Brit.Pat.Abstrs., 1967, **7**, No.43, 1.2.
100. Japanese P.21 759/68 (1968); Derwent Japanese, 1968, **7**, No.37, part 1.6.
101. BRD Appl.1 570 912 (1969); Auszüge Offenlegungsschr., 1969, **2**, No.35, 2209.
102. B.P.1 179 247 (1970); The Official Journal (Patents), 1970.
103. US P.3 578 691 (1971).
104. BRD P.1 813 172 (1969); Chem.Abs., 1969, **71**, 124 643.
105. French P.1 501 551 (1967); Chem.Abs., 1968, **69**, 97 362.
106. US P.3 803 086 (1974); Chem.Abs., 1974, **81**, 79 104.
107. US P.3 702 317 (1972).
108. BRD Appl.1 645 047 (1969); Patentblatt, 1969.
109. W.Fink, J.Paint.Technol., 1970, **42**(543), 220.
110. French P.1 546 594 (1968); Chem.Abs., 1969, **71**, 50 203.
111. K.A.Andrianov, N.A.Tebeneva, I.M.Petrova, and V.G.Kotrelev, Dokl.Akad.Nauk SSSR, 1975, **222**, 1101.

112. B.Dejak, J.Kulpinski, Z.Lasocki, and S.Piechucki, "Trudy V Mezhdunarodnogo Simpoziuma 'Polikondensatsionnye Protsessy', Varna, 1975" (Proceedings of the Vth International Symposium on "Polycondensation Processes", Varna, 1975), Izd.Bolg.Akad.Nauk, Sofia, 1976, p.213.
113. French P.1 505 664 (1967); Bulletin officiel de la Propriété industrielle, 1967, 15 décembre, No.50 du.
114. Swiss Appl.16 649/65 (1965); Industrial Property, 1965.
115. B.P.1 171 786 (1960); Brit.Pat.Abstrs., 1969, **9**, No.51, 1.2.
116. US P.3 498 949 (1970)l Offic.Faz.U.S., 1970, 3 mar., **872**, No.1.
117. BRD Appl.1 645 050 (1970); Chem.Abs., 1970, **69**, 107 671.
118. K.A.Andrianov, I.I.Tverdokhlebova, S.-S.A.Pavlova, P.A.Kurginyan, T.A.Larina, V.M.Kopylov, Zh.S.Syrtsova, and E.G.Khoroshilova, Vysokomol. Soed., 1977, **19A**, 2305.
119. BRD Appl.1 668 373 (1970); Chem.Abs., 1970, **71**, 50 203E.
120. Swiss Appl.4756/66 (1966); Industrial Property, 1966.
121. K.A.Andrianov, G.V.Kotrelev, E.A.Zhdanova, T.V.Strelkova, E.S.Obolonkova, V.A.Martirosov, and N.I.Pankov, Vysokomol.Soed., 1978, **20A**, 2355.
122. USSR P.574 453 (1977); Byul.Izobret., 1977, No.36.
123. K.A.Andrianov, M.I.Shkol'nik, V.M.Kopylov, L.M.Khananashvili, and P.L.Prikhod'ko, Vysokomol. Soed., 1977, **19A**, 2300.
124. USSR P.657 038 (1978); Byul.Izobret., 1979, No.14.
125. D.Ya.Zhinkin, I.S.Shragin, V.M.Kopylov, Zh.S.Syrtsova, V.V.Yastrebov, and M.G.Zaitseva, Vysokomol. Soed., 1980, **22A**, 1541.
126. E.A.Zhdanova, V.S.Svistunov, and G.V.Kotrelev, Vysokomol.Soed., 1980, **22A**, 1973.
127. K.A.Andrianov, I.I.Tverdokhlebova. S.-S.A.Pavlova, T.A.Larina, P.A.Kurginyan, G.V.Kotrelev, N.A.Tebeneva, N.V.Pertsova, and E.G.Khoroshilova, Vysokomol.Soed., 1977, **19A**, 2300.
128. K.A.Andrianov, G.V.Kotrelev, N.A.Tebeneva, N.V.Pertsova, I.I.Tverdokhlebova, P.A.Kurginyan, T.A.Larina, and E.G.Khoroshilova, Vysokomol.Soed., 1978, **20A**, 692.
129. Papers presented at the 157th Meeting, Minneapolis, 1969; Amer.Chem.Soc., Div.of Organic Coatings and Plastics Chem., 1969, **29**, No.1, 125.
130. Plastics, 1968, **33**(368), 611.
131. Chem.Eng., 1968, **75**(13), 95.
132. Oil, Paint a.Drug Reporter, 1968, **193**(24), 7.
133. Chemical Age, 1968, **98**(2552), 14.
134. Farbe und Lack, 1969, **75**(11), 1075.
135. B.P.1 063 086 (1967); Brit.Pat.Abstrs., 1967, **7**, No.16, 5.1.
136. B.P.1 228 874 (1971); Chem.Abs., 1971, **75**, 36 330.
137. B.P.1 203 622 (1970); Chem.Abs., 1970, **72**, 32 015.
138. US P.3 539 609 (1970); Offic.Gaz.U.S., 1970, 10 nov., **880**, No.2.
139. BRD.P.2 226 069 (1973); Chem.Abs., 1973, **78**, 159 838.
140. Swiss Appl.11 547/66 (1966); Industrial Property, 1966.
141. US P.3 553 242 (1971); Chem.Abs., 1971, **75**, 20 604.
142. US P.3 565 934 (1971); Chem.Abs., 1971, **75**, 36 325.
143. BRD P.1 811 497 (1970); Chem.Abs., 1970, **73**, 26 077.
144. L.Parkanyi, M.Dunaj-Jurco, L.Bihatsi, and P.Hencsei, Cryst.Struct.Comm., 1980, **9**, 1049.
145. S.N.Gurkova, A.I.Gusev, N.V.Alekseev, Yu.M.Varezhkin, M.M.Morgunova, and D.Ya.Zhinkin, Zhur.Strukt.Khim., 1981, **22**, 173.
146. U.Wannagat and S.Klemke, Monatsh., 1979, **110**, 1089.
147. U.Wannagat, S.Klemke, D.Mootz, and H.D.Reski, J.Organometal.Chem., 1979, **178**, 83.
148. L.Skoda, U.Klingebiel, and A.Meller, Chem.Ber., 1980, **113**, 2342.
149. L.Skoda, U.Klingebiel, and A.Meller, Z.anorg.Chem., 1980, **467**, 131.
150. M.G.Zaitseva, V.V.Kravchenko, and M.I.Shkol'nik, "V Vsesoyuznaya Konferentsiya po Khimii i Primeneniyu Kremniiorganicheskikh Soedinenii, Tbilisi, 1980" (The Vth All-Union Conference on the Chemistry and Applications of Organosilicon Compounds, Tbilisi, 1980), Vol.2, No.470.
151. L.M.Khananashvili, V.M.Kopylov, M.I.Shkol'nik, M.G.Zaitseva, J.Šraml, J.Souček, and V.Chvalovsky, Zhur.Obshch.Khim., 1980, **50**, 1565.
152. Yu.M.Varezhkin, D.Ya.Zhinkin, and M.M.Morgunova, Vysokomol.Soed., 1980, **22B**, 453.
153. Yu.M.Varezhkin, M.M.Morgunova, V.L.Kostikina, and D.Ya.Zhinkin, Vysokomol.Soed., 1981, **23A**, 1171.
154. G.V.Kotrelev and E.A.Zhdanova, "V Vsesoyuznaya Konferentsiya po Khimii i Primeneniyu Kremniiorganicheskikh Soedinenii, Tbilisi, 1980", (The Vth All-Union Conference on the Chemistry and Applications of Organosilicon Compounds, Tbilisi, 1980), Vol.1, No.178.
155. K.A.Andrianov, V.N.Talanov, and M.M.Il'in, "V Vsesoyuznaya Konferentsiya po Khimii i Primeneniyu Kremniiorganicheskikh Soedinenii, Tbilisi, 1980" (The Vth All-Union Conference on the Chemistry and Applications of Organosilicon Compounds, Tbilisi, 1980), Vol.1, No.228.
156. Yu.M.Varezhkin, "V Vsesoyuznaya Konferentsiya po Khimii i Primeneniyu Kremniiorganicheskikh Soedinenii, Tbilisi, 1980" (The Vth All-Union Conference on the Chemistry and Applications of Organosilicon Compounds, Tbilisi, 1980), Vol.1, No.253.
157. I.S.Shragin and Zh.S.Syrtsova, "V Vsesoyuznaya Konferentsiya po Khimii i Primeneniyu Kremniiorganicheskikh Soedinenii, Tbilisi, 1980" (The Vth All-Union Conference on the Chemistry and Applications of Organosilicon Compounds, Tbilisi, 1980), Vol.1, No.251.
158. E.A.Zhdanova and V.S.Svistunov, "V Vsesoyuznaya Konferentsiya po Khimii i Primeneniyu Kremniiorganicheskikh Soedinenii, Tbilisi, 1980" (The Vth All-Union Conference on the Chemistry and Applications of Organosilicon Compounds, Tbilisi, 1980), Vol.1, No.290.
159. Zh.S.Syrtsova and I.S.Shragin, "V Vsesoyuznaya Konferentsiya po Khimii i Primeneniyu Kremniiorganicheskikh Soedinenii, Tbilisi, 1980" (The Vth All-Union Conference on the Chemistry and Applications of Organosilicon Compounds, Tbilisi, 1980), Vol.1, No.233.
160. Yu.M.Varezhkin, M.M.Morgunova, and D.Ya.Zhinkin, Zhur.Obshch.Khim., 1980, **50**, 1083.
161. D.Ya.Zhinkin, Yu.M.Varezhkin, and M.M.Morgunova, "V Vsesoyuznaya Konferentsiya po Khimii i Primeneniyu Kremniiorganicheskikh Soedinenii, Tbilisi, 1980" (The Vth All-Union Conference on the Chemistry and Applications of Organosilicon Compounds, Tbilisi, 1980), Vol.1, No.71.
162. Yu.M.Varezhkin, M.M.Morgunova, and D.Ya.Zhinkin, Zhur.Obshch.Khim., 1980, **50**, 1355.
163. Yu.M.Varezhkin, M.M.Morgunova, and D.Ya.Zhinkin, Zhur.Obshch.Khim., 1980, **50**, 2487.
164. Yu.M.Varezhkin, M.M.Morgunova, and D.Ya.Zhinkin, Zhur.Obshch.Khim., 1981, **51**, 425.