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The Structure of Organocyclosiloxanes

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X-Ray results form the basis of a discussion of the stereochemistry of monocyclic siloxanes—monomers yielding polyorganosiloxanes—as well as the structure of higher polycyclic siloxanes, simple oligomers. A list of 105 references is included.

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I. INTRODUCTION

The practical usefulness of two classes of polymers having inorganic main chains—polycyclosiloxanes and polyphosphazens—is firmly established. Both hetero-organic and macromolecular aspects of the chemistry of organosiloxanes and organophosphazens have been studied in some detail.

Among the main lines of attack on which investigators attempting to produce novel polymers with inorganic main chains concentrate their efforts, three are directly related to the subject of the present Review—firstly the production of polymeric molecules having a non-traditional structure (cyclolinear, spirocyclic, etc.),[1,2] secondly a transition to polymers having main chains differing in composition (polysilazanes, polyheterosiloxanes, polyphosphoxans, polysilthians, polyborazens, etc.),[1-4] and thirdly study of the influence of the framework both on the character of the bond and the conformation of the inorganic unit and on the overall properties of the polymeric product[5].

There is no doubt about the importance of structural investigations for these three lines of research. The increasing number of studies, consequent mainly on the growth in instrumental physicochemical methods, have been made at different structural levels, from the simplest molecules containing only one silicon (phosphorus, etc.) atom in the organic framework to polymeric macromolecules of molecular mass $\sim 10^6$. The investigators usually attempt to relate their structural information to the observed (or supposed) properties of the compounds. The transferability of such conclusions to real compounds depends, of course, on the level at which the structural investigation has been made. Research on the structure of polymers is "closer to life" than that on simple molecules, but the information is considerably more complicated to interpret than in the latter case. Therefore the qualitative aspect predominates in the former, and the quantitative aspect in the latter studies.

The present Review summarises results of X-ray structural investigations on organocyclosiloxanes, which have been more thoroughly studied in relation to polymers than have other types of hetero-organic monomers (although numerically organophosphazens predominate), which helps to reveal several rules useful in analysing the structure of other classes of monomers.

In analysing and comparing structures it has been borne in mind that these compounds serve either as monomers or as oligomers of polymers containing common structural units. The following restrictions must, of course, be taken into account in elucidating correlations between the properties of the lower monomeric (and oligomeric) structures and those of the polymers. (i) The properties of polymers depend on their structure at all levels, i.e. on the primary, secondary, and tertiary structures (crystal-chemical analysis of the structure of the monomer will give information only on the primary and to some extent the secondary structures). (ii) Crystal-chemical analysis applies to molecules situated in a crystal field, which may change the equilibrium conformation of the free (reacting) molecule. (iii) It is improbable that the solid-phase polymerisation of siloxanes will have a purely topochemical mechanism: it will most likely occur in amorphous zones, while the elements of the crystalline order will be retained.

These and perhaps other limitations on crystal-chemical conclusions regarding the structure of polymeric products and reactivity in the solid phase must be borne in mind by the reader of the Review. However, it appears to the Reviewers that such restrictions do not so much diminish the practical value of the crystal-chemical approach as emphasise the complexity of the problems and thereby justify the idealised approach employed in the Review.

The chemistry of organosiloxanes is largely that of organosiloxane rings. Very great variation in size is characteristic of $(SiO)_n$ rings†, which may be either isolated (monocyclic siloxanes) or fused, with extremely diverse modes of fusion (spirocyclic, cyclolinear, and other polycyclosiloxanes).[1] The natural sequence in which cyclosiloxane structures are discussed in this Review (initially monocyclic, and then more complicated fused polycyclic systems) enables the structure of complex polycycles to be analysed in terms of results for their simpler constituents.

†The existence of disiloxane rings $(SiO)_2$[6,7] has not yet been confirmed by means of X-rays. Rings $(SiO)_n$ having $n = 10$–15 are probably of practical value, although there are indications of the existence of rings with n up to 400.[8]

II. MONOCYCLIC SILOXANES

Table 1 gives the most important structural constants for trisiloxane rings D_3# in monocyclic cyclotrisiloxane derivatives investigated by X-ray structural analysis. These rings have an approximately planar structure in which the maximum divergence of atoms from the planes of the rings is $\Delta = 0.01$ Å. Such a planar structure is evidence of some steric strain in these rings. Indeed the SiOSi bond angles in trisiloxane rings (131–134°) are among the smallest known. However, disruption of the planarity of the rings would have implied a still greater decrease in these bond angles, which, as will be shown below, would have weakened the silicon–oxygen bonds and diminished the stability of the rings. Even in complicated sterically strained fused polycyclic systems the departure of atoms from the planes of the trisiloxane rings does not exceed 0.4 Å (see below).

Table 1. Data on trisiloxane rings in monocyclotrisiloxanes.

No.	Formula	l_{Si-O}, Å	α_{SiOSi}	Δ, Å	Ref.
(I)*	$(Me_2SiO)_3$	1.61	136°	0**	9
(II)	$(Ph_2SiO)_3$	—1.64	131.9°	0.07	10
(III)	*cis*-$(MePhSiO)_3$	1.65	132.3°	0.10	11
(IV)	*trans*-$(MePhSiO)_3$	1.65	132°	0.05	12
(V)	$Na_3[PhSi(O)O]_3$	1.647	133.5°	0.029	***

*Determination of this structure was inaccurate, and has been disregarded in the comparison with others.
**Molecule in a special position (see text).
***This compound crystallises as the octahydrate $Na_3(C_6H_5SiOO)_3.8H_2O$. Some of the results of this investigation have appeared in Ref. 13.

The molecule (I) has an ideally planar structure. Its great intrinsic symmetry (D_{3h}) is retained even in the crystal, where the molecules occupy unique positions (space group $R3m$, $Z = 1$). The impossibility of packing a large number of bulky phenyl substituents in a sufficiently highly symmetrical space group probably prevents realisation in the crystal of the potentially high intrinsic symmetry of molecule (II). An example of the geometrical isomerism of cyclosiloxanes is provided by molecules (III) and (IV). Organosiloxanes are often formed as mixtures of geometrical isomers. In some cases clear identification of isomers acquires practical importance, e.g. with isomers (III) and (IV), which differ sharply in their polymerisation properties[14]. Other examples of the use of X-ray structural analysis to solve problems of the identification of isomers will be found in the Review.

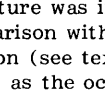
#The notation adopted for the configurations of organosiloxanes combines the symbols for the four structural units[8]

Functionality	Symbol	Unit
Mono	*M*	$R'R''R'''SiO_{1/2}$
Di	*D*	$R'R''SiO_{2/2}$
Tri	*T*	$RSiO_{3/2}$
Tetra	*Q*	$SiO_{4/2}$

The subscript following the oxygen atom denotes the number of oxygen atoms per silicon atom (e.g. $\frac{3}{2}$ indicates that the silicon atom is attached to three oxygen atoms, each of which is combined with another silicon atom).

Great interest attaches to the structure of the siloxane anion in sodium *cis*-1,3,5-triphenylcyclotrisiloxane-1,3,5-triolate (V). The distance Si–O^- to the ionised oxygen atom was first determined (on the average 1.586(2) Å). The T_3 ring in structure (V) is appreciably "flattened" in comparison with the D_3 rings in molecules (II)–(IV), and has well defined C_{3v} symmetry (crown conformation), with the plane of the three cyclic oxygen atoms located farther from the exocyclic oxygen atoms than is the parallel plane of the three silicon atoms. If the conformation of the ring can be explained by the *T* character of the cyclic silicon atoms (C_{nv} symmetry is characteristic even of larger T_n rings—see below), the great "flatness" is probably due to mutual electrostatic repulsion of Si–O^- groups. The cyclic silicon–oxygen bond lengths in (V) are the same as in other trisiloxane rings.

Table 2. Data on tetrasiloxane rings in monocyclotetrasiloxanes*.

No.	Formula	l_{Si-O}, Å	α_{SiOSi}	Symmetry of ring	Conformation of ring	Angles of fold	Ref.
(VI)	$(Me_2SiO)_4$ (β-form)	1.65	142.5	C_i	chair	31.3°	15
(VII)	$[(Me_2SiO)(Ph_2SiO)_2]_2$	1.62	148.5°	S_4	boat	27.5° и 31	16
(VIII)	*cis*-$[(MePhSiO)(Me_2SiO)]_2$	1.63	144.2°	C_2	boat	35.5°	17
(IX)	*trans*-$[(MePhSiO)(Me_2SiO)]_2$	1.622	145.2°	C_i	chair	31°	18
(X)	$(R_2SiO)_4$	1.62	149°	C_i	chair	34.2°	19, 20
(XI)	*cis*-$[(Me(OH)SiO(Ph_2SiO)]$	1.622	144°	S_4	boat	40.2°	см.*
(XII)		1.636	140°	C_i	chair	24°	см.*

*The angle of fold of the ring in (IX) is close to that found for structure (VI); the chair conformation in structure (X) differs (see text) from the chair conformation in (VI); for the structures (XI) and (XII) see Refs. 100 and 101 respectively; $R_2 = [CH_2]_4$; and $R' = CH_2.C(COOC_2H_5)_2.CH_2$.

The rings in organocyclosiloxanes $(RR'SiO)_n$ with $n > 3$ are non-planar, and hence may be expected to exist in different conformations. Table 2 gives data on structures having eight-membered tetrasiloxane rings. Comparison of Tables 1 and 2 shows§ that silicon–oxygen bonds are shorter in tetrasiloxane than in trisiloxane rings (on the average respectively 1.62 and 1.65 Å), and the SiOSi angles are larger (respectively 142–149° and 131–134°). Thus the silicon–oxygen bonds are more stable in D_4 than in D_3 rings.

Fig. 1 shows diagrammatically possible conformations of cyclic systems $(AB)_4$ comprising alternating atoms, which include tetrasiloxane rings. With the SiOSi bond angles observed in tetrasiloxanes (142–149°) all the conformations indicated in Fig. 1 (with the exception of D_{4h}) are possible, as well as conformational transitions between them.

X-Rays have been used to study the structure of the low-temperature β modification of octamethylcyclotetrasiloxane, which at −16.3 °C passes into the high-temperature α modification melting at 17.5 °C. In a crystal of the β modification

§It must be borne in mind when making the comparison that structures (I) and (VI) have not been determined with great accuracy.

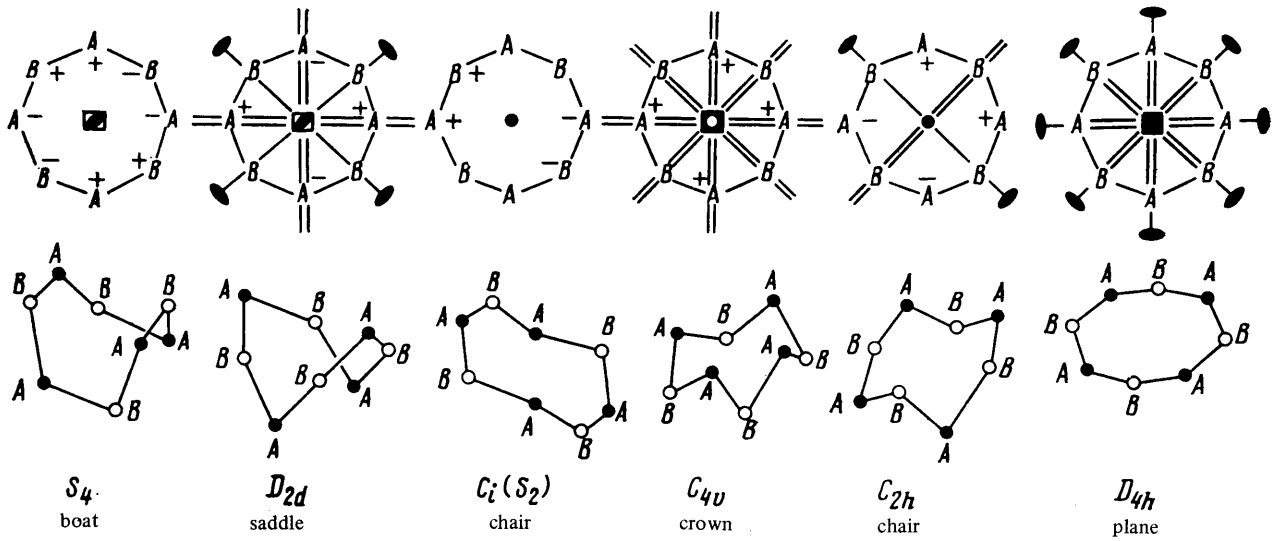


Figure 1. Possible ideal conformations of $(AB)_4$ rings comprising alternating atoms[16]. The plus and minus signs show the divergence of atoms above and below the mean plane of the ring.

the molecules are located at centres of symmetry, and the D_4 ring has a chair conformation (Fig. 1).[15] The molecule is located at a special position also in a crystal of the α modification, but now on a fourfold axis: i.e. it has a boat or saddle conformation[15]. It was supposed originally[15] that the phase transition involved the appearance of orientational disorder, since it was assumed by analogy with organic rings that the heat of transition would be too small to change the conformation of the molecule. A later spectroscopic investigation showed[21] that conversion into the high-temperature modification was a conformational transition with a change in the intrinsic symmetry of the molecule.

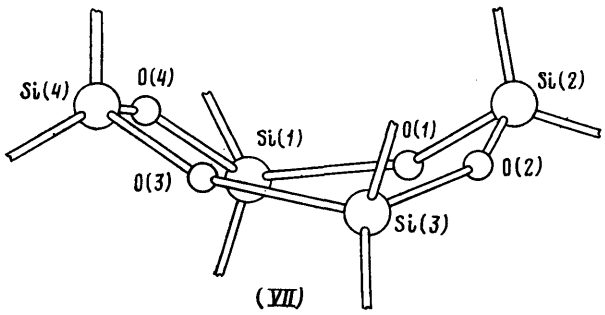


Figure 2. Conformation of D_4 ring in molecule (VII).[16]

The D_4 ring in molecule (VII) has non-crystallographic symmetry intermediate between S_4 and D_{2d} (closer to S_4), with a boat conformation (Fig. 2). The $Si_{(1)}O_{(1)}Si_{(3)}O_{(3)}$ plane, which constitutes the "bottom" of the boat, forms with the $Si_{(1)}O_{(4)}Si_{(4)}O_{(3)}$ and $O_{(1)}Si_{(2)}O_{(2)}Si_{(3)}$ planes dihedral angles of 27.5° and 31° respectively.

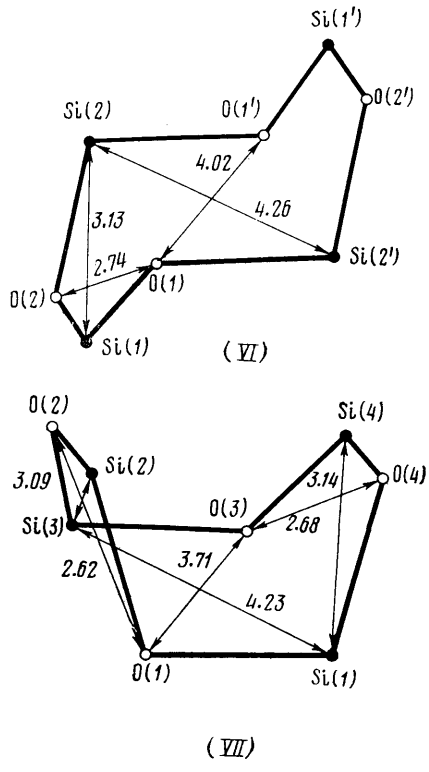


Figure 3. Non-bonded endocyclic distances in D_4 rings in molecules (VI) and (VII).[16]

Ideally chair–isomerism involves rotation of only one diatomic Si–O group relative to the remaining part of the ring. However, Fig. 3 shows that the real molecules (VI) and (VII) differ

also in the geometry of the central portion of the D_4 ring (the "bottom" of the boat). In particular, the difference between the diagonal Si...Si and O...O distances in the central portion is smaller in (VI) (4.26 and 4.02 Å) than in (VII) (4.23 and 3.71 Å). Furthermore, this portion is planar in (VI) (the molecule is situated at a centre of symmetry), whereas in (VII) the atoms forming the central four-membered portion depart by ±0.11 Å from its median plane[16].

Further discussion of the geometry of siloxane rings involves consideration of the nature of the silicon–oxygen bond in this group of compounds. These questions are not examined in detail in the present Review, since they have been covered exhaustively in several papers, cited e.g. in reviews[4,22]. Although the concept of silicon–oxygen p_π–d_π interaction has been increasingly criticised during recent years by several quantum chemists[23–25], this approach is nevertheless adopted in the present Review for the following two reasons.

(1) This approach provides a good explanation of the observed geometry even of extremely complicated organocyclosiloxane molecules. However, a serious problem for the concept of p_π–d_π interaction was presented by the $[(C_6H_5)_2Si]_2O$ molecule[28], in which the SiOSi angle had increased to 180° (the molecule was located at a centre of symmetry), while the silicon–oxygen bond had contracted only to 1.616(1) Å.¶

(2) An alternative approach, in which the silicon–oxygen bond length is assumed to be constant (the sum of the covalent radii corrected for the difference in electronegativity between silicon and oxygen atoms), and the SiOSi bond angle is explained by the separation of electron-pairs located in valency orbitals (the VSEPR method[27])†, is actually applicable only to a narrow range of compounds[27,28], in particular silicates having a Q unit as a structural element. There are other quantum-chemical treatments of the bonds formed by Group IVb elements (in particular silicon–oxygen bonds)[23,29,30], but as before the concept of p_π–d_π interaction remains the most popular for interpreting the geometry of organosiloxanes.

The rule of the interrelationship between the SiOSi angle and the length of the silicon–oxygen bonds forming it, which has been most sharply criticised by opponents of the hypothesis that p_π–d_π interaction is important, is well satisfied in organocyclosiloxanes, as shown below.

The set of almost isoenergetic chain conformations with bonds almost identical in character is considerably extended by the involvement in bonding of *d* orbitals of silicon atoms differently oriented relative to the axis of the siloxane chain[31], with a consequent diminished rigidity of the SiOSi bond angles and enhanced chain flexibility. This feature makes possible the appearance of geometrical isomers of siloxane chains, whose structures result from a compromise between the repulsion of non-bonded groups and the requirement of maximum p_π–d_π interaction[22,32].

The relation between the structure of the rings and the requirement of maximum p_π–d_π interaction was examined in detail by Craig and Paddock[31], who calculated the overlap integrals of *d* and *p* (or hybrid *sp*) orbitals for various conformations of the rings. They established the possibility of the existence of several energetically approximately equivalent conformations of rings formed by atoms possessing vacant *d* orbitals and atoms with lone pairs in *p* orbitals. Thus conformations of symmetry S_4, C_{2h}, C_{4v}, and D_{2d} are almost equally probable for eight-membered rings, e.g. D_4, with comparatively weak p_π–d_π interaction. The corresponding conformational transitions do not appreciably affect the degree of p_π–d_π interaction, since the silicon–oxygen bond lengths do not change with different conformations of the D_4 ring characterised by roughly the same SiOSi angles (142–149°).

This conclusion is supported also by numerous spectral investigations. Transition from the high-temperature crystalline modification of (VI) to the liquid phase is accompanied by a substantial change in spectra: the molecule acquires C_{4v} symmetry[21,32]. Electron diffraction by (VI) in the gas phase indicates S_4 molecular symmetry[33]. The conclusion that a conformation of C_{4v} symmetry is present in the liquid phase is consistent with the dipole moments of liquid cyclosiloxanes D_n with $n = 4–8$.[32] Among the types of symmetry possible for the tetramer only C_{4v} is consistent with the observed non-zero dipole moment.

Thus variation in the set of substituents, polymorphic transitions, and change in the state of aggregation may lead to a change in the conformation of the D_4 ring. Such rings in crystallographically independent molecules in the same crystal may also have different conformations, as has been observed e.g. with octamethylcyclotetrasilazane[34].

The molecule (XI) has non-crystallographic symmetry C_2 (approximately S_4 for the T_2D_2 ring—see Fig. 4). The planes of the phenyl rings $C_{(3)}...C_{(8)}$ and $C_{(21)}...C_{(26)}$ are almost parallel (dihedral angle 172.6°) and interact sterically, as is confirmed by the C...C distances between the ring atoms (3.17–3.50 Å). Such a molecular structure favours the development of activity by the *cis*-silanolic groups, since the approach of reagent molecules in solution is not subject to steric hindrance. Although the positions of the phenyl and methyl hydrogen atoms have been determined objectively, the hydrogen atoms of the silanolic groups could not be located. They probably undergo extremely vigorous thermal motion. It is interesting that the silanolic oxygen atoms have almost the same hybridisation as in the ring (mean Si–O(H) distance 1.643 Å).

Molecules (X) and (XII) are of interest in connection with the possible distorting influence on the structure of the D_4 ring of the "chelate" substituents, with ring closure at one or two silicon atoms (Figs. 5 and 6). The parameters of the D_4 ring in (X) have normal values (Si–O bond length 1.62 Å, SiOSi and OSiO bond angles 149° and 109°). The CSiC bond

¶ The fact that the MOM bond angles in $[(C_6H_5)_3C]_2O$ and $[(C_6H_5)_3Ge]_2O$ (128° and 135.2° respectively) are determined by non-bonded El...El interaction (where El = C, Ge) has led to surprise[26] that a linear geometry could occur in $[(C_6H_5)_3Si]_2O$. An "electronic" influence of the phenyl substituents should apparently be excluded in view of the quite long Si–C(C_6H_5) bonds (1.860–1.870 Å). Nevertheless, the Reviewers consider that steric factors are responsible for the geometry of this last molecule. Although intramolecular contacts between the phenyl groups are not critical here (the shortest C...H distance is 2.81 Å), the "pushing apart" of phenyl groups is fully able to affect the molecular geometry in such a fundamental fashion, as a consequence of the advantageous centrosymmetrical arrangement of the bulky phenyl groups and the relative ease of deformation of the SiOSi bond angles (in comparison with COC and GeOGe angles). The steric character of the factors governing the geometry of the $[(C_6H_5)_3Si]_2O$ molecule explains also the insufficient contraction (in a scheme with p_π–d_π interaction) of the silicon–oxygen bonds.

† Cases of linearity of oxy-bridges in $(R_3Si)_2O$ molecules are explained by the donor properties of the trialkylsilyl groups, which suppress the tendency of the oxygen bridge to assume a bent structure[102].

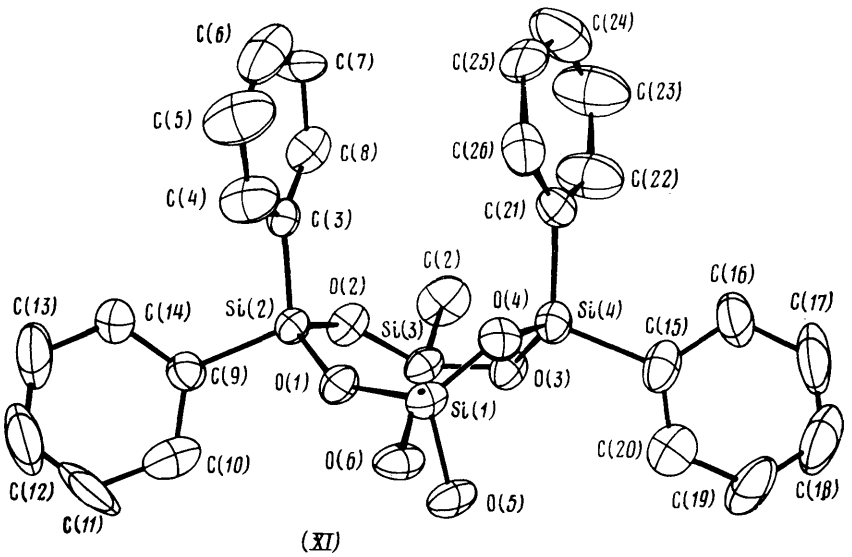


Figure 4. Structure of molecule (XI). The $Si_{(1)}$ ellipsoid shows the point of entry of the $Si_{(1)}-C_{(1)}$ bond with its methyl group.

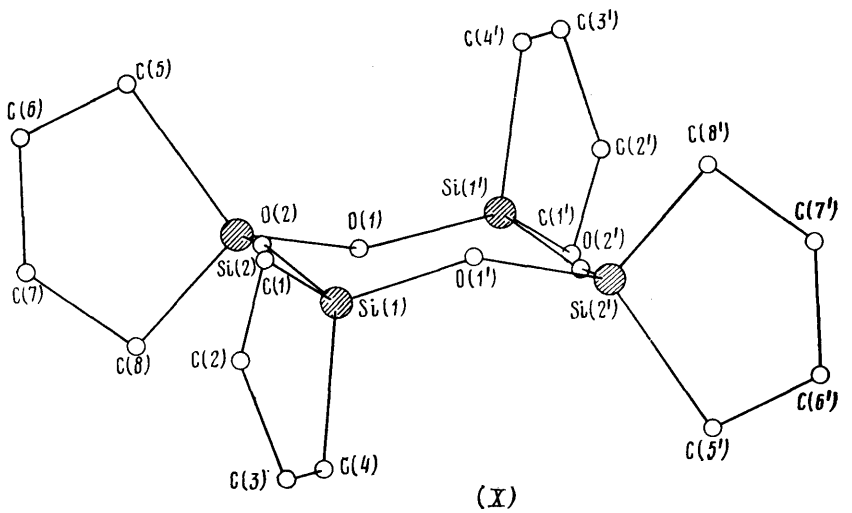


Figure 5. Structure of molecule (X) located at a centre of symmetry[20].

angles have decreased on the average to 97° owing to entry into five-membered heterocycles.

However, the D_4 conformation of the ring found in molecule (X) had not been observed for cyclotetrasiloxanes before the appearance of this recent work[19,20]. This is a particular case of the chair conformation (C_i symmetry), in which six ring atoms $[O_{(1)}Si_{(2)}O_{(2)}O_{(1')}Si_{(2')}O_{(2')}]$ are situated in the same plane (in (X) the emergence of atoms from this plane does not exceed 0.03 Å), from which the diametrically opposite silicon atoms (1) and (1') depart markedly on opposite sides (by ±0.53 Å—Fig. 5). Thus here the chair conformation is formed by the deflections of opposite triatomic groups from the remainder of the ring. The same conformation as in (X) and (XII) is exhibited by the mixed siloxazane ring of 1,3,5',7'-tetramethyl-1',3',5,7-tetraphenylcyclo-1,3,5,7-tetrasila-2,6-diaza-4,8-dioxane[35] and the silazane ring in 1,3,5',7'-tetramethyl-1',3',5,7-tetraphenylcyclotetrasilazane[36]. Both these rings have completely different sets of substituents from those in (X) and (XII).

The same conformation is found for the next D_4 derivative with "ring-closed" chelate substituents (XII), but here, instead of silicon atoms, oxygen atoms are deflected ($O_{(1)}$ and $O_{(1')}$ by ±0.69 Å) from the plane of the hexatomic fragment $Si_{(1)}Si_{(2)}O_{(2')}Si_{(1')}Si_{(2')}O_{(2)}$ (Fig. 6).

Before passing to cyclosiloxanes with >4 SiO units we note that derivatives of the D_4 ring have a special role in the

stereochemistry of organosiloxanes. These rings, which are the most frequently encountered among cyclosiloxane rings¶, form the most popular fragment in various organosiloxane polymers. Eight-membered rings based on SiO_4 tetrahedra are met quite often also among silicates (within infinite silicon–oxygen bridges, in which the silicon atoms usually have a *Q* configuration)[37].

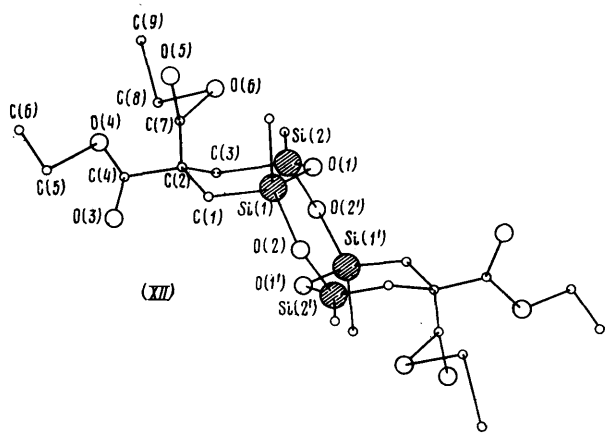


Figure 6. Structure of molecule (XII) located at a centre of symmetry.

Research on the biological activity of cyclic siloxanes of type $(C_6H_5CH_3SiO)_x[(CH_3)_2SiO]_y$ begun at the start of the 1970s has shown that several of them affect the reproductive function of mammals[38–40]. The D_4 derivatives (VIII) and $(C_6H_5CH_3SiO)_2[(CH_3)_2SiO]_3$ have proved the most active. The results of this work, which are significant from the point of view of a possible stereochemical analysis of the biological activity of organic derivatives of D_4 cyclosiloxanes, can be summarised: (1) the activity of organosiloxanes is due to the presence of arylsilicon groups; (2) the conformation and the configuration of D_4 derivatives are important (compound (VIII) has considerable oestrogenic activity, and (IX) is almost inactive); and (3) bioactivation in the animal organism does not involve conversion of chemically different organosiloxanes into chemically and (biologically) similar compounds.

Very little is known about the structure of D_n cyclosiloxanes having $n > 4$. The crystalline "octamer" $[(CH_3)_2SiO]_8$ has been examined by X-ray diffraction[32]. The molecules occupy positions having S_4 symmetry (space group $P\bar{4}2_1c$), while the conformation of the ring probably resembles that found for the D_4 ring in the α modification of (VI). Even these data indicate that the conformation of the D_8 ring may change on melting, since in the liquid phase these compounds have a non-zero dipole moment, which would be impossible with S_4 symmetry[32]. Spectral data[21] suggest that in the liquid phase the octamer molecule has C_8 symmetry.

X-Ray examination of decamethylcyclopentasiloxane $[(CH_3)_2SiO]_5$ in the liquid phase indicated[41] that the siloxane ring was buckled. However, the molecular parameters obtained (Si–O and Si–C 1.66 and 1.85 Å; SiOSi, OSiO, and CSiC respectively 145°, 115°, and 110°) suggest that this work was inaccurate (doubtful parameters are underlined).

Spectroscopic investigation shows[32] that the $[(CH_3)_2SiO]_6$ molecule can be assigned to the point groups D_{3d} and C_{6v} respectively in the crystal and in the liquid. In the crystal the dimethylsilylene groups face alternately above and below a plane perpendicular to the threefold (sixfold) axis, but in the liquid all these groups face the same direction. The diminution in symmetry from C_{6v} to D_{3d} is probably due to steric interaction of neighbouring dimethylsilylene groups. With the SiOSi angle remaining constant in C_{nv} conformations of $[(CH_3)_2SiO]_n$ molecules the distance between the methyl groups decreases with increase in n, and a decrease in symmetry to D_{3d} may prove energetically advantageous.

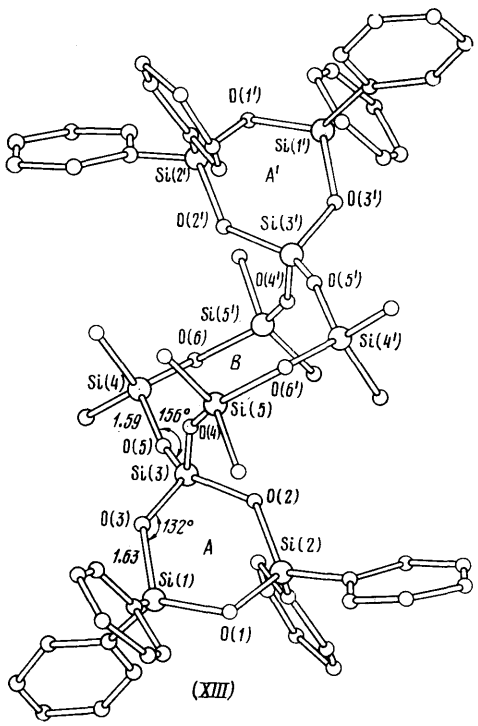


Figure 7. Structure of molecule (XIII) located at a centre of symmetry[43].

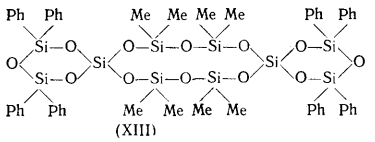
In contrast to rings in which n is even, the spectra of crystals with odd values of n differ little from those of the liquid phase: i.e. the conformation of the rings is the same in the liquid and in the crystal. Only groups D_n and C_n are consistent with the spectral data: the former can be rejected, since it has zero dipole moment, so that the molecules of pentamer and heptamer possess C_5 and C_7 symmetry, although certain features of the spectra indicate that the dimethylsilylene groups are arranged in conformity with a lower degree of symmetry.

Electron diffraction results for methyl derivatives of cyclopentasiloxane and cyclohexasiloxane in the gas phase[42] are not really consistent with any definite models. Better agreement is obtained with C_{5v} and D_{3d} symmetry respectively, with the oxygen atoms located in the same plane. Special

#See discussion at end of Section II.

attention was paid to C_5 and C_6 symmetry models, since they were based on spectral data[42]. We can pass from C_{nv} to C_n symmetry by rotating the dimethylsilylene plane relative to the corresponding OSiO fragment. However, this lower symmetry is less consistent than C_{nv} symmetry with the experimental results. It is supposed[42] that, owing to the large amplitudes of the low-frequency vibrations, molecules having large siloxane rings possess no definite conformation.

An X-ray structural investigation has been made[43] on 8,8,10,10,19,19,21,21-octamethyl-2,2,4,4,14,14,16,16-octaphenyldispiro[5,5,5,5] decasiloxane



(XIII)

whose molecule is located at a centre of symmetry and comprises three cyclosiloxane fragments (Fig.7), two six-membered (A and A') and one twelve-membered (B). The configurations of rings A and B are respectively D_2Q and D_4Q_2. The central twelve-membered siloxane ring B has the general chair conformation (symmetry C_i), with eight atoms $Si_{(4)}Si_{(5)}Si_{(4')}Si_{(5')}O_{(4)}O_{(6)}O_{(4')}O_{(6')}$ located approximately in the same plane (deviations do not exceed 0.3 Å). The deflection from it of the "chair-backs" (i.e. of the atomic planes $Si_{(3)}Si_{(4)}O_{(4)}O_{(5)}$ and $Si_{(3')}Si_{(4')}O_{(4')}O_{(5')}$) is 78°.

A most interesting feature of the structure of ring B is a sharp increase in the SiOSi angles (to an average of 156°) in comparison with e.g. eight-membered siloxane rings (Table 2). This value also exceeds the SiOSi angle of 149.6° in $[(CH_3)_2SiO]_6$ found by electron diffraction in the gas phase[42]. The increase in the angles leads to enhanced mobility of the oxygen atoms[43], which correlates with their larger temperature factors (7.6–9.6 Å^2) relative to the oxygen atoms in ring A (5.5–6.2 Å^2), in which the SiOSi angles are on the average 132°.

Structural comparison of the minerals bustamite (Ca,Mn)SiO_3 and wollastonite $CaSiO_3$ reveals a similar feature[32]. Both crystals are constructed of infinite chains $[SiO_3O_{9/2}]_\infty$ containing three silicon–oxygen tetrahedra in a repeating unit. The three non-equivalent SiOSi angles in the chain have the values

(Ca, Mn) SiO_3 : 161°, 135°, 137°;
$CaSiO_3$: 149°, 139°, 141°.

In the bustamite molecule the isotropic temperature factor of the oxygen atom in the grouping with the SiOSi angle straightened out to 161° was double that for the remaining oxygen atoms. In the wollastonite chain the temperature factor of the corresponding oxygen atom only slightly exceeded the mean value for all the remaining atoms[32].

In the structure of thortveitite $Sc_2Si_2O_7$ [44] the isotropic temperature factor of the bridging oxygen atom with the SiOSi bond angle 180° (the pyrosilicate group is located at a centre of symmetry) is almost double those for the terminal oxygen atoms (respectively 0.98, 0.55, and 0.65 Å^2), which are involved in the coordination of scandium atoms. The silicon–oxygen distance is shorter to the oxygen bridge than to the terminal atoms (respectively 1.605(1) and 1.629(1) Å).

In structures with abnormally large oxygen bond angles (>150°) the retardation of internal rotation in ElOEl bridges is weakened[32]. This is favoured firstly by increase in the distance between substituents attached to the El atoms and secondly by decrease in the potential barrier to internal rotation due to increasing overlap of d orbitals of the element El with p orbitals of oxygen, whose nodal plane is perpendicular to the ElOEl plane. In the limiting case, with an ElOEl angle of 180°, rotation about the ElOEl bond is probably entirely free and will depend only on steric interaction of the framing groups.

Quantum-chemical examination of these problems showed[45] that the barriers to internal rotation are zero in the chains of organic cumulenes $H_2C{:}C{:}...{:}C{:}CH_2$, and only the relative rotations of the two terminal groups can be fixed: this distinguishes a system of cumulative bonds fundamentally from a system of conjugated bonds, where internal rotation is retarded. However, in such cumulative systems in which the chain has a framework (as in many polymers having an inorganic main chain) internal rotation may be hindered by the repulsion of atoms in the framing groups. Although it was considered[45] that such retardation could not be essential (since not every atom carries substituents), it may play a large part with bulky (e.g. phenyl) substituents. Furthermore, spectral data[32] indicate that, in structures with ElOEl angles close to 180°, slight retardation of internal rotation is accompanied by diminished rigidity of these angles, so that a considerable increase in mobility of the oxygen atoms can be expected both in the ElOEl plane (perpendicular to the El...El axis) and perpendicular to it.

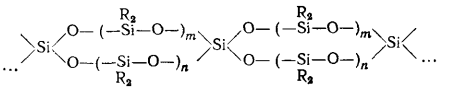
The flexibility of the SiOSi fragments entails a general conformational non-rigidity of the ring B [(XIII)], which probably accounts for the higher temperature factors of the silicon atoms than in the ring A (respectively 5.1–6.7 and 5.0–5.1 Å^2).[43] Flexibility of the ring B is promoted also by the packing of the molecules in the crystal. Of a total of 29 independent intermolecular contacts < 4 Å some 25 are formed by phenyl groups, i.e. by substituents in rings A and A'. Four methyl groups are completely uninvolved in intermolecular contacts < 4 Å. Thus the conformation of ring B is almost completely determined by intramolecular interactions, with methyl groups situated in the "rarefied" (with respect to intermolecular contacts) zone along the periphery of the central ring.

The specific packing combined with the large free displacement of oxygen atoms in structures having "abnormally" large SiOSi angles leads to enhanced mobility of fragments of the molecule (including substituents attached to the silicon atoms) relative to the Si...Si axes. This may explain also the high temperature factors (11–17 Å^2) of the methyl carbon atoms in (XIII). In this compound, as in comparable silicate structures, enhanced mobility of the oxygen atoms characterises SiOSi bridges with the largest SiOSi angles together with the shortest silicon–oxygen interatomic distances, which indicate increased bond orders.

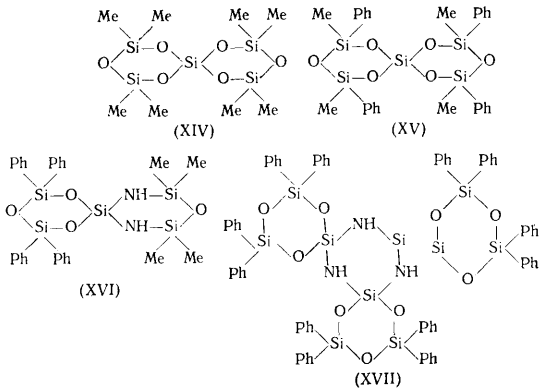
The conclusion that silicon–oxygen bonds are more stable in D_n rings with $n > 4$ than in a D_4 ring is consistent with a study of the polymerisation⇌depolymerisation (cyclisation) equilibrium of dimethylsiloxanes, which indicated that the concentration of D_4 is higher than those of all other cyclic dimethylsiloxanes present in the mixture. Indeed, the lower content of more flexible and stable rings with higher values of n can be explained by the smaller probability of their closure than with the shorter D_4 chains. The greater abundance of D_4 than of D_3 rings is attributed to some strain in the latter[2,3], as well as to greater instability of their silicon–oxygen bonds (Tables 1 and 2). The advantage of eight-membered Q_4 rings in silicates has been mentioned by O'Keefe and Hyde[24], who have analysed a large number of structural investigations of silicates and concluded that the conformations of silicon–oxygen fragments in them are determined by non-bonded Si...Si interaction with almost constant silicon–oxygen bond lengths. The Si...Si distances have their most favourable values (3.08–3.10 Å) in Q_4 rings.

III. SPIROCYCLIC SILOXANES

Organospiropolycyclosiloxanes, a novel class of organopolysiloxanes[1,46], have the general formula



Structures have been determined for the five spirocyclosiloxanes (XIII)–(XVII)



whose geometrical parameters are given in Table 3. Like D_3 rings (Table 1) the D_2Q rings present in spirocyclosiloxanes have an approximately planar structure. According to Table 3 the silicon–oxygen bonds in the spiro-units of the D_2Q rings are somewhat shorter, which indicates that they are more stable than the usual siloxane bonds§. Such contraction is due to more complete involvement of the central silicon atom (than of the silicon atoms in ordinary siloxanes) in π coupling with the four surrounding oxygen atoms; the polarising effect of the latter leads to the appearance of a positive charge on the silicon atom, which diminishes the energy of its 3*d* orbitals. Such an explanation has been used, for example, in analysing the character of the bonds in siloxanes[22].

When the oxygen atoms forming the spiro-environment of silicon atoms are replaced by the less electronegative nitrogen atoms, of course, the positive charge on the silicon atoms diminishes, and the remaining silicon–oxygen bonds become weaker. As a result, for example, the D_2T spiro-ring in the molecule (XVI) has the same parameters as have D_3 rings. On passing to compound (XVII), however, the difference in the silicon–oxygen bond lengths again becomes appreciable. This indicates that in mixed siloxane–silazane polycycles the silicon–oxygen bonds in the spiro-units are stronger than the remaining silicon–oxygen bonds provided that the spiro-units involve silicon atoms of an inner silazane ring. The molecule (XVII) (Fig.8) exhibits a fairly sharp difference in planarity of the trisiloxane rings (Table 3): the $Si_{(9)}$ atom emerges markedly (by 0.43 Å) from the plane of the remaining five atoms of the ring $Si_{(3)}O_{(10)}Si_{(8)}O_{(11)}Si_{(9)}O_{(12)}$.

§The absence of this effect in the molecule (XIV) is probably due to inaccuracy in the investigation[47].

The presence of spiro-silicon atoms should enhance not only the three-dimensional rigidity¶ but also the thermal stability of the organopolycyclosiloxane chain. Two modes of construction of such chains are of interest in connection with the molecular mechanism of deformation. The first involves a chain of spiro-linked siloxane rings with a small number (3 or 4) of SiO units in each. Such chains should be characterised by strong intramolecular organisation and great rigidity. The second method incorporates into the general spirocyclolinear molecule siloxane rings with >4 SiO (or linear siloxane links with >4 SiO). The strengthening in such molecules of the silicon–oxygen bonds involving spiro-silicon atoms is combined with enhanced stability of the other silicon–oxygen bonds as a consequence of their entry into long siloxane chains, distinguished by stronger p_π–d_π interaction[32,45].

Table 3. Data on spirocyclic siloxanes (d_1 and d_2 are the mean Si–O bond lengths within and outside the spiro-group in the D_2Q ring, Δ_{max} is the maximum divergence of atoms from the D_2Q plane, and α is the mean SiOSi bond angle in the D_2Q ring).

No.	d_1, Å	d_2, Å	Δ_{max}, Å	α	Ref.
(XIII)	1.61 (1)	1.64 (1)	0.11	132°	43
(XIV)	1.64	1.64	0*	132.3°	47,22
(XV)	1.611 (6)	1.634 (6)	0.11	132.5°	48
(XVI)	1.637 (6)	1.638 (6)	0.11	132.6°	49
(XVII)	1.62 (1)	1.64 (1)	0.07; 0.11; 0.20***	132.5°	см.**

*Molecule located in the special position 42*m*.
**See Ref.103; some of the results will be found in Ref.50.
***The divergence is given separately for each of the D_2Q rings in the (XVII) molecule.

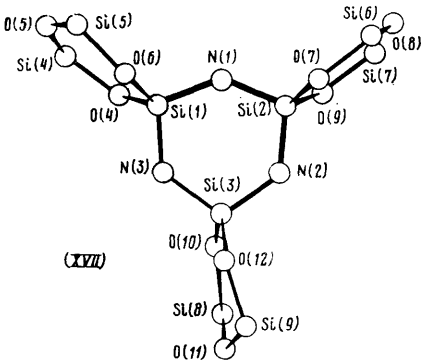
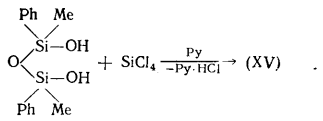


Figure 8. Tetracyclic fragment of molecule (XVII).

¶As already remarked, the rigid spiro-units in the molecule (XIII) stabilise the conformation of the inner twelve-membered siloxane ring, which enables single crystals of this compound to be obtained.

Organopolysiloxane chains of the second type, while retaining the rigidity inherent in organospirocyclosiloxanes, should possess better chemical and thermal stability. Phenyl substituents enhance the rigidity and the crystallisability of both types of organopolysiloxanes[51]. On the other hand, the presence of sterically rigid segments diminishes the thermal mobility of the molecular skeleton, with a consequent impairment of, for example, the resistance of the polymer to thermal oxidation. However, this adverse effect can be suppressed by incorporating into the general polyspirocyclosiloxane system extremely flexible extended polysiloxane segments (large rings).

The compound (XV) can exist as five stereoisomers depending on the orientation of the substituents relative to the planes of the siloxane rings (Fig. 9). Reaction with the *meso*-form of the diol accompanied by retention of configuration[52] gives the *cis,cis*-isomer of (XV) as a racemic mixture of the two enantiomers (XVa) and (XVb), for which the only element of molecular symmetry is a twofold axis:



The methyl groups in each of the siloxane rings of these enantiomers are diastereotopic, as is confirmed by the nuclear magnetic resonance spectra, in which two separate signals are observed from methyl protons. Reaction with silicon tetrachloride of the optically active forms *SS* and *RR* of the diol, and also of their racemic mixture†, should lead to formation of the *trans,trans*-isomer of (XV) as a mixture of the enantiomers (XVe) (conventionally the *d*-isomer) and (XVf) (conventionally the *l*-isomer) and the diastereomeric *meso*-form (XVg) (in the proportions 1 : 1 : 2). The molecules (XVe) and (XVf) have D_2 symmetry, i.e. three twofold axes, while the *meso*-form (XVg) has a fourfold inversion axis, and is thus optically inactive. When the reaction mixture contains both the *meso*-form and the *SS* and *RR* forms of the diol the isomers (XVc) and (XVd) may appear[48].

One of the *trans,trans*-forms of (XV) was isolated. The n.m.r. spectra did not distinguish whether this compound was a *trans-meso*-isomer (XVe) or (XVf), the racemate (XVe) + (XVf), or the *meso*-form (XVg). X-Ray structural analysis showed that the form of (XV) isolated was the *trans,trans-dl*-isomer (Fig. 10). Since the compound crystallised in the non-enantiomorphic space group $P2_1/a$, both optical antipodes (XVe) and (XVf) were present in the crystal[48].

IV. CYCLOLINEAR SILOXANES

The structure of cyclolinear organopolysiloxanes# (Fig. 11)[1] can be represented by various combinations of *cis*- and *trans*-linkings of tetrasiloxane rings. Structure (*b*), for example, has an alternation of *cis,trans,trans* linkages, whereas structure (*c*) has *trans,trans,trans*. From a study of the properties of solutions, X-ray powder data, and infrared spectra Brown[53] demonstrated the *cis*-syndiotactic structure of each $Si_{(1)}Si_{(2)}$... strand of the double chain of cyclolinear organopolysiloxanes corresponding to polymer (*c*), which is usually termed ladderlike. In such polymers, containing silsesquioxane fragments in a chain unit, every third silicon atom of each of the two chains repeats translationally the first (in structure (*b*) the first, fifth, ninth, etc. atoms are repeated).

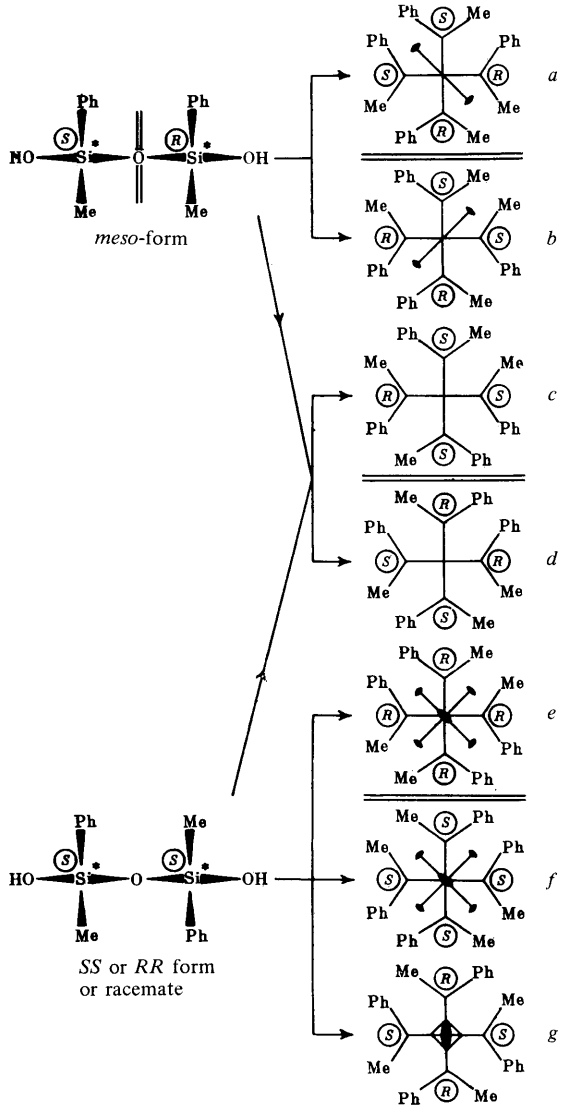


Figure 9. Possible stereoisomers of (XV). The molecules are shown diagrammatically (only substituents and their bonds with the ring, represented by a vertical or horizontal line) as a projection along the straight line passing through the spiro-atom and the two oxygen atoms most remote from it; *R* and *S* denote the configurations of the substituted silicon atoms. The symmetry elements of the molecules are indicated, as well as the mirror plane between the optical antipodes (by a pair of parallel lines).[48]

†Actually the reaction has been conducted only with the racemate of the diol.

#Such cyclolinear structures, in contrast to monocyclic structures, contain *T* units, and are usually termed silsesquioxanes.

Cyclolinear polyphenylsilsesquioxanes comprise semi-rigid macromolecules (persistent length§ 200–900 Å). The flexibility of such macromolecules is due to small fluctuations in torsional and bond angles, in contrast to flexible macromolecules (persistent length ~10–20 Å), e.g. polymethylphenylsiloxane, the mechanism of whose flexibility involves rotational isomerism[55].

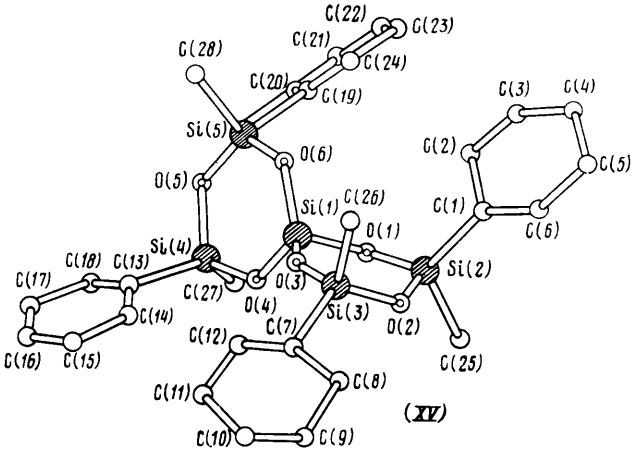
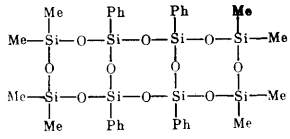
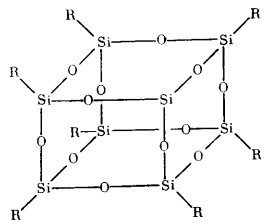


Figure 10. Structure of molecule (XV).[48]

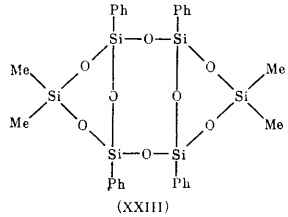
An important factor in the study of the preparation and properties of ladderlike organopolysiloxanes is their lowest oligomers, the octa(organosilsesquioxanes) $(RSiO_{1.5})_8$ (Fig. 11*d*), which are formed as by-products[56] and can also serve as starting materials for the synthesis of macromolecular polyorganosilsesquioxanes[57,58]. Table 4 gives data on the T_4 rings in the series of cyclolinear organocyclosiloxanes (XVIII)–(XXIII)



(XVIII)



(XIX), R = H; (XX), R = Me; (XXI), R = Ph; (XXII), R = C_2H_3



(XXIII)

The structure of (XVIII) is disordered[59,60]: silicon atoms 2, 3, 6, and 7, together with their methyl substituents, can each occupy two positions with approximately equal probability (Fig. 12). Passage from one position to the other can be effected by rotation of the dimethylsilylene group through an angle Ω about an axis passing through the oxygen atoms, whose positions remain unchanged. For the four dimethylsilylene groups the angle Ω has a mean value of 60°, which corresponds to displacement of the silicon atoms along an arc ~1.0 Å in length, while the attached methyl carbon atoms move ~3.0 Å.

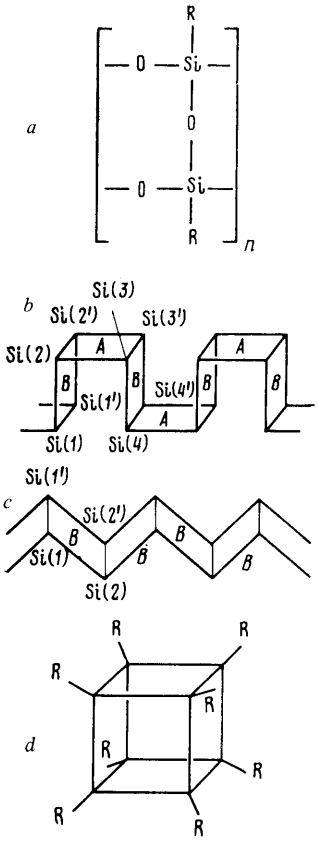


Figure 11. General formulae of: *a*) polyorganosilsesquioxane; *b*,*c*) two possible structures of a cyclolinear organopolysiloxane (a segment of a straight line corresponds to one tetrasiloxane ring; organic substituents are not shown); *d*) diagram of molecule of octa(silsesquioxane).[60]

§ This quantity characterises the rigidity of a polymer chain. A strict definition will be found in Ref. 54.

Of the sixteen possible conformations (on the assumption that the four dimethylsilylene groups can each occupy two positions independently of the others) fourteen are forbidden because they would involve short intramolecular contacts (denoted in Fig.12 by the symbol ↓‾↓) between methyl groups attached to different silicon atoms. Thus the molecule has only two energetically equivalent conformations of its silicon atoms, i.e. 1–2–3–4–8–7–6–5 and 1–2′–3′–4–8–7′–6′–5¶.

Table 4. Data on T_4 rings in structurally studied simple cyclolinear polysiloxanes (α = mean SiOSi bond angle; d = mean Si–O bond length; and Δ_{max} = maximum emergence of O atoms from plane of four Si atoms).

No.	α	d, Å	Symmetry of ring	Conformation of ring	Δ_{max}, Å	Ref.
(XVIII)	151.7 (3)°	1.609 (6)	S_4	saddle*	0.37	59,60
(XIX)	—	—	C_{4v}	crown	—	61
(XX)	145.3°	1.61	C_{4v}	crown	0.34	62
(XXI)	149.2 (4)°	1.614 (7)	C_{4v}	crown	0.30	63
(XXII)	150°	1.609	C_{4v}	crown	—	64
(XXIIIa)	127.5 (4)** 145.5 (4)°	1.618 (7)** 1.638 (7)	S_4	boat	0.72	65
(XXIIIb)	132.5	1.626 (6)	C_i	chair	0.56	104

*The four silicon atoms are almost coplanar.
**Relates to the SiOSi fragment common to the DT_2 and D_2T_2 rings.

In a free state (solution) the molecule (XVIII) may perform frequent transitions, under the influence of thermal vibrations, from one conformation to the other. This view is supported by the very prolate character and appropriate orientation of the ellipsoids representing the thermal vibrations of the atoms of disordered dimethylsilylene groups (Fig.12). Each conformational transition can be regarded as a simultaneous change in direction of twist of the two lateral D_2T_2 rings, which can be twisted only to one side in each of the permitted conformations.

The disorder of structure (XVIII) is interesting in connection with Brown's hypothesis on the condensation of cyclosiloxanes that identical functional groups attached to mobile portions of molecules, and therefore structurally non-equivalent, differ in reactivity[56]. The principle of equal reactivity of identical functional groups, on which the statistical theory of polycondensation is based, does not apply to such systems.

Fig.13 shows that, after initial formation of a dimer (*3*), condensation of the tetraol (*1*) can occur either intramolecularly to give (*4*) and (*5*) or intermolecularly in the sequence (*3*) → (*6*) → (*7*). The statistics of intermolecular vibrations, suggested as the decisive factor in intermolecular cyclisation[56], is probably less important in the present case owing to the relatively small number of degrees of freedom in each successive primary act of intermolecular condensation with formation of a polymeric cyclolinear structure, e.g. (*7*).

¶These conformations have intrinsic (non-crystallographic) symmetry C_2 and form a pair of optical antipodes.

If the compound differing from the tricyclic derivative (*3*) in the presence of methyl instead of phenyl groups in the lateral D_2T_2 rings is assumed to have the same type of disorder as the molecule (XVIII), the smaller steric interactions between substituents will result in preferential conversion of (*3*) into (*4*) instead of (*6*). This is explained by the shorter Si...Si distances, greater frequency of collisions (as shown by analysis of the thermal ellipsoids), and hence greater probability of chemical interaction along the lines $Si_{(2)}...Si_{(6)}$ (as well as $Si_{(2')}...Si_{(6')}$—Fig.12) and $Si_{(3)}...Si_{(7)}$ (and $Si_{(3')}...Si_{(7')}$) than along the lines $Si_{(2)}...Si_{(7)}$ (and $Si_{(2')}...Si_{(7')}$) and $Si_{(3)}...Si_{(6)}$ (and $Si_{(3')}...Si_{(6')}$), corresponding respectively to edges and two-dimensional diagonals of the silsesquioxane cube (Fig.13). The presence in compounds (*1*)–(*3*) of phenyl instead of methyl groups changes the mobility of the D_2T_2 rings and leads to greater probability of process (*3*) → (*6*) than of (*3*) → (*4*), i.e. to formation of a polymer of high molecular weight (the yields of the products are indicated in Fig.13).

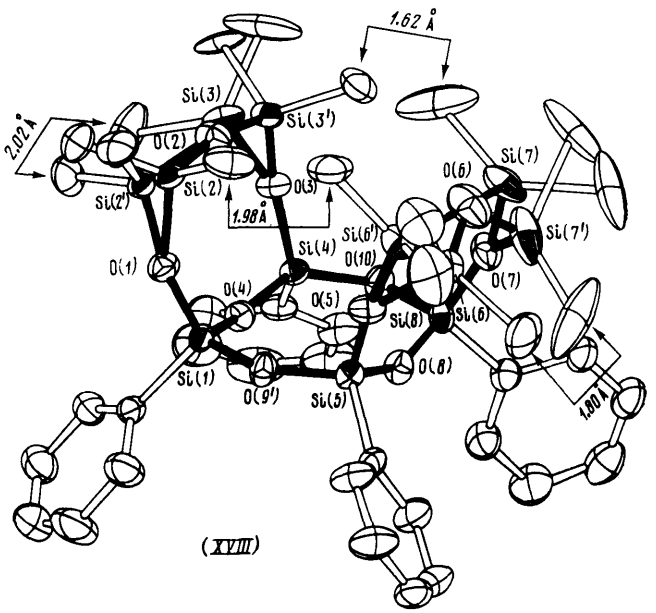


Figure 12. Structure of (XVIII) molecule[60] (explanation in text).

Neither of the "structurally" confirmed mechanisms of the deformation of tetrasiloxane rings [rotation of diatomic Si–O fragments or twisting of triatomic fragments in (XVIII)] explains the conformational transition (*a*) → (*b*) of T_4 rings (Fig.14 and Table 4). On the other hand, both mechanisms revealed for D_4 rings or the D portions of D_2T_2 rings, i.e. for siloxanes, involve the displacement of substituted silicon atoms, which is difficult to envisage in the more rigid silsesquioxanes. Conformational rearrangements probably have different mechanisms in D_4 and in T_4 rings. The conformational transitions of T_4 rings can be represented as the displacement of two *trans*-oxygen atoms. Such a mechanism of the conformational transition $S_4 \rightarrow C_{4v}$ had been suggested earlier (though in D_4 rings) in a spectroscopic paper[21].

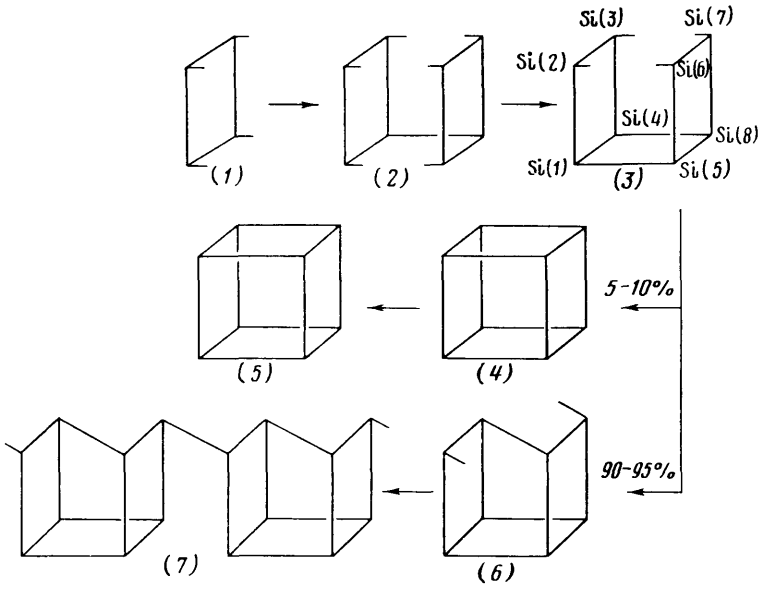


Figure 13. Scheme of condensation[56] of the tetraol (*1*) (tetraphenylcyclotetrasiloxanetetraol) via the tricyclic compound (*3*) into an octa(silsesquioxane) (*5*) and via the tetracyclic compound (*6*) into a poly(silsesquioxane) (*7*). The structures of (*3*) and (*5*) have been confirmed by X-ray examination[60,63]. Products (*4*) and (*6*) can exist as epimers with a different orientation of hydroxy-groups.

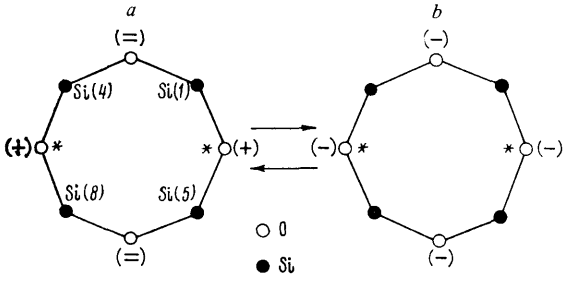


Figure 14. Scheme illustrating the differences and interrelationship between conformations of T_4 rings in the molecules: *a*) (XVIII), approximate symmetry S_4; *b*) (XXI), C_{4v}.[60] For simplicity the silicon atoms are shown in (XVIII) as lying in the same plane; the symbols (+), (−), and (=) indicate the positions of oxygen atoms above, and below, and in this plane. Asterisks denote oxygen atoms whose movements are perpendicular to the plane of the diagram and essentially determine the transitions (*a*) ⇌ (*b*). The silicon atoms are numbered in conformity with Fig. 12.

The two conformers of (XVIII) are characterised by closely similar dihedral angles of deflection of the planes of the lateral D_2T_2 eight-membered rings from that of the central T_4 ring (on the average 108°). As was to be expected, the silicon–oxygen bonds are shorter in silsesquioxane *T* units than in siloxane *D* units (on the average 1.606(3) and 1.621(6) Å respectively). Yet the difference in the mean silicon–oxygen bond lengths in T_4 and D_2T_2 rings is small (respectively 1.609(3) and 1.614(6) Å), just like the difference in mean SiOSi bond angles in these rings (151.7(2)° and 148.1(3)°).

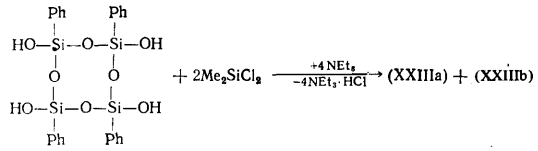
Since the conformation of the siloxane ring (infrared spectra[66]) remains unchanged when the polymer chain is extended, the parameters (bond lengths and angles) of the T_4 ring are probably maintained even in the corresponding cyclolinear polymer.

Conformational analysis has been used to determine the most probable angular parameters for *cis*-syndiotactic poly(phenylsilsesquioxane)[67]. The SiOSi angles in the "strand" (along an infinite polysiloxane chain) are 145–150°, rather smaller than the 155–170° in the "binder" (the cross-link between the polysiloxane chains). Experimental X-ray structural data[60] indicate that in the T_4 ring of (XVIII) the SiOSi angles are also somewhat smaller in the strand than in the binder (on the average 148.7° and 154.7° respectively).

As a consequence of the inductive effect the addition of aromatic substituents to the silsesquioxane cube [conversion of (XIX) and (XX) into (XXI)] strengthens appreciably the π interaction, which is apparent in an increase in the SiOSi angles in (XXI) and also in a "flattening" of the T_4 rings forming the cube (the mean emergence of the T_4 cyclic oxygen atoms from the plane through the four silicon atoms is respectively 0.34 and 0.30 Å in (XX) and in (XXI)—Table 4). This "flattening" should diminish the dipole moment of the T_4 ring and enhance d_π–p_π interaction in the silicon–oxygen bonds, but the lengths of the latter are closely similar in the T_4 rings in (XX) and in (XXI) (Table 4).

Passage from (XX) to (XXI) should be accompanied by a decrease in stability of the silsesquioxane skeleton towards radical reagents and an increase towards ionic reagents, as well as an enhancement of thermal stability. This is important in the choice of conditions for the polymerisation of octa(organosilsesquioxanes).

Compound (XXIII) is a cyclolinear oligosiloxane containing DT_2 as well as T_4 rings. Its preparation involves the isolation[65] of two products—(XXIIIa) and (XXIIIb)—differing in yield, melting point (respectively 162–163 and 222–223 °C), solubility, and physical properties:



Data have been published on (XXIIIa),[56,68,69] but (XXIIIb) has been isolated for the first time. A conformational difference is assumed between them. X-Ray examination indicates that (XXIIIa) is a *cis*-isomer of the D_2T_4 tricyclic system, and (XXIIIb) a *trans*-isomer (Fig.15).

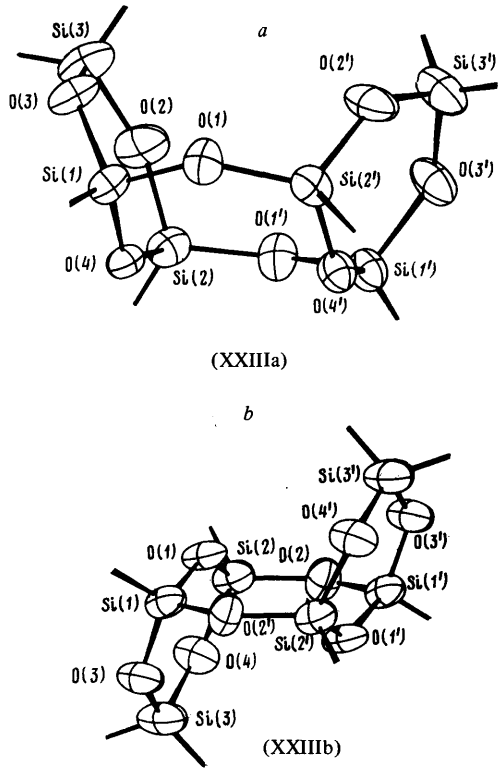


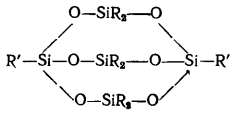
Figure 15. Structures of D_2T_4 tricyclic siloxane systems (Table 4) in the molecules: *a*) (XXIIIa)[65]; *b*) (XXIIIb).

The structure of (XXIIIa)† is characterised by "anomalous" parameters of its tetrasiloxane and trisiloxane (T_4 and DT_2) rings (Fig.15): (i) the $Si_{(1)}O_{(4)}Si_{(2)}$ and $Si_{(1')}O_{(4')}Si_{(2')}$ bond angles are 127.5°, unusually small for tetrasiloxanes (cf. Tables 2 and 4), so that the T_4 ring in (XXIIIa) is considerably more strongly deformed than, for example, the T_4 ring in (XVIII), which has a similar chemical environment and the same symmetry S_4 (Table 4); and (ii) steric interaction of methyl groups attached to $Si_{(3)}$ and $Si_{(3')}$ (C...C distance 3.713 Å) leads to deformation of the DT_2 rings (departure of the cyclic atoms from their mean planes reaches 0.33 Å–cf. D_3 rings in Table 1). Furthermore, as a consequence of this steric interaction the angle of deflection of the lateral DT_2 rings in (XXIIIa) from the central ring (115°) exceeds that in (XVIII) (108°); the ideal symmetry C_{2v} of the tricyclic siloxane system in (XXIIIa) degenerates to C_2.[65]

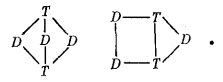
In the *trans*-isomer (XXIIIb), the molecule is located at a centre of symmetry in the crystal, the lateral DT_2 rings have a more planar structure than in (XXIIIa) (departure of the atoms from the plane of these rings does not exceed 0.1 Å), and they conform approximately to C_{3v} symmetry. The eight-membered T_4 ring has a general chair conformation (symmetry C_i); the atoms $Si_{(1)}$ and $Si_{(1')}$ deviate by ±0.56 Å on opposite sides of the general plane of the ring. The SiOSi bond angles in the T_4 ring of (XXXIIIb) have a mean value of 132.5°, markedly smaller (by ~10°) than in other derivatives of eight-membered siloxane rings (Tables 2 and 4). The dihedral angle between the planes of DT_2 and T_4 rings is 82.4°.

V. OTHER POLYCYCLIC SILOXANES

Structures have been determined for two bicyclo[3,3,3]pentasiloxane D_3T_2 derivatives



(in (XXIV) R = C_6H_5 and R' = CH_2.CH (Fig.16)[70]; in (XXV) R = R' = CH_3 (Fig.17)[71]) obtained in different ways. Whereas the structure (XXIV) alone is possible for the D_3T_2 product of the reaction between vinyltrichlorosilane and diphenylsilanediol[72], the D_3T_2 product of the thermal decomposition of branched polydimethylsiloxanes may have the two structures[71]



However, X-ray examination indicates that the two products have the same siloxane skeleton. These molecules are characterised by a non-crystallographic threefold axis passing through the silsesquioxane silicon atoms, but the silicon–oxygen skeleton has the overall non-crystallographic symmetry $\bar{6}2m$.

The three tetrasiloxane D_2T_2 rings in (XXIV) and (XXV) exhibit considerably greater "non-planarity" than do D_4 and T_4 rings. For example, in (XXIV) the mean dihedral angle between tetratomic fragments of D_2T_2 rings is 44° (in D_4 rings it is 27.5–40.2°, Table 2). As a consequence the mean SiOSi angle is 14°, smaller than in D_4 rings (142.5–149°). The considerable deformation of D_2T_2 rings in (XXIV) prevents development of their silsesquioxane nature, i.e. strengthening of silicon–oxygen bonds; the mean silicon–oxygen distance in (XXIV) is 1.63 Å, but no differences in length are observed between siloxane and silsesquioxane bonds[70].

Because of the smaller bulk of the substituents the D_2T_2 rings are less deformed in (XXV) than in (XXIV), but the mean SiOSi angle (145.6°) corresponds to this value in the D_4 rings, while being smaller than the SiOSi angles in T_4 rings. The silicon–oxygen distance (1.618 Å) is close to those found in T_4 rings (above). Yet the non-bonded diagonal Si...Si distances in (XXIV) and (XXV) are closely similar. Diagonals of type $Si_{(3)}...Si_{(5)}$ in (XXIV) (Fig.16) and of type $Si_{(2)}...Si_{(4)}$

†The molecule is located on a twofold axis.

in (XXV) (Fig.17) are respectively 4.21–4.26 and 4.236–4.256 Å, while the Si...Si distances along non-crystallographic threefold axes in (XXIV) and (XXV) ($Si_{(1)}...Si_{(2)}$ in Fig.16 and $Si_{(1)}...Si_{(3)}$ in Fig.17) are 3.71 and 3.76 Å. Thus a silicon–oxygen "skylight" of this type is "compressed" along an approximate threefold axis.

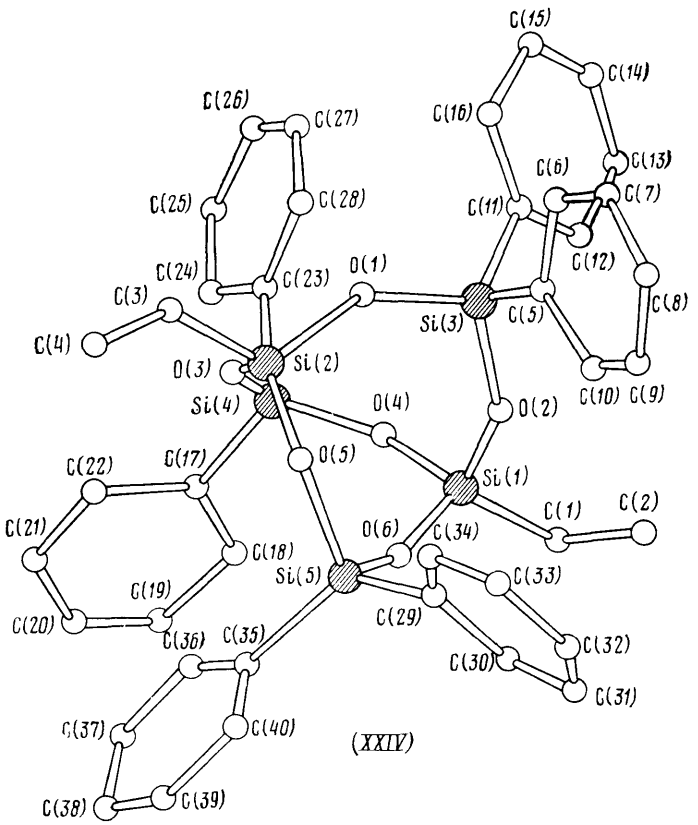


Figure 16. Structure of molecule (XXIV).[70]

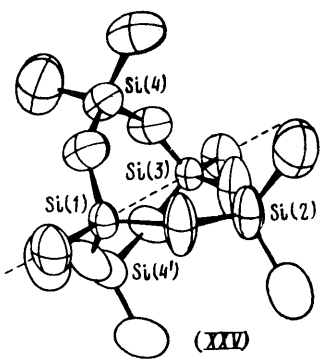


Figure 17. Structure of molecule (XXV).[71] The broken line shows the approximate threefold axis.

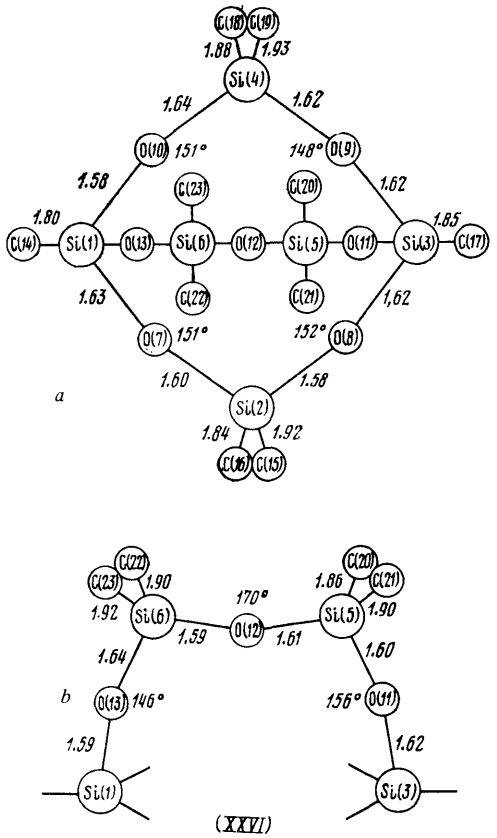
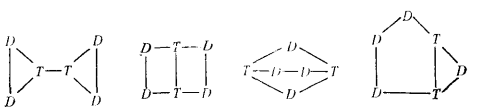


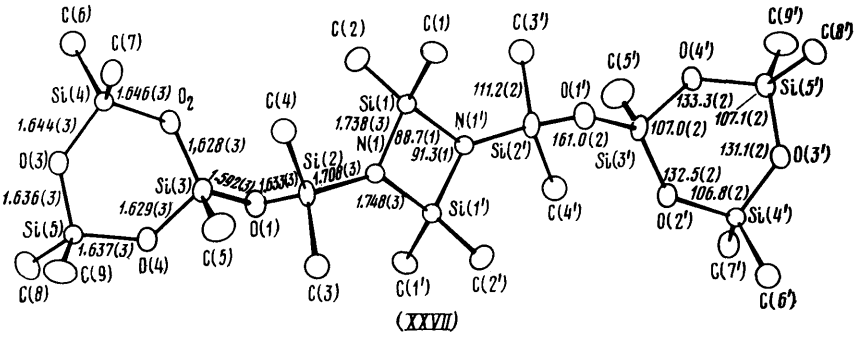
Figure 18. Structure of: *a*) molecule (XXVI); *b*) "semicircle".[73]

The thermal decomposition of branched polydimethylsiloxanes has led to the chromatographic isolation of three products (*a*)–(*c*) having the configuration D_4T_2, for which the structures



are possible[8]. X-Ray examination of one of the products has confirmed the suggested structure (*c*), i.e. (XXVI) in Fig.18.[73] In the molecule with approximate C_{2v} symmetry one D_2T_2 tetrasiloxane ring and two D_3T_2 pentasiloxane rings can be distinguished. The D_2T_2 ring has approximate D_{2d} symmetry (saddle conformation), with the atoms emerging rather less (up to 0.30 Å) from the plane of this eight-membered ring than in isolated D_4 rings, e.g. 0.49 Å in (XI). The atoms forming the "semicircle" $Si_{(1)}O_{(13)}Si_{(6)}O_{(12)}Si_{(5)}O_{(11)}.Si_{(3)}$ lie to within 0.13 Å in the same plane, which is approximately perpendicular (dihedral angle 84.9°) to the mean plane of the D_2T_2 ring. The planarity of the "semicircle" $Si_{(1)}...Si_{(3)}$ and also the unexpectedly large SiOSi bond angle (170°) at the $O_{(12)}$ atom are the most interesting stereochemical features of the molecule (XXVI).[73]

The molecule (XXVII) (Fig.19) represents a completely different type of polycyclic organosiloxane[74]. It is located at a centre of symmetry and contains two D_2T rings joined by an extended siloxazane bridge. In a D_2T ring the mean



(XXVII)

Figure 19. Structure of molecule (XXVII).[74]

silicon–oxygen distance in the *T* unit 1.628(3) Å is shorter than in the *D* units (on the average 1.641(3) Å) or in D_3 rings (Table 1). The maximum departure of atoms from the plane of the D_2T rings (0.08 Å) is of the same order as in D_3 rings. The bond lengths and angles (Fig.19) indicate an interesting strengthening of the linear bonding between siloxane and silazane rings due to intensified p_π–d_π interaction particularly in these parts of the molecule. Hence these siloxazane bridges should be not only the most stable energetically but also the most resistant to the action of ionic reagents. The silazane ring in (XXVII) has the usual geometry#.

VI. CRYSTALLINE STRUCTURE OF ORGANOCYCLOSILOXANES

Crystals of organosiloxanes usually have loose packing and weak intermolecular interaction[51]. Nevertheless, the some thirty crystalline structures known for organosiloxanes include several non-trivial examples related to the stereochemical peculiarities of such compounds and important from the point of view of their practical application.

In a crystal comprising conformationally disordered molecules of (XVIII) the methyl groups of identical§ conformers, the molecules of which are related by the translation *c* and also a centre of symmetry at ½,½,0, are separated by C...C distances of 3.58 (translation *c*), 3.52, 3.52, and 3.64 Å (centre at ½,½,0).[60]

The van der Waals radius of the methyl group is generally assumed to be ~2 Å.[9,75] However, in a crystal of *DL*-*N*-chloroacetalanine[76], for example, with a $C(CH_3)...C(CH_3)$ distance of 3.72 Å between molecules related by centres of symmetry, the H...H distances (the hydrogen atoms have been identified objectively) between these methyl groups are 2.88 Å, i.e. ~0.5 Å greater than double the van der Waals radius of the hydrogen atom[77]. If it is supposed that, with the shortened $C(CH_3)...C(CH_3)$ distances found in a crystal of (XVIII), orientations of the methyl groups are possible for which the H...H and C...H distances are not shortened, a random distribution of conformers of (XVIII) may occur in the crystal: i.e. both identical and different conformers may be neighbours. If, however, such orientations are impossible, some of the intermolecular contacts between identical conformers are forbidden. Unfortunately, X-ray structural analysis has not yet answered the question of the possible juxtaposition of conformers of the same or different types, or indicated the character of the disorder (statistical or dynamic) in a crystal of (XVIII). This requires investigations at low temperatures with location of the hydrogen atoms.

Two problems in organic crystal chemistry—the crystallisation of molecules with porous packing and the chemical interaction of molecules densely packed in a crystal—have special significance for crystals of organocyclosiloxanes. In a crystal of (XXI) cavities of volume ~150 Å³¶ have been observed around symmetry centres 0,½,0 (Fig.20). Clearly, the shape of molecules of (XXI) permits only two-dimensional dense packing: compact superposition of layers is impossible, and the above cavities, which may be filled with small solvent molecules, appear in the crystal. Indeed, differential synthesis of electron density has revealed in the cavities several peaks of electron density corresponding to disordered small molecules of solvents used in preparation and crystallisation[63].

The high temperature factors for atoms present in a solvent molecule are consistent with results obtained for clathrates. For example, the atoms of the dioxan molecules in the clathrate complex $Cd(NH_3)_2.Ni(CN)_4.2C_4H_8O_2$ have isotropic temperature factors of 23 and 14 Å².[78] The volume of a cavity considerably exceeds the molecular volume[80] of the solvents used in the preparation of (XXI) (pyridine 91 Å³, *o*-dichlorobenzene 100 Å³)†, so that the packing coefficient in the cavities is low ($k \approx 0.63$). Then, of course, the (XXI)...Solv intermolecular distances exceed the sum of the van der Waals radii. This explains the possible disorder in the arrangement of solvent molecules in the cavities[63]. When the occluded solvent molecules are taken into account, good agreement is obtained between calculated and measured densities of a crystal of (XXI). If, however, the occupation of the cavities is ignored, the calculated value is smaller than the measured density (1.29 and 1.34 g cm^{-3}), as for the second (not studied structurally) monoclinic modification[79].

#We intend to survey the structure of cyclosilazanes in a subsequent review.

§Corresponding distances between different conformers are considerably longer than 3.8 Å.

¶This quantity has been determined by means of a special programme of search for the positions and volumes of cavities in a crystal, established by L.M.Borisanova (Faculty of Chemistry, Moscow State University, 1976).

†Molecular volumes were calculated from the contributions by atomic groupings[80].

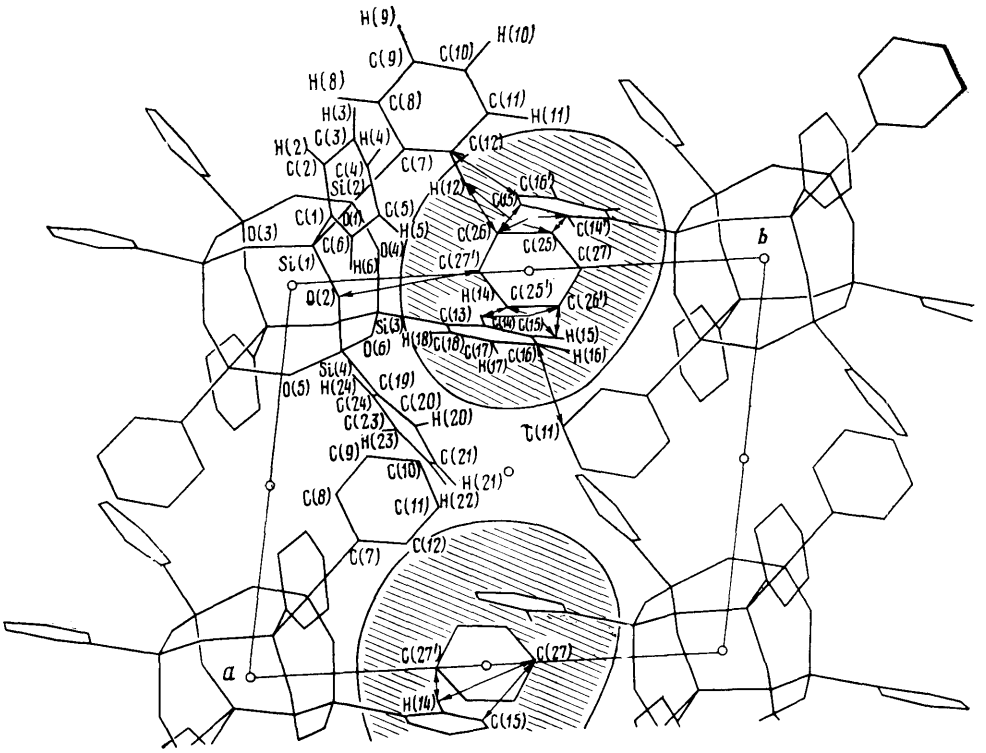


Figure 20. Projection [001] of structure (XXI). The arrows show distances between (XXI) and solvent molecules. Cross-sections of the cavities made by the plane of projection are shaded[63].

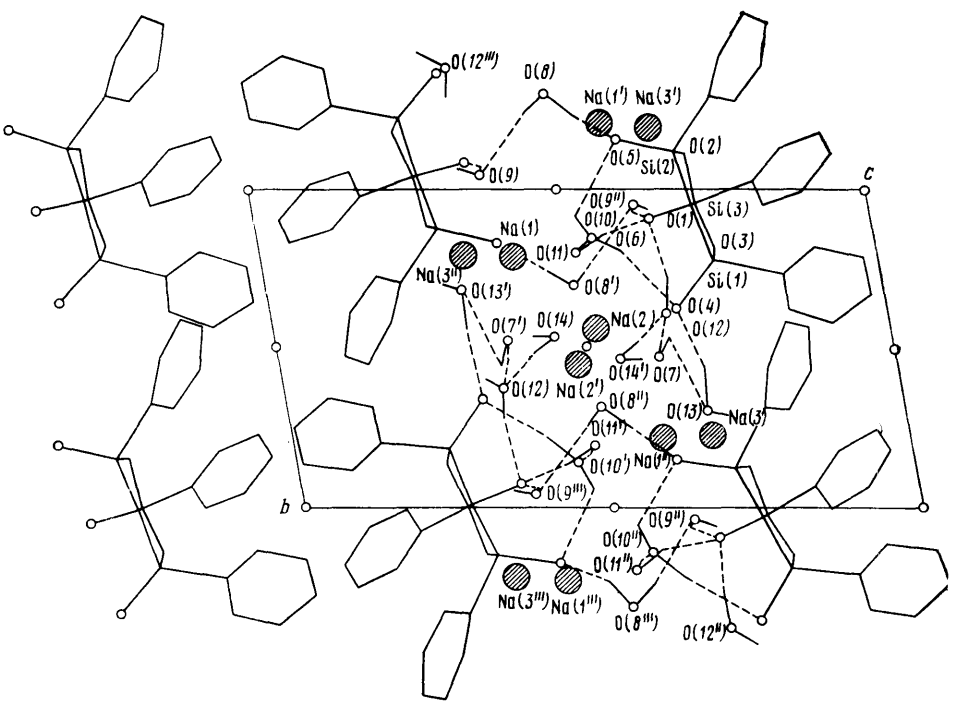


Figure 21. Projection on the face *bc* of the packing of molecules in a crystal of (V). Hydrogen bonds O–H...O are shown by broken lines[105].

Molecules of (XVII) also crystallise with porous packing. Centres of symmetry $0,\frac{1}{2},0$ (the crystals belong to space group $P\bar{1}$) are located in cavities filled with solvent (benzene) molecules. As with crystals of (XXI), the volume of a cavity exceeds that of a benzene molecule, so that the latter is slightly "disordered", which is evident in somewhat increased isotropic temperature factors (~50% larger than for phenyl substituents in the (XVII) molecule).[50]

Among all the crystalline structures of organosiloxanes investigated (around thirty have been determined) voids have been found only in crystals of (XVII) and XXI), which differ from other organocyclosiloxanes in a rigid silicon–oxygen skeleton and from siloxanes having such a skeleton [e.g. from the methyl derivative (XX)] in the presence of bulky phenyl substituents. These latter, by sharply increasing distances between siloxane skeletons, diminish the polar interaction inherent in, for example, crystals of octa(silsesquioxanes) with small substituents[61], as well as promoting the formation of cavities in the crystal.

The ability of several large skeletal siloxane molecules with bulky framing groups to pack with the formation of cavities acquires special interest in the light of the specific gas-permeability of certain cyclolinear organosiloxanes, which has found practical application[81–83]. Although the character of the system of cavities in crystals of (XXI) excludes the possibility of migration of even the simplest molecules from one cavity to another, it may be expected in principle that, by varying the substituents, we shall be able to obtain monolayers or double layers (and perhaps even three-dimensional structures) possessing the necessary permeability.

Many chemical reactions of siloxanes involve intermediate ionic structures. Interest therefore attaches to the results of the first X-ray structural investigation of the ionic sodium salt (V) of a siloxane[13]. The siloxane rings of the anions form layers parallel to the plane *ab*. The gaps between the layers are filled alternately with phenyl groups of the anions (van der Waals interaction between layers) and with sodium cations and water molecules (ionic interaction and hydrogen bonds) (Fig. 21). Interlayer spaces of the second type are characterised by strong electrostatic interaction, which is not found in ordinary molecular crystals of organosiloxanes. The coordination of the sodium ions and their distribution relative to charged fragments of the anion in a crystal of (V) are important for understanding the initial stages in the reactions of organosiloxanes in hydrophilic alkaline media.

Chemical reactions (including polymerisation) of molecules densely packed in a crystal have begun to be studied relatively recently. Several important papers on the crystal chemistry of these processes have been cited in a review[84]. A necessary condition for the occurrence of topochemical solid-phase reactions is that shifts in the equilibrium positions of atoms in the reactant molecules should be minimal with fairly intense vibrational thermal motion of the atoms. This is the fundamental principle of lattice-controlled reactions formulated

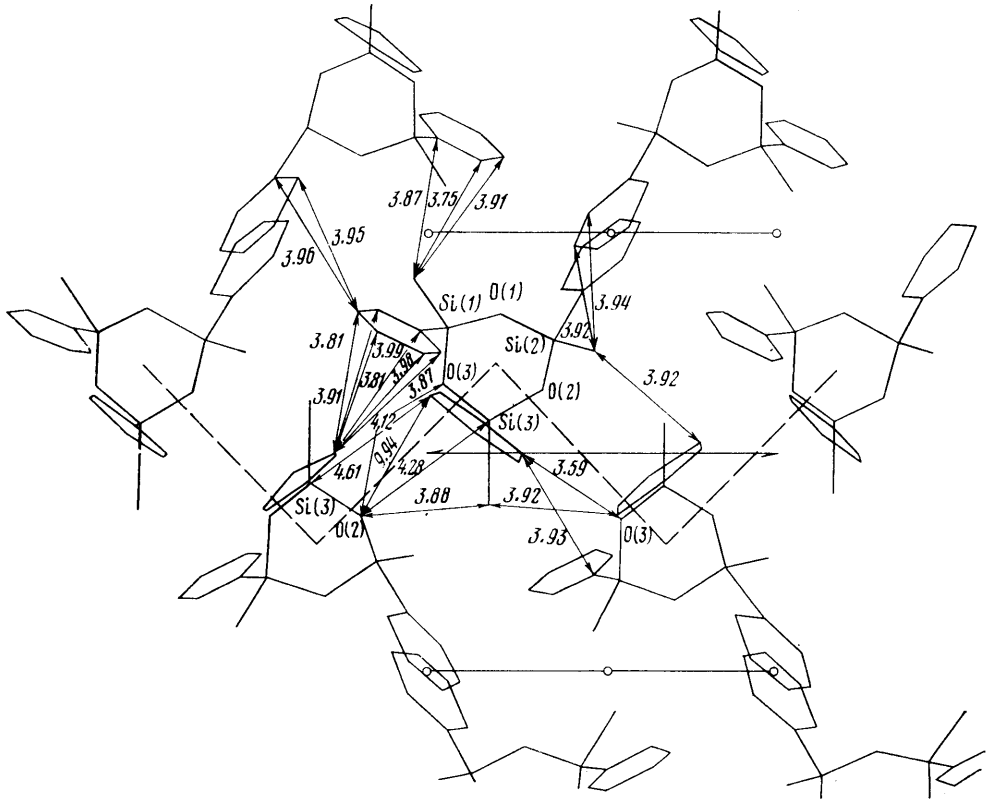


Figure 22. Arrangement of molecules in a layer in structure (IV). The broken lines join centres of D_3 rings in molecules forming chains. The numerals indicate intermolecular distances[12].

by Schmidt[85,86]. In application to solid-phase polymerisation this principle was formulated by Kargin and Kabanov[87].

Derivatives of D_3 rings—(I), (III), and (IV)— are capable of solid-phase polymerisation at room temperature or above in the presence of potassium trimethylsilanolate as initiator[88]. X-Ray examination of compounds (I)–(IV)[9–12] has led to several interesting conclusions on the possibility and the mechanism of the polymerisation of D_3 derivatives in the solid phase. Unfortunately, in contrast to, for instance, oligomers of formaldehyde, for which a molecular mechanism of polymerisation is based on numerous experimental confirmations of the formation of an oriented crystalline polyoxymethylene[89–91,84], results on the formation of ordered polysiloxanes by solid-phase polymerisation have not yet been obtained. Therefore discussion of the mechanism of the solid-phase polymerisation of siloxanes is tentative in character.

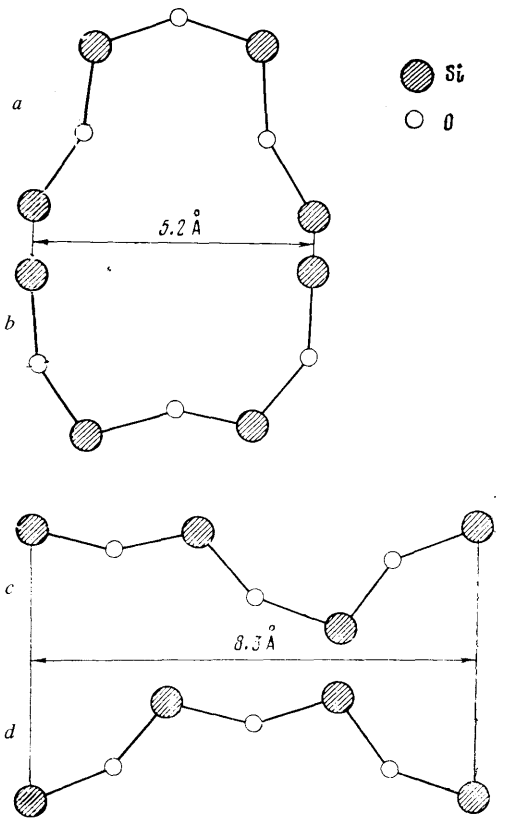


Figure 23. Some possible conformations of a planar monomeric unit in a polysiloxane chain: *a*) *trans,cis,cis,trans*; *b*) *cis,trans,trans,cis* ("shortest" units); *c*) *trans,trans,cis, trans*; *d*) *trans,trans,trans,trans* ("longest" units)[11,12].

In a crystal of (IV)[12] layers of molecules can be clearly distinguished, whose siloxane rings are very accurately coplanar. These layers have an interplanar spacing of 9.52 Å and are parallel to the $(1\bar{2}0)$ face. Fig.22 shows that a layer in turn contains distinct chains of molecules connected by a screw axis lying in the plane of the layer (e.g. 2_1 [$\frac{1}{2}$ $\frac{1}{4}$ z]). Within the layers the distances between silicon and oxygen atoms of neighbouring molecules in the same chain (4.28 and 4.61 Å) are appreciably shorter than the distances between chains (5.46 and 5.63 Å).

The structure of (III)[11] also contains distinct layers of molecules, parallel to the (100) face, but in contrast to (IV) the planes of the D_3 rings are non-coplanar, forming an angle of 27.5° with the plane of the layer. The Si...O distances between the rings of molecules in a layer are 5.46–7.54 Å (no well defined chains present), and those between rings in molecules of neighbouring layers ~9 Å.

In a crystal of (I) the molecules have a disordered distribution, which indicates that their number in a cell is anomalous (space group $R3m$, $z = 1$) with strong diffuse scattering on the X-ray photographs[9]. Layers having $z = 0$, $\frac{1}{3}$, and $\frac{2}{3}$ prove to be identical but displaced statistically one relative to the other along $\mathbf{a}\sqrt{3}/3$ vectors. In the layers the Si...O distances between the initial and each of the six neighbouring siloxane rings have been determined as 4.62 Å; the distance between layers is 6.4 Å.[9]

The packing of molecules of (II), which does not polymerise in the solid state[10], exhibits the following features: (i) all distances between atoms of siloxane rings in neighbouring molecules exceed 7 Å; (ii) although shorter intermolecular contacts are present in the structure of (II) than in that of (IV), they are all effected by atoms of the framing phenyl substituents (only one short C...O contact, of 3.38 Å, is present); (iii) the phenyl groups are so oriented that they shield siloxane rings in neighbouring molecules from each other; and (iv) the coplanar arrangement of D_3 rings in neighbouring molecules characteristic of the structure of (IV) is not observed in the crystal.

A layered distribution of D_3 rings, which in all cyclotrisiloxanes[9–12] have a somewhat strained planar configuration, is especially significant. Indeed, with such an arrangement the framing substituents are distributed between the layers and do not prevent interaction of siloxane rings within layers during polymerisation, which is especially important with such bulky substituents as phenyl. Thus a layered arrangement of D_3 rings favours the solid-phase polymerisation of an organocyclotrisiloxane monomer. Therefore compound (II), for example, whose crystals do not have a layer structure, does not polymerise in the solid phase. Consequently the scheme of polymerisation of cyclic monomers[92], suggested in particular for (I), according to which molecules are arranged in stacks in a crystal of the monomer, and polymerisation occurs with ring opening and formation of extended helices of a crystalline polymer, does not apply to D_3 rings.

The possibility of the polymerisation of a cyclic monomer in a given crystallographic direction can sometimes be assessed by comparing the distance between neighbouring rings in this direction with the length of a unit formed topochemically on opening of the rings. In view of the inevitable increase# in SiOSi angles from 132° to ~160° when a D_3 ring is opened, the resulting polysiloxane chain acquires a planar conformation, and the length of a unit in this chain, formed from a single ring, will vary from ~5.2 Å (*trans,cis, cis,trans*- or *cis,trans,trans,cis*-conformation) to ~8.3 Å (*trans,trans,cis,trans*- or *trans,trans,trans,trans*-conformation) (Fig.23). The distances between centres of siloxane rings corresponding to these limits are (*a*) in structure (IV)[12] respectively ~6.9 and ~8.1 Å between neighbouring molecules

#Since the SiOSi angles in D_3 rings are considerably smaller (~130°) than those in siloxanes with a large number of units, where these angles vary between 140° and 160°, polymerisation with ring opening should be accompanied by an increase in the angles.

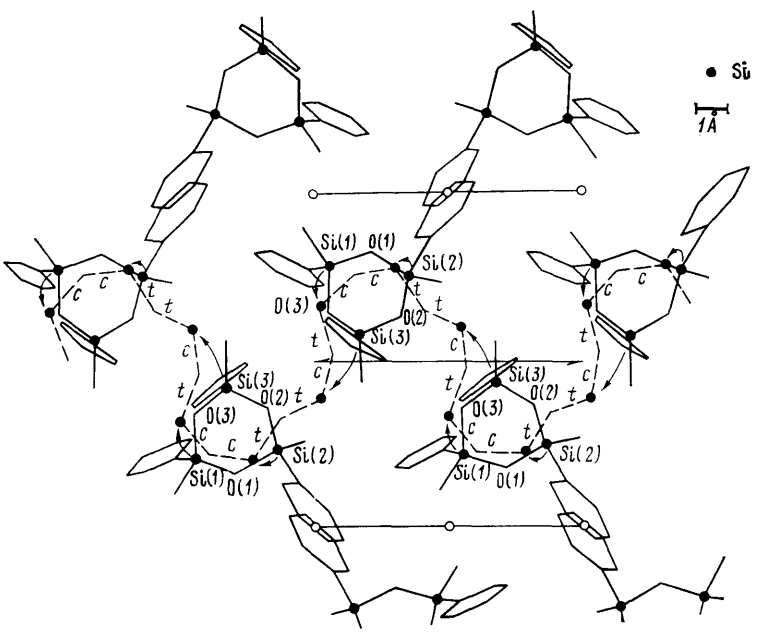


Figure 24. A layer in structure (IV). The broken line shows a planar polysiloxane chain which may be formed on the cleavage of rings at $Si_{(3)}-O_{(2)}$ bonds and the closure of $Si_{(3')}-O_{(2')}$ intermonomer bonds at the sites of the shortest intermolecular Si...O contacts (the arrows indicate the displacement of atoms on polymerisation). The letters *c* and *t* denote units in the polymer chain having *cis* and *trans* conformations respectively. The polymer chain formed has a *cis,cis,trans, trans,cis,trans* conformation of the monomeric unit[11,12].

in the chain and between molecules of neighbouring chains in the same layer related by centres of symmetry 0,0,0, (*b*) in structure (III)[11] ~8.6 and ~8.5 Å between molecules in the same layer related by translations *b* and *c*§, and (*c*) in structure (I) respectively ~7.6 and ~6.4 Å between neighbouring molecules in a layer and between molecules in neighbouring layers¶. The OSiO bond angles in mono- and poly-organosiloxanes are approximately constant and differ from the tetrahedral angle (109.5°) by at most 2–3°.

In relation to the solid-phase polymerisation of (IV) the main condition of topochemical polymerisation (retention by most atoms of their approximate positions during polymerisation[84]) leads to the requirement of maximum similarity of the configuration of the resulting polymer chain to that of the siloxane rings of the monomer. Fig. 24 shows that this requirement is met by a *cis,cis,trans,trans,cis,trans*-conformation of the monomeric unit in a polymeric chain constructed by changes in the SiOSi bond angles with the OSiO angles constant. It must be emphasised that this polymer chain is formed by opening the rings at the $Si_{(3)}-O_{(2)}$ bonds, which in a crystal of (IV) corresponds to the shortest intermolecular distance $Si_{(3)}...O_{(2')}$ (4.28 Å) of all the Si...O distances in the chain of molecules. Thus the suggested scheme of formation of the polymer chain satisfies both the condition of topochemical polymerisation and the condition of closest spatial proximity of chemically interacting atoms. It should lead to considerable compression of the crystal in the direction of the polymer chain. Actually the distance between the centres of siloxane rings in adjacent monomeric molecules in the chain is 6.9 Å, while the length of a unit in the resulting polymer chain (i.e. the distance between the centres of gravity of the trios of silicon atoms from one former ring) is ~5.9 Å.[11,12]

Thus analysis of the packing shows that the distances between the centres of neighbouring siloxane rings in structural layers of (I), (III), and (IV) probably permit chemical interaction of the rings with formation of polymer chains. The structure of (IV) is more favourable to the propagation of polymerisation in chains of molecules, which may lead (with a topochemical mechanism) to formation of an oriented polymer. In a crystal of (III) polymerisation in layers is most likely, while the direction of chain growth within a layer may vary, with formation of different macrocycles D_n. In contrast to a crystal of (IV), polymerisation in layers in (I) and (III) requires considerable three-dimensional rearrangement in the crystals of these monomers.

With regard to a possible mechanism for the initiation of polymerisation it is reasonable to assume[11,12] that deposition of the initiator on crystal faces parallel to the planes of layers of siloxane rings in crystals of (I), (III), and (IV), i.e. respectively on the faces (001), (100), and ($1\bar{2}0$), would lead to rapid two-dimensional polymerisation in these planes, leaving deep-seated portions of the crystal unaffected. Deposition of the initiator on faces perpendicular to the layer planes, however, will lead to development of polymerisation

§ A difference of ~0.3 Å from the upper limit is insignificant and "surmountable" by the thermal motion of the atoms at ordinary temperatures[80].

¶ The absence from a crystal of (I) of preferred directions (in the chain and in the layer) is consistent with the formation of an amorphous polymer by its solid-phase polymerisation[88].

in all densely packed layers of molecules, i.e. to the spread of polymerisation throughout the crystal†.

In a crystal of (XXVII) the D_2T rings in chains of molecules related by centres of symmetry $0,\frac{1}{2},\frac{1}{2}$ are significantly closer together (Fig.25). The $Si_{(4)}...O_{(3')}$ and $Si_{(4')}...O_{(3)}$ distances between these molecules are 4.12 Å, considerably less than any other Si...O intermolecular distance, the shortest of which is 5.46 Å. The layers are situated in $(01\bar{1})$ planes. The Si...O distances between D_2T rings in different layers exceed 7 Å.[74,94] The question arises whether the localisation of deformation of D_2T rings in the structure of (XXVII) and the relative weakening of $Si_{(4)}-O_{(3)}$ bonds are not caused by the observed closer approach of these particular parts of neighbouring molecules in the crystal. Such approach is probably due to electrostatic interaction of the antiparallel $Si_{(4)}-O_{(3)}$ and $Si_{(4')}-O_{(3')}$ dipoles.

It must then be ascertained whether such specific interaction of the molecules in the crystal does not affect the mechanism of polymerisation. If solid-phase polymerisation of (XXVII) is possible, this intermolecular interaction may lead to a polymer having a cyclolinear structure of alternating disilazane and D_4T_2 rings joined by trimeric siloxazane bridges with the polymer chain extended along the [011] direction of the monomer crystal (Fig.25).[94]

It follows from the crystal and molecular structure of (XXVII) that, if local attack by a nucleophilic species (with substantial initiation of solid-phase polymerisation) takes place at silicon–oxygen bonds in D units of the cyclic portion of a molecule located on the crystal surface, leading to cleavage of the siloxane ring and migration of the active centre to the oxygen atom, then rupture of a silicon–oxygen bond in an adjacent molecule (related to the initial centre of symmetry $0,\frac{1}{2},\frac{1}{2}$) should be facilitated. However, further transfer of the active centre to the other end of the molecule is impossible because of its great length, and all other distances between rings in the crystal are too large for topochemical interaction. "Chemical" intermolecular interactions other than the above interaction of D units are possible only in lattice defects.

In fact[74] solid-phase polymerisation in the presence of an ammonium catalyst involves 6–7% formation of an insoluble product, but >90% of the initial compound remains unchanged. In benzene solution at the same temperature (~50 °C) a polymer of predominantly network structure is formed together with a gel fraction (62%). Polymerisation goes similarly in the melt at higher temperatures#.

A crystal of (XXIV) contains infinite chains of molecules in contact at their vinyl side-chains with C...C distances of ~4 Å (Fig.26).[70] At such distances molecules are able to

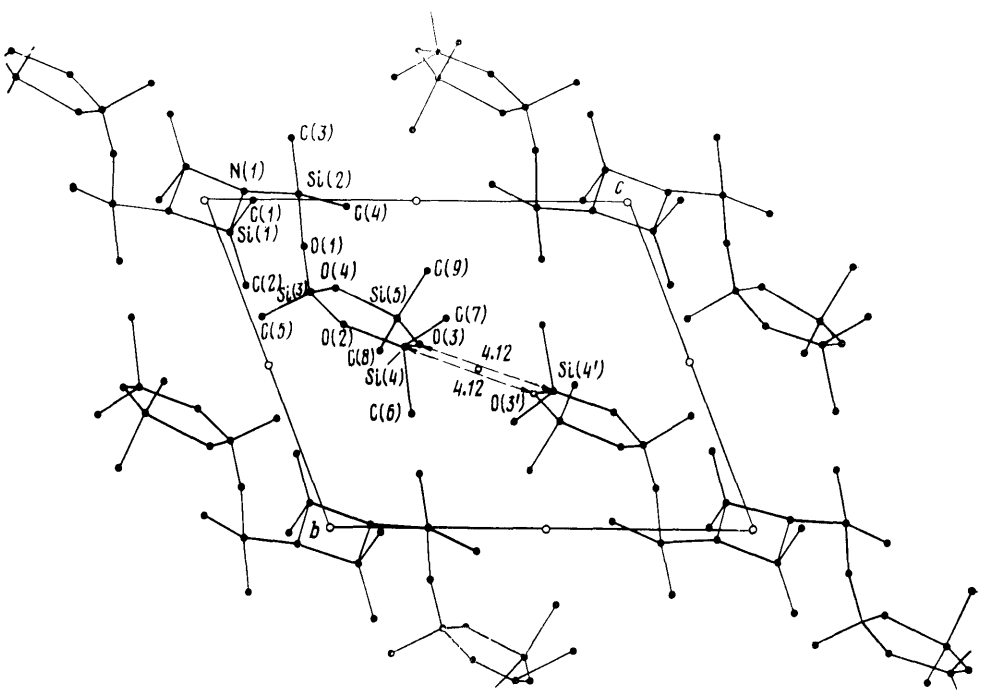


Figure 25. Projection (100) of structure (XXVII).[94]

†An analogous mechanism of initiation was suggested and confirmed by polarisation data and electron microscopy, as well as by measurements of infrared dichroism, for the solid-phase polymerisation of *p*-acetamidostyrene and *p*-benzamidostyrene, whose crystals also have a layer structure[93].

#A study is now being made of the possibility of radiation-induced solid-phase polymerisation of (XXVII), which would eliminate difficulties associated with the transfer of active centres: on exposure they are generated throughout the crystal.

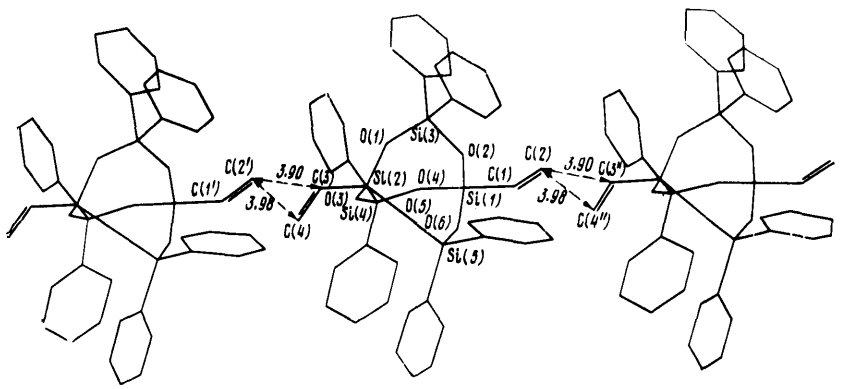


Figure 26. Diagram of chain of molecules in a crystal of (XXIV). Contacts C...C between vinyl groups in neighbouring molecules are indicated.

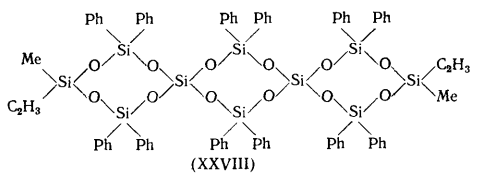
interact in the crystal by a topochemical mechanism[84]. It was therefore suggested[70] that (XXIV) is able to polymerise in the crystal through the vinyl groups with formation of a "bead" type of polymer. An attempt is now being made to confirm experimentally this crystal-chemical conclusion.

VII. CONCLUSION

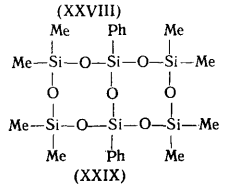
It may be concluded not so much from the quantity of papers published on the crystal structure of organocyclosiloxanes (though it is quite convincing) as from the character of the problems tackled and the importance of several of the findings that X-ray structural (and physicochemical in general) investigation of this class of compounds is being vigorously pursued. Although it is difficult to expect the preparation of novel monomers in this field, while synthetic work is aimed mainly at improving and modifying known structures, the growth in the number of structural investigations on organocyclosiloxanes is undoubtedly justified, since it not only promotes further successful development of this field of macromolecular hetero-organic chemistry but also leads to the accumulation of the valuable factual and procedural information required for the analysis of novel or little-studied classes of hetero-organic monomers.

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During the preparation of this Review for publication structural information has appeared on the spirocyclic siloxane (XXVIII),[95] the bicyclic siloxane (XXIX),[96]



(XXVIII)



(XXIX)

and also a tetragonal modification (XXX)[97] of octa(phenylsilsesquioxane) $(C_6H_5SiO_{1.5})_8$. The form of the tetrasiloxane rings in (XXVIII) and (XXIX) has been described by the Cremer–Pople method[98] and specified by the Hendrickson method[99].

In the centrosymmetric molecule (XXVIII) the outer D_3Q rings form dihedral angles of 83.2° with the plane of the inner D_2Q_2 ring. The latter ring has a form close to *LC*, and the outer rings are intermediate between *B* and *BB*. As in other spirocyclosiloxanes (Section III) the mean distance between a spiro-silicon atom and an oxygen atom (*Q* units) is 1.598(8) Å, rather less than the remaining silicon–oxygen distances (*D* units, 1.62(1) Å). The terminal vinyl groups, *trans* with respect to the tricyclic silicon–oxygen system, are disordered[95].

The form of the D_2T_2 rings constituting the molecule (XXIX) is close to *BB*, with a dihedral angle of 125.9°. The silicon–oxygen bond lengths in *D* and *T* units differ little (on the average they are respectively 1.630(8) and 1.62(1) Å).[96]

The $(C_6H_5SiO_{1.5})_8$ molecules in a crystal of (XXX) are situated on fourfold axes (in (XXI) at centres of symmetry). The mean silicon–oxygen and silicon–carbon distances (1.613 and 1.833 Å), and also the SiOSi bond angle (148.5°), are closely similar to those found in a crystal of the triclinic modification of (XXI). As in the latter compound, disordered solvent (acetone) molecules are found in a crystal of (XXX), which do not escape from the crystal in air, despite the absence of specific intermolecular interaction. The packing of molecules in a crystal of (XXX) is fairly free, with a shortest intermolecular C...C distance of 3.752 Å.[97]

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