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Review

RECENT DEVELOPMENTS IN STRUCTURAL CHEMISTRY OF ORGANOSILICON COMPOUNDS

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Contents

1. Introduction

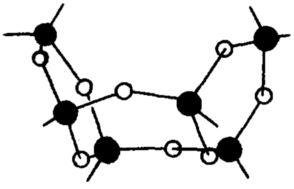
The present review summarizes the results of X-ray structural investigations of organosilicon compounds (OSC) carried out in the last 3-5 years. In view of the limited space, only the main structural results out of a vast amount published in this period are included. The classification used is, of course, somewhat arbitrary, but we believe that it properly represents the main trends in the development of structural OSC chemistry. For the reason mentioned the review does not include a wide field of

X-ray investigations of small Si-containing molecules, which is relevant to the problem of the bonding nature at the Si atom, as well as a number of more specific branches of structural OSC chemistry (carbosiloxanes, "aromatic" Si-heterocycles, and some others).

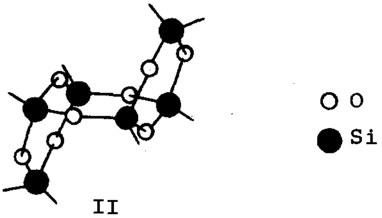
2. Siloxanes

Among siloxanes, representing the most thoroughly studied class of OSC, we discuss the silsesquioxanes, which are important from the practical point of view.

In the tricyclic molecules I-IV the main interest is in the geometry of the internal rings, which can be regarded as elementary units of cyclolinear polyorganosilsesquioxanes. In the



I



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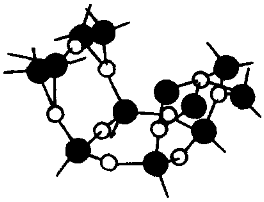

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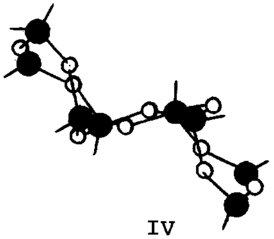

IV

cis-tricyclic units of I and III the form of internal T_4^x ring is close to LB^x and in trans-tricyclic units of II and IV it

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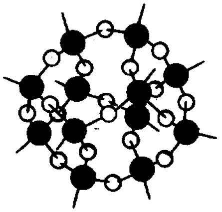
[x] The following set of canonical conformations of 8-membered rings is used [1] : crown (CR), boat (B), boat-boat (BB), chair (C) and long chair (LC).

[xx] Organosiloxane molecules may be regarded as a definite combinations of the following four structural units [2] :

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

is close to LC; moreover, according to force field calculations, the conformation of internal T_4 rings in I-IV is retained on fusion of the additional siloxane rings to both sides [2-7].

In the series of cisoid molecules a transition from the closed, cubane-like molecule $(PhSiO_{1.5})_8$ (V) [8] to the molecule $(PhSiO_{1.5})_{12}$ (VI) with the expanded cubane framework [9], then to the "open contracted cubane" (VII) [1] , and, finally to an "open cubane" (III) leads to successive decrease in the contribution of the crown form (CR) to the internal T_4 ring conformation from 43% (V) to 24% (III) [6]. Transition from the cubane-like framework in V and VI to the open form in VII and VIII results also in a bending of the cyclic system around the O...O middle line of the internal cycle (e.g. O(1)...O(5) in VII;), accompanied by helical twisting of the last two molecules (by an angle of ca. 20° in VII) around the longitudinal molecular axis (i.e. the other middle line of the internal ring, i.e. O(8)...O(9) in VII).



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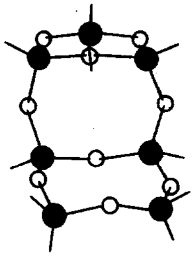

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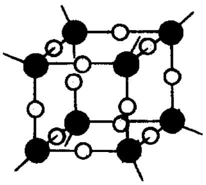
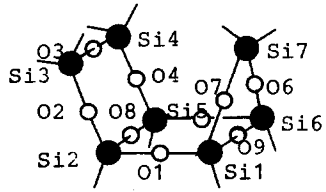
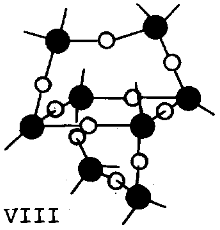


V



VII



VIII

In the lowest oligomer VIII [6] of cyclolinear silsesquioxanes of a new type (with cross-linking side rings), the "chelating" seven-atomic moieties (for instance, Si_1, O_5, ... O_7, Si_3) of the side rings are approximately planar, with the internal T_4 ring in the BB form.

The Q_4 ring of the molecule IX (Fig. 1) [11], a typical representative of the very large class of spirocyclosiloxanes, is characterized by an essentially planar form, rarely observed among

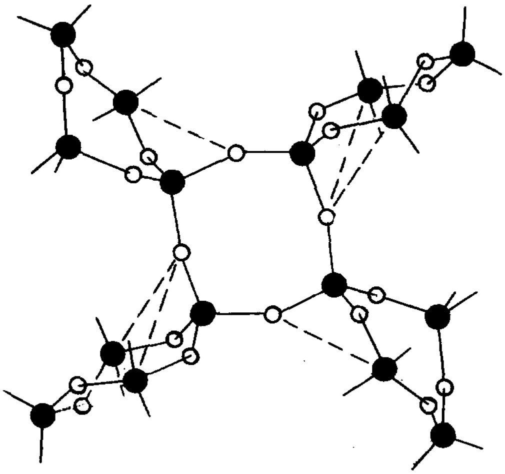


Fig. 1 Structure of the molecule IX (C_i symmetry). Dashed lines show shortened intramolecular Si...O contacts [11]

the tetrasiloxane rings. The planarity of this ring is evidently imposed by shortened intramolecular Si...O contacts, which lead to increasing of the bond angles at O atoms to 166.9(4)°, and, therefore, to shortening (strengthening) of the Si-O bonds in this ring to 1.607(4) Å (cf. [12] for correlation between Si-O bond lengths and SiOSi bond angles in siloxanes).

The structure of hexadecamethylcyclooctasiloxane (X) (Fig. 2) [13] was determined in a search of the structural correspondence between cyclic dimethylsiloxanes $[(CH_3)_2SiO]_n$ and isoelectronic dimethylphosphazenes $[(CH_3)_2PN]_n$ (XI) and, indeed, the molecular structure of X closely resembles that of XI [14]. The relatively

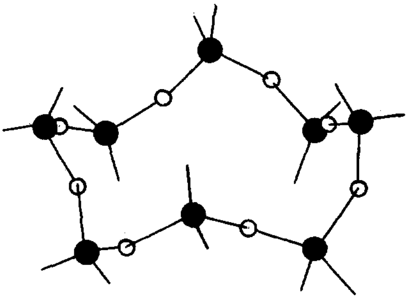


Fig. 2 Structure of the molecule X [13]

rigid conformation of X, wherein the $(SiO)_8$ ring has a crown form, is controlled by efficient van der Waals interactions between two sets of four methyl groups at the C...C distances of 3.96 Å (3.92 Å in XI).

From the point of view of polymer chemistry, there is special interest in the "mixed" element-siloxanes, whose siloxane moieties usually retain their characteristic geometry. Thus, in the planar 6-membered chelate rings of the zirconiumsiloxane anion XII (Fig. 3), the Si-O distances and SiOSi bond angles are unexceptional for siloxane rings [15]. The geometrical parameters of the six Ph_3SiO groups, linking Pb atoms in the adamantane-like core of the molecule XIII (Fig. 4), are also typical for siloxanes [16].

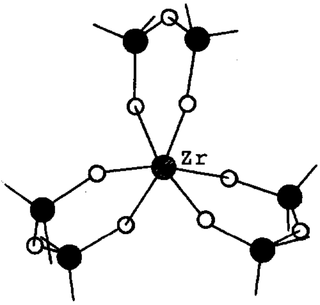


Fig. 3 Structure of the anion XII (C_2 symmetry) [15]

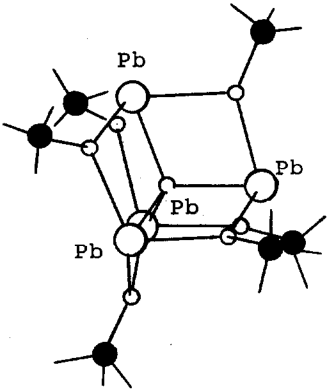


Fig. 4 Structure of the molecule XIII [16]

The mixed siloxane-germoxane rings of the molecules of trans-$[(Ph_2Ge)O(Ph_2Si)O]_2$ (XIV) and trans-$[(Me_2Ge)O(Ph_2Si)O]_2$ (XV) [17] have boat and distorted chair conformations, respectively, and are characterized by the greater puckering than in

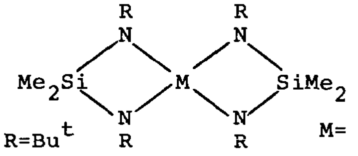
8-membered siloxane rings (the sum (S) of the endocyclic bond angles is 996° in XIV and 983° in XV, whereas in the $(SiO)_4$ ring of the trans-$[(PhMeSi)O(Me_2Si)O]_2$ with a distorted chair conformation S = 1017° [18] and in the planar $(SiO)_4$ ring of $[(Ph_2Si)O(Ph_2Si)O]_2$ S = 1078° [19] in contrast to S = 928° in still more puckered cyclooctane [19]). The greater puckering of 8-membered siloxane-germoxane rings as compared with cyclotetrasiloxane rings is explained by smaller values of the bond angles at O atoms in the mixed rings (137-144° in XIV and 135.8-138.0° in XV) [17].

One of the "anomalies" of siloxane geometry is the occurrence of linear O-bridges in disiloxanes (e.g. in $(Ph_3Si)_2O$ [21], $(Ph_3Si)_2O.C_6H_6$ [12], $[(Me_3SiO)_2(HCB_{10}H_{10}CCH_2)Si]_2O$ [22]), which is due to the electronic properties of substituents at the Si atoms [23].

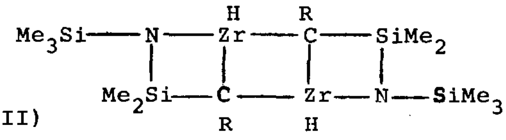
3. Silazanes

As in the case of the siloxanes, most of the structurally studied silazanes have cyclic molecules. Among non-cyclic silazanes we would like to mention the compounds $Cl_3AlN(Me)_2Si(Cl)(NMe_2)_2$ (XVI) [24] and $(C_5H_5)_2VNSiMe_3$ (XVII) [25], which contain the M-N-Si group with M-N distances of 1.990 and 1.972(5) Å in XVI and 1.736(6) Å in XVII. The Si-N(tetrahedral) and Si-N(trigonal) bond lengths in XVI (2 unique molecules) are different (1.832, 1.835(5) Å and 1.674-1.684(6) Å); the former are much longer and the latter shorter than the range of usual Si-N bond lengths of 1.69-1.77 Å in silazanes, though the Si-N distance of 1.736(6) Å in XVII is within this range.

The Si_2N_2 rings, which are the most thoroughly studied among cyclosilazanes, adopt in different molecules a strictly [26] or approximately [26] planar structure (this is also true for other 4-membered rings with Si-N bonds, e.g. for molecules XVIII-XXI [28-30]).

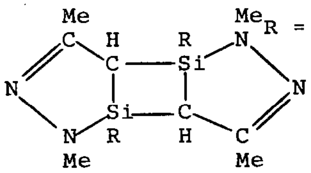


M= Ti (XVIII)
Zr (XIX)
Sn (XX)



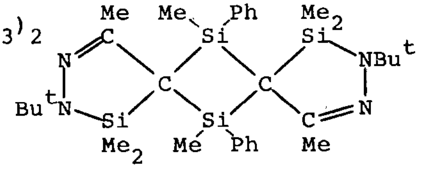
R = $N(SiMe_3)$ XXI

The Si-N bonds in silazanes with Si_2N_2 rings are somewhat elongated, while the exocyclic Si-N bonds are somewhat shortened [31]. The deviation from planarity of 5-membered SiN_2C_2 rings (7 structures) varies from 0.065 Å (XXII) [32,33] to 0.65 Å (XXIII) [32], [34] and is governed by the conjugation of the 3-coordinated N atom, adjacent to the Si atom, and the endocyclic N=C bond [32].



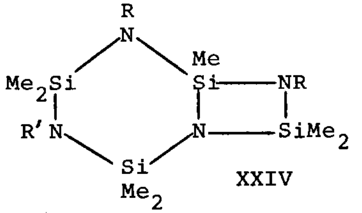
R = $N(SiMe_3)_2$

XXII



XXIII

6-Membered trisilazane rings, depending on the electronic and steric properties of substituents, can be either planar (molecule $[PhFSiN(Me)]_3$ [35]), or non-planar (XXIV, deviation from planarity up to 0.29 Å, boat conformation [31]).



XXIV

R = $SiMe_3$

R' = $Si(Me,F)N(SiMe_3)_2$

8-Membered tetrasilazane rings are always non-planar, like their tetrasiloxane analogues. Various conformations are reported for these rings (LC in $[(PhMeSi)(NH)]_4$ [35], LC←BB←CR [1] in three equivalent $(SiN)_4$ rings of the molecule $N(SiMe_2NHSiMe_2)_3N$ (XXV, Fig. 5) [37]. The Si-N bond lengths in 6- and 8-membered silazanes, as well as the forms of the rings, depend on the properties of substituents [36,37].

4. Silicon peroxides

Silicon peroxides are of interest, because of their ability to undergo decomposition into radicals and unusual rearrangements [38]. The properties of silicon peroxides and siloxanes differ significantly, in particular the energy of Si-O bonds in siloxanes and O-O bonds in peroxides is equal to 422-493 and 192-204 $kJ.mol^{-1}$ respectively [38].

In the monoperoxides XXVI and XXVII (Table 1), as in other symmetric peroxides with bulky substituents, the -O-O- torsion angle, τ, equals 180^o (C_i symmetry). In the bis-peroxides XXXI the value of τ 135.6^o is governed by the incorporation of pero-

TABLE 1

Geometrical parameters of the SiOOSi and coplanar OSiC moieties of silicon peroxides and of the corresponding COOC and OCC moieties in related organoperoxides (d - the O-O bond length (Å), τ - the SiOOSi torsion angle (degr.), r - the Si-O bond length (Å), α - the SiOO bond angle (degr.), ω - the torsion angle around the O-Si bond in OOSiC moiety (degr.), β - the decreased OSiC bond angle in this moiety (degr.))

Compound		d	τ	r	α	ω	β	Ref.
$[(p\text{-}ClC_6H_4)Me_2SiO]_2$	(XXVI)	1.498(2)	180	1.691(1)	105.48(9)	178.5	100.88(8)	39
$[(C_6H_5CH_2)Me_2SiO]_2$	(XXVII)	1.501(1)	180	1.687(1)	104.47(6)	179.1(1)	102.43(6)	39
$(Ph_3SiO)_2$	(XXVIII)	1.500(5)	180	1.668(6)	103.6(5)	180	99.7(4)	40
$Ph_3SiOOGePh_3$	(XXIX)	1.489(5)	180	1.742(6) ^{x}	104.4(4)	180 ^{x}	100.4(3)	41
$(Me_3SiO)_2$	(XXX)	1.481(8)	143(6)	1.681(3)	107(1)	156(3)	^{xx}	42
$(Me_2SiOO)_2$	(XXXI)	1.492(2)	135.6(1)	1.674(1)	104.9(1)	176.6	102.4(1)	43
$[(\overset{t}{B}uOO)_3Si]_2O^{xxx}$	(XXXII)	1.477(8)	138	1.640(8) 1.454(9)	106(2) 108(1)	174(1) 175(2)	101(2) 105(2)	44

^{x}The Si and Ge atoms replace each other statistically, therefore the r, α, ω and β values represent average parameters

^{xx}The β value is not given in [42].

^{xxx}The upper line corresponds to the SiOO and the lower line to the COO moieties.

xide group into the ring (in the carbon analogue of XXIX also, $\tau = 135.6^{\circ}$ [45]). 9-Membered rings of both molecules have a TBC conformation [46].

At the Si atoms of silicon peroxides there are planar transoid -O-O-Si-C- units, wherein the OSiC bond angles are decreased by 5-10° (Table 1). Thus, in the planar group C(1)Si(1)O(1)O(1′)Si(1′)C(1′) of the molecule XXVII (Fig. 6) the bond angles C(1)Si(1)O(1) and C(1′)Si(1′)O(1′) are equal to 102.43(6)°.

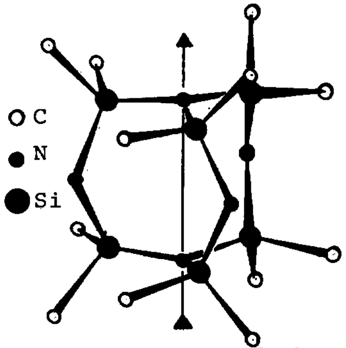


Fig. 5 Structure of the molecule XXV (C_3 symmetry) [37]

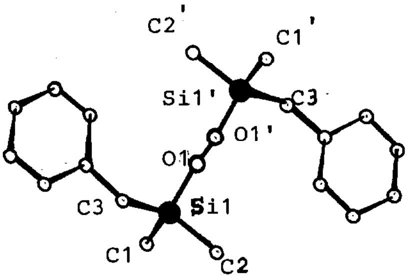


Fig. 6 Structure of the molecule XXVII (C_i symmetry) [39]

The O-O bond lengths in silicon peroxides (1.49-1.50 Å) are somewhat larger than the corresponding values in organic peroxides. The Si-O bond lengths (1.67-1.69 Å) are larger than in siloxanes, where they do not exceed 1.65 Å.

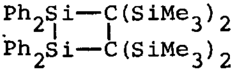
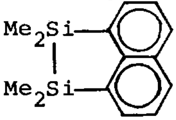
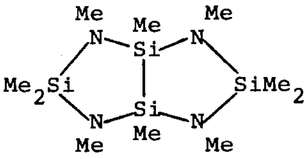
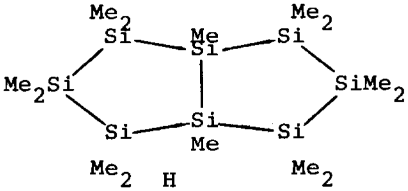
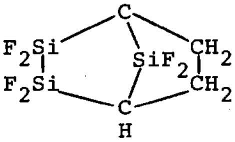
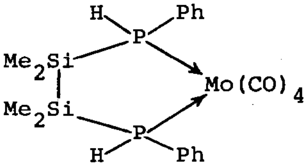
5. Compounds with Si-Si bonds

A number of interesting compounds of this kind have been investigated (Table 2). With the exception of compounds XLIII and XXXVII, where the Si-Si bond lengths equal 2.314(2) and 2.511(3) Å respectively, these values in OSC are within a rather narrow range from 2.34 to 2.41 Å (Table 2).

The comparison of the Si-Si bond lengths shows that the values of 2.407, 2.391 and 2.511(3) Å in cyclotrisilanes XXXV-XXXVII are among the largest observed in alkyl- and aryl-substituted cyclopolysilanes. It is noteworthy that in the peralkylcyclopolysilane series, the smaller the ring size, the longer the Si-Si bond length. The increasing in the Si-Si bond lengths on going from Si_6 to Si_5, Si_4 and Si_3 rings is probably the result of the increasing steric repulsions between the substituents at the Si atoms

TABLE 2

Bond lengths Si-Si (d, Å) in polysilanes

Compound		d	Ref.
$Cl_2MeSi—SiMeCl_2$	(XXXIII)	2.367(5)	47
$Me_3Si—SiMe[C_6H_5(SiMe_3)_4]SiMe_3$	(XXXIV)	2.35	48
$[(2,6\text{-}Me_2C_6H_3)_2Si]_3$	(XXXV)	2.407	49
$[(Bu^tCH_2)_2Si]_3$	(XXXVI)	2.391	50
$(Bu^t_2Si)_3$	(XXXVII)	2.511(3)	51
$(R^1R^2Si)_4$, $R^1 = Me$, $R^2 = Bu^t$	(XXXVIII)	2.377	52
$R^1 = R^2 = Ph$	(XXXIX)	2.377	53
 $Ph_2Si—C(SiMe_3)_2$ $Ph_2Si—C(SiMe_3)_2$	(XL)	2.344(9)	54
$(Ph_2Si)_5$	(XLI)	2.395	55
	(XLII)	2.338(2)	56
	(XLIII)	2.314(2)	57
	(XLIV)	2.34(2)	58
	(XLV)	2.342(3)	59
	(XLVI)	2.378(2)	60
$(Me_2Si)_6$	(XLVII)	2.339	61

and hence of the ring strain. For a particular ring size the Si-Si bond length depends on the steric requirements of substituents. Thus, the Si-Si bond length in cyclopentasilanes, Si_5, increases with the volume of substituents in the order H<Me<Ph [49]. Similarly, the Si-Si bond in $(Ph_2Si)_4$ and $(Bu^tMeSi)_4$ is longer than in $(Me_2Si)_4$ (2.377, 2.377 and 2.363 Å respectively) [50].

The longest Si-Si distance of 2.511(3) Å is found in the 3-membered ring of hexa-tert-butylcyclotrisilane XXXVII [51]. This molecule has D_3 symmetry andexhibits also very long Si-C distances of 1.970(5) Å . These distances exceed those observed, e.g. in hexa-(2,6-dimethyl)cyclotrisilane by 0.10 and 0.06 Å, respectively, and, on the basis of comparison with the standard single bond lengths (2.35 for Si-Si and 1.88 for Si-C), correspond to the Pauling bond orders of 0.60 and 0.75 [51]. Thus, the molecule XXXVII is highly strained and energy rich. The strain is also displayed in the bond angle values, viz. SiCC (112.1°), CCC (106.7°) and CSiC (105.7°) [50].

The increasing of the Si-Si bond lengths in complexes of the type XLVI is also probably due to steric strain in the 5-membered metallarings. Electronegative F-substituents in the molecule XLV do not affect the Si-Si distance. The reason for the considerable decrease of the Si-Si bond length in XLIII is not clear.

6. The Si-C bond and carbosilanes

The Si-C bond lengths in OSC vary in a wide range from 1.84 to 1.93 Å and are governed by electronic and steric factors. The dependence of this bond length on the stereochemical features of the particular molecule evidently accounts for its apparent indepedence on the state of C atom hybridization.

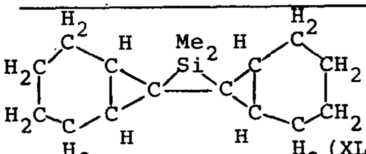
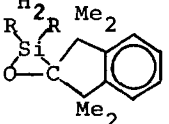
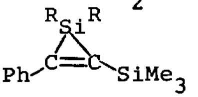
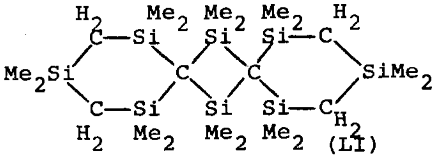
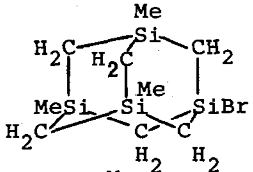
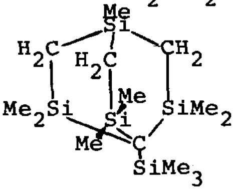
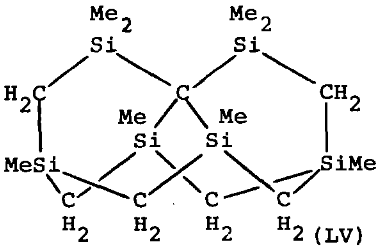
An evident increase of the Si-C bond length because of steric factors is observed in crystalline $(Me_3SiCH_2NMe_3)^+I^-$ ($Si-CH_2$ distance 1.934 Å, SiCN bond angle 123°, one of $Si-CH_3$ distances 1.926 Å) [62].

The increase of Si-C distances in the overcrowded moieties (4-membered rings, spiro-units) of the molecule LI (Table 3) is also probably explained by steric factors, although the molecule XLVIII, whose endocyclic CSiC bond angle is decreased to 49.2(1)°, has normal Si-C bond lengths both within and outside the ring.

The endocyclic Si(1)-C(1) bond length of 1.800(2) Å in the mo-

TABLE 3

Geometrical parameters of carbosilanes (bond lengths d, Å)

Compound		Bond	d	Ring conformation	Ref.
	(XLVIII)	Si-C_{endo}	1.826(3)		63
		Si-C_{exo}	1.858(3)		
		C-C_{ring}	1.520(4)		
 R=Mes	(XLIX) Fig. 7	Si-C	1.849		64
		Si-O	1.668		
 R=Mes	(L) Fig. 8	Si-C_{ring}	1.800(2)		65
			1.839(2)		
	(LI)	Si-C_A	1.922	A - planar	66
		Si-$C_{B,spiro}$	1.918	B - boat	
		Si-$C_{B,non-spiro}$	1.826		
	(LII)	Si-C_{ring}	1.87	Chair	67
	(LIII)	Si-C	1.893(7)	Boat	68
		Si-CH_2	1.872(7)		
		Si-CH_3	1.886		
$Si_6C_6H_8Cl_8$	(LIV) Fig. 9	Si-C (CH_2-bridge)	1.90(2)		69
		Si-C ($SiCl_2$-bridge)	1.81(1)	Boat	
		Si-C (4-memb. ring)	1.89(2)		
	(LV)	Si-C_{endo}	1.884	Boat	70
		Si-C_{Me}	1.876		
$Si_8C_{17}H_{36}$	(LVI) Fig. 10	Si-C_{endo}	1.889(3)	Twist-boat	71
		Si-C_{Me}	1.874(8)		

lecule of substituted silacyclopropene L (Fig. 8) [65] is considerably shorter than the second Si(1)-C(2) bond length of 1.839(2) Å and the Si-C bond distances usually observed in derivatives of the tetrahedral silicon (1.84-1.89 Å, Table 3). Nevertheless the Si(1)-C(2) bond length and other ring parameters, viz. the C(1)Si(1)C(2) angle (43.5(1)°), the main value of two SiCC angles (68.3(1)°) and the C(1)-C(2) bond length (1.349(3) Å), are compatible with the results of silacyclopropene calculations by the SCF method [72]. A significant difference between the Si(1)-C(1) and Si(1)-C(2) bond lengths and between the Si(1)C(1)C(2) and Si(1)C(2)C(1) angles may be due to the effect of substituents at the C(1) and C(2) atoms. It is noteworthy that the silacyclopropene and phenyl rings are almost coplanar with a dihedral angle of 6.5(1)° [65].

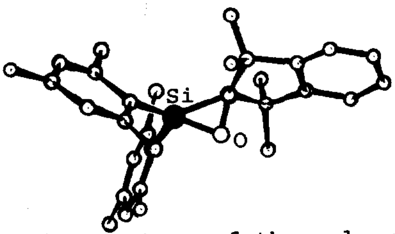


Fig. 7 Structure of the molecule XLIX [64]

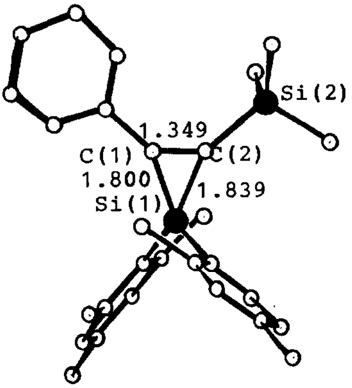


Fig. 8 Structure of the molecule L [65]

The bond lengths in the framework of carbosilanes LI-LVI are in the upper part of the Si-C distance range. It is to be noted that the Si-C distances to $SiCl_2$ bridges in the molecule LIV (Fig. 9) are considerably shortened.

In the scaphane series (viz. hexasilahexascaphane LV, the product of tetrasilatriscaphane LII condensation, which further leads to octasiladodecascaphane LVI) the boat-like shape of the 6-membered rings is noteworthy. The substitution of C atoms in 6-mem-

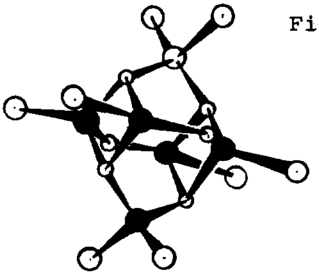


Fig. 9 Structure of the molecule LIV (C_i symmetry) [69]

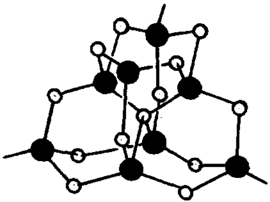


Fig. 10 Structure of the molecule LVI [71]

bered ring for Si atoms reduces the energy difference between the chair and boat forms (from ca. 29.3 kJ.mol^{-1} for cyclohexane to 14.6 kJ.mol^{-1} for 1,3,5-trisilacyclohexane [68]), but still results in increased Si-C distances as observed in scaphanes.

The molecules XLVIII-L including the 3-membered Si-containing ring, belong to the small ring compounds which are of a great current interest in silicon chemistry owing to their high reactivity resulting from the molecular strain, displayed mainly in distorsions of bond angles. The distorsions are caused by bulky substituents which are used for the stabilization of such molecules.

7. Compounds with Si-Element bonds

The stereochemistry of OSC with Si-Element bonds still needs to be studied in more detail. Nevertheless, among these compounds the representatives with Si-P bonds are well known.

In the structure of the adduct of $Mg(SiMe_3)_2$ with dimethoxyethane, the bond lengths are: Si-Mg 2.630(2) Å and Si-C 1.879(4) Å [73]. The Si-Hg distances in anions of Li-salts, $(Me_2PhSi)_4HgLi_2$ and $(Me_3Si)_4HgLi_2$ are similar (2.521 and 2.544 Å respectively) [74].

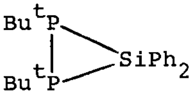
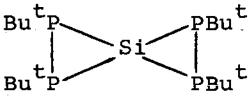
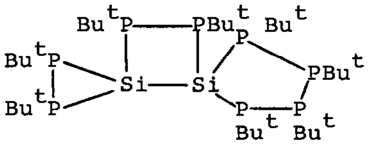
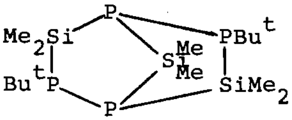
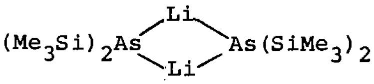
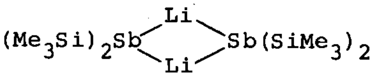
The shortest Si-P bonds (Table 4) are observed in the 3-membered Si_2P rings of molecules LVII-LIX. In the sterically strained molecules LIX-LXI with polycyclic systems and bulky substituents the Si-P distances are increased. Sensitivity to steric factors is also exhibited by the Si-As bond length (molecules LXII-LXIV). This bond in LXIV is in the lower part of the Si-As distance range. The Si-Sb distance in the molecule LXV is also shortened.

Relatively constant Si-Element bond lengths in OSC with considerably varying bond angles at the Si atom (from 60 to 120° in P-containing OSC; cf. also structures XLVIII-L in Table 3) are also observed in S-containing OSC (in the molecule $(Me_2SiS)_2$ the Si-S distance of 2.152(2) Å is close to the values of 2.126-2.153(3) Å in $(MePhSiS)_3$ [85]).

The Si-M (M = transition metal) bond lengths vary to an even greater degree (Si-Mn of 2.497(5) Å in $Me_3Si\text{-}Mn(CO)_5$ and of 2.564(6) Å in $(Me_3Si)_3Si\text{-}Mn(CO)_5$ [86]; in Re-analogues 2.600(1) and 2.665(9) Å [87]).

TABLE 4

Si-Element (P, As, Sb) bond lengths (d, Å)

Compound		Bond	d	Ref.
	(LVII)	Si-P	2.225	75
	(LVIII)	Si-P	2.201[x] 2.216[x]	76
	(LIX)	Si-P	2.240[xx] 2.292[xx] 2.287[xx]	77
	(LX)	Si-P	2.258- -2.291	78
$(Me_3Si)_3P_7$	(LXI, Fig. 11)	Si-P	2.288	79
$(Me_3Si)_2As—As(SiMe_3)_2$	(LXII)	Si-As	2.364	80
$(Me_3Si)_3As_7$	(LXIII, Fig. 11)	Si-As	2.397(3)	81
 .DME[xxx]	(LXIV)	Si-As	2.307(7)	82
$(Me_3Si)_2Sb—Sb(SiMe_3)_2$	(LXV)	Si-Sb	2.594	83
 .DME[xxx]	(LXVI)	Si-Sb	2.532	84

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[x] Bond lengths in two isomers with different orientation of substituents at pyramidal P atoms

[xx] In 3-, 4- and 5-membered rings respectively.

[xxx] DME = dimethoxyethane

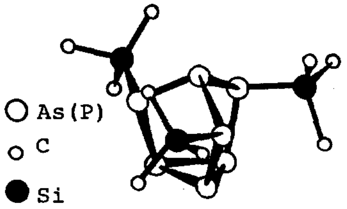
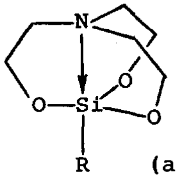


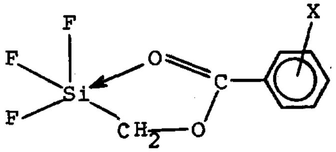
Fig. 11 Structures of the heptaphosphane LXI [79] and heptaarsane LXIII [81]

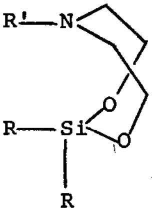
8. Derivatives of penta-coordinated silicon

An X-ray study of the dimethylsilylamine pentamer [88] provided an explanation of the anomalously high melting point (276 K) of this compound and simultaneously furnished the first crystallographic identification of penta-coordinated Si. Whereas the structure of the isolated Me_2NSiH_3 molecule in the vapour is characterized by pyramidal geometries at both N and Si atoms and by N-Si and N-S bond lengths of 1.712(3) and 1.459(3) Å respectively [89], the Si atom coordination in the solid state is trigonal bipyramidal and these distances are increased to 1.976(4) and 1.476(4) Å respectively (redetermination of the structure [89]). In the crystal the N atoms of the dimethylsilylamine pentamer occupy the corners of a regular pentagon with Si atoms slightly displaced outwards from the midpoints of its sides.

Silatranes (a), aroyloxymethyltrifluorosilanes (b) and dioxazasilacyclooctanes (c) are among the most thoroughly studied compounds with a penta-coordinated Si atom. In these compounds, as


(a)


(b)


(c)

in other penta-coordinated silicon derivatives, the Si atom has a somewhat distorted trigonal-bipyramidal geometry.

The main features of silatrane molecular geometry can be illustrated by the structures of three ionic compounds $[RCH_2Si(OCH_2CH_2)_3N]^+I^-$ with R = Me_2S (LXVII) [90], Me_3N (LXVIII) and Ph_3P (LXIX) [91]. The transannular Si←N bond length in LXVII-LXIX depends on the electronic properties of R substituents and is equal to 2.046(2) Å (LXVII), 2.08(1) Å (LXVIII) and 2.07 2.12(1) Å (LXIX, 2 unique molecules). The N→Si-C moiety is almost linear, the angle NSiC being 179.1(1), 175.7(4) and 178.6, 178.0(4)°, respectively. The intramolecular steric silatranyl...R interaction is observed only in LXVIII: the Si-C-R bond angles equal 114.4(1), 121.2(9) and 113.6, 115.3(5)°, respectively. Some differences in geometry of the cations in crystal LXVIII are due to the different orientation of the N→Si-C axes relative to the layers of I^- anions.

The nature of the interaction between nitrogen and silicon in silatranes was elucidated in a precision X-ray study of 1-fluorosilatrane [92]. A section of the deformation electron density map through the Si-N line (Fig. 12) clearly shows a maximum of bonding electron density.

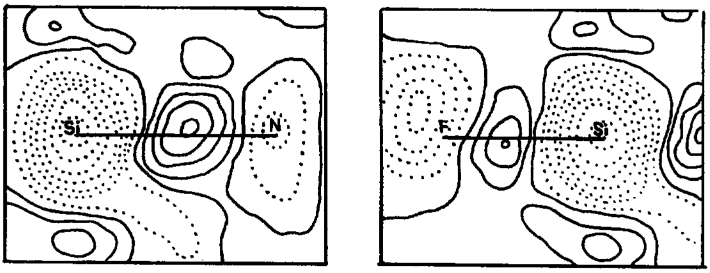


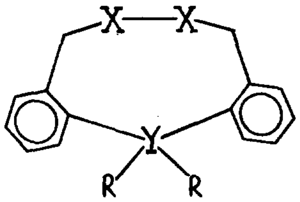
Fig. 12 Deformation electron density map in the Si(1), O(2), N(1) (a) and the Si(1), O(2), F plane (b). Contours are drawn at 0.1 e.Å^{-3} interval and broken lines represent negative values (estimated error is ca. 0.1 e.Å^{-3}) [92]

The length of the coordinate Si←O bond in aroyloxymethyltrifluorosilanes LXX (X p-H), LXXI (p-F), LXXII (p-Cl), LXXIII (p-Br) and LXXIV (o-Cl) varies from 1.95(2) to 2.08(2) Å. An increase in the axial Si-F bond length by 0.03 Å to 1.59(2)-1.62(1) Å is in agreement with the concept of the three-centered hypervalent F—Si—O bonding. In LXXII the presence of the substituent results in the mutual rotation of the planes of the 5- and 6-membered rings by 17.5° [93].

In the 1,3-dioxa-6-aza-2-silacyclooctane series (7 structures), depending on the electronic and steric properties of the substituents at the Si and N atoms, the Si...N distance gradually increases from 2.30 Å (R = Ph, R' = H, transannular interaction) to 3.19 Å (R = Me, R' = Ph, no interaction) and simultaneously the Si atom tetrahedral geometry is recovered [94]. The sterically overcrowded equatorial position of the R substituent in the trigonal bipyramid of the Si atom corresponds to an energetically unfavourable axial position in the 8-membered heterocycle. For this reason the preferred orientation of the R substituent and the position of the conformational equilibrium of the heterocycle strongly depend on the N→Si bond energy.

The heterocycles of 1,3-dioxa-6-aza-2-silacyclooctanes in solution have boat-chair (BC) and/or chair-chair (CC) conformations. Weakening of the N→Si bond results in an increase in the dihedral angle φ_{ON} between the planes OCC and CCN and shift of the coformational equilibrium to the CC form of the heterocycle. The exchange between the Si substituent positions in the trigonal bipyramid, observed at low temperatures, proceeds through the inversion of the heterocycle and reqires a dissociation of the N→Si bond [95].

In the molecules LXXV, LXXVI and LXXVII the intramolecular Si...X distances are noticeably different (3.438 and 4.190(3) Å in LXXV, 3.372 and 4.193(1) Å in LXXVI, 3.608 and 4.382(2) Å in LXXVIII) indicating transannular Si←S and Si←Se interactions, observed here for the first time. These interactions are confirmed by a characteristic trigonal-bipyramidal distortion of the Si atom coordination [96,97]. Previously an attractive, but in this case intermolecular, Si...S interaction at distances of 3.55 and 3.56(1) Å was noted in the crystal of $(H_3Si)_2S$ [98]. In LXXVII and LXXIX the pairs of Si...Se and Ge...Se intramolecular distances are almost equal and significantly exceed the sum of the corresponding van der Waals radii. The 9-membered heterocycles in LXXV-LXXIX have a distorted TBB conformation, but the positions of the heteroatoms in this form are different.



	X	Y	R	
LXXV	S	Si	Me	(Fig. 13)
LXXVI	S	Si	Ph	
LXXVII	Se	Si	Me	
LXXVIII	Se	Si	Ph	
LXXIX	S	Si	Ph	

The structure LXXX is the first example of OSC with hexa-coordinated Si atom [99]. The Si atom in LXXX has slightly distorted octahedral [4+2] geometry with two "long" Si←N distances (2.051 and 2.089(9) Å) and nearly "normal" Si-O and Si-C distances (1.772; 1.772(7) Å and 1.93 and 1.91(1) Å respectively).

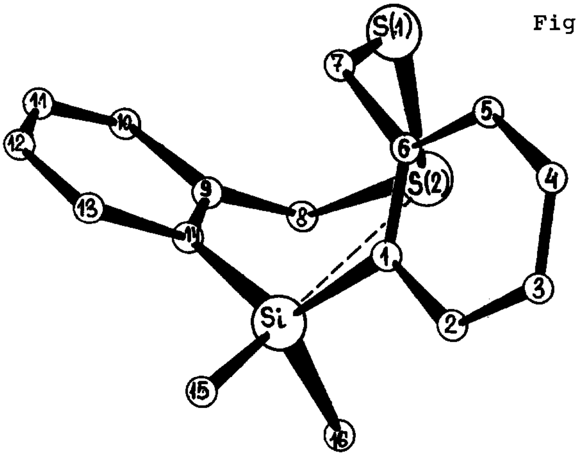
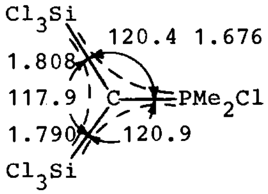


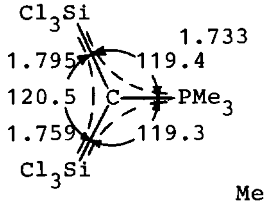
Fig. 13 Structure of the molecule LXXV [96]

9. Compounds with multiple bonds at the Si atom

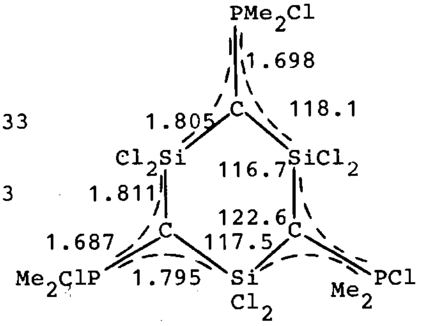
Even before the appearance of X-ray structural data on compounds with actual double Si ═ C and Si ═ Si bonds, the structures of stable ylides LXXXI-LXXXIII, obtained from perchlorinated carbosilanes, were solved [100]. The ylide C atoms have a planar-trigonal geometry, with the Si-C and P-C bond lengths being much shorter than standard single bonded values and thus indicating a higher order of these bonds.



LXXXI



LXXXII



LXXXIII

Actual double Si=C and Si=Si bonds were discovered in molecules where these bonds are shielded by bulky substituents. The Si=C distance of 1.764(3) Å in the adamantylsilaethylene molecule LXXXIV (Fig. 14) [101] is much shorter than the ordinary Si-C bonds (1.84-1.92 Å) and, at the same time, somewhat longer than the double bond length value of 1.69-1.73 Å predicted by quantum chemistry calculations of the molecules $H_2Si{=}CH_2$ and $Me_2Si{=}CH_2$

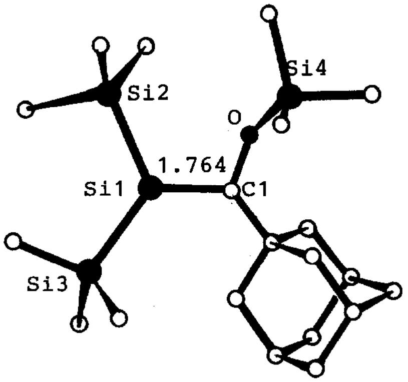


Fig. 14 Structure of the molecule LXXXIV [99]

[101]. All the other Si-C distances in LXXXIV (1.829-1.877(4) Å) are typical of ordinary bonds. A slight torsion around the double bond, as well as mutual 15° rotation of coordination planes of the Si(1) and C(1) atoms, is due to steric interaction of the adamantyl and $SiMe_3$ groups at the Si atom, which is confirmed by the distribution of bond angles at the Si(1) and C(1) atoms [101].

The Si=Si bond length of 2.160(1) Å in tetramesityldisilene (LXXXV) [102] is 0.19-0.20 Å shorter than in tetramesityldisilane (two unique distances of 2.350 and 2.362 Å) [103]. This contraction is slightly smaller than found on going from a C-C single bond to a C=C double bond, viz. ca. 9 % for silicon compounds and ca. 12 % for carbon analogues. The observation is consistent with theoretical studies which place the bond strength in Si_2H_4 at roughly 7.2 $kJ.mol^{-1}$.

Theoretical calculations of the Si=Si bond length in Si_2H_4 leads to the value of ca. 2.15 Å in good agreement with the observed bond lengths in LXXXV and 1,2-di-tert-butyl-1,2-dimesityldisilene (LXXXVI) of 2.160(1) and 2.143(1) Å [102]. The presence of bulky substituents apparently has no significant effect on the Si=Si distances. It is interesting that the double bonded covalent Si radius in LXXXIV (1.09 Å) is slightly larger than in the two disilenes LXXXV and LXXXVI. The Si=C double bond in LXXXIV is probably elongated due to conjugation with the adjacent oxygen of the SiO-group [102].

The two Si and four bonded C atoms in LXXXV deviate from planarity. The degree of pyramidalization at the Si atom can be gauged by the 18° angle formed by the CSiC plane and the Si=Si bond axis. The torsional distortion around the Si=Si bond results in a twist angle of 6.5(1)°. Distortions of the double bond of the type found in LXXXV (twisting and pyramidalization) are sometimes observed in olefins with extremely bulky substituents (e.g. [104]). However, LXXXVI, which should be at least as sterically hindered as LXXXV, does not show these distortions. Besides, LXXXVI has a lower reactivity than LXXXVI in addition reactions [102].

In the molecule of silaethene tetrahydrofuranate (LXXXVII, Fig. 15a) an essentially planar, sp^2-hybridized C(1) atom is engaged in bonding with a tetracoordinated Si atom of unusual geometry [105]. This Si atom bearing two methyl groups (Si(1)-C(2)

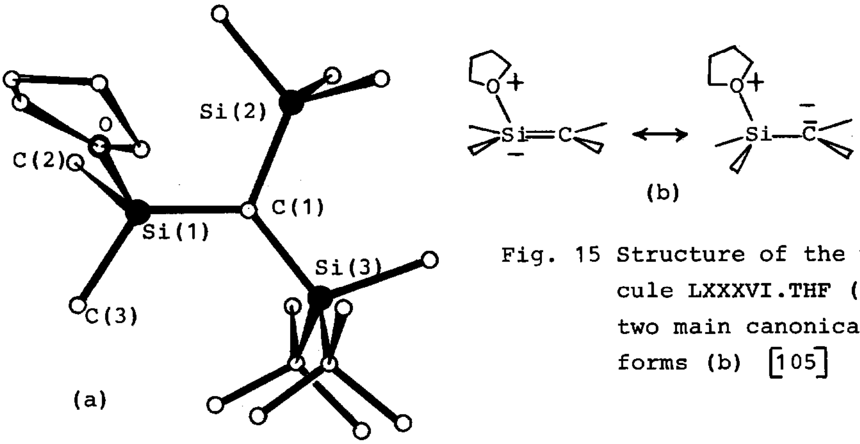


Fig. 15 Structure of the molecule LXXXVI.THF (a), two main canonical forms (b) [105]

1.850, Si(1)-C(3) 1.858(5) Å) is closely approaches by the oxygen atom of THF (Si(1)-O 1.878(4) Å) and forms a drastically shortened Si-C(1) bond of 1.747(5) Å. It is even slightly shorter than the value of 1.764(3) Å found in the silaenol ether LXXXIV (Fig. 14) [101] but close to the range of 1.69-1.73 Å predicted on the basis of MO calculations for sterically unhindered S=C double bonds [106]. The C(1)Si(1)C(2) and C(1)Si(1)C(3) angles (119.7(3) and 124.1(3)$^\circ$ respectively) show surprisingly little deviation from the value of 120°, normal for an sp^2hybridized atom, which is assumed to represent the bonding model for the free silaethene LXXXVII in the absence of complexing THF.

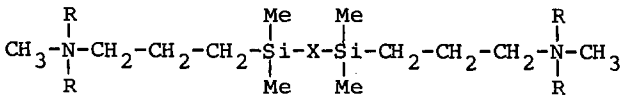
However, the angle C(2)Si(1)C(3) of 104.9(3)$^\circ$ is significantly compressed. The angles involving the THF oxygen atom may be divided into two groups: the OSiC(1) angle of 107.9(2)$^\circ$ is much larger than the OSi(1)C(2) and OSi(1)C(3) angles involving the methyl groups, which are 97.9 and 96.5(2)$^\circ$, respectively. The Si(1)-O distance of 1.878(4) Å is much longer than the values 1.63-1.66 Å found for Si-O bonds with two-coordinated O atom [2-5] and even 1.66-1.76 Å with three-coordinated O atoms [107]. The Si(1)-C(2) and Si(1)-C(3) bond lengths (1.850 and 1.858(5) Å) agree reasonably well with those of the C(1)-Si(2) and C(1)-Si(3) bonds (1.835 and 1.836(5) Å). The latter are slightly shorter than the Si-C(Me) bonds (1.879-1.907(6) Å in silyl groups wherein both Si and C atoms show a distinct sp^3 hybridization.

The bonding situation in LXXXVII.THF can be described in terms of two canonical forms (Fig. 15b). The left hand form implies adduct formation between THF and the Si atom engaged in a Si=C double bond and means d-orbital participation. The other canonical form can be regarded as structurally related to phosphorus ylides R_3P-CR_2. The rather long Si-O bond in LXXXVII.THF is consistent with a relatively weak adduct, represented by the (a) form. The approximately tetrahedral substituent geometry around Si(1), on the other hand, is consistent with the zwitterionic form (b) [105].

10. Bioactive compounds

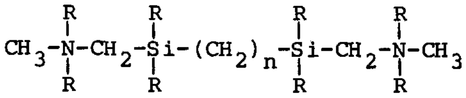
Here we consider several examples illustrating a relationships between the structure and bioactivity of OSC with various biological effects [108, 109].

The study of compounds of the LXXXVIII and LXXXIX type, which exhibit a curare-like activity , has shown that (a) biological action is governed by the character and orientation of substituents at the N atoms; (b) substitution of the internal CH_2 group by the O atom somewhat lowers bioactivity; (c) bioactivity depends on the length of the bridge between the N and Si atoms. The main



$$CH_3\text{-}\overset{R}{\underset{R}{N}}\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}\overset{Me}{\underset{Me}{Si}}\text{-}X\text{-}\overset{Me}{\underset{Me}{Si}}\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}\overset{R}{\underset{R}{N}}\text{-}CH_3$$

R = NMe_2, X = -, -CH_2-, -CH_2-CH_2- LXXXVIII



$$CH_3\text{-}\overset{R}{\underset{R}{N}}\text{-}CH_2\text{-}\overset{R}{\underset{R}{Si}}\text{-}(CH_2)_n\text{-}\overset{R}{\underset{R}{Si}}\text{-}CH_2\text{-}\overset{R}{\underset{R}{N}}\text{-}CH_3$$

n = 4, 5, 6 LXXXIX

functionally important parameter of molecular geometry is the intramolecular N...N distance, which in compounds of the series studied is 12.4, 13.5, 14.8 Å in LXXXVIII and 12.3, 13.5, 14.8 Å in LXXXIX. However, this distance can be change on transition to solution due to the conformational flexibility of the molecules [110].

Unlike pridinole (XC), silapridinole (XCI) (Fig. 16), which has 5 times greater anticholinergic activity, is characterized by the presence in the crystal of only intermolecular hydrogen O-H...N bonds that link molecules into dimers. In non-polar solvents both compounds are present in a monomeric form with the intramolecular H bonds, and in polar solvents they form associates with the solvent. The acidity of silanole XCI explains its greater affinity for the acetylcholine receptor, and, therefore, its greater anticholinergic activity [111].

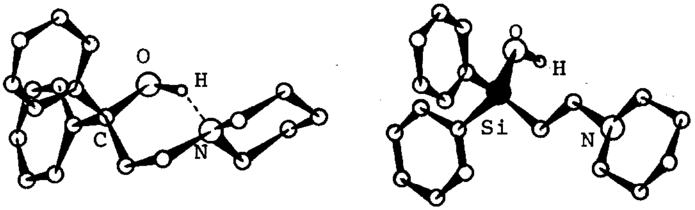
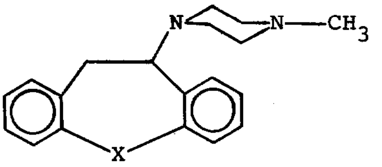


Fig. 16 Molecular structure of pridinole XCI (intramolecular H-bond shown)and silapridinol XCI [111]

In non-polar solvents the molecule of (2-morpholinoethyl)diphenylsilanol XCII, which is almost identical to XCI, also exists as a monomer with the strong intramolecular O-H...N hydrogen bond forcing the Si-CH$_2$-CH$_2$-N group to adopt a gauche conformation [112]. In the crystal the torsion angle Si-CH$_2$-CH$_2$-N is 178.1°, and thus the silyl moiety and morpholine rings are in a trans conformation to each other, as in XCI. Nevertheless, in contrast to XCI, the molecules XCII are linked by intermolecular hydrogen bonds into infinite chains.

(3-Piperidinopropyl)diphenylsilanol (XCIII) and 2-(dimethylamino)ethylthiomethyldiphenylsilanol (XCIV) are closely related to the anticholiergic drugs difenidol (1,1-diphenyl-4-piperidino-1-butanol, XCV) and siladifenidol((3-piperidinopropyl)diphenylsilanol, XCVI) [113]. In the crystal the morpholinopropyl chain of the molecule XCIII has an extended conformation, the torsion angles SiCCC and CCCN being 169.8 and 175.7(2)°, respectively [114]. In the crystal the SiCSCCN moiety of the molecule XCIV has also an extended conformation with the torsion angles SiCSC, CSCC, SCCN of 178.1, 177.2 and 168.0(4)°. The intramolecular distances between the centroids of the phenyl rings and the N atom are 6.4 and 8.2 Å in the crystal structure XCIII and 7.9 and 9.5 Å in XCIV. The hydrogen bond system in crystalline XCIII (infinite chains of O-H...O hydrogen bonded molecules) is very similar to that of XCII but differs completely from that found in siladifenidol XCVI with a strong intramolecular O-H...N hydrogen bond [111].

Silepine (XCVII), the Si-analogue of parathiepine (XCVIII), which has a weaker neuroleptic activity than XCVII, is characterized by a greater planarity of the 7-membered ring and pseudoaxial orientation of the piperazinyl substituent at the ethylene bridge, which makes it roughly equidistant from both benzene rings, while in XCVII (pseudoequatorial orientation), the piperazinyl substituent is closer to one of the benzene rings. The difference in orientation of the piperazinyl substituent probably plays an important role in controlling of the bioactivity of the compounds of types XCVII and XCVIII [116].



X = $SiMe_2$ (XCVII)
S (XCVIII)

11. Intermolecular distances, H-bonding and ionic interactions

Calculations of intermolecular contacts in crystals in crystals of organosiloxanes have shown [117] that molecules of "non-rigid" siloxanes occupy a greater effective volume than that determined by the generally accepted van der Waals radii. At the same time, in crystals of more rigid siloxanes, which are hydrogen bonded or have bulkier substituents, intermolecular contacts are realized at distances that are normal for organic molecular crystals . This implies differences in density of molecular packing in crystals of "rigid" and "non-rigid" siloxanes [117].

Hydrogen bonds in crystals of siloxanes, for instance XCIX [118], are of an intermediate strength and exert little effect on the geometry of the SiO molecular frameworks [119].

N-Lithium and N-sodium hexamethyldisilazanes $Li[N(SiMe_3)_2]$ (C) and $Na[N(SiMe_3)_2]$ (C) exhibit properties of covalent compounds, but, unlike solutions where they probably have a dimeric structure, in crystals these molecules are linked into trimers (C, [120]) or polymers (CI, [121]). The framework of trimer C represents an approximately planar 6-membered Li_3N_3 ring (Li-N 2.00(2) Å), wherein each N atom is bonded to two Me_3Si groups (av. Si-N 1.729(4) Å). Infinite -Na-N-Na-N- chains in the crystal of C have Na-N and Si-N bond lengths of 2.352(2) and 1.690(5) Å. In the ionic crystal of $K[N(SiMe_3)_2].C_4H_8O_2$ (CII) [122] the K^+ cation is coordinated, besides the N atom, by four oxygen atoms of dioxane solvate molecules. Although on going from the Li and Na to the K derivative a qualitative change in bonding nature occurs, the M-N distances differ approximately by the same values as the Li^+, Na^+ and K^+ ionic radii.

In the trimeric $[(Me_3SiNNa)_2SiMe_2]_3$ cluster one $Na(3)^+$ cation is situated approximately in the centre, while five other Na^+ cations are arranged around the central one at the vertices of a trigonal bipyramid (Fig. 17) [123]. At first sight the Na^+ cations

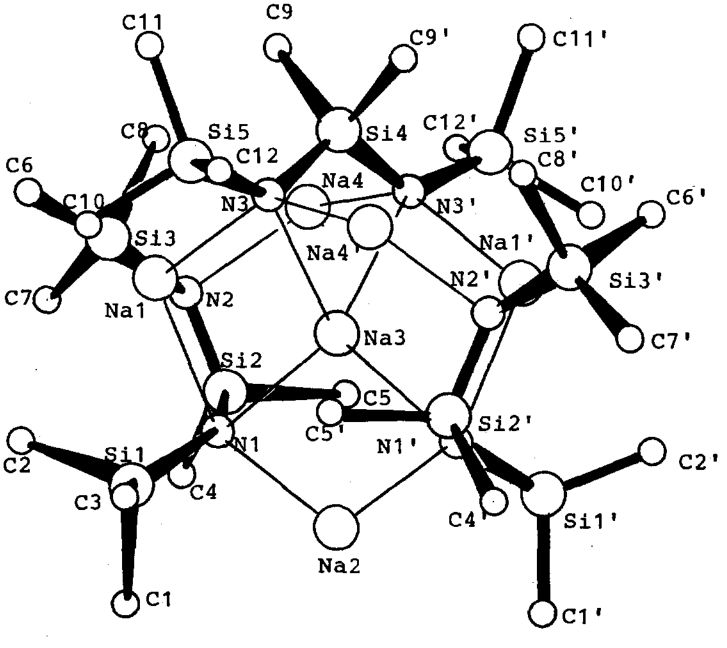


Fig. 17 Structure of the ionic cluster $[(Me_3SiNNa)_2SiMe_2]_3$ (C_2 symmetry) [123]

seem to be coordinatively unsaturated (a distorted tetrahedral coordination of the Na(3)$^+$ cation, non-linear two-fold coordination of the Na(2)$^+$ and Na(4)$^+$ cations), but the rest of the octahedral coordination sites are not vacant but filled with Me-groups.

In crystals of ionic silanolates and siloxanolates the spatial segregation of different structural regions is observed with separate areas of ionic and van der Waals interactions (hydrophilic and hydrophobic regions). Layer structures are thus realized in crystals of $Na_3[PhSi(O)O]_3.8H_2O$ [124], $[Na(Me_3SiO)].3H_2O$ [125] and $Na_2[(Me_2SiO)_2O].4H_2O$ [125], while crystals of the anhydrous complex $10[Na(Me_3SiO)].NaOH$ [126] are built of cluster associates (Fig. 18).

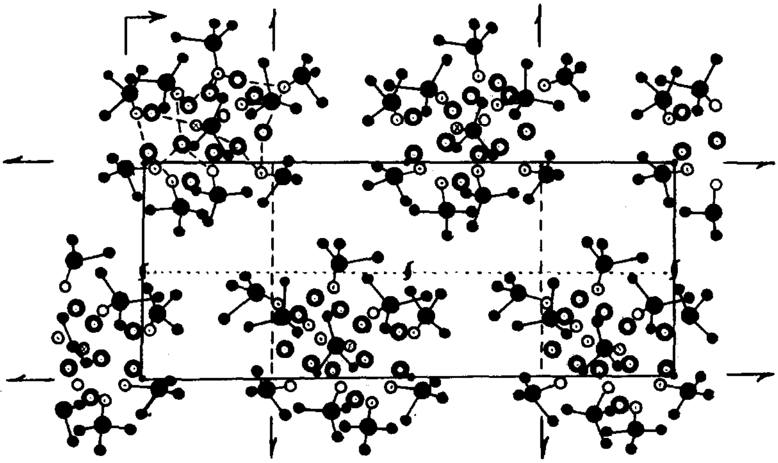


Fig. 18 Crystal structure of $10[Na(Me_3SiO)].NaOH$ built of cluster associates (● - C, o - O, ⬤ - Si, **O** - Na, ⊗ - O of the HO group, dashed lines - ionic Na...O interactions [126]

12. Conclusion

Structural investigations of the following classes of OSC may be regarded as the "hot spots" of organosilicon structural chemistry: siloxanes and related compounds, representing models of polymer elementary units; OSC with novel heteroatoms, e.g. metal atoms; OSC with highly coordinated Si atoms; compounds with multiple bonds at the Si atom. It is possible to foresee a growing interest in structure-bioactivity relationships in the above mentioned and other classes of OSC, as well as in a deeper insight in the nature of chemical bonds, formed by the Si atom, and also in attractive intra- and intermolecular interactions, organosilicon intermediates and ionic OSC, the studies of which can assist a better and more profound understanding of mechanism and pathways of chemical reactions.

13. References

1 V.A.Palyulin,N.S.Zefirov,V.E.Shklover and Yu.T.Struchkov, J. Molec. Struct., 1, 70 (1980) 65.

2 G.Garzo,J.Tamas,T.Szekely and K.Ujszaszi, Acta Chim. Acad. Sci. Hung., 69 (1971) 273.

3 V.E.Shklover,Yu.T.Struchkov,I.Yu.Klementiev,V.S.Tikhonov and Yu.T.Struchkov, Zh. Strukt. Khim., 20 (1979) 302.

4 V.E.Shklover,I.Yu.Klementiev and Yu.T.Struchkov, Zh. Strukt. Khim., 3, 22 (1981) 76.

5 V.E.Shklover,A.N,Chekhlov,Yu.T.Struchkov,N.N.Makarova and K.A.Andrianov, Dokl. Akad. Nauk SSSR, 234 (1977) 614.

6 V.E.Shklover,I.Yu.Klementiev and Yu.T.Struchkov, Dokl. Akad. Nauk SSSR, 259 (1981) 131.

7 V.E.Shklover,T.V.Timofeeva,Yu.T.Struchkov and A.A.Zhdanov, Vysokomolek. Soed., A25 (1983) 1405.

8 V.E.Shklover,Yu.T.Struchkov,N.N.Makarova and K.A.Andrianov, Zh. Strukt. Khim., 19 (1978) 1107.

9 W.Clegg,G.M.Sheldrick and N.Vater, Acta Cryst., B36 (1980) 3162.

10 V.E.Shklover,Yu.T.Struchkov,N.N.Makarova and A.A.Zhdanov, Zh. Strukt. Khim., 4, 22 (1981) 103.

11 V.E.Shklover,Yu.T.Struchkov,A.B.Zachernyuk and A.A.Zhdanov, Cryst. Struct. Commun., 11 (1982) 1771.

12 I.L.Dubchak,V.E.Shklover,and Yu.T.Struchkov, Zh. Strukt. Khim., 5, 24 (1983) 121.

13 N.L.Paddock,S.J.Rettig and J.Trotter, Can. J. Chem., 61 (1983) 541.

14 D.W.J.Cruichshank, Acta Cryst., 14 (1961) 896.

15 M.A.Hossain and M.B.Hursthouse, Inorg. Chim. Acta, 44 (1980) L259.

16 C.Gaffney,P.G.Harrison and T.J.King, Chem. Commun., (1980) L251.

17 H.Puff,M.P.Bockmann,T.R.Kok and W.Schuh, J. Organomet. Chem., 268 (1984) 197.

18 M.Soderholm and D.Carlstrom, Acta Chem. Scand., B31 (1977) 193.

19 M.A.Hossain,M.B.Hursthouse and K.M.A.Malik, Acta Cryst., B35 (1979) 522.

20 J.B.Hendrickson, J. Amer. Chem. Soc., 86 (1964) 4854; 89 (1967) 7036.

21 C.Glidewell and D.C.Liles, Acta Cryst., B34 (1978) 124.

22 A.I.Yanovsky,I.L.Dubchak,V.D.Myakushev,L.I.Zakharkin,V.E.Shklover,Yu.T.Struchkov, V.N,Kalinin and B.A.Izmailov, Zh. Strukt. Khim., 5, 23 (1982) 88.

23 C.Glidewell, Inorg. Chem., 29 (1978) L283.

24 A.H.Cowley,M.C.Cushner and P.E.Riley, J. Amer. Chem. Soc., 102 (1980) 624.

25 N.Wiberg and H.-W.Haring, Z. Naturforsch., 35B (1980) 599.

26 V.E.Shklover,P.Ad'yasuren,G.V.Kotrelev,E.A.Zhdanova,V.S.Svistunov and Yu.T.Struchkov, Zh. Strukt. Khim., 2, 21 (1980) 94.

27 H.Rosenberg,T.T.Tsai,W.W.Adams,M.T.Gehatia,A.V.Frantini and D.R.Wiff, J. Amer. Chem. Soc., 98, (1976) 8083.

28 D.J.Brauer,H.Burger,E.Essig and W.Geschwandter, J. Organomet. Chem., 190 (1980) 343.

29 M.Veith, Z. Anorg. Allg. Chem., 446 (1978) 227.
30 R.P.Planalp, R.A.Andersen and A.Zalkin
31 W.Clegg, Acta Cryst., B36 (1980) 2830.
32 W.Clegg, Acta Cryst., C39 (1983) 1106.
33 W.Clegg, U.Klingebiel, G.M.Sheldrick and P.Werner, Angew. Chem., Int. Ed., 20 (1981) 384.
34 W.Clegg, U.Klingebiel, S.Pohlmann, G.M.Sheldrick and P.Werner, Angew. Chem., Int. Ed., 20 (1981) 383.
35 W.Clegg, M.Noltemeyer, G.M.Sheldrick and N.Fater, Acta Cryst., B36 (1980) 2461.
36 V.E.Shklover, Yu.T.Struchkov, B.A.Astapov and K.A.Andrianov, Zh. Strukt. Khim., 1, 20 (1980) 102.
37 V.E.Shklover, Yu.T.Struchkov, G.V.Kotrelev, V.V.Kazakova and K.A.Andrianov, Zh. Strukt. Khim., 1, 20 (1980) 96.
38 V.A.Yablokov, N.V.Yablokova, V.E.Mikhlin and D.Ya.Zhinkin, Organosilicon Peroxides. In: Organoelement compounds, NIITEKhim, Moscow, 1978.
39 V.E.Shklover, T.V.Timofeeva, Yu.T.Struchkov, A.V.Ganyushkin and V.A.Yablokov, Zh. Strukt. Khim., 3, 22 (1981) 68.
40 V.A.Lebedev, Yu.N.Drozdov, E.A.Kuzmin, A.V.Ganyushkin, V.A.Yablokov and N.V.Belov, Kristallographiya, 1, 26 (1981) 192.
41 V.A.Lebedev, Yu.N.Drozdov and E.A.Kuzmin, Dokl. Akad. Nauk SSSR, 248 (1979) 601.
42 D.Kass, H.Oberhammer, D.Brandes and A.Blashette, J. Molec. Strukt., 40 (1977) 65.
43 V.E.Shklover, P.Ad'yasuren, I.Cynker, V.A.Yablokov and A.V.Ganyushkin, Zh. Strukt. Khim., 3,21 (1980) 112.
44 V.E.Shklover, Yu.T.Struchkov, A.V.Ganyushkin, V.A.Yablokov and G.A.Razuvaev, Dokl. Akad. Nauk SSSR, 253 (1980) 341.
45 P.Groth, Acta Chem. Scand., 23 (1969) 1311.
46 J.B.Hendrickson, J. Amer. Chem. Soc., 89 (1967) 7047.
47 G.Sawitzky and H.G.Schnering, Chem. Ber., 109 (1976) 3728.
48 T.A.Beineke and L.L.Martin, J. Organomet. Chem., 20 (1969) 65.
49 H.Watanabe, M.Kato, T.Okawa and Y.Nagai, J. Organomet. Chem., 271 (1984) 225.
50 S.Masamure, Y.Hanzava, S.Murakami, Z.Bally and J.F.Blount, J. Amer. Chem. Soc., 104 (1982) 302.
51 A.Schafer, M.Weidenbruch, K.Peters and H.G.Schnering, Angew. Chem., Int. Ed., 23 (1984) 302.
52 C.J.Hurt, J.C.Calabrese and R.J.West, J. Organomet. Chem., 91 (1975) 273.
53 L.Parkanyi, K.Saswari and I.Barta, Acta Cryst., B34 (1978) 883.
54 M.Ishokawa, T.Fuchikami, M.Kumada, T.Higuchi and S.Miyamoto, J. Amer. Chem. Soc., 101 (1979) 1348.
55 L.Parkanyi, K.Saswari, J.P.Declercq and G.Germain, Acta Cryst., B34 (1978) 3678.
56 O.A.D'yachenko, S.V.Soboleva and L.O.Atovmyan, Zh. Strukt. Khim., 17 (1976) 350.
57 U.Wannagat, S.Klemke, D.Mootz and H.D.Reski, J. Organomet. Chem., 178 (1979) 83.
58 W.Stallings and J.Donohue, Inorg. Chem., 15 (1976) 524.
59 C.S.Liu, S.C.Nyburg, J.C.Nyburg, J.T.Szymanski and J.C.Thompson, J. Chem. Soc. Dalton Trans., (1972) 1129.
60 G.M.Sheldrick and A.Borkenstein, Acta Cryst., B33 (1977) 2916.
61 H.L.Carrell and J.Donohue, Acta Cryst., B28 (1972) 1566.
62 S.N.Gurkova, A.I.Gusev, A.T.Abrosimova, N.V.Alekseev and M.G.Voronkov, Dokl. Akad. Nauk SSSR, 260 (1981) 1115.
63 G.K.Delker, Y.Wang, G.D.Sticky, R.L.Lambert, C.K.Haas and D.Seyeferth, J. Amer. Chem. Soc., 98 (1976) 1779.
64 W.Ando, Y.Hamada and A.Sekiguchi, Tetrahedron Lett., 23 (1982)

65 K.Hirotsu, T.Higuchi, M.Ishikawa, H.Sugisawa and M.Kumada, Chem. Commun., (1982) 726.
66 K.Peters, E.-M. Peters and H.G.Schnering, Z. Anorg. Allg.Chem., 502 (1983) 61.
67 S.N.Gurkova, A.I.Gusev, V.A.Sharapov, T.K.Gar and N.V.Alekseev, Zh. Strukt. Khim., 20 (1979) 356.
68 A.Lipka and H.G.Schering, Z. Anorg. Allg. Chem., 419 (1976) 20.
69 G.Sawitzky, H.G.Schnering, Z. Anorg. Allg. Chem., 399 (1973) 257.
70 G.Fritz, H.Volk, K.Peters, E,-M.Peters and H.G.Schnering, Z. Anorg. Allg. Chem., 497 (1983) 119.
71 H.G.Schnering, G.Sawitzky, K.Peters and K.-J.Tebbe, Z. Anorg. Allg. Chem., 404 (1974) 38.
72 J.C.Barthelat, G.Tringuir and G.Bertrand, J. Amer. Chem. Soc., 101 (1979) 3785.
73 A.R.Clagett, W.H.Ilsley, T.J.Anderson, M.D.Glick and J.P.Oliver, J. Amer. Chem. Soc., 99 (1977) 1797.
74 W.H.Ilsley. M.J.Abright, T.J.Anderson, M.D.Glick and J.P.Oliver, Inorg. Chem., 19 (1980) 3577.
75 K.-F.Tebbe, Z. Anorg. Allg. Chem., 468 (1980) 202.
76 M.Feher, T.Heinlein, K.-F.Tebbe, Abstr. Europ. Cryst. Meet., Liege, 1983, p. 92.
77 M.Bandler, T.Pontzen, U.Schings, K.-F.Tebbe and M.Feher, Angew. Chem., Int. Ed., 22 (1983) 775.
78 H.Wolfgang, H.G.Schnering, Z. Anorg. Allg. Chem., 442 (1978) 107.
79 W.Honle and H.G.Schnering, Z. Anorg. Allg. Chem., 440 (1978) 171.
80 G.Becker, G.Gutenkunst and C.Witthauer, Z. Anorg. Allg. Chem., 486 (1982) 90.
81 H.G.Schnering, D.Fenske, W.Honle, M.Binneweis and K.Peters, Angew. Chem., Int. Ed., 18 (1979) 679.
82 G.Becker and C.Wittenhauer, Z. Anorg. Allg. Chem., 492 (1982) 28.
83 G.Becker, H.Friedenbaum and C.Wittenhauer, Z. Anorg. Allg. Chem., 492 (1982) 37.
84 G.Becker, A.Munch and C.Wittenhauer, Z. Anorg. Allg. Chem., 492 (1982) 15.
85 W.E.Schklower, Yu.T.Struchkow, L.E.Guselnikow, W.W.Wolkowa, W.G.Awakyan, Z. Anorg. Allg. Chem., 501 (1983) 153.
86 M.C.Couldwell, J.Simpson and W.T.Robinson, J. Organomet. Chem., 107 (1976) 323.
87 B.K.Nicholson, J.Simpson and W.T.Robinson, J. Organomet. Chem., 47 (1973) 403.
88 R.Rudman, W.C.Hamilton, S.Novick and T.D.Goldfarb, J. Amer. Chem. Soc., 89 (1967) 5157.
89 A.J.Blake, E.A.V.Ebsworth and A.J.Welch, Acta Cryst., C40 (1984) 895.
90 V.E.Shklover, Yu.T.Struchkov, M.S.Sorokin and M.G.Voronkov, Dokl. Akad. Nauk SSSR, 274 (1984) 615.
91 M.P.Demidov, V.E.Shklover, Yu.T.Struchkov, Yu.L.Frolov, A.A.Kashaev and M.G.Voronkov, Zh. Strukt. Khim., (1985) in press.
92 L.Parkanyi, P.Hencsei, L.Bihatsi and T.Muller, J. Organomet. Chem., 269 (1984) 1.
93 E.A.Zelbst, V.E.Shklover, Yu. . truchkov, Yu.L.Frolov, A.A.Kashaev, L.I.Gubanova, V.M.D'yakov and M.G.Voronkov, Zh. Strukt. Khim., 3, 22 (1981) 82.
94 A.A.Kemme, J.Bleidelis, I.Urtane, G.Zelchan and E.Lukevics,

95 E.Kupce, E.Liepins and E.Lukevics, J. Organomet. Chem., 248 (1983) 131.

96 V.E.Shklover, Yu.T.Struchkov, V.F.Traven', O.G.Rodin, V.I.Rokitskaya, M.Yu.Eismont and B.I.Stepanov, Abstr. 7th. Int. Symp. Organosilicon Chemistry, Jap., 1984, p. 121.

97 V.E.Shklover, Yu.T.Struchkov, O.G.Rodin, V.F.Traven' and B.I.Stepanov, J. Organomet. Chem., 266 (1984) 117.

98 M.J.Barrow, and E.A.V.Ebsworth, J. Chem. Soc. Dalton Trans., 211 (1982).

99 W.B.Farnham and J.F.Whitney, J. Amer. Chem. Soc., 106 (1984) 3992.

100 G.Fritz, U.Braun, W.Schick, W.Honle and H.G.Schnering, Z. Anorg. Allg. Chem., 472 (1981) 45.

101 A.G.Brook, S.C.Nyburg, F.Abdesaken, B.Gutenkunst, G.Gutenkunst, R.K.Kallury, Y.C.Poon, Y.-M.Chang and W.Wong-Ng, J. Amer. Chem. Soc., 104 (1982) 5667.

102 M.J.Fink, M.J.Michalczyk, K.J.Haller, R,West and J.Michl, Organometallics, 3 (1984) 793.

103 S.G.Baxter, K.Mislow and J.F.Blount, Tetrahedron, 36 (1980) 605.

104 H.Sakurai, Y.Nakadaira, H.Tohita, T.Ito, K.Torumi and H.Ito, J. Amer. Chem. Soc., 104 (1982) 300.

105 N.Wiberg, G.Wagner, G.Muller and J.Riede, J. Organomet. Chem., 271 (1984) 381.

106 H.F.Schaefer, Acc. Chem. Res., 15 (1982) 283.

107 M.Bonamico and G.Dessy, J. Chem. Soc., A, (1968) 291.

108 M.G.Voronkov, Chem. Brit., 9 (1973) 411.

109 M.G.Voronkov, Ann. Rep. Med. Chem., 11 (1975) 265.

110 R.Tacke, R.Niedner, J.Frohnecke, L.Ernst and W.S.Sheldrick, Liebigs Ann. Chem., (1980) 1859.

111 R.Tacke, M.Strecker, W.S.Sheldrick, L.Ernst, E.Heeg, B.Berndt, G.-M.Knapstein and R.Niedner, Chem. Ber., 113 (1980) 1962.

112 M.Soderholm, Acta Chem. Scand., B38 (1984) 31.

113 R.Tacke and U.Wannagat, Fortschr. Chem. Forsch., 84 (1979) 1.

114 M.Soderholm, Acta Chem. Scand., B38 (1984) 95.

115 M.Soderholm, Acta Chem. Scand., B38 (1984) 303.

116 E.R.Corey, W.F.Paton, J.Y.Corey and M.D.Glick, J. Organomet. Chem., 179 (1979) 241.

117 I.L.Dubchak, T.V.Timofeeva, V.E.Shklover, Yu.T.Struchkov and A.A.Zhdanov, Zh. Strukt. Khim., 6, 22 (1981) 112.

118 V.E.Shklover, I.L.Dubchak, Yu.T.Struchkov, E.S.Khynku and A.A.Zhdanov, Zh. Strukt. Khim., 2, 22 (1981) 104.

119 V.E.Shklover and Yu.T.Struchkov, Usp. Khim., 49 (1980) 518.

120 R.Coning and J.C.Atwood, J. Organomet. Chem., 137 (1977) 101.

121 R.D.Rogers and J.C.Atwood, J. Organomet. Chem., 157 (1978) 229.

122 A.M.Domingos and G.M.Sheldrick, Acta Cryst., B30 (1974) 517.

123 D.J.Brauer, J. Organomet. Chem., 248 (1983) 1.

124 I.L.Dubchak, V.E.Shklover, M.M.Levicky, A.A.Zhdanov and Yu.T.Struchkov, Zh. Strukt. Khim., 6, 21 (1980) 103.

125 I.L.Dubchak, V.E.Shklover, M.Yu.Antipin, Yu.T.Struchkov, V.M.Kopilov, A.M.Muzafarov, P.L.Prikhod'ko and A.A.Zhdanov, Zh. Strukt. Khim., 2, 23 (1982) 63.

126 I.L.Dubchak, V.E.Shklover, Yu.T.Struchkov, V.M.Kopylov and P.L.Prikhod'ko, Zh. Strukt. Khim., 2, 24 (1983) 59.