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Organic compounds of silicon with non-standard types of coordination

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ABSTRACT. **The structures of organosilicon compounds in which the coordination number of silicon is other than 4 are examined. Derivatives of pentacoordinate silicon, in which silicon has a trigonal-bipyramidal geometry, have been most thoroughly investigated among them. Appreciably much less information is available about the unstable derivatives of tricoordinate silicon, whose structure is close to being planar. Examples of compounds in which the coordination number of silicon is greater than five are also examined. Attention is concentrated on the geometry of compounds with an increased coordination number of silicon atoms as intermediates in chemical reactions.**
The bibliography includes 111 references.

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I. Introduction

The main advances in the chemistry of organosilicon compounds (OSC) are associated with studies on derivatives of traditional tetrahedral silicon. This is why the commonest valence and coordination state of silicon is in fact mainly considered in the structural chemistry of OSC.[1,2] However, compounds in which the coordination number of silicon is higher (in the first place silatranes[3,4]) have been synthesised comparatively recently and have now ceased to be unique, while in the last 5–7 years it has been possible to obtain compounds with multiple bonds at the silicon atom.[5–10] The structures of these new OSC have been investigated in fair detail (see, for example, the relevant reviews[1–6]), but so far there has been no general survey of these investigations. The aim of the present review is the examination of the structural features of all the known OSC with a non-tetrahedral coordination of the silicon atom or a coordination which differs appreciably from the tetrahedral. Attention is concentrated on compounds with a silicon–carbon bond, but certain new interesting compounds without such bonds are also considered.

The review does not claim to cover all the structural data on OSC with a non-tetrahedral silicon atom. Preference is given to X-ray diffraction studies (the most reliable method for the investigation of new structures), new results, and the authors' own data.

II. Tricoordinate silicon compounds

1. Silaethylenes

The available data on the structures of compounds with Si=C double bonds (silaethylenes) are summarised in Table 1. Their Si=C bond lengths are in the range close to the length (1.69–1.73 Å) predicted by MO calculations for sterically unhindered silaethylenes.[11] The molecule of compound (I) with the shortest Si=C bond [1.702(5) Å] has a virtually planar core $C_2Si=CSi_2$ (Fig. 1), the sum of the valence angles at each of the atoms Si(1) and C(1) being 360°. The torsional distortion (twisting) relative to the Si=C bond is only 1.6°. The deviations of the valence angles at the unsaturated Si(1) and C(1) centres from the standard values for the sp^2 hybridisation can be fairly well accounted for by the steric strain introduced by the $SiMe_3$ and especially $SiMe(Bu_t)_2$ groups at the C(1) atom.[8]

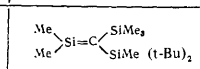
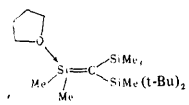
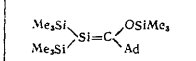
The differences between the Si=C bond lengths and the torsional distortions in the silaethylenes (I)–(III) are probably caused by the greater size of the substituents and also by their electronegativity [the $OSiMe_3$ group in compound (III)]. Since the silaethylene (I) contains less bulky and not unduly electronegative substituents, its Si=C bond length [1.702(5) Å] can be regarded as characteristic of the silaethylene $R_2Si=CR_2$ with moderately large substituents.

The most interesting feature of the silaethylene tetrahydrofuranate (II) molecule is the presence in it of a significantly planar bond system at the sp^2-hybridised C(1) atom, which forms a double bond with the tetracoordinate Si(1) atom which is involved in an unusual coordination (Fig. 2). The sum of the valence angles of the C(1) atom is 358.8° and the atom is displaced from the Si(1)Si(2)Si(3) plane by only 0.11 Å. Large valence angles at the C(1) atom are probably caused by the steric interaction between the substituents. The largest Si(1)C(1)Si(3) angle, which is 126.7(3)°, is due to the extremely bulky $Si(3)MeBu_2$ group whose Si(3)–C(8) and Si(3)–C(12) bonds are in the *gauche*-conformation relative to the Si(1)–C(1) bond.

The coordination involving the Si(1) atom does not correspond to the ideal tetrahedral geometry, which can be difficult to explain by steric hindrance. The C(1)Si(1)C(2) and C(1)Si(1)C(3) angles, which are respectively 119.7° and 124.1(3)°, unexpectedly differ little from 120°, the usual value of the angle in the sp^2-hybridisation. The C(2)Si(1)C(3) = 104.9(3)° angle is appreciably smaller than the tetrahedral value. The angles at the oxygen atom in the THF

molecule can be divided into two groups: the OSi(1)C(1) = 107.9(2)° angle is much greater than the OSi(1)C(2) = 97.9° and OSi(1)C(3) = 96.5(2)° angles. The Si(1)–O = 1.878(4) Å distance is much greater than the Si–O bond lengths characteristic of the dicoordinate O atom in siloxanes (1.68 Å) [12–15] and the bonds involving a tricoordinate O atom aluminosiloxanes (1.66–1.76 Å),[16] although in the latter the O atom is incorporated in some cases in a strained four-membered Al_2O_2 ring.

Table 1. The principal geometrical parameters of molecules with Si=C double bonds.

No. of compound	Compound	Molecular symmetry	r (Si=C), Å	τ*, deg	Refs.
(I)		C_1	1.702 (5)	1.6	[8]
(II)		C_1	1.747 (5)	22.4	[9]
(III)	 Ad = 1-adamantyl	C_1	1.764 (3)	14.6	[10]

*τ = angle of twist about the Si=C double bond.

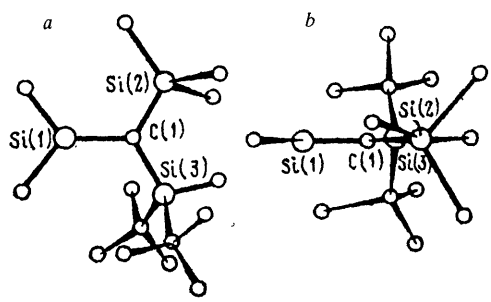
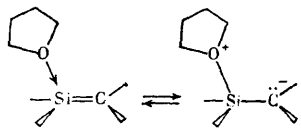


Figure 1. The structure of the molecule of compound (I): projection onto the Si_3C plane (*a*) and onto a surface perpendicular to the plane of the π-system of the C(1)=Si(1) double bond (*b*).[8]

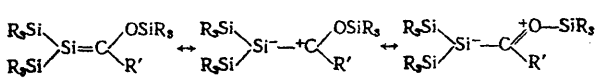
The Si(1)–C(2) and Si(1)–C(3) bond lengths [1.850 and 1.858(5) Å respectively] are somewhat greater than the C(1)–Si(2) and C(1)–Si(3) bond lengths [1.853 and 1.836(5) Å] and are much smaller than the Si–Me bond lengths in silyl groups [1.879 Å to 1.907(6) Å]. The Si(3)–C(Bu_t) [Si(3)–C(8) and Si(3)–C(12)] bonds are even longer [1.939 and 1.927(6) Å], which may be caused by steric strain.[9] The usual geometry of compound (II) can be explained by equilibrium between the forms (A) and (B):[9]



The canonical form (A) corresponds to the formation of an adduct with THF, as a consequence of which the Si atom acquires ten electrons, which requires the participation of *d* orbitals in the bonding. It is important to emphasise that the presence of an excess Si–O bond in compound (II) does not induce a sharp increase in the length of the Si=C bond, which remains shorter than, for example, in the silaethylene (III), with bulky substituents (Table 1). The second canonical form (B) presupposes charge separation between the atoms in the 1- and 3-positions as a consequence of the formation of the covalent Si–O bond, as happens in the phosphorus ylides $R_3P^+-\dot{C}R_2^-$. The increased Si–O bond length in the molecule of compound (II) agrees with a relatively low stability of the adduct (A), in which suitable *d* orbitals of the Si atom can overlap with the donor orbitals of the O atom and the approximately tetrahedral form (albeit distorted) coordination of the Si(1) atom agrees with the zwitter-ionic form (B).

The conformation of the molecule of compound (II) is apparently determined by the steric interactions of the substituents at the Si(1) and C(1) atoms. In particular, the twisting around the double bond [the C(3)Si(1)C(1)Si(3) angle is 22.4°] is probably caused by the minimisation of the steric interactions between the methyl groups at Si(1) and the t-butyl groups at the Si(3) atom. According to ^{1}H NMR data, both Me groups at the Si(1) atom in the molecule of compound (II) in solution in THF at 30 °C are equivalent.[9] This is a powerful argument in support of form (B), the ylide type of bonding in which presupposes free rotation about the Si(1)–C(1) bond.

The high stability of the silaethylene (III) can be explained partly by steric causes (bulky substituents, especially the adamantyl substituent, prevent dimerisation and other reactions) and partly by the electronic influence of the substituents Me_3SiO and Me_3Si at the double bonded C and Si atoms respectively. As a consequence of the inductive effect of the substituents and the existence of resonance forms, the polarisation of the double bond is found to be much smaller than would have been expected from the difference between the electronegativities of the Si and C atoms:



Quantum-chemical calculations confirm the stabilising influence of the silyl group at the Si atom and of the siloxy-group at the C atom on the Si=C double bond (as a consequence of electronic effects).[9]

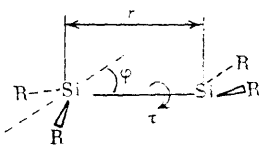
2. Disilenes

The first stable disilene, investigated by X-ray diffraction, proved to be tetramesityldisilene (IV),[17] synthesised by the photolysis of the polysilane precursor.[17] The Si–Si = 2.160(1) Å distance in the molecule of compound (IV) is shorter by 0.19–0.20 Å than in tetramesityldisilane,[19] which is consistent with the presence of a double bond in compound (IV).

It follows from the X-ray diffraction data for the heteroethylenes M_2R_4 that, with increase in the atomic number of the M atom, there arises a tendency towards an increase in the pyramidal form of

its coordination {the sum of the valence angles of the M atom is 360° in C_2Ph_4, 355.3° in compound (IV), 348.5° in $Ge_2[CH(SiMe_3)_2]_4$, and 342° in $Sn_2[CH(SiMe_3)_2]_4$} and towards the shortening of the M–M bond compared with the standard $M(sp^3)-M(sp^3)$ bond lengths adopted in the diamond-like modification of M [C(12%) > Si(8%) > Ge(4%) > Sn(2%)].[20]

Table 2. The principal geometrical parameters of molecules with Si=Si double bonds



No. of compound	Compound	Molecular symmetry	r, Å	τ, deg	φ*, deg	Refs.
(IV)	Mes(Mes)Si=Si(Mes)Mes; Mes = 2,4,6-$Me_3C_6H_2$	C_2	2.160 (1)	6.5	15	[17]
(V)	Mes(t-Bu)Si=Si(Bu-t)Mes	C_i	2.143 (1)	0	0	[21]
(VI)	R(R)Si=Si(R)R; R = 2,6-$Et_2C_6H_3$	C_i	2.15	0	10	[5]

*φ = angle between the plane and the Si=Si bond.

Both these features indicate the presence of a large, albeit smaller than in alkenes, π-contribution to the Si–Si bond in disilenes.[21] These conclusions agree with the results of a large number of theoretical studies in which the energy of the π-bond in the Si_2H_4 model disilene was estimated as approximately 30 kcal mol^{-1},[22,23] which is smaller by a factor of approximately two than the π-bond energy in ethylene.

The weaker π-interaction in disilenes compared with alkenes is usually attributed to the less effective overlap of the 3*p* orbitals of the Si atoms.[21] The overlap of 4*p* or 5*p* orbitals of Ge or Sn analogues of olefins should be even weaker. The distinctly antipyramidal structure of distannenes probably arises as a consequence of the ineffectiveness of the $p_\pi-p_\pi$ bonding: the Sn–Sn distance in tetrakis(trimethylsilyl)distannene agrees with the length of a single Sn–Sn bond in hexaphenyldistannane.[21]

As can be seen from Table 2, the molecules of the three disilenes listed in it are characterised by very similar Si=Si bond lengths, but differ significantly in the deformability of the central fragment. According to the results of *ab initio* calculations, disilenes are appreciably more susceptible to deformations than alkenes and the differences between the molecular geometries of the environments of the Si=Si double bonds in compounds (IV)–(VI) can be explained by packing effects.[21] It is therefore entirely possible that other conformations of compounds (IV)–(VI) predominate in solution rather than in the solid phase. According to calculations of the structure of the Si_2H_4 molecule in the ground state, its potential energy level is described by a low-slope surface with two minima corresponding to antipyramidal and planar geometries, the first form being more stable than the second by ~0.5 kcal mol^{-1}.[21]

Quantum-chemical calculation[24] of the energies of the M_2H_4 molecules (M = C, Si, or Ge) as a function of the pyramidalisation angle φ showed that "for ethylene this function is a parabola with a minimum at φ = 0°, for disilene it is a U-shaped curve with low-slope bottom, indicating a contribution by a structure with a large angle φ, while for digermene the curve has a maximum at φ = 0° and a minimum at φ = ±40°. The latter can be regarded as an indication of the possibility of an intermediate structure with a single Ge–Ge bond and the resonance of the unshared electron pair, which corresponds to the angle φ ≃ 55°".[25]

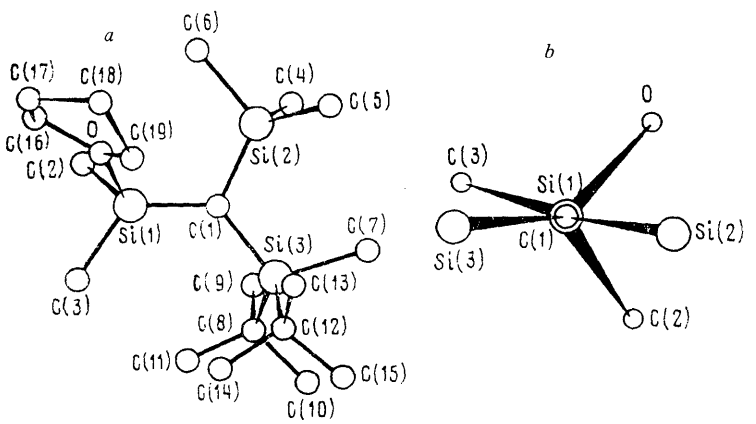
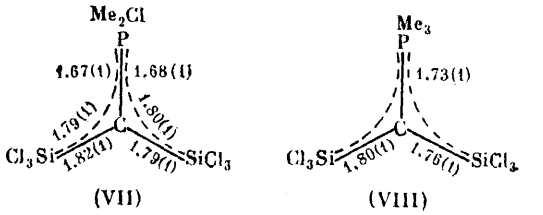


Figure 2. The structure of the molecule of compound (II): projection onto the Si_3C plane (*a*) and view along the C(1)=Si(1) bond (*b*).[10]

III. Compounds of tetracoordinate silicon with an appreciably distorted structure

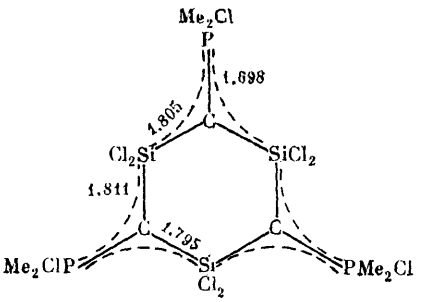
1. Disilaphosphorane ylides

An unexpected feature of the disilaphosphorane ylides (VII)–(IX) [26]



(VII)

(VIII)



(IX)

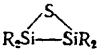
proved to be appreciably smaller lengths of the Si–C (1.76–1.82 Å) and P–C (1.67–1.73 Å) bonds involving central planar-trigonal C atoms compared with the standard Si–C (1.84–1.87 Å) [12–15] and P–C (1.78–1.82 Å) distance.[27] This indicates an increased order of the ylide bonds for what is actually an undistorted tetrahedral coordination of the Si and P atoms. Using the equations $n_i = (d_1/d_i)^5$ (d_1 is the length of the bond whose order is $n = 1$, assumed to be equal to the sum of the covalent radii with a Shomaker–Stevenson correction for the difference between the electronegativities),[28,29] the authors[26] calculated the approximate orders n_i of the shortened bonds Si–C and P–C. For all three structures (VII)–(IX), the average sum of the bond orders involving the ylide carbon atoms is ~4 and that for the Si and P atoms is ~4.33. Thus the orders of the shortened Si–C and P–C bonds are close to one another and amount to $n \simeq 1.33$. Consequently, the intensification of the interaction of the ylide C atoms with the surrounding Si and P atoms is caused not by the weakening of the interaction of the latter with the peripheral substituents [for example the Si–Cl distances in the molecules of compounds (VII)–(IX) have the usual values of 2.024–2.098 Å] but are caused by additional $p_\pi - d_\pi$ bonding.[26]

The concept of the $p_\pi - d_\pi$ interaction has also been used to explain the shortening of the Si–C bonds with participation of the carbanionic C atom [to 1.799(2) and 1.816(4) Å] in the dimeric organolithium-silicon compound $[Li^+C^-(SiMe_2OMe)_3]_2$.[30]

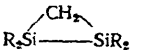
2. Small rings

Many organosilicon compounds containing small three-, four-, and five-membered Si-heterocycles are known in which the valence angles at the Si atoms are much smaller than the standard values. In these systems, the Si atom retains a distorted tetrahedral coordination and the lengths of the bonds involving it usually have the normal values characteristic of unstrained rings. However, in certain cases, for example in cyclodisiloxanes $(R_2SiO)_2$ and cyclodisilathiiranes $R_2\overset{\frown}{Si}-SiR_2-\underset{\frown}{S}$, the molecular geometry is less trivial and the presence in these compounds of some kind of coordination of the Si atom other than the distorted tetrahedral coordination may be postulated.

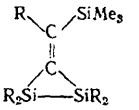
The small length of the Si–Si bond proved to be an unexpected structural feature of the 1,1,2,2-tetramesityl-1,2-disilathiiran (X) molecule.[31] It is 2.289(2) Å, which is smaller by 0.05 Å than the typical Si–Si bond length in disilane derivatives (2.34 Å).[1]



(X): R = mesityl



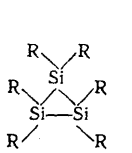
(XI): R = 2,6-dimethylphenyl



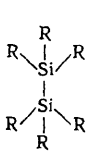
(XII): R = mesityl

The Si–Si distance in disilacyclopropane (XI) is even smaller (2.272 Å),[32] while the corresponding bond in the molecule of compound (XII) (2.327 Å) [33] has almost the normal length. In all three compounds (X)–(XII), the disposition of the second Si atom and of the exocyclic C atoms around the first Si atom of the three-membered ring is almost planar.[31] For example, in compound (X) the sum of the two CSiSi valence angles and of the CSiC angle around both Si atoms is 357.4(4)°. The corresponding values in compound (XI) are 357.4(2)° and 357.7(1)°, while in compound (XII) it is 356.6°. These structural features show that in all three molecules the hybridisation of the Si atom is of the sp^2-p-type rather than the sp^3-type. The interaction of the Si atom with the S and C atoms of the three-membered rings then takes place mainly via the 3p orbital of silicon. Furthermore, the small length of the Si–Si bond in compounds (X)–(XII) suggests that there is some overlap of the 3p orbitals of the neighbouring Si atoms leading to the π interaction between them and hence to an increase in the Si–Si bond order ($n > 1$).[31]

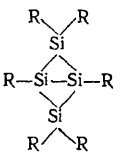
A small length of the Si–Si bond is not characteristic of all compounds containing a three-membered ring: thus in hexakis(2,6-dimethylphenyl)cyclotrisilane (C_1 symmetry) [34] and especially in hexa(t-butyl)cyclotrisilane [35] (XIII) (D_3 symmetry), the Si–Si bond lengths are greater than the normal values [2.407(4) and 2.511(3) Å respectively]. The greater length of the Si–Si bond [2.511(3) Å] in the cyclotrisilane (XIII) molecule containing more bulky substituents is striking.



(XIII): R = Bu-t



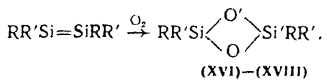
(XIV): R = Bu-t



(XV): R = 2,6-$Et_2C_6H_3$

An appreciable increase in the length of the Si–Si bond to 2.697 Å has been observed in the sterically greatly hindered acyclic molecule of compound (XIV); the Pauling order of this bond is $n = 0.45$.[36] The variability of the Si–Si bond length is as a rule explained by the characteristic features of the steric structure of the molecules. Thus in the bicyclosilane (XV) [37] the central Si–Si bridge bond is somewhat lengthened (it is readily ruptured by oxygen and chlorine; furthermore, the bicyclic system undergoes rapid inversion), while the peripheral bonds are on the whole somewhat shortened.

1,3-Cyclodisiloxanes (Table 3) are formed when the corresponding disilenes are oxidised in air:[38,39]



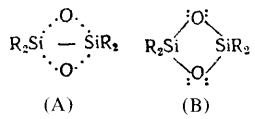
(XVI)–(XVIII)

A characteristic feature of these structures is the small transannular Si...Si distance: it amounts to 2.349(1) Å in compound (XVIII), i. e. it is the same as the length of a single Si–Si bond (2.34 to 2.35 Å),[38] it is somewhat shorter in compound (XVI) 2.306(3) Å, while in compound (XVII) it is somewhat longer (2.396 Å) than the normal Si–Si bond. The transannular O...O distances in compounds (XVI)–(XVIII) are also smaller than twice the van der Waals radius of the oxygen atom (3.40 Å).[40] The Si–O bond lengths in cyclodisiloxanes are somewhat greater than in cyclosiloxanes with a larger ring (1.61–1.65 Å).[1,2] Their SiOSi angles are forced to assume values reduced to 86.2(3)° in compound (XVI), 91.13(7)° in compound (XVII), and 89.7° and 89.4° in compound (XVIII) (in cyclosiloxane the SiOSi valence angles are usually 130–150° [1,2]).

Table 3. The principal geometrical parameters of 1,3-cyclodisiloxanes $(RMeSiO)_2$.[38,39]

Compound	R	Molecular symmetry	Interatomic distances, Å				OSiO' angle, deg	SiOSi angle, deg
			Si...Si	O...O	Si–O	Si–O'		
(XVI)	Me	C_2	2.306 (3)	2.480 (8)	1.721 (4)	1.658 (4)	95.5 (1)	86.2 (2)
(XVII)	t-Bu	C_i	2.396 (1)	2.349 (3)	1.676 (2)	1.679 (2)	88.87 (7)	91.13 (7)
(XVIII)	$(Me_3Si)_2N$	C_1	2.349 (1)	2.358 (4)	1.663	1.668	90.2	89.7
					1.667 (3)	1.672 (3)	89.8 (1)	89.4 (1)

There exist two alternative points of view on the structure of cyclodisiloxanes.[38,39] According to the first, there is a σ-bond between the Si atoms and the Si–O bonds are therefore electron-deficient [structure (A)]; according to the second, there is strong repulsion between the O atoms, which forces the Si atoms to approach one another, but there is no bond between them [structure (B)].



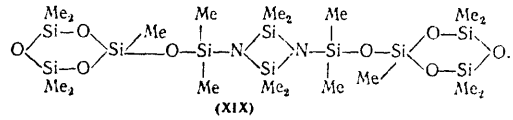
(A) (B)

If the first point of view is adopted, then the addition of oxygen to disilenes during the oxidation reaction induces the dissociation not only of the π-component of the Si=Si double bonds but also of the σ-component.[38] The first calculation by the MNDO method for the model H_4SiO_2 molecule failed to confirm the presence of a bond between the Si atoms but, as pointed out by Fink and co-workers,[38,39] this question has not yet been finally resolved.

In order to explain the structure of cyclodisiloxanes, the model of the bonding in cyclobutadiene is also used.[39] There is a 3*p* orbital (of the π-type) on the silicon atom, which is characterised by a smaller electron density than the 2*p* orbital of the O atom and the diagonal antibonding interactions of the O atoms are therefore stronger than those of the Si atoms, which leads to the rhombic distortion observed in the cyclodisiloxane molecules, for example, in compound (XVI). The differences between the SiOSi angles and the Si...Si distances in the molecules of compounds (XVI)–(XVIII) are a result of the operation of packing forces or steric factors.

The distortions observed in cyclodisiloxanes are characteristic also of cyclodisilthianes, for example of $(Me_2SiS)_2$,[41] in which the SiSSi angle, amounting to 82.41(6)°, is even smaller than in $(Me_2SiO)_2$ [86.2(2)°], because the van der Waals angle of the sulphur is even greater than that of the oxygen atom.

On the other hand, in the cyclodisilazanes $(R_2SiNR)_2$ the SiNSi angles are always greater than 90°—for example, in compound (XIX) this angle is 91.3(1)°:[42]



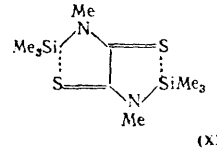
(XIX)

The stretching of the cyclodisilazanes rings in the opposite direction (along the Si...Si diagonal) may be caused by the tendency towards an increase in the valence angles at the N atoms as a result of the movement of the unshared electron pairs of the N atoms away from one another. This is associated with the fact that the Si–N bond lengths in cyclodisilazanes (1.71–1.75 Å) are somewhat greater than the Si–O bond lengths in cyclodisiloxanes [1.663(3)–1.721(4) Å—see Table 3].[39]

IV. Compounds of pentacoordinate silicon

1. Dibenzochalcogensilonins

The additional intramolecular Si ← Si interaction was first observed in the molecule of compound (XX), where the Si...S distances are 3.718 and 3.719 Å (for two symmetrically independent molecules).[43]

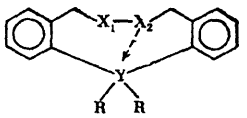


(XX)

A stronger intramolecular transannular Si ← S interaction has been observed in dibenzochalcogensilonins (Table 4). The Si...S and Si...Se distances in compounds (XXI)–(XXIII) are smaller than the sums of the corresponding van der Waals radii by 0.4–0.5 Å. The intermolecular secondary (donor–acceptor) bonds in the $H_3SiSSiH_3$ and $H_3SiSeSiH_3$ crystals are characterised by approximately the same Si...S and Si...Se distances (3.55 and 3.60 Å respectively).[48] The energy of this interaction is low.

Analysis of the conformations of the heterocycles considered using the foldability parameters[47] showed that they all have a form intermediate between the twisted double boat and double boat conformations. However, the disposition of the heteroatoms along the perimeter of the rings of this form common to them depends on the transannular donor–acceptor interaction between the silicon and chalcogen atoms: the ring in which such interaction takes place

differs from that where it does not by the shift of the X_1, X_2, and Y atoms by two positions:



It is of interest that the dihedral angle between the phenylene rings is actually the same in all the compounds (XXI)–(XXIII) of this series (97–99°). Despite this, the overall form of the molecule depends greatly on the presence of the donor–acceptor bond (between the silicon and chalcogen): if this bond is absent, the molecule has the approximate C_2 symmetry; if it is present, the molecule becomes asymmetric (Fig. 3).

Table 4. The transannular Si ← S interactions in the molecules of dibenzochalcogensilonins

Compound	$X_1 = X_2$	Y	R	Interatomic distances, Å		Σ*	$X_2 \rightarrow Y$ interaction	Refs.
				$X_1 \ldots Y$	$X_2 \ldots Y$			
(XXI)	S	Si	Ph	4.193	3.372	3.90	present	[44]
(XXII)	S	Si	Me	4.190	3.438	3.90	»	[45]
(XXIII)	Se	Si	Ph	4.382	3.608	4.00	»	[46]
(XXIV)	Se	Si	Me	4.322	4.228	4.00	absent	[47]
(XXV)	Se	Ge	Me	4.327	4.216	4.10	»	[46]

*Σ = sum of van der Waals radii.

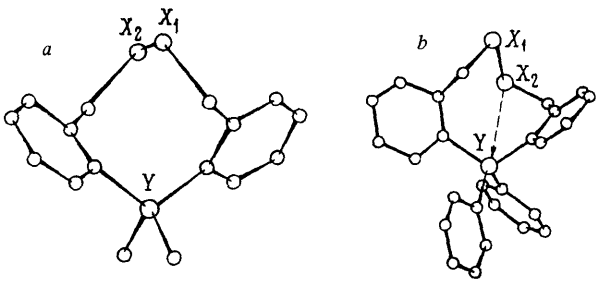


Figure 3. General view of the molecules of the (XXI)–(XXV) series in the presence (*b*) and absence (*a*) of the $X_2 \rightarrow$ Si donor–acceptor bond.[44–47]

Comparison of the lengths of the donor–acceptor bonds in compounds (XXI)–(XXIII) leads to the following conclusions: (1) the X → Si interaction is greatly intensified on passing from X = Se to X = S; (2) the replacement of the methyl groups at the Si and Ge atoms by phenyl groups also strengthens the donor–acceptor bonds; (3) the Ge atom has the same electron-accepting properties (as regards strength) as the Si atom. The replacement of the methyl groups by phenyl groups has different effects in the (XXI)–(XXII) and (XXIV)–(XXIII) pairs: in the latter case, such replacement leads to the appearance of a donor–acceptor bond, while in the former the corresponding $X_2 \ldots$Si distance is shortened by only 0.06 Å.

Furthermore, in the structure of compound (XXII), where the S...S intermolecular distance is only 3.456 Å (twice the van der Waals radius of the S atom is 3.60 Å [40]), there is a possibility of a more complex Si ← S...S → Si intermolecular interaction.[44]

2. The (dimethylamino)silane pentamer and the chloro(dimethylamino)silane dimer

One of the first pieces of evidence for the quinary coordination of the Si atom was provided by an X-ray diffraction study of (dimethylamino)silane (XXVI), whose structure in the crystalline state proved to be pentameric (Fig. 4), while in the gas phase its molecules are monomeric.[49] This made it possible to explain the anomalously high melting point of compound (XXVI) (again 276 K) compared with other compounds $Me_{3-n}N(SiH_3)_n$ (n = 0–3),[50] which are monomeric in the solid state.[51] The crystal structure of compound (XXVI) is discussed here on the basis of a more accurate reinvestigation by X-ray diffraction.[51]

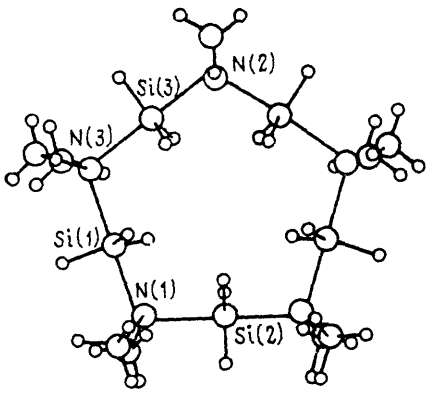


Figure 4. The structure of the (dimethylamino)silane pentamer (XXVI).[51] The molecule has the C_s symmetry.

In the crystal, the molecule of compound (XXVI) occupies a special position on the symmetry plane and has an extremely unusual structure: the N atoms are located at the vertices of a regular pentagon, while the Si atoms are in the centres of its sides, being slightly displaced from the centre of the ring. The average planes of the two crystallographically independent halves of the pentamer molecule intersect the Si(2)...N(2) line, forming a dihedral angle of 170.5°.

Whereas in the gas phase the "isolated" Me_2NSiH_3 molecule is characterised by a pyramidal geometry of the N atom and a tetrahedral geometry of the Si atom or Si–N and N–C bond lengths of 1.712(3) and 1.459(3) Å respectively,[21] in the crystalline state, the Si atoms are involved in a trigonal-bipyramidal coordination, while the N atoms are involved in a tetrahedral coordination; the average interatomic Si–N and N–C distances then increase to 1.976(4) and 1.476(4) Å respectively. Thus the Si–N distances in the pentamer, corresponding to a pentacoordinate Si atom, are

greater by 0.26 Å than the corresponding distance in the monomeric molecule in the gas phase with a tetrahedral coordination of Si. On the other hand, the N–C distances increase by only 0.02 Å when the coordination of N changes from pyramidal to tetrahedral.

We may note yet again that the silicon atom in the structure of this pentacoordinate derivative has a rigorously trigonal-bipyramidal geometry and is located precisely in the plane of the three equatorial H atoms, while both axial Si–N bonds have the same lengths. Thus the Si atom in this compound has the [3 + 2] coordination.

The distortions of the geometry of the tetrahedral molecules as a consequence of the interaction of their central atoms with a relatively close nucleophile can be described as the initial stages of S_N2 nucleophilic substitution reactions whose transition states or intermediates have a trigonal-bipyramidal geometry.[51–53] In this context, the dimethylsilylamine pentamer can be regarded as a "frozen" ensemble of five molecules of a fully symmetrical intermediate.

The vibrational spectra of chloro(dimethylamino)silane (XXVII) in the gaseous and solid states differ sharply, especially in the region of stretching vibrations of the Si–N bond (600–900 cm^{-1}).[54] According to electron diffraction data, compound (XXVII) is monomeric in the gas phase and contains a tetrahedral Si atom (Fig. 5*a*). The Si–N and Si–Cl bond lengths, which are 1.689(4) and 2.070(2) Å respectively, are close to those found in related compounds. The coordination of the N atom is slightly pyramidal and the ClSiN and CNC planes are almost perpendicular to one another.

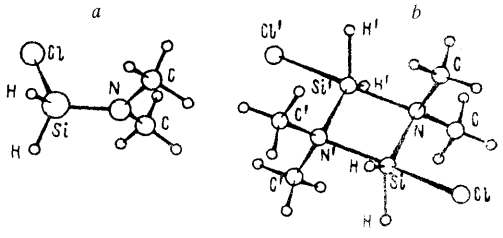
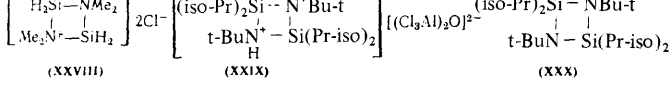


Figure 5. The structure of chloro(dimethylamino)silane (XXVII) in the gas (*a*) and solid (*b*) phases.[54]

The crystal structure of compound (XXVII) includes discrete dimers (Fig. 5*b*) [54] having the C_{2h} crystallographic symmetry: the symmetry plane coincides with the plane of the Si_2N_2 ring. In this ring, the two opposite Si–N distances are 1.81(1) Å, while the other two Si–N distances are much greater [2.05(1) Å]. Consequently the dimer can be described as a species produced by the association of two strongly interacting monomeric molecules. This interaction is manifested by a strong distortion of the tetrahedral coordination of the Si atom in the dimer. The N–Si–Cl angle in the dimer [96.1(5)°] is much smaller than the angle of 113.0(6)° in the monomer, which entails the possibility of the formation of a coordinate bond between the Si and N atoms. The N...Si–C angle is 179.0(4)°, i.e. it is in fact linear and the Si atom acquires a trigonal-bipyramidal coordination, although the N...Si–Cl line, passing through the axial N and Cl atoms, is not rigorously perpendicular to the equatorial plane in which the N atom and the two H atoms linked to the Si atom are located. The axial (and not equatorial) position of the Cl atom creates conditions for the formation of a hypervalent bond, listed by Tandura et al.,[3] and, in particular, it corresponds to the tendency by the most electro-negative substituents to occupy axial positions in a trigonal-bipyramidal molecule. The Si...N coordination interaction leads to an appreciable lengthening of the Si–Cl and Si–N bonds in the crystal (by 0.16 and 0.12 Å respectively) compared with the gas phase, the S–Cl bond being in the *trans*-position relative to the Si–N coordinate bond, while the Si–N′ bond is almost perpendicular to it. The Si–Cl bond length approaches the Si–Cl bond lengths in other derivatives of pentacoordinate (2.148–2.307 Å) or hexacoordinate Si (2.199–2.392 Å).[55] The Si–N...Si = 97.0(6)° angle proved to be intermediate between linear and tetrahedral angles.

It has been suggested[54] that the dimer (XXVII) be regarded as a "frozen" intermediate in an S_N2 reaction, which reduces to attack by the Si atom on the N atom. The Cl atom behaves as the leaving group and the tentative reaction "product" [compound (XXVIII)] represents the ionic form of the dimer with Si–N bonds of equal length:



The equalisation of the Si–N distances in the $(SiN)_2^{2+}$ ring has demonstrated by an X-ray diffraction study of the salt (XXIX).[56] It is of interest that these distances in compound (XXIX) (the average value is 1.792 Å) are appreciably greater than in the usual silazanes, for example, in compound (XXX) (1.747 Å).[56]

3. Silatranes

Silatranes constitute the most thoroughly investigated class of pentacoordinate silicon derivatives, including also the structural aspect (see, for example, the relevant reviews[1–4]). The transannular Si ← N interaction in silatranes with participation of the Si atom involved in a trigonal-bipyramidal coordination has been explained by the participation of the *d* orbitals of the silicon atom in bonding (see, for example, Tandura et al.[3]) and the hypervalent interaction in the N → Si–R fragment.[3,57] It has also been considered from the standpoint of the interaction of Lewis acids and bases.[4]

The strength of the transannular Si ← N bond depends on the structure of the silatranes, in the first place on the electron-accepting properties of the axial substituents at the Si atom. The enhancement of the electron-accepting properties (for any of the three explanations mentioned above) should strengthen the Si ← N bond.

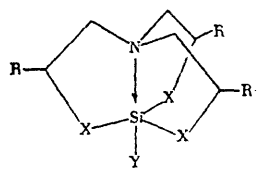
Since there are many reviews on the structure of silatranes (see, for example, Refs. 1–4), we concentrated attention here on the very latest (predominantly our own) results.

The structures of two silatranes in which the Si atom is linked to four O atoms have been determined: 1-(*m*-chlorophenoxy)silatrane (XXXI) [58] and 1-(t-butoxy)silatrane (XXXII).[59] By virtue of the greater electron-accepting capacity of the *m*-chlorophenoxy-group, the Si ← N distance in the silatrane (XXXI) [2.079(2) Å] is appreciably smaller than in compound (XXXII) [2.189(4) Å], where it is actually identical with the Si ← N distance in the α-modification of 1-phenylsilatrane (XXXIII).[60] On the other hand, the axial Si–O distance in compound (XXXI) is greater than in compound (XXXII) [1.690(2) and 1.659(4) Å respectively]. Since, judging from

the interatomic distances, the axial bond orders in compound (XXXI) are closer to one another than in compound (XXXII), the shift of the Si atom (Δ_{Si}) from the plane of the three equatorial O atoms in the silatrane (XXXI) is smaller than in compound (XXXII) [0.136(1) and 0.201(2) Å respectively]. The shift of the N atom from the plane of the three C atoms linked to it (Δ_N) is, on the other hand, smaller in compound (XXXII) than in compound (XXXI) [0.371(4) and 0.407(2) Å respectively], although the decrease in Δ_N is less distinct than the increase in Δ_{Si}. The values of Δ_{Si} and Δ_N observed in compound (XXXII) agree well with those calculated from the empirical equations[59]

$$\Delta_{Si} = 0.479 d_{Si-N} - 0.840 = 0.206 Å,$$
$$\Delta_N = -0.385 d_{Si-N} + 1.200 = 0.357 Å.$$

The replacement of the equatorial O atoms in 1-phenylsilatrane by NH groups [transition to 1-phenyltriazasilatrane (XXXIV)] does not actually affect the transannular interaction: the Si—N = 2.132(4) Å bond length in the silatrane (XXXIV) [60] is the same as the corresponding bond length in the γ-modification of compound (XXXIII) [61] and is somewhat smaller than in two other (α and β) modifications of this compound [2.193(5) Å [62] and 2.156(4) Å [63] respectively]:



(XXXIII): X = O, Y = Ph, R = H;
(XXXIV): X = NH, Y = Ph, R = H;
(XXXV): X = O, Y = C_6H_4Me-*p*, R = H;
(XXXVI): X = O, Y = C_6H_4Me-*p*, R = Me.

(XXXIII) – (XXXVI)

On the other hand, the Si—C(Ph) bond length in compound (XXXIV), which is 1.922(5) Å, is greater than in the α-, β-, and γ-modifications of compound (XXXIII) [1.882(6), 1.908(4), and 1.894(5) Å respectively]. The displacement of the Si atom from the plane of the three equatorial atoms towards the phenyl group in compound (XXXIV) is greater (0.24 Å) than in the α-, β-, and γ-forms of compound (XXXIII) (0.20, 0.20, and 0.18 Å respectively), which leads, for approximately the same Si ← N distances, to an appreciable shift of the axial N atoms from the plane of the three C atoms linked to it towards the Si atom (0.42 Å against 0.34, 0.38, and 0.39 Å).

The somewhat different parameters characterising the transannular interaction in the α, β-, and γ-modifications of compound (XXXIII) indicate their lability, a possible dependence on the packing effects, and the necessity of using in the interpretation the data for a large number of compounds.

The lengths of the equatorial Si—N bonds in compound (XXXIV) [1.731–1.756(4) Å] are close to the upper limit of the range of the Si—N distances in silazanes[64] and agree with the length of the equatorial bond [1.746(2) Å] in 1-(trichlorosilyl)-1,2,3,4-tetrahydro-1,10-phenanthroline (see subsection 5), which contains a pentacoordinate Si atom. Such increase in the lengths of the equatorial bonds in compounds (XXXIV) is analogous to a slight increase in the lengths of the equatorial Si—O bonds characteristic of "oxygen" silatranes [thus they amount to 1.656, 1.657, and 1.656 Å in the α-, β-, and γ-modifications of compound (XXXIII) respectively], whereas the range 1.61–1.65 Å is typical for the tetrahedral silicon derivatives $(RO)_nSiR_{4-n}$ with $n > 1$.[2]

The Si ← N transannular interaction is weakened when methyl groups are introduced in the 3-, 7-, and 10-positions of the silatrane nucleus: the Si—N distances in two symmetrically independent molecules of 1-(*p*-tolyl)silatrane (XXXV) are 2.171 and 2.167(1) Å, while the corresponding distance in 3,7,10-trimethyl-1-(*p*-tolyl)-silatrane (XXXVI) is 2.236(3) Å.[65] This effect is explained both by the electron-donating influence of the CH_3 group (which reduces the electron-accepting effect of the equatorial O atoms) and by the conformational difference between the five-membered chelate rings in the silatranes (XXXIV) and (XXXV) caused by them.

The breakdown of the C_3 symmetry of the silatrane ring, induced by the different directions of the deviation of the C_β atoms (and hence of the methyl groups attached to them) from the planes of the remaining atoms of the five-membered rings, observed for the first time in compound (XXXVI), is also remarkable.[65,66]

Naturally the introduction of C atoms in the equatorial positions relative to the Si atom (transition to tricarbasilatranes) weakens the transannular Si ← N interactions. Thus the Si...N distance in the $[Si(CH_2CH_2CH_2)_3N]_2O$ molecule[67] is 2.477(5) Å, which indicates a weak Si ← N coordination (a formal bond order of 0.35). The coordination of the Si atom in this compound is intermediate between tetrahedral and trigonal-bipyramidal (the difference between the sums of the equatorial and apical valence angles is 40.2°). The NSiO and SiOSi valence angles are 180° (C_{3i} intrinsic symmetry of the molecule).

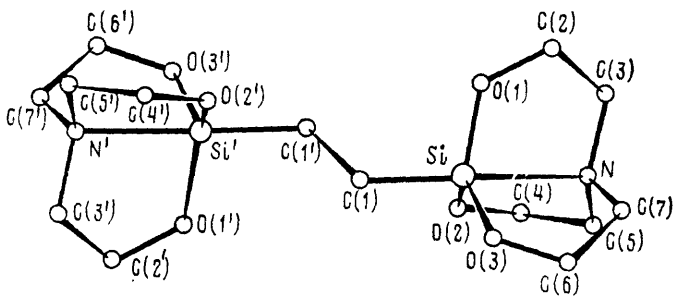


Figure 6. The structure of the centrosymmetrical molecule of compound (XXXVII).[64]

The linking of the two silatranyl groups in 1,2-bis(1-silatranyl)-ethane (XXXVII) by the CH_2CH_2 bridge is hardly reflected in their geometry. The length of the Si ← N transannular bond [2.230(5) Å] and the shift of the Si atom from the plane of the equatorial O atoms (Δ_{Si} = 0.24 Å) of the centrosymmetric molecule of compound (XXXVII) (Fig. 6) [64] are close to those observed in 1-ethylsilatrane, which are respectively 2.21(1) and 0.23 Å.[68] Thus there is virtually no mutual influence of the silatranyl groups in compound (XXXVII). On the other hand, the presence of the methylene bridge ensures this influence to some extent. The Ge ← N bond length and Δ_{Ge} in bis(1-germatranyl)methane [69] are greater than in 1-ethylgermatrane by 0.05 and 0.08 Å respectively.

In the series of onium derivatives of the type $[RCH_2Si(OCH_2CH_2)_3N]^+I^-$ [R = Me_2S^+ (XXXVIII),[70] Me_3N^+ (XXXIX),[71] and Ph_3P^+ (XL) [72]], the lengths of the transannular

Si ← N bonds, correlated with electron-accepting properties of the substituent R, are respectively 2.046(2) Å in compound (XXXVIII), 2.08(1) Å in compound (XXXIX), and 2.07 and 2.12(1) Å in compound (XL) (in the last case there are two independent molecules). In fact, the l_{Si-N} distance in compound (XXXIX) for example, should be 2.08(2) Å according to the equation $l_{Si-N} = 2.20(1) - 0.063(6)\sigma_X^*$ [71] (σ_X^* is the Taft inductive constant) for $\sigma^*_{Me_3NCH_2} = 1.90$, which agrees with X-ray diffraction data.[71] Among all the onium compounds considered, intramolecular steric hindrance has been observed only in the molecule of compound (XXXIX). Thus the SiCR angles in these compounds have the following values: 114.4(1)° in compound (XXXVIII), 121.2(9)° in compound (XXXIX), and 113.6° and 115.3(6)° in compound (XL).

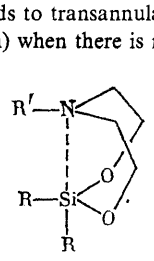
Among the silatranes whose structures have been investigated, the shortest Si ← N distance (l = 2.023 Å) has been noted in 1-chlorosilatrane, although, according to the correlation equations used to predict the values of l from the Taft inductive constant σ^* [73] and the average electronegativity of the substituent in the 1-position,[4] this distance in 1-fluorosilatrane (XLI) should be even smaller (2.007 and 1.927 Å respectively).[74] However, according to X-ray diffraction data, the Si ← N distance in compound (XLI) proved to be 2.042(1) Å, which is somewhat greater than in 1-chlorosilatrane.

Since the mechanism of the interaction of the N and Si atoms in silatranes still remains controversial, the experimental (X-ray diffraction) study of the distribution of electron density in the region of the Si ← N bond assumes special importance.[74] Two maps of the deformation electron density in the planes passing through the Si ← N and Si–F bonds are presented in Fig. 7. In the region between N and Si atoms, there is a distinct maximum with a height of 0.4 eÅ^{-3} actually on the lines connecting them, its distances from the Si and N atoms corresponding approximately to the ratio of the covalent radii. The reliability of this experimental manifestation of the hypervalent Si ← N interaction is confirmed by the presence of a comparable maximum on the line corresponding to the Si–F covalent bond.

A precision X-ray diffraction study made it possible to investigate also the distribution of deformation electron density in the chloromethylsilatrane crystal.[75] The peak corresponding to the unshared electron pair of the N atom is separated from it in the direction towards the Si atom by 0.7 Å, which is greater than the distances usually observed between the N atom and the peaks due to its unshared electron pairs (0.40–0.42 Å). This finding can be interpreted as confirmation of the transannular Si ← N interaction.

4. 1,3-Dioxa-6-aza-2-silacyclo-octanes

Depending on the electronic and steric properties of the substituents at the Si and N atoms in 1,3-dioxa-6-aza-2-silacyclo-octanes, the Si...N distance varies from 2.30 Å (for R = Ph and R′ = H), which corresponds to transannular interaction, to 3.19 Å (for R = Me and R′ = Ph) when there is no such interaction.[76]



As the Si...N interaction intensifies, the coordination of the Si atom deviates increasingly from the tetrahedral and there is an increase in the contribution of the "crown" conformation to the shape of the eight-membered ring.[76] The replacement of the N atom in the molecules considered, where R = Ph and R′ = H, by the O atom (transition to 1,3,6-trioxa-2-silacyclo-octane) weakens appreciably the transannular interaction. The corresponding Si...O distance is 2.976(5) Å, which is smaller by only 0.5 Å than the sum of the van der Waals radii of Si and O.[40,44–47] As a result of the Si ← O interaction, the eight-membered ring in 1,3,6-trioxa-2-silacyclo-octane assumes the unfavourable crown conformation.[77]

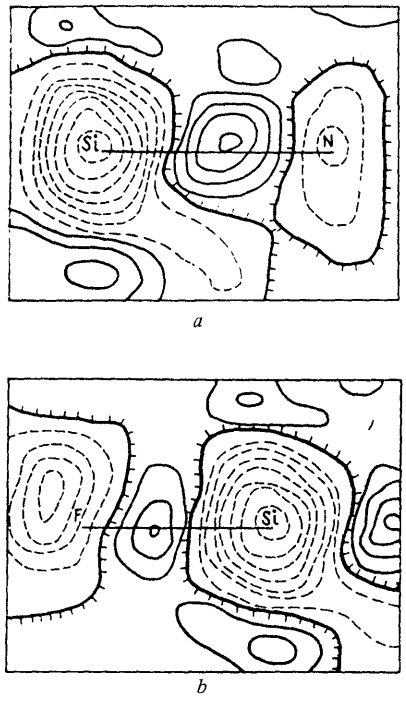


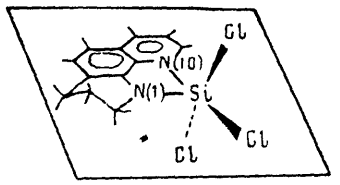
Figure 7. The distribution of deformation electron density in the Si(1)O(2)N(5) (*a*) and Si(1)O(2)F (*b*) planes in the molecule of compound (XLI) in the crystalline state. The isolines are drawn at 0.1 e Å^{-3} intervals, the dashed lines correspond to negative values of the density, and the "spiked" line corresponds to zero density.[74]

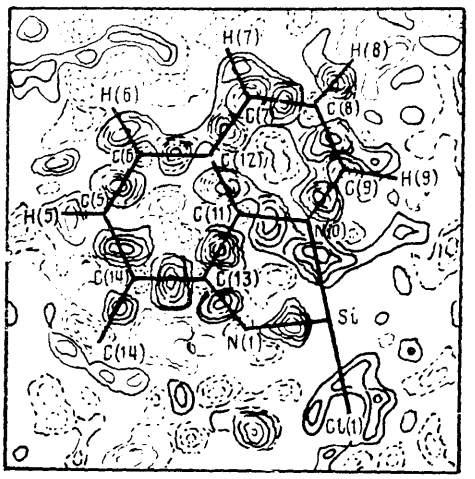
5. 1-(Trichlorosilyl)-1,2,3,4-tetrahydro-1,10-phenanthroline

In order to elucidate the electronic nature of the sharp difference between the lengths of the axial (donor–acceptor) and equatorial (covalent) Si–N bonds involving the pentacoordinate Si atom in the 1-(trichlorosilyl)-1,2,3,4-tetrahydro-1,10-phenanthroline (XLII) molecule (Fig. 8) [1.979(2) and 1.746(2) Å respectively], a precise X-ray diffraction study has been made of the distribution of electron density in a crystal of compound (XLII).[78]

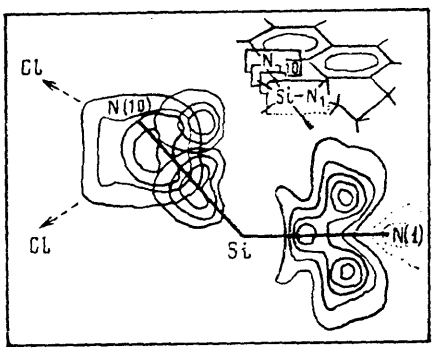
The molecule of compound (XLII) is located in a crystallographic plane with symmetry *m*, while the Si atom is involved in a trigonal-bipyramidal coordination with the N(10) and Cl(1) atoms in the axial positions. Fig. 8*a* shows that the unshared electron pair of the pyridine N(10) atom is highly polarised by the neighbouring Si atom. The maximum deformation electron density between these atoms is separated from the N(10) atom by a distance of ~0.7 Å, is

highly distorted, and decreases more gently in the direction of the Si atom than in the direction of the N(10) atom. On the other hand, the electron density maximum on the Si–N(1) bond decreases much faster in the direction of the Si atom than the N(1) atom and is located at a distance of ~1 Å from the latter. A similarity is observed in the character of the distribution of electron density of the unshared electron pair of the N(10) atom and of the pyridine nitrogen atom in the structure of 2-amino-5-chloropyridine involved in the formation of the intermolecular N–H...N bond.[79]





a



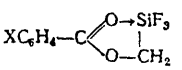
b

Figure 8. Distribution of deformation electron density in the molecule of compound (XLII) in the crystalline state: *a*, section by the crystallographic plane *m* through the molecule as shown at the top of the figure (two C atoms of the tetrahydropyridine ring are arranged above and below this plane); *b*, sections perpendicular to the Si–N(10) bond (on the left) and the section along the Si–N(1) bond (on the right). The isolines are drawn at 0.1 e Å^{-3} intervals.[78]

It is believed[78] that the donor–acceptor N(10) → Si bond in compound (XLII) is formed by the unshared electron pair of the pyridine N(10) atom and is highly polarised by the Si atom. This interaction can increase the barrier to the rotation of the $SiCl_3$ group about the Si–N(1) bond. Furthermore, the unshared electron pair of the amine N(1) atom of the saturated heterocycle is displaced towards the Si atom and towards the Si–N(1) bond (Fig. 8*b*). Such anisotropic distribution of electron density between the Si and N(1) atoms can also increase the barrier to rotation about the Si–N(1) bond, which has been confirmed by NMR data for solutions.[78]

6. (Aroyloxymethyl)trifluorosilanes

The length of the Si ← O bond in (aroyloxymethyl)trifluorosilanes (XLIII)–(XLVII) varies in the range from 1.95(2) to 2.08(2) Å:[72,80,81]



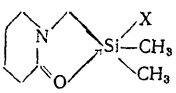
(XLIII)–(XLVII)

(XLIII): X = 4-H,
(XLIV): 4-F,
(XLV): 4-Cl,
(XLVI): 4-Br,
(XLVII): 2-Cl.

It amounts to 2.029(2) Å in the structure of compound (XLV), which has been established most precisely. The length of the Si–F axial bond in compounds (XLIII)–(XLVII) is greater than that of the equatorial bonds by ~0.03 Å and reaches 1.59(2)–1.61(1) Å, which agrees with the concept of the three-centre hypervalent F–Si ← O bond. The introduction of the Cl atom in the *ortho*-position of the benzene ring [compound (XLVII)] increases the angle between the plane of the ring and the average plane of the five-membered ring, resulting from the cyclisation via the Si ← O bond, from 5–7° to 17.5°.[81]

7. *N*-(Halogenodimethylsilylmethyl)lactams

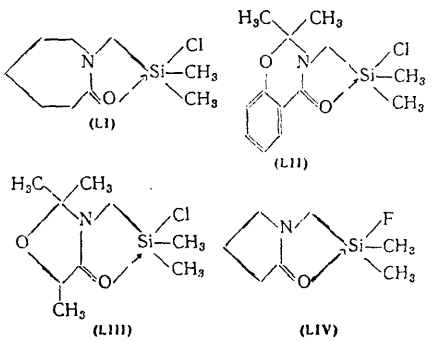
Compounds (XLVIII)–(L) constitute a new class of derivatives of pentacoordinate silicon. Measurements of the electrical conductivities of solutions and analysis of IR spectra showed that the Si ← O interaction weakens with decrease in the atomic number of the halogen X in the sequence I → Br → Cl:[57,82]



(XLVIII)–(L)

(XLVIII): X = I,
(XLIX): X = Br,
(L): X = Cl.

The authors of the present review carried out an X-ray diffraction study of compounds (XLVIII)–(L) and the related compounds (LI)–(LIV), differing in the structure of the lactam fragment:[82]

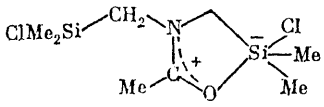


The Si atom has in fact an undistorted trigonal-bipyramidal [3 + 2]-coordination in the chloro-derivatives (L)–(LII) and an appreciably distorted, almost tetrahedral [4 + 1]-coordination in the iodo-derivative (XLVIII), the bromo-derivative (XLIX), the fluoro-derivative (LIV), and the chloro-derivative (LIII) with a modified bicyclic lactam system (Table 5).

The axial positions at the Si atoms are occupied in all the structures investigated by the O and X atoms and the equatorial positions are occupied by three C atoms. The Si–O distance in the axial O–Si–X fragments varies within very wide limits [from 1.749(2) Å in the iodo-derivative (XLVIII), which is close to the Si–O distances in compounds of tetrahedral silicon, for example, 1.690(5) Å in the 2,2′-dimethyl-5,10-dioxoanthra-[1,2-*e*]-1′,4′,2′-dioxasilin,[83] to 2.316–2.461(8) Å in the fluoro-derivative (LIV)]. The character of the lactam ring and the nature of the substituent also have a strong influence on the Si ← O interaction: the Si ← O distance in the chloro-derivatives varies from 1.954(2) Å in compound (L) to 2.425(4) Å in compound (LIII).[82,84]

It has been found that the stronger the Si ← O interaction, the weaker the Si–X interaction. Thus the Si–I distance in compound (XLVIII) is smaller by only 0.3 Å than the sum of the van der Waals radii of the Si and I atoms (4.08 Å [85]); on the other hand, in compound (LIV) the Si–F = 1.652 Å distance is close to the length of the Si–F covalent bond (1.55 Å) in derivatives of tetrahedral silicon.[37]

An increase in the size of the lactam ring [to the seven-membered ring in compound (LIII)] and the fusion with the latter of the benzene ring [as in compound (LII)] hardly influence the structure of the axial fragment. Thus the Si–O distances, amounting to 1.950(2) Å in compound (LII) and 1.989(4) Å in compound (LIII), differ little from the distance of 1.954(2) Å in compound (L). On the other hand, according to Onan et al,[86] the length of the Si–O bond in the related structure (LV), where there is no lactam ring, is appreciably smaller [1.918(3) Å] than in the lactam chloro-analogue (L) with a six-membered lactam ring [1.954(2) Å].



The replacement of the I atom by Br, Cl, and F in the series of compounds (XLVIII)–(L) and (LIV) entails, as it were, a "migration" of the Si atom along the O...X line from the O atom to the X atom relative to the plane of the three equatorial C atoms (Fig. 9). It is remarkable that in this migration the distance from the carbonyl O atom to the equatorial plane remains almost unaltered [2.097 Å in compound (XLVIII) and 2.109 Å in compound (LIII)].

The crystal of compound (LIV) (with a weak Si ← O interaction) is made up of four symmetrically independent molecules whose different environments lead to a difference between the geometrical parameters of the axial O–Si–F fragment. In particular, the Si ← O bond length changes appreciably, from 2.316 to 2.461(8) Å, although the Si–F bond length remains actually unaltered.

We may note yet again the unusual nature of the structure of compound (LIII). In contrast to the structures of compounds (L)–(LII), the Si–Cl distance in compound (LIII) is close to values typical for derivatives of tetrahedral silicon, while the Si ← O distance approaches the values observed in the fluoro-derivative

Table 5. The principal geometrical parameters of the molecules of *N*-(halogenodimethylsilylmethyl)lactams.

Compound	*l*, Å	*r*, Å	Δ*l*, %	Δ*r*, %	ω, deg	Δ, Å	n_0	n_X
(XLVIII)	1.749 (2)	3.734 (1)	7.3	51.8	161.90 (7)	0.348 (1)	0.82	0.12
(XLIX)	1.800 (4)	3.122 (2)	10.4	41.3	162.6 (6)	0.218 (2)	0.71	0.18
(L)	1.954 (2)	2.307 (2)	19.9	13.3	171.16 (5)	−0.058 (2)	0.46	0.55
(LI)	1.950 (2)	2.315 (1)	19.6	13.7	171.70 (7)	−0.055 (1)	0.47	0.53
(LII)*	1.989	2.313	22.0***	13.4***	172.06	−0.074 (1)	0.43	0.55
	1.990 (2)	2.305 (2)			170.67 (9)	−0.060 (1)		
(LIII)	2.425 (4)	2.148 (2)*e*	48.8	5.5	171.8 (1)	−0.451 (1)	0.16	0.79
(LIV)**	2.316	1.656	46.9***	6.6	172.8***	−0.238	0.17	0.73
	2.350	1.665				−0.305		
	2.451	1.658				−0.302		
	2.461 (8)	1.630 (7)				−0.297 (3)		

Note. Notation adopted: *l* is the Si–O bond length, *r* the Si–X bond length, Δ*l* and Δ*r* are the increments in *l* and *r* relative to the lengths of the covalent bonds of tetrahedral Si,[13,83] ω is the axial OSiX angle, Δ the shift of the Si atom from the equatorial plane in the direction towards the O atom, and n_0 and n_X are the Si–O and Si–X bond orders calculated as described by Allmann.[28]

* Data for two independent molecules are quoted.

** Data for four independent molecules are quoted.

*** The average value for independent molecules is quoted.

(LIV). It may be that this is caused by the conjugation of the unshared electron pair of the ether oxygen atom with the π-electron density of the carbonyl bond. A decrease in the size of the lactam ring [or its absence as in the structure (LIV)] is less significant.

A very large and concerted change in the lengths and orders of the O–Si and Si–X bonds is observed in compounds (XLVIII)–(LIV). It is also accompanied by the "inversion" of the coordination polyhedron of the Si atom, which makes it possible to regard the geometry of these compounds as a component part of the model of the hypothetical S_N2 reaction at the Si atom.

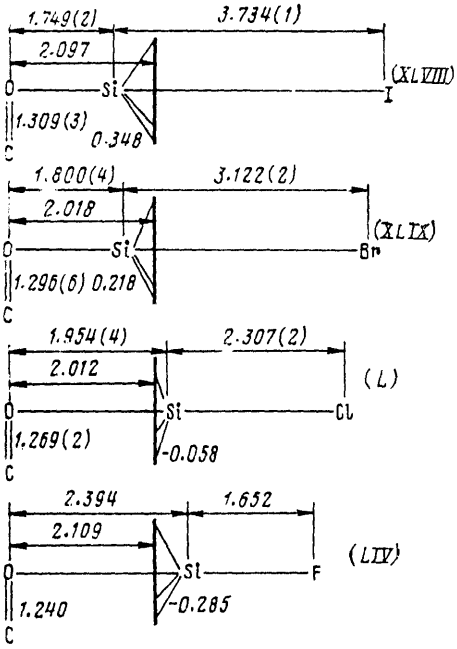
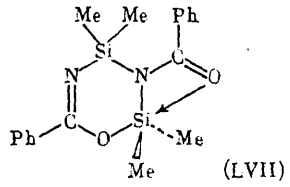


Figure 9. Variation of the coordination of the silicon atom as a function of the nature of the axial halogen atom in *N*-(halogenodimethylsilylmethyl)lactams. The plane of three equatorial C atoms is indicated by a bold line. The deviations of the Si atom from this plane and the lengths of the C=O carbonyl bond, diminishing in succession with intensification of the Si–O interaction, are indicated.[57,82]

strength.[88] The weak additional Si...O interaction in compound (LVII) is accompanied by an appreciable deviation of the O_a–Si...O_a angle from 180°, which amounts to 161°.



(LVII)

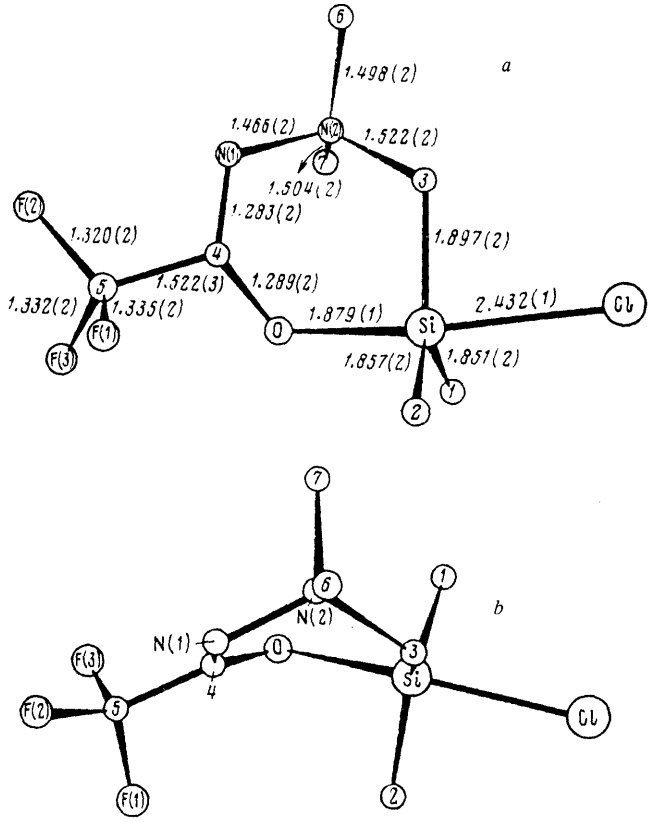


Figure 10. The structure of the molecule of compound (LVI): *a*, projection onto the average plane; *b*, projection onto the plane perpendicular to the average plane and passing through the N(1) and C(3) atoms.[87]

8. (O–Si)-Chloro-[1-(1,1-dimethyl-2-trifluoroacetylhydrazonium)methyl]dimethylsilane

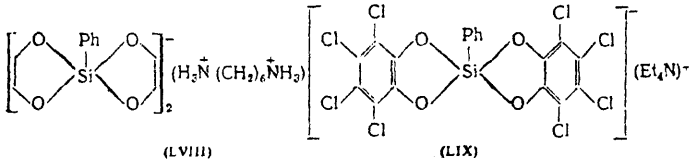
(O–Si)-Chloro-[1-(1,1-dimethyl-2-trifluoroacetylhydrazonium)-methyl]dimethylsilane (LVI) (Fig. 10) is the first example of a pentacoordinate silicon derivative in which the "additional" (coordinate) Si ← O bond is part of a six-membered, and not a five-membered, chelate ring.[87] Admittedly, in the molecule of compound (LVII) the pentacoordinate Si atom is also incorporated in a six-membered heterocycle, but in this case the additional O → Si interaction with the carbonyl group is very weak [the Si...O distance is 2.613(2) Å] and the endocyclic (second axial) Si–O bond is close to the usual covalent bond as regards length [1.670(2) Å] and

The coordination of the Si atom in compound (LVI), namely the [3 + 2]-coordination, is close to its coordination in the pentacoordinate silicon derivatives, examined above, with an axial O–Si–X fragment, where the O–Si bond is incorporated in a five-membered ring. The shift of the Si atom from the equatorial plane (in the direction towards the Cl atom) is very small [Δ_{Si} = 0.078(1) Å]. The lengthening of the Si–Cl axial bond [2.432(1) Å] relative to the "normal" Si–Cl = 2.048(1) Å bond in the H_3SiCl molecule[89] is somewhat greater than the increase in the

length of the Si–O = 1.879(1) Å axial bond relative to the Si–O = 1.68 Å "normal" bond in the molecule of 2′,2′-dimethyl-5,10-dioxoanthra[1,2-*e*]-1′,4′,2′-dioxasilin.[83] The O–Si–Cl angle is 172.20(5)°. However, despite the similarity of the coordination of the Si atom in compound (LVI) and in the lactam derivatives (L) and (LV), the Si ← O interaction in compound (LVI) is somewhat stronger, which may be caused by the greater electron density in the conjugated N⋯C⋯O fragment in compound (LVI).

9. Phenyl spirosilicates

The change in the coordination geometry of the Si atom in the cyclic anionic phenyl spirosilicates of type (LVIII) and (LIX) from that of a square pyramid (SP) to that of a trigonal bipyramid (TBP) makes it possible to trace the hypothetical path followed in the ligand rearrangement of the Berry pseudorotation type:[90]



(LVIII) (LIX)

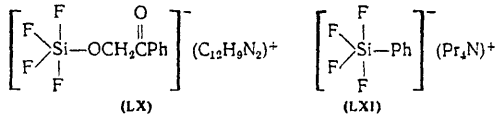
The coordination polyhedron of the Si atom in both phenyl spirosilicates, (LVIII) and (LIX), represents a distorted SP, although the structure of the latter is much closer to the ideal geometry.[91] This is indicated best by the *trans*-basal 1-Si-5 (θ_{15}) and 2-Si-4 (θ_{24}) angles which are closer to one another in compound (LIX) [152.9° and 147.3(2)°] than in compound (LVIII) [159.2° and 143.6(1)°] (Fig. 11). The Si–O bond lengths in these compounds also indicate that the coordination polyhedron of the Si atom in compound (LIX) is closer to the ideal SP. If the structure of compound (LVIII) is described as a TBP, then the average lengths of the axial and equatorial Si–O bonds should be 1.748(3) and 1.701(3) Å respectively. The corresponding values for the spirosilicate (LIX) are 1.756(6) and 1.752(6) Å, i.e. they are identical within the limits of the error of the determination. In compound (LIX), the four atoms forming the basal plane of the SP are coplanar to within 0.05 Å with the Si atom displaced from this plane in the direction of the apical C atom. The Si–C distances in compounds (LVIII) and (LIX), amounting to 1.854(4) and 1.883(3) Å, are close to the values typical for tetrahedral silicon derivatives.[84]

For a more rigorous quantitative description of the structural distortions in related compounds, the dependence of the *trans*-basal angles θ_{15} and θ_{24} in the SP (which become the axial and equatorial angles respectively in the TBP) on the angle δ_{24} between the normals to the (124) and (245) faces of the TBP with a common equatorial edge (24) was examined.[85] The above dihedral angle, which can be regarded as a coordinate of the Berry pseudorotation, is 53.1° in the ideal TBP and becomes zero when the (24) edge in the SP vanishes.

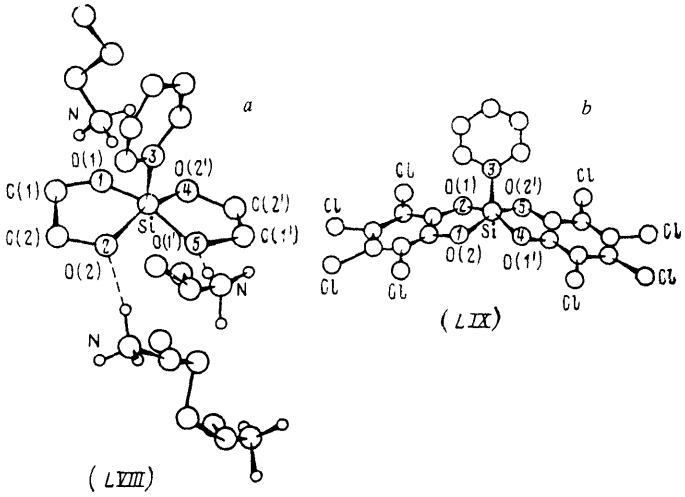
The results of the application of the method of the sums of the dihedral angles[92] to the estimation of the geometrical distortion of the molecules of pentacoordinate silicates have been published.[91] This method makes it possible to estimate (in percentages) the degree of transition of the real structure from the TBP to the SP. For example, the degrees of the TBP → SP transition are 72.1 and 89.8% respectively for compounds (LVIII) and (LIX).

10. Organyl tetrafluorosilicates

The Si atoms in both compounds of this class whose structures have been investigated, 1,10-phenanthrolinium benzoyloxymethyltetrafluorosilicate (LX) [93] and tetrapropyl-ammonium phenyltetrafluorosilicate (LXI),[94] form similar trigonal-pyramidal systems with the organic ligands in the equatorial positions:



(LX) (LXI)



(LVIII) (LIX)

Figure 11. The structure of the anions (LVIII) (*a*) and (LIX) (*b*).[91]

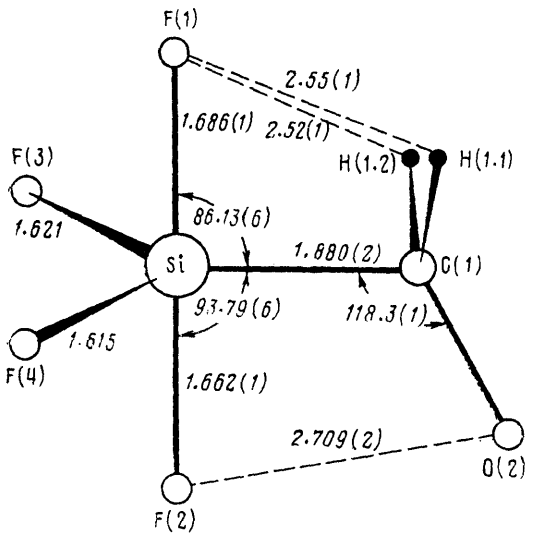
The Si–F axial bonds [1.686 and 1.662(1) Å] in compound (LX) are longer by 0.05–0.06 Å than the equatorial bonds [1.615 and 1.621(1) Å]. Approximately the same picture is observed also in the anion of compound (LXI), where the difference is 0.067 Å. The axial Si–F distances in the anions of compounds (LX) and (LXI) are also greater than in the derivatives of hexacoordinate silicon (see below). For example, the Si–F_a bond length in dipyridinesilicon tetrafluoride is 1.656(3) Å, while the Si–F_e bond length is 1.630(2) Å.[95]

The Si–F = 1.602(2) Å axial bond in compound (XLIV) is also longer than the equatorial bonds [1.582 and 1.585(2) Å], but the difference is smaller than in the anions of compound (LX) and (LXI). Overall, the Si–F distances in compound (LXIV) are appreciably shorter than in the anions of compounds (LX) and (LXI), although they do in fact exceed the Si–F distances in derivatives of tetrahedral silicon [for example, 1.56 Å in SiF_4 or 1.55(1) Å in $F_3SiOSiF_3$ [93]].

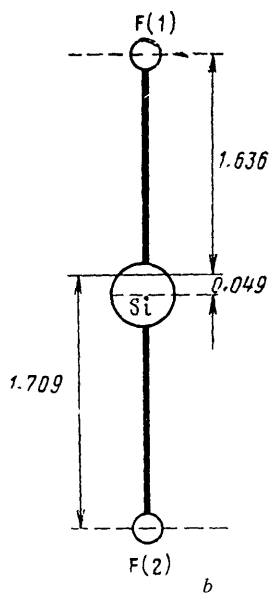
The F(1)–Si–F(2) group in the anion of compound (LX) is actually linear [the F(1)SiF(2) angle is 179.74(5)°]. On the other hand, owing to the presence of non-valence contacts of the type $F_a \ldots$ H-*o*(Ph) as in the anion of compound (LXI) (2.48 and 2.55 Å, while the sum of the van der Waals radii of F and H is 2.67 Å [40]), the F_aSiF angle in this species is 174.6(2)°, as in the molecule of the compound $PhPF_4$ isoelectronic with compound (LXI) (174.0°).[96]

The non-valence contacts F(1)...H in the anion of compound (LX) (Fig. 12*a*) lead to the appearance of the eclipsed orientation of the Si–F(2) and C(1)–O(2) bonds [the torsional angle

F(2)SiC(1)O(2) is 3.29(9)°]. However, such coordination of the anion of compound (LX) promotes in its turn the appearance of a short F(2)...O(2) contact [2.709(2) Å], while the sum of the van der Waals radii of O and F is 2.99 Å,[40] which induces an increase in the F(2)SiC(1) and SiC(1)O(2) valence angles. The latter can be interpreted as a shift of the Si atom from the equatorial plane (Fig. 12*b*). On the other hand, the shift of the Si atom in the direction of the F(2) atom intensifies the non-valence interactions with participation of the F(1) atom, which increases the Si–F(1) distance.



a



b

Figure 12. The coordination environment of the Si atom in the anion (LX) (*a*) and the shifts of the F(1), Si, and F(2) atoms from the equatorial plane passing through the F(3), F(4), and C(1) atoms (continuous horizontal line) (*b*).[93]

11. Complexes of the three-centre Mn–H–Si bond

The oxidative addition of the silanes $HSiR_3$ to the 16-electron coordinatively unsaturated manganese complex $C_5R_5(CO)(L)Mn$ [R = H, or Me; L = CO, PR_3, $P(OR)_3$, or CNR] leads to the formation of the compounds $C_5R_5(CO)(L)Mn(H)SiR_3$ with the two-electron three-centre bond Mn–H–Si. They can be regarded as "frozen" intermediates in this reaction.[97]

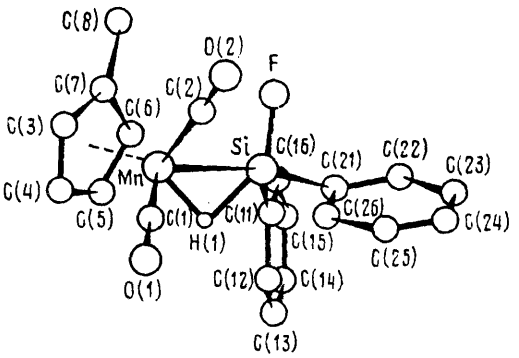


Figure 13. The structure of the molecule of compound (LXII).[99]

In complexes of this type, the "agostic" H atom[98] occupies a bridging position between the Mn and Si atoms. In the structure of the compound $C_5H_4Me(CO)_2Mn(H)SiFPh_2$ (LXII), the Mn–H(1) and Si–H(1) distances are 1.569(4) and 1.802(5) Å respectively according to neutron diffraction data (Fig. 13).[99] The observed Si–H(1) distance is appreciably smaller than the sum of the van der Waals radii of the Si and H atoms (about 3.20 Å [40,85]) and exceeds by only ~0.40 Å the length of the covalent Si–H bond, which is 1.40 ± 0.02 Å according to electron diffraction and microwave spectroscopic data for tetrahedral silane derivatives. The Mn–H(1) distance in compound (LXII) was actually found to be somewhat smaller than the Mn–H = 1.601(16) Å distance in $(CO)_5Mn–H$, where H is the terminal ligand.[100] The Mn–Si = 2.352(4) Å distance in compound (LXII) corresponds to approximately the middle of the range of variation of the Mn–Si distances [2.254(1)–2.461(7) Å] in complexes of the type $MeC_5H_4(CO)_2Mn(H)SiR_3$ with the three-centre Mn–H–Si system.[99]

Owing to the Mn–H–Si interaction indicated above, the Si atom in the complex (LXII) requires quinary coordination. The coordination polyhedron of the Si atom can be described as a strongly distorted trigonal bipyramid with the H(1) and F atoms in the axial positions [the H(1)SiF valence angle is 148.8(2)°] and the Mn, C(11), and C(21) atoms (see Fig. 13) in the equatorial positions [MnSiC(11) = 115.8(1)°, MnSiC(21) = 117.3(1)°, and C(11)SiC(21) = 109.0(1)°]. The absence of an appreciable lengthening of the axial Si–F bond in compound (LXII) [1.634(3) Å compared with 1.624(2) Å in $C_5H_5(CO)_2FeSiFPh_2$ [99]] does not conflict with such a description in view of the large difference between the electronegativities of the apical H and F atoms.

Comparison of the adduct (LXII) with the related complexes $C_5Me_5(CO)_2Mn(H).SiR_3$ shows that, if the substituents R shorten the Mn—Si distance, then the Mn—H distance also diminishes, while the Si—H distance increases slightly. The oxidative addition of the silane $HSiR_3$ to the $C_5Me_5(CO)_2Mn$ fragment proceeds tentatively in accordance with the scheme

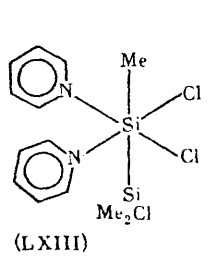
$$L_nMn + \overset{H}{\diagdown}SiR_3 \rightleftarrows L_nMn\cdots H\cdots SiR_3 \rightleftarrows L_nMn\overset{H}{\diagup}\!\!\diagdown SiR_3 \rightleftarrows L_nMn\overset{H}{\diagup}\!\!\diagdown SiR_3 .$$

It agrees with the observed changes in the distances between the Mn, H, and Si atoms in the series of complexes of type (LXII).

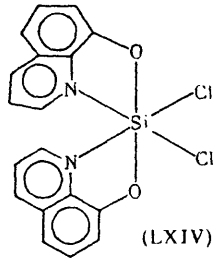
V. Compounds of silicon with coordination numbers of six and above

1. Derivatives of hexacoordinate silicon

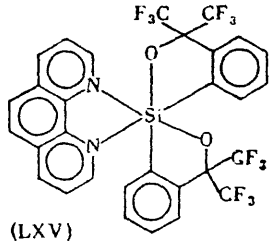
Only three examples of organosilicon compounds with a hexacoordinate silicon atom whose structures have been confirmed are known [compounds (LXIII)—(LXV)].[102-104] Their structure provides important information for the understanding of the structures of the intermediates formed as a result of the wide variety of reactions of organosilicon compounds.



(LXIII)



(LXIV)



(LXV)

According to the hypervalent bonding model, the silicon atom in a hexacoordinate state forms two covalent and two three-centre four-electron bonds.[3] Its coordination polyhedron is therefore an octahedron with four equatorial bonds longer than the axial bonds.

Table 6 shows that the equatorial bonds in compounds (LXIII) and (LXIV) are indeed lengthened compared with the corresponding bonds of tetrahedral silicon, relative to the axial bonds. However, in compound (LXV) the situation is more complicated: the increase in the length of the equatorial and axial bonds is almost the same in this instance. This structure can be described as a trigonal bipyramid with the phenanthroline ligand occupying one coordination site. This treatment agrees with the ability of the complex (LXV) (according to ^1H NMR data) to undergo enantiomeric and diastereoisomeric transformations in solution as a result of the dissociation of the Si—N bond with the phenanthroline ligand.[104]

In contrast to compounds of pentacoordinate silicon, whose coordination can be in most cases described approximately as of the [4 + 1] type with only one lengthened axial bond (for example the Si ← N bond in silatranes), an increase in the length of four [compound (LXIII)], three [compound (LXIV)], or two [compound (LXV)] equatorial bonds has been observed in compounds of hexacoordinate silicon.

Table 6. The lengths of the bonds involving the Si atom in its hexacoordinate derivatives (LXIII)—(LXV) [102-104] and the difference between them and the lengths of the bonds involving tetrahedral silicon.

Compound	Axial bond	*l*, Å	Δ, Å	Equatorial bond	*l*, Å	Δ, Å
(LXIII)	Si—Si	2.367	0.03	Si—Cl	2.274	0.24
	Si—C	1.888	0.02		2.392	0.36
				Si—N	2.007	0.28
					2.029	0.30
(LXIV)	Si—O	1.763	0.08	Si—Cl	2.199	0.17
		1.766	0.09	Si—N	2.016	0.29
					2.014	0.28
				Si—C	1.940	0.07
(LXV)	Si—O	1.772 (7)	0.09	Si—O	1.772 (7)	0.09
	Si—C	1.93 (1)	0.06	Si—N	2.051 (9)	0.33
					2.089 (9)	0.36
				Si—C	1.91 (1)	0.04

Note. Typical lengths of the bonds involving tetrahedral silicon: Si—Si = 2.34 Å,[1] Si—Cl = 2.03 Å,[89] Si—N = 1.73 Å,[66] Si—O = 1.68 Å,[81] and Si—C = 1.87 Å.[1] The subdivision into axial and equatorial bonds is based on the literature data.[102-104]

2. The cluster $[Co_9Si(CO)_{21}]^{2-}$

The great possibilities inherent in the silicon atom as regards coordination can be illustrated in relation to the cobalt carbonyl cluster $[Co_9Si(CO)_{21}]^{2-}$ with an encapsulated silicon atom (Fig. 14).[105] Nine cobalt atoms form a one-cap tetragonal antiprism with the Si atom occupying a cavity within the latter. Eight Si—Co distances are in the range usual for Si—Co bond lengths [cf. 2.299(2) Å]. The Si—Co(1) distance to the atom of the cap is much greater [2.527(4) Å] and can correspond only to a weak interaction. The distances between the cobalt atoms, Co(1)—C(2) = 2.613 Å, Co(2)—Co(2′) = 2.940 Å, Co(2)—Co(3) = 2.688 Å, Co(2)—Co(3′) = 2.593 Å, and Co(3)—Co(3′) = 2.808(1) Å, indicate an appreciable expansion of the core made up of the Co atoms when the Si atom is incorporated in it. The cavity within the regular square antiprism made up of Co atoms (the covalent radius of cobalt is 1.35 Å) has a radius of ~0.85 Å, which is much less than the covalent radius of the Si atom (1.12 Å) [sic]. It is not surprising that the attempt to obtain an analogous cluster with encapsulation of the larger Ge atom (r_{Ge} = 1.22 Å) was unsuccessful.[106] On the other hand, the C atom, whose size is smaller (r_C = 0.77 Å) forms a stable encapsulated square-antiprismatic cluster $(Co_8C(CO)_{18}]^{2-}$, in which the Co—Co distances are 2.47—2.59 Å.[107]

3. Sandwich complexes of silicon

Unexpected results have been obtained in an X-ray diffraction study of the recently synthesised decamethylsilicocene $(C_5Me_5)_2Si$ (LXVI).[108] This is the first silanediyl which is stable under the usual conditions and the first π-complex with a central silicon atom. In the crystal of compound (LXVI), there are two crystallographically independent molecules of A and B (A : B = 1 : 2, Fig. 15). One of them is at the centre of symmetry and the other is in a common position (space group $C2/c$, $Z = 12$). In the A molecule, the pentamethylcyclopentadienyl rings are antiparallel, i.e. are in the crossed conformation. On the other hand, in the B molecule the rings form a dihedral angle of 25.3° whilst retaining the crossed conformation. Whereas the Si–C distances in the A ring are equalised [cf. 2.42(1) Å], in the B molecule they are unequal and amount to 2.324(8) Å [Si(2)–C(22) and Si(2)–C(28)], 2.526(7) Å [Si(2)–C(25)], and 2.541(7) Å [Si(2)–C(26)]. The approximate intrinsic symmetry of this molecule is C_{2h}. On the other hand, the distances from the Si atoms to the centres of the C_5Me_5 rings in the A and B molecules are very close (2.11 and 2.12 Å). The character of the disposition of the molecules in the crystal of compound (LXVI) shows that the non-parallel arrangement of the C_5Me_5 rings in the B molecule is caused by intermolecular interactions.[108]

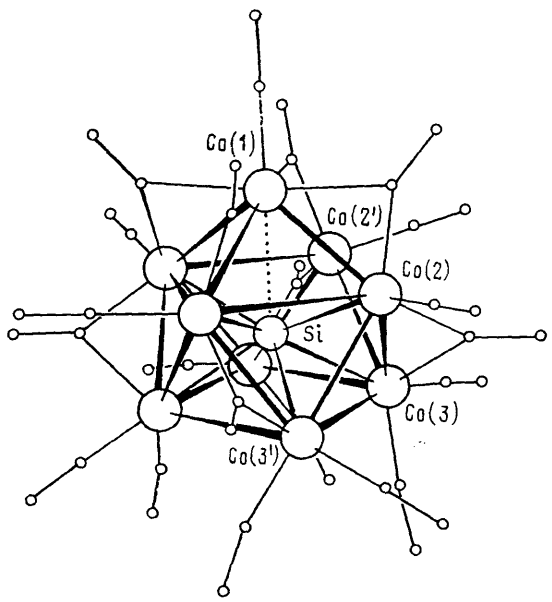


Figure 14. The structure of the anion $[Co_9Si(CO)_{21}]^{2-}$.[105] The Si–Co(1) vector coincides with the fourfold crystallographic axis.

It is of interest that bis[(1,2,4-trimethylsilyl)cyclopentadienyl]-germanium (LXVII) also exists in the crystal as two conformers[109] in which the Cp–Ge–Cp angles of similar size differ little from the linear angle of 180° (by 10.5 and 8.2° respectively). The Ge–Cp distances (Cp corresponds to the centre of the ring) are also almost identical (2.250–2.256 Å) and the Ge–C distances differ very little for all four unsubstituted Cp rings (2.556–2.574 Å).

Using the EENY2 program, the conformational energy of the molecule of compound (LXVII) was calculated by varying the Cp–Ge–Cp angle, the Ge–Cp–C angles of inclination, and the orientations of the rings and $SiMe_3$ groups.[109] It was found that the conformation arising in the crystal does indeed have a low energy, which, however, does not have a distinct minimum. Thus one cannot rule out the possibility of certain changes in the molecular geometry of compound (LXVII) under the influence of the crystal field.

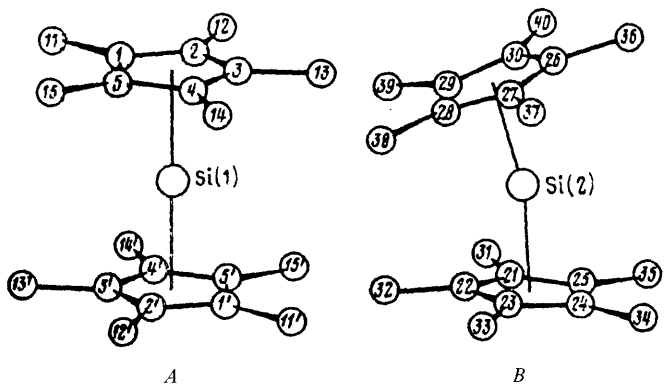


Figure 15. The structure of the crystallographically independent molecules of compound (LXVI) in the crystal:[108] *A*, at the centre of symmetry; *B*, in the common position.

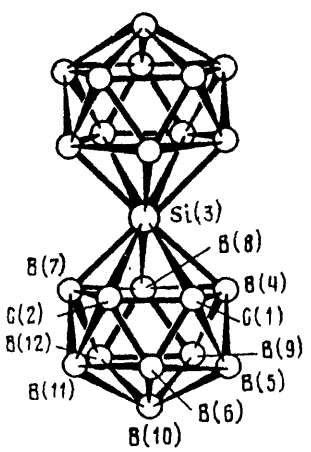


Figure 16. The structure of the centrosymmetrical molecule of compound (LXVIII).[110]

A second confirmation of the possibility of the existence of stable silicon π-complexes has been provided by an X-ray diffraction study of a sandwich derivative of *o*-carbaborane—*commo*-3,3-Si-(1,2-$C_2B_9H_{11}$) (LXVIII) (Fig. 16).[110] The molecule of compound (LXVIII) is centrosymmetrical and the Si(3) atom is

therefore separated by equal distances from the planes of both antiparallel five-membered C_2B_3 rings to which it is coordinated but is displaced relative to their centres towards the B(8) and B(8′) atoms: Si–B(8) = 2.05(1) Å, Si–B(4) and Si–B(7) = 2.14(1) Å, and Si–C(1) and Si–C(2) = 2.22(1) Å. Thus the Si–C distances in compound (LXVIII) are appreciably smaller than in compound (LXVI).

A model has been proposed for the bonding of the Si atom to the dicarbaboryl ligands in compound (LXVIII).[111] At the instant of bonding, these ligands are characterised by the presence of a combination of occupied ligand orbitals (LO): a_g, a_u, e_{1g}, and e_{1u}. The ligand orbitals e_{1u} are suitable as regards symmetry for the π-type bonding interaction with the silicon atomic orbitals (AO) p_x and p_y, while the a_u LO undergoes a σ-type interaction with the p_z AO of the Si atom. If the participation of the silicon *d* AO in bonding is postulated, then the silicon d_{xz} and d_{yz} AO have a symmetry suitable for a π-type overlap with the e_{1g} LO. On the other hand, if the difference between the energies of these AO and LO is large, the two electron pairs of the Si atom remain non-bonding and the ligand electrons remain in the e_{1g} LO. Finally, either the combination of the silicon *s* and d_{z^2} AO or only the *s* AO can interact with the a_g LO, which leads to σ-bonding.

VI. Conclusion

During recent years, extensive information has been obtained about the structure of a wide variety of organosilicon compounds in which a coordination of silicon other than the tetrahedral is realised. Silatranes have been undoubtedly most thoroughly investigated among these compounds. We have obtained recently data on the structure of *N*-(halogenodimethylsilylmethyl)lactams. On the other hand, other classes of compounds of non-tetrahedral silicon have been studied inadequately and are represented by one–two structures.

It is remarkable that the interpretation of the structures of organic silicon compounds with a non-trivial geometry of the Si atom (disilaphosphorane ylides, the complex of silaethylene with THF, and others) is difficult without resorting to the idea of $p_\pi - d_\pi$ bonding with participation of the *d* orbitals of the Si atom. On the other hand, if one uses the results of a precise study of the distribution of electron density, as was done for 1-(trichlorosilyl)-1,2,3,4-tetrahydro-1,10-phenanthroline and 1-fluorosilatrane, then there is no need to consider the *d* orbitals of the pentacoordinate Si atom in order to explain the mechanism of the formation of bonds with its participation.

Analysis of the geometry of compounds with an expanded coordination of the Si atom as intermediates in chemical reactions provides information of greatest chemical interest. The structural correlations of a series of compounds examined have been investigated to different extents. They have been studied in greatest detail for *N*-(halogenodimethylsilylmethyl)lactams (S_N2 reactions) and phenyl spirosilicates (Berry pseudorotation).

Thus structural studies on derivatives of non-tetrahedral silicon not only deepen our ideas about the coordination and valence possibilities of this element but are also of definite general importance for the modelling and mapping of reaction pathways.

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