Influence of a valent environment on the hypervalent bond of a silicon atom

3.* Crystal structure of four (O—Si)-chelate (lactamo-*N*-methyl)dichloro- and -trichlorosilanes**

*Yu. T. Struchkov,[a†] Yu. E. Ovchinnikov,[a] A. G. Shipov,[b] and Yu. I. Baukov[b]**

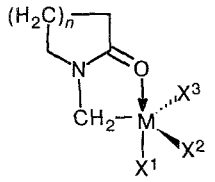
[a]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 117813 Moscow, Russian Federation. Fax: +7 (095) 135 5085*

[b]*Russian State Medical University, 1 ul. Ostrovityanova, 117869 Moscow, Russian Federation. Fax: +7 (095) 434 4787*

X-ray structural study of two (O—Si)-chelate (lactamo-*N*-methyl)dichlorosilanes and two (O—Si)-chelate (lactamo-*N*-methyl)trichlorosilanes with the hypervalent O—Si—Cl bond has been carried out. Introduction of more electronegative substituents into equatorial positions of the trigonal-bipyramidal valent environment of a silicon atom increases the hypervalent bond rigidity. It has been concluded that the influence of nonspecific (including electrostatic) intermolecular interactions on geometric parameters of the hypervalent fragment is insignificant.

Key words: organic derivatives of pentacoordinated silicon; hypervalent interaction; X-ray study.

In the first communication of this series we reported[2] that the introduction of highly electronegative substituents (halogens instead of carbon atoms) at the equatorial positions of the trigonal-bipyramidal (TBP) coordinative polyhedron of a pentacoordinated silicon atom considerably affects the hypervalent O—Si—F bond parameters. However, the Si—F_{ax} component of the three-center four-electron (hypervalent) bond is extraordinarily rigid. As the silicon coordination changes from tetrahedral to ideal TBP, the Si—F distance increases by no more than 0.1 Å. In this paper the role of the equatorial substituents at the hypervalent atom is considered for the case of (O—M)-chelate (lactamo-*N*-methyl)monochloro-, -dichloro- and -trichlorosilanes and -germanes. Compounds **1**—**4** have been investigated by X-ray analysis for the first time,* and the previously investigated compounds **5**—**9** are their chemical and structural analogs.



1—9

Compound	X^1	X^2	X^3	*n*	M
1	Cl	Cl	Me	3	Si
2	Cl	Cl	Cl	3	Si
3	Cl	Cl	OMe	3	Si
4	Cl	Cl	Cl	2	Si
5 [3]	Cl	Me	Me	3	Si
6 [4]	Cl	Me	Me	3	Ge
7 [5]	Cl	Cl	Cl	3	Ge
8 [6]	Cl	Me	Me	2	Si
9 [7]	Cl	Me	Me	2	Ge

* For Communication 2, see Ref. 1.

** Dedicated to Academician of the RAS N. S. Zefirov (on his 60th birthday).

† Deceased in August, 1995.

Experimental

The crystal data and main the X-ray diffraction characteristics of compounds **1**—**4** are given in Table 1. All experiments were carried out on a four-circle automatic Syntex $P2_1$ diffractometer at low temperature (λMo-Kα, graphite monochromator, θ/2θ-scanning, $2\theta_{max}$ = 54 to 56°). The structures were solved by the direct method and refined by the full-matrix least-squares technique in the anisotropic approximation for nonhydrogen atoms. The H atoms in structures **1**—**3**

* The synthesis of compounds **1**—**4** will be published in a separate communication.

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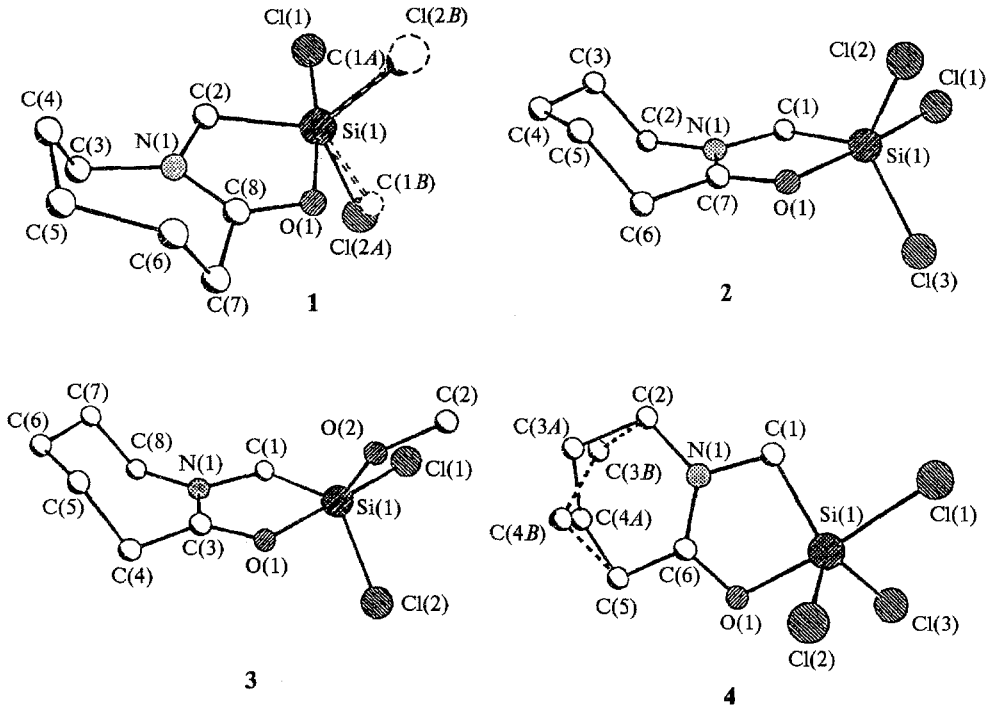

Fig. 1. General view of molecules **1**—**4** in the crystal. In structures **1** and **4**, the disorder in the molecules is shown. The H atoms are not shown.

Table 1. Crystal data and main characteristics of the X-ray diffraction experiments for compounds **1**—**4**

Parameter	1	2	3	4
Empirical formula	$C_8H_{15}NOSiCl_2$	$C_7H_{12}NOSiCl_3$	$C_8H_{15}NO_2SiCl_2$	$C_6H_{10}NOSiCl_3$
T/K	195	180	185	195
a/Å	6.167(3)	6.188(2)	9.242(2)	9.729(3)
b/Å	8.707(4)	8.524(3)	10.160(2)	9.821(2)
c/Å	11.457(5)	11.274(3)	12.587	11.125(3)
α/deg	111.21(3)	107.74(2)	90	9
β/deg	91.30(4)	92.63(2)	94.26(2)	90
γ/deg	93.09(4)	94.21(2)	90	90
V/Å^3	572(1)	563.4(7)	1178.6(8)	1063.0(8)
Space group (Z)	$P\bar{1}$ (2)	$P\bar{1}$ (2)	$P2_1/c$ (4)	$P2_12_12_1$ (4)
d_{calc}/g cm^{-3}	1.394	1.536	1.444	1.541
N_{refl}	2500	2442	2468	2603
N_{refl} (least squares)	1863 ($I > 2\sigma$)	2077 ($I > 3\sigma$)	1756 ($I > 3\sigma$)	1717 ($I > 3\sigma$)
R, R_w	0.034, 0.036	0.035, 0.038	0.039, 0.041	0.056, 0.05

were located in a difference synthesis and were refined isotropically (except for those of the disordered over two positions methyl group in structure **1**, which were fixed in the calculated positions); in structure **4** H atoms were placed in the calculated positions. Upon structure refinement essential disorder was found in crystals **1** and **4**. In molecule **1**, the equatorial Me- and Cl-substituents at the TBP silicon environment show similar stereochemical parameters, resulting in two isomers **1*A*** and **1*B*** for every crystallographic position (Fig. 1). The Cl(2*A*) and C(1*B*), Cl(2*B*) and C(1*A*) positions were separated by artifical means and were refined by imposing extra conditions, namely, the Si—Cl(2*A*) and Si—Cl(2*B*), Si—C(1*A*) and Si—C(1*B*) bond lengths are regarded as equal. The populations of the *A* and *B* positions were taken as 0.75 and 0.25, respectively, because the weighted average values of the thermal parameters of the Cl(2) and C(1) atoms in the *A* and *B* positions are nearly the same when these magnitudes are assumed.

A different disorder is found in structure **4**, where two conformers are present in each crystallographic position. These conformers are distinguished by the location of two carbon atoms of the six-membered cycle (see Fig. 1). The populations

Table 2. Coordinates of atoms ($\times10^4$, $\times10^3$ for H atoms) in structure **1**

Atom	*x*	*y*	*z*
Si(1)	4244.2(8)	1734.8(7)	2447.4(5)
Cl(1)	4088.3(9)	3120.6(7)	1124.5(5)
Cl(2*A*)*	7571(1)	1721(1)	2450(1)
Cl(2*B*)*	2983(8)	3561(6)	3911(4)
O(1)	4216(3)	349(2)	3410(1)
N(1)	2173(3)	−1335(2)	1793(2)
C(1*A*)*	3162(11)	3365(7)	3735(5)
C(1*B*)*	7158(5)	1954(17)	2746(13)
C(2)	2545(3)	−34(3)	1277(2)
C(3)	812(4)	−2861(3)	1094(2)
C(4)	−1211(4)	−3052(3)	1757(2)
C(5)	−830(4)	−3681(3)	2819(2)
C(6)	639(4)	−2544(3)	3904(2)
C(7)	2941(4)	−2220(3)	3556(2)
C(8)	3123(3)	−1033(3)	2891(2)
H(21)	117(2)	27(2)	108(1)
H(22)	322(2)	−47(2)	51(2)
H(31)	175(2)	−375(2)	95(2)
H(32)	43(2)	−275(2)	31(2)
H(41)	−192(2)	−205(2)	206(1)
H(42)	−220(2)	−379(2)	113(2)
H(51)	−14(2)	−468(2)	251(2)
H(52)	−224(2)	−382(2)	314(2)
H(61)	77(2)	−303(2)	453(2)
H(62)	0(2)	−160(2)	425(2)
H(71)	393(2)	−177(2)	429(2)
H(72)	343(2)	−319(2)	302(2)

* The populations of the *A* and *B* positions are 0.75 and 0.25, respectively.

Table 3. Coordinates of atoms ($\times10^4$, $\times10^3$ for H atoms) in structure **2**

Atom	*x*	*y*	*z*
Cl(1)	4163.4(8)	3070.0(6)	6055.8(4)
Cl(2)	3303.8(9)	3371.0(6)	8817.4(4)
Cl(3)	7728.8(7)	1649.4(6)	7365.1(5)
Si(1)	4386.4(7)	1585.3(6)	7353.9(4)
O(1)	4453(2)	191(2)	8346(1)
N(1)	2219(3)	−1468(2)	6795(1)
C(1)	25553(3)	−143(2)	6238(2)
C(2)	762(4)	−2977(2)	6168(2)
C(3)	−1218(3)	−3159(3)	6876(2)
C(4)	−753(4)	−3785(3)	7988(2)
C(5)	828(4)	−2659(3)	9022(2)
C(6)	3130(4)	−2389(3)	8611(2)
C(7)	3264(3)	−1193(2)	7886(2)
H(11)	116(5)	29(4)	607(3)
H(12)	328(4)	−55(3)	549(2)
H(21)	34(4)	0291(3)	542(2)
H(22)	167(4)	−388(3)	607(2)
H(31)	−194(5)	−210(4)	717(3)
H(32)	−232(4)	−403(3)	627(2)
H(41)	−1(5)	−487(4)	726(3)
H(42)	−201(6)	−391(4)	831(3)
H(51)	28(4)	−157(4)	939(3)
H(52)	98(5)	−311(4)	964(3)
H(61)	357(4)	−351(3)	810(2)
H(62)	404(5)	−197(4)	933(3)

Table 4. Coordinates of atoms ($\times10^4$, $\times10^3$ for H atoms) in structure **3**

Atom	*x*	*y*	*z*
Si(1)	3654.6(9)	4582.1(7)	2950.5(6)
Cl(1)	6029.8(8)	4229.5(8)	3303.3(6)
Cl(2)	3839.1(8)	4458.1(8)	1319.4(5)
O(1)	1695(2)	5073(2)	2680(2)
O(2)	3081(2)	3198(2)	3518(2)
N(1)	2419(3)	6836(2)	3615(2)
C(1)	3830(3)	6202(3)	3671(2)
C(2)	3716(5)	2068(5)	3716(3)
C(3)	1375(3)	6183(3)	3086(2)
C(4)	−153(4)	6657(4)	2978(3)
C(5)	−842(4)	6732(4)	4039(3)
C(6)	−370(4)	7918(4)	4723(3)
C(7)	1236(4)	7984(4)	5063(3)
C(8)	2200(4)	8103(3)	4152(3)
H(11)	417(4)	609(3)	439(3)
H(12)	450(4)	674(3)	341(3)
H(21)	478(8)	212(6)	387(5)
H(22)	295(6)	136(6)	401(5)
H(23)	358(8)	145(7)	289(6)
H(41)	−70(4)	604(4)	252(3)
H(42)	−16(4)	756(5)	260(3)
H(51)	−65(4)	600(4)	446(3)
H(52)	−186(5)	678(4)	393(4)
H(61)	−90(4)	789(4)	535(3)
H(62)	−67(4)	872(4)	434(3)
H(71)	147(4)	719(4)	552(3)
H(72)	141(4)	865(4)	551(3)
H(81)	315(4)	839(3)	437(3)
H(82)	178(4)	870(4)	362(3)

Table 5. Coordinates of atoms ($\times10^4$) in structure **4**

Atom	*x*	*y*	*z*
Si(1)	11(1)	2821(1)	1129(1)
Cl(1)	−944(1)	3574(1)	2801(1)
Cl(2)	1959(1)	2727(2)	1879(1)
Cl(3)	−418(2)	4582(2)	267(2)
O(1)	715(4)	2053(4)	−261(3)
N(1)	−839(4)	454(4)	108(3)
C(1)	−1192(4)	1309(4)	1131(4)
C(2)	−1563(4)	−833(4)	−113(3)
C(3*A*)*	−797(5)	−1733(3)	−968(4)
C(3*B*)*	−1351(5)	−1311(6)	−1377(4)
C(4*A*)*	−286(5)	−941(5)	−2029(3)
C(4*B*)*	139(5)	−1253(4)	−1714(6)
C(5)	685(5)	161(4)	−1644(4)
C(6)	178(5)	915(5)	−554(4)

* The populations of the *A* and *B* positions are 2/3 and 1/3, respectively.

of *A* (2/3) and *B* (1/3) positions for disordered over two positions C(3) and C(4) atoms were defined in the same manner as for structure **1**. Similarly, the lengths of the corresponding C—C bonds and C—C—C valent angles were equalized upon structure refinement. The atom coordinates in structures **1**—**4** are listed in Tables 2—5, respectively. All calculations were carried out on an IBM PC/AT computer using SHELXTL PLUS programs.[8]

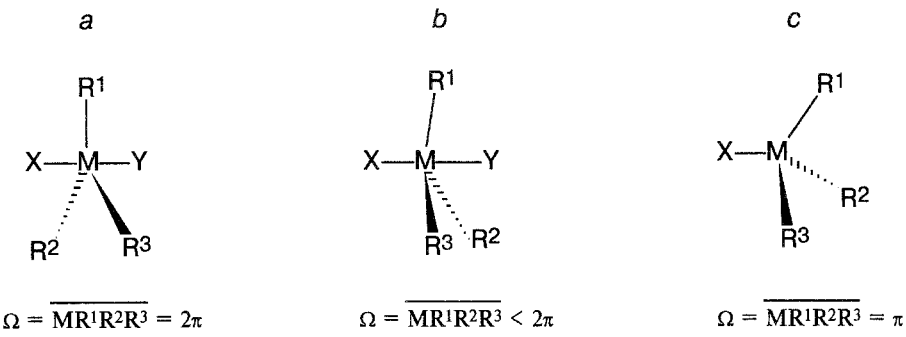

Fig. 2. Solid angle Ω for pentacoordination: *a*, ideal trigonal bipyramid; *b*, distorted trigonal bipyramid, a coordination polyhedron is "opened" towards a good leaving group Y; *c*, ideal tetrahedron, no additional interaction.

Table 6. Bond lengths (*d*) in molecules **1**—**4**

Bond	*d*/Å	Bond	*d*/Å
	Molecule **1**		
Si(1)—Cl(1)	2.256(1)	N(1)—C(2)	1.466(3)
Si(1)—Cl(2*A*)	2.052(1)	N(1)—C(3)	1.480(3)
Si(1)—Cl(2*B*)	2.051(4)	N(1)—C(8)	1.306(3)
Si(1)—O(1)	1.907(2)	C(3)—C(4)	1.507(4)
Si(1)—C(1*A*)	1.808(5)	C(4)—C(5)	1.523(4)
Si(1)—C(1*B*)	1.808(4)	C(5)—C(6)	1.518(3)
Si(1)—C(2)	1.881(2)	C(6)—C(7)	1.523(4)
O(1)—C(8)	1.278(2)	C(7)—C(8)	1.491(4)
	Molecule **2**		
Cl(1)—Si(1)	2.213(1)	N(1)—C(2)	1.478(2)
Cl(2)—Si(1)	2.052(1)	N(1)—C(7)	1.309(2)
Cl(3)—Si(1)	2.064(1)	C(2)—C(3)	1.517(3)
Si(1)—O(1)	1.865(2)	C(3)—C(4)	1.529(4)
Si(1)—C(1)	1.880(2)	C(4)—C(5)	1.520(3)
O(1)—C(7)	1.291(2)	C(5)—C(6)	1.541(2)
N(1)—C(1)	1.458(3)	C(6)—C(7)	1.489(2)
	Molecule **3**		
Si(1)—Cl(1)	2.236(1)	N(1)—C(3)	1.311(4)
Si(1)—Cl(2)	2.077(1)	N(1)—C(8)	1.474(4)
Si(1)—O(1)	1.885(2)	C(3)—C(4)	1.489(5)
Si(1)—O(2)	1.680(2)	C(4)—C(5)	1.523(5)
Si(1)—C(1)	1.880(3)	C(5)—C(6)	1.526(6)
O(1)—C(3)	1.282(3)	C(6)—C(7)	1.516(5)
O(1)—C(2)	1.305(5)	C(7)—C(8)	1.508(5)
N(1)—C(1)	1.452(4)		
	Molecule **4**		
Si(1)—Cl(1)	2.207(2)	N(1)—C(6)	1.313(6)
Si(1)—Cl(2)	2.073(2)	C(2)—C(3*A*)	1.498(6)
Si(1)—Cl(3)	2.021(3)	C(2)—C(3*B*)	1.498(6)
Si(1)—O(1)	1.852(4)	C(3*A*)—C(4*A*)	1.498(6)
Si(1)—C(1)	1.890(4)	C(3*B*)—C(4*B*)	1.498(6)
O(1)—C(6)	1.276(6)	C(4*A*)—C(5)	1.498(6)
N(1)—C(1)	1.456(6)	C(4*B*)—C(5)	1.498(6)
N(1)—C(2)	1.468(6)	C(5)—C(6)	1.504(6)

Results and Discussion

The lengths of the hypervalent bond components O—M—Cl (M = Si, Ge) and the corresponding valent angles in molecules **1**—**4** (Tables 6 and 7) and their analogs **5**—**9** (see Refs. 3—7) vary slightly due to an insubstantial distinction in the effect of the weak strained γ- and δ-lactam cycles on the hypervalent bond parameters.[9] Therefore, one can observe the effects of modification of the M atom equatorial environment in the molecules considered in a nearly pure form. The O_{ax}—Si distance in monochlorides **5** and **8**, dichloride **1**, and trichlorides **2** and **4** becomes shorter by ~0.04 and ~0.09 Å, respectively, due to introduction of one and two chlorine atoms into this environment. Accordingly, a shortening of the Si—Cl axial bond is about the same (0.05 and 0.10 Å). In the case of the germanium derivatives, the O_{ax}—Ge bond becomes even shorter (by ~0.13 Å in trichloride **7**) in comparision with monochlorides **6** and **9**, whereas the length of the Ge—Cl_{ax} bond decreases to a smaller degree (by 0.09 Å) upon introducing two chlorine atoms into the equatorial positions. In molecule **3**, the shortening of the Si atom axial bonds (by 0.07—0.08 Å) is intermediate between those observed in the dichlorides and trichlorides. This is in agreement with the fact that the inductive constant of the MeO group is approximately an average of those for Cl and Me.[10]

We suggested previously[11,12] to use the solid angle Ω between the equatorial bonds of the hypervalent atom (pseudoequatorial in a hexacoordinate structure) as a characteristic of its state. The change in the solid angle Ω depending on the extent of a coordinative interaction in the case of pentacoordination is shown in Fig. 2. Accordingly, the dependences of the hypervalent bond components lengths on Ω are described by the single-valued curves if the steric conditions for atoms of the hypervalent fragment are equal. It is convenient to use the deviation ΔΩ of the solid angle Ω from the 2π value corresponding to the "equivalent" components of a hypervalent bond, *e.g.*, when the chelate cycle at the M atom is the same for all structures discussed. These curves based on the data obtained by us and other authors[14—16] are presented in Fig. 3. Some of the curves were published previously,[13] however, with a somewhat different parameterization. The points *d*(ΔΩ) for structures **1**—**9** are also shown in Fig. 3. Note that the curves for a hypervalent germanium with the different equato-

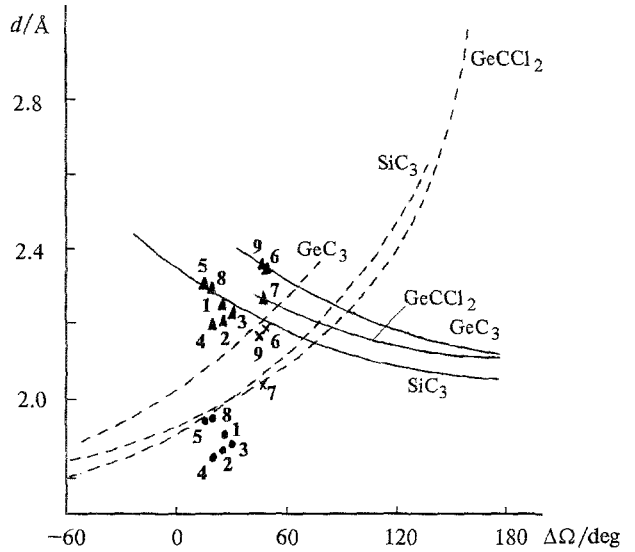

Fig. 3. Dependences of the distances M—Cl (solid lines) and M—O_{endo} (dashed lines) (M = Si, Ge) on ΔΩ for a series of compounds with different equatorial environments of the hypervalent M atom (the value of ΔΩ is given in solid angle degrees: 2π = 360°): • — O→Si bonds; × — O→Ge bonds; ▲ — Ge—Cl_{ax} and Si—Cl_{ax} bonds. Numeration of compounds is given.

rial environment are built on a basis of a very limited number of structures. Moreover, the latter don't meet the criterion of the steric conditions equality. Hence, these curves are most likely correlative. Nevertheless, the presented dependences are sufficiently reliable and in a good agreement with the parameters of molecules **6**, **7**, and **9**. On the contrary, the curves for the hypervalent Si atom with three carbon atoms in an equatorial environment are built on a large series of similar molecule structures. However, little is known about the structures of analogs with a different equatorial environment of the Si atom.

A comparision of the $d(\Delta\Omega)$ dependences and the data for structures **1**—**9** suggests the absence of essential differences under variation of the equatorial environment of the pentacoordinated Si and Ge atoms. It is to be expected, that the $d(\Delta\Omega)$ curves for the hypervalent SiC_2Cl and $SiCCl_2$ fragments with an equatorial coordinaton of the silicon atom are analogous to those for pentacoordinated Ge derivatives. With stronger electronegative equatorial substituents, the relatively short axial bonds (d(M—Cl) < 2.4 Å, d(M—O) < 2.2 Å) become not only shorter, but more rigid as well. By contrast, a slope of the curves $d(\Delta\Omega)$ increases in the region of a weak coordination. This effect is likely due to a decreased mobility of the hypervalent bond electrons caused by the shift of an electron density from the M atom to its equatorial substituents.

A much lesser rigidity of the hypervalent bond components as compared to usual covalent bonds explains why the parameters of this bond can vary under the effect of weak interactions, such as van der Waals forces.

Table 7. Relevant valent angles (ω) in molecules **1**—**4**

Angle	ω/deg	Angle	ω/deg
	Molecule **1**		
Cl(1)—Si(1)—Cl(2*A*)	93.5(1)	C(1*A*)—Si(1)—C(2)	124.3(2)
Cl(1)—Si(1)—Cl(2*B*)	94.6(2)	C(1*B*)—Si(1)—C(2)	128.8(4)
Cl(1)—Si(1)—O(1)	173.3(1)	Si(1)—O(1)—C(8)	114.3(1)
Cl(2*A*)—Si(1)—O(1)	89.0(1)	C(2)—N(1)—C(3)	121.0(2)
Cl(2*B*)—Si(1)—O(1)	89.8(2)	C(2)—N(1)—C(8)	115.0(2)
Cl(1)—Si(1)—C(1*A*)	94.1(2)	C(3)—N(1)—C(8)	123.9(2)
Cl(2*A*)—Si(1)—C(1*A*)	115.6(2)	Si(1)—C(2)—N(1)	108.9(1)
O(1)—Si(1)—C(1*A*)	90.4(2)	N(1)—C(3)—C(4)	113.0(2)
Cl(1)—Si(1)—C(1*B*)	97.9(6)	C(3)—C(4)—C(5)	114.2(2)
Cl(2*B*)—Si(1)—C(1*B*)	106.3(4)	C(4)—C(5)—C(6)	115.0(2)
O(1)—Si(1)—C(1*B*)	85.7(6)	C(5)—C(6)—C(7)	114.7(2)
Cl(1)—Si(1)—C(2)	89.5(1)	C(6)—C(7)—C(8)	114.0(2)
Cl(2*A*)—Si(1)—C(2)	119.6(1)	O(1)—C(8)—N(1)	117.8(2)
Cl(2*B*)—Si(1)—C(2)	123.6(2)	O(1)—C(8)—C(7)	119.6(2)
O(1)—Si(1)—C(2)	83.9(1)	N(1)—C(8)—C(7)	122.5(2)
	Molecule **2**		
Cl(1)—Si(1)—Cl(2)	93.9(1)	C(1)—N(1)—C(7)	114.9(1)
Cl(1)—Si(1)—Cl(3)	93.4(1)	C(2)—N(1)—C(7)	123.7(2)
Cl(2)—Si(1)—Cl(3)	113.7(1)	Si(1)—C(1)—N(1)	108.3(1)
Cl(1)—Si(1)—O(1)	175.3(1)	N(1)—C(2)—C(3)	113.3(1)
Cl(2)—Si(1)—O(1)	89.2(1)	C(2)—C(3)—C(4)	113.8(2)
Cl(3)—Si(1)—O(1)	88.6(1)	C(3)—C(4)—C(5)	115.5(2)
Cl(1)—Si(1)—C(1)	90.4(1)	C(4)—C(5)—C(6)	114.1(2)
Cl(2)—Si(1)—C(1)	123.6(1)	C(5)—C(6)—C(7)	112.6(2)
Cl(3)—Si(1)—C(1)	122.2(1)	O(1)—C(7)—N(1)	117.7(2)
O(1)—Si(1)—C(1)	84.9(1)	O(1)—C(7)—C(6)	119.2(2)
Si(1)—O(1)—C(7)	114.2(1)	N(1)—C(7)—C(6)	123.1(2)
C(1)—N(1)—C(2)	121.4(2)		
	Molecule **3**		
Cl(1)—Si(1)—Cl(2)	92.0(1)	C(1)—N(1)—C(3)	115.1(2)
Cl(1)—Si(1)—O(1)	173.8(1)	C(1)—N(1)—C(8)	121.2(2)
Cl(2)—Si(1)—O(1)	89.2(1)	C(3)—N(1)—C(8)	123.7(3)
Cl(1)—Si(1)—O(2)	96.7(1)	Si(1)—C(1)—N(1)	108.7(2)
Cl(2)—Si(1)—O(2)	114.9(1)	O(1)—C(3)—N(1)	117.7(3)
O(1)—Si(1)—O(2)	88.2(1)	O(1)—C(3)—C(4)	119.6(3)
Cl(1)—Si(1)—C(1)	89.8(1)	N(1)—C(3)—C(4)	122.7(3)
Cl(2)—Si(1)—C(1)	121.3(1)	C(3)—C(4)—C(5)	113.0(3)
O(1)—Si(1)—C(1)	84.4(1)	C(4)—C(5)—C(6)	114.4(3)
O(2)—Si(1)—C(1)	123.1(1)	C(5)—C(6)—C(7)	115.2(3)
Si(1)—O(1)—C(3)	114.1(2)	C(6)—C(7)—C(8)	114.3(3)
Si(1)—O(2)—C(2)	131.7(3)	N(1)—C(8)—C(7)	112.8(3)
	Molecule **4**		
Cl(1)—Si(1)—Cl(2)	93.4(1)	C(2)—N(1)—C(6)	124.4(4)
Cl(1)—Si(1)—Cl(3)	91.5(1)	Si(1)—C(1)—N(1)	107.8(3)
Cl(2)—Si(1)—Cl(3)	114.7(7)	N(1)—C(2)—C(3*A*)	112.0(3)
Cl(1)—Si(1)—O(1)	174.9(1)	N(1)—C(2)—C(3*B*)	111.1(4)
Cl(2)—Si(1)—O(1)	88.8(1)	C(2)—C(3*A*)—C(4*A*)	111.1(3)
Cl(3)—Si(1)—O(1)	91.7(1)	C(2)—C(3*B*)—C(4*B*)	111.1(4)
Cl(1)—Si(1)—C(1)	90.1(1)	C(3*A*)—C(4*A*)—C(5)	111.1(3)
Cl(2)—Si(1)—C(1)	122.0(2)	C(3*B*)—C(4*B*)—C(5)	111.1(4)
Cl(3)—Si(1)—C(1)	123.0(2)	C(4*A*)—C(5)—C(6)	112.3(4)
O(1)—Si(1)—C(1)	84.8(2)	C(4*B*)—C(5)—C(6)	112.7(4)
Si(1)—O(1)—C(6)	114.7(3)	O(1)—C(6)—N(1)	117.8(4)
C(1)—N(1)—C(2)	120.9(3)	O(1)—C(6)—C(5)	120.2(4)
C(1)—N(1)—C(6)	114.7(4)	N(1)—C(6)—C(5)	122.0(4)

In four crystallographically independent molecules of *N*-(dimethylfluorosilylmethyl)pyrrolidone-2,[17] the lengths of the O—Si bonds vary from 2.35 to 2.45 Å.

Such a pronounced effect is not observed in the case of the shorter bonds (d(Si—O) < 2.2 Å), but it doesn't imply its absence. In fact, rather high dipole moments (~5 D) of the molecules under consideration generate a slowly changing electric field in a crystal, which can effect the hypervalent fragment parameters. The previously revealed[18] correlation between the spectral characteristics of the hypervalent fragment and the solvent dielectric constant provides indirect evidence of such a possibility. In crystals, a similar confirmation would be true in the case of essentially different hypervalent fragment parameters for polymorphic modifications (a different average field owing to a different orientation of the dipole moments of molecules) or, alternatively, if there were an analogous difference in the isostructural compounds, *i.e.*, a different value and orientation of the dipole moments of molecules.

Compounds **1**—**9**, except **3**, belong to two isostructural groups: **1**, **2**, **5**—**7** and **4**, **8**, **9**. On the one hand, the curves presented in Fig. 3 are based on data obtained for other structures, and small nonsystematic deviations of the parameters of molecules **5**—**9** from these curves reveals that the effects of changes in the dipole moments of molecules and their orientation in crystals are not so important at least in the ranges of d(M—Cl) < 2.4 Å, d(M—O) < 2.2 Å. On the other hand, a comparison of the geometric fragment parameters within the isostructural groups doesn't reveal any specific deviations from the simple regularities described above. So, we can consider the influence of the intramolecular interactions on the lengths of hypervalent bond components exceeding the length of the usual covalent bond by ~0.3 Å (M—Cl) or ~0.6 Å (M—O) as being immaterial. The effect observed in solution may be attributed to dynamic factors.

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