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Physical Chemistry

Chemical bonding in isolated molecules and crystals of zwitterionic pentacoordinate silicon chelates

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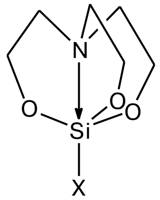
The electronic structures of a number of zwitterionic pentacoordinate silicon chelates were investigated using the results of X-ray diffraction studies and quantum-chemical calculatoins by the MPW1PW91/6-311G(d) method. The topological analysis of the electron density distribution function and the study in the framework of the natural bond orbital partitioning scheme showed that the character of chemical bonding in the axial fragments of the molecules under consideration changes from dative to three-center, four-electron as the silicon atom assumes a trigonal-bipyramidal coordination.

Key words: zwitterionic pentacoordinate silicon compounds, S_N2 nucleophilic substitution, dative bond, three-center four-electron interaction, electron density distribution, *ab initio* quantum-chemical calculations, NBO method.

The structure correlation method (SCM) is a popular and actively used theoretical approach to the description of reaction pathways.[1] Most of investigations by the structure correlation method were devoted to analysis of S_N2 nucleophilic substitution reactions based on X-ray diffraction data for series of similar crystal structures of pentacoordinate germanium, tin, cadmium, and, particularly, silicon compounds.[2] Hypercoordinate silicon compounds are used for simulating different steps of S_N2 nucleophilic substitution reactions (Nu:→Si—X, where the substituent X is considered as a leaving group and Nu: is a nucleophile) due to a correlation between the bond lengths in their axial fragments. In the course of the reaction, the coordination about the Si atom changes from 4 + 1 to 3 + 2 (in the transition state) and then to 1 + 4, *i.e.*, its configuration undergoes inversion.[3] Apparently, these changes in the geometry must be accompanied by a substantial change in the character of chemical bonding in the axial fragment. However, this problem has not been adequately explored.



The most abundant spectroscopic[4—7] and structural[8,9] information on different series of pentacoordinate silicon compounds concerns silatranes and chelate derivatives.[5,8] The electronic structures of silatranes, in particular, the nature of the Si—N transannular bond, have received considerable attention.[4,10—13]

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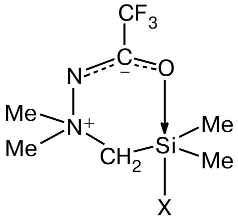
An important structural feature of silatranes is a substantial elongation (by ~0.3 Å) of the Si—N transannular bond in the gas phase as compared to that observed in the crystals.[14,15] This allowed one to classify all these bonds as dative bonds,[16,17] *i.e.*, those characterized by transfer of an electron from the lone electron pair of the N atom to the antibonding orbital of the axial Si—X bond. This is in good agreement with the results of quantum-chemical calculations of silatranes[10—13,17] and other compounds[12] with Si—N transannular bonds.

The electronic structures of compounds with the Si—O dative bond have been little studied and only the data for a series of solvated tetracoordinate silicon complexes are available.[18]

Among numerous pentacoordinate silicon chelates with the Si—O dative bond, hydrazine derivatives **1—5** containing a six-membered ring are of particular interest.[19,20] Unlike most of five-membered chelates, in the crystal these compounds simulate the final rather than initial step of the S_N2 reaction. In their molecules, the Si—O bonds are substantially longer than the standard bonds (~1.64 Å) but are much shorter than the analogous bonds in most of other chelate derivatives.[5] By contrast, the Si—Cl bond in molecule **3** is so elongated (2.6 Å [20]) that it can be characterized as a weak coordination bond and the molecules in crystal are generally considered as zwitterions.[20] Quantum-chemical calculations of compound **3** demonstrated[21] that, analogously to silatranes, the transition from the gas phase to solution must be accompanied by shortening of the Si—O bond by 0.2 Å. The similarity of the character of the Si—O and Si—N bonds was also evidenced from the analysis of the deformation electron density (DED) in the crystal of compound **3**.[22]



1—5

X = OMe (**1**), F (**2**), Cl (**3**), Br (**4**), OSO_2CF_3 (**5**)

Thus, information on the character of chemical bonding in the axial fragments of pentacoordinate silicon compounds is based on the results of quantum-chemical calculations, according to which the Si—O bond in the isolated molecules is much longer than that in the crystals. In turn, the structure correlation method reflects structural rearrangements in the OSiX fragment, completely ignoring changes in its electronic structure. Therefore, it was of interest to carry out a theoretical study of changes in the chemical bonding during the simulated S_N2 reaction and to compare the results obtained with the SCM predictions. For this purpose, the spatial and electronic structures of five inner salts, *viz.*, 1,1-dimethyl-1-(X-dimethylsilyl)methyl-2-(2,2,2-trifluoroethylidene-hydrazinium-1-olates) **1—5** (Fig. 1), and of cation **6** modeling the removal of the substituent X were studied by quantum-chemical methods using the density functional theory. To estimate the effect of the crystal field on the character of chemical bonding, we compared the results of calculations and experimental studies of the electron density distribution in the crystal of compound **3** (see Fig. 1).

Calculation procedure

All calculations were carried out with full geometry optimization using the Gaussian 98W program suite[23] with the MPW1PW91 hybrid functional and the 6-311G(d) basis set. The topological analysis of the theoretical (calculated) electron density distribution was performed with the use of the EXTREME[24] and AIM2000 programs.[25] The orbitals were localized using the NBO method[26] incorporated into the Gaussian 98W program suite.

The experimental electron density distribution in the crystal of compound **3** was obtained by the multipole refinement of the X-ray diffraction data[22] using the XD program package.[27] The refinement was carried out based on F using 6449 reflections ($I > 4\sigma(I)$, $\theta_{max} = 53°$). For the C and N atoms, the coordinates, thermal parameters, and multipole parameters up to the octupole level ($l = 3$) were refined. For the O, Si, and Cl atoms, the populations of multipoles were refined up to the hexadecapole level ($l = 4$). The local symmetry C_{3v} was assigned to the F atoms of the CF_3 group and to the C(1) and C(2) atoms of the Me groups. Before the refinement, the C—H distances were normalized to 1.07 Å (the value obtained in neutron diffraction studies[28]). For the H atoms, only the populations of dipoles were refined ($l = 1$), while the coordinates and thermal parameters were fixed. The multipole refinement gave the following results: $R = 0.0295$, $wR = 0.0271$, and GOF = 1.65 using 6449 reflections with $I > 4\sigma(I)$.

Results and Discussion

Geometry of molecules 1—5 and cation 6. In all the molecules under study, the coordination polyhedron about the Si atom is a distorted trigonal bipyramid. In molecules **1—5**, the deviation (Δ_{Si}) of the Si atom from the plane passing through the C atoms bound to this atom varies from 0.03 (**5**) to 0.33 Å (**1**) (Table 1). In molecule **3**, the Δ_{Si} value (0.14 Å) is close to that calculated by the HF/6-31G(d) method (0.15 Å).[29] The exception is cation **6** in which the coordination polyhedron about the Si atom is a distorted tetrahedron ($\Delta_{Si} = -0.47$ Å).

In the axial fragments of molecules **1—5**, the O—Si—X bond angles are in the range of 168.4—174.2°. On going from poor leaving groups (X = F or OMe) to good leav-

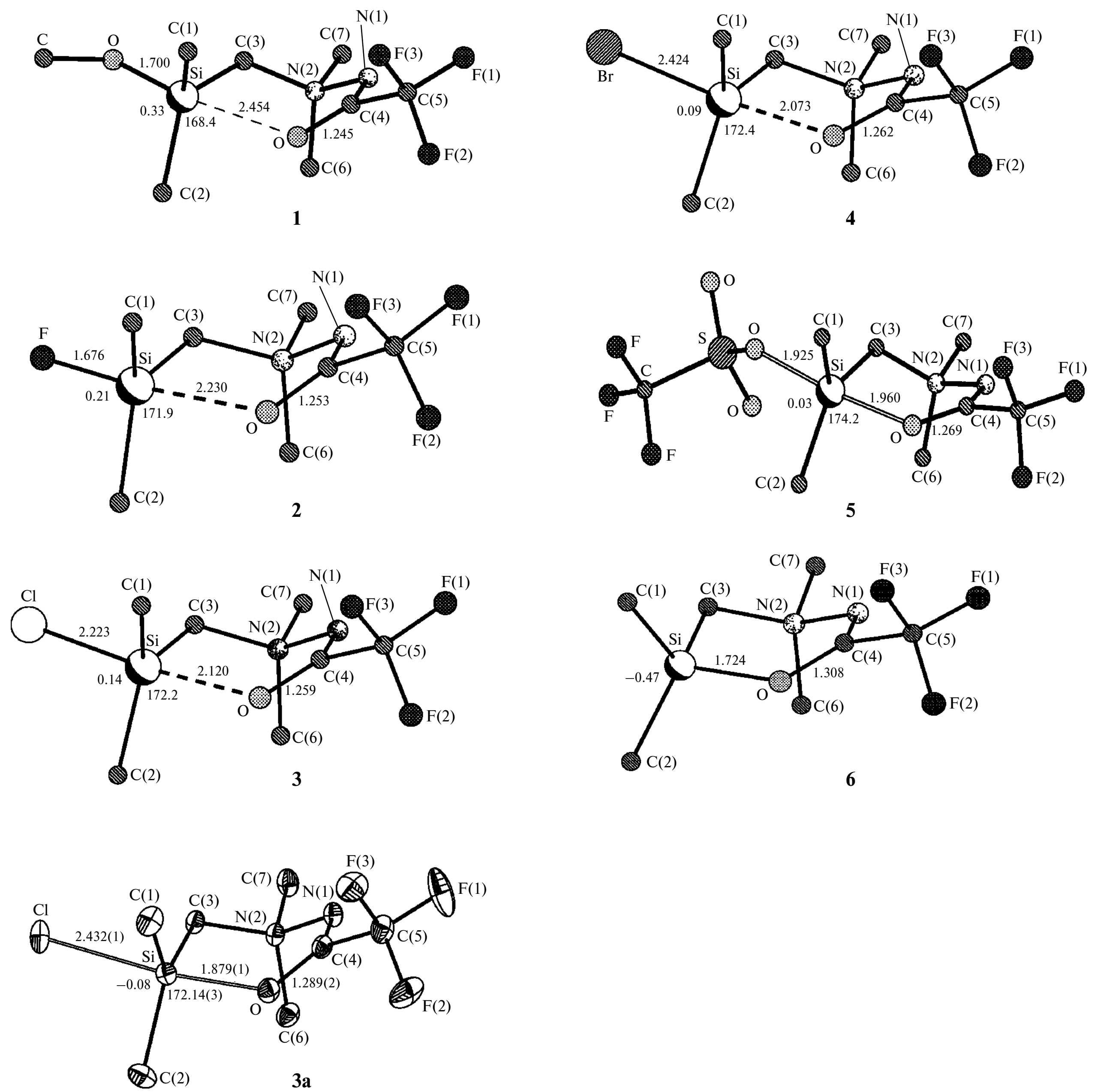


Fig. 1. Overall views and principal geometric parameters (bond lengths/Å, bond angles/deg, and deviations of the Si atoms/Å) of molecules **1—5** and cation **6**. The atoms of molecule **3a** are represented by thermal ellipsoids (p = 50%).

ing groups (X = Cl, Br, or OSO_2CF_3), the deviation from 180° is decreased. Such distortions of the geometry of the axial fragment are typical of all pentacoordinate silicon compounds including silatranes.

The deformation of the coordination polyhedron about the Si atom is manifested primarily in changes in the geometry of the O—Si—X fragment and is determined by the electronic effects of the substituents X. The Si—O and Si—X bond lengths in molecules **1—5** change in opposite directions. According to calculations, the shortest Si—O bond (1.960 Å) occurs in molecule **5**, whereas molecule **1** has the longest Si—O bond (2.454 Å) (see Table 1). Shortening of the Si—O bond leads to a sharp increase in the C(4)—O—Si angle (*cf.* ~120.7° for molecules **1—4** and 130.1° for molecule **5**). In cation **6**, this angle is 124.1°. Close inspection of the data on the Si—O bond lengths showed that the inductive effect of the substituent at the Si atom is of minor importance. For instance, the Si—O bond in molecule **2** (2.230 Å) is among the longest in such compounds despite the highest electronegativity of the substituent (X = F). Such an elongation is commonly attributed to polarizability of

Table 1. Principal geometric parameters (bond lengths, bond angles, and deviations of the Si atom (Δ_{Si}) from the plane passing through the C atoms bound to Si) in molecules **1—5** and cation **6**

Parameter	Compound						
	1	**2**	**3**	**3a**	**4**	**5**	**6**
Bond/Å							
Si—X	1.700	1.676	2.223	2.432(1)	2.424	1.925	—
Si—O	2.454	2.230	2.120	1.879(1)	2.073	1.960	1.726
Si—C(3)	1.922	1.925	1.926	1.897(2)	1.926	1.925	1.913
Si—C_{exo}*	1.873	1.869	1.871	1.854	1.873	1.868	1.846
O—C(4)	1.245	1.253	1.259	1.289(2)	1.262	1.269	1.308
N(1)—N(2)	1.451	1.451	1.450	1.466(2)	1.449	1.447	1.451
C(4)—N(1)	1.310	1.305	1.300	1.283(2)	1.298	1.293	1.277
Angle/deg							
X—Si—O	168.4	171.9	172.2	172.14(3)	172.4	174.2	—
Δ_{Si}/Å	0.33	0.21	0.14	−0.08**	0.09	0.03	−0.47

* The bond length was averaged over the Si—C(1) and Si—C(2) bonds.

** The minus sign corresponds to the deviation of the Si atom toward the O atom.

the chemical bond between the Si atom and the leaving group.[30]

As mentioned above, the geometry of isolated molecules of pentacoordinate silicon compounds differs substantially from their geometry in condensed state. Of compounds **1—5**, the crystal structure was established only for compound **3** in which the Si—O bond is ~0.22 Å shorter, whereas the Si—Cl bond is 0.20 Å longer than the corresponding bonds in the isolated molecule (see Table 1). In the subsequent discussion, the molecular geometry in the crystal will be considered separately and molecule **3** in the crystal will be denoted as **3a** (see Fig. 1) to distinguish two points on the potential surface of the S_N2 reaction.

Unlike the bond lengths in the axial fragment, the bond lengths in the equatorial plane of the trigonal bipyramid are independent of both the nature of the substituent X and aggregation state. Apparently, an insignificant increase in the calculated Si—C bond lengths as compared to the experimental values results from the incompleteness of the basis set employed and the drawbacks of the level of theory used.[31] It should be noted that the endocyclic Si—C(3) bond is ~0.04—0.05 Å longer than the Si—C(1) and Si—C(2) bonds both in the crystal and isolated molecule (see Fig. 1). This can be associated with the charge transfer from the O—C(4) carbonyl group not only to the antibonding orbital of the Si—X bond but also to the antibonding orbital of the Si—C(3) bond.

A comparison of the Si—X bond lengths in molecules **1—5** with the standard values[1] in tetracoordinate silicon compounds demonstrated that the elongation of the Si—X bond is maximum for isolated molecules **3** and **5** (~0.28 Å), whereas this elongation in isolated molecules **1** and **2** is an order of magnitude smaller. Since an elongation of the Si—X bond for the same leaving group is larger in the crystal than in the isolated molecule,[14,21] it can be assumed that free molecules **1—5** are not zwitterions regardless of the nature of the substituent X.

Changes in the geometry of the electron-excess N(1)—C(4)—O group are also quite expectable. The geometry of this group is determined primarily by the nature of the substituent at the Si atom and by the presence of the CF_3 group at the C(4) atom, resulting in a decrease in the electron-donating ability of this fragment. In particular, the O—C(4) bond length in molecule **1** is close to the standard value, whereas the C(4)—N(1) bond length has the maximum value. As the Si—O interaction in cation **6** is strengthened, the O—C(4) bond is elongated to 1.308 Å and the C(4)—N(1) bond is shortened to 1.277 Å. It should be noted that for X = Cl the replacement of the CF_3 group by the methoxybenzoyl fragment[31] leads to the O—C(4) and C(4)—N(1) bond lengths of 1.320 and 1.290 Å, respectively, which are virtually equal to the analogous parameters of cation **6**.

The conformation of the six-membered ring varies depending on the nature of the substituent X. In molecules with X = F or OMe, this ring adopts a boat conformation with the O and N(2) atoms deviating from the plane passing through the Si, C(3), N(1), and C(4) atoms, on the average, by 0.62 and 0.38 Å, respectively, whereas the deviation of the O atom from this plane in compounds **5** and **6** is much smaller (0.16 and 0.20 Å, respectively) and the rms deviation of the Si, C(3), N(1), and C(4) atoms from the mean plane (0.08 and 0.07 Å in **5** and **6**, respectively) is much larger than the analogous values (~0.01 Å) for the other compounds.

Analysis of the geometric parameters of molecules **1—5** and cation **6** showed that these molecules describe all possible rearrangements in the axial fragment occur-ring in the course of the S_N2 reaction. Hence, these molecules can be used in studies of changes in chemical bonding. The characteristic structural features of the molecules in the gas phase and condensed state suggest that the character of the Si—O dative bond in molecules **1—5** is qualitatively similar to that observed for the Si—N dative bond in silatranes and their analogs.

Electron density distribution in molecules 1—5 and cation 6. The experimental and calculated electron density distributions in molecules **1—5** and cation **6** were studied within the framework of the DED model and using the topological analysis of the electron density distribution function, ρ(*r*). The static DED maps constructed in the multipole refinement of **3a** (Fig. 2) are virtually identical with the analogous dynamic DED maps[22] characterized by accumulation of the electron density in the regions of almost all bonds including the Si—O dative bond.

Two DED peaks of approximately equal heights (0.70 and 0.60 e Å^{-3}) localized in the vicinity of the O atom correspond to the lone electron pair of this atom (see Fig. 2). These peaks are at distances of ~0.31 Å from the O atom and are located on the Si—O line and the bisector of the Si—C(3)—N(2) angle, respectively. The largest accumulation of ρ(*r*) is observed in the region of the amide N(1)—C(4)—O fragment (see Fig. 2). The high DED on the N(1)—C(4) bond (0.60 e Å^{-3}) corresponds to high multiplicity of this bond.

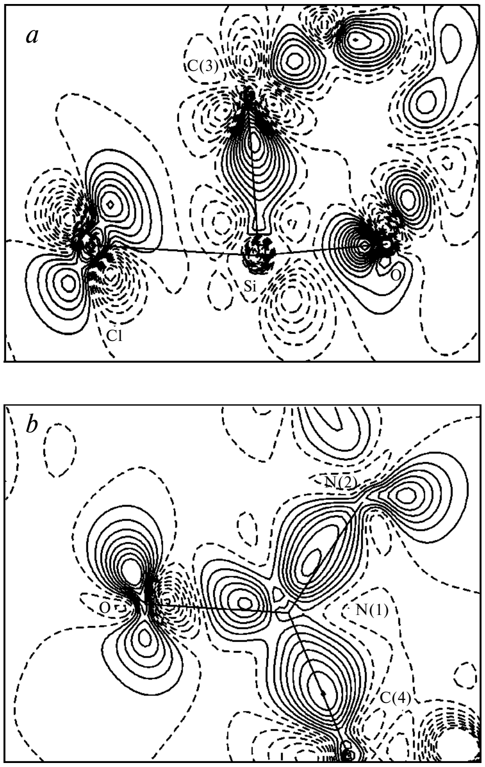


Fig. 2. Experimental deformation electron density in the crystal of **3a**; sections through the O—Si—Cl (*a*) and O—C(4)—N(1) (*b*) planes (positive contours are solid lines, negative contours are dashed lines, the maps are contoured at 0.05 (*a*) and 0.1 e Å^{-3} intervals (*b*)).

In spite of substantial elongation of the Si—O bond in the isolated molecule, the qualitative DED distribution in molecule **3** is analogous to that in the region of the Si—N transannular bond in 1-methylsilatrane, where no substantial charge transfer from the lone electron pair of the N atom to the antibonding orbital of the Si—Me bond is observed.

The DED distribution in the region of the Si—Cl bond is more sensitive to changes in the interatomic distance. In the crystal (**3a**), no DED maximum is observed on the Si—Cl bond (DED ≤0.1 e Å^{-3}), which is dramatically different from the Si—Cl bond in trichlorosilyltetrahydrophenanthroline.[32] In the section of the calculated DED, the maximum in the Si—Cl line is only slightly higher (~0.15 e Å^{-3}) (Fig. 3).

The positions of the lone electron pairs of the Cl atom were analyzed based on the DED maps for crystal **3a**. It was demonstrated that only two electron pairs form shortened intermolecular contacts (Fig. 4), whereas the remaining electron pairs lie off the region of the Si—Cl bond. Hence, the positions of the electron pairs of the Cl atom in the crystal are dictated not only by the possibility for the Si—Cl bonding to occur but also by the nonbonded interactions this atom is involved in.

The qualitative and quantitative analysis of the experimental and calculated ρ(*r*) distributions was carried out within the framework of the "Atoms in Molecules" (AIM theory).[33] We chose this approach because it allows one to unambiguously reveal chemical bonding from the presence of a critical point (CP) (3, −1) of the ρ(*r*) function in the bonding region. A shortened Si—O inter-

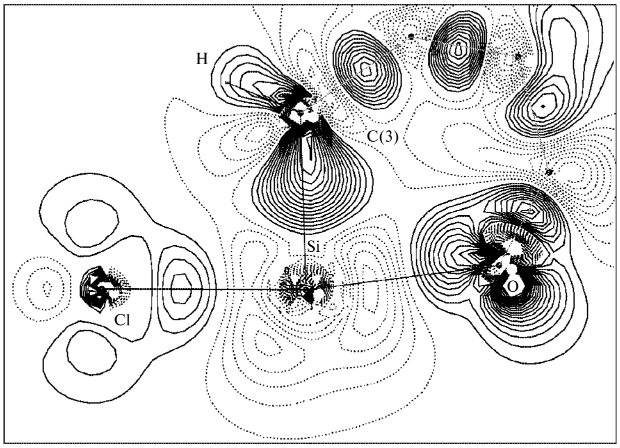


Fig. 3. Calculated deformation electron density in molecule **3**; section through the O—Si—Cl plane (positive contours are solid lines, negative contours are dashed lines, the maps are contoured at 0.034 e Å^{-3} intervals).

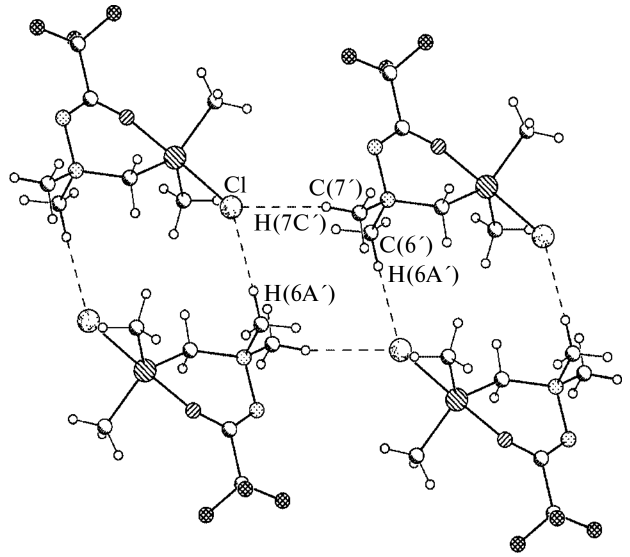


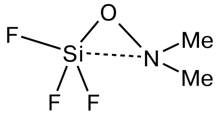
Fig. 4. Scheme of a doubled chain formed by shortened intermolecular C—H...Cl contacts: C(6)—H(6A)...Cl (2 – *x*, 2 – *y*, 1 – *z*) (H(6A)...Cl, 2.63 Å; C(6)H(6A)Cl, 154°) and C(7)—H(7C)...Cl (*x*, *y* – 1, *z*) (H(7C)...Cl, 2.67 Å; C(7)H(7C)Cl, 163°) in the crystal of **3a**.

Table 2. Topological characteristics of molecules **1—5** and cation **6**

Bond	**1**	**2**	**3**	**3a**	**4**	**5**	**6**
			$\rho(r)$ at (3, –1) CP/e Å^{-3}				
Si—X	0.81	0.74	0.47	0.32	0.40	0.47	—
Si—O	0.20	0.27	0.34	0.55	0.34	0.40	0.74
Si—C	0.74	0.74	0.74	0.69	0.74	0.74	0.74
O—C(4)	2.56	2.50	2.50	2.57	2.43	2.43	2.16
			$\nabla^2\rho(r)$ at (3, –1) CP/e Å^{-5}				
Si—X	17.35	18.07	2.41	0.27	0.24	6.51	—
Si—O	1.20	1.45	2.41	2.60	3.13	5.54	15.66
Si—C	5.06	5.06	5.06	2.92	5.06	5.06	5.30
O—C	–7.71	–8.19	–8.19	–24.08	–8.19	–7.47	–6.99
			$-E^{e}(r)$ at (3, –1) CP/hartree Å^{-3}				
Si—X	0.20	0.13	0.27	0.11	0.20	0.13	—
Si—O	0.03	0.07	0.13	0.24	0.13	0.13	0.20
Si—C	0.40	0.40	0.40	0.37	0.47	0.47	0.47
O—C	4.18	4.05	3.98	4.45	3.91	3.78	3.24

Note. $\rho(r)$ is the electron density, $\nabla^2\rho(r)$ is the Laplacian of the electron density, $E^{e}(r)$ is the local energy density, and CP is a critical point.

atomic distance and an elongated Si—X bond cannot serve as reliable criteria for dative bonding in the O—Si—X fragment.



As an example, we refer to (*N*,*N*-dimethylaminooxy)trifluorosilane.[34] In the molecule of this compound, the Si atom has a distorted trigonal-bipyramidal configuration, the Si...N interatomic distance (1.963(1) Å) is shorter than the corresponding distances in all other known silatranes, and one of the Si—F bonds is noticeably elongated. Based on the geometric characteristics, the Si...N transannular interaction seems not to be improbable. However, the topological analysis of the distribution function $\rho(r)$ revealed the absence of the (3, –1) CP in the region of the Si...N bond. This is also confirmed by the position of the lone pair electron of the N atom, which is substantially shifted from the Si...N line, and by the fact that the dipole moment vector is directed at an angle of 45° with respect to this line.

In contrast, analysis of the theoretical and experimental distribution functions $\rho(r)$ (Table 2) in molecules **1—5** and cation **6** demonstrated that the (3, –1) CPs are localized in the regions of all expected bonds including Si—O. In addition to the (3, –1) CPs, the (3, +1) CPs corresponding to the presence of a six-membered ring were found in all compounds. Hence, the Poincaré—Hopf relationship[33] is obeyed by molecules **1—5** and cation **6**. In the crystal, two (3, –1) CPs corresponding to intermolecular C—H...Cl contacts are observed along with the characteristic set of CPs of the isolated molecules (see Fig. 4).

The sections of the Laplacian of the calculated and experimental electron densities, $-\nabla^2\rho(r)$, in molecules **3** and **3a** (Fig. 5) exhibit accumulation of the electron density in the regions of all bonds of the six-membered ring, except for the Si—O bond. For this bond, depletion of $\rho(r)$ is observed at the (3, –1) CP in spite of a substantial difference in the bond lengths in the crystal and isolated molecule. This suggests that the character of the Si—O dative bond is independent of its length and is analogous to that of the Si—N dative bond and B—N and Al—N bonds in donor-acceptor complexes of boron and aluminum.[35]

Unlike the examination of the DED maps, analysis of the $\nabla^2\rho(r)$ distribution (see Fig. 5) showed that the character of the electron density distribution in the region of the Si—Cl bond changes on going from the isolated molecule to the crystal. According to calculations, this region is characterized by accumulation of $\rho(r)$. This situation is similar to that observed for bonds with high polarity (for example, the Si—O bond in 1-methylsilatrane[10]). By contrast, the analogous accumulation of $\rho(r)$ is virtually absent in the crystal (**3a**) (see Fig. 5, *a*) and the electron density is accumulated in the vicinity of the Cl atom so that all maxima of the Laplacian, $-\nabla^2\rho(r)$, corresponding to the lone electron pairs of the Cl atom lie off the Si—Cl line.

With the aim of comparing the electron density distributions in the axial fragments of molecules **1—5**, revealing the dependence of the electron density distribution on the nature of the substituents, and obtaining

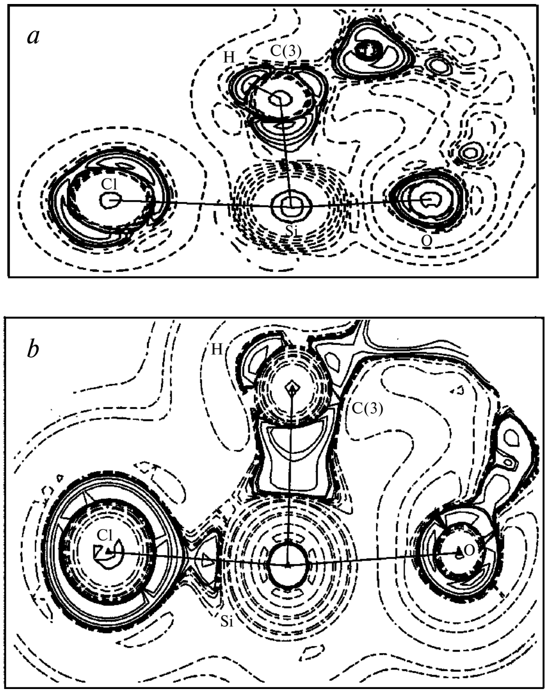


Fig. 5. Sections of the experimental (*a*) and theoretical (*b*) Laplacians of the electron density, $-\nabla^2\rho(r)$, through the O—Si—Cl plane in the crystal of **3a** (*a*) and in molecule **3** (*b*). Regions of positive and negative electron density accumulation ($-\nabla^2\rho(r) > 0$) are indicated by solid and dashed lines, respectively. The maps are contoured in the 2 logarithmic scale.

qualitative estimates of the Si—O and Si—X interactions, we analyzed the topological characteristics of molecules **1—5** and cation **6**, *viz*., $\rho(r)$, $\nabla^2\rho(r)$, and the local energy density $E^e(r)$, at the corresponding (3, −1) CPs (see Table 2). The energies $E^e(r)$ were calculated from the experimental data using a method based on a semiqualitative approximation of the kinetic energy density as a function of $\rho(r)$ and $\nabla^2\rho(r)$.[36]

The topological parameters of the bonds, except for those formed by the Si atom, are characterized by negative values of $\nabla^2\rho(r)$ and $E^e(r)$ (see Table 2). Within the framework of the AIM theory,[33] these bonds belong to the shared type of interatomic interactions corresponding to conventional covalent bonds. On the whole, the calculated and experimental values of $\nabla^2\rho(r)$ and $E^e(r)$ are in good agreement with each other and with the results of topological analysis of the $\rho(r)$ functions for different organic compounds.[37—39]

By contrast, the Si—C, Si—O, and Si—X bonds are characterized by the positive values of $\nabla^2\rho(r)$ (local depletion) at the (3, −1) CPs though the energies $E^e(r)$ remain negative. Based on their topological characteristics, these bonds can be considered as interactions of intermediate type.[33]

At the (3, −1) CPs corresponding to the formation of weak C—H...Cl contacts, $\nabla^2\rho(r)$ and $E^e(r)$ have small positive values (on the average, 0.6 e Å^{-5} and 0.04 hartree Å^{-3}, respectively) typical of closed-shell interactions. The energy of these contacts estimated using a correlation between the interaction energy and the potential energy density[40] is ~0.4 kcal mol^{-1}.

Analysis of the calculated $\rho(r)$ and $E^e(r)$ values for molecules **1—5** and cation **6** (see Table 2) demonstrated that the topological characteristics of the endocyclic bonds are virtually independent of the nature of the substituent, which exerts the most substantial effect on the O—C(4) carbonyl group involved in the O—Si—X dative bonding. The exceptions are the Si—O bonds.

In spite of the fact that the O—C(4) bond length changes substantially (~0.03 Å) on going from X = OMe (**1**) to OSO_2CF_3 (**5**), the $\rho(r)$ and $E^e(r)$ values at the (3, −1) CP correlating with the bond order decrease only slightly (the changes are 0.13 e Å^{-3} and 0.3 hartree Å^{-3}, respectively). Consequently, none of the substituents in the isolated molecules can cause a substantial withdrawal of the electron density toward the region of the dative bonding. The formation of the "normal" Si—O bond leads to a sharp weakening of the O—C(4) bond, which is manifested in a decrease in the absolute values of $\rho(r)$ and $E^e(r)$ at the (3, −1) CP.

The axial O—Si—X fragment is of particular interest from the viewpoint of chemical bonding. The values of $\rho(r)$ and $E^e(r)$ at the (3, −1) CPs for the Si—O and Si—X bonds change in opposite directions, like the bond lengths by themselves (see Tables 1 and 2).

Despite the substantial variations in the Si—O bond length (~0.45 Å), the $\rho(r)$ and $E^e(r)$ parameters of molecules **1—5** vary over rather narrow ranges (from 0.20 to 0.40 e Å^{-3} and from −0.03 to −0.13 hartree Å^{-3}, respectively). An analogous situation is observed for solvated donor-acceptor complexes of tetracoordinate silicon compounds.[17] Since the energy of the dative bond depends on the bond length to a lesser extent than the energies of conventional covalent bonds,[29,31] the fact that $\rho(r)$ and $E^e(r)$ vary over narrow ranges is quite explicable. The exception is the Si—O bond in cation **6** whose topological characteristics differ substantially from those of molecules **1—5** and are close to the corresponding values for the Si—X bond in molecule **1** (see Table 1) and the Si—O bonds in the simplest siloxanes and silicates.[41—43] This suggests that the Si—O bond in cation **6** is more similar to the normal bond than to the dative one. The topological characteristics of the Si—O bond in crystal **3a** are intermediate between those of isolated cation **6** and molecules **1—5**, which, apparently, results from the crystal packing effect.[15,44]

Thus, the influence of the leaving group in an isolated molecule is insufficient for a strengthening of the Si—O bond such that this bond can be considered as a normal rather than dative bond. This requires the cleavage of the Si—X bond.

The topological characteristics of the Si—X bonds at the (3, −1) CPs vary over substantially wider ranges than those of the Si—O bonds at the (3, −1) CPs (see Table 2). This reflects the different nature of the substituents X in molecules **1—5**. In molecule **1**, the Si—O(Me) bond length differs only slightly from the normal Si—O bond length in methylsilatrane.[10] The Si—X bonds in the other compounds are much weaker as evidenced by a decrease in the $\rho(r)$ and $E^{e}(r)$ values at the (3, −1) CP as compared to the corresponding values for the standard bonds.[1] Molecule **5** (X = OSO_2CF_3) is a special case. Here, the topological characteristics of the axial Si—O bonds have so close values that these bonds cannot be unambiguously treated as normal and dative bonds.

Investigation of the electronic structures of molecules 1—5 and cation 6 within the framework of the localized orbital scheme. Analysis of the electron density distributions within the framework of the AIM theory allowed us to study the character of interatomic interactions in molecules **1—5** and cation **6** in detail. However, the AIM formalism can not always be successfully combined with the schemes commonly accepted in chemistry. It was of interest to supplement the above-described data with the results of investigation of the electronic structures in the localized orbital approximation according to the NBO scheme.[26] The set of localized orbitals includes core-electron orbitals, two-center (both bonding and nonbonding) orbitals of the bonds, and the orbitals of the lone electron pairs and enables one to estimate the energy of stereoelectronic interactions.[26]

Analysis of the valence electron orbitals of the C(4)—O—Si—X fragment and orbitals of the lone pairs of the O atoms in molecules **1—5** and cation **6** is of most interest. The atomic charges (δ), the sum of the partial orbital energies of the $n_O \to \sigma^*_{Si-X}$ interactions ($\Sigma E^*_{O\to Si-X}$) involving all lone electron pairs of the O atom, and the population of the antibonding orbital of the Si—X bond ($P(\sigma^*_{Si-X})$) were examined (Table 3). The two last-mentioned values serve as a measure of the strength of the Si—O dative bond. Thus, the values of $\Sigma E^*_{O\to Si-X}$ characterize the possible gain in energy due to the involvement of the electron pairs of the O atom in the dative interaction, and $P(\sigma^*_{Si-X})$ characterizes the degree of charge transfer from the O atom to the antibonding orbital of the Si—X bond.

As can be seen from Table 3, the atomic charges in the C(4)—O—Si—X fragment are virtually independent of the nature of the substituent. The charge on the Si atom changes to the greatest extent. However, this change seems to be associated with the characteristic features of the MO localization scheme used in the NBO method rather than is caused by charge transfer. Hence, the atomic charges cannot serve as a criterion of charge transfer in the analysis of the electronic structure of the fragment under consideration.

Table 3. Principal characteristics of the localized orbitals of the C(4)OSiX fragment and atomic charges (δ) in this fragment

Compound	δ/e				$P(\sigma^*_{Si-X})$ /e	$\Sigma E^*_{O\to Si-X}$ /kcal mol^{-1}
	C(4)	O	Si	X		
1	0.50	−0.71	1.87	−0.91	0.08	12.2
2	0.50	−0.71	1.86	−0.66	0.10	23.4
3	0.51	−0.73	1.61	−0.49	0.12	41.7
3a	0.50	−0.75	1.69	−0.61	0.11	56.0
4	0.50	−0.73	1.60	−0.48	0.13	50.1
5	0.51	−0.73	1.80	−1.01	0.22	78.6
6	0.52	−0.78	1.81	—	—	—

Note. $P(\sigma^*_{Si-X})$ is the population of the antibonding orbital of the Si—X bond and $\Sigma E^*_{O\to Si-X}$ is the sum of partial energies of the $n_O \to \sigma^*_{Si-X}$ interactions.

The $\Sigma E^*_{O\to Si-X}$ and $P(\sigma^*_{Si-X})$ parameters are much more sensitive to the nature of the substituent X. There is a correlation between these parameters and the Si—O bond length analogous to the dependence on the topological characteristics ($\rho(r)$ and $E^{e}(r)$ at the (3, −1) CP). The charge transfer—population relationship is not true only for the isolated molecule of compound **5**.

Differences in the interatomic bonding are observed also in the analysis of the geometry of crystal **3a** by the NBO method. In this case, $P(\sigma^*_{Si-X})$ is much smaller than that for compound **5** in spite of the shorter Si—O bond. This suggests that the chemical bonding in the C(4)—O—Si—X fragments of molecules **1—5** and cation **6** cannot be adequately described by the dative bonding model. This is also evidenced by the analysis of the populations of the antibonding orbitals of the Si—O bonds ($P(\sigma^*_{Si-O})$).

In molecules **1—4**, the populations of these orbitals are low (<0.04) and, hence, the energy of the possible $\sigma_{Si-X} \to \sigma^*_{Si-O}$ interaction is also low. Consequently, in these compounds we deal with virtually unidirectional charge transfer from the carbonyl group to the antibonding orbital of the Si—X bond, as in the case of the Si—N dative bond in 1-methylsilatrane.[12] Therefore, the dative bonding model is more suitable for compounds **1—4**.

In contrast, the partial energies of the $\sigma_{Si-X} \to \sigma^*_{Si-O}$ interactions in molecules **5** and **3a** are 73.6 and 46.1 kcal mol^{-1}, respectively, and the populations of the σ^*_{Si-X} and σ^*_{Si-O} orbitals have comparable values (0.29 and 0.15 e, respectively). It should also be noted that the antibonding orbitals of the Si—O and Si—X bonds are very similar in composition. Thus the contribution of AOs of the Si atom is 85—96% (3s, 3p, and 3d orbitals account for 15—20, 50—85, and 2—3%, respectively), whereas the contributions of the X and O AOs are 4—15% (15—20% (3s), 50—85% (3p), 0—3% (3d)), the contribution of the Si AOs to the antibonding orbital of the

Si—O bond being somewhat larger than the contribution to the orbital of the Si—X bond. The above-considered data demonstrate that the charge transfer from the bonding orbital of the Si—X bond to the antibonding orbital of the Si—O bond in molecules **5** and **3a** is almost as energetically favorable as $n_{\mathrm{O}} \to \sigma^*_{\mathrm{Si-X}}$. Consequently, the charge transfer can proceed in both directions and the Si—O and Si—X bonds cannot be unambiguously treated as dative or normal bonds. An analogous situation was observed in the analysis of the topological characteristics of the $\rho(r)$ function.

Taken altogether, the impossibility of unambiguous treatment of the axial bonds as dative and normal bonds, the compositions of the antibonding orbitals (the predominant contribution of the Si AOs), and the large sum of the partial energies of charge transfer to the antibonding orbitals of the axial bonds suggest that a three-center four-electron interaction (3c-4e) occurs in the O—Si—X fragments of molecule **5** and crystal **3a**. It should also be noted that the coordination environment about the Si atom in these compounds is most similar to a trigonal bipyramid, which is most favorable for the 3c-4e interactions.

Our study demonstrated that the pentacoordinate silicon chelates under consideration can be classified into three types according to the characteristic features of the chemical bonding in the O—Si—X fragment. In the first type of compounds (**1—4**), the chemical bonding can be described as the $n_{\mathrm{O}} \to \sigma^*_{\mathrm{Si-X}}$ dative interaction. Despite a substantial weakening of the Si—X bond, the Si—O bonds in these compounds can be characterized as weak coordination interactions. Cation **6** simulating the removal of the leaving group belongs to the second type. Here, the Si—O bond differs only slightly from the normal bond as regards all the parameters under consideration. In the third type of compounds (**5** and **3a**), the axial bonds cannot be unambiguously treated as dative and normal bonds. Their topological characteristics are closer to each other than the parameters of the corresponding bonds in the first type of compounds, and the 3c-4e interaction can serve as the most adequate model for the description of chemical bonding in the O—Si—X fragment.

To summarize, the rearrangement of the geometry and changes in the chemical bonding in the axial O—Si—X fragments of the compounds under study, which are predicted by quantum-chemical calculations, are in agreement with the results obtained within the framework of the structure correlation method for the crystal state.

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