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Nature of Coordination Bond in Silatranes and Its Formation Dynamics According to the Ab Initio Calculations

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Abstract—Quantum-chemical calculations of 1-hydrosilatrane molecule with complete optimization of its geometry and at various fixed Si···N distances (2.0 to 3.7 Å) has been carried out at the MP2/6-31G(d) level. The silatranes coordination bond is formed of different atomic orbitals of Si and N atoms participating in a series of molecular orbitals. With the Si···N distance decreasing, contributions of the atomic orbitals in these molecular orbitals have been changed, number of the molecular orbitals has increased, and total energy of the molecule has decreased. At the coordination centers are getting closer, population of the nitrogen valence *s* and p_z orbitals have changed due to the corresponding bond angle change; the populations of Si and H orbitals are not significantly changed.

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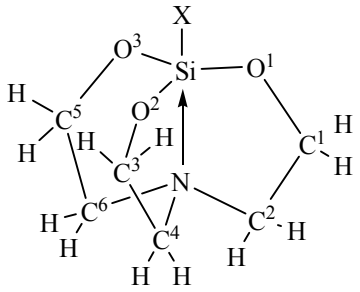
Silatrane **I** derivatives have been the first representatives of stable organic chelates of pentacoordinated silicon. Therefore, they have been thoroughly studied by a variety of physical methods [1–3].



I

The nature of Si←N bond in silatranes has been a matter of numerous discussions [(e.g., [1, 2, 4])]. According to earliest hypothesis, this bond is formed as a result of interaction of the lone-electron pair of nitrogen with the free *d*-orbitals of silicon suitable in symmetry. Later hypothesis has postulated interaction of three atoms of the axial fragment of molecule to form hypervalent four-electron three-center bond [1, 2, 4]. In the cases of other organosilicon compounds, the intramolecular coordination bonds have been believed to be formed via donor-acceptor interaction of the lone-electron pair the heteroatom with the electron-accepting Si atom [5, 6]. We propose that the coordination bond in silatranes (and in other compounds with intra- and intermolecular coordination) is initiated by electrostatic interaction of the coordination centers leading to their approaching, polarization of their bonds, and the transfer of electron density from the donor frag-ment to the acceptor when the atoms get sufficiently close [7–9].

The non-empiric methods of quantum chemistry are efficient to investigate the nature and formation dynamics of coordination bonds in silatranes and other coordination compounds. 1-Hydrosilatrane **I** (X = H) is a convenient model compound. According to the X-ray diffraction data [1, 10], the coordination polyhedron of silicon in silatranes is trigonal bipyramid with axial positions occupied by X, Si, and N atoms, and equatorial positions occupied by three oxygen atoms. Silicon atom is off the equatorial plane of the molecule towards X.

The H–Si←N angle in 1-hydrosilatrane is practically equal to 180°, that is, H, Si, and N atoms are aligned. For quantum-chemical calculations, it is

natural to take the position of X = H nucleus as the origin of coordinates, then the X atom as well as Si and N atoms are located at the *z* axis of coordinate system. It this case, the changes in population of the lone-electron pair and the valence *s* orbital of N atom, of valence *s* and p_z orbitals and the vacant d_{z^2} orbital of Si atom, and the valence *s* orbital of H atom can be analyzed at the varied Si···N distance. Such analysis, along with the analysis of molecular orbitals, is expected to give the valuable information on formation of the coordination Si←N bond and its nature.

We performed the quantum-chemical calculations of 1-hydrosilatrane molecule at the MP2/6-31G(d) level implemented in Gaussian 03 W software [11]. The modeling with complete geometry optimization revealed that the three five-membered cycles of the molecule were practically equal. The basic geometry parameters of the molecule are listed in the Table 1. The modeling demonstrated the absence of molecular orbital corresponding to the hypervalent four-electron three-center bond. In 1-hydrosilatrane there were no molecular orbitals formed predominantly of the orbitals of the molecule axial fragment. All the bonds were multicenter, typical of the polyatomic molecules. Several orbitals of the molecules revealed the significant contribution from the p_z valence orbital of N atom. For example, that orbital strongly contributed to the molecular orbitals with energies of –10.867 eV (φ_{47}) and –11.744 eV (φ_{46}). First φ_{47} orbital is HOMO. The contribution of *s* orbitals of N and H to that orbital was significantly lower, and the contribution of p_z orbital of Si atom was even lower. Contribution of the latter in HOMO was of the same order as that of *d* orbitals of Si. The oxygen, carbon, and some of hydrogen atoms orbitals contributed substantially to the both above-mentioned molecular orbitals, as followed from the calculated coefficients of molecular orbitals [Eqs. (1) and (2)].

Table 1. Bond lengths (*d*), bond (α) and torsion (β) angles in the molecule **I** with X = H as calculated by means of MP2/6-31G(d)

Bond	*d*, Å	Angle	α, deg	Angle	β, deg
H–Si	1.475	HSiO	99.65	HSiOC	–159.35
O–Si	1.691	SiOC	121.95	SiOCC	–45.09
O–C	1.415	OCC	108.90	OCCN	46.22
C–C	1.525	CCN	106.36		
C–N	1.465	CNC	114.80		
Si···N	2.315	OSiO	117.25		

$$\varphi_{47} = 0.757\mathrm{N}p_z - 0.173\mathrm{N}s - 0.113\mathrm{Si}s + 0.077\mathrm{Si}p_z + 0.036\mathrm{Si}dx^2 + 0.036\mathrm{Si}dy^2 - 0.096\mathrm{Si}d_{z^2} - 0.193\mathrm{H}s + 0.067\mathrm{O}^1s - 0.217\mathrm{O}^1p_x - 0.261\mathrm{O}^1p_y - 0.1\mathrm{O}^1p_z + 0.065\mathrm{C}^1s - 0.033\mathrm{C}^1p_x + 0.095\mathrm{C}^1p_y + 0.126\mathrm{C}^1p_z + 0.071\mathrm{C}^2s - 0.186\mathrm{C}^2p_z + 0.067\mathrm{O}^2s - 0.117\mathrm{O}^2p_x + 0.318\mathrm{O}^2p_y - 0.1\mathrm{O}^2p_z + \ldots, \quad (1)$$

$$\varphi_{46} = 0.632\mathrm{N}p_z - 0.24\mathrm{N}s + 0.063\mathrm{Si}s - 0.145\mathrm{Si}p_z - 0.008\mathrm{Si}dx^2 - 0.008\mathrm{Si}dy^2 + 0.026\mathrm{Si}dz^2 + 0.152\mathrm{H}s - 0.046\mathrm{O}^1s - 0.051\mathrm{O}^1p_x + 0.402\mathrm{O}^1p_y + 0.226\mathrm{O}^1p_z - 0.099\mathrm{C}^1p_x - 0.052\mathrm{C}^1p_y + 0.015\mathrm{C}^1p_z - 0.023\mathrm{C}^2s - 0.113\mathrm{C}^2p_x + 0.057\mathrm{C}^2p_y - 0.073\mathrm{C}^2p_z - 0.046\mathrm{O}^2s + 0.373\mathrm{O}^2p_x - 0.156\mathrm{O}^2p_y + 0.225\mathrm{O}^2p_z + \ldots \quad (2)$$

In order to study the nature of silatranes coordination bond and dynamics of its formation, we modeled the 1-hydrosilatrane molecule at different Si···N distances. The longest Si···N distance was of 3.7 Å when top of the trigonal pyramid (N atom) was

Table 2. Charges (*q*) of atoms and bond lengths *d*(Si–H) in the molecule **I** with X = H calculated at the MP2/6-31G(d) level at different Si···N distances

d(Si···N), Å	*d*(Si–H), Å	*q*(N), *e*	*q*(Si), *e*	*q*(X), *e*	*q*(O), *e*	*q*(C^1), *e*	*q*(C^2), *e*
2.0	1.480	–0.743	1.449	–0.173	–0.747	0.026	–0.174
2.315[a]	1.475	–0.735	1.471	–0.166	–0.753	0.020	–0.148
2.5	1.473	–0.717	1.480	–0.161	–0.761	0.016	–0.135
2.8	1.471	–0.690	1.493	–0.156	–0.774	0.010	–0.120
2.919[b]	1.470	–0.679	1.494	–0.155	–0.776	0.006	–0.117
3.1	1.469	–0.657	1.490	–0.153	–0.779	0.000	–0.120
3.4	1.467	–0.608	1.483	–0.145	–0.782	–0.005	–0.143
3.7	1.465	–0.562	1.482	–0.130	–0.790	–0.005	–0.171

[a] After complete optimization of molecular geometry. [b] At CNSi angles of 90°.

Table 3. Population of orbitals of N, Si, and H atoms in the molecule **I** with X = H, full energies of molecule (E = –21888.X, eV), and difference (Δ) between the highest and lowest populations as calculated at the MP2/6-31G(d) level at different Si···N distances

d(Si···N), Å	X, eV	N(s), e	N(p_z), e	Si(s), e	Si(p_z), e	Si(d_{z^2}), e	H(s), e
2.0	.815	1.645	1.611	0.672	0.629	0.153	0.653
2.315[a]	.984	1.633	1.723	0.702	0.610	0.117	0.648
2.5	.959	1.605	1.777	0.708	0.606	0.109	0.646
2.8	.850	1.548	1.842	0.709	0.599	0.108	0.644
2.919[b]	.794	1.534	1.855	0.710	0.598	0.108	0.644
3.1	.703	1.532	1.851	0.713	0.598	0.109	0.643
3.4	.484	1.578	1.794	0.719	0.604	0.110	0.637
3.7	.006	1.644	1.716	0.726	0.614	0.112	0.624
Δ		0.113	0.240	0.054	0.031	0.046	0.029

[a] After complete optimization of molecular geometry. [b] At CNSi angles 90°.

Table 4. Coefficients (C) of atomic orbitals of N, Si, and H atoms in molecular orbital (φ) of molecule **I** with X = H, and energies (E) of the molecular orbitals calculated at the MP2/6-31G(d) level at different Si···N distances

φ	d(Si···N), Å	E, eV	C(Ns)	C(Np_z)	C(Sip_z)	C(Sid_{z^2})	C(Hs)
φ_{47}	2.0	–11.034	0.058	–0.351	–0.291	0.132	0.326
	2.315	–10.867	–0.173	0.757	0.077	–0.096	–0.193
	2.5	–10.347	–0.227	0.947	–0.019	–0.063	–0.112
	2.8	–9.507	–0.145	1.008	–0.059	–0.041	–0.078
	2.919	–9.298	–0.082	1.012	–0.066	–0.037	–0.077
	3.1	–9.157	–0.026	1.002	–0.073	–0.034	–0.080
	3.4	–9.311	0.175	0.957	–0.073	–0.030	–0.085
	3.7	–9.666	0.259	0.900	–0.063	–0.028	–0.084
φ_{46}	2.0	–11.491	–0.070	–0.017	0.161	–0.047	–0.166
	2.315	–11.744	–0.240	0.632	–0.145	0.026	0.152
	2.5	–11.712	–0.150	0.375	–0.158	0.065	0.214
	2.8	–11.964	–0.073	0.284	–0.131	0.076	0.216
φ_{43}	2.919	–11.996	0.0	0.0	0.0	0.0	0.0
	2.0	–12.518	–0.247	0.726	–0.079	–0.028	0.119
	2.315	–12.456	–0.003	0.104	–0.305	0.085	0.288
	2.5	–12.702	0.0	0.0	0.0	0.0	0.0

directed away from Si atom, and N atom could not participate in the coordination interaction. The shortest Si···N distance was of 2.0 Å when top of the trigonal pyramid was directed towards Si, and N atom could participate in coordination interaction. As the Si···N distance was decreasing from 3.7 to 2.0 Å, the CNSi angles increased from 72.1° to 106.9° and the XSiO angles decreased from 113.74° to 95.08° at the average. The N atom is flat at the Si···N distance equaling 2.919 Å (the CNSi angles equaled 90º).

Modeling of 1-hydrosilatrane molecule at different Si···N distances confirmed that the XSiN angle remained practically equal to 180°. According to the calculations, as the coordination centers (Si and N atoms) got closer, the Si–H bonds were elongated independently of the nitrogen lone-electron pair orientation (that is, independently of its ability to interact with Si). Simultaneously, the partial negative charge at nitrogen, oxygen atoms, and X = H atom increased, whereas the partial positive charge at Si

atom first slightly increased (Table 2), and then sharply decreased passing of N atom by the planar state. The partial charge of C atom bound to O, being small and negative at Si···N > 2.919 Å, became positive after nitrogen had passed through the planarity state. Simultaneously, the negative charge of C atom bound to N one decreased at Si···N > 2.919 Å and then started growing. Evidently, elongation of the Si–H bond, increase of the electron density at X = H atom, and decrease of the electron density at O and Si atoms was due to polarization of the O–Si and Si–X bonds caused by the partial negative charge of N atom directly through the space [12].

From the computed population of the valence orbitals of N, Si, and X = H atoms (Table 3) it followed that approach of the coordination centers caused noticeable population changes only in the cases of *s* and p_z orbitals of N and (to a much lesser degree) in the cases of Si and H orbitals. In particular, the population of *s* orbital of Si linearly decreased, whereas that of p_z and d_{z^2} orbitals decreased at Si···N > 2.919 Å and increased at Si···N < 2.919 Å. The changes of populations of the valence *s* and p_z orbitals of N were opposite: with Si···N distance decreasing from 3.7 Å to 2.919 Å, population of p_z orbital of N increased and that of *s* orbital decreased; with Si···N distance further decreasing to 2.0 Å, vice versa, population of p_z orbital of N decreased, and that of *s* orbital increased. Thus, in the case of the nitrogen lone-electron pair orientation towards Si atom, transfer of electron density from N atom to p_z and d_{z^2} orbitals of Si atom as well as to X = H atom was possible. The highest population of the lone-electron pair orbital of N atom and the lowest population of its valence *s* orbital were observed at Si···N distance of 2.919 Å. Therefore, the populations of those orbitals of N significantly depended on its bond angles.

Thus, decrease of the Si←N distance in 1-hydrosilatrane caused transformation of all the molecular orbitals, including change of their energy and the corresponding contributions of atomic orbitals. For example, when the lone-electron pair of N was oriented towards Si atom, the approach of coordination centers led to decrease in HOMO energy (Table 4). The highest contribution of p_z orbital of N atom was observed at Si–N distance of 2.919 Å. At Si···N < 2.919 Å the contribution significantly decreased, whereas at Si···N > 2.919 Å the contribution increased only slightly. When the lone-electron pair of N was oriented from Si atom and at Si···N = 2.919 Å, the atoms of the molecule axial fragment (H, Si, N) did not participate in the formation of φ_{46} molecular orbital; vice versa, when the lone-electron pair of N was oriented towards Si, the atom orbitals of the above-mentioned atoms contributed to the molecular orbital, the contributions being significant at lower Si···N distance. Those atoms contributed to the φ_{43} molecular orbital as well, if Si···N distance was below 2.5 Å (Table 4). With decreasing Si···N distance, the total energy of the molecule decreased (Table 3).

To conclude, on convergence of the coordination centers due to their electrostatic interaction, variation of the molecule geometry occurs. Simultaneously, the electron density was redistributed, and polarization of O–Si and Si–X bonds changed leading to displacement of the electronic density from O and Si atoms to the X atom and to elongation of the Si–X bond [12]. The described changes in geometry and the electron density were accompanied by the change of the molecular orbitals energy and the contributions of atomic orbitals. In particular, number of molecular orbitals formed with participation of coordination centers atomic orbitals increased, and total energy of the molecule decreased. Thus, coordination bond in silatranes was formed with participation of various atomic orbitals of Si and N atoms in several molecular orbitals. It could not be described as a result of interaction of single atomic orbitals of the coordination centers, for example, as the interaction of the lone-electron pair of N atom and the vacant *d*-orbital of Si atom or its p_z-orbital. It could not be described either as the three-center four-electron bond.

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