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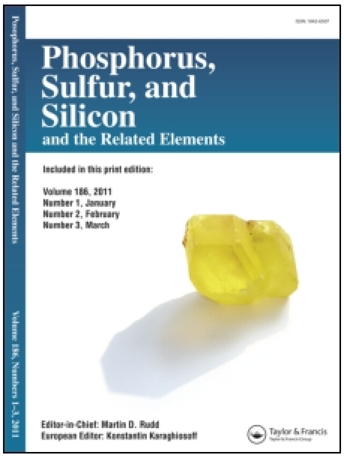

Phosphorus, Sulfur, and Silicon and the Related Elements

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Eleonora A. Ishmaeva[a]; Alina P. Timosheva[b]; Aisylu A. Gazizova[c]; Denis V. Chachkov[d]; Yana A. Vereshchagina[ac]; Vladimir E. Kataev[b]; Natalya V. Timosheva[e]
[a] Kazan State University, Kazan, Russia [b] A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan, Russia [c] Kazan State Technological University, Kazan, Russia [d] Kazan Scientific Center of Russian Academy of Sciences, Kazan, Russia [e] University of Massachusetts, Amherst, Massachusetts, USA

To cite this Article Ishmaeva, Eleonora A. , Timosheva, Alina P. , Gazizova, Aisylu A. , Chachkov, Denis V. , Vereshchagina, Yana A. , Kataev, Vladimir E. and Timosheva, Natalya V.(2009) 'Polarity and Structure of Silatranes with Planar Fragments', Phosphorus, Sulfur, and Silicon and the Related Elements, 184: 6, 1406 — 1412

To link to this Article: DOI: 10.1080/10426500902947500

URL: http://dx.doi.org/10.1080/10426500902947500

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Phosphorus, Sulfur, and Silicon, 184:1406–1412, 2009
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ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500902947500

Polarity and Structure of Silatranes with Planar Fragments

Eleonora A. Ishmaeva,[1] Alina P. Timosheva,[2] Aisylu A. Gazizova,[3] Denis V. Chachkov,[4] Yana A. Vereshchagina,[1,3] Vladimir E. Kataev,[2] and Natalya V. Timosheva[5]
[1]Kazan State University, Kazan, Russia
[2]A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan, Russia
[3]Kazan State Technological University, Kazan, Russia
[4]Kazan Scientific Center of Russian Academy of Sciences, Kazan, Russia
[5]University of Massachusetts, Amherst, Massachusetts, USA

The structure of silatranes $N[CH_2(RMeC_6H_2)O]_3SiR^1$ with planar fragments in six-membered semi-rings was established by the methods of dipole moments and density functional theory calculations. They are endo-structures with transannular interaction N→Si in which the oxygen atoms located adjacent to the silicon participate besides the nitrogen and silicon atoms.

Keywords Density functional theory; dipole moments; silatranes; transannular interaction

INTRODUCTION

Structure and intramolecular transannular interactions in the triethanolamine derivatives of boron, germanium, and silicon have been studied relatively well. The general name for this class of compounds was proposed in Voronkov and Zelchan[1]: atranes. The most studied atranes are the derivatives of silicon.

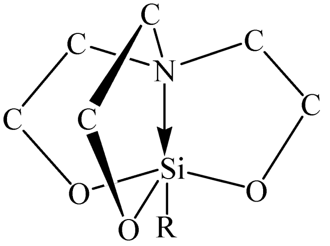
High values of dipole moments (5.73–7.1 D)[2,3] of 1-substituted organylsilatranes (Scheme 1) were identified as evidence of almost full

Received 17 December 2007; accepted 25 January 2008.

Dedicated to Professor Marian Mikołajczyk, CBMiM PAN in Łódź, Poland, on the occasion of his 70th birthday.

Investigated compounds were synthesized by N. V. Timosheva under the supervision of Professor Robert R. Holmes (University of Massachusetts, Amherst, Massachusetts, USA), and we want to express our deep gratitude to him.

Address correspondence to Professor Eleonora A. Ishmaeva, Kazan State University, Kremlevskaya St., 18, Kazan 420008, Russia. E-mail: yavereshchagina@yahoo.com



SCHEME 1

electron transfer from the nitrogen atom to the silicon atom. But later, on the basis of critical analysis of additive calculation on silatranes polarity using X-ray data,[4,5] the authors have drawn a conclusion about the incorrectness of this conception. The polarity of N→Si bond in 1-methylsilatrane is not great, which corresponds to the 0.1 $\bar{e}$ charge transfer from the nitrogen atom to the silicon atom. Numerous works of Voronkov and co-workers as well as other researchers (e.g.,[6–10]) have confirmed this conclusion.

Now a model of three-center four-electron (hyper valence) bonds N→Si–X is more recognized. Despite a number of obvious assumptions, this model describes electronic and spatial structures of silatranes in reality as compared with the hypothesis about sp^3d-hybridization of the silicon atom, which was widely propagated in 1970–80s. Modern theoretical calculations confirm that. Nevertheless, in spite of increasing possibilities of quantum chemical study on this problem, it is not finally solved, because there are still different points of view. In Milov et al.,[11] computational data obtained by the DFT B3LYP/6-311+G** and ab initio MP2(full)/6-311G** methods have showed that attractive interaction N→X(R) is conditioned by donation of the lone pair of electrons of the nitrogen atom to the antibonding orbital σ^*(XR). The same interaction O→Y (Y = N, P, As, Sb, and Bi) is also discussed in Minkin et al.[12] (DFT method) and Makoto et al.[13]

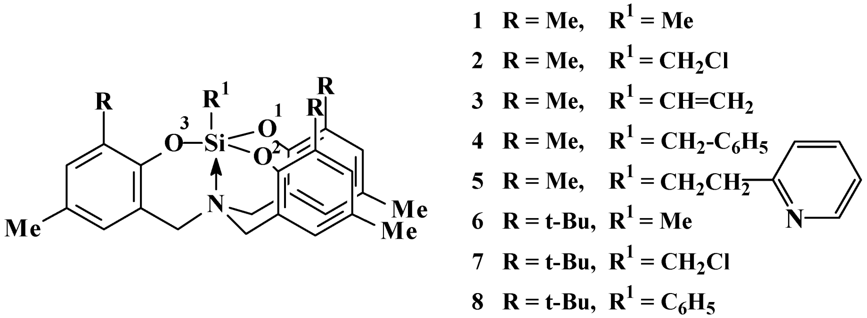
At the same time, Chernyshov et al.[14] have revealed an important role of not only the Si, Ge, and N atoms but also the O and other atoms of framework in stabilization of *endo*-configuration of silatranes and germatranes. It was shown that a model of "hyper valence" or "dative" interaction between N and Si or Ge is not exhaustive for an explanation of their structure. The authors have considered that the stability of these molecules is explained by total contribution of all atoms of the atrane part of the molecule into bonding molecular orbitals, and first and foremost atomic orbitals of the oxygen atom. Also electrostatic interactions between Si or Ge atoms bearing considerable positive charge and the electrons localized on the nitrogen atom are of importance. The entropy of the system increases, and the free energy of molecules decreases. So, the problem is complicated. In any case, there can be no doubt that atrane systems are exceptionally stable, and the nitrogen atom is not drawn in complexation, i.e., its basicity is very low.

RESULTS AND DISCUSSION

Recently a new class of silatranes $N[CH_2(MeRC_6H_2)O]_3Si{-}R^1$ containing unsaturated six-membered cycles in cyclic part of the molecules was prepared.[15–17] On the basis of data of X-ray analysis and dynamic NMR spectroscopy (^{29}Si and ^{1}H), the authors have concluded that these compounds have *endo*-form, and there is transannular bonding N→Si in their molecules, just as for atranes with five-membered semi-rings in cyclic part of the molecules.[3]

In the present work, we have determined polarity and structure of $[4.4.4.0^{1,6}]$ tricyclotetradecane derivatives **1–8** (Scheme 2) in benzene solution by the method of dipole moments and quantum chemical calculations. Experimental, calculated according to the vector-additive scheme, and theoretical dipole moments as well as experimental and theoretical values of N–Si and O–Si bond lengths for compounds **1–8** are shown in Table I.

As is obvious from Table I, the considerable exaltation (0.93–1.7 D) between the experimental and calculated data using additive scheme dipole moments is observed for all compounds, and this tendency remains for theoretical moments too. In accordance with data for 1-organylsilatranes,[4] it is evidence of the presence of transannular N→Si bonding in compounds **1–8**. Note that *exo*-structure does not exist according to results of quantum chemical calculations. An attempt of optimization of initial *exo*-structure results in optimum *endo*-structure.



1 R = Me, R^1 = Me
2 R = Me, R^1 = CH_2Cl
3 R = Me, R^1 = $CH{=}CH_2$
4 R = Me, R^1 = CH_2-C_6H_5
5 R = Me, R^1 = CH_2CH_2–
6 R = t-Bu, R^1 = Me
7 R = t-Bu, R^1 = CH_2Cl
8 R = t-Bu, R^1 = C_6H_5

SCHEME 2

TABLE I Experimental, Calculated Using Vector-Additive Scheme, Theoretical Dipole Moments (D), and Selected Bond Lengths (Å) for 1–8

	μ_{expt}	μ_{calc}	μ_{theor}	$\Delta\mu$	r_{expt} (N–Si)	r_{theor} (N–Si)	r_{theor} (O^1–Si)	r_{theor} (O^2–Si)	r_{theor} (O^3–Si)
1	2.07	2.17	0.94	0.10	2.746[15]	2.870	1.661	1.661	1.661
2	5.67	4.74	5.60	0.93	2.130[16]	2.280	1.685	1.676	1.675
3	3.26	2.13	1.13	1.13	2.636[16]	2.843	1.661	1.660	1.659
4	3.75	2.79	1.81	0.83	2.563[16]	2.803	1.664	1.664	1.658
5	3.43	2.44	1.14	0.99	2.781[16]	2.833	1.662	1.663	1.665
6	4.88	3.39	3.84	1.47	2.211[17]	2.236	1.699	1.699	1.699
7	6.73	5.03	6.21	1.70	2.045[17]	2.132	1.706	1.697	1.697
8	4.84	3.06	4.48	1.75	2.120[17]	2.177	1.707	1.707	1.701

Theoretical data are in a good agreement with N→Si bond lengths established by X-ray analysis.[15–17] The presence of a chlorine atom in the exocyclic methylene group of compounds **2** and **7** affects their polarity and asymmetry of molecule. The dipole moments of **2** and **7** are higher than ones of compounds without chlorine atom (Table I). The N→Si distance in molecules **1–8** is in a good agreement with interaction moments according to the data of the method of dipole moments. It is minimum in compounds **7** (2.045 Å) and **8** (2.120 Å), where the exaltation between the experimental and calculated dipole moments is maximum (1.70 D, 1.75 D). Note that the N→Si distance decreases in compounds **6–8** with *tert*-butyl substituents in planar fragments as compared with **1–5** (Table I). Apparently, the hydrogen atoms of *tert*-butyl groups are displaced close enough to the oxygen atoms, which are adjacent to the silicon atom, that promotes their inclusion into the general system of electronic density distribution in these molecules.

Thus, on the basis of obtained data, we can conclude that in the examined silatranes, there is transannular N→Si interaction, in which the nitrogen and silicon atoms as well as the oxygen atoms located adjacent to the silicon atom participate. The substitution of five-membered semi-rings in the framework of 1-organylsilatranes[5] for six-membered semi-rings with planar fragments does not affect their structures in solution—they are *endo*-structures with transannular N→Si bonding.

EXPERIMENTAL

Syntheses of silatranes **1–8** were reported earlier: 1-methylsila -2,10,11-trioxa-6-aza-3,4;8,9;12,13-tris(4′,6′-dimethylbenzo) [4.4.4.$0^{1,6}$]

tricyclotetradecane **1**,[15] 1-chloromethylsila-2,10,11-trioxa-6-aza-3,4;8,9;12,13-tris(4′,6′-dimethylbenzo)[4.4.4.$0^{1,6}$]tricyclotetradecane**2**,[16] 1-vinylsila-2,10,11-trioxa-6-aza-3,4;8,9;12,13-tris(4′,6′-dimethylbenzo) [4.4.4.$0^{1,6}$]tricyclotetra-decane**3**,[16] 1-benzylsila-2,10,11-trioxa-6-aza-3,4;8,9;12,13-tris(4′,6′-dimethylbenzo) [4.4.4.$0^{1,6}$]tricyclotetradecane**4**,[16] 1-(2-pyridylethyl)sila-2,10,11-trioxa-6-aza-3,4;8,9;12,13-tris(4′,6′-dimethylbenzo) [4.4.4.$0^{1,6}$]tricyclotetradecane **5**,[16] 1-methylsila-2,10,11-trioxa-6-aza-3,4;8,9;12,13-tris(4′-methyl,6′-*tert*-buthylbenzo) [4.4.4.$0^{1,6}$]tricyclotetradecane **6**,[17] 1-chloromethylsila-2,10,11-trioxa-6-aza-3,4;8,9;12,13-tris(4′-methyl,6′-*tert*-buthylbenzo) [4.4.4.$0^{1,6}$]tricyclotetradecane **7**,[17] and 1-phenylsila-2,10,11-trioxa-6-aza-3,4;8,9;12,13-tris (4′-methyl,6′-*tert*-buthylbenzo) [4.4.4.$0^{1,6}$]tricyclotetradecane **8**.[17]

The dipole moments were determined in benzene at 20°C on an IDM-2 instrument according to a procedure in the literature.[18] Benzene was purified using standard procedure.[19] In the calculations of dipole moments according to vector-additive scheme, we used the following moments of the bonds and groups: m(Si–O) = 2.25 D[20]; m(Si–$C_{sp}{}^3$) = 1.48 D[20]; m(Si–C^2_{spAr}) = 0.79 D[21]; m(H–$C_{sp}{}^3$) = 0.28 D[21]; m(H–$C_{sp}{}^2$) = 0.70 D[21]; m(Si–Vinyl) = 0.88 D (calculated from μ_{expt} of vinyltrimethylsilane)[22]; m(Me–C_{Ar}) = 1.08 D and m($C_{sp}{}^3$–C_{Ar}) = 0.75 D were calculated from μ_{expt} of toluene[22]; m(*t*-Bu–C_{Ar}) = 1.18 D (calculated from μ_{expt} of *tert*-butylbenzene)[22]; m($C_{sp}{}^2{}_{Ar}$–N) = 1.51 D (calculated from μ_{expt} of pyridine)[22]; m($C_{sp}{}^2{}_{Ar}$–O) = 0.34 D (calculated from μ_{expt} of anisole)[22]; m($C_{sp}{}^3$–Cl) = 1.58 D[4]; m($C_{sp}{}^3$–N) = 0.53 D.[23] Bond angles determined by X-ray diffraction analysis of compounds **1–8**[15–17] were used. The coefficients of the equations used for calculations, the orientational polarizations, and experimental dipole moments of silatranes **1–8** are given in Table II.

TABLE II Coefficients of the Computational Equations, Orientational Polarizations, and Experimental Dipole Moments of Compounds 1–8

	α	γ	P_{or}, cm^3	μ_{expt}, D
1	1.033	0.0215	87.626	2.07
2	7.262	0.0345	657.442	5.67
3	2.654	0.0313	217.333	3.26
4	3.039	0.1701	287.577	3.75
5	2.609	0.0485	240.591	3.43
6	4.646	0.0223	487.002	4.88
7	8.307	0.0380	928.235	6.73
8	4.156	0.0280	479.051	4.84

Quantum chemical calculations were carried out by the GAUSSIAN 03 program[24] at the B3LYP level of the hybrid density functional theory with the 6-31G(d) basis set. All calculations were performed in Joint Supercomputer Center of Kazan Scientific Center of Russian Academy of Sciences (http://wt.knc.ru).

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