ISSN 1070-3632, Russian Journal of General Chemistry, 2008, Vol. 78, No. 7, pp. 1350–1353. © Pleiades Publishing, Ltd., 2008.
Original Russian Text © E.A. Ishmaeva, A.P. Timosheva, A.A. Gazizova, D.V. Chachkov, Ya.A. Vereshchagina[a], V.E. Kataev, N.V. Timosheva, 2008, published in Zhurnal Obshchei Khimii, 2008, Vol. 78, No. 7, pp. 1114–1117.

Dipole Moments, Structure, and Transannular Interactions in Silatranes Containing Planar Fragments

E. A. Ishmaeva[a], A. P. Timosheva[b], A. A. Gazizova[c], D. V. Chachkov[d], Ya. A. Vereshchagina[a,c], V. E. Kataev[b], and N. V. Timosheva[e]

[a] *Kazan State University, ul. Kremlevskaya 18, Kazan, 420008 Tatarstan, Russia*
e-mail: EleonoraIshmaeva@ksu.ru

[b] *Arbuzov Institute of Organic and Physical Chemistry, Kazan Research Center, Russian Academy of Sciences, Kazan, Tatarstan, Russia*

[c] *Kazan State Technological University, Kazan, Tatarstan, Russia*

[d] *Kazan Research Center, Russian Academy of Sciences, Kazan, Tatarstan, Russia*

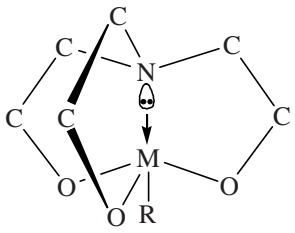
[e] *University of Massachusetts, Amherst, Massachusetts, USA*

Received December 28, 2007

Abstract—The method of dipole moments and theoretical calculations (DFT B3LYP/6-31G*) were used for structural assessment of silatranes $N[CH_2(RMeC_6H_2)O]_3SiR^1$ containing planar fragments in the six-membered semirings. They are endo structures with transannular N→Si interaction which involves, along with nitrogen and silicon, oxygen atoms adjacent to silicon.

DOI: 10.1134/S1070363208070116

By present the structure and intramolecular transannular interactions in triethanolamine derivatives of boron, germanium, and silicon are sufficiently thoroughly studied. Voronkov and D'ykov [1] have offered to call this class of compounds by a general name "atranes": silatranes (M = Si), boratranes (M = B), ferratranes (M = Fe), phosphatranes (M = P), arsatranes (M = As), vanadatranes (M = V), etc.



Silicon derivatives are the best studied among atranes. Apart from general theoretical problems, this is caused by the fact that silatranes are more interesting and promisimg due to their specific (and often unique) biological activity [2]. Furthermore, unlike many other atranes, silatranes exhibit a higher solubility, what is important for physicochemical studies. The high dipole moments (5.3–7.1 D) [3, 4] of 1-substituted organylsilatranes were considered as evidence for an almost complete electron transfer from nitrogen to silicon. But later on the basis of the critical analysis of the vector additive calculations of the polatiry of silatranes [2, 5] and X-ray diffraction data, this conclusion was ruled out. The polarity of the N→Si bond in 1-methylsilatrane is not too high (1.38 D), which suggests that the charge transfer from nitrogen to silicon is about 0.1 ē. This suggestion was confirmed in numerous works (see, for example, [6–10]).

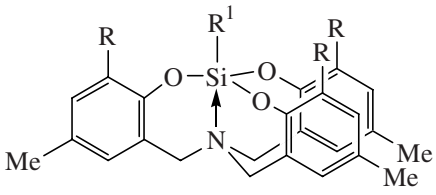
The most acknowledged model of the N→Si bond in silatranes is a three-centered four-electron (hypervalent) N→Si–X bond. In spite of some evident admissions, this model gives a more adequate description of the electron and steric structure of silatranes as compared to the hypothesis of an sp^3d-hybridized the silicon atom, which was the most widespread in 1970–80s. Modern theoretical calculations give analogous evidence. Nevertheless, despite enhanced possibilities for quantum-chemical investigation of this problem, it cannot be considered completely solved, because there are different points of view still exist. Milov et al. [11] performed DFT B3LYP/6-311+G** and ab initio MP(2)(full)/6-311G**

calculations to show that the (R)X←N interaction is caused by donation of the nitrogen lone electron pair onto the antibonding σ(XR) orbital. Analogous Y←O interactions (Y = N, P, As, Sb, and Bi) was considered in [12] (DFT and B3LYP methods) and [13].

At the same time, Chernyshev et al. [14] established that an important role in the stabilization of the *endo* configuration of silatranes and germatranes is played not only by Si, Ge, and N, but also by oxygen and other carcass atoms, which reveals itself in MO parameters. The AM1 and PM3 methods with the STO-3G, 631G, 631G*, and B3LYP basis sets were used. It was shown that the model of "hypervalent" or "dative" interaction of N and Si or Ge fails to exhaustively explain the structure of silatranes. The referees suggested that the stability of these molecules is better explained in terms of a joint contribution of all atoms of the atrane frame, primarily oxygen, into bonding MOs. An important role is also played by electrostatic interactions of Si and Ge, which bear a significant positive charge, and electrons localized on nitrogen. The entropy of the system increases, and the free energy of molecules decreases. The aforesaid shows that the problem is quite intricate and ambiguous. In any case, atrane systems are of no doubt extremely stable, and their nitrogen atom cannot be involved in complex formation, i.e. it possesses quite a low bacility.

Over the past years a new class of silatranes of the general formula $N[CH_2(RMeC_6H_2)O]_3SiR^1$ containing unsaturated six-membered rings in the cyclic part of the molecule was synthesized. Based on X-ray diffraction and dynamic ^1H and ^{29}Si NMR data, a conclusion was drawn that these compounds exist in the *endo* form and certain a transannular N→Si bond, like atranes with five-membered semirings in the cyclic part of the molecule [4].

In the present work we determined the polarity of atranes **I–VIII** in solutions by the method of dipole moments. The resulting data in combination with quantum-chemical calculations were used to assess the structure of these compounds.



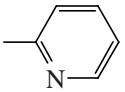
I, R = Me, R^1 = Me; **II**, R = Me, R^1 = CH_2Cl; **III**, R = Me, R^1 = $CH{=}CH_2$; **IV**, R = Me, R^1 = $CH_2{-}C_6H_5$; **V**, R = R^1 = CH_2CH_2–  ; **VI**, R = *t*-Bu, R^1 = Me; **VII**, R = *t*-Bu, R^1 = CH_2Cl; **VIII**, R = *t*-Bu, R^1 = C_6H_5.

Table 1 lists the experimental, vector-additive, and theoretical dipole moments of compounds **I–VIII**, as well as the experimental and theoretical N–Si and O–Si interatomic distances.

As seen from Table 1, all the compounds feature a significant exaltation (0.93–1.79 D) of the experimental and vector-additive dipole moments. The same trend is observed in the theoretical dipole mo-

Table 1. Experimental, vector-additive, and theoretical dipole moments (D) of compounds **I–VIII** and selected N–Si and O–Si distances (Å)

Comp. no.	μ_{exp}	μ_{calc}	μ_{theor}	$\Delta\mu$	r_{exp} (N–Si)	r_{theor} (N–Si)	r_{theor} (O^1–Si)	r_{theor} (O^2–Si)	r_{theor} (O^3–Si)
I	2.07	2.17	0.94	0.10	2.746 [15]	2.870	1.661	1.661	1.661
II	5.67	4.74	5.60	0.93	2.130 [16]	2.280	1.685	1.676	1.675
III	3.26	2.13	1.13	1.13	2.636 [16]	2.843	1.661	1.660	1.659
IV	3.75	2.79	1.81	0.83	2.563 [16]	2.803	1.664	1.664	1.658
V	3.43	2.44	1.14	0.99	2.781 [16]	2.833	1.662	1.663	1.665
VI	4.88	3.39	3.84	1.47	2.211 [17]	2.236	1.699	1.699	1.699
VII	6.73	5.03	6.21	1.70	2.045 [17]	2.132	1.706	1.697	1.697
VIII	4.84	3.06	4.48	1.75	2.120 [17]	2.177	1.707	1.707	1.701

ments. By analogy with 1-organylsilatranes [5], these results can be treated as evidence for transannular N→Si bonding. Note that quantum-chemical calculations show that the *exo* structure is not realized. Attempted optimization of the starting *exo* structure leads to an optimal *endo* structure. Theoretical calculations sufficiently well reproduce the X-ray diffraction N→Si distances reported in [15–17]. The presence of the chlorine atom in the exocyclic methylene group (compounds **II** and **VII**) affects the polarity and asymmetry of the molecule. This reveals itself in the dipole moments which are higher than in chlorine-free compounds, as well as in the Si–O distances (Table 1). The N→Si distance in the molecules under investigation well correlates with their interaction moments established from the dipole moments. This distance is the shortest in **VII** and **VIII** (2.045 and 2.120 Å, respectively), where the exaltation of the experimental and calculated dipole moments is the greatest (1.70 and 1.75 D). Furthermore, the N→Si distance in **VI–VIII** having *tert*-butyl substituents in the planar fragments is shorter than in **I–V** (Table 1), which is probably explained by the fact that the *tert*-butyl hydrogen atoms are fairly proximate to the oxygen atoms adjacent to silicon and thus included in the common electron density distribution system.

Hence, our present results provide evidence for the existence in silatranes having planar fragments in the six-membered semirings of transannular N→Si interaction involving, along with nitrogen and silicon, the oxygen atoms adjacent to silicon. The replacement of the five-membered semirings in the 1-organylsilatrane frame [2] by six-membered semirings with planar fragments produces no significant changes in their structures in solutions. They are *endo* structures with transannular N→Si bonding.

Table 2. Coefficients of the calculation equations, orientational polarization, and experimental dipole moments of compounds **I–VIII**

Comp. no.	α	γ	P_{or}, cm^3	μ_{exp}, D (benzene)
I	1.033	0.0215	87.626	2.07
II	7.262	0.0345	657.442	5.67
III	2.654	0.0313	217.333	3.26
IV	3.039	0.1701	287.577	3.75
V	2.609	0.0485	240.591	3.43
VI	4.646	0.0223	487.002	4.88
VII	8.307	0.0380	928.235	6.73
VIII	4.156	0.0280	479.051	4.84

EXPERIMENTAL

The synthesis and analytical data of silatranes **I–VIII** are presented in the following publications: 1-methyl-1-sila-2,10,11-trioxa-6-aza-3,4,8,9;12,13-tris-(4',6'-dimethylbenzo)[4.4.4.$0^{1,6}$]tricyclotetradecane **I** [15], 1-chloromethyl-1-sila-2,10,11-trioxa-6-aza-3,4,8,9;12,13-tris(4',6'-dimethylbenzo)[4.4.4.$0^{1,6}$]tricyclotetradecane **II** [16], 1-vinylsila-2,10,11-trioxa-6-aza-3,4,8,9;12,13-tris(4',6'-dimethylbenzo)[4.4.4.$0^{1,6}$]tricyclotetradecane **III** [16], 1-benzyl-1-sila-2,10,11-trioxa-6-aza-3,4,8,9,12,13-tris(4',6'-dimethylbenzo[4.4.4.$0^{1,6}$]tricyclotetradecane **IV** [16], 1-(2-pyridyl-1-ethyl)sila-2,10,11-trioxa-6-aza-3,4,9,12,13-tris(4',6'-dimethylbenzo)[4.4.4.$0^{1,6}$] tricyclotetradecane **V** [16], 1-methyl-1-sila-2,10,11-trioxa-6-aza-3,4,8,9;12,13-tris(4'-methyl,-6'-*tert*-butylbenzo)-[4.4.4.$0^{1,6}$]tricyclotetradecane **VI** [17], 1-chloro-methyl-1-sila-2,10,11-trioxa-6-aza-3,4,8,9;12,13-tris(4'-methyl,6'-*tert*-butylbenzo)[4.4.4.$0^{1,6}$]tricyclotetradecane **VII** [17], and 1-phenylsila-2,10,11-trioxa-6-aza-3,4;8.9;12.13-tris(4'-methyl,6'-*tert*-butylbenzo) [4.4.4.$0^{1,6}$]-tricyclotetradecane **VIII** [17].

The dipole moments of compounds **I–VIII** were measured in benzene at 20°C, according to [18]. In calculations by the vector additive scheme, the following group and bond increments were used, D: m(Si–O) 2.25 D [19], m(Si–C_{sp3}) 1.48 [19], m(Si–C_{sp2Ar}) 0.79 [20], m(H–C_{sp2}) 0.70 [20], m(Si–Vinyl) 0.88 (calculated from the dipole moment of vinyltrimethylsilane [21]), m(Me–C_{Ar}) 1.08 and m(C_{sp3}–C_{Ar}) 0.75 (calculated from the experimental dipole moment of toluene [21]), m(*t*-Bu–C_{Ar}) 1.18 (calculated from the experimental dipole moment of *tert*-butylbenzene [21]), m(C_{sp2Ar}–N) 1.51 (calculated from the experimental dipole moment of pyridine [21], m (C_{sp2Ar}–O) 0.34 D calculated from the experimental dipole moment of anisole [21]), m(C_{sp3}–Cl) 1.58 (calculated from the experimental dipole moment of methylene chloride [5]), and m(C_{sp3}–N) 0.53 [22]. The X-ray diffraction bond angles of compounds **I–VIII** were also used [15–17].

The coefficients of the calculation equations, orientational polarization, and experimental dipole moments are listed in Table 2. Benzene was purified by the standard procedure described in [23].

ACKNOWLEDGMENTS

The quantum-chemical calculations were carried out by the DFT B3LYP/6-31G method using the GAUSSIAN 03 program [24]. All the calculations were performed in the Supercomputer Center for Collective Use, Kazan Research Center, Russian Academy of Sciences (http://wt.knc.ru).

The authors express their gratitude to Robert R. Holmes (University of Massachusetts, Amherst, USA) in whose laboratory N.V. Timosheva prepared the compounds investigated in this work.

REFERENCES

1. Voronkov, M.G. and Zelchyan, G.I., *Khim. Geterotsikl. Soedin.*, 1965, no. 1, p. 51.
2. Voronkov, M.G. and D'yakov, V.M., *Silatrany* (Silatranes), Novosibirsk: Nauka, 1978.
3. Voronkov, M.G., Mazheika, I.B., and Zelchyan, G.I., *Khim. Geterotsikl. Soedin.*, 1965, no. 1, p. 58.
4. Voronkov, M.G., *Pure Appl. Chem.*, 1966, vol. 13, no. 1, p. 35.
5. Ishmaeva, E.A., Samarina, O.A., D'yakov, V.M., Voronkov, M.G., and Pudovik, A.N., *Dokl. Akad. Nauk SSSR*, 1975, vol. 222, no. 4, p. 878.
6. Hencset, P. and Marsmann, H.S., *Acta Chim. Acad. Sci. Hung.*, 1980, vol. 105, no. 1, p. 79.
7. Hensei, P., Csonka, G., Zsombok, Gy., and Gergo, E., *Period. Polytech. Chem. Eng.*, 1983, vol. 27, no. 4, p. 263.
8. Tandura, S.N., Pestunovich, V.A., Zelchyan, G.I., Baryshok, V.P., Lukina, Yu.A., Sorokin, M.S., and Voronkov, M.G., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, no. 2, p. 295.
9. Pestunovich, V.A., Shternberg, B.Z., Tandura, S.N., Zelchyan, G.I., Baryshok, V.P., Urtane, I.P., Solomennikova, I.I., Lukevics, E.Ya., and Voronkov, M.G., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, no. 2, p. 467.
10. Pestunovich, V.A., Shternberg, B.Z., Lippmaa, E.T., Myagi, M.Ya., Alla, M.A., Tandura, S.N., Baryshok, V.P., Petukhov, L.P., and Voronkov, M.G., *Dokl. Akad. Nauk SSSR,* 1981, vol. 258, no. 6, p. 1410.
11. Milov, A.A., Minyaev, R.M., and Minkin, V.I., *Zh. Org. Khim.*, 2003, vol. 39, no. 3, p. 372.
12. Minkin, V.I., Minyaev, R.M., Milov, A.A., and Gribanova, T.N., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 2001, no. 11, p. 1938.
13. Makoto, Ya., Yohsuke, Ya., Kinya, A., Daisuke, H., Fuyiko, I., Mozomi, T., and Shiger, N., *J. Am. Chem. Soc.*, 2005, vol. 127, no. 12, p. 4354.
14. Chernyshev, E.A., Knyazev, S.P., Kirin, V.N., Vasil'ev, I.M., and Alekseev, N.V., *Zh. Obshch. Khim.*, 2004, vol. 74, no. 1, p. 65.
15. Chandrasekaran, A., Day, R.O., and Holmes, R.R., *J. Am. Chem. Soc.,* 2000, vol. 122, no. 6, p. 1066.
16. Timosheva, N.V., Chandrasekaran, A., Day, R.O., and Holmes, R.R., *Organometallics*, 2000, vol. 19, no. 26, p. 5614.
17. Timosheva, N.V., Chandrasekaran, A., Day, R.O., and Holmes, R.R., *Organometallics*, 2001, vol. 20, no. 11, p. 2331.
18. Vereshchagin, A.N. and Grozina, L.A., *Teor. Eksp. Khim.*, 1968, vol. 4, no. 3, p. 361.
19. Yuldasheva, L.K., Arshinova, R.P., Samitov, Yu.Yu., Romadan, Yu.P., and Voronkov, M.G., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1974, no. 2, p. 323.
20. Gribov, L.A. and Popov, E.M., *Dokl. Akad. Nauk SSSR*, 1962, vol. 145, no. 4, p. 761.
21. Osipov, O.A., Minkin, V.I., and Garnovskii, A.D., *Spravochnik po dipol'nym momentam* (Handbook on Dipole Moments), Moscow: Vysshaya Shkola, 1971.
22. Ishmaeva, E.A., Podovik, M.A., Terent'eva, S.A., and Pudovik, A.N., *Dokl. Akad. Nauk SSSR*, 1971, vol. 196, no. 3, p. 630.
23. Weissberger, A. and Proskauer, E.S., *Organic Solvents: Physical Properties and Methods of Purification*, Riddick, J.A. and Toops, E.E., Jr., Eds., New York: Interscience, 1955.
24. Frish, M.L., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Montgomery, J.A., Vreven, T.Jr., Kudin, K.N., Burant, J.C., Millam, J.M., Iyengar, S.S., Tomasi, J., Barone, V., Menucci, B., Cossi, M., Scalmani, G., Rega, N., Petersson, G.A., Nakatsuji, H., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegava, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Klene, M., Li, X., Knox, J.E., Hratchian, H.P., Cross, J.B., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R.E., Yazyev, O., Austin, A.J., Cammi, R., Pomelli, C., Ochterski, J.W., Ayala, P.Y., Morokuma, K., Voth, G.A., Salvador, P., Dannenberg, J.J., Zakrzewski, V.G., Dapprich, S., Daniels, A.D., Strain, M.C., Farkas, O., Malick, D.K., Rabuch, A.D., Raghavachari, K., Foresman, J.B., Ortiz, J.V., Cui, Q., Baboul, A.G., Clifford, S., Cioslowski, J., Stefanov, B.B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, J., Martin, R.L., Fox, D.J., Keith, T., Al-Laham, M.A., Peng, C.Y., Narayakkara, A., Challacombe, M., Gill, P.M.W., Johnson, B., Chen, W., Wong, M.W., Gonzalez, C., and Pople J.A., *Gaussian 03. Rev. B. 03*, Pittsburgh, PA: Gaussian, 2003.