UDC 541.67 + 546.287

ATRANES. II*. DIPOLE MOMENTS AND STRUCTURE OF SILATRANES

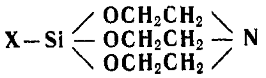
M. G. Voronkov, I. B. Mazheika, G. I. Zelchan

Khimiya geterotsiklicheskikh soedinenii, Vol. 1, No. 1, pp. 58-63, 1965

Possible steric configurations of 1-organyl- and 1-organoxysilatranes, $XSi(OCH_2CH_2)_3N$., are considered.

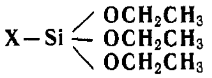
The dipole moments of six compounds of this type (X = CH_3, $(CH_3)_2CH$, $CH_2{=}CH$, C_6H_5, C_2H_5O, C_6H_5O) have been found experimentally to be extremely high, 5.3-7.1 D. They conclusively show that the silatranes contain a semipolar transannular coordinate bond Si←N between the negatively charged 5-covalent silicon atom in the middle of the planar SiO_3 group and the tetrahederal onium nitrogen atom.

The monomeric organyl (2, 2', 2"-aminotriethoxy)silanes (I, X = alkyl, aryl) and organoxy(2, 2', 2"-aminotriethoxy)-silanes (I, X = alkoxy or aryloxy group) differ markedly in their resistance to hydrolysis, and in respect to many other properties, from the corresponding organyl- (II, X = alkyl, aryl) and, in particular, organoxytriethoxysilanes (II, X = alkoxy or aryloxy group).



$$X-Si\begin{matrix} \diagup OCH_2CH_2 \diagdown \\ - OCH_2CH_2 - \\ \diagdown OCH_2CH_2 \diagup \end{matrix} N$$

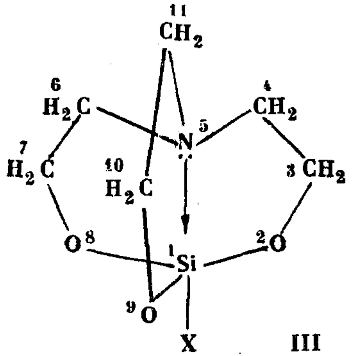
I



$$X-Si\begin{matrix} \diagup OCH_2CH_3 \\ - OCH_2CH_3 \\ \diagdown OCH_2CH_3 \end{matrix}$$

II

The readiness with which compounds of type I (and not polymers of analogous composition) are formed, their high melting points, low volatility, solubility in water, and the sharp decrease in the electron donor properties of their nitrogen atom strongly suggest that they contain an intramolecular transannular coordination link between the electron donor (nitrogen) and electron acceptor (silicon) atoms, i.e., that its structure is that of a silatrane of type III**.



III

It is of particular interest that molecule III has a coordinate bond between the nitrogen and the 5-covalent silicon atom, since so far formation of stable coordination complexes between alkoxysilanes and ammonia or amines has not been observed. However, in work carried out by one of the authors [2, 3], it is shown that labile complexes may exist in solution between alkoxysilanes and certain amines. Monomeric complexes between halogenosilanes and ammonia or amines, of the type $R_{4-n}SiX_n \cdot B$ (X = F, Cl; R = H, CH_3; n = 1 - 4; B = amine, NH_3) and containing a 5-covalent silicon atom, are certainly unknown***.

On the other hand, $R_{4-n}SiX_n \cdot 2B$-type complex compounds, with an octahedral 6-covalent silicon atom, have been quite extensively investigated [8-11]. Their formation is due to transfer of an unshared electron pair of the nitrogen atom to vacant 3d orbitals of the central silicon atom.

In accordance with the classical tetrahedral theory of the structure of organic compounds, Si-substituted 2, 2', 2"-aminotriethoxysilanes can be assigned two 3-dimensional structures with a tetrahedral $XSiO_3$ group: an unstrained biconvex structure (IV), and an almost unstrained concavo-convex structure (V). It is obvious that only in the case of structure V can there be a donor-acceptor transannular link between the nitrogen and silicon atoms. Consideration of the Stewart-Brigleb (atom) models leads to the conclusion that it is possible to have only one concavo-convex form Va (see Fig. 3),

---

*Part I, see [1].

** Internal complex heterocyclic compounds of the type $X_{n-3}M(OCH_2CH_2)_3N$, where M is an element of valence 3 or higher with incomplete p or d electron shells, X is a substituent, and n is the valence of the atom M, have been named [1] atranes: silatrane (M = Si), boratrane (M = B), ferratrane (M = Fe), etc.

*** Compounds of this composition described in the literature [4-7] are either ammonia salts or have a polymeric structure.

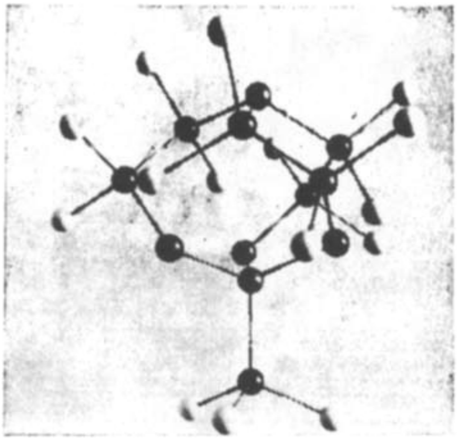


Fig. 1. Biconvex unstrained space model of the 1-methylsilatrane (IV) molecule

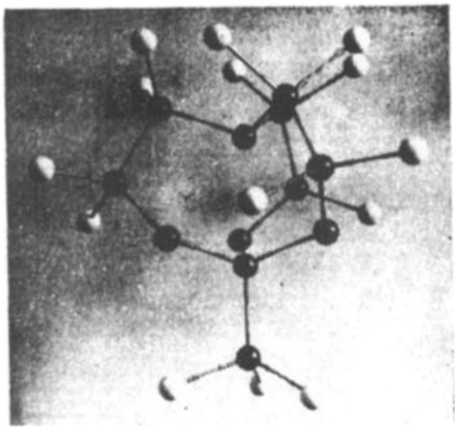


Fig. 2. Concavo-convex, almost unstrained space model of the 1-methylsilatrane (V molecule.

in which the nitrogen and silicon atoms are separated by a distance, such that a coordinate link can be formed between them*. Still, the conclusion that silatranes have structure V, shown in the photo, appears premature. The point is that with the transannular donor-acceptor link Si←N in the silatrane molecule, the covalence of the silicon atom rises to 5; then the hybridization of its valence orbitals must be sp^3d and not the usual tetrahedral sp^3, and this corresponds to 5 valence bonds directed toward the vertices of a trigonal bipyramid. Consequently, the molecular configuration of the silatranes must be represented by structure VI, containing a planar SiO_3 group, and a tetrahedral 4-covalent nitrogen atom.

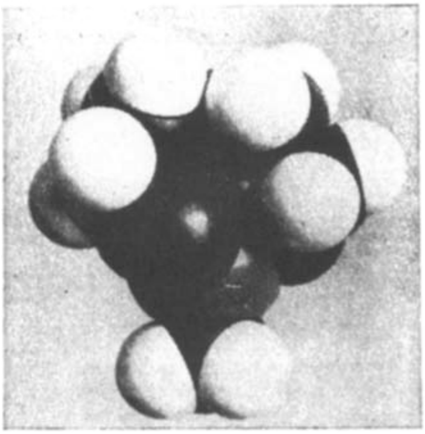


Fig. 3. Concavo-convex three dimensional Stewart-Brigleg model of the 1-methylsilatrane molecule (Va).

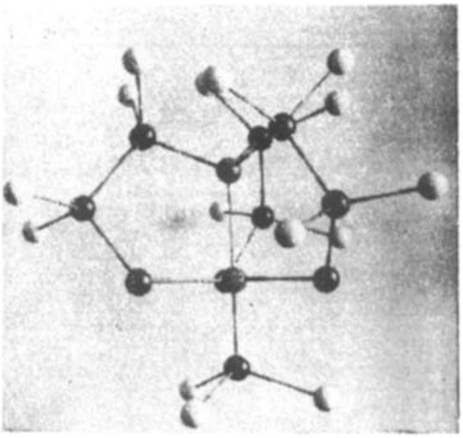


Fig. 4. Three-dimensional structure of the 1-methylsilatrane molecule (VI).

The decisive proof that the silatranes have a configuration like (VI) consists in establishing the presence of a dipolar transannular link between the silicon and nitrogen atoms. In addition to indirect arguments previously put forward [1, 13], the present paper gives a more convincing confirmation of the existence of a transannular donor-acceptor bond Si←N, based on measurements of the dipole moments.

Measurements have been made of the electric dipole moments of six 1-organyl- and 1-organoxysilatranes $\mathrm{XSi(OCH_2CH_2)_3N}$ (X = CH_3, $(CH_3)_2CH$, $CH_2{=}CH$, C_6H_5, C_2H_5O, C_6H_5O) (see table 1).

The moment of the group $-Si(OCH_2CH_2)_3N$ without a transannular donor-acceptor link $\overset{-}{\mathrm{Si}}\leftarrow\overset{+}{\mathrm{N}}$ (structure IV), as calculated from the bond moments, is 0.93 D, the vector moment being directed from silicon to nitrogen**.

The dipole moments of organyl- and organoxy(2,2',2"-aminotriethoxy)silanes, calculated on the basis of this value and Si–X bond moments, and assuming structure IV, are rather lower than those found experimentally (e.g., by 5 D).

The dipole moments of the organyl- and organoxytriethoxysilanes (II), which have similar structures, are also considerably lower than those of the corresponding silatranes (by 3.5-4.5 D).

TABLE 1

Dipole moments of 1-organyl and 1-organoxysilatranes, $\mathrm{X}\underleftarrow{\mathrm{Si(OCH_2CH_2)_3N}}$

X	μ, D		μ $XSi(OC_2H_5)_3$ [14]	μ SiX	μ $-\underleftarrow{\mathrm{Si(OCH_2CH_2)_3N}}$
	Found (±0.15D)	Calculated for structure IV			
CH_3	5.30	0.66	1.70	0,27	5,03
$(CH_3)_2CH$	5,55	0.66	—	0,27	5,28
$CH_2{=}CH$	5.88	0.5	—	0.4	5,5
C_6H_5	5.98	0,09	1.67	0.84	5.14
C_2H_5O	6.29	0.49	1,82	1.42	4,87
C_6H_5O	7.13	—	—	—	—
				Average value	5.2±0,2 D

The much greater experimental values of the dipole moments of organyl- and organoxysilatranes (5.3-7.1 D), which indicates their high polarity, is not only unequivocal evidence against their having the biconvex structure IV, but also affords conclusive evidence that these compounds contain the polar transannular link $\overset{-}{\mathrm{Si}}\leftarrow\overset{+}{\mathrm{N}}$ with an onium nitrogen atom and a negatively charged 5-covalent silicon atom. The average experimental value of the dipole moment of the group $-\underleftarrow{\mathrm{Si(OCH_2CH_2)_3N}}$ is 5.2±0.2 D, the vector being directed from nitrogen to silicon.

TABLE 2

Dipole measurement data for $\mathrm{X}\underleftarrow{\mathrm{Si(OCH_2CH_2)_3N}}$ in benzene at 25°

X	f, mole fract.	ε	d	P_{total}, cm^3	MR_D, cm^3	P_{or}, cm^3	μ, D
	0,000000	2,2730	0,8734				
CH_3	0,001012 0.000714 0.000534	2.3145 2,3016 2,2943	0,8741 0,8739 —	633.72	43.25	583,98	5.30
$(CH_3)_2CH$	0.001006 0.000653 0,000331	2,3171 2,3016 2.2886	0,8743 0.8741 —	704.37	53,84	650,53	5,55
$CH_2{=}CH$	0.000786 0,000534 0,000485 0.000329	2,3109 2.2994 2.2948 2.2901	0,8740 0,8739 0,8738 —	775.82	49.18	719,27	5.88
C_6H_5	0,000800 0.000301 0.000175	2.3124 2.2896 2,2823	0,8743 0,8738 —	820,07	64.86	745,52	5,98
C_2H_5O	0,000779 0,000568 0,000396	2,3160 2,3072 2.2953	0,8742 0,8740 —	884,24	49,41	824,94	6,29
C_6H_5O	0.000598 0,000512 0.000322	2.3174 2,3106 2,2967	0.8770 0.8741 0.8738	1131.60	64,78	1057.10	7.13

The approximate value of the bond moment for $\overset{-}{\mathrm{Si}}\leftarrow\overset{+}{\mathrm{N}}$ can be calculated as 8.6 D (shift of an electron having charge 4.80×10^{-10} esu, with 1.8 A N–Si (sp^3d) bond interatomic distance). Starting from this, the moment for the group $-\underleftarrow{\mathrm{Si(OCH_2CH_2)_3N}}$ must amount to 8.6-1.1 = 7.5 D (the calculated dipole moment for this group, assuming it to have structure Vi but not the transannular bond Si←N, is 1.06 D). The somewhat lower experimental value of the dipole moment for this group (5.2 D) is due to the effect of reverse polarization, induced by the intrinsic dipole moment, to the induction of a moment in the substituent X* linked to the silicon atom, and, of course, to the fact that the unshared pair

---

*On the other hand, consideration of analogous molecular models of the boratranes $\underleftarrow{\mathrm{B(OCH_2CH_2)_3N}}$ with a planar BO_3 group shows the possible existence of both concavo-convex and biconvex structures [12].

** In the calculations the valence angles C–N–C, Si–O–C, and O–Si–O are assumed tetrahedral, and the bond moments for C–H, C–N, Si–O and C–O are taken as 0.37, 0.45, 1.54, and 0.74 D, respectively.

of electrons of the nitrogen atom is not completely shifted onto the silicon atom. This phenomenon is a general one for semipolar bonds, the experimental values of μ being always less than the calculated ones based on electron shift between coordinated atoms [15].

All molecules with semipolar bonds of the same type as those in the silatranes (amine complexes, complexes of ethers and sulfides with halides of boron, aluminum, titanium, tin, etc.) likewise have high dipole moments of the same order [16].

EXPERIMENTAL

The stock 1-methyl-, isopropyl-, vinyl-, and phenylsilatranes are described in the preceding paper [1]. Ethoxysilatrane is prepared in 90% yield by transesterification of tetraethoxysilane with triethanolamine in the presence of KOH. Recrystallized from heptane it melts at 102-103°. 1-Phenoxysilatrane is obtained by reacting together equimolecular amounts of tetraethoxysilane, triethanolamine, and phenol, in the presence of KOH as a catalyst (yield 98%). Recrystallized from heptane-chloroform it melted at 228.0-229.2°.

Silatrane dipole moments were determined in benzene at 25° by the heterodyne beat method. The method of measurement has previously been described [17]. Total polarization was calculated by Hederstrand's method. Molecular refractions were calculated from refraction values for benzene and chloroform solutions. The atomic polarization was assumed equal to 15% MR_D. The experimental data is given in Table 2.

---

*Here it must be emphasized that the experimental value for the group $-\mathrm{Si(OCH_2CH_2)_3N}$ (5.2 D) is obtained starting from the Si–X (sp^3d) bond moments of Table 1. Certainly, the Si–X^3(sp^3d) moments must differ appreciably from the latter.

REFERENCES

1. M. G. Voronkov, G. I. Zelchan, KhGS, 1, 51, 1965.
2. M. G. Voronkov, A. Ya. Deich, Izv. AN Latv. SSR, ser. khim., 145, 1964.
3. M. G. Woronkow [Voronkov], A. J. Deitsch, J. pr. Chem., [4]22, 214, 1963.
4. J. E. Fergusson, D. K. Grant, R. H. Hickford, C. J. Wilkins, J. Chem. Soc., 99, 1955.
5. A. B. Burg, J. Am. Chem. Soc., 76, 2674, 1954.
6. H. J. Emeleus, N. Miller, J. Chem. Soc., 819, 1939.
7. B. J. Aylett, H. J. Emeleus, A. G. Meddock, J. Inorg. Nucl. Chem., 1, 185, 1955.
8. U. Wannagat, R. Schwarz, Z. anorg. Chem., 277, 73, 1954.
9. T. S. Piper, E. G. Rochow, J. Am. Chem. Soc., 76, 4318, 1954.
10. E. Schnell, Mon., 92, 1055, 1961; 93, 65, 1962.
11. V. Gutmann, P. Heilmayer, K. Utvary, Mon., 92, 322, 1961.
12. Fr. Hein, R. Burckhardt, Z. anorg. Chem., 268, 159, 1952.
13. C. L. Frye, G. E. Vogel, J. A. Hall, J. Am. Chem. Soc., 83, 996, 1961.
14. E. Larsson, Trans. Chalm. Univ., no. 115, 25, 15, 1951.
15. C. K. Ingold, Structure and Mechanism in Organic Chemistry [Russian Translation], IL, Moscow, 81-82, 1959.
16. O. A. Osipov, V. I. Minkin, Yu. B. Kletenik, Handbook of Dipole Moments (in Russian), Rostov State University, Rostov-on-Don, 34-40, 1961.
17. I. B. Mazheika, L. Kh. Avota, G. P. Sokolov, S. A. Giller, ZhOKh, 34, 3380, 1964.

10 April 1964

Institute of Organic Synthesis AS Latvian SSR, Riga