

# Structural Features of Silatranes and Germatranes

E. A. Chernyshev, S. P. Knyazev, V. N. Kirin, I. M. Vasilev, and N. V. Alekseev

Lomonosov Moscow State Academy of Fine Chemical Technology, Moscow, Russia

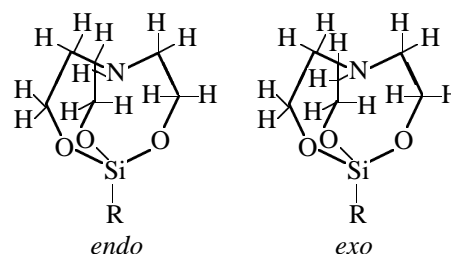
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**Abstract**—In stabilization of the *endo* configuration of silatranes and germatranes, a major role is played not only by the Si (or Ge) and N atoms, but also by oxygen and other atoms of the atrane core, which is manifested in molecular orbital parameters. Calculation of the system of interacting methyltrimethoxysilane and trimethylamine shows that the energy of the system grows as the distance between the Si and N atoms is decreased from 5 to 2 Å. The Si–N interaction in methylsilatrane, according to the calculations and precision X-ray diffraction studies, is the interaction of filled electronic shells and is electrostatic in nature. Analysis of the thermodynamic functions of formation of 1-methyl- and 1-hydroxysilatranes and -germatranes reveals an increase in the enthalpy and the decisive contribution of the entropy factors to stabilization of the reaction products. A  $^1\text{H}$  NMR study of ethylgermatrane in aqueous solution revealed its equilibrium with the hydrolyzed form. The transition state in the first step of hydrolysis of methyl- and hydroxysilatranes and -germatranes was studied by methods of quantum chemistry (AM1, PM3; basis sets STO-3G, 6-31G, 6-31G\*, 6-31G\*\*; B3LYP method).

Among organosilicon and organogermanium compounds, atrane derivatives are of particular interest. Silatranes and germatranes are ethers of triethanolamine and the corresponding organosilanetriols and organogermanetriols [1–4]. Virtually all the silatranes and germatranes studied show high biological activity; plant growth regulators, cosmetics, and drugs (e.g., effective immunomodulators) have been developed on their basis.

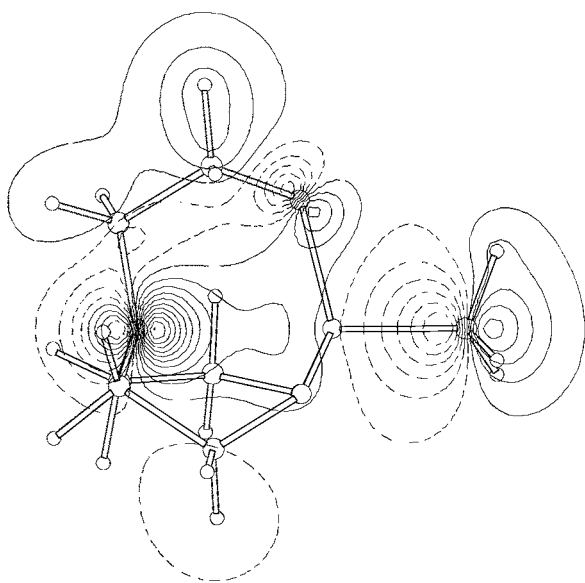
A common feature of atrane compounds is an increase in the coordination number of Si or Ge to 5. Silatranes and germatranes can exist in two main conformations: *exo* and *endo* (Scheme 1). The Si–N interatomic distance in the *endo* form of silatranes is 2–2.7 Å, being considerably shorter than the sum of the van der Waals radii of these atoms. A characteristic feature of silatranes and germatranes is stabilization of their molecules in the *endo* configuration. It is this fact that stimulated numerous studies on the nature of bonding of nitrogen with the element (Si, Ge, etc.) in atrane structures and generally in compounds with extended coordination sphere of elements of Group IV and other groups. It is commonly believed that the “transannular” interaction makes a decisive contribution to the thermodynamic stability and high yields of atrane structures under conditions of equilibrium synthesis and that this interaction is largely responsible for stabilization and decreased reactivity of silatranes and germatranes as compared to common alkoxy derivatives of Si and Ge, e.g., under conditions of hydrolysis.

Scheme 1.



Thus, the existence of silatranes and germatranes in the *endo* configuration and their relative stability are the most important theoretical problems in the chemistry of atrane compounds. Various causes of these effects were discussed in the literature: transfer of the nitrogen lone electron pair to the silicon *d* orbitals [5], conformational effects [6], dipole–dipole (electrostatic) interactions [7], etc. In 1970–1990, these concepts gave way to the concept of hyperbonding due to formation of a three-center bond [8], and in 1990s the concept of “dative” interaction of nitrogen and silicon was put forward [9].

Our studies of the molecular and electronic structures of silatrane and germatrane molecules revealed new features of their structure and possible causes of enhanced stability. We found that stabilization of the *endo* form of silatranes and germatranes may be due to the whole set of factors related to conformational, dipole–dipole (electrostatic), and covalent interactions. For example, we found that the bonding molecular



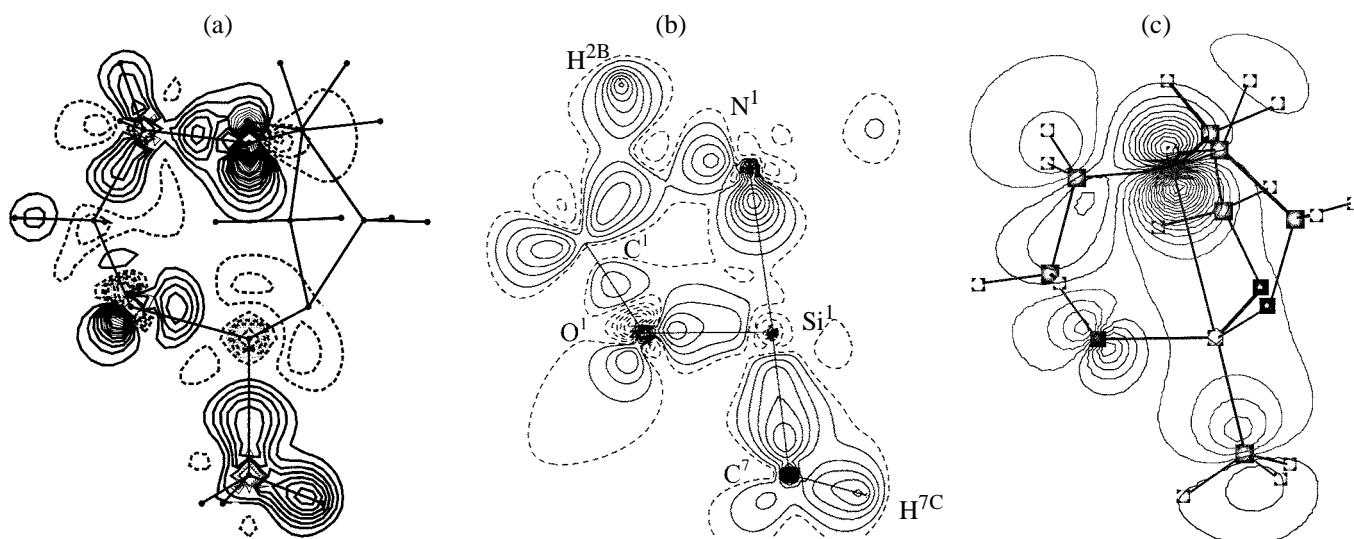
**Fig. 1.**  $MO_{32}$  orbital in methylsilatrane, binding the N and Si atoms.  $E -10.79$  eV [ $-0.32p_xN + 0.19p_xSi \pm 3(0.32p_zO) - 0.22p_xC_{Me}$ , AM1 calculation].

orbitals involving the atomic orbitals of nitrogen and silicon or germanium necessarily involve also the atomic orbitals of oxygen. One of such orbitals in methylsilatrane is shown in Fig. 1. The structure of this orbital suggests bonding interaction between the nitrogen, silicon, and methyl carbon atoms, with the oxygen atomic orbitals making a significant contribution to this orbital. The highest occupied molecular orbital (HOMO) of silatranes and germatranes containing no donor functional groups is mainly formed

by the atomic orbitals of nitrogen. Figure 2c shows the HOMO of methylsilatrane.

The stabilization of the *endo* configuration of silatranes and germatranes is also revealed in the features of their frontier molecular orbitals: the HOMOs in the *endo* configuration lie lower, and the lowest unoccupied molecular orbitals (LUMOs), higher than the respective orbitals in the *exo* configuration. Correspondingly, the energy gap between HOMO and LUMO increases in going from the *exo* to *endo* structures, which is also indicative of the higher configurational stability of the *endo* form compared to the *exo* form (Table 1).

A precision X-ray diffraction study of methylsilatrane molecule [10], performed by us in cooperation with the Center for X-ray Structural Studies, Nesmeyanov Institute of Organoelemental Compounds, Russian Academy of Sciences, gave important results. It was found that the characteristic feature of this molecule is the electron density localized on the nitrogen atom and oriented toward the silicon atom. The electron density maximum is at a distance of  $0.45$  Å from the nitrogen atom (Fig. 2b). Analysis of the topology of the electron density distribution in methylsilatrane suggests electrostatic interaction of filled electronic shells of the nitrogen and silicon atoms, rather than covalent bonding. Similar results were obtained in calculations of the electron density distribution (Fig. 2a) and HOMO (Fig. 2c) in the methylsilatrane molecule. Thus, the results obtained indicate that a significant contribution to stabilization of the *endo* configuration is made by electrostatic interactions arising from the electron density on the N atom and excess positive



**Fig. 2.** 1-Methylsilatrane: (a) electron density map (6-31G\*/B3LYP calculation), (b) electron density map (X-ray diffraction data) [10], and (c) HOMO of methylsilatrane ( $E -6.03$  eV, 6-31G\*/B3LYP calculation).

**Table 1.** Parameters of the methylsilatrane molecule in the *endo* and *exo* configurations, calculated by various methods

Parameter	AM1		STO-3G		6-31*		B3LYP/6-31G*	
	<i>endo</i>	<i>exo</i>	<i>endo</i>	<i>exo</i>	<i>endo</i>	<i>exo</i>	<i>endo</i>	<i>exo</i>
$\Delta E_{\text{tot}}$ , au	-86.6634	-86.6640	-831.6082	-831.5993	-841.8930	-841.8869	-845.8120	-845.8072
$\Delta E$ , kcal mol <sup>-1</sup>		-0.37		5.58		3.83		3.01
$\Delta E_{\text{HOMO}}$ , eV	-9.56	-8.71	-7.99	-6.83	-9.47	-8.99	-6.03	-5.40
$\Delta E_{\text{LUMO}}$ , eV	1.69	1.22	12.26	12.21	6.10	5.95	2.18	2.10
$\Delta E_{\text{MO}}$ , eV	11.25	9.93	20.25	19.04	15.57	14.94	8.21	7.50
$\Delta \Delta E_{\text{MO}}$ , eV		1.32		1.21		0.63		0.71
$l(\text{E-N})$ , Å	2.61	3.25	2.39	3.25 <sup>a</sup>	2.74	3.25 <sup>a</sup>	2.68	3.25 <sup>a</sup>
Charge on Si, e	1.60	1.57	1.27	1.25	1.57	1.57	1.11	1.12
Charge on O, e	-0.57	-0.58	-0.45	-0.45	-0.76	-0.77	-0.56	-0.57
Charge on N, e	-0.35	-0.36	-0.32	-0.31	-0.69	-0.64	-0.44	-0.39
$\mu$ , D	4.076	0.55	4.81	0.63	3.86	1.80	3.85	1.63

<sup>a</sup> The structure has no local minimum on the potential energy surface.

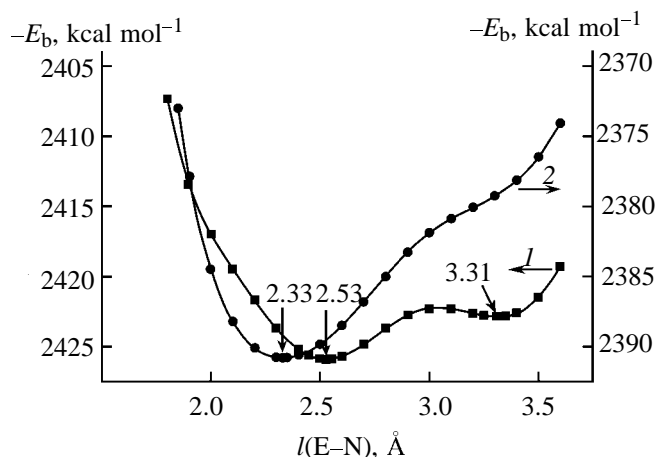
charge on the Si atom, estimated by various methods at 1–1.6 units (Table 1).

The higher stability of germatrane structures compared to silatrane structures is an interesting trend. Figure 3 shows how the energies of the silatranol and germatranol molecules depend on the element (Si, Ge)–nitrogen interatomic distance (AM1 calculation). A striking feature is the higher stability of the *endo* form of germatranes compared to silatranes, which is manifested in the shorter interatomic distance Ge–N (2.33 Å) compared to Si–N (2.53 Å) (Table 2) and in the absence of the local minimum for the *exo* configuration of germatranol. The inflection on the coordinate of the *endo*–*exo* conformational transition in the ger-

matranol molecule, corresponding to the *exo* structure, is located by 11 kcal mol<sup>-1</sup> higher on the energy scale as compared to the *endo* structure (Fig. 3).

The *ab initio* calculations of the silatrane and germatrane molecules (STO-3G, 6-31G\*, 6-31G\*\*, B3LYP/6-31G\*, B3LYP/6-31G\*\*, etc.) give the results consistent with those of semiempirical calculations (AM1, PM3): In all the calculation versions, the *endo* configuration is more advantageous than the *exo* configuration, and the equilibrium interatomic distance Si–N (or Ge–N) is within 2.3–2.7 Å. The principal result of the *ab initio* calculations of silatranes and germatranes is the absence of the potential minimum corresponding to the *exo* configuration on the coordinate of the conformational transition between the *endo* and *exo* forms. The energy of the system is only weakly dependent on the Si–N and Ge–N interatomic distance in the range 2–3 Å, which accounts for major differences between the results of determining this parameter for, e.g., methylsilatrane by X-ray diffraction (crystal, Si–N 2.1604 [10], 2.175 Å [11]), electron diffraction (gas phase, Si–N 2.453 Å [12]), and quantum-chemical calculations (AM1, 2.63 Å; PM3, 2.54 Å; STO-3G, 2.39 Å; 6-31G\*, 2.74 Å; B3LYP/6-31G\*, 2.67 Å; and MP2/6-31G\*, 2.38 Å). In the range of N–Si distances in methylsilatrane 2.3–3.0 Å, the potential energy varies within a ~1.5 kcal mol<sup>-1</sup> range. Thus, the Si–N coordinate is “soft” and readily deformable, e.g., in a crystal field.

To reveal the character of the covalent component in interaction of the N and Si atoms in silatranes, we studied a model system of trimethylamine and methyltrimethoxysilane molecules, simulating the methylsilatrane structure (Fig. 4). The energy of the system

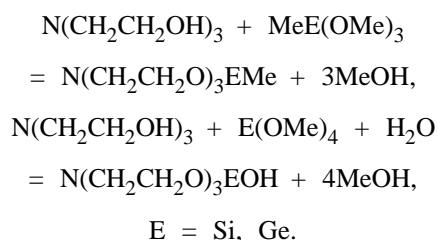


**Fig. 3.** Binding energy  $E_b$  as a function of the distance between the Ge (or Si) and N atoms in (1) silatranol and (2) germatranol (AM1 calculations).

considerably increased at the N–Si distances corresponding to the *endo* configuration in silatranes (2.4 Å) as compared to the isolated molecules. The energy growth (kcal mol<sup>-1</sup>) determined by various methods was as follows: PM3, 16.7; STO-3G, 6.63; 6-31G, 7.56; and 6-31G\*, 17.62.

The enhanced thermodynamic stability of silatranes and germatranes was repeatedly postulated in the literature on the basis of their virtually quantitative formation in equilibrium synthesis reactions, relative stability to hydrolysis, and some other properties. The experimentally determined enthalpies of formation of silatranes suggest, in the opinion of Voronkov *et al.* [13], the stabilizing effect of the N–Si interaction whose energy is estimated at 7–20 kcal mol<sup>-1</sup>. This parameter was calculated as the difference between the enthalpies of formation determined experimentally and calculated by the additive scheme.

We calculated the thermodynamic parameters of formation of methylsilatrane, methylgermatrane, silatranol, and germatranol:



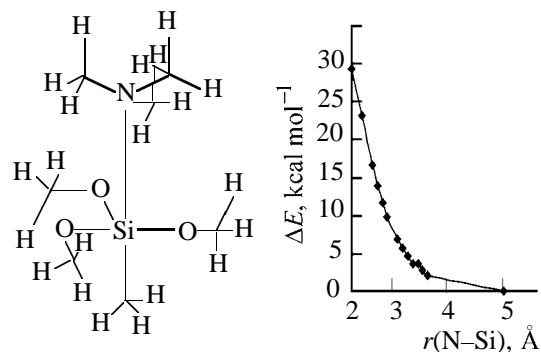
The calculations were performed *ab initio* for isolated molecules in the 6-31G\* basis taking into account the electron correlation by the DFT method in the B3LYP approximation. The calculation results for the reactants and products are listed in Table 3.

The thermodynamic characteristics of the reactions were determined as the differences between those of the products and initial reactants (Table 4):

$$\begin{aligned} \Delta H_r^0 &= \Sigma H_{\text{prod}}^0 - \Sigma H_{\text{in}}^0, \\ \Delta S_r^0 &= \Sigma S_{\text{prod}}^0 - \Sigma S_{\text{in}}^0, \\ \Delta G_r^0 &= \Sigma G_{\text{prod}}^0 - \Sigma G_{\text{in}}^0 \quad (\Delta G^0 = \Delta H^0 - T\Delta S^0). \end{aligned}$$

The calculation results (Table 4) show that the reaction enthalpy is positive ( $\Delta H^0 > 0$ ), but its free energy is negative ( $\Delta G^0 < 0$ ). Thus, formation of silatranes and germatranes (shift of the equilibrium) is exclusively due to the increase in the entropy ( $\Delta S^0 > 0$ ).

We also calculated the enthalpy of formation of methylsilatrane from the experimental enthalpies of formation of the reactants and products (Table 3).



**Fig. 4.** Coordinate of mutual approach of the trimethylamine and methyltrimethoxysilane molecules (the sum of the energies of isolated molecules is taken as zero).

The calculated and experimental parameters coincide within the experimental error (Table 4).

Our results disagree with the commonly accepted views that the shift of the equilibrium of silatrane and germatrane formation toward the reaction products is due to stabilization of the atrane structures by hyperbonding of the N and Si (or Ge) atoms. According to the calculation results, in all the systems under consideration the internal energy of the system grows upon formation of silatranes and germatranes (the system gets destabilized). The negative free energies of formation of methylsilatrane, methylgermatrane, silatranol, and germatranol are determined by the entropy factors. As a result, the reaction equilibrium is fully shifted toward the reaction products ( $\log K >$

**Table 2.** Calculated parameters of the silatranol and germatranol molecules in the *endo* and *exo* configurations (AM1 calculations)

Parameter	Silatranol		Germatranol	
	<i>endo</i>	<i>exo</i>	<i>endo</i>	<i>exo</i>
$E_b$ , kcal mol <sup>-1</sup>	-2425.90	-2422.86	-2390.79	-2379.8
$\Delta E$ , kcal mol <sup>-1</sup>	-3.04		-11.0	
$E_{\text{HOMO}}$ , eV	-10.02	-8.97	-10.50	-9.04
$E_{\text{LUMO}}$ , eV	1.40	0.90	0.15	-0.41
$\Delta E_{\text{MO}}$ , eV	11.42	9.87	10.65	9.45
$\Delta \Delta E_{\text{MO}}$ , eV	1.55		1.20	
$l(\text{E-N})$ , Å	2.53	3.31	2.33	3.24
Charge on Si(Ge) atom, e	1.65	1.64	1.61	1.53
Charge on O atom, e	-0.58	-0.59	-0.57	-0.53
Charge on N atom, e	-0.34	-0.33	-0.30	-0.35

**Table 3.** Thermodynamic parameters of reactants and products in the reactions of synthesis of methylsilatrane, methylgermatrane, silatranol, and germatranol

Compound	$-\Delta E_{\text{tot}}$ , au	$-H^0$ , au	$-\Delta H(\text{exp})$ , kcal mol $^{-1}$	$S^0$ , kcal mol $^{-1}$ K $^{-1}$	$-G^0$ , au
N(CH <sub>2</sub> CH <sub>2</sub> OH) <sub>3</sub>	518.0487	517.8116	133.44 [14]	96.29	517.8574
MeSi(OMe) <sub>3</sub>	674.9314	674.7510	225.62 [15]	113.95	674.8052
MeGe(OMe) <sub>3</sub>	2460.3734	2460.1944	–	111.72	2460.2476
Si(OMe) <sub>4</sub>	750.1811	749.9934	–	119.647	750.0503
Ge(OMe) <sub>4</sub>	2535.5943	2535.4088	–	119.207	2535.4655
MeOH	115.7144	115.6587	48.07 [16]	56.73	115.6856
H <sub>2</sub> O	76.4089	76.3840	–	45.14	76.4055
N(CH <sub>2</sub> CH <sub>2</sub> O) <sub>3</sub> SiMe	845.8119	845.5677	201.00 [13]	102.95	845.6166
N(CH <sub>2</sub> CH <sub>2</sub> O) <sub>3</sub> GeMe	2631.2671	2631.0239	–	106.43	2631.0745
N(CH <sub>2</sub> CH <sub>2</sub> O) <sub>3</sub> SiOH	881.7533	881.5325	–	103.94	881.5818
N(CH <sub>2</sub> CH <sub>2</sub> O) <sub>3</sub> GeOH	2667.1868	2666.9676	–	107.78	2667.0188

**Table 4.** Thermodynamic characteristics of formation of methylsilatrane, methylgermatrane, silatranol, and germatranol (6-31G\*/B3LYP)

Compound	$\Delta H^0$ , kcal mol $^{-1}$ (experiment)	$\Delta S^0$ , kcal mol $^{-1}$ K $^{-1}$	$\Delta G^0$ , kcal mol $^{-1}$
Methyl- silatrane	11.82 (13.79 ± 1.96)	62.90	–6.94
Silatranol	13.68	69.79	–7.13
Methyl- germatrane	3.82	68.61	–16.64
Germatranol	1.30	74.06	–20.80

<sup>a</sup> Value calculated from the experimental data.

9–15). Stabilization of atranes toward hydrolysis is apparently also due to this factor. Notably, the free energy of formation of germatranes is much more negative than that of silatranes.

The reactivity of silatranes and germatranes may also be determined by kinetic factors. The PM3 calculations suggest the possibility of formation of stable hydrated germatrane (especially germatranol) molecules (Table 5). At the same time, hydration of silatranols, according to our calculations, increases the energy of the system compared to isolated molecules. In all the calculated hydrates, the water oxygen atom coordinates with the element (Si, Ge) atom. The *ab initio* calculations in the 6-31G\*\* basis, however, suggest the absence of such coordination. Hydration occurs as hydrogen bonding between the water molecule and the oxygen atom of the atrane core. The hydrated germatrane species are more stable than the silatrane derivatives. This is consistent with the experimental data on isolation of germatranol crystal hydrates [17].

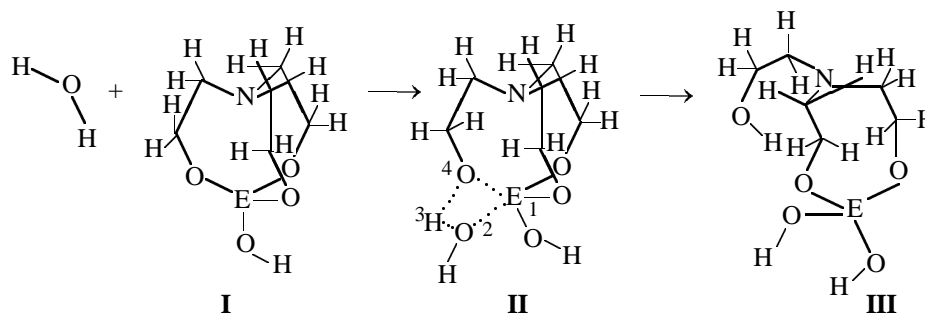
**Table 5.** Energy of “coordination” of atranes with a water molecule, kcal mol $^{-1}$ 

Compound	Method		
	PM3	STO-3G	6-31G**
Silatranol	0.91	–9.48	–6.43
Germatranol	–3.58	–9.56	–9.81
Ethyl- silatrane	9.76	–6.73	–6.41
Ethyl- germatrane	–0.41	–6.98	–8.50

Computer simulation of hydrolysis of silatranes and germatranes gave interesting results. We found that the potential barriers of these reactions are comparable and amount to 15–35 kcal mol $^{-1}$  depending on the approximation level. A search for transition state was performed for the first step of the model reaction of silatranol and germatranol hydrolysis. Calculations were performed in the HF/6-31G\*\* approximation using QST-2 and TS methods, with calculation of normal vibrational modes. The calculated reaction model involves the silatranol and water molecules brought to the distance of 2.6 Å between the Si and water oxygen atoms as the reactants and structure **III** as the product (addition of one water molecule with formation of a covalent bond Si–O<sup>H<sub>2</sub>O</sup>, with cleavage of one of the Si–O bonds in the silatrane and proton transfer from the water molecule to the leaving oxygen atom, Scheme 2).

The parameters of the transition states for silatranol and germatranol are listed in Table 6. The structures

Scheme 2.



found lie higher in the energy (enthalpy) relative to the isolated reactant molecules by 34.89 and 20.00 kcal mol<sup>-1</sup>, respectively; consideration of the hydration energy increases the barrier height to 41.37 and 29.81 kcal mol<sup>-1</sup>, respectively. The difference between the free energies of the transition state and reactants is somewhat larger: ~48 kcal mol<sup>-1</sup> for silatranol and 33 kcal mol<sup>-1</sup> for germatranol.

The validity of the revealed transition state structures is confirmed by the analysis of their vibration frequencies. In both cases (hydrolysis of silatranol and germatranol), there is a single imaginary frequency, which corresponds to a first-order saddle point on the potential energy surface (transition state). The normal mode analysis for the imaginary frequencies shows that they correspond to the coordinate of the hydrogen atom transfer from the water molecule to the “leaving” oxygen atom (Scheme 2, Table 6). The calculated potential barriers are apparently somewhat overestimated, as the solvent effect is not taken into account in the model.

On the whole, the results of computer simulation of hydrolysis of silatranes and germatranes suggest that these reactions are not kinetically forbidden. The lower potential barrier of the model reaction for germatranes suggests that their enhanced hydrolytic stability is mainly due to the thermodynamic factors, especially in the case of germatranol compared to silatranes. We believe that the hydroxy group at the Ge atom markedly stabilizes the molecule as regards formation and hydrolysis in aqueous solution. The stabilization may also be due to formation of hydrogen-bonded molecular associates.

Our results are consistent with the results of an NMR study of hydrolysis of germatranes and silatranes: Aqueous solutions of germatranol are hydrolytically stable; with ethylgermatrane, an equilibrium is attained between germatrane and its hydrolysis products (5 : 4 ratio in 20–30 min and 2 : 3 ratio in 48 days); silatranes are completely hydrolyzed in

aqueous solutions within several hours or days, in agreement with data of Voronkov *et al.*

Thus, our results revealed new factors responsible for stabilization of atrane structures and higher stability of germatranes compared to silatranes. It was shown that the models of “hypervalent” or “dative” interactions of the N and Si (or Ge) atoms in these molecules do not exhaustively account for their structural features. The stability of silatranes and germatranes in the *endo* configuration is mainly due to the total contribution of all the atoms of the atrane moiety and primarily of the oxygen atomic orbitals, stabilizing this configuration, rather than to the N–Si or N–Ge bonding interaction [in many bonding molecular orbitals, this interaction is antibonding, which is confirmed by data for the model system Me<sub>3</sub>N–MeSi(OMe)<sub>3</sub>]. An appreciable role in stabilization of the *endo* form of atrane structures is also played by electrostatic interactions of the Si or Ge atom bearing a significant positive charge with the electrons localized on the N atom. Thus, stability of silatranes and germatranes in formation and hydrolysis reactions is determined by

**Table 6.** Parameters of the transition state (Scheme 2) of the first step of hydrolysis of silatranol and germatranol (calculation, GAUSSIAN 98, 6-31G\*\*/QST2/Freq)

Parameter	Silatranol	Germatranol
$\Delta E$ , kcal mol <sup>-1</sup>	34.89	20.00
$\Delta H^0$ , kcal mol <sup>-1</sup>	34.53	19.49
$\Delta S^0$ , cal mol <sup>-1</sup> K <sup>-1</sup>	-44.94	-44.14
$T\Delta S^0$ , kcal mol <sup>-1</sup> ( $T$ 298.15 K)	-13.40	-13.16
$\Delta G^0$ , kcal mol <sup>-1</sup>	47.93	32.65
$l(E^1-O^2)$ , Å	1.902	1.995
$l(O^2-H^3)$ , Å	1.175	1.200
$l(H^3-O^4)$ , Å	1.194	1.174
$l(E^1-O^4)$ , Å	1.925	2.001
$l(E^1-N)$ , Å	2.163	2.239
$\nu$ , cm <sup>-1</sup> (imaginary frequency)	-1503	-1492
	(O←H→O)	(O←H→O)

external (positive entropy and negative free energy of formation) rather than internal factors (positive enthalpy of formation).

## EXPERIMENTAL

Quantum-chemical calculations were performed with HyperChem and GAUSSIAN 98 program complexes [18].

The NMR spectra were recorded on a Bruker AM-360 spectrometer from 6% solutions in acetone- $d_6$ ,  $CDCl_3$ , or  $D_2O$  relative to TMS.

The hydrolytic stability of silatranol, ethylsilatranol, germatranol, and ethylgermatranol was studied by NMR spectroscopy. Spectra of 6% solutions of silatranes and germatranes in  $D_2O$  were recorded at definite time intervals at 300 K. The occurrence and degree of hydrolysis were judged from the appearance of the triethanolamine methylene proton signals at 3.76 and 2.82 ppm and from the ratio of their intensity to that of the methylene proton signals of the starting atranes.

**1-Hydroxysilatranol** was prepared according to [19] by the reaction of tetraethoxysilane with triethanolamine, followed by selective hydrolysis of the forming tri(silatranoyloxyethyl)amine. Yield 60%, mp 203–205°C (200–205°C [19]).

The  $^1H$  NMR spectrum of 1-hydroxysilatranol in  $CDCl_3$  consists of three signals with the relative intensity of 6 : 6 : 1. The  $CH_2O$  and  $CH_2N$  groups of the atrane core give two triplets at 3.82 and 2.85 ppm, respectively, and the OH group gives a singlet at 1.87 ppm.

The  $^1H$  NMR spectrum of 1-hydroxysilatranol in  $D_2O$  irreversibly changes in time: Along with two triplets of the  $CH_2O$  and  $CH_2N$  groups of the atrane core at 3.85 and 3.05 ppm, two triplets of the  $CH_2O$  and  $CH_2N$  groups of the forming triethanolamine appear at 3.73 and 2.81 ppm, respectively, and grow with time. The conversion half-time is 0.5 h. Aqueous solutions of 1-hydroxysilatranol and its hydrolysis products remain transparent for 3 months; no signs of gelation were observed.

**1-Ethylsilatranol** was prepared by the reaction of triethanolamine with ethyltriethoxysilane in the presence of a catalyst (sodium ethylate) following the procedure described in [20]; yield 60%, mp 132–133°C (132–133°C [20]).

The  $^1H$  NMR spectrum of 1-ethylsilatranol in acetone- $d_6$  consists of four signals with the relative intensities of 6 : 6 : 3 : 2. The  $CH_2O$  and  $CH_2N$  groups of

the atrane core give two triplets at 3.63 and 2.81 ppm, respectively, and in the ethyl substituent the methyl group gives a triplet (0.86 ppm), and the methylene group, a quartet (0.22 ppm).

The  $^1H$  NMR spectrum of 1-ethylsilatranol in  $D_2O$  undergoes irreversible changes in time: Along with two triplets of the  $CH_2O$  and  $CH_2N$  groups of the atrane core at 3.81 and 3.02 ppm, two triplets of the  $CH_2O$  and  $CH_2N$  groups of the forming triethanolamine appear at 3.74 and 2.81 ppm, respectively, and grow with time. The concentration variation follows a first-order equation, with the conversion half-time of 10.7 h; after 11 h, gelation is observed.

**1-Hydroxygermatranol** was prepared according to [17] by the reaction of germanium dioxide with triethanolamine and water; yield of 1-hydroxygermatranol monohydrate 97%, mp 154–156°C (154–156°C [17]).

The  $^1H$  NMR spectrum of 1-hydroxygermatranol in acetone- $d_6$  consists of three signals with the relative intensity of 6 : 6 : 1. The  $CH_2O$  and  $CH_2N$  groups of the atrane core give two triplets at 3.69 and 2.91 ppm, respectively, and the OH group gives a singlet at 2.76 ppm.

The  $^1H$  NMR spectrum of 1-hydroxygermatranol in  $D_2O$  contains two triplets of equal intensity at 3.87 and 3.11 ppm, belonging, respectively, to the  $CH_2O$  and  $CH_2N$  groups. The  $^1H$  NMR spectrum of 1-hydroxygermatranol in  $D_2O$ , measured over a period of 60 days, remained unchanged.

**1-Ethylgermatranol**. An equimolar amount of tris(trimethylsiloxyethyl)amine was added to a solution of 15 g of ethyltrichlorogermane in 50 ml of heptane at 60–70°C. The mixture was stirred at room temperature until the distillation of trimethylchlorosilane stopped; the mixture was vacuum-evaporated, and the residue was recrystallized from toluene. Yield of 1-ethylgermatranol 12.3 g (70%), mp 146–147°C (146–147°C [17]).

The  $^1H$  NMR spectrum of 1-ethylgermatranol in acetone- $d_6$  consists of four signals with the relative intensities of 6 : 6 : 3 : 2. The  $CH_2O$  and  $CH_2N$  groups of the atrane ring give two triplets at 3.63 and 2.81 ppm, respectively; in the ethyl substituent, the  $CH_3$  group gives a triplet at 1.02 ppm, and the  $CH_2$  group, a quartet at 0.74 ppm.

The  $^1H$  NMR spectrum of 1-ethylgermatranol in  $D_2O$  changes with time: Along with the two triplets of the  $CH_2O$  and  $CH_2N$  groups of the atrane ring at 3.81 and 3.04 ppm, two triplets of the  $CH_2O$  and  $CH_2N$  groups of the forming triethanolamine appear

at 3.76 and 2.82 ppm, respectively. In 28 min, the intensity ratio of the signals of the methylene protons in the atrane core and triethanolamine (hydrolysis product) reached 5 : 4, after which it varied insignificantly (in 48 h, the ratio of the starting compound to the hydrolysis product approached 2 : 3). The 1-ethylgermatrane solution remained transparent throughout the monitoring period; no signs of gelation were observed.

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