

Concerning the transannular bond in silatranes and germatranes: a quantum chemical study

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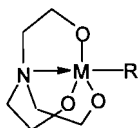
Abstract

For a series of silatranes and germatranes the structure of isolated molecules was investigated by the quantum chemistry molecular orbital method. The transannular bond $N \rightarrow M$ lengthens with the strengthening of a substituent + I-effect, however, in the solid state the bond length depends considerably on the crystal field effects. Due to the latter, this transannular bond in crystals is shorter than that in isolated molecules. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

The structures and properties of silatranes (**I**) and germatranes (**II**)—organic compounds of the pentacoordinated silicon and germanium—have been studied extensively [1–3].



I M=Si, **II** M=Ge

The intramolecular $N \rightarrow M$ donor–acceptor bond is the common characteristic feature for both types of compounds. This bond length in silatranes and germatranes is similar, while the remaining Si–X bonds in silatranes are shorter by 0.05–0.10 Å than the corresponding Ge–X bonds in germatranes, because the covalent radius for Ge is larger than that for Si.

The experimental data on the molecular structure of silatranes and germatranes were obtained mainly apply-

ing X-ray crystallographic measurements, i.e. the compounds were studied in the solid state. The N–Si distances lie between 1.965 and 2.24 Å [3]. The exception is silatranyl complexes with noble metals [4,5], where the geometry of atranes approaches to the *exo* structure, in which the transannular bond is absent. Unfortunately, up to now there are only two experimental investigations on the structures of these molecules in the gas phase: methylsilatrane (**I**, R = Me) and fluorosilatrane (**I**, R = F) are studied using electron diffraction [6,7]. N–Si distances equalling 2.453 Å for **I** (R = Me) and 2.324 Å for **I** (R = F) are longer than those found for these compounds in the solid state. According to X-ray diffraction analysis these values are 2.175 Å [8] for **I** (R = Me) and 2.042 Å [9] for **I** (R = F). Using ab initio quantum chemical calculations it has been shown that the N–Si distances for molecules **I** (R = Me and R = F) [10] are also longer than those observed in crystals. The theoretical work [11] showed that the ab initio calculated potential curve for deformation of the N–Si distance in molecule **I** (R = F) is very shallow.

The aim of the present paper is a quantum chemical investigation of the electronic structure of silatranes and germatranes by the molecular orbital (MO)

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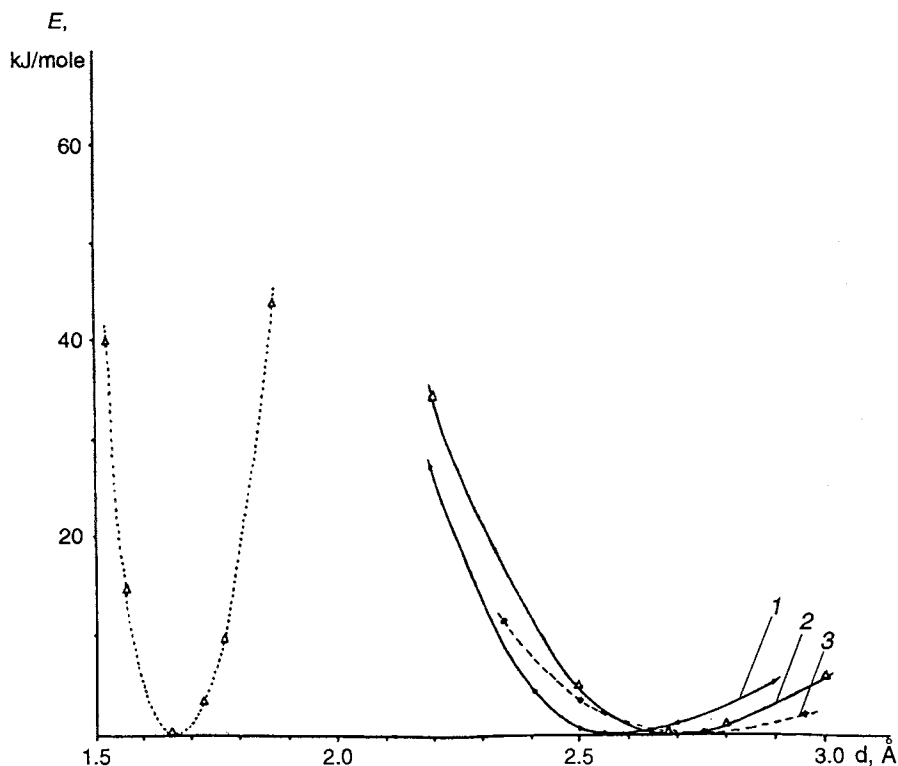


Fig. 1. AM1 (curve 1), MNDO (curve 2) and ab initio (curve 3) variation of the molecule I ($R = \text{Me}$) energy function of $\text{N} \rightarrow \text{Si}$ bond length and MNDO variation of the $\text{Si}-\text{O}$ bond length (dotted line) (in all cases the equilibrium is taken as 0).

method. The interpretation of the results has revealed some peculiarities in the molecular structures of silatranes and germatranes.

2. Computations

The most precise magnitudes of the geometrical parameters are obtained using the fully optimized ab initio calculations. Such calculations are called the representing theoretical experiment, as their exactness is sometimes higher than that obtained by means of the diffraction methods [12]. However, this accuracy requires considerable efforts: the calculations are very cumbersome and often an extension of the basis sets is needed. It is hard to realize even if electronic correlation energies are excluded. The systems studied are very complex and of relatively low symmetry, especially in the germatrane molecules, where germanium contributes 32 electrons in the system.

Because of the complications associated with the interpretation of ab initio calculations the semiempirical calculations have been employed in the present study. The ab initio calculations of methylsilatrane have been performed for calibrating the semi-empirical calculation results. The MO methods based on the zero differential overlap (ZDO) approximation have turned out to be of little use for silatranes and germatranes.

ZDO patterns with full optimization of the geometrical parameters for these compounds lead to physically unreal results. Therefore, the more strict variants of the self-consistent field theory have been chosen and the calculations with full geometry optimization have been performed by MNDO [13] and AM1 [14] methods, based on the neglect of diatomic differential overlap (NDDO) approximation. The quantum chemical parameters for germanium were taken from [15]. The package of programs MOPAC [16] and the program [17] were used for the calculations.

Ab initio calculations using a minimal basis did not give satisfactory results. Therefore, following [10] the basis set was extended but not balanced: this basis had d-functions only on the silicon atom. As in Ref. [10],

Table 1
Bond lengths (Å) in the molecule of methylsilatrane

Bond	MNDO	AM1	ab initio ^a
$\text{N} \rightarrow \text{Si}$	2.684	2.554	2.756
$\text{Si}-\text{C}$	1.814	1.787	1.855
$\text{Si}-\text{O}$	1.664	1.778	1.639
$\text{O}-\text{C}$	1.363	1.387	1.433
$\text{C}-\text{C}$	1.562	1.547	1.536
$\text{C}-\text{N}$	1.473	1.446	1.458

^a The ab initio values for the equilibrium configuration are obtained also in Ref. [10].

Table 2
MNDO results in comparison with X-ray analysis values for compounds **I**

R	MNDO					X-ray			Ref.
	N→Si	Si–O	Si–R	q_R	q_N	N→Si	Si–O	Si–R	
H	2.665	1.665	1.385	–0.268	–0.456				
F	2.505	1.665	1.591	–0.498	–0.441	2.042(1)	1.645(2)	1.622(1)	[9]
Cl	2.526	1.655	2.121	–0.448	–0.444	2.023(8)	1.649(8)	2.153(4)	[21]
Br	2.612	1.655	2.233	–0.388	–0.451				
I	2.707	1.656	2.405	–0.227	–0.461				
Me	2.684	1.664	1.814	–0.265	–0.456	2.175(4)	1.670(4)	1.870(6)	[8]
						2.193(5)	1.656(5)	1.882(6)	[22]
Ph	2.718	1.664	1.794	–0.364	–0.463	2.156(4)	1.657(5)	1.908(5)	[23]
						2.132(4)	1.656(4)	1.894(5)	[24]

Table 3
Dependence of the transannular bond lengths on the packing effect in compound **I** (R = Ph)

Crystal modification	N–Si bond length (Å)	Density (g cm ^{–3})	Packing coefficient
α	2.193(5)	1.357(2)	0.735
β	2.156(4)	1.361(1)	0.738
γ	2.132(4)	1.368(1)	0.742

the basis set 3-21G* was adopted. The calculations were carried out applying the program GAUSSIAN 92 [18].

3. Results and discussion

The dependence of the methylsilatrane (**I**, R = Me) molecule energy on the transannular bond length is shown in Fig. 1. It should be noted that the equilibrium lengths of N–Si bonds semiempirically calculated (AM1, 2.554 Å; MNDO, 2.684 Å) are closer to the experimental value (2.453(47) Å [6]), than the ab initio value, 2.756 Å. Nevertheless, the character of the energy variation is identical in all three cases: potential energy surface is shallow, i.e. only small energy changes are associated with the N→Si bond length. So, the change of this length by 0.4 Å requires an energy of about 10–30 kJ mol^{–1}. This is comparable with a lattice energy for molecular crystals [19]. Thus, in a solid state this bond length differs considerably due to the crystal field. That is why, the N–Si bond length is substantially shorter in the crystal of this substance and equals 2.175(4) Å [8].

Table 1 lists the principal bond lengths obtained by MNDO, AM1 and ab initio calculations for molecule **I** (R = Me) at the equilibrium configuration. The AM1 method gives the N→Si bond length which is closer to the experimental data, and given the experimental error this value could be considered satisfactory. But still this method produces unreal values of the Si–O bond lengths. That is why only MNDO results will be discussed further.

Changes in the bond energies in silatranes do not differ from those for the covalent bonds [19] (except for the N→Si bond). Consequently, the bond lengths (except for the N→Si) in the free state are near to the values in the solid state. The variation in the molecule **I** (R = Me) energy as a function of the Si–O bond length is presented in comparison with the N→Si bond length (see Fig. 1).

MNDO-calculated Si–X bond lengths (in Å) for the silatranes studied have been compared with the X-ray crystallographic data (Table 2). The effective charges on the nitrogen atoms (q_N) and the net effective charge of the R substituent (q_R) in silatranes are also represented. These values have been defined on the basis of Mulliken's population analysis [20].

According to the calculations the N→Si bond lengths with strengthening of the substituent + I-effect and, consequently, with increasing absolute charge on N. There is a linear dependence between the last value and the N→Si bond length (d_{N-Si}), which is described by the equation $d_{N-Si} = 10.305|q_N| - 2.039$ with correlation coefficient $r = 0.989$. Thus, in contrast to the work [25], the shortest N→Si bond in this series occurs for the fluorosilatrane (**I**, R = F) molecule. In the solid state the N→Si bond length depends considerably on the crystal field effects. Due to the latter, this length in the chlorosilatrane (**I**, R = Cl) crystal structure is shorter than that in the fluorosilatrane. It may be explained by the closer packing in the chlorosilatrane crystal. Its packing coefficient calculated on the basis of Kitaigorodsky's approach [26] is 0.708; for the fluorosilatrane structure this coefficient equals 0.673.

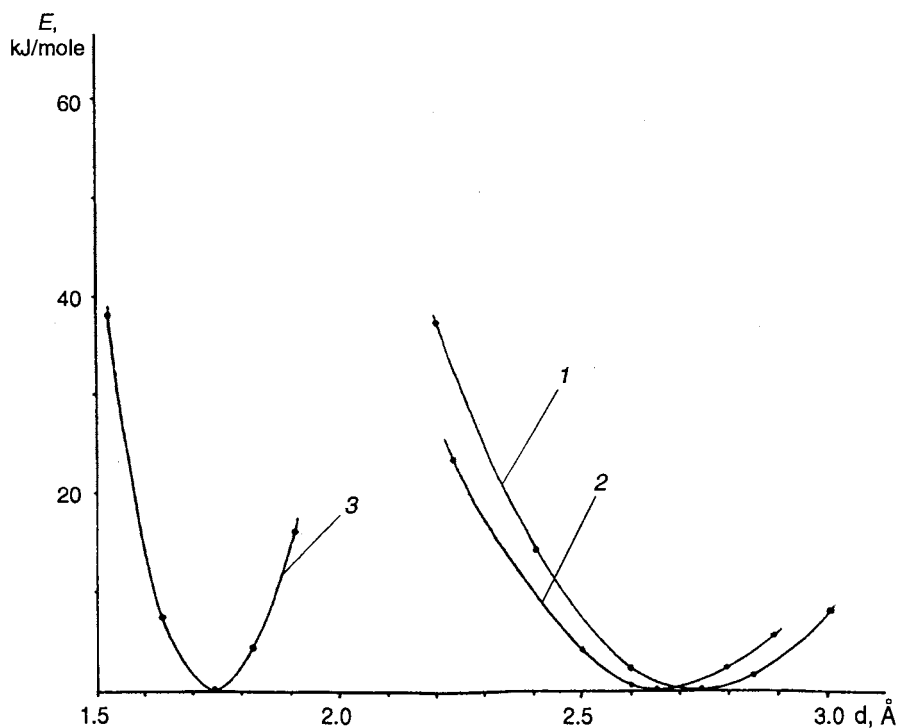


Fig. 2. MNDO variation of the molecule energy function of N→Ge, N→Si and N→B bond lengths for **II** (R = H) (curve 1), **I** (curve 2) and boratrane (curve 3) (in all cases the equilibrium is taken as 0).

The influence of the crystal field is especially pronounced in phenylsilatrane (**I**, R = Ph), where in different crystal modification there exists different N→Si bond lengths. The denser packing promotes the intensification of crystal field and, hence, compression of the molecules. As follows from Table 3, the N→Si bond length decreases with the increase of crystal density and packing coefficient.

Germatranes exhibit the same properties for the transannular bond as silatranes. The dependence of the variants in the molecular energy on the N→Ge bond length does not differ qualitatively from the N→Si bond in silatranes. The dependence of the germatrane (**II**, R = H) molecule energy on the donor–acceptor bond length and the analogous curve for the compound **I** (R = H) are shown in Fig. 2.

Table 4 lists the calculated characteristics for the germatrane molecules structure in comparison with X-ray values. There is a linear dependence between the calculated N→Ge bond length and $|q_N|$ value (the least squares equation is $d_{N-Ge} = 13.589|q_N| - 3.322$) with a high correlation coefficient ($r = 0.994$). Due to the crystal field effect the N→Ge bond lengths in crystals are considerably shorter. The extremely short N→Ge bond in the fluorogeratrane (**II**, R = F) crystal can be explained not only by the presence of electron-acceptor substituents, but by the strong crystal field as well. The crystal structure of **II** (R = F) (the packing coefficient is equal to 0.718) is not isomorphous to the rather incoherent structure of fluorosilatrane (**I**, R = F), while it is isomorphous to the more dense crystal structure of chlorosilatrane (**I**, R = Cl).

Table 4
Comparison of MNDO results with X-ray analysis values for compounds **II**

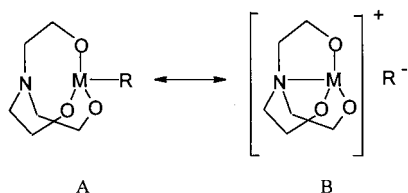
R	MNDO					X-ray			Ref.
	N→Ge	Ge–O	Ge–R	q_R	q_N	N→Ge	Ge–O	Ge–R	
H	2.742	1.811	1.498	–0.352	–0.446				
F	2.578	1.822	1.739	–0.563	–0.434	2.011(9)	1.768(6)	1.78(1)	[27]
Cl	2.618	1.801	2.268	–0.514	–0.437				
Br	2.643	1.799	2.388	–0.463	–0.440	2.09(1)	1.78(1)	2.42(1)	[28]
I	2.704	1.799	2.565	–0.316	–0.443				
Me	2.732	1.814	1.941	–0.344	–0.445				
Ph	2.759	1.814	1.915	–0.411	–0.448	2.212(5)	1.797(4)	1.947(5)	[29]

Table 5
Bond orders and the diatomic contributions with their components (in eV) to full energy of molecule for some bonds in **I** (R = H), **II** (R = H) and boratrane

Bond	Resonance term	Exchange term	Sum of Coulomb's components	Total diatomic energy	Bond order
N→Si	-0.62	-0.12	-4.26	-5.00	0.041
Si-H	-7.23	-4.13	-1.19	-12.55	0.852
N→Ge	-1.02	-0.22	-4.45	-5.67	0.067
Ge-H	-5.59	-3.90	-2.88	-12.37	0.835
N→B	-8.63	-2.73	2.84	-8.52	0.553

The calculated transannular bond lengths in germatranes are relatively close to the corresponding values in silatranes. The same can be observed for the crystal structures. This phenomenon can be interpreted using the expansion of a molecule energy into one- and two-atomic contributions. The two-atomic contributions and their components for N→M and M-H bonds in silatrane **I** (R = H) and germatrane **II** (R = H) are listed in Table 5. The same characteristics for the N→B bond in the 2,2',2''-nitrilotriethylborate (boratrane) molecule are also given for a comparison.

The first two terms characterize the covalent part of energy: it is larger for the N→Ge bond than for the N→Si one (the sum of the covalent members is -1.2 eV for N→Ge and -0.74 eV for N→Si). In contrast, the covalent part for Si-H is more considerable than for Ge-H. At the same time, the ionic part of energy for Si-H is smaller than for Ge-H (the sum of Coulomb's addends is -1.19 eV for Si-H and -2.88 eV for Ge-H). Thus, presenting schematically the structure of **I** and **II** as two mesomeric forms one can infer that the specific weight of the B form in germatranes is higher than that in silatranes. This conclusion is confirmed by the bond orders for N→M given in Table 5.



The N→Ge bond lengths in **II** are closer to those in the germatranyl-cation than the N→Si bond lengths in **I** to that in the silatranyl-cation. The calculated N→M bond lengths in these cations are equal 1.885 Å for N→Si and 1.959 Å for N→Ge. Obviously, in the crystal state for both silatranes and germatranes the specific weight of the B form increases. In its turn, it leads to lengthening of the M-R bonds.

The peculiarities for the N→M bond in silatranes and germatranes do not seem to be present for the N→B bond in boratrane. In this case the covalent terms are considerable (see Table 5), but ionic contribution is destructive, as it is positive (the sum is equal 2.84 eV). The donor-acceptor bond in boratrane is a con-

ventional covalent polar bond. The variation of energy as function of N→B length is shown in Fig. 2; the character of the variation is ordinary for most of the covalent bonds, and it differs from N→Si and N→Ge. That is a principal difference between the transannular N→Si and N→Ge bonds and the N→B bond.

4. Conclusions

The quantum chemical MNDO method gives physically reasonable results for silatranes and germatranes, i.e. it describes these systems in their ground states well.

The contribution of the covalent component of molecular energy, sensitive to the changes in bond lengths, is not large in the transannular bonds of silatranes and germatranes, that is why, only low energy is needed for the considerable change in the donor-acceptor bond length in silatranes and germatranes.

The N→Si and N→Ge bonds in solids are far shorter than those in the free state due to the crystal field influence.

As the lengths of N→Si and N→Ge bonds are more or less interchangeable, these values are not good parameters for structure-property correlations.

The Ge-X bonds are longer than the corresponding Si-X bonds, however, the lengths of the transannular N→Si and N→Ge bonds are rather close; and this has been attributed to the covalent contribution to the N→Ge bonds.

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