Physical Chemistry

Study of the electronic structure of organogermanes with extended coordination sphere of germanium

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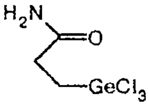
The spatial and electronic structures of some organogermanes with extended coordination spheres of the metal were calculated using AMPAC and HYPER CHEM 4.0 program packages. Interatomic distances, bond angles, torsion angles, atomic charges, electron densities, bond orders, parameters of localized and canonical molecular orbitals, *etc.* were determined. The nature of the additional intramolecular O→Ge interaction in the molecules of these compounds was considered.

Key words: germanium, quantum-chemical calculations, electronic structure.

A series of organic derivatives of trichlorogermane (**1**—**4**) containing a C=O group separated from the germanium atom by three covalent bonds has been studied by X-ray diffraction analysis and vibrational spectroscopy.[1—5]



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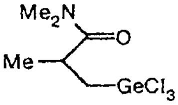

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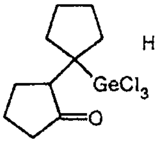

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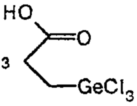

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The Ge atoms in these compounds interact with the O atoms (of the C=O group), and thus the coordination number of the metal increases to five. However, detailed electronic structure of this type of molecules or the nature of the interaction between the Ge and O atoms have not yet been studied. Therefore, we carried out calculations of their electronic structures using AMPAC and HYPER CHEM 3.0 program packages.[6,7]

There are relatively few publications presenting the results of calculations of electronic structures of organogermanium compounds. Data on the calculations of the electronic structures of molecules in which the coordination sphere of Ge has been extended by additional interactions with electron-donating atoms are even more scarce. In order to evaluate the potentialities of the most widely used semiempirical approaches, we carried out calculations for the molecule of 3-trichlorogermylpropionamide (**1**), in which the Ge...O distance in the solid phase (2.166 Å) is one of the shortest in the series of compounds under consideration[1]. We used the CNDO, INDO, MNDO, AM1 and PM3 methods implemented in the HYPER CHEM 4.0 program package. Our task was to estimate the degree to which these methods are able to reproduce the specific structural features of these molecules, namely:

— the decrease in the d(Ge....O) distance down to the value specified by the sum of the covalent radii of the Ge and O atoms (~1.88 Å);

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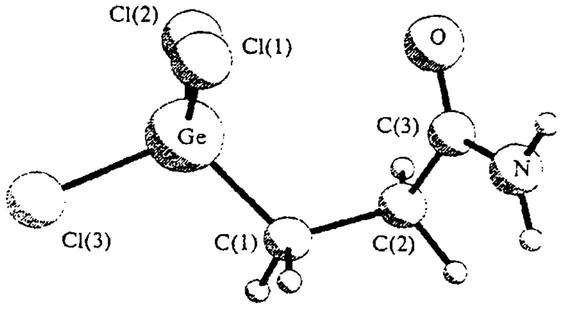

Fig. 1. Structure of the 3-trichlorogermylpropionamide molecule (**1**).

— the replacement of the tetrahedral configuration of the valence bonds of Ge by a nearly trigonal-bipyramidal configuration in which the Cl(3) and O atoms occupy axial positions and the Cl(1), Cl(2), and C(1) atoms are equatorial (the axial Ge—Cl bond is longer than the analogous equatorial bonds) (Fig. 1);

— the increase in the C=O bond length with respect to its average value;

— the envelope-like structure of the Ge—C(1)—C(2)—C(3)—O five-membered ring (in which the Ge, O, C(2) and C(3) atoms are located almost exactly in one plane, whereas the C(1) atom is slightly lifted above it) (see Fig. 1).

The results of calculations (Table 1) showed that within the framework of the CNDO and INDO methods, the "additional" Ge...O interaction cannot be reproduced: the corresponding distance amounts to 2.8—3.0 Å. The use of MNDO, AM1, and PM3 methods leads to much more correct results. Before we discuss these data, the following facts should be mentioned.

On the one hand, as the *d*(Ge...O) distance varies from the value specified by the sum of the van der Waals radii of Ge and O to that close to the sum of their covalent radii, the curve of the dependence of the heat of formation of the molecule ΔH_f on *d*(Ge...O) may exhibit two minima that would correspond to the coordination and valence bonds between the Ge and O atoms. It is clear that the method that reproduces these minima most adequately should be regarded as being the most suitable for our purposes. Figure 2 shows these curves constructed in terms of the MNDO (*a*), AM1 (*b*), and PM3 (*c*) methods. It can be seen from the Figure that only the PM3 method clearly reproduces the two minima.

On the other hand, interatomic coordination interactions including the Ge...O interaction considered here are very sensitive to the influence of the environment of the molecule. Besides, the distances between the atoms interacting in a molecule are normally shorter in the solid phase than in the gas phase. Numerous examples confirming this statement can be found in monographs;[8,9] however, for our purposes, the following fact is the most interesting. The length of the Si...N bond in the crystal of ethylsilatrane is 2.223 Å, while that in the gas is 2.435 Å.[10] Since the nature of the Ge...O bonds in the compounds in question is most likely similar to that of the Si...N bonds in silatranes, it should be expected that the calculated Ge...O bond lengths would be greater than those found in the crystals, because our calcula-

Table 1. Experimental and calculated bond lengths (*d*), bond angles (φ), and dihedral angles (ω) in molecule **1**

Structural parameter	Experiment[1]	Calculations					
		CNDO	INDO	MNDO	AM1	PM3*	PM3**
Bond				d/Å			
Ge—Cl_{ax}	2.253(6)	2.505	2.529	2.289	2.178	2.254	2.219
Ge—Cl_{eq}	2.147 (av.)	2.505	2.529	2.271 (av.)	2.167	2.227 (av.)	2.172 (av.)
Ge—C(1)	1.938(15)	2.361	2.416	1.978	2.023	1.985	1.958
C(1)—C(2)	1.535(19)	1.453	1.445	1.534	1.496	1.500	1.500
C(2)—C(3)	1.475(20)	1.461	1.469	1.535	1.514	1.511	1.514
C(3)=O	1.262(17)	1.277	1.286	1.265	1.276	1.264	1.237
C(3)—N	1.330(19)	1.385	1.361	1.359	1.351	1.366	1.398
Ge...O	2.166(9)	3.012	2.698	2.118	2.123	1.926	2.429
Bond angle				φ/deg			
Cl_{ax}—Ge—Cl_{eq}	101.85 (av.)	107.3 (av.)	102.9 (av.)	95.6 (av.)	97.3 (av.)	93.6 (av.)	100.7 (av.)
Cl_{eq}—Ge—C(1)	115.2 (av.)	112.8 (av.)	116.7 (av.)	117.2 (av.)	18.6 (av.)	117.6 (av.)	116.3 (av.)
Ge—C(1)—C(2)	109.7(1.6)	114.4	111.1	115.6	112.8	105.9	108.3
C(1)—C(2)—C(3)	110.3(1.1)	113.9	117.2	109.4	109.5	109.7	111.5
O—C(3)—N	120.1(1.9)	118.5	118.7	118.9	118.7	115.6	117.3
O—Ge—Cl_{ax}	175.7(1.0)	172.6	171.6	179.2	175.8	175.5	179.1
Dihedral angle				ω/deg			
C(1)—Ge—O—C(3)	11.4(1.5)	13.5	21.5	1.8	10.0	9.9	11.0
Ge—C(1)—C(2)—C(3)	24.4(2.0)	58.1	41.2	6.0	21.4	19.4	25.8

* The refinement of the structure was begun with *d*(Ge...O) = 2.3 Å.

** The refinement of the structure was begun with *d*(Ge...O) = 3.1 Å.

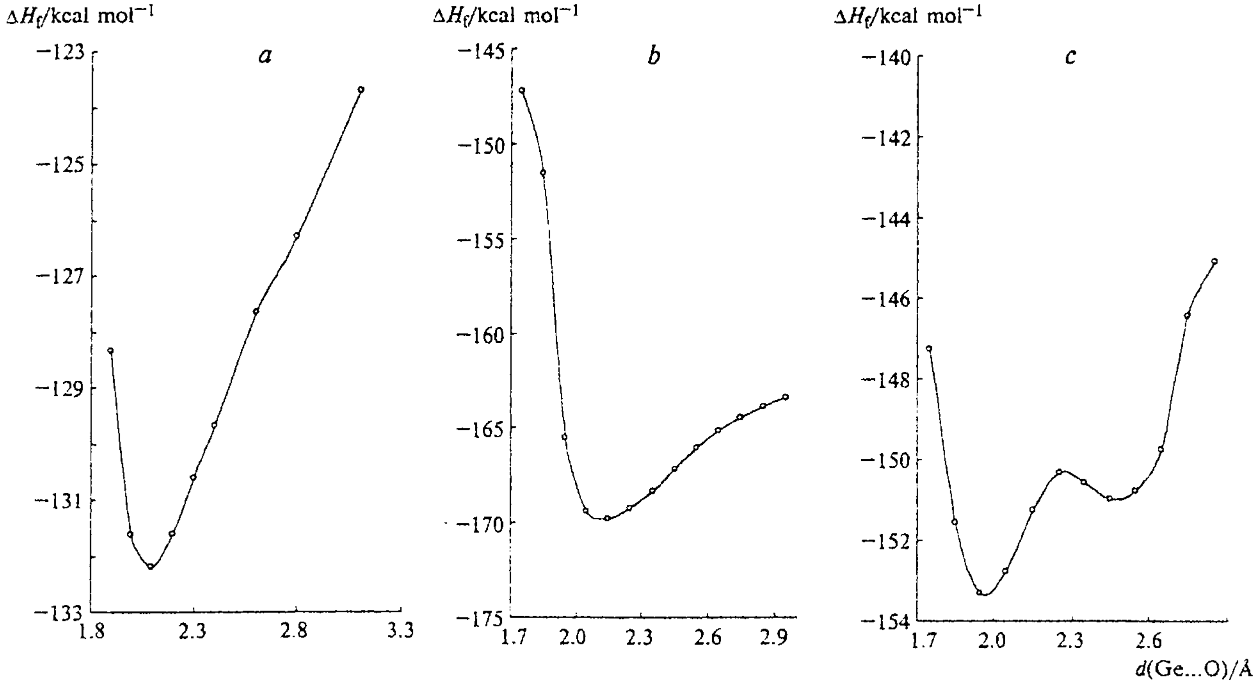

Fig. 2. Dependences of the heats of formation (ΔH_f) of molecule **1** on *d*(Ge...O) found by MNDO (*a*), AM1 (*b*), and PM3 (*c*) calculations.

tions are valid for free molecules. If we assume that on going from the solid phase to the gas, the *d*(Ge...O) distance changes similarly to *d*(Si...N) in silatranes, then this distance in the gas should be ~2.4 Å. It is just this value that results from the PM3 calculations.

Regarding reproduction of other typical features of the structure of molecule **1**, it can be seen from Table 1 that, according to MNDO calculations, all the Ge—Cl bonds are equal (their lengths are substantially greater than those found experimentally), and the Ge—C(1)—C(2)—C(3)—O five-membered ring is nearly planar. The AM1 method also leads to identical Ge—Cl bond lengths. However, the shape of the Ge—C(1)—C(2)—C(3)—O five-membered ring found by AM1 calculations is close to that found experimentally.

According to the profile of the dependence of ΔH_f on *d*(Ge...O) obtained in terms of the PM3 method (see Fig. 2, *c*), these calculations can lead to two dissimilar structures. If the refinement of the geometry starts with *d*(Ge...O) ≈ 2.8—3.0 Å, then the calculation procedure yields *d*(Ge...O) ≈ 2.43 Å; if the refinement starts with *d*(Ge...O) ≈ 2.0—2.2 Å, then the calculations afford *d*(Ge...O) ≈ 1.93 Å. In the structure characterized by the shorter *d*(Ge...O) distance, the lengths of all the Ge—Cl bonds are nearly identical and are somewhat longer than the experimental values. The difference between the lengths of the axial and equatorial Ge—Cl bonds can be reproduced more or less adequately only for the structure with *d*(Ge...O) ≈ 2.43 Å, which corresponds to the coordination bond between these two atoms. It can be seen from Table 1 that the theoretical results obtained for this structure are in good agreement with experimental data almost for all the interatomic distances and dihedral and bond angles. Thus, taking all the foregoing into account, it is expedient to carry out the subsequent calculations for the organogermanes of interest using the PM3 method.

To describe the electronic structures of these compounds in terms of localized molecular orbitals (MO), the LOCALIZE procedure included in the AMPAC program package was used. The energies and the composition of the localized MOs of molecule **1** are listed in Table 2. The valence MOs of this molecule contain 54 electrons distributed over 27 localized MOs corresponding to bonds and lone pairs (two- and one-center orbitals). Twelve mostly one-center MOs of molecule **1** correspond to the lone electron pairs of the Cl, O, and N atoms (see Table 2, MOs 1—8 and 24—27). In terms of their energies, they can be divided into two groups. Four almost purely atomic one-center orbitals of the Cl and O atoms (MOs 24—27) occupy the lowest-energy positions. Conversely, the rest of the mostly one-center MOs are located higher in energy than all the other above-mentioned orbitals; they are no longer purely atomic orbitals but contain noticeable contributions of the atomic orbitals (AO) of the neighboring atoms.

Since the Ge and O atoms are not linked by a valence bond, no two-center MO is formed in this case. Therefore, the characteristics of the MO corresponding to the second electron lone pair of the O atom, which participates in the Ge...O interaction (MO 8), are of particular interest. This orbital incorporates contribu-

Table 2. Characteristics of the localized MO of 3-trichlorogermylpropionamide (**1**)

MO	*E*/eV	Contributions of AOs (%)	Number of centers
1	−10.5	Cl(1) 98.3; Ge 1.1	1.03
2	−10.6	Cl(1) 98.6	1.03
3	−10.7	Cl(2) 97.9; Ge 1.6	1.04
4	−10.8	Cl(2) 98.3; Ge 1.1	1.03
5	−10.8	Cl(3) 98.2; Ge 1.4	1.04
6	−10.8	Cl(3) 98.5	1.03
7	−12.9	N 82.3; C(3) 15.8; O(1) 1.2	1.24
8	−14.5	O 87.3; Ge 8.6; C(5) 1.5	1.23
9	−14.6	O 72.8; C(3) 26.4	1.66
10	−15.0	Cl(2) 66.7; Ge 32.9	1.80
11	−15.4	Cl(1) 62.0; Ge 37.8	1.89
12	−15.4	Cl(3) 63.2; Ge 36.5	1.87
13	−15.7	C(1) 53.8; Ge 45.6	2.00
14	−18.5	C(1) 53.7; H 45.5	2.01
15	−18.6	C(1) 54.1; H 45.1	2.01
16	−19.2	C(2) 53.3; H 45.5	2.03
17	−19.2	C(2) 53.2; H 45.9	2.02
18	−20.3	C(2) 50.2; C(1) 48.9	2.03
19	−20.8	N 53.7; H 45.6	2.01
20	−21.1	N 52.6; H 46.6	2.02
21	−22.2	C(3) 52.9; C(2) 46.2	2.02
22	−23.5	N 50.2; C(3) 48.9	2.03
23	−26.9	O 53.1; C(3) 46.4	2.01
24	−27.3	O 99.5	1.01
25	−51.4	Cl(2) 99.9	1.02
26	−51.6	Cl(1) 99.9	1.01
27	−51.6	Cl(3) 99.9	1.02

tions of the s-, p_x-, p_y-, and p_z-AOs of oxygen, p_x-AO of germanium, and p_x-AO of the carbonyl carbon atom; the proportion of the oxygen AOs amounts to ~87%, and those of the germanium and carbon AOs are ~8.6% and ~1.5%, respectively (see Table 2). In the case of *N*,*N*-dimethyl-2-methyl-3-trichlorogermylpropionamide (**2**), in which the *d*(Ge...O) distance (2.123 Å) was found to be the shortest among the molecules considered, the proportion of the AO of the Ge atom in this MO is even larger and amounts to 9.3%. For 1′-trichlorogermyl-1,1′-bicyclopentan-2-one (**3**) (*d*(Ge...O) = 2.770 Å), this value is ~1.5%, and in the case of 3-trichlorogermylpropionic acid (**4**) (*d*(Ge...O) = 3.228 Å), it is close to zero.

The variation of the proportion of the AO of the Ge atom in the MO of the electron lone pair of the O atom correlates well with the variation of the characteristics of the Ge...O bond. The higher this proportion, the higher the bond order and the greater the energy of the pair interaction (Table 3). It is noteworthy that even for fairly large *d*(Ge...O) distances (for example, for those found in molecule **4**), the energy of this interaction is still relatively large, despite the fact that the bond order and the proportion of the AO of the Ge atom in the MO of the lone pair of the O atom are close to zero. Apparently, in this case, it is a purely electrostatic interaction.

Table 3. Characteristics of the interatomic bonds in the molecules of organogermanes **1**—**4**

Molecule	Bond	Δ*Q**	Bond order (according to Wiberg)	Partial energy/eV
1	Ge—Cl_{ax}	1.04	0.80	−8.7
	Ge—Cl_{eq}	0.92	0.92	−9.1
	Ge—C	0.98	0.88	−9.8
	C—C	0.14	1.01	−13.8
	C=O	0.56	1.52	−21.6
	C—N	0.05	1.33	−17.6
	Ge...O	1.07	0.28	−5.3
2	Ge—Cl_{ax}	1.03	0.80	−8.7
	Ge—Cl_{eq}	0.95	0.91	−9.1
	Ge—C	0.96	0.88	−9.8
	C—C	0.19	1.00	−13.7
	C=O	0.58	1.51	−21.5
	C—N	0.10	1.31	−17.3
	Ge...O	1.08	0.29	−5.4
3	Ge—Cl_{ax}	0.91	0.90	−9.1
	Ge—Cl_{eq}	0.87	0.95	−9.3
	Ge—C	0.84	0.91	−9.8
	C=O	0.58	1.88	−25.1
	Ge...O	0.97	0.05	−1.5
4	Ge—Cl_{ax}	0.89	0.93	−9.1
	Ge—Cl_{eq}	0.84	0.95	−9.2
	Ge—C	0.90	0.95	−10.3
	C—C	0.15	0.99	−13.7
	C=O	0.76	1.79	−24.9
	C—O	0.67	1.06	−16.2
	Ge...O	1.06	0.01	−1.1

*Magnitudes of the differences between the effective charges on the atoms forming the bond.

The donor-acceptor Ge...O bond should be markedly influenced by the character of substituents at the Ge atom. In fact, our calculations showed that the replacement of electronegative substituents such as Cl atoms by methyl or phenyl groups results in a substantial lengthening of this bond, which reflects weakening of the Ge...O interaction. The *d*(Ge...O) distances for various sets of three substituents at the Ge atom are presented below.

Substituents at the Ge atom	3 F	3 H	3 Me	3 Cl	2 HPh
d(Ge...O)/Å	2.311	2.671	2.566	2.429	2.552

In the studies dealing with the interaction between the Si and N atoms in silatranes and related molecules, the concept of "hypervalent three-center bond" combining the axial substituent and the Si and N atoms is often invoked. The character of the Ge...O bonds in molecules **1**—**4** should be similar to the character of Si...N bonds in silatranes. However, the above-presented data indicate that there is no full analogy, because AOs of the axial Cl atom do not participate in the Ge...O interaction (although it follows from the data of Table 1 that

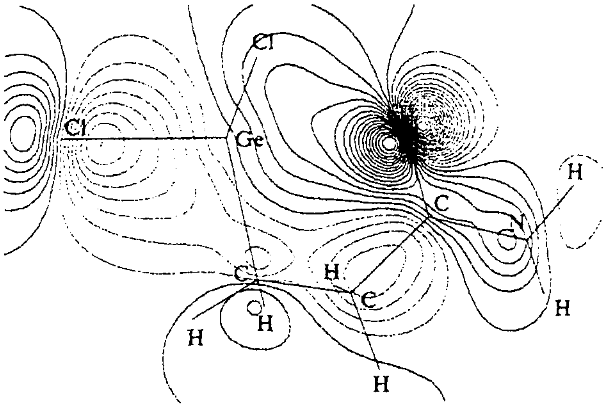

Fig. 3. Form of MO 17 of molecule **1**.

AOs of the Ge atom do participate in the MOs of the electron lone pairs of the Cl atoms).

The composition of the one-center MO that describes the lone pair of the N atom is equally complicated. This orbital is formed by the s- and p-AOs of the N atom (82.5%), the p_z-AO of the C atom linked to the N atom (15.8%), and the p_z-AO of the O atom (~1.2%). Thus, the N atom, which forms the N—C covalent bond (MO 22), participates simultaneously in the donor-acceptor interaction with the atoms of the C=O group. Consequently, the overall order of the N—C bond increases to 1.3 (see Table 3). An increase in the N—C bond order has also been observed in the spectroscopic studies of these molecules.[11]

Attention is attracted by the composition of some two-center MOs that form valence bonds. For example, the MOs of the Ge—Cl bonds contain relatively low proportions of the Ge AO (especially the MO of the axial Ge—Cl bond in which this proportion is as low as ~33%). All these bonds are relatively "weak" and are polar (they are characterized by the largest ΔQ values, *i.e.*, differences between the effective atomic charges) (see Table 3).

The carbonyl C=O bond is described by two MOs (8 and 23). The former orbital (π-MO) consists almost completely of the p_z-AOs of the O and C atoms; their proportion is ~26%. The latter orbital (σ-MO) is formed from s-, p_x-, and p_y-AOs of these atoms, whose contributions are nearly equal. As shown above, the C=O bond is an electron acceptor rather than an electron donor; therefore, its order is less than two and its length is larger than the standard value.

Analysis of the composition and the form of the canonical MOs of the molecule **1** implies an intricate nature of the Ge...O interaction. According to PM3 calculations, the molecule contains 27 bonding MOs and 15 virtual MOs, three of which (MOs 28—30) lie in the region of negative energies: −0.9, −0.8, and −0.7 eV. The major contributions to these MOs are made by the AOs of the Ge atom. The energies of MOs 9, 14, and 17, which ensure the binding between the Ge and O atoms, are relatively low: −18.4, −14.6, and −13.1 eV. Their composition depends on the molecular system of coordinates chosen. When the plane that passes through the C=O group and the Ge atom is combined with the *xy* plane, and the Ge...O line is combined with the *x* axis, the composition of MO 17, which makes the major contribution to the linking of the Ge and O atoms, is the following: $0.41\ p_x\text{Ge} - 0.17\ p_y\text{Ge} + 0.10\ p_x\text{O} + 0.24\ p_y\text{O} - 0.36\ p_x\text{Cl}_{ax}$.(the contributions of those AOs are presented, the coefficients at which are greater than 0.1). The form of this MO is shown in Fig. 3. Similar electronic structures are typical of other molecules of this series, in which a fairly strong interaction between the O and Ge atoms occur.

References

1. S. N. Gurkova, A. I. Gusev, and N. V. Alekseev, *Dokl. Akad. Nauk SSSR*, 1982, **266**, 1399 [*Dokl. Chem.*, 1982 (Engl. Transl.)].
2. S. N. Gurkova, A. I. Gusev, and N. V. Alekseev, *Zh. Strukt. Khim.*, 1985, **26**, 148 [*J. Struct. Chem.*, 1985, **26** (Engl. Transl.)].
3. S. N. Gurkova, A. I. Gusev, and N. V. Alekseev, *Zh. Strukt. Khim.*, 1985, **26**, 183 [*J. Struct. Chem.*, 1985, **26** (Engl. Transl.)].
4. S. N. Gurkova, A. I. Gusev, and N. V. Alekseev, *Zh. Strukt. Khim.*, 1985, **26**, 136 [*J. Struct. Chem.*, 1985, **26** (Engl. Transl.)].
5. S. N. Tandura, S. N. Gurkova, A. I. Gusev, and N. V. Alekseev, *Stroenie biologicheski aktivnykh soedinenii germaniya s rasshirennoi koordinatsionnoi sferoi* [*Structures of Biologically Active Germanium Compounds with Extended Coordination Spheres*], NIITEKhIM, Moscow, 1983, 46 pp. (in Russian).
6. P. Stewart, *J. Computer-Aided Mol. Design*, 1990, **4**, 1; M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, and J. J. P. Stewart, *J. Am. Chem. Soc.*, 1985, **107**, 3902.
7. *HYPER CHEM Release 3 for WINDOWS. Autodesc*, Inc. Publication, 10036-01, 1993.
8. M. Hargittai and I. Hargittai, *Geometriya molekul koordinatsionnykh soedinenii v paroobraznoi faze* [*Molecular Geometry of Coordination Compounds in the Vapor Phase*], Mir, Moscow, 1978, 282 pp. (in Russian).
9. L. V. Vilkov, V. S. Mastryukov, and N. I. Sadova, *Opredelenie geometricheskogo stroeniya svobodnykh molekul* [*Determination of the Geometrical Structures of Free Molecules*], Khimiya, Leningrad, 1978, 354 pp. (in Russian).
10. S. N. Tandura, M. G. Voronkov, and N. V. Alekseev, *Molecular and Electronic Structures of Penta- and Hexacoordinated Silicon Compounds*, in *Topics in Current Chemistry*, Springer-Verlag, 1986, **131**, 99; Q. Shen and R. L. J. Hilderbrandt, *Mol. Struct.*, 1980, **64**, 257.
11. N. A. Chumaevskii, D. A. Ivashchenko, T. K. Gar, O. A. Dombrova, and N. A. Minaeva, *Koord. Khim.*, 1988, **14**, 1071 [*Sov. J. Coord. Chem.*, 1988, **14** (Engl. Transl.)].

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