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The structural peculiarities and chemical bonding in three organogermanes $Cl_3GeCH_2OC(O)R$ with rigid coordination centre

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Abstract

The molecular and crystal structure of three organogermanes $Cl_3GeCH_2OC(O)R$ (where $R = –NHC_6H_{11}$, $–C_{10}H_{15}$, and $–NH_2$) has been determined by X-ray diffraction method in order to investigate geometrical regularities of these molecules. The nature of Ge–O bonding in these molecules was investigated by quantum chemistry method. It was shown that the influence of the nature of ligand, attached to carbon atom of the carbonyl group, on Ge···O interatomic distance is incidentally small in isolated molecule while in the crystal it is much more pronounced due to the crystal packing effect. The nature of Ge···O bonding corresponds to intermediate type of interatomic interaction in terms of "Atoms in molecules" theory.

Keywords: Organogermanes; Pentacoordinated germanium; Single-crystal X-ray studies; Quantum chemical calculations; Electron density distribution

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1. Introduction

Organogermanes $X_3Ge–CH_2–Y–C(O)–R$ (where $X = Cl$, CH_3 or C_6H_5 and $Y = CH_2$, O or N) with the pentacoordinated germanium atom have attracted the attention of researchers in synthetic and theoretical organic chemistry for a long time. Pioneering studies of the molecular structures of these compounds was carried out in the early 1980s [1,2]. Since then, the crystal and molecular structures of 23 such compounds (in which $X = Cl$ or CH_3, and $Y = CH_2$ or N) were studied by X-ray single crystal diffraction [Cambridge Structural Database (CSD, [3])]. However, the crystal and molecular structure as well as chemical bonding in related compounds with $Y = O$ are not adequately studied.

For this reason we carried out the detailed study of the crystal and molecular structures of (trichlorogermyl) methyl *N*-cyclogexylcarbamate **I**, (trichlorogermyl)methyl 1-adamantanecarboxylate **II** and (trichlorogermyl)methyl carbamate **III** (Fig. 1). Preliminary information about molecular structure of **II** and **III** was already published [4,5]. The results of single crystal X-ray experiments and quantum chemical calculations of crystal structures and isolated molecules of **I–III** were used to define the characteristics of Ge···O bonding and influence of crystal packing on geometrical parameters as well as peculiarities of electron structure of those molecules.

2. Experimental

2.1. Preparation

Compounds **I–III** were prepared by interaction of (trichlorogermyl)methanol with isocyanatocyclohexene, 1-adamantanecarboxylic acid chloride and isocyanatotri-

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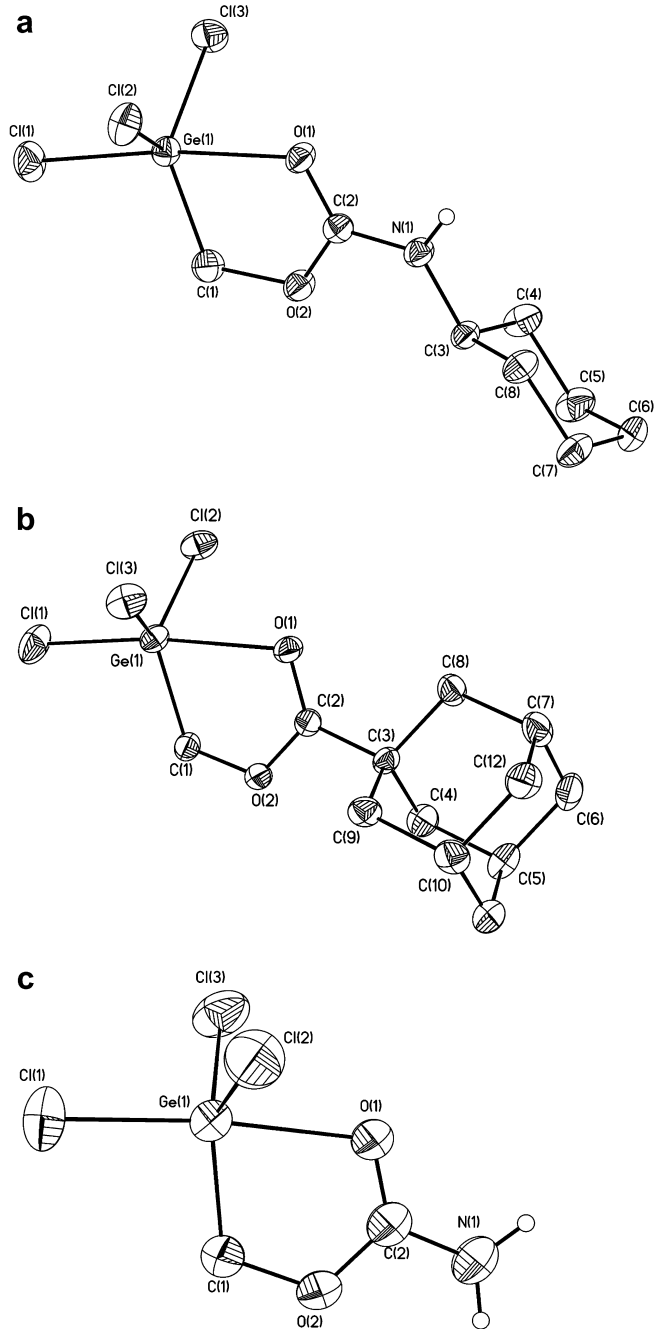

Fig. 1. Molecular structure of **I** (a), **II** (b) and **III** (c) presented by thermal ellipsoids with 50% probability.

methylsilane correspondingly. All reactions accompanied by significant heat evolution. Trichlorogermylmethanol was prepared according to method published in literature (see [6] and references therein). All manipulations were performed under an argon atmosphere using standard Schlenk techniques. Solvents were dried by standard methods and distilled prior to use.

2.1.1. (Trichlorogermyl)methyl N-cyclogexylcarbamate (*I*)

The trichlorogermylmethanol (21.0 g, 0.1 mol) was added dropwise to the solution (12.5 g, 0.1 mol) of isocyanatocyclohexene in 100 ml. of diethyl ether. The reaction mixture was stirred for 2 h and then 10.6 g (0.33 mol) of methanol was added. Finally the triethylamine (33.4 g, 0.33 mol) was added dropwise with stirring. After 1 hour the stirring was interrupted and reaction mixture washed out with 30 mol of benzene two times and then triethanolamine (14.0 g, 0.9 mol) was added. After cooling of reaction mixture the precipitated crystals (17.6 g, 46.9%, m.p. 145–155 °C) were filtered and dried in vacuum. Analytical data are as follows. Found (%): C, 28.8; H, 4.1; Cl, 31.9; Ge, 21.5; N, 4.2; O, 9.6; $C_8H_{14}Cl_3GeNO_2$. Calcd (%): C, 28.67; H, 4.21; Cl, 31.73; Ge, 21.67; N, 4.18; O, 9.55%. ^1H NMR spectra (25 °C, $CDCl_3$) δ, ppm: 1.20, 1.43, 1.95, 3.58 (all m, 11H, cyclohexyl), 4.63 (s, 2H, CH_2), 6.74 (d, 1H, NH).

2.1.2. (Trichlorogermyl)methyl 1-adamantanecarboxylate (*II*)

Trichlorogermylmethanol (20.9 g, 0.1 mol) was added dropwise with stirring to 1-adamantanecarboxylic acid chloride (19.6 g, 0.1 mol). Then the reaction mixture was heated until gas evolution completely accomplished. After cooling of the reaction mixture to room temperature, crystallization have occurred. Crystals of compound **II** were obtained after recrystallization from hexane (31.7 g, 85%, m.p. 85–88.5 °C). Anal. Found (%): C, 38.75; H, 4.55; Cl, 28.60; Ge, 19.47. $C1_2H_{17}Cl_3GeO_2$. Calcd (%): C, 38.72; H, 4.60; Cl, 28.57; Ge, 19.51. ^1H NMR (25 °C, CDC13), δ ppm: 1.68–1.77, 1.92, 1.93, and 2.05 (all m, 15 H, $C_{10}H_{15}$); 4.37 (s, 2 H, CH_2O).

2.1.3. (Trichlorogermyl)methyl carbamate (*III*)

Cooled (trichlorogermyl)methanol (38.8 g, 0.185 mol) was added dropwise with stirring to isocyanatotrimethylsilane (10.7 g, 0.093 mol). The reaction accompanied by heat evaluation. Reactionary mixture then cooled, until a gas emission finished completely. The crystallization of **III** was very slow. In order to improve the yield of compound **III** the reaction mass was kept at room temperature during 10 days, and then precipitate was filtered out. Finally, compound **III** was flushed by chloroform (~10 ml) and dried in a vacuum (11.7 g, 49.8%, m.p. 77–87 °C). The crystals suitable for X-ray analysis were obtained by recrystallization from benzene (m.p. 112–114). Anal. Found (%): C 10.0; H 1.8; Ge 28.1; Cl 41.4; $C_2H_4Cl_3GeNO_2$. Calcd (%): C 9.5; H 1.6; Ge 28.7; Cl 42.0. ^1H NMR (25 °C, CDC13), δ ppm: 4.28 s (2H, OCH_2Ge); 7.20 s (1H, NH).

All ^1H NMR spectrums were recorded on a Bruker AM-360 spectrometer (360 MHz).

2.2. X-ray crystallographic study

X-ray diffraction measurements of **I**–**III** were carried out with a SMART 1000 CCD diffractometer at 100 K and monitored by SMART program [7]. The frames were integrated and corrected for absorption by the SAINT and SADABS programs [7]. The details of crystallographic data and experimental conditions are presented in Table 1. Important structural parameters of structures **I–III** are summarized in Table 2.

The structures were solved by the direct method and refined by full-matrix least-squares technique against F^2 in the anisotropic approximation. The hydrogen atoms were located from difference electron density syntheses and refined in rigid body model. All calculations were performed using the SHELXTL PLUS 5.10 program package [8]. Atomic coordinates, bond lengths, bond angles and thermal parameters of **I–III** have been deposed at the Cambridge Crystallographic DataBase (Deposition Nos.: 264020, 606570 and 629736).

Table 2
Important experimental bond lengths and angles in compounds **I–III**

Bond lengths and angles	**I**[a]	**II**	**III**
Ge(1)···O(1)	2.188(2)	2.324(3) (A) 2.376(3) (B)	2.251(2)
Ge(1)–Cl(1)	2.2172(7)	2.190(1) (A) 2.189(1) (B)	2.2082(8)
Ge(1)–Cl(2)	2.1416(8)	2.136(1)	2.1264(8)
Ge(1)–Cl(3)	2.1322(7)	2.126(1)	2.1320(8)
Ge(1)–C(1)	1.950(2)	1.950(3)	1.942(3)
O(1)–C(2)	1.253(3)	1.228(4)	1.223(3)
O(2)–C(1)	1.433(3)	1.437(4)	1.430(3)
O(2)–C(2)		1.339(4)	
N(1)–C(2)	1.321(3)		1.319(4)
Cl(1)–Ge(1)–O(1)	173.55(5)	173.15(7) (A) 172.81(6) (B)	173.95(5)
O(2)–C(1)–Ge(1)	113.94(15)	115.4(3)	114.9(2)
O(1)–C(2)–O(2)	121.5(2)	120.0(3)	121.7(2)
C(2)–N(1)–C(3)	125.20(19)		
O(1)–C(2)–N(1)	123.7(2)		125.1(3)

[a] The values for independent molecules A and B are presented, otherwise averaged values are shown.

2.3. Calculations

The quantum chemical calculations of **I–III** structures in the crystal were carried out using the VASP 4.6.28 code [9]. Conjugated gradient technique was used for optimizations of the atomic positions (started from experimental data) and minimization of total energy. Projected augmented wave (PAW) method was applied to account for core electrons while valence electrons were approximated by plane-wave expansion with 400 eV cutoff [9]. Exchange and correlation terms of total energy were described by PBE [10] exchange-correlation functional. In case of crystals **I** and **II** Kohn–Sham equations were integrated using Γ-point approximation, while for crystal of **III**, 4 × 4 × 4 Monkhorst-Pack k-point mesh [11] have been applied. We believe that Γ-point approximation is sufficient for **I** and **II** because of their large crystal unit cells. Using DFT method it's not possible to take into account dispersion interactions. For this reason calculated cell parameters may be

Table 1
Crystal data and experimental conditions for compounds **I–III**

	I	**II**	**III**
Molecular formula	$C_8H_{14}Cl_3GeNO_2$	$C_{12}H_{17}Cl_3GeO_2$	$C_2H_4Cl_3GeNO_2$
Formula weight	335.14	372.20	253.00
Color, shape	cube	Plate	prism
Dimension (mm)	0.3 × 0.3 × 0.3	0.3 × 0.3 × 0.02	0.3 × 0.3 × 0.2
Crystal system	Orthorombic	Monoclinic	Monoclinic
Space group	*Pbca*	$P2_1/n$	$P2_1/n$
a (Å)	10.599(3)	17.997(5)	8.1768(10)
b (Å)	13.682(4)	9.049(2)	10.0604(13)
c (Å)	17.854(5)	18.335(4)	9.7887(11)
β (°)		90.043(7)	91.086(3)
V (Å^3)	2589.0(13)	2985.7(13)	805.09(17)
Z	8	8	4
ρ_{calc} (g cm^{-1})	1.72	1.656	2.087
Temperature (K)	120	120	120
Scan type	ω	ω	ω
2θmax (°)	60.14	60.06	59.92
Radiation, λ(Mo-Kα) (Å)	0.71073	0.71073	0.71073
Linear absorption (μ) (cm^{-})	29.66	25.80	47.32
Absorption correction	SADABS	SADABS	SADABS
T_{min}/T_{max}	0.53/0.53	0.51/0.95	0.45/0.33
$F(000)$	1344	1504	488
Total refl. (R_{int})	28811	18550	7325
Number of independent refl.	3777	8485	2304
Number of indepent refl. with $I > 2(\sigma)$	3128	4435	1623
Parameters	136	325	82
wR_2	0.0795	0.0847	0.0487
R_1 [$I > 2(\sigma)$]	0.0333	0.0442	0.0308
GOF	0.965	0.988	0.982
ρ_{max}/ρ_{min} (e Å^{-3})	1.05/−0.54	1.39/−0.51	0.45/−0.45

systematically overestimated or underestimated up to 5%. Thus, the experimental values of cell parameters were used in the calculations. At a final step of our calculations atomic displacements converged were better than 0.02 eV Å^{-1}, as well as energy variations were less than 10^{-3} eV. In order to carry out the topological analysis of electron density distribution function in terms of R.F Bader's theory "Atoms in molecules" (AIM) [12] the dense FFT (fast Fourier transformation) grid was used (corresponding to cutoff 1360 eV). The latter was obtained by separate single point calculation of optimized geometry with hard PAWs for each atom type. The topological analysis of electron density distribution function was carried out using AIM program – part of ABINIT software package [13].

The isolated molecules of **I–III** were simulated utilizing the Gaussian 98 Release A7 software [14]. Optimization of atomic positions was carried out using B3LYP hybrid functional and 6-311G(d,p) local basis set. The structures of isolated molecules of **I–III** were tested on stability by calculation of vibrational frequencies. The topological analysis of electron density distribution function of isolated molecules was carried out utilizing AIMPAC program package [15].

3. Results and discussion

Previously investigated trichloroorganogermane molecules can be classified into two groups according to the nature of the substituent Y. In compounds, with Y = CH_2, the Ge–O distances vary over a wide range from 2.123 Å (in 3-(trichlorogermyl)-*N*,*N*′-dimethylpropan-amide) [2] to 3.228 Å (in 3-(trichlorogermyl)propionic acid [1]). The five-membered rings Cl_3Ge-C-Y-C(O)-R in these molecules adopt an envelope conformation where the carbon atom adjacent to the Ge atom deviates from the plane formed other four atoms. In the molecules with Y = N, the Ge–O distances vary over a much smaller range, from 2.080 to 2.354 Å (in most cases, *ca.* 2.2 Å). The above-mentioned five-membered rings (Y = N) in are nearly planar (for example, in *N*-methyl-4-*N*-trichlorogermylmethyl methylbenzamide [16]).

The elongation of the axial Ge(1)–Cl(1) bond in comparison with equatorial Ge–Cl bonds does not exceed 0.1 Å in all trichloroorganogermanes investigated earlier. Therefore the $CGeCl_3$-coordination centre in the above-mentioned compounds can be described as rigid. This feature makes a distinguish between $CGeCl_3$ and C_3GeCl coordination centers. The compounds with C_3GeCl coordination centre are investigated extensively [17]. In their molecules, O···Ge and Ge–Cl axial distances vary in much wider ranges and so that the C_3GeCl coordination centre can be described as soft (non-rigid). Such difference can be explained in terms of Lewis acidity of the $CGeCl_3$ and C_3GeCl fragments. The softness of the C_3GeCl moiety as Lewis base is more than that of $CGeCl_3$ moiety. Therefore the axial Ge–Cl bond is more prone to the elongation in the case of $CGeCl_3$ fragment.

The form of five-membered rings Cl_3Ge-C-Y-C(O)-R in **I–III** correspond to neither the former nor the latter type. These rings adopt an envelope conformation with the Ge atoms deviating from the plane of the O—C=O fragment (the deviation is within ~0.02 Å). The corresponding values of Ge atom deviation are equal to 0.08 Å in **I**, 0.45–0.56 Å in **II** and 0.24 Å in **III**. Therefore the shortest Ge···O distance correspond the most planar five-membered ring.

Such conformations of five-membered rings in molecules under consideration are due to the fact that the C–H and equatorial Ge–Cl bonds tend to arrange so as to minimize the torsion strain in the Cl–Ge–C–H fragments. This can be achieved if either the C or Ge atom deviates from the plane of the ring. However, the C atom is a part of the ester fragment R–C(O)OCH_2– in which all the atoms appear, as a rule, in the same plane (for example, in methyl acetate [18] and methyl (3-chloro-4-hydroxyphenyl)glyoxylate [19]). Therefore, Ge atoms deviates significantly from the plane of the ring. As a result, the Cl–Ge–C–H torsion angles are close to those observed in methyltrichlorogermane, in which the Ge–Cl bond is staggered with respect to the C–H bond (60°). It is also necessary to mention, that one cannot exclude the influence of crystal packing on conformation of five-membered ring in **I–III**. Hovewer, based only on structural data it is impossible to study this influence in detail.

The expansion of coordination polyhedron of Ge in molecules under consideration occurs as a result of additional Ge···O interaction. Unfortunately the analysis of structural parameters could not give the necessary information about the nature of this interaction. Using the quantum chemical methods allows one to get the information on this problem. Previously the chemical bonding in trichloroorganogermanes was studied using only semi-empirical (PM3 and AM1) level [20]. In this study we carried out quantum chemical calculations of the crystal packing of **I–III** using PBE exchange correlation functional and plane wave basis set as well as quantum chemical calculations of the isolated molecules **I–III** based on B3LYP/6-311G(d,p) level of theory. R.F. Bader's theory "Atoms in molecules" (AIM) [12] was chosen as theoretical approach to analyze the electronic structures of **I–III**. Previously, we successfully utilized such a methodological background for studying series of silicon compounds with expanded coordination polyhedron of the Si atom [21–23].

The experimental and calculated structural parameters of the crystals **I–III** are in satisfactory agreement. The main differences are observed for intermolecular distances corresponding to weak N–H···O, C–H···O bonds and Cl···Cl interatomic contacts which are equal, on average 0.1 Å. All the bonds formed by Ge atom are elongated up to 0.03 Å compared to experimental ones. Probably, the reasons of such a deviations are disadvantages of the DFT theory which cannot account for weak van der Waals interactions. Nevertheless the calculations reproduced well the differences between two independent molecules in structure of **II**.

The geometry of isolated molecules **I–III** agrees well with experimental one (except for Ge···O distances). Mean-square deviations of calculated and experimental values of bond lengths are equal to *ca.* 0.02Å. For bond angles, this value is equal to *ca.* 2.0°. The discrepancy between experimental and calculated values of Ge···O distances is expected as result of influence of crystal field. It's very probably, that Ge–O bonds in studied molecules are similar to Si···N and Ge···N bonds in silatranes and germatranes. As it is known at transferring from solid to gas phase Si···N and Ge···N interatomic distances in this molecules are enlarged by ~0.2–0.3 Å [24–27]. Apparently, the behavior of Ge···O interatomic distances in molecules under consideration appears to be similar. And really, calculated values of Ge···O interatomic distances in **I–III** exceed the experimental ones by ~0.2Å as it is possible to see from data of the Table 3. It should be noted that in isolated molecules **I–III** the variation of Ge···O interatomic distances (0.07 Å) is less pronounced than in crystal. So one can expect that in isolated molecules **I–III** Ge···O bonds have almost equal energies (Table 4).

Both in crystals and isolated molecules **I–III** the topological analysis of electron density distribution function $\boldsymbol{\rho}(r)$ have shown the presence of critical points $CP(3,-1)$ in region of all expected bonds as well as for Ge···O coordination bonds. Besides, the $CP(3,-1)$ critical points corresponding to the N–H···O, C–H···O, C–H···Cl weak hydrogen bonds and Cl···Cl, Cl···O, Cl···N contacts were also found. The C–O, N–C, C–C, C–H and N–H bonds are characterized by negative values of laplacian $\nabla^2\boldsymbol{\rho}(r)$ and local energy density $E^e(r)$. These bonds correspond to shared type (ordinary covalent bonds) in terms of AIM theory. In turn, all bonds formed by the Ge atom are characterized by positive value of $\nabla^2\boldsymbol{\rho}(r)$ and negative one of $E^e(r)$, that is typical for interatomic interactions of intermediate type. Weak intermolecular interactions found in crystal may be described as closed shell interactions (for them $\nabla^2\boldsymbol{\rho}(r) > 0$, $E^e(r) > 0$, in $CP(3,-1)$).

One of the useful advantages of AIM theory is the possibility to evaluate the energy of closed shell interactions as well as interactions of intermediate type using correlation formula proposed by Espinosa, Mollins and Lecomte [28]:

$$E_{\mathrm{A-B}} \approx 1/2V^{e}(r) \qquad (1)$$

where $E_{\mathrm{A-B}}$ is the energy of weak interatomic contacts or coordination bond and $V^e(r)$ is potential energy density in $CP(3,-1)$. The value of $V^e(r)$ can be calculated from values $\rho(r)$ and $\nabla^2\rho(r)$ in $CP(3,-1)$ using Kirzhnitz formula for kinetic energy density and local virial theorem expression [29]. We utilized this methodological background for detailed analysis the influence of the crystal packing on geometry and electron structure.

Both in experimental and calculated crystal packing, the molecules of **I** are assembled into centrosymmetric dimers via N(2)–H(2B)···O(1) hydrogen bonds (Fig. 2). The energy of latter bond is equal to 4.84 kcal/mol (calculated N···O, H···O distances are equal to 2.02 and 3.041 Å, the experimental N···O distance is 3.074(4) Å). Similar dimers in crystal packing of **III** are formed by more strong N(2)–H(2)···O(1) bonds (5.65 kcal/mol), the calculated H···O and N···O distances are 1.96 and 2.979 Å (the experimental value of latter distance is larger by 0.06 Å).

The energy of numerous weak C–H···O(Cl) bonds and Cl···Cl, Cl···O, Cl···N contacts vary in range 0.2 ÷ 1.5 kcal/mol. The topological analysis of $\boldsymbol{\rho}(r)$ allowed us to found in **II** rather strong C(2)···Cl(3′) and C(2′)···Cl(3) contacts with energies being equal to

Table 3
Structural parameters of calculated crystal structures and isolated molecules of **I–III**

Bond lengths and angles	Crystal			Isolated molecules		
	I[a]	**II**	**III**	**I**	**II**	**III**
Atomic bondings (Å)						
Ge(1)···O(1)	2.222	2.300 (A) 2.362 (B)	2.255	2.403	2.443	2.377
Ge(1)–Cl(1)	2.242	2.230 (A) 2.217 (B)	2.252	2.220	2.207	2.224
Ge(1)–Cl(2)	2.176	2.164	2.167	2.167	2.167	2.164
Ge(1)–Cl(3)	2.164	2.168	2.168	2.167	2.167	2.164
Ge(1)–C(1)	1.978	1.976	1.975	1.991	1.969	1.990
O(1)–C(2)	1.267	1.243	1.261	1.223	1.225	1.222
O(2)–C(1)	1.424	1.429	1.429	1.434	1.402	1.429
O(2)–C(2)	1.351	1.346	1.354	1.343	1.360	1.344
N(1)–C(2)	1.325		1.326	1.349		1.339
Valence angles (°)						
Cl(1)–Ge(1)–O(1)	174.07	172.29	174.79	170.2	174.0	170.6
O(2)–C(1)–Ge(1)	113.69	115.17	114.15	117.5	117.5	116.9
O(1)–C(2)–O(2)	121.18	120.95	121.25	123.3	117.4	123.0
C(2)–N(1)–C(3)	125.33			125.5		
O(1)–C(2)–N(1)	123.94		124.84	122.9		124.8

[a] The values for independent molecules A and B are presented, otherwise averaged values are shown.

Table 4
Topological properties of selected chemical bonds in crystal and isolated molecules of **I**–**III**

Chemical bond	Compound											
	I				**II**				**III**			
	ρ(r)	$\nabla^2\rho(r)$	$E^e(r)$	$V^e(r)$	$\rho(r)$	$\nabla^2\rho(r)$	$E^e(r)$	$V^e(r)$	$\rho(r)$	$\nabla^2\rho(r)$	$E^e(r)$	$V^e(r)$
Crystal												
Ge(1)···O(1)	0.43	4.23	−0.10	−0.49	0.37	3.38	−0.07	−0.38 (A)	0.40	3.89	−0.09	−0.44
					0.32	2.84	−0.06	−0.31 (B)				
Ge(1)–Cl(1)	0.68	3.61	−0.34	−0.93	0.71	3.57	−0.37	−0.99	0.67	3.52	−0.34	−0.92
Ge–Cl_{eq}	0.80	3.74	−0.46	−1.18	0.80	3.88	−0.46	−1.20	0.80	3.90	−0.47	−1.21
Ge(1)–C(1)	0.95	0.22	−0.72	−1.50	0.95	0.69	−0.73	−1.50	0.96	0.73?	−0.73	−1.51
N(1) –H(1)···O(1)	0.15	0.46	0.005	−0.10					0.17	1.79	0.002	−0.12
Isolated molecule												
Ge(1)···O(1)	0.23	2.42	−0.02	−0.22	0.24	2.20	−0.01	−0.17	0.25	2.54	−0.03	−0.24
Ge(1)–Cl(1)	0.61	2.67	−0.29	−0.75	0.56	3.42	−0.18	−0.59	0.58	3.47	−0.26	−0.75
Ge–Cl_{eq}	0.68	2.66	−0.34	−0.86	0.59	3.41	−0.19	−0.62	0.65	3.77	−0.30	−0.87
Ge(1)–C(1)	0.87	0.12	−0.54	−1.07	0.78	1.27	−0.35	−0.79	0.83	2.03	−0.47	−1.08

The values of $V^e(r)$ are given in a.u. while $\rho(r)$, $E^e(r)$ and $\nabla^2\rho$(r) are given in e Å^{-3} and Å^{-5}, respectively.

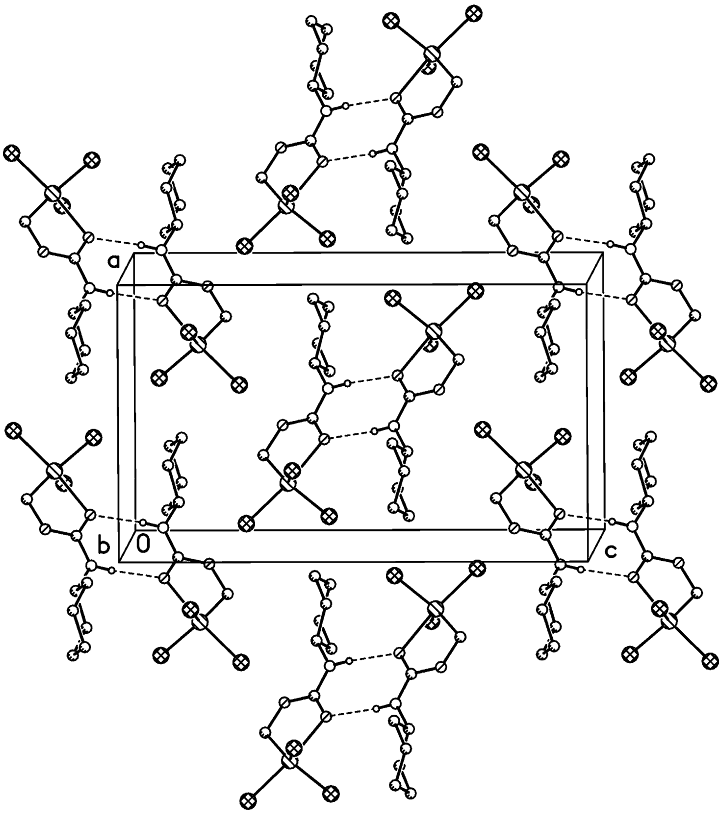

Fig. 2. H-bonded dimers in crystal structure of **III**.

5.65 kcal/mol, on average. The calculated C(2)···Cl(3′) and C(2′)···Cl(3) distances are 3.378 and 3.331 Å are less than sum of van der Waals radii of C and Cl atoms (3.57 Å) [30]. The experimental values for such distances are 3.419(3) and 3.400(3) Å. In terms of AIM theory C(2)···Cl(3′) and C(2′)···Cl(3) contacts corresponds to so-called “peak and hole” interactions, that is interaction of a lone electron pair of Cl atom with antibonding orbital of C(2′)–O(2′) bond (Fig. 3).

Thus, the presence of C(2)···Cl(3′) contacts and C–H···O(2) weak hydrogen bonds causes the distortion of planarity of five-membered helate cycle in comparison to the form of latter in isolated molecule **II**. Actually, in isolated molecule of **II** the conformation of such cycle is considerably flattened in comparison to molecule in crystal.

On the base of AIM theory it is of interest to analyze the differences between two independent molecules in the crystal structure of **II**. This can be done by the summation of the

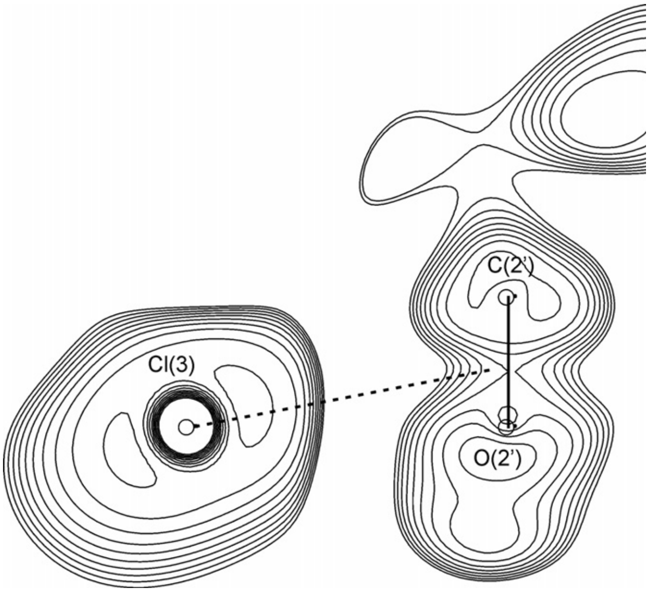

Fig. 3. The section of electron localization function illustrating the interaction of lone electron pair of the Cl(2) with antibonding orbital of the C(2′)–O(2′) bond of adjacent molecule in crystal structure of **II**.

energies of contacts of each independent molecule considering them separately. The sum of contacts energies for molecule A is 21.2 kcal/mol while for B this value is equal to 22.6 kcal/mol. Indeed the difference is rather small, but one should keep in mind that potential function of Ge···O interatomic distance is very flat therefore weak intermolecular contacts can significantly affect it. The evaluation of the energy of Ge···O coordination bond in crystal of **I–III** have revealed that it vary in rather narrow range (14.4–22.9 kcal/mol). Unfortunately in literature we could not find the results of evaluation of Ge···O(N) coordinative bonds energies by means of theoretical or spectral methods. Hovewer, for comparison we can use the articles describing the silatranes [31,32]. According to this literature data the energy of Si···N coordination bonds in different silatranes vary in the range of 10–20 kcal/mol that is close to calculated values for **I–III**. The strongest Ge···O bond found in **I**, while the weakest one is observed in **II** (14.4 kcal/mol in molecule B). It is interesting to note that the energies of Ge(1)···O(1) (17.71 kcal/mol) and Ge(1′)···O(1′) bonds differs by $\sim$3 kcal/mol, the discrepancy in interatomic distance between Ge and O atom is 0.07 Å. The value of Ge···O coordination bond energy in **III** is 20.6 kcal/mol that is close to corresponding value for **I**. In isolated molecules of **I–III** the energy of Ge···O coordination bonds vary in range of the 9.3–10.1 kcal/mol (Table 4). So one may propose that the influence of nature of exocyclic substituent at carbonyl group in isolated molecules **I–III** is negligible.

4. Conclusion

Similarly to Ge–N bonds in germatranes [24–27] the Ge···O coordination bonds in studied molecules can be described as weak interatomic interaction with high ionic contribution. The energy of such bonds mostly depends on crystal packing effects in more extent than the nature of ligand. In isolated molecules **I–III** the geometrical parameters and peculiarities of electron structure are nearly the same as in case of those crystal structures. The only significant difference is the strengthening of Ge···O coordinative bonds to 5–11 kcal/mol in crystal compared to those in isolated molecules. In addition the influence of crystal packing lead to some distortion of five-membered Ge-containing ring.

Thus, the usage quantum chemical calculations both for crystal structures obtained by single crystal X-ray diffraction and isolated molecules **I–III** allowed one to study in details the nature of Ge···O bond and describe the role of crystal packing.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2007.04 .019.

References

[1] S.N. Gurkova, A.I. Gusev, N.V. Alekseev, T.K. Gar, Dokl. Akad. Nauk SSSR (Proc. Nat. Acad. Sci. USSR) 266 (1982) 6 1399 (in Russian).
[2] S.N. Tandura, S.N. Gurkova, A.I. Gusev, N.V.Alekseev, Stroenie biologicheski aktivnykh soedinenii germaniya s rasshirennoi koordinatsionnoi sferoi [Structures of Biologically Active Germanium Compounds with Extended Coordination Sphere], NIITEKhIM, Moscow, 1983 (in Russian).
[3] Cambridge Structural Database, release October 2005.
[4] A.A. Korlyukov, N.V. Alekseev, K.V. Pavlov, O.V. Krivolapova, V.G. Lakhtin, E.A. Chernyshev, M.Yu. Antipin, Russ. Chem. Bull. 7 (2005) 1623.
[5] A.A. Korlyukov, N.V. Alekseev, K.V. Pavlov, O.V. Krivolapova, V.G. Lakhtin, E.A. Chernyshev, M.Yu. Antipin, Dokl. Chem. 397 (2004) 161.
[6] K.V. Pavlov, N.A. Viktorov, V.F. Mironov, Organomet. Chem. USSR 5 (4) (1992) 552.
[7] Programs SMART (1998), SAINT (1999), Bruker-AXS Inc., Madison, WI (USA); G.M. Sheldrick, SADABS, v.2.01 Bruker/Siemens Area Detector Absorption Correction.
[8] G.M. Sheldrick, SHELXTL-97 V5.10, Bruker AXS, Madison, WI-53719, USA, 1997.
[9] (a) G. Kresse, J. Hafner, Phys. Rev. B 47 (1993) RC558;
(b) G. Kresse, Thesis, Technische Universitat Wien, 1993;
(c) G. Kresse, J. Furthmuller, Comput. Mat. Sci. 6 (1996) 15–50;
(d) G. Kresse, J. Furthmuller, Phys. Rev. B 54 (1996) 11169.
[10] J.P. Perdew, S. Burke, M. Ernzerhopf, Phys. Rev. Let. 77 (1996) 3865.

[11] H.J. Monkhorst, J.D. Pack, Phys. Rev. B13 (1976) 5188.

[12] R.F.W. Bader, Atoms In molecules A Quantum Theory, Clarendron Press, Oxford, 1990.

[13] X. Gonze, J.-M. Beuken, R. Caracas, F. Detraux, M. Fuchs, G.-M. Rignanese, L. Sindic, M. Verstraete, G. Zerah, F. Jollet, M. Torrent, A. Roy, M. Mikami, Ph. Ghosez, J.-Y. Raty, D.C. Allan, Comput. Mater. Sci. 25 (2002) 478.

[14] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez, J.A. Pople, Gaussian 98W, Rev A.8; Gaussian Inc., Pittsburgh, PA, 1998.

[15] (a) J. Cheeseman, T.A. Keith, R.W.F. Bader, AIMPAC Program Package, McMaster University, Hamilton, Ontario, 1992;
(b) F.W. Biegler-König, R.F.W. Bader, J. Comput. Chem. 3 (1982) 317.

[16] A.K. Nuridzhanyan, S.N. Gurkova, A.I. Gusev, Russ. Chem. Bull 4 (1993) 762 (Engl. Transl.).

[17] I. Yu, Baukov A.G. Shipov, Yu. E. Ovchinnikov, Yu. T. Struchkov, Russ. Chem. Bull 6 (1994) 917 (Engl. Transl.).

[18] M.J. Barrow, S. Creadoc, E.A. Ebsworth, D.W.H. Rankin, J. Chem. Soc. Dalton Trans. (1981) 1988.

[19] W.J. McGahren, J.H. Martin, G.O. Morton, R.T. Hargreaves, R.A. Leese, F.M. Lovell, G.A. Ellestad, E. O'Brien, J.S.E. Holker, J. Am. Chem. Soc. 102 (1980) 1671.

[20] N.V. Alekseev, S.P. Knyazev, E.A. Chernyshev, I.A. Abronin, Russ. Chem. Bull. 47 (1998) 3367.

[21] A.A. Korlyukov, K.A. Lyssenko, M.Yu. Antipin, V.N. Kirin, E.A. Chernyshev, S.P. Knyazev, Inorg. Chem. 41 (2002) 5043.

[22] A.A. Korlyukov, K.A. Lyssenko, M.Yu. Antipin, A.G. Shipov, O.A. Zamyshlyaeva, E.P. Kramarova, Vad.V. Negrebetsky, S.A. Pogozhikh, Yu.E. Ovchinnikov, Yu.I. Baukov, Russ. Chem. Bull. 53 (2004) 1924.

[23] A.A. Korlyukov, K.A. Lyssenko, M.Yu. Antipin, Russ. Chem. Bull. 51 (2002) 1423.

[24] P.L. Shutov, S.S. Karlov, K. Harms, D.A. Tyurin, M.V. Zabalov, A.V. Churakov, J.A.K. Howard, J. Lorberth, G.S. Zaitseva, J. Mol. Struct. 689 (2004) 261.

[25] S.S. Karlov, D.A. Tyurin, M.V. Zabalov, A.V. Churakov, G.S. Zaitseva, J. Mol. Struct.: THEOCHEM 724 (2005) 31.

[26] A.A. Milov, R.M. Minyaev, V.I. Minkin, Russ. J. Org. Chem. 39 (2003) 340.

[27] S. Belyakov, L. Ignatovich, E. Lukevics, J. Organomet. Chem. 577 (1999) 205.

[28] E. Espinosa, E. Molins, C. Lecomte, Chem. Phys. Letts 285 (1998) 170.

[29] Yu.A. Abramov, Acta Crystallogr. A53 (1997) 264.

[30] R.S. Rowland, R. Taylor, Phys. Chem. 100 (1996) 7384.

[31] F. Rioux, M.W. Schmidt, M.S. Gordon, Organometallics 16 (1997) 158.

[32] E.I. Brodskaya, M.G. Voronkov, Bull. Acad. Sci. USSR, Chem. Sci. (Engl. Transl.) (1986) 1546.