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Structure of 3,3'-Bis-(tribromogermyl)propionic Acid According to the Results of *ab initio* Calculations

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Abstract—The nonempirical quantum-chemical calculations of the molecule of 3,3-bis-(tribromogermyl)-propionic acid by RHF/6-31G(d) and MP2/6-31G(d) methods were performed with full optimization of its geometry. The results of calculations by the two methods do not differ fundamentally. The calculations showed that two forms of this molecule are stable: one containing two tetrahedrally coordinated Ge atom and another with one tetrahedrally coordinated and one pentacoordinated Ge atom. The first form is typical of the crystalline state of the matter, the second is the most energy-effective for the gas. At the intramolecular interaction between the carbonyl oxygen atom and the Ge atom in the second form leading to its pentacoordination the corresponding Ge–Br bonds are polarized in such a way that the negative charges on the Br atoms and a positive charge on the Ge increase. No transfer of electron density from the oxygen to the germanium was revealed.

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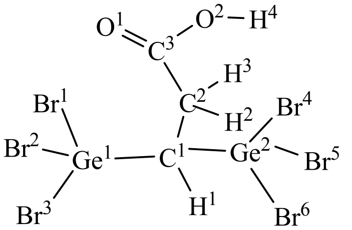
In a significant number of organyltrichlorogermanes obeying the conditions of the Ge atom pentacoordination [1–3] the coordination interaction of the germanium occurs with the heteroatom of the organic substituent. Such an interaction is presumable in the molecule of 3,3-bis-(tribromogermyl)propionic acid between the oxygen atom of the carbonyl group and one or two Ge atoms, because the structure of this molecule allows their pentacoordination [1–3]. However, XRD data for the 3,3-bis-(tribromogermyl)-propionic acid [4] indicate the absence of such interaction. According to these data, the nonvalent distances between the carbonyl oxygen atom and Ge atoms are significantly greater than the sum of their van der Waals radii, 3.69 and and 4.57 Å, respectively. At the same time this interaction can be assumed in the gaseous state of the matter, since the structure of the matter may significantly depend on its aggregative state. For example, the quantum-chemical calculations of the system $SiCl_4$–$N(CH_3)_3$ and $GeCl_4$–$N(CH_3)_3$ show [5, 6] that in the gaseous state they exist practically as individual components, while the spectra of nuclear quadrupole resonance (NQR) on the ^{35}Cl nuclei at 77 K clearly indicate [7, 8] that these systems in the crystalline state are complexes, the coordination polyhedron of the electron-acceptor central atom has the structure of a trigonal bipyramid. For the complex $GeCl_4 \leftarrow N(CH_3)_3$ the same structure has also been established by XRD analysis [9]. These and other complexes of the tetrachlorides of group IVA elements with organic ligands of trigonal-bipyramidal structure usually are energetically less favorable than the individual components of the systems [5, 6, 10].

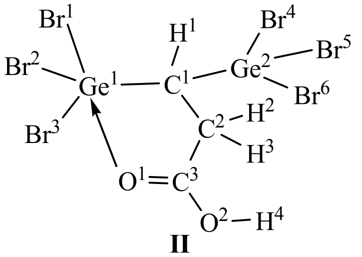
The ^{35}Cl NQR data [11] and quantum chemical calculations [12] showed that in 2,6-dimethoxyphenyltrichlorostannane the Sn atom became pentacoordinated as a result of intramolecular interaction with only one oxygen atom, despite the equal probability of its interaction with the other oxygen atoms. A similar situation exists in the molecule of 3,3-bis(tribromogermyl)propionic acid. However, in this molecule, unlike the previous case, there are two electron-withdrawing and one electron-donating center.

The aim of this work was to reveal the structure of 3,3-bis(tribromogermyl)propionic acid in the gaseous state and the possibility of formation of the Ge←O coordination bond in this molecule with one or two Ge atoms. To solve the problem, we performed a nonempirical quantum-chemical calculations of the molecule of 3,3-bis(tribromogermyl)propionic acid by RHF/6-31G(d) and MP2/6-31G(d) methods with full optimization of its geometry using GAUSSIAN 03W software [13].

According to the RHF/6-31G(d) calculation, the molecule of 3,3-bis-(tribromogermyl)propionic acid has two stable forms: one with two tetrahedrally coordinated Ge atoms (**I**) and the other with one tetra- and one pentacoordinated Ge atoms (**II**).



I



II

The imaginary frequencies of stretching vibrations in these structures are absent. In structure **I** the Ge^1···O^1 and Ge^2···O^1 distances (Table 1) are close to those found by XRD [4]. These distances are considerably greater than the sum of the van der Waals radii of Ge and O atoms (3.4 Å [4]). In structure **II** the Ge^1···O^1 distance is considerably shorter, while Ge^2–O^1 longer than the sum of the van der Waals radii of Ge and O atoms (Table 2). Consequently, the Ge^1 atom is penta-, while the Ge^2 is tetracoordinated. The calculated Ge–Br and O^1–C^1 bonds in the structure **I**, taking into account the zero point energy, is by 1.36 kcal mol^{-1} higher than that of structure **II**. However, in the crystalline state the molecule of 3,3-bis-(tri-bromogermyl)propionic acid is in the energetically less favorable form **I**. Its geometric characteristics are in accordance with the XRD data (Table 1). However, quite naturally, the full compliance of the data calculated for individual molecules and the experimental data for the crystalline state of matter is not observed. The calculated bond distances of Ge–Br and O^1–C^3 in the structure **I** are somewhat longer, while Ge–C^1, O^2–C^3 and C–C, on the contrary, shorter than the experimental ones. The calculated and experimental values of bond angles in this structure are close, with the exception of the angles C^{1}C^{2}C^3 and C^{2}C^{3}O^2.

In structure **II** the lengths of all three Ge^1–Br bonds are significantly different, which is not typical of the coordination polyhedron of tetracoordinated Ge atom with the trigonal–bipyramidal structure. Two Ge^2–Br bonds of tetrahedrally coordinated Ge atom are identical, and the third is much longer, that, on the

Table 1. Bond lengths (*d*), bond (ω) and torsion (β) angles in structure **I** calculated by the RHF/6-31G(d) and MP2/6-31G(d) methods, as well as XRD data [4]

Bond	*d*, Å			Angle	ω, deg			Angle	β, deg	
	RHF	MP2	XRD		RHF	MP2	XRD		RHF	MP2
Ge^1–Br^1	2.289	2.302	2.272	Br^{1}Ge^{1}C^1	109.66	108.75	106	Br^{1}Ge^{1}C^{1}C^2	–82.38	–82.30
Ge^1–Br^2	2.287	2.298	2.271	Br^{1}Ge^{1}Br^2	106.02	105.86	108.4	Br^{1}Ge^{1}C^{1}Ge^2	43.53	40.91
Ge^1–Br^3	2.276	2.288	2.267	Br^{1}Ge^{1}Br^3	109.39	109.96	109.1	Br^{1}Ge^{1}C^{1}H^1	158.75	157.46
Ge^1–C^1	1.932	1.923	1.98	Br^{2}Ge^{1}Br^3	108.96	110.51	106.5	Br^{2}Ge^{1}C^{1}C^2	34.68	33.99
Ge^2–Br^4	2.285	2.297	2.261	Br^{2}Ge^{1}C^1	111.42	111.38	116	Br^{3}Ge^{1}C^{1}C^2	156.48	157.07
Ge^2–Br^5	2.272	2.285	2.249	Br^{3}Ge^{1}C^1	111.25	110.27	112	Br^{2}Ge^{1}C^{1}Ge^2	160.58	157.20
Ge^2–Br^6	2.293	2.305	2.274	Ge^{1}C^{1}C^2	111.61	110.98	107	Br^{3}Ge^{1}C^{1}Ge^2	–77.61	–79.73
Ge^2–C^1	1.931	1.923	1.94	Br^{4}Ge^{2}C^1	113.70	113.57	113	Br^{4}Ge^{2}C^{1}C^2	44.49	40.65
C^1–C^2	1.537	1.529	1.67	Br^{5}Ge^{2}C^1	111.22	110.35	112	Br^{5}Ge^{2}C^{1}C^2	168.51	164.50
C^2–C^3	1.520	1.523	1.61	Br^{6}Ge^{2}C^1	106.30	105.67	105	Br^{6}Ge^{2}C^{1}C^2	–70.94	–73.82
O^1–C^3	1.181	1.213	1.15	Ge^{2}C^{1}C^2	109.74	110.98	107	Ge^{1}C^{1}C^{2}C^3	–85.87	–83.47
O^2–C^3	1.328	1.356	1.35	Ge^{1}C^{1}H^1	105.76	106.87	–	Ge^{2}C^{1}C^{2}C^3	145.35	151.63
C^1–H^1	1.084	1.099	–	Ge^{2}C^{1}H^1	104.85	106.49	–	C^{1}C^{2}C^{3}O^1	–14.64	–14.24
C^2–H^2	1.085	1.098	–	C^{1}C^{2}C^3	111.60	109.93	101.0	C^{1}C^{2}C^{3}O^2	167.70	168.22
C^2–H^3	1.088	1.101	–	C^{2}C^{3}O^1	123.47	106.83	130.0	C^{2}C^{3}O^{2}H^4	–3.87	–3.87
O^2–H^4	0.948	0.975	–	C^{2}C^{3}O^2	115.33	123.52	104.0	C^{3}C^{2}C^{1}H^1	30.82	34.74
Ge^1···O^1	3.722	3.621	3.69	O^{1}C^{3}O^2	121.15	120.86	126.0	Ge^{1}C^{1}C^{2}H^2	37.44	38.87
Ge^2···O^1	4.469	4.505	4.57	C^{3}O^{2}H^4	112.84	110.15	–	Ge^{1}C^{1}C^{2}H^3	155.54	157.23
				C^{1}C^{2}H^2	110.67	110.26	–			

Table 2. Bond lengths (*d*), bond (ω) and torsion (β) angles in structure **II** calculated by the RHF/6-31G(d) and MP2/6-31G(d) methods

Bond	*d*, Å		Angle	ω, deg		Angle	β, deg	
	RHF	MP2		RHF	MP2		RHF	MP2
Ge^1–Br^1	2.312	2.344	$Br^1Ge^1C^1$	104.35	99.77	$Br^1Ge^1C^1C^2$	144.75	154.77
Ge^1–Br^2	2.290	2.302	$Br^1Ge^1Br^2$	104.40	102.65	$Br^1Ge^1C^1Ge^2$	–84.64	–82.10
Ge^1–Br^3	2.272	2.295	$Br^1Ge^1Br^3$	104.88	101.68	$Br^1Ge^1C^1H^1$	26.30	31.53
Ge^1–C^1	1.946	1.945	$Br^2Ge^1Br^3$	112.44	115.53	$Br^2Ge^1C^1C^2$	32.44	45.66
Ge^2–Br^4	2.306	2.314	$Br^2Ge^1C^1$	111.90	115.33	$Br^3Ge^1C^1C^2$	–99.73	–96.38
Ge^2–Br^5	2.274	2.278	$Br^3Ge^1C^1$	117.37	117.80	$Br^2Ge^1C^1Ge^2$	163.05	168.80
Ge^2–Br^6	2.274	2.296	$Ge^1C^1C^2$	115.33	115.02	$Br^3Ge^1C^1Ge^2$	30.88	26.75
Ge^2–C^1	1.936	1.931	$Br^4Ge^2C^1$	105.92	105.92	$Br^4Ge^2C^1C^2$	–61.03	–66.41
C^1–C^2	1.535	1.528	$Br^5Ge^2C^1$	112.49	117.22	$Br^5Ge^2C^1C^2$	–179.17	170.92
C^2–C^3	1.514	1.515	$Br^6Ge^2C^1$	113.62	108.33	$Br^6Ge^2C^1C^2$	55.60	47.28
O^1–C^3	1.185	1.223	$Ge^2C^1C^2$	111.62	109.15	$Ge^1C^1C^2C^3$	50.67	36.74
O^2–C^3	1.321	1.341	$Ge^1C^1Ge^2$	113.54	109.26	$Ge^2C^1C^2C^3$	–80.85	–86.45
C^1–H^1	1.086	1.097	$Ge^1C^1H^1$	103.22	104.80	$C^1C^2C^3O^1$	–22.20	–23.16
C^2–H^2	1.085	1.099	$C^1C^2C^3$	112.61	110.44	$C^1C^2C^3O^2$	160.80	161.31
C^2–H^3	1.087	1.099	$C^2C^3O^1$	121.77	121.50	$C^2C^3O^2H^4$	–4.45	–7.40
O^2–H^4	0.948	0.976	$C^2C^3O^2$	116.92	118.19	$C^3C^2C^1H^1$	166.0	156.14
$Ge^1\cdots O^1$	2.805	2.481	$O^1C^3O^2$	121.25	120.16	$Ge^1C^1C^2H^2$	174.85	160.10
$Ge^2\cdots O^1$	3.705	3.749	$C^3O^2H^4$	112.90	110.22	$Ge^1C^1C^2H^3$	–67.30	–80.64
			$C^1C^2H^2$	110.61	111.69			

contrary, is characteristic of the coordination polyhedron of the trigonal–bipyramidal structure. The longest Ge^2–Br^4 bond in the Ge^2Br_3 group with tetrahedrally coordinated Ge atoms is shorter than the longest Ge^1–Br^1 bond in the Ge^1Br_3 group with tetracoordinnated Ge atom, as expected (Table 2). The length of the Ge^2–Br_4 bond is much more different from the other two bonds in the Ge^2Br_3 group, as compared with the difference between the bond lengths in the Ge^1Br_3 group.

Table 3. Atomic charges (*q*, e) on the atoms in structures **I** and **II** calculated by the RHF/6-31G(d) and MP2/6-31G(d) methods

Atom	**I**		**II**	
	RHF	MP2	RHF	MP2
Br^1	–0.214	–0.215	–0.235	–0.270
Br^2	–0.190	–0.188	–0.211	–0.203
Br^3	–0.180	–0.182	–0.195	–0.210
Ge^1	0.715	0.715	0.799	0.832
Br^4	–0.198	–0.200	–0.223	–0.221
Br^5	–0.173	–0.172	–0.167	–0.146
Br^6	–0.217	–0.222	–0.184	–0.217
Ge^2	0.711	0.712	0.694	0.689
C^1	–0.593	–0.589	–0.605	–0.609
C^2	–0.503	–0.505	–0.489	–0.479
C^3	0.818	0.839	0.819	0.850
O^1	–0.522	–0.542	–0.538	–0.573
O^2	–0.691	–0.703	–0.683	–0.685
H^1	0.305	0.309	0.268	0.277
H^2	0.219	0.224	0.220	0.223
H^3	0.243	0.249	0.255	0.261
H^4	0.471	0.470	0.475	0.478

For more reliable establishment of the structure of 3,3-bis-(tribromogermyl)propionic acid we performed calculations of structures **I** and **II** on a higher level, by MR2/6-31G(d) method. The results of calculations by both methods do not differ fundamentally. According to the MR2/6-31G(d) calculations, in structure **I** the Ge^1–O^1 and Ge^2–O^1 distances are also greater than the sum of the van der Waals radii of Ge and O atoms (Table 1), while in the structure **II** the Ge^1–O^1 distance is considerably shorter and the Ge^2–O^1 distance is longer than this sum (Table 2). The of Ge^1–O^1 distance in structure **II** calculated by the MR2.6-31G(d) method is significantly less than obtained in the RHF/6-31G(d) calculation. The structure of **I** calculated by MR2/6-31G(d) is energetically less favorable than the structure **II**, like in the RHF/6-31G(d) calculation. The total energy of the latter is by 4.71 kcal mol^{-1} lower than the former. Judging from the dihedral angles, the steric structures of **I** are obtained almost equal in both calculations, the same concerns structure **II**. The difference in bond lengths and bond angles in each of these structures, calculated by both methods, insignificant.

According to the MR2/6-31G(d) calculations of structure **II** the coordination polyhedron of the Ge^1 atom is a distorted trigonal bipyramid with the axial

Ge^1–Br^1 bond much longer than the two equatorial bonds, Ge^1–Br^2 and Ge^1–Br^3, which only slightly differ in length. The bond angles of pentacoordinated Ge atom are closer to those of an ideal coordination polyhedron of the trigonal–bipyramidal structure than the corresponding angles obtained in the RHF/6-31G(d) calculation of the structure **II**. All three Ge^2–Br bonds of tetracoordinated Ge atom in this structure, as well as the bond angles of the Ge atom calculated by the MP2/6-31G(d) method, differ greatly.

Mulliken charges of atoms in structure **I** calculated by both methods do not differ practically, except for the atoms O^1 and O^2, whereas the atomic charges in the Ge–Br and C=O groups in structure **II** differ significantly (Table 3). In going from structure **I** to structure **II**, the total negative charge of the three Br atoms in the group Ge^2Br_3 and the positive charge of the atom Ge^2 are changed insignificantly, whereas the partial negative charges on the Br atoms in the Ge^1Br_3 group, the axial in particular, and of one O atom, as well as the positive charge on the Ge atom increase substantially. These data do not agree with the transfer of electron density from the carbonyl oxygen atom on the Ge atom through their non-valence interaction. If such an interaction occurred, the Ge^1–Br covalent bonds should be polarized, resulting in increased electron density on the Br atoms. A similar situation exists in organyltrichlorgermanes: here this interaction leads to an increase in the electron density on the chlorine, especially axial, and oxygen atoms, as well as to a significant decrease in the electron density on the Ge atom [14, 15]).

Thus, the molecules of 3,3-bis-(tribromogermyl)-propionic acid in crystalline state have structure **I** with two tetrahedrally coordinated Ge atoms, while in the gas state structure **II** with one tetra- and one tetracoordinated Ge atom is energetically more favorable. Therewith, the coordination polyhedron of the pentacoordinated Ge atom in the structure **II** is a distorted trigonal bipyramid. In the case of non-valent intramolecular interaction between the carbonyl oxygen atom and the Ge atom, leading to pentacoordination of the latter in structure **II**, its Ge–Br bonds are polarized in such a way that the partial negative charges on the Br atoms and the positive charge on the Ge atom increase. At the same time the negative charge of the carbonyl oxygen atom also increases. This is not consistent with the idea of the electron density transfer from the oxygen atom on the Ge atom in such a non-valence interaction.

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