Synthesis and structure of (trichlorogermyl)methyl adamantane-1-carboxylate

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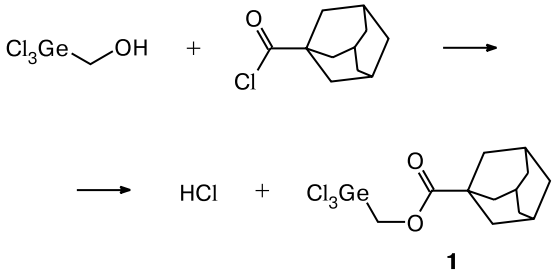
The reaction of adamantane-1-carboxylic acid chloride with trichlorogermylmethanol afforded (trichlorogermyl)methyl adamantane-1-carboxylate, whose molecular structure was established by ^{1}H NMR spectroscopy and X-ray diffraction analysis.

Key words: organogermanium compounds, X-ray diffraction analysis, ^{1}H NMR spectroscopy, esters.

Organogermanes of the general formula $X_3Ge—CH_2—Y—C(O)—R$ with the pentacoordinate germanium atom have long attracted the attention of researchers in synthetic and theoretical organic chemistry. Pioneering studies of the molecular structures of these compounds have been performed in the early 1980s.[1,2] Since then the crystal and molecular structures of 23 compounds belonging to this class, in which X = Cl or Me, and Y = CH_2 or N, were studied (data from the latest release of the Cambridge Structural Database[3]). Besides, several molecules with X = Ph, in which additional Ge...O interactions are absent, were investigated. Up to now, the crystal and molecular structures of related compounds with Y = O have remained unknown. In the present study, we synthesized a compound of the latter type, *viz.*, (trichlorogermyl)methyl adamantane-1-carboxylate (**1**), starting from adamantane-1-carboxylic acid chloride and trichlorogermylmethanol.



1

The structure of compound **1** was confirmed by ^{1}H NMR spectroscopy and X-ray diffraction analysis (Fig. 1, Table 1).

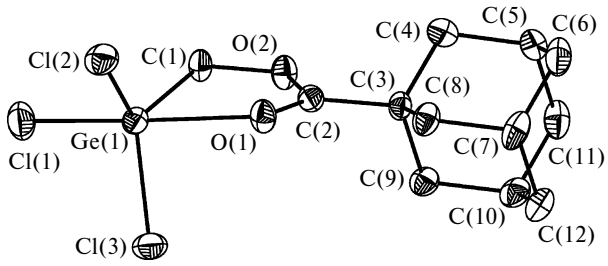


Fig. 1. Molecular structure of (trichlorogermyl)methyl adamantane-1-carboxylate.

In the unit cell of **1**, two crystallographically independent molecules (A and B) occupy two fourfold general positions. The structural parameters of two independent molecules are slightly different.

In both independent molecules, the germanium atoms are pentacoordinate. Their coordination polyhedra can be described as slightly distorted trigonal bipyramids, whose equatorial planes are formed by the C(1), Cl(2), Cl(3) and C(1′), Cl(2′), Cl(3′) atoms and the axial positions are occupied by the Cl(1) and Cl(1′) atoms and the O(1) and O(1′) atoms of the carbonyl groups. The germanium atoms deviate from the equatorial planes toward the axial chlorine atoms by 0.34 and 0.36 Å in molecules A and B, respectively. The Ge—O distances are 2.322(2) Å (in molecules A) and 2.374(3) Å (in molecules B). These distances are much smaller than the sum of the van der Waals radii of the germanium and oxygen atoms (~3.4—3.7 Å)[2,4,5] but are larger than the sum of the covalent radii of these elements (~1.88 Å).[6] Slight differences in the Ge—O distances have virtually no effect on the

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Table 1. Principal interatomic distances (*d*) and bond angles (ω) in molecule **1**

Bond	*d*/Å	Angle	ω/deg
Ge(1)—C(1)	1.963(3)	C(1)—Ge(1)—Cl(1)	98.6(1)
Ge(1)—Cl(1)	2.190(1)	Cl(3)—Ge(1)—Cl(1)	99.7(4)
Ge(1)—Cl(2)	2.136(1)	Cl(2)—Ge(1)—Cl(1)	100.4(5)
Ge(1)—Cl(3)	2.130(1)	C(1)—Ge(1)—Cl(3)	119.9(1)
Ge(1)—O(1)	2.322(2)	C(1)—Ge(1)—Cl(2)	119.9(1)
O(1)—C(2)	1.229(4)	Cl(3)—Ge(1)—Cl(2)	112.2(4)
O(2)—C(1)	1.421(4)	Cl(1)—Ge(1)—O(1)	173.1(6)
O(2)—C(2)	1.341(4)	O(2)—C(1)—Ge(1)	115.4(2)
C(2)—C(3)	1.498(5)	C(2)—O(2)—C(1)	117.5(2)
Ge(1′)—C(1′)	1.947(3)	O(1)—C(2)—O(2)	120.0(3)
Ge(1′)—Cl(1′)	2.189(1)	O(1)—C(2)—C(3)	126.3(3)
Ge(1′)—Cl(2′)	2.137(1)	C(2)—C(3)—C(4)	112.3(3)
Ge(1′)—Cl(3′)	2.121(1)	C(2)—C(3)—C(8)	110.1(3)
Ge(1′)—O(1′)	2.374(3)	C(1′)—Ge(1′)—Cl(1′)	99.0(1)
O(1′)—C(2′)	1.228(4)	Cl(3′)—Ge(1′)—Cl(1′)	100.7(4)
O(2′)—C(2′)	1.338(4)	Cl(2′)—Ge(1′)—Cl(1′)	100.5(5)
C(2′)—C(3′)	1.502(5)	C(1′)—Ge(1′)—Cl(3′)	119.7(1)
C—C_{av}*	1.533(5)	C(1′)—Ge(1′)—Cl(2′)	119.8(1)
		Cl(3′)—Ge(1′)—Cl(2′)	111.6(4)
		Cl(1′)—Ge(1′)—O(1′)	172.8(6)
		O(2′)—C(1′)—Ge(1′)	115.8(2)
		C(2′)—O(2′)—C(1′)	117.5(2)
		O(1′)—C(2′)—O(2′)	121.6(3)
		O(1′)—C(2′)—C(3′)	125.7(3)
		C(2′)—C(3′)—C(4′)	112.6(3)
		C(2′)—C(3′)—C(8′)	110.0(3)
		C—C—C_{av}*	109.7(3)

* In the adamantane fragments.

Cl_{ax}—Ge—O angles (173.1(1)° and 172.8(1)°; the larger angle corresponds to the shorter distance). The differences in the analogous (Cl, O)$_{eq}$—Ge—Cl_{ax} angles in both independent molecules are small, all differences being smaller than the experimental confidence intervals.

In both molecules, the axial Ge—Cl bonds are virtually equal (2.190 Å), whereas the equatorial Ge—Cl bonds are slightly different in length and are shorter than the axial bonds by *ca.* 0.06 Å. The larger differences are observed in the Ge—C bond lengths. As can be seen from Table 2, the Ge—C bond is slightly longer in the molecule, in which the Ge—O distance is shorter. The Ge—Cl and Ge—C interatomic distances averaged over two molecules are very similar to those observed in trichloro- and trimethylorganogermanes.[7]

The trichloroorganogermane molecules can be classified into two groups according to the nature of the substituent Y. In compounds, where Y = CH_2, the Ge—O distances vary over a wide range from 2.123 Å (in 2-methyl-3-(trichlorogermyl)propionic acid *N*,*N*′-dimethylamide[8]) to 3.228 Å (in 3-(trichlorogermyl)propionic acid[1]). The five-membered rings Cl_3Ge—C—Y—C(O)—R adopt an envelope conformation, where the carbon atom adjacent to Ge deviates from the plane through other four atoms. In the molecules with Y = N, the Ge—O distances vary over a much smaller range, from 2.080 Å to 2.354 Å (in most cases, *ca.* 2.2 Å). The above-mentioned five-membered rings in these molecules are nearly planar (for example, in *N*-trichlorogermylmethyl-*N*-methyl-4-methylbenzamide[9] and *N*-(dimethylchlorogermylmethyl)-*N*-(1-phenylethyl)acetamide[10]).

The structures of two independent molecules in the crystals of **1** correspond to neither the former nor the latter type. The Ge—O distances in these molecules are close to the upper limit of the values typical of molecules of the second type, whereas the five-membered rings in molecules A and B are nonplanar. These rings adopt an envelope conformation with the Ge atoms deviating from the plane of the H_2C—O—C=O fragment (planar within 0.01 Å) by 0.45 and 0.56 Å in molecules A and B, respectively. Therefore, the conformation of this ring is significantly different from that observed in the first type of molecules due to the fact that the C—H and Ge—Cl_{eq} bonds are arranged so as to minimize the torsional strain in the Cl_{eq}—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 involved in the ester fragment R—C(O)OCH_2—, in which all atoms lie, as a rule, in a single plane (for example, in methyl acetate[11] and methyl (3-chloro-4-hydroxyphenyl)glyoxylate[12]). Hence, it is the Ge atom that, most likely, deviates from the plane of the ring. As a result, the Cl_{eq}—Ge—C—H torsion angles ($63.5°_{av}$) are close to those observed in methyltrichlorogermane, in which the Ge—Cl bond is staggered with respect to the C—H bond (60°). It should be noted that the five-membered ring is more planar in molecule A with the shorter Ge—O distance.

Table 2. Hydrogen bonds in the crystal of **1**

Bond D—H...A	Symmetry transformation	Distance/Å		D—H—A angle /deg
		D...A	H...A	
C(1′)—H(1′A)...O(2′)	[$-x+2$, $-y+2$, $-z+1$]	3.284(4)	2.49	139
C(6′)—H(6′B)...Cl(1′)	[$-0.5+x$, $1.5-y$, $0.5+z$]	3.854(5)	2.87	164
C(1)—H(1A)...Cl(2′)	[x, y, z]	3.769(5)	2.90	143

It is interesting to compare the structure of the molecule under consideration with the structures of its silicon analogs. Data on the structures of about 30 molecules containing such fragments are available in the literature.[3] In molecules, where X are either F or F and Me, and R are substituted phenyl groups, the Si—O distances are in the range of 1.9—2.1 Å, and the five-membered rings Si—C—Y—C(O)—R are planar (for example, in (4-fluorophenyloxymethyl)trifluorosilane[13] and (phenyloxymethyl-C,O)difluoromethylsilane[14]). In molecules, in which the methyl, phenyl, or isopropyl groups are bound to the silicon atom in different combinations, the Si—O distances are at most 3.5 Å and the five-membered rings are not formed.

The intermolecular contacts formed by molecules A are typical of van der Waals interactions. Molecules B are linked by the C(1′)—H(1′A)...O(2′) and C(6′)—H(6′A)...Cl(1′) hydrogen bonds to form chains extended along the crystallographic [110] direction (see Table 2). The Cl(2′) atoms form weak bonds with the H(1A) atoms of the endocyclic methylene group of molecule A. It is the formation of C—H...Cl hydrogen bonds that is, most likely, responsible for a small difference in the equatorial Ge(1′)—Cl(3′) and Ge(1′)—Cl(2′) bond lengths (2.121(1) and 2.138(1) Å, respectively).

Since the radii of the sp^3-hybridized C(1) and C(1′) atoms are larger than the radii of the C(2) and C(2′) atoms of the carbonyl groups, the C—O bond lengths are noticeably different. The involvement of the oxygen atom of the carbonyl group in the Ge—O interaction does not lead to an essential change in its length.

The structure of the adamantyl fragment remains unchanged. Thus, the bond lengths, the bond angles, and the torsion angles are approximately equal to those observed in other substituted adamantanes.

Experimental

The ^{1}H NMR spectrum was recorded on a Bruker AM-360 spectrometer (360 MHz, $CDCl_3$). The results of single-crystal X-ray diffraction study of **1**, crystallographic data, and characteristics of structure refinement are given in Table 3. The structure was solved by direct methods and refined by the full-matrix least-squares method in the anisotropic-isotropic approximation against F^2. The hydrogen atoms were located from difference electron density syntheses and refined isotropically. All calculations were carried out with the use of the SHELXTL PLUS program package (version 5.0) on an IBM PC.

(Trichlorogermyl)methyl adamantane-1-carboxylate (1). Trichlorogermylmethanol (20.9 g, 0.1 mol) was added dropwise with stirring to adamantane-1-carboxylic acid chloride (19.6 g, 0.1 mol). The reaction mixture warmed up, which was accompanied by gas evolution and dissolution of the precipitate. After 15—20 min, adamantane-1-carboxylic acid chloride was completely dissolved. Then the reaction mixture was heated until gas evolution completely ceased. After cooling of the reaction mixture to room temperature, crystallization accompanied by heat evolution occurred. After recrystallization from hexane, (trichlorogermyl)methyl adamantane-1-carboxylate (**1**) was obtained in a yield of 31.7 g (85%), m.p. 85—88.5 °C. Found (%): C, 38.75; H, 4.55; Cl, 28.60; Ge, 19.47. $C_{12}H_{17}Cl_3GeO_2$. Calculated (%): C, 38.72; H, 4.60; Cl, 28.57; Ge, 19.51. ^{1}H NMR (25 °C, $CDCl_3$), δ: 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).

Table 3. Crystallographic data and parameters of the structure refinement of **1**

Parameter	Characteristic
Molecular formula	$C_{12}H_{17}Cl_3GeO_2$
Molecular weight	372.20
T/K	120(2)
Diffractometer	SMART 1000K
Scan type	ω scans
Scan range/deg	1.59—30.03
Radiation	Mo-Kα
λ/Å	0.71073
Crystal system	Monoclinic
Space group	$P2(1)/n$
a/Å	17.997(5)
b/Å	9.049(2)
c/Å	18.335(4)
α/deg	90.0
β/deg	90.043(7)
γ/deg	90.0
V/Å^3	2985.7(13)
Z	8
ρ_{calc}/mg m^{-3}	1.656
μ/mm^{-1}	2.580
F(000)	1504
Total number of measured reflections	18550
independent reflections	8485 (R_{int} = 0.0343)
R_1 ($I > 2\sigma(I)$)	0.0424
R factor based on all reflections	0.0909

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