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SYNTHESIS AND CRYSTAL STRUCTURE OF 1-(4-FLUOROPHENYL)-AND 1-(4-DIMETHYL-AMINO)PHENYLGERMATRANES

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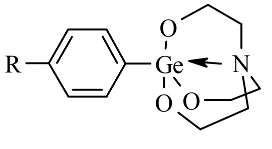
The X-ray crystal structure of 1-(4-fluorophenyl)- and 1-(4-dimethylaminophenyl)germatranes reveals that the germanium atom is pentacoordinated and adopts a trigonal bipyramidal geometry. The fluorophenyl and dimethylaminophenyl groups and the nitrogen atom each occupy an apical position with the transannular N→Ge bond of 2.192(3) and 2.249(3) Å; the deviation of the Ge atom from the O(2)–O(8)–O(9) plane is 0.2306(4) and 0.2693(3) Å, correspondingly.

Keywords: germatranes, crystal structure, synthesis, transannular N→Ge bond.

The transannular N→Ge bond length in 1-substituted germatranes containing the Ge–C bond depends on the hybridization state of the C atom and the electronegativity of the substituents bound to this atom. For C_{sp3} substituents (alkyl, cycloalkyl) it is in the range 2.24–2.27 Å [1] being the longest in 1-ada- mantylgermatrane (2.266 Å) [2]. Introduction of electronegative substituents into the alkyl group significantly shortens the N→Ge bond (2.167 for CH_2Cl, 2.146 for $CHCl_2$, and 2.108 Å for CF_3) [1]. This bond is shorter for germatranes with C_{sp2} substituents (aryl) but it is less influenced by the substituents in the aryl group, e.g. 2.156 for C_6F_5 [3] and 2.212 Å for C_6H_5 [3, 4]. The difference is even smaller for monosubstituted arylgermatranes (Table 1). This may be due to the relatively small substituent electronic effects in the investigated arylgermatranes. Therefore we decided to synthesize and investigate the molecular structure of arylgermatranes containing substituents with different electronic effects (F and Me_2N).

The 4-fluorophenylgermatrane (**1**) was prepared from 1-fluoro-4-iodobenzene by the germanium dibromide insertion method [4] and 4-dimethylaminophenylgermatrane (**2**) from N,N-dimethylaniline by the substitution reaction with germanium tetrachloride [5] followed by hydrolysis and cyclization with triethanolamine.



1 R = F, **2** R = NMe_2

In the crystal structure of germatrane **1** (Fig. 1) the molecules are packed as on a chessboard: the center of negative charges of one molecule corresponds to the positive center of another molecule (Fig. 2). The molecules are packed approximately parallel to the main symmetry axis (space group $P\ 2_1$). Thus, the crystal

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structure of germatrane **1** is chiral in spite of the absence of asymmetric atoms. Compound **1** is characterized by a significant value of the dipole moment (calculated value 4.99 D), which is directed along N–Ge–C_6H_4F bonds. This direction is almost coaxial to the positive direction of the monoclinic axis (*y* axis). Therefore, in crystals **1** the dipole moments are summarized and these crystals possess the piezoelectric effect: they are polarized and stick to the internal surface of vessels.

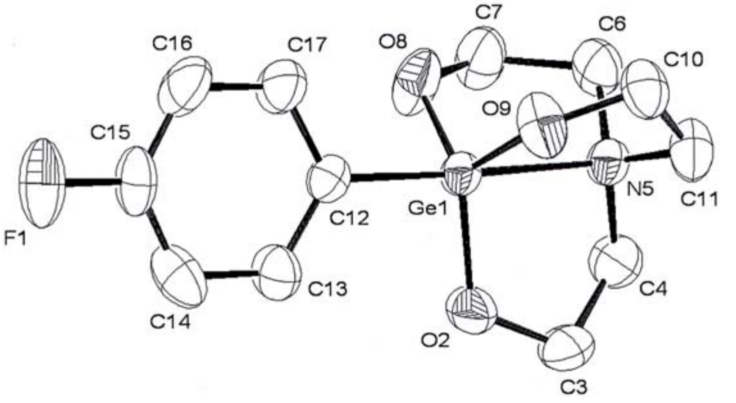

Fig. 1. Molecular structure of 1-(4-fluorophenyl)germatrane (**1**).

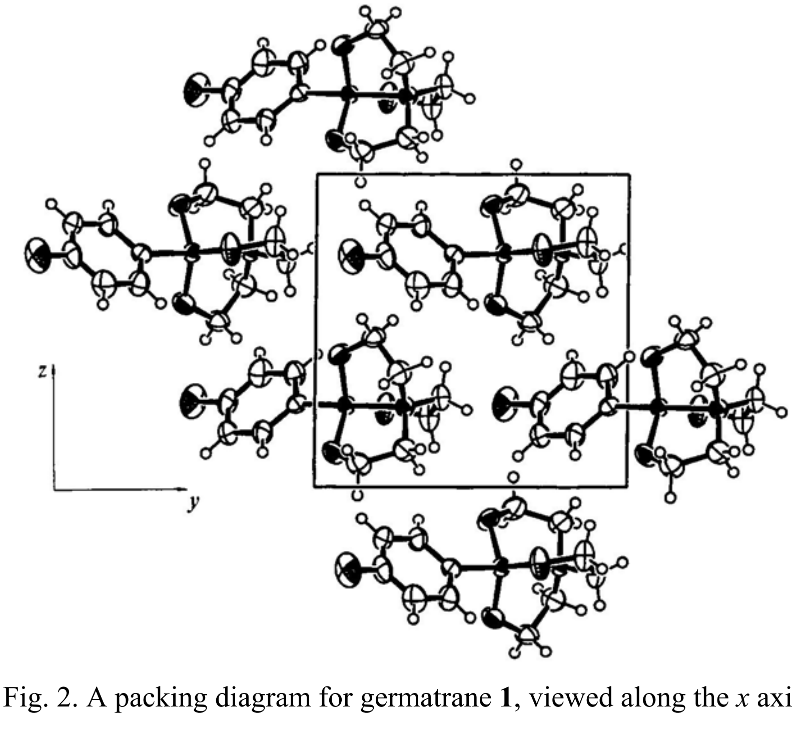

Fig. 2. A packing diagram for germatrane **1**, viewed along the *x* axis.

The length of the intramolecular transannular N→Ge bond for 4-fluorophenylgermatrane **1** equals 2.192(3) Å. It is a relatively short value for arylgermatranes (Table 1). The deviation (ΔGe) of the Ge atom from the three oxygen atoms plane in compound **1** is 0.2306(4) Å. The mean bond length for Ge−O is 1.789(4), and the length of Ge−C bond is 1.949(5) Å; the value of N→Ge−C valence angle is 176.8(2)°, and the mean values of angles N−Ge−O, O−Ge−C, and O−Ge−O are 82.6(1), 97.4(2), and 118.4(2)°, correspondingly.

TABLE 1. The Principal Geometrical Parameters of $R{-}Ge(OCH_2CH_2)_3N$

R	*d* (Ge–N), Å	*d* (Ge–C), Å	∠C–Ge–N, deg	ΔGe, Å	Refe-rences
4-$Me_2NC_6H_4$	2.249	1.941	179.8	0.269	This work
2-MeC_6H_4	2.230	1.940	144.2	0.263	[4]
4-MeC_6H_4	2.217	1.946	179.0	0.245	[4]
3-MeC_6H_4	2.214	1.947	176.3	0.253	[4]
C_6H_5	2.212	1.947	177.5	0.238	[4]
4-FC_6H_4	2.192	1.949	176.8	0.231	This work
C_6F_5	2.156	1.990	176.3	0.2	[3]
4-$EtOOCC_6H_4$	2.211	1.961	178.7	0.238	[7]
4-BrC_6H_4	2.208	1.948	177.6	0.227	[8]
4-(2-Thienyl)C_6H_4	2.219	1.948	178.9	0.263	[9]
	2.247			0.231	

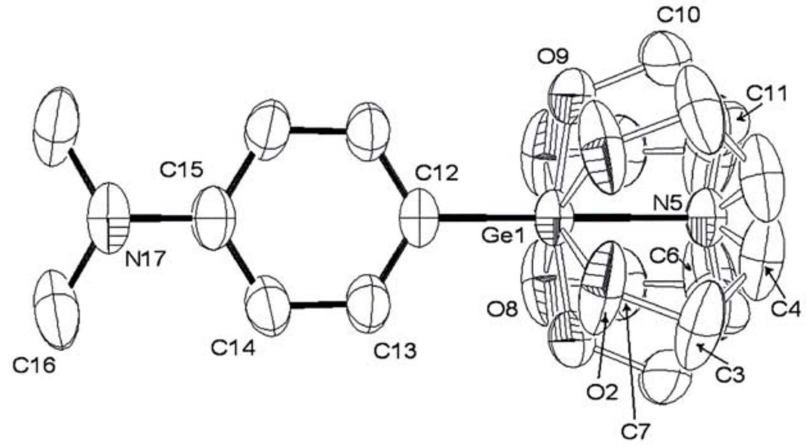

Fig. 3. Molecular structure of 1-(4-dimethylaminophenyl)germatrane (**2**).

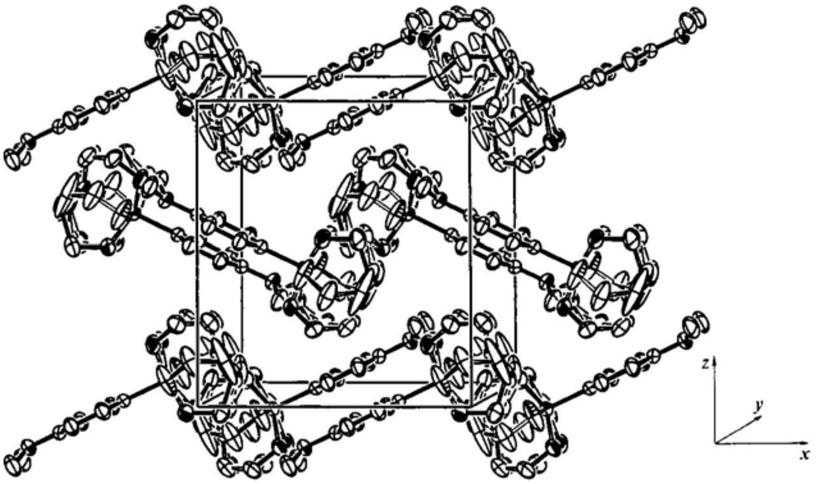

Fig. 4. A packing diagram for germatrane **2** (for the sake of clarity, H atoms have been omitted, the bonds between disordered atoms are shown by double thin lines).

The form and volume of compound **2** molecules are near to these in compound **1**. At the same time, for molecules **2** the dipole moment (1.398 D) is three and a half times smaller than that for molecule **1**. Possibly, it is why the molecular packing of germatrane **1** is not realized for the germatrane **2**, and the crystal structure **2** (Fig. 3) is not isomorphous to the structure **1**. The molecules **2** are packed in a centrosymmetrical orthorhombic lattice (space group *Pnma*); each molecule lies in a special position (symmetry plane *m*). However, the germatrane cage does not possess symmetry planes. Thus, packing of molecules **2** in this space group is possible only if structure disorder occurs (Fig. 4). The symmetry planes *m* are perpendicular to the phenyl rings of germatrane **2**. Two carbon atoms of the phenyl group and both nitrogen atoms, and germanium atoms lie in the symmetry plane. All oxygen and carbon atoms of the atrane cage are disordered. The occupation *g*-factors for these atoms are 0.5.

The value of the N→Ge donor-acceptor bond for germatrane **2** is 2.249(3) Å. It is the longest bond found for arylgermatranes (Table 1). The Ge–C bond (1.941(3) Å) in germatrane **2** is shorter than in germatrane **1** in accordance with the conclusions of [6], where it has been shown that lengthening of transannular N→Ge bonds leads to shortening of Ge–C bonds. The bond angle N→Ge–C in compound **2** (179.8(1)°) is practically flat, and the mean values of angles N–Ge–O, O–Ge–C, and O–Ge–O are 81.4(1), 98.6(2), and 117.8(3)°, respectively; the ΔGe value is 0.2693(3) Å and the mean value of Ge–O bond lengths is 1.774(3) Å.

Thus the introduction of fluorine substituent into position 4 of the aryl ring of phenylgermatrane shortens the N–Ge distance, but the introduction of the electron-donor dimethylamino group, on the contrary, lengthens it. However, the differences between them and unsubstituted phenylgermatrane are still small.

EXPERIMENTAL

^{1}H NMR spectra were measured on a Varian Mercury-200 instrument (200 MHz) using $CDCl_3$ as a solvent and TMS as the internal standard. Mass spectra were registered on an GC-MS HP 6890 (70 eV). Elemental analyses were performed on a EA 1108 Carlo Erba instrument.

The molecular dipole moments for germatranes **1** and **2** were calculated by the quantum-chemical MNDO method using an approach analogous to [6].

1-(4-Fluorophenyl)germatrane (1). A mixture of 1-fluoro-4-iodobenzene (17 mmol) and the dioxane complex of germanium(II) dibromide (5 mmol) was boiled in "Pierce" for 18 h under Ar. The reaction mixture was analyzed by GC. The resultant yellow solution was transported to a 3-neck flask under Ar. An ethanolic solution of triethylamine (17 mmol) was added dropwise to 4-fluorophenyldibromoiodogermane solution in abs. Et_2O (5 ml), cooled to 0°C, followed by heating to room temperature and boiling for 2 h. After cooling, pentane (10 ml) was added and the triethylamine salt was filtred off. Triethanolamine (5 mmol) in an ethanol solution (8 ml) was added dropwise to the filtrate cooled to 0°C. The reaction mixture was stirred at room temperature for 1 h, cooled to 0°C, and 1-(4-fluorophenyl)germatrane (58%) was filtered off. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.93 (6H, t, $J = 6.0$, CH_2N); 3.90 (6H, t, $J = 6.0$, CH_2O); 6.82-7.86 (4H, m, C_6H_4). GC-MS (*m/z*): 408 [M^+] (5), 327 [M^+ –Br] (100), 234 (5), 153 [GeBr] (30), 75 (15), 50 (10). The single crystals were grown from chloroform by slow evaporation of the solvent, mp 188-189°C. Found, %: C 45.34; H 4.98; N 4.40. $C_{12}H_{16}FGeNO_3$. Calculated, %: C 45.92; H 5.14; N 4.46.

1-(4-Dimethylaminophenyl)germatrane (2). Germatrane **2** was synthesized by the known method [5]. Crystals of germatrane **2** suitable for X-ray study were grown from ethanol solution, mp 236-238°C (235-238°C [5]). Found, %: C 49.24; H 6.48; N 8.10. $C_{14}H_{22}GeN_2O_3$. Calculated, %: C 49.61; H 6.54; N 8.27.

X-Ray crystallography. For X-ray crystal structure analysis of compounds **1** and **2** an automatic single-crystal Nonius Kappa CCD diffractometer with MoKα radiation ($\lambda = 0.71073$ Å) was used for intensity data collection. Reflection intensities were collected at room temperature (293K) using the φ and ω scan technique. Other crystallographic, measurement, and refinement data for compounds **1** and **2** are given in Table 2.

TABLE 2. Crystal Data, Measurement Conditions and Refinement Data for Compounds **1** and **2**

	1	**2**
Molecular formula	$C_{12}H_{16}FGeNO_3$	$C_{14}H_{22}GeN_2O_3$
Molecular weight, M_r	313.85	338.93
Crystal size, mm^3	0.10×0.12×0.25	0.13×0.17×0.22
Crystal system	Monoclinic	Orthorhombic
Space group	$P\,2_1$	*Pnma*
Cell parameter:		
a, Å	6.7526(3)	11.0570(2)
b, Å	9.6962(3)	11.2904(2)
c, Å	9.9677(5)	12.1708(3)
β, deg	102.524(1)	90.0
Unit cell volume, V, Å^3	637.10(5)	1519.35(5)
Molecular multiplicity, Z	2	4
$F(000)$	320	704
Crystal density, D_{calc}, g/cm^3	1.636	1.482
Absorption coefficient, μ, mm^{-1}	2.416	2.025
Data collection:		
$2\theta_{max}$	55.0	57.0
h	-8→8	-14→14
k	-12→12	-15→15
l	-12→12	-16→16
Number of		
measured reflections	3085	3716
independent reflections	2795	2047
reflections with $I > 2\sigma(I)$	2520	1741
Refinement data:		
R-factor	0.0377	0.0369
wR on F^2 for all data	0.0931	0.1105
Goodness of fit	1.057	1.051
Number of parameters	163	139
$\Delta\rho_{max}$, e/Å^3	0.342	0.418
$\Delta\rho_{min}$, e/Å^3	-0.481	-0.534
Flack's x parameter	-0.03(2)	—
Solution and refinement programs	SIR93 [10], SHELXL97 [11]	SIR93 [10], SHELXL97 [11]
CCDC deposition numbers	643598	643599

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