1-Fluorogermatrane—germatrane with the shortest intramolecular N → Ge bond

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Abstract

1-Hydroxygermatrane readily reacts with boron trifluoride etherate in acetonitrile to give 1-fluorogermatrane in good yield. The length of the N → Ge donor–acceptor bond equals 2.011(9) Å, which is the shortest among all studied for germatranes. © 1997 Elsevier Science S.A.

Keywords: 1-Fluorogermatrane; Germatrane; Bond length

1. Introduction

Intramolecular bond length N → Si in silatranes (1.965–2.24 Å) depends on the electronic structure of the substituent bound to the silicon atom: the increase of electron–acceptor properties shortens the N → Si bond [1]. The shortest transannular N → Si bonds have been found in dimethylsilatranyl oxonium cation (1.965 Å) [2] and in 1-chlorosilatrane (2.023 Å) [3].

It seems to be true also for germatranes. The N → Ge bond in 1-bromogermatrane (2.09 Å) is shorter than that in alkyl [4], aryl [5,6] and siloxygermatranes [7].

For further study of this phenomenon we have synthesized 1-fluorogermatrane and investigated its crystal and molecular structure.

2. Experimental

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-360 spectrometer in CDCl$_3$/TMS. Crystals of 1-fluorogermatrane suitable for the X-ray study were obtained from ethanol:water (1:1).

2.1. Synthesis of 1-fluorogermatrane (2)

A solution of boron trifluoride etherate (0.008 mol) in 20 ml of acetonitrile was added to a solution of

1-hydroxygermatrane (0.024 mol) in 40 ml of acetonitrile at 50°C. After 15–20 min compound 2 precipitated. The mixture was cooled to room temperature. 1-Fluorogermatrane was filtered off and crystallized from ethanol:water (1:1). Colourless crystals with m.p. 225°C were obtained in 82% yield.

Found: C, 30.31; H, 5.10; N, 5.85. Calc. for GeC$_6$H$_{12}$FNO$_3$: C, 30.31; H, 5.09; N, 5.89%. ^{1}H NMR (360.1 MHz, CDCl$_3$/TMS, 303 K) δ (ppm): 2.96 (6H, t, ^3J = 5.73 Hz); 3.738 (6H, dt, ^3J = 5.73 Hz, ^4J = 1.51 Hz). ^{13}C NMR(90.56 MHz, CDCl$_3$/TMS,303 K) δ (ppm): 50.71(t); 56.44(t).

2.2. Structure determination of 2

Crystal data for **2**: monoclinic; a = 7.188(1), b = 7.263(2), c = 8.031(1) Å, β = 93.82(1)°; V = 418.3(2) Å^3, Z = 2; D_{calc} = 1.888(1) g/cm^3; F(000) = 240; space group P2$_1$. A total number of 810 independent intensities was collected at room temperature on a Syntex P2$_1$ four-circle computer-controlled single-crystal diffractometer with graphite-monochromated MoK$_\alpha$ radiation (λ = 0.71069 Å), μ = 3.65 mm^{-1}; $2\theta_{max}$ = 50°, sin Θ/$\lambda \le 0.595$ Å^{-1}; $\theta/2\theta$ scan technique; crystal size 0.15 × 0.20 × 0.25 mm. Two standard reflections showed no significant decay. Lorentz, polarization and absorption corrections by the azimuth scanning method [8] were applied to the processing of the data obtained.

Position of the germanium atom was determined from the Patterson function. The other non-hydrogen

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atoms were found by the following Fourier syntheses. For the structure refinement 732 reflections with $|F_o| > 4\sigma(F)$ were used. The full-matrix least-squares method on F with weighting scheme $w = 1/[\sigma^2 + (0.07P)^2]$, where $P = (|F_o|^2 + 2|F_c|^2)/3$, was used in the refinement procedure. The Ge, F, O, N and C atoms were refined in anisotropic approximation. All hydrogen atoms have been located from difference syntheses and refined isotropically. Extinction correction [9] was employed in the refinement procedure.

The absolute structure for crystals 2 has been determined using the Flack method [10]. The value of Flack's x parameter is 0.05(66) (the expected values are 0 within 3 esds for the corrected structure and 1 for inverted absolute one).

Calculations were carried out with the program SHEXL-93 [9] and AREN complex of programs [11] for crystallographic calculations. Atomic scattering factors were taken from the International Tables for X-ray Crystallography [12]. The final value of R-factor is 0.0388.

3. Results and discussion

We have found that 1-hydroxygermatrane (1) readily reacts with boron trifluoride etherate in acetonitrile to give 1-fluorogermatrane (2) in good yield (82%).

3 N(CH₂CH₂O)₃GeOH + BF₃·Et₂O ⟶

1

3 N(CH₂CH₂O)₃GeF + B(OH)₃

2
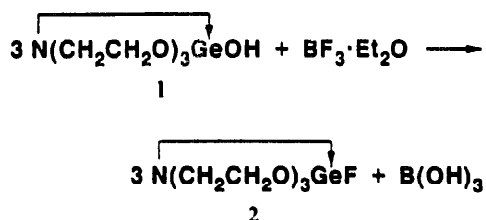
To continue our previous investigations on the atrane molecules structure [3,5–7,13] germatrane 2 has been studied using X-ray diffraction method.

The perspective view of the molecular structure with the atomic labels for the compound is shown in Fig. 1. Tables 1 and 2 give the coordinates of non-hydrogen atoms with thermal parameters, and principal bond lengths, and valence angles in the molecule 2.

The peculiarity of this structure is the strong transannular interaction between the Ge and N atoms. The length of the N → Ge donor–acceptor bond equals 2.011(9) Å, which is the shortest among all studied for atranes [3,14].

The coordinated polyhedron of the germanium atom in the structure 2 as in the other atrane systems appears to be a trigonal pyramid. However, in this case the Ge atom lies practically in the plane compiled by the O2,

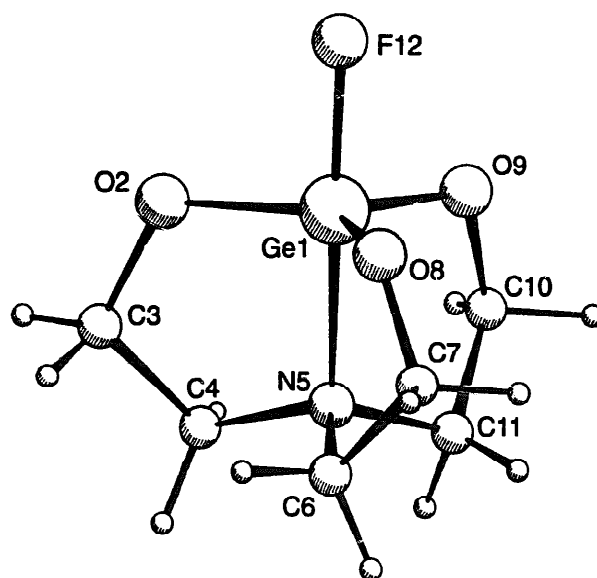Fig. 1. Molecular structure of 1-fluorogermatrane.

Table 1
Coordinates and equivalent isotropic thermal parameters (Å) of non-hydrogen atoms for structure 2

	x	y	z	Beq
Ge1	0.3030(1)	0.5(0)	0.7417(1)	2.34(3)
O2	0.2062(9)	0.4930(12)	0.5326(7)	3.6(2)
C3	0.1463(6)	0.3141(17)	0.4794(12)	3.8(3)
C4	0.2789(14)	0.1695(14)	0.5585(11)	3.1(3)
N5	0.3116(12)	0.2233(13)	0.7421(9)	2.0(3)
C6	0.1623(14)	0.1588(13)	0.8427(12)	3.3(3)
C7	0.1530(13)	0.3022(16)	0.9815(12)	3.4(3)
O8	0.1571(8)	0.4849(11)	0.9110(7)	3.2(2)
O9	0.5483(7)	0.5090(12)	0.7817(6)	3.5(2)
C10	0.6330(14)	0.3234(18)	0.7585(13)	4.4(3)
C11	0.5004(14)	0.1737(15)	0.8029(13)	3.5(3)
F12	0.2993(14)	0.7452(14)	0.7417(10)	5.4(4)

Table 2
Bond lengths (Å) and valence angles (in degrees) for molecule 2

N5–Ge1	2.011(9)	N5–C4	1.528(12)
O2–Ge1	1.775(6)	C6–N5	1.463(13)
O8–Ge1	1.755(6)	C11–N5	1.456(13)
O9–Ge1	1.772(5)	C7–C6	1.530(14)
F12–Ge1	1.781(10)	O8–C7	1.444(14)
C3–O2	1.425(15)	C10–O9	1.496(15)
C4–C3	1.528(15)	C11–C10	1.505(16)
Ge1–O2–C3	113.7(6)	O8–Ge1–F12	93.0(4)
O2–Ge1–N5	89.0(3)	Ge1–O9–C10	110.7(6)
O2–Ge1–O8	120.6(3)	O9–Ge1–F12	88.7(4)
O2–Ge1–O9	119.7(3)	O2–C3–C4	109.5(8)
O2–Ge1–F12	91.4(4)	C3–C4–N5	106.1(8)
Ge1–N5–C4	104.5(6)	C4–N5–C6	112.3(8)
Ge1–N5–C6	107.3(6)	C4–N5–C11	109.9(8)
Ge1–N5–C11	106.0(6)	N5–C6–C7	104.7(8)
N5–Ge1–O8	87.5(3)	C6–N5–C11	115.9(8)
N5–Ge1–O9	90.4(4)	N5–C11–C10	109.5(9)
N5–Ge1–F12	179.1(5)	C6–C7–O8	109.7(8)
Ge1–O8–C7	112.7(6)	O9–C10–C11	110.6(8)
O8–Ge1–O9	119.6(2)		

O8, O9 atoms. The deviation in atranes so far is considered to be 0.095 Å [15] (structure of 1-chlorosilatrane). Thus, the values of the bond angles X–Ge–O (X = N or F) in 2 are about 90° (see Table 2). At the same time the distance from the N atom to the plane formed by C4, C6 and C11 atoms equals 0.408(9) Å, somewhat longer than that in the 1-fluoro-(0.0390 Å) and 1-chloro-silatranes (0.0396 Å) [15]. This distance characterizes the degree of approach of the nitrogen lone electron pair to the germanium atom.

On the whole, the molecule 2 has the approximate symmetry C3 with zigzag conformation of the atrane system. The values of Ge1–O2–C3–C4, Ge1–O8–C7–C6 and Ge1–O9–C10–C11 torsion angles are −35.6(9), −36.0(8) and −1.6(8)°, respectively.

The crystal structures of germatranes are usually isomorphous to the corresponding silatranes [7,13]. However, the crystal structure of 2 is not isomorphous to the structure of 1-fluorosilatrane; the crystals of the latter belong to the space group Pc [14], whilst the crystals of 2 are of the space group P2$_1$.

Acknowledgements

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