

A new pathway for the synthesis of 1,3-dioxo-6-aza-2-germacyclooctanes: molecular structure of 2,2-di(2-thienyl)-6-methyl-1,3-dioxo-6-aza-2-germacyclooctane

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Abstract

A novel reaction pathway has been applied for the synthesis of 1,3-dioxo-6-aza-2-germacyclooctanes. Compounds of this type were obtained by the dehydrocondensation of di(2-thienyl)germane and diethanolamines without a catalyst. The molecular structure of 2,2-di(2-thienyl)-6-methyl-1,3-dioxo-6-aza-2-germacyclooctane has been determined by X-ray diffraction study. The interatomic N → Ge distance of 2.446 Å indicates the presence of a weak transannular bond.

Keywords: Germanium; X-ray diffraction; 1,3-Dioxo-6-aza-2-germacyclooctane

1. Introduction

The five-coordinated germanium compounds, such as germatranes (2,8,9-trioxo-5-aza-1-germatricyclo-[3.3.3.0^{1,5}]undecanes) and germocanes (1,3-dioxo-6-aza-2-germacyclooctanes), have attracted much attention due to their peculiar structure [1–6] and wide variety of biological activity [7–9]. Five synthetic methods have been used for the formation of the germatrane and germocane backbone. The most investigated pathway is the transesterification of alkoxygermanes with di- and triethanolamines [1,7,10]. Alkylaminogermanes may be used instead of alkoxygermanes for the synthesis of germatranes [11]. Germanium dioxide GeO₂ and germesquioxanes (RGeO_{1.5})_n also react with di-[12,13] and triethanolamines [12,14] to give germatranes and germocanes in high yield. The interaction of halogenogermanes with stannyl ethers of triethanolamine N(CH₂CH₂OSnR₃)₃ (stannyl method) has limited application for the introduction of germatrane cage into the molecules [15]. The silyl method (the reaction of halogenogermanes with silyl ethers of triethanolamine) [16] is more convenient due to the lower toxicity of silyl compounds. In the present communication we report a new route for the synthesis of germo-

cane by the dehydrocondensation of di(2-thienyl)germane with diethanolamines.

2. Results and discussion

It has been found that di(2-thienyl)germane (1) reacts immediately with diethanolamine derivatives without any catalyst and solvent to afford 2,2-di(2-thienyl)-1,3-dioxo-6-aza-2-germacyclooctanes (2, 3) in high preparative yield (78–81%). The reaction has exothermic character. Germocane (2) was also obtained in 75% yield by transesterification of di(2-thienyl)diethoxygermane (4) with N-methyldiethanolamine:

For the synthesis of the starting di(2-thienyl)germane (1) the reduction of di(2-thienyl)diethoxygermane (4) by lithium aluminum hydride in pentane under phase transfer conditions [17,18] at room temperature has been used. The formation of dihydrogermane (1) occurred in 76% yield and was not accompanied by Ge–C bond cleavage.

To continue our structural investigations of the atrane molecules and their analogues [2,19–21] an X-ray diffraction study was carried out on germane (2). Fig. 1 shows a perspective view of the compound 2 with atom labels in accordance with X-ray analysis data. Tables 1 and 2 give the atomic coordinates for non-hydrogen atoms and the values of bond lengths and angles for 2

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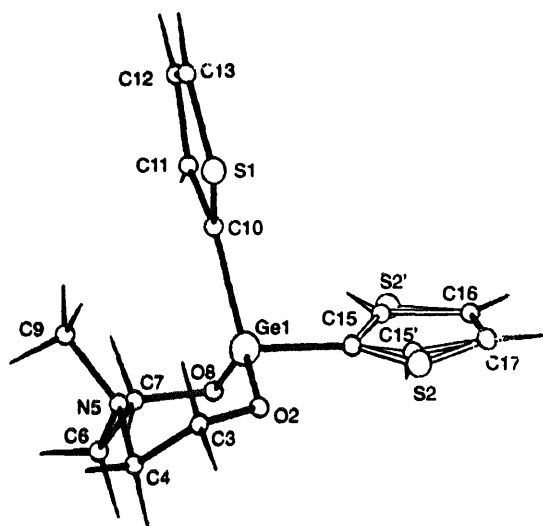


Fig. 1. Molecular structure of germocane (2).

respectively. Besides S2 and C15 we have managed to reveal S2' and C15' atoms in the refinement procedure by Fourier synthesis. Thus, there are two molecular forms for compound 2 in the crystal. For one form the value of the torsion angle C10–Ge1–C14–S is 99(1)°, for the other it is 289(2)°. Both molecules exist in the same crystallographic position and the disorder is not removed by a fall in symmetry of the space group, so the structure of 2 may be described with the help of the occupation *g*-factors. For disordered S2, S2', C15 and C15' atoms the value of the *g*-factor is 0.5. For this value the isotropic thermal parameters of these atoms are 3.5(3), 2.7(7), 1.6(8) and 3.6(10) Å² respectively.

To our knowledge compounds 5 and 6 are the only examples of five-coordinated germanium derivatives with a 1,3-dioxo-6-aza-2-germacyclooctane ring that have been characterized by X-ray analysis [4,5]. Contrary to the spirocyclic derivatives 5 and 6 with a very

short N → Ge distance (2.161 and 2.143 Å) comparable with these values in germatranes, germocane (2) is characterized by a considerable lengthening of the N → Ge transannular bond (2.446 Å). However, this distance is shorter than the N → Si coordination in 2,2-diphenyl-6-methyl-1,3-dioxo-6-aza-2-silacyclooctane (2.68(1) Å) [22]. The coordination polyhedron of the germanium atom in germocane (2) is a strongly distorted trigonal bipyramid, whose base is formed by two oxygen atoms and a carbon atom of one thiophene ring located equatorially. The upper vertices are occupied by the nitrogen atom and the second thiophene substituent (N–Ge–C_{ax} = 162.1°). At the same time in compounds 5 and 6 the germanium atom has a trigonal bipyramidal environment.

The eight-membered ring has a crown conformation, the oxygen atoms and two carbon atoms in the α-position with respect to nitrogen are almost coplanar and the remaining atoms depart from the plane in the same direction ($\Delta\text{Ge} = 0.637$ Å, $\Delta\text{N} = 0.739$ Å, $\Delta\text{C}(3) = 0.288$ Å, $\Delta\text{C}(7) = 0.306$ Å).

3. Experimental

¹H NMR spectra were recorded on a Bruker WH-90/DS spectrometer in CDCl₃. Mass spectra were obtained with a Kratos MS-25 GC-MS instrument (70 eV).

3.1. 2,2-Di(2-thienyl)-1,3-dioxo-6-aza-2-germacyclooctanes (2, 3)

N-Methyldiethanolamine (0.6 g, 5 mmol) was added to di(2-thienyl)germane (1.2 g, 5 mmol). Immediately the white precipitate was obtained. Recrystallization from the mixture of dry Et₂O and CHCl₃ (1:1) gave 1.5 g (81%) of compound 2, m.p. 161°C. Anal. Found:

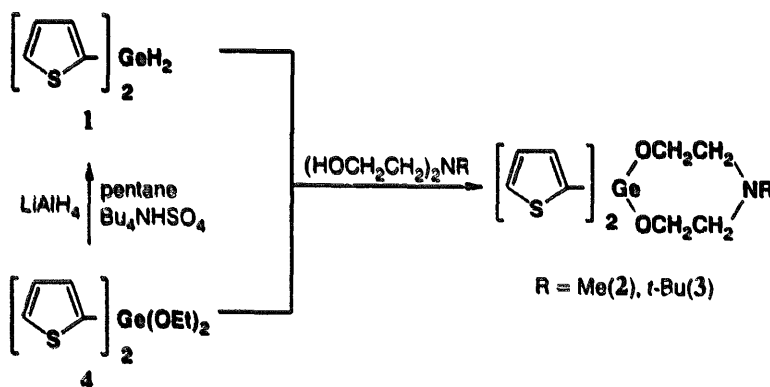


Table 1
Atomic coordinates for non-hydrogen atoms in germocane (2)

Atom	x	y	z
Ge(1)	0.5614(1)	0.1951(1)	0.1419(1)
O(2)	0.5867(10)	0.3097(6)	0.2095(4)
C(3)	0.4582(15)	0.3973(9)	0.1877(6)
C(4)	0.2616(16)	0.3511(10)	0.1591(7)
N(5)	0.2424(11)	0.2719(8)	0.0933(5)
C(6)	0.1339(16)	0.1715(10)	0.0960(7)
C(7)	0.2292(14)	0.0745(10)	0.0754(7)
O(8)	0.4214(9)	0.0733(6)	0.1285(4)
C(9)	0.1808(17)	0.3204(11)	0.0143(7)
C(10)	0.5889(13)	0.2356(9)	0.0408(6)
C(11)	0.5493(10)	0.1567(6)	-0.0318(4)
C(12)	0.6027(17)	0.2218(13)	-0.0925(7)
C(13)	0.6580(17)	0.3266(13)	-0.0700(8)
S(1)	0.6632(5)	0.3592(3)	0.0210(2)
C(14)	0.7964(14)	0.1237(10)	0.2107(6)
C(15)	0.8613(96)	0.0280(57)	0.1932(58)
C(15')	0.9423(94)	0.1548(32)	0.2832(42)
C(16)	0.0604(15)	0.0015(10)	0.2590(7)
C(17)	0.1090(15)	0.0874(12)	0.3042(7)
S(2)	0.9629(21)	0.1963(11)	0.2861(10)
S(2')	0.8525(39)	-0.0087(19)	0.1855(18)

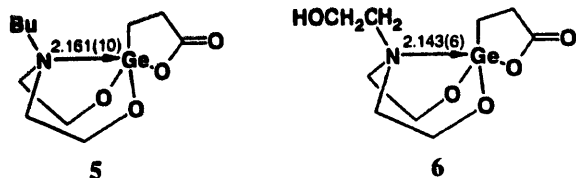
C, 43.58; H, 4.76; N, 4.02; S, 18.09. C₁₃H₁₇NO₂S₂Ge (356.00) Calc.: C, 43.86; H, 4.81; N, 3.93; S, 18.01%. ¹H NMR (CDCl₃) δ (ppm): 1.83 (s, 3H, N-Me); 2.68 (t, 4H, N-CH₂); 4.00 (t, 4H, OCH₂); 7.16 (2H, H(4));

7.30 (2H, H(3)); 7.55 (2H, H(5)). MS: *m/z* (%) 357 (M⁺, 4); 273 (17), 157 (28), 140 (100), 97 (62), 70 (18), 57 (54), 42 (48).

Germocane (3) was prepared by the same method.

Table 2
Bond lengths (Å) and angles (deg) in the molecule 2

N(5)-Ge(1)	2.446(0.008)	O(8)-C(7)	1.417(0.011)
O(2)-Ge(1)	1.782(0.007)	S(1)-C(10)	1.678(0.011)
O(8)-Ge(1)	1.782(0.007)	C(12)-C(11)	1.491(0.017)
C(10)-Ge(1)	1.912(0.011)	C(13)-C(12)	1.347(0.022)
C(14)-Ge(1)	1.954(0.009)	C(15)-C(14)	1.336(0.080)
C(3)-O(2)	1.398(0.013)	C(15')-C(14)	1.394(0.057)
C(4)-C(3)	1.504(0.016)	S(2)-C(14)	1.698(0.016)
C(6)-N(5)	1.479(0.016)	S(2')-C(14)	1.754(0.029)
C(9)-N(5)	1.409(0.015)	C(17)-C(15')	1.439(0.062)
C(7)-C(6)	1.491(0.018)	S(2)-C(17)	1.678(0.019)
Ge(1)-O(2)-C(3)	120.9(6)	C(6)-C(7)-O(8)	109.2(9)
O(2)-Ge(1)-O(8)	129.9(4)	C(10)-C(11)-C(12)	103.7(8)
O(2)-Ge(1)-C(10)	112.8(4)	C(11)-C(10)-S(1)	111.4(7)
O(2)-Ge(1)-C(14)	94.8(4)	C(10)-S(1)-C(13)	95.5(7)
Ge(1)-O(8)-C(7)	120.2(6)	C(11)-C(12)-C(13)	115.2(12)
O(8)-Ge(1)-C(10)	110.6(4)	C(12)-C(13)-S(1)	113.9(12)
O(8)-Ge(1)-C(14)	94.9(4)	C(14)-C(15)-C(16)	110.5(51)
Ge(1)-C(10)-C(11)	123.3(7)	C(15)-C(14)-C(15')	101.5(39)
Ge(1)-C(10)-S(1)	125.2(6)	C(15)-C(14)-S(2)	112.9(31)
C(10)-Ge(1)-C(14)	106.9(4)	C(14)-C(15')-C(17)	114.5(40)
Ge(1)-C(14)-C(15)	125.1(32)	C(15')-C(14)-S(2')	106.5(23)
Ge(1)-C(14)-C(15')	133.2(23)	C(14)-S(2)-C(17)	89.7(9)
Ge(1)-C(14)-S(2)	120.2(8)	S(2)-C(14)-S(2')	118.9(11)
Ge(1)-C(14)-S(2')	120.1(9)	C(14)-S(2')-C(16)	89.4(13)
O(2)-C(3)-C(4)	108.8(9)	C(15)-C(16)-C(17)	105.7(29)
C(3)-C(4)-N(5)	107.7(11)	C(16)-C(17)-S(2)	120.0(9)
C(4)-N(5)-C(6)	114.1(10)	C(15')-C(17)-C(16)	105.8(22)
C(4)-N(5)-C(9)	113.3(9)	C(17)-C(16)-S(2')	121.6(13)
N(5)-C(6)-C(7)	108.0(10)	N(5)-Ge(1)-C(10)	90.9(4)
C(6)-N(5)-C(9)	112.4(8)	N(5)-Ge(1)-C(14)	162.1(4)



Anal. Found: C, 48.33; H, 5.77; N, 3.47; S, 16.27. $C_{16}H_{23}NO_2S_2Ge$ (398.09) Calc.: C, 48.28; H, 5.82; N, 3.47; S, 16.11%. 1H NMR ($CDCl_3$) δ (ppm): 0.86 (s, 9H, N- 1Bu); 2.72 (t, 4H, N- CH_2); 3.99 (t, 4H, OCH_2); 7.17 (2H, H(4)); 7.32 (2H, H(3)); 7.59 (2H, H(5)). MS: m/z (%) 399 (M^+ , 3), 384 (55), 354 (56), 312 (28), 157 (49), 134 (58), 108 (27), 97 (40), 84 (30), 57 (100), 41 (94), 39 (83).

The reaction of N-methyldiethanolamine with di(2-thienyl)diethoxygermane gave germocane (2) in 75% yield.

3.2. Di(2-thienyl)germane (1)

Di(2-thienyl)diethoxygermane (3.30 g, 10 mmol) was added to the suspension of $LiAlH_4$ (0.5 g) and Bu_4NHSO_4 (0.2 g) in pentane under argon. After stirring the reaction mixture at room temperature during 2 h the solid was filtered off and the filtrate distilled. Distillation gave 1.84 g (76%) di(2-thienyl)germane (1), b.p. $93^\circ C$ (3 Torr). 1H NMR ($CDCl_3$) δ (ppm): 5.49 (s, 2H, Ge=H); 7.20 (2H, H(4)); 7.32 (2H, H(3)); 7.57 (2H, H(5)). MS: m/z (%) 242 (M^+ , 41), 157 (80), 97 (59), 85 (59), 74 (45), 52 (100), 39 (35).

3.3. Determination of the crystal and molecular structure of 2

Crystal data for 2: monoclinic; $a = 7.626(2)$, $b = 12.085(4)$, $c = 17.422(4)$ Å, $\beta = 111.52(2)^\circ$; $V = 1493.7$ Å³, $Z = 4$, $\mu = 5.38$ mm⁻¹, $D_{calc} = 1.58$ g cm⁻³; $F(000) = 728$; space group $P2_1/c$. Monocrystals were grown from $Et_2O-CHCl_3$ mixture (1:1), a crystal of size $0.30 \times 0.20 \times 0.15$ mm³ was used for intensity data collection on a Syntex P2₁ four-circle computer-controlled single-crystal diffractometer with graphite-monochromated Cu K α ($\lambda = 1.54051$ Å) radiation; lattice parameters were refined from 20 reflections with $50 < 2\theta < 55^\circ$. A total of 1668 reflection intensities were collected at room temperature using the $\theta/2\theta$ scan technique up to $2\theta_{max} = 100^\circ$ ($\sin \theta/\lambda < 0.497$ Å⁻¹); one standard reflection showed no significant decay; Lorentz and polarization corrections were applied to the data.

For structure solution, the initial phases of ten strong reflections were determined by the maximum-determinant method [23]. The phase values obtained were

introduced into the starting set of the MULTAN programme [24]. Two variants were calculated, one of them yielding the model. For structure refinement, 1331 independent reflections with $|F| > 4\sigma(F)$ were used. Fourier synthesis and full-matrix least-squares with unit weighting scheme were used for refinement. The Ge, S, O, N and C atoms were refined anisotropically. The hydrogen atoms of the methyl group were located from difference synthesis. All the other H atom coordinates were calculated geometrically.

The correction for absorption was carried out by the DIFABS method [25].

Calculations were carried out with the AREN complex of programs [26] for crystallographic computations. Atomic scattering factors were taken from the *International Tables for X-ray Crystallography* [27]. The final R-factor is 0.0796.

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