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Synthesis, X-ray Diffraction Studies, and DFT Calculations on Hexacoordinated Germanium Derivatives: The Case of Germaspirobis(ocanes)

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Synthesis of the title compounds, viz. $[RN(CH_2CHR'O)_2]_2Ge$ (**1**, R = Me, R′ = H; **2**, R = Me, R′ = Ph; **3**, R = Ph, R′ = H), by the reaction of 2 equiv of corresponding dialkanolamines $RN(CH_2CHR'OH)_2$ (**4**, R = Me, R′ = H; **5**, R = Me, R′ = Ph; **6**, R = Ph, R′ = H) with $(AlkO)_4Ge$ is reported. Composition and structures of all novel compounds were established by ^1H and ^{13}C NMR spectroscopy and mass spectrometry as well as elemental analysis data. The single-crystal X-ray diffraction of **2** has clearly indicated the presence of two transannular interactions Ge←N in the compound. N atoms are cis-orientated. The compound **3** possesses long Ge···N distances. The structural data obtained from geometry optimizations by DFT calculations on **1**–**3** reproduces experimental results. Both cis- and trans-isomers were studied, and cis-configuration was found to be more thermodynamically stable for all three compounds. The transition states for possible cis ↔ trans rearrangement processes in **1**–**3** were calculated. The properties of the Ge–O and Ge←N bonds in **1**–**3** were analyzed by the AIM approach. The interactions between the Ge atom and N atoms as well as O atoms possess predominantly ionic character.

Introduction

The structure and chemical behavior of the metallatranes, cyclic ethers of trialkanolamines, have been extensively studied, and compounds of elements have been reported throughout the periodic table.[1] Among these, metallatranes derivatives of group 14 elements, $N(CH_2CH_2O)_3MX$ (**I**, M = Si, Ge, Sn), are the most heavily investigated. [2−4] The main focus of the research is the elucidation of the nature of the transannular M←N bond, which is strongly affected by the design of the atrane building block and the substituents at the metal atoms.[1,3,4] In contrast, metallocanes, $RN(CH_2CH_2O)_2MX(X')$ (M = Si, Ge, Sn) (**II**)—closely related analogues of **I**—have been little studied.[5−12] It is possible that these compounds possess even greater chemical and structural flexibility than the metallatranes (**I**) since the substituents R, X, and X′ can be varied readily along with their influence on structures and chemical properties of substances. Among compounds of type **II**, derivatives where

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both substituents X and X′ form one tridentate ligand containing an additional donor group are of particular interest due to the possible formation of an additional transannular interaction, leading to hexacoordination at the central atom M. The structural study of these compounds may allow new information to be obtained for the transannular M←N bond. We expect the spirobis(ocanes), $[RN(CH_2CH_2O)_2]_2M$ (M = Si, Ge, Sn) (**C**), to be the most interesting in this regard. However, only few papers have dealt with their synthesis,[13−18] and the structures of only two compounds have been determined by single-crystal X-ray diffraction.[14,15,18] On the other hand, it is well-known that hypercoordinated group 14 elements derivatives display a wide range of biological activity, which makes them interesting for medicinal chemistry and pharmacology.[3,18,19] Thus, spirobis(ocanes) (**III**) may also be potentially useful as therapeutic agents. As a part of our program to investigate the structure and chemical behavior of hypercoordinated germanium molecules, especially germatranes and germocanes, and to compare the degree of strength of the transannular M←N interactions with those in the derivatives of other main group elements,[6,20−28] we present the synthesis of three novel 1,7,9,15-tetraoxa-4,12-diaza-8-germaspiro[7.7]pentadecanes, i.e., $[RN(CH_2CHR'O)_2]_2Ge$ (**1**−**3**), which are the derivatives of *N*-methyldiethanolamine (**4**), *N*-methyl-*N*-(2-hydroxy-2-phenylethyl)ethanolamine (**5**), and *N*-phenyldiethanolamine (**6**), respectively. The motivation in our work was to study structural changes in hypercoordinated germanium compounds arising from the replacement of substituents at the different positions of the ligand cage.

Compounds **1**−**3** were prepared via reaction of 2 equiv of the corresponding dialkanolamine with tetraalkoxygermane. The crystal structures of two of them have been established by X-ray diffraction confirming the hexacoordination of the Ge atom in these compounds (**2** and **3**). These data have been compared with those obtained from DFT calculations.

Experimental Section

General Procedures. All manipulations were performed under a dry, oxygen-free argon atmosphere using standard Schlenk techniques. Solvents were dried by standard methods and distilled prior to use. $PhN(CH_2CH_2OH)_2$ (**6**) (Aldrich) and $MeN(H)CH_2CH_2OH$ (Aldrich) were used as supplied. $Ge(OEt)_4$, $Ge(OMe)_4$,[29] $MeN(CH_2CH_2OH)_2$ (4),[30] and $MeN(CH_2CH_2OSiMe_3)_2$[31] were prepared according to the literature. $CDCl_3$ was obtained from Deutero GmbH and dried over P_4O_{10}. ^1H and ^{13}C NMR spectra were recorded on a Varian VXR400 spectrometer (in $CDCl_3$ at 295 K). Chemical shifts in the ^1H and ^{13}C NMR spectra are given in ppm relative to internal Me_4Si. Mass spectra (EI-MS) were recorded on a Varian CH-7a device using electron impact ionization at 70 eV; all assignments were made with reference to the most abundant isotopes. Elemental analyses were carried out by the Microanalytical Laboratory of the Chemistry Department of the Moscow State University. In this work, the nonempirical generalized gradient approximation (GGA) for the exchange-correlation functional of Perdew et al. was employed.[32,33] Calculations were performed using the program "PRIRODA" developed by Laikov, which implements an economical computational procedure.[34] Large orbital basis sets of contracted Gaussian-type functions of the size (5s1p):[3s1p] for H, (11s6p2d):[4s3p2d] for C, (11s6p2d):[4s3p2d] for N, (11s6p2d):[4s3p2d] for O, and (19s16p9d):[6s5p3d] for Ge were used. The present method has been used and has given very useful results in the organometallic chemistry of Si, Ge, Sn, Sb, and Bi.[21,35] The chemical bonds were analyzed by using the topological analysis of the wave function. All critical point calculations were performed using AIMPAC95 software package.[36,37]

***N*-Methyl-*N*-(2-hydroxy-2-phenylethyl)ethanolamine, $MeN(CH_2CH_2OH)CH_2CH(Ph)OH$ (5).** A mixture of *N*-methylethanolamine (8.26 g, 0.11 mol) and styrene oxide (12.02 g, 0.10 mol) was stirred for 24 h at room temperature. The distillation of the reaction mixture gave a colorless oil (17.80 g, 91%; 132−136 °C, 0.02 Torr) as a mixture of **5** (95%) and $MeN(CH_2CH_2OH)CHPhCH_2OH$ (5%). This mixture was used without further purification. Analytical data for **5** are as follows. NMR spectra: ^1H, δ 2.36 (s, 3H, NCH_3), 2.52−2.66 (m, 4H, NCH_2), 3.25 (br s, 2H, OH), 3.58−3.68 (m, 2H, OCH_2), 4.75 (dd, 1H, OCH), 7.30−7.37 (m, 5H, C_6H_5); $^{13}C\{^1H\}$, δ 42.30 (NCH_3), 59.25 (NCH_2), 59.54, 65.94 (NCH_2, OCH_2), 70.27 (OCH), 125.86, 127.52, 128.32, 142.15 (C_6H_5). Analytical data for $MeN(CH_2CH_2OH)CHPhCH_2OH$ are as follows. NMR spectra: ^1H, δ 2.20 (s, 3H, NCH_3), other signals overlapped with signals of protons of **5**; $^{13}C\{^1H\}$, δ 37.48

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(NCH_3), 54.90 (NCH_2), 58.92 (OCH_2), 61.36 ($OC\mathit{H}_2NCH$), 69.19 (NCH), 127.83, 128.28, 128.71 (C_6H_5, signal of one carbon has not been found).

4,12-Dimethyl-1,7,9,15-tetraoxa-4,12-diaza-8-germaspiro[7.7]-pentadecane, $[MeN(CH_2CH_2O)_2]_2Ge$ (1). A mixture of alkanolamine **4** (1.71 g, 14.4 mmol), $(MeO)_4Ge$ (1.42 g, 7.2 mmol), and benzene (10 mL) was refluxed for 2 h, and all volatiles were removed under reduced pressure to give a white waxy solid **1** (2.21 g, 100%). NMR spectra: ^1H, δ 2.46 (s, 6H, NCH_3), 2.58 (t, 8H, NCH_2), 3.71 (t, 8H, OCH_2); ^1H (223 K), δ 2.49 (br s, 6H, NCH_3), 2.56−2.72 (br m, 8H, NCH_2), 3.75−3.65 (br s, 8H, OCH_2); $^{13}C\{^1H\}$, δ 45.46 (NCH_3), 57.26 (NCH_2), 58.05 (OCH_2). Mass spectrum (EI-MS) [*m*/*e* (rel int)]: 308 (1, M^+), 207 (22, $M^+ - OCH_2CH_2 - 2OCH_2$). Anal. Calcd for $C_{10}H_{22}GeN_2O_4$: C, 39.14; H, 7.23; N, 9.13. Found: C, 39.48; H, 7.51; N, 9.18.

4,12-Dimethyl-2,10-diphenyl-1,7,9,15-tetraoxa-4,12-diaza-8-germaspiro[7.7] pentadecane, $[MeN(CH_2CH_2O)(CH_2CHPhO)]_2Ge$ (2). A mixture of alkanolamine **5** (1.80 g, 9.2 mmol), $(EtO)_4Ge$ (1.17 g, 4.6 mmol), and benzene (15 mL) was refluxed for 50 h, and all volatiles were removed under reduced pressure. The residue was recrystallyzed from toluene mixture to give colorless microcrystals of **2** (1.75 g, 83%) as a mixture of three diastereomers. NMR spectra: ^1H, δ 2.56, 2.58, 2.59 (s, 6H, NCH_3), 2.58−2.78 (m, 8H, NCH_2), 3.78−3.90 (m, 4H, OCH_2), 4.79−4.91 (m, 2H, OCH), 7.09−7.22, 7.31−7.35 (m, 10H, C_6H_5); $^{13}C\{^1H\}$, δ 47.73 (broad, $3NCH_3$), 58.03, 58.22, 58.26, 59.10, 59.16, 59.49 (NCH_2), 65.20, 65.41, 65.47 (NCH_2CHO), 69.44, 69.52, 69.70 (OCH), 125.73, 125.92, 125.99, 126.86, 126.92, 127.05, 127.96, 127.99, 128.05, 143.07, 143.26, 143.42 (C_6H_5). Mass spectrum (EI-MS) [*m*/*e* (rel int)]: 460 (5, M^+), 354 (46, $M^+ - PhCHO$), 266 (31, $M^+ - CH_2PhCHO - CH_2CH_2O - OCH_2$). Anal. Calcd for $C_{22}H_{30}GeN_2O_4$: C, 57.56; H, 6.59; N, 6.10. Found: C, 57.53; H, 6.67; N, 6.15.

4,12-Diphenyl-1,7,9,15-tetraoxa-4,12-diaza-8-germaspiro[7.7]-pentadecane, $[PhN(CH_2CH_2O)_2]_2Ge$ (3). A mixture of alkanolamine **6** (0.80 g, 4.4 mmol), $(EtO)_4Ge$ (0.56 g, 2.2 mmol), and toluene (20 mL) was refluxed for 50 h. The resulting solution was reduced in volume to 4 mL and stored at −18 °C to give colorless microcrystals of **3** (0.42 g, 44%). NMR spectra: ^1H, δ 3.38 (t, 8H, NCH_2), 3.89 (t, 8H, OCH_2), 6.89−6.94, 7.28−7.32 (m, 10H, C_6H_5); $^{13}C\{^1H\}$, δ 56.29 (NCH_2), 62.82 (OCH_2), 115.52, 119.30, 128.70, 149.86 (C_6H_5). Mass spectrum (EI-MS) [*m*/*e* (rel int)]: 432 (5, M^+). Anal. Calcd for $C_{20}H_{26}GeN_2O_4$: C, 55.74; H, 6.08; N, 6.50. Found: C, 55.40; H, 5.92; N, 6.36.

$MeN(CH_2CH_2O)_2Ge(OH)_2$ (7). Water (3 mL) was added to a stirred solution of the compound **1** (2.00 g, 6.5 mmol) in toluene (10 mL) at room temperature. The reaction mixture was stirred at room temperature during 72 h, and all volatiles were removed under reduced pressure. The residue was recrystallized from the mixture of methanol/acetone (1:3) to give **7** (1.30 g, 89%). NMR spectra: ^1H, δ 2.58 (s, 3H, NCH_3), 2.65−2.71 (m, 4H, NCH_2), 3.75−3.79, 3.85−3.90 (m, 4H, OCH_2), signals of OH groups have not been found in the spectrum; $^{13}C\{^1H\}$, δ 44.59 (NCH_3), 55.82 (NCH_2), 58.10 (OCH_2).

Attempted Synthesis of 1 via $MeN(CH_2CH_2OSiMe_3)_2$. A mixture of $MeN(CH_2CH_2OSiMe_3)_2$ (10.54 g, 0.04 mol) and $GeCl_4$ (4.29 g, 0.02 mol) in $CHCl_3$ solution (15 mL) was refluxed for 9 h. No traces of **1** have been found in reaction mixture according to NMR data.

X-ray Crystallography. Crystal data, data collection, structure solution, and refinement parameters for compounds **2** and **3** are given in Table 1. Both experiments were performed at 120 K on Bruker SMART 1K diffractometer using Mo Kα radiation (0.710 73 Å). Semiempirical absorption corrections based on the measurements of equivalent reflections were applied. The structures were solved by direct methods[38] and refined by full-matrix least squares based on F^2 with anisotropic thermal parameters for all non-hydrogen atoms.[39] All hydrogen atoms were found from difference Fourier syntheses and refined isotropically for both **2** and **3**. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications nos. CCDC-247115 and -247116. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [fax, +44−1223-336-033; E-mail, deposit@ccdc.cam.ac.uk].

Table 1. Crystal Data, Data Collection, Structure Solution, and Refinement Parameters for **2** and **3**

	2	3
formula	$C_{22}H_{30}GeN_2O_4$	$C_{20}H_{26}GeN_2O_4 \cdot C_7H_8$
fw	459.07	523.15
cryst system	tetragonal	monoclinic
space group	$P4_12_12$	$P2_1/n$
a, Å	11.6124(1)	17.0253(7)
b, Å	11.6124(1)	18.4791(7)
c, Å	15.5183(2)	17.4343(7)
β, deg		118.135(1)
V, Å^3	2092.61(4)	4836.9(3)
Z	4	8
d(calcd), g·cm^{-3}	1.457	1.437
abs coeff, mm^{-1}	1.495	1.303
F(000)	960	2192
θ range, deg	2.19−27.99	1.38−28.00
index ranges	$-15 \le h \le 13$	$-22 \le h \le 9$
	$-15 \le k \le 13$	$-24 \le k \le 23$
	$-19 \le l \le 20$	$-15 \le l \le 23$
reflcns collcd	15 351	27 669
indpdt reflcns	2540	11 658
R_{int}	0.0418	0.0333
data/param	2540/192	11 658/885
GOOF on F^2	1.068	0.950
R1 [$I > 2\sigma(I)$]	0.0246	0.0424
wR_2 (all data)	0.0570	0.1109
largest diff peak/hole (e·Å^{-3})	0.323/−0.250	1.568/−0.639

Results and Discussion

Synthesis. According to the literature, only two of compounds **III** (M = Ge) were synthesized so far, $[HN(CH_2CH_2O)_2]_2Ge$ and $[HN(CH_2CHMeO)_2]_2Ge$, but no structural information was reported.[13] These compounds have been synthesized via reaction of GeO_2 or $HN(CH_2CHR'O)_2Ge(OH)_2$ with the corresponding dialkanolamine. The treatment of GeO_2 with **4** did not lead to the expected **1**.[13] Moreover, the authors have suggested the impossibility of the synthesis of derivatives with electron-donating groups at the nitrogen atoms as "the germanium center will be too electron-rich and become unstable".[13] Two closely related compounds where the hexacoordination of the Ge atom is possible, $[S(CH_2CH_2S)_2]_2Ge$ and $[O(CH_2CH_2S)_2]_2Ge$, have been studied by X-ray diffraction, but the Ge atom in the compounds was found to be tetracoordinated.[40] In addition, the examples of structural investigations of neutral germanium compounds

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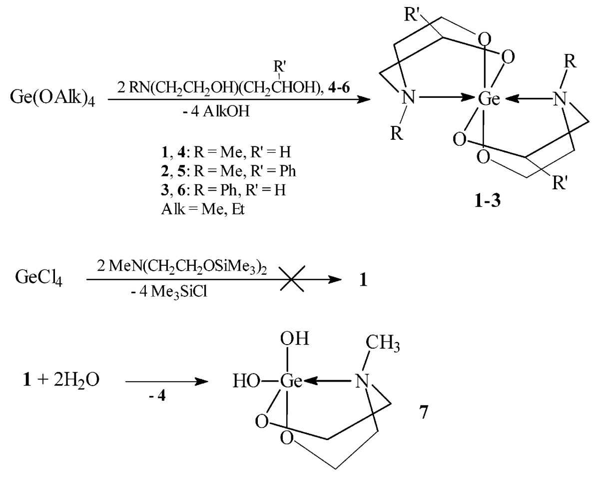
Scheme 1



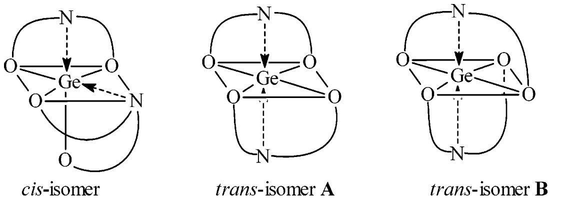
with hexacoordinated Ge atom are very rare.[41] The hexacoordinated tin derivative $[HOCH_2CH_2N(CH_2CH_2O)_2]_2Sn$ (according to crystallographic data) has been obtained from the reaction of $SnCl_4$ with triethanolamine,[14,15] while another stannaspirobis(ocane), $[CH_3N(CH_2CH_2O)_2]_2Sn$, has been prepared by transalkoxylation reaction between **4** and adduct $Me_2NH{\cdot}Sn(OMe)_4$. The authors have found from Mössbauer spectroscopy data that the tin atom is hexacoordinated in $[CH_3N(CH_2CH_2O)_2]_2Sn$.[17] Lukevics et al. have reported that several silaspirobis(ocanes) are formed in reactions of $Si(OAlk)_4$ with dialkanolamines, but yields have not been reported. The authors suggested the weakening of $Si\leftarrow N$ interaction in silaspirobis(ocanes) in comparison with that in "usual" silocanes (**B**) from mass-spectrometry data.[18]

We have also used this reaction for the syntheses of spirobis(ocanes) **1**−**3**. Dialkanolamines **4**−**6** react in refluxing toluene or benzene with $Ge(OAlk)_4$ (Alk = Me or Et) to give the corresponding spirobis(ocanes) **1**−**3**, which were isolated in high or moderate yields (Scheme 1). The substances are very moisture sensitive. The reaction of controlled hydrolysis of **1** led to dihydroxygermocane **7** with high yield. Dialkanolamine **5** has been prepared by the treatment of $MeN(H)CH_2CH_2OH$ with styrene oxide. The product was a mixture of the expected **5** (95%) and $MeN(CHPhCH_2OH)CH_2CH_2OH$ (5%) and was used in the next reaction without further purification. We have also tested another approach to the spirobis(ocane) **1**. Recently, we have reported the reaction of $GeHal_4$ (Hal = Cl, Br) with 1 equiv of $MeN(CH_2CH_2OSiMe_3)_2$ readily led to the dihalogermocanes $MeN(CH_2CH_2O)_2GeHal_2$.[6] However, our attempts to prepare **1** via reaction of $GeCl_4$ with 2 equiv of $MeN(CH_2CH_2OSiMe_3)_2$ failed.

The composition and structures of **1**−**3** and **7** were established by ^1H and ^{13}C NMR spectroscopy, mass spectrometry and elemental analysis data.

NMR Studies. ^1H and ^{13}C NMR spectra are in accord with the suggested structures. In the ^1H NMR spectra of **1** and **3** the signals of the methylene protons of the "ocane" skeleton appear as a set of two pseudotriplets, forming an AA′XX′ spin system ($J \sim 6$ Hz). The ^1H NMR spectrum of **2** is more complicated due to the nonequivalence of all H atoms in one dialkanolamine moiety. It should be noted that this compound exists as a mixture of three diastereomers. The diastereomers differ in position of phenyl groups toward the "ocane" skeleton. The proton resonances of the Me−N and NCH_2 groups in **1** and **2** are downfield shifted in comparison to those in the model compounds **4** and **5** [**4**, δ 2.23 (CH_3), 2.50 (NCH_2); **5**, see Experimental Section]. These shifts may be explained by hexacoordination of the Ge atoms in **1** and **2** in $CDCl_3$ solutions.[42] In contrast, no downfield shift of the NCH_2 group signal in the ^1H NMR spectrum of **3** was observed in comparison with that for model alkanolamine **6** [**6**, δ 3.41 (NCH_2)]; i.e., the transannular interactions $Ge\leftarrow N$ in **3** ($CDCl_3$ solution) are expectedly weaker than those in **1** and **2**.

Chart 1. Three Possible Isomers for Hexacoordinate **1**−**3**



cis-isomer *trans*-isomer **A** *trans*-isomer **B**

In the ^{13}C NMR spectra of **1**−**3** the signals of the carbon atoms of the "ocane" skeleton have the expected values.[42] There are three different signals for the C atoms of compound **1**, six signals for those of **3**, and 25 signals for the three diastereomers of **2** ($27 = 9 \times 3$ required peaks). The hexacoordinate compounds **1**−**3** may exist as three possible isomers, e.g., cis- and trans-isomers as shown in Chart 1, but it should be noted that in the trans- and cis-isomers of **1** and **3**, two dialkanolamine groups are equivalent. Thus, in theory it is impossible to define what kind of isomer exists in $CDCl_3$ solution, but we can conclude that only one isomer is present for both compounds under these conditions. The conclusion was supported by ^1H NMR data of **1** at −50 °C. Little change in the ^1H NMR spectrum of **1** at −50 °C was found in comparison to that at 23 °C; only a partial broadening of signals was detected.

Although different sets of signals should be present in the ^{13}C NMR spectrum of the trans- and cis-isomers for compound **2**, it is very difficult to determine unambiguously the type of isomer in this case due to the presence of three diastereomers in solution.

X-ray Studies. To the best of our knowledge compounds **2** and **3** are the first derivatives of germanium containing two dialkanolamine moieties that have been structurally characterized. To our knowledge only $[PhN(CH_2CH_2O)_2]_2Si$[18] [Si atom is tetracoordinated; Si−N distances are 3.16(1)−3.345(9) Å for two independent molecules] and $[HOCH_2CH_2N(CH_2CH_2O)_2]_2Sn$ [two modifications, Sn atom is hexacoordinated; the Sn−N distances are 2.33(1)−2.38(1) Å][14,15] have been crystallographically studied among spirobis-

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Table 2. Selected Bond Lengths (Å) and Angles (deg)[a]

2		**3a**[b]		**3b**[b]	
Ge(1)−N(1)	2.307(2)	Ge(1)−N(1)	3.016(2)	Ge(2)−N(3)	3.055(2)
		Ge(1)−N(2)	2.795(2)	Ge(2)−N(4)	2.779(2)
Ge(1)−O(1)	1.821(1)	Ge(1)−O(11)	1.761(2)	Ge(2)−O(31)	1.761(2)
Ge(1)−O(2)	1.834(1)	Ge(1)−O(12)	1.753(2)	Ge(2)−O(32)	1.756(2)
		Ge(1)−O(21)	1.744(2)	Ge(2)−O(41)	1.749(2)
		Ge(1)−O(22)	1.755(2)	Ge(2)−O(42)	1.753(2)
intraligand (cis)		O−Ge−O			
O(1)−Ge(1)−O(2)	103.56(6)	O(21)−Ge(1)−O(12)	124.19(8)	O(41)−Ge(2)−O(42)	113.52(8)
O(1)−Ge(1)−N(1)	81.79(6)	O(21)−Ge(1)−O(22)	112.10(8)	O(41)−Ge(2)−O(32)	122.40(8)
O(2)−Ge(1)−N(1)	80.26(6)	O(12)−Ge(1)−O(22)	106.16(7)	O(42)−Ge(2)−O(32)	107.01(8)
interligand (cis)		O(21)−Ge(1)−O(11)	101.78(7)	O(41)−Ge(2)−O(31)	101.08(7)
O(1)−Ge(1)−O(1)$^{\#1}$	92.25(9)	O(12)-Ge(1)−O(11)	109.72(7)	O(42)−Ge(2)−O(31)	99.90(8)
O(1)−Ge(1)−O(2)$^{\#1}$	93.99(6)	O(22)−Ge(1)−O(11)	100.28(8)	O(32)−Ge(2)−O(31)	110.47(7)
O(2)−Ge(1)−N(1)$^{\#1}$	84.40(6)	O−Ge−O(av)	109.04	O−Ge−O (av)	109.06
N(1)−Ge(1)−N(1)$^{\#1}$	105.06(9)				
cis-angle (av)	91.62	O-Ge-N (trans)			
interligand (trans)		O(11)−Ge(1)−N(2)	172.23(7)	O(31)−Ge(2)−N(4)	171.71(6)
O(1)−Ge(1)−N(1)$^{\#1}$	170.44(6)	O(22)−Ge(1)−N(1)	165.37(7)	O(42)−Ge(2)−N(3)	162.59(7)
O(2)−Ge(1)−O(2)$^{\#1}$	154.67(9)				
ΔN[c]	0.468(2)	ΔN(1)[c]	0.207(3)	ΔN(3)[c]	0.176(2)
		ΔN(2)[c]	0.263(2)	ΔN(4)[c]	0.271(2)

[a] Symmetry transformations used to generate equivalent atoms: (#1) *y*, *x*, −*z*. [b] **3a**,**b** are two crystallographically independent molecules of **3**. [c] ΔN denotes the deviation of nitrogen atom from the plane of three neighboring carbon atoms.

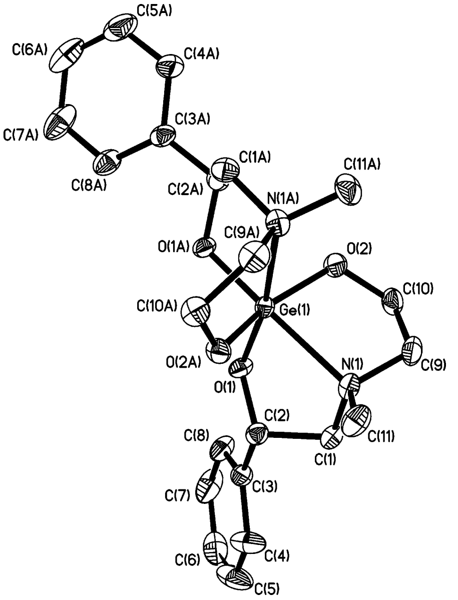

Figure 1. Molecular structure of **2**. Hydrogen atoms are omitted for clarity.

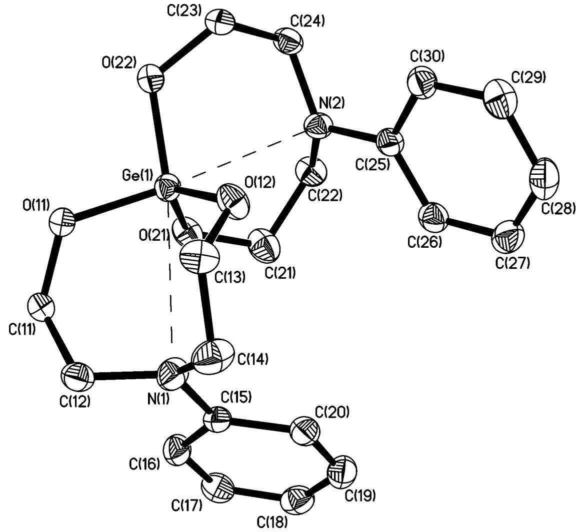

Figure 2. Molecular structure of **3**. One independent molecule is presented. Hydrogen atoms are omitted for clarity.

(ocanes) of the 14 group elements. Analysis of the Cambridge Structural Database (July 2004)[43] shows that only five structures with O_4GeN_2 structural fragment have been documented. All of them contain ethylenediaminetetraacetic acid moiety, and it is characteristic that the Ge−N contacts are very short due to the bonding of the Ge atom with carboxylate groups.

The molecular structures of **2** and **3** (one independent molecule) are shown in Figures 1 and 2. Table 2 lists selected geometrical parameters for these compounds. The molecules of **2** lie on a crystallographic 2-fold axis. In the structure of **3**, the asymmetric unit contains two independent molecules of the germocane and two independent solvate toluene molecules. The coordination polyhedron of Ge atom in compound **2** represents a distorted octahedral geometry with N(1) and N(1A) atoms in cis-orientation. The O−Ge−N angles [except O(1)−Ge(1)−N(1A) and O(1A)−Ge(1)−N(1), 170.44(6)°] and O−Ge−O angles [except O(2)−Ge(1)−O(2A), 154.67(9)°] range between 80.26(6) and 105.06(9)°. Previously studied $[HOCH_2CH_2N(CH_2CH_2O)_2]_2Sn$ also possesses cis-geometry.[14,15] In contrast, trans-orientation of intermolecular donor molecules is usual for $MX_4{\cdot}2D$ (M = Si, Ge, Sn; D = external donor)[41] except some cases with special steric requirements of donor molecule, such as $SiF_4{\cdot}$2,2′-bipy where the cis-structure realizes.[44] The Ge←N bonds [2.307(2) Å] in **2** are much longer than usual covalent Ge−N bonds (1.80−1.90 Å).[22] At the same time this value is close to those previously found for Ge←N transannular bonds in

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molecules with pentacoordinated Ge atom like germatranes and germocanes which also are based on alkanolamine moiety. For example, in germatranes with the $N\rightarrow GeO_{3-}O$ fragment the Ge←N bond distance lies within 2.105−2.156 Å.[4] The Ge←N bond length in $HN(CH_2CH_2O)_2Ge(OH)_2$ equals 2.123(4) Å.[45] On the other hand, the Ge←N distance in a germocane with two donor substituents, $MeN(CH_2CH_2O)_2Ge(2\text{-thienyl})_2$, is substantially longer [2.446(8) Å].[11] Thus, the electron-donor properties of the Me group in **2** lead to the formation of two sufficiently strong transannular Ge←N bonds.

The presence of nitrogen atoms [N(1) and N(1A)] in trans-positions to O(1) and O(1A) effects very little change in the length of Ge−O(1) and Ge−O(1A) bonds (1.821(1) Å) in comparison to the Ge−O(2) and Ge−O(2A) bonds [1.834-(1) Å]. However, the Ge−O bonds in **2** are longer than those in Ge(O−*i*-Pr)$_4$, [1.745(1) Å], which is the only tetraalkoxygermane studied crystallographically.[46] The elongation results from additional electron density donation from two MeN groups on the GeO_4 fragment. Comparison of the Ge−O bond lengths in **2** with those in closely related $MeN(CH_2CH_2O)_2Ge(-OCH_2CH_2O-)$ with a pentacoordinated germanium atom shows that the coordination polyhedron of the Ge atom in the latter compound represents a distorted trigonal bipyramid.[47] This compound contains two different types of Ge−O bonds: three equatorial bonds [1.776(6)−1.795(6) Å] and one axial bond [1.808(6) Å] which are situated on the opposite side to the N atom and is slightly longer than the three others. The Ge←N distance in the compound is quite short (2.159(7) Å).[47] However, all four Ge−O bonds are noticeably shorter than those found in **2**. Thus, we can note a large influence of two internal donor groups on the GeO_4 fragment in **2** in comparison with the same influence of the one MeN group in $MeN(CH_2CH_2O)_2Ge(-OCH_2CH_2O-)$.[47]

The coordination environment of the both N atoms in compound **2** is approximately tetrahedral, and the Ge−N−C and C−N−C angles range between 102.1(1) and 118.1(1)°. The nitrogen atoms are displaced by 0.47 Å from the plane defined by three carbon atoms toward the Ge atom. The conformation of the eight-membered rings −Ge−O−C−C−N−C−C−O− in **2** may be regarded as a boat−chair, similar to that recently found for $MeN(CH_2CH_2O)_2GeBr_2$,[6] while previously studied spirogermocanes, such as *n*-BuN$(CH_2CH_2O)_2Ge[CH_2CH_2C(O)O-]$ and $MeN(CH_2CH_2O)_2Ge(-OCH_2CH_2O-)$ exhibit boat−boat conformation.[47,48]

In contrast to what is found for **2**, the primary coordination environment of the Ge atom in **3** is formed by four covalent bonded oxygen atoms and may be treated as a distorted tetrahedron. The O−Ge−O angles range between 99.90(8) and 124.19(8)°. The Ge−O distances [1.744(2)−1.761(2) Å] are shorter than those in **2** and are comparable with those found for closely related Ge(O−*i*-Pr)$_4$ [1.745(1) Å].[46] It confirms the absence of the considerable donation of the electron density from the PhN group on the GeO_4 fragment as it was found from NMR data (vide supra). However, the Ge−N distances [2.779(2)−3.055(2) Å] are significantly shorter than the sum of the van der Waals radii of the germanium and the nitrogen (3.72 Å) and are comparable with the lengths of Ge←N weak secondary interactions found in the structures of azagermatranes $N[(CH_2CH_2N(SiMe_3)]_3$-Ge−X [2.743(2) Å, X = *n*-Bu; 2.766(2) Å, X = Ph].[22] As well, N atoms in **3** are slightly shifted *toward* the Ge atom by 0.18−0.27 Å. Consequently, the germanium atom in **3** can be regarded as [4 + 2]-coordinated. If we consider the coordination polyhedron of the Ge atom as a strongly distorted octahedron, N atoms will occupy cis-positions. It should be noted that the GeO_4 fragment is more attractive for electron donation from the PhN group than SiO_4 moiety.[18] The Si←N distances in closely related $[PhN(CH_2CH_2O)_2]_2Si$ range between 3.16(1) and 3.345(9) Å (two independent molecules), and distortions of tetrahedron (coordination polyhedron of the Si atom) are noticeably smaller (O−Si−O angles: 106.9−114.4°). The approximate equality of the Si−O bond lengths in $[PhN(CH_2CH_2O)_2]_2Si$ (1.61−1.62 Å)[18] with those in closely related silicon tetraalkoxides [Si(O−*i*-Pr)$_4$ 1.615(1) Å, Si(O-Menthoxy)$_4$ 1.615(5)−1.624(5) Å][49,50] is an additional confirmation of the appropriateness of the assertion about the weakness or absence of a transannular interaction in $[PhN(CH_2CH_2O)_2]_2M$, where M = Si and Ge. The eight-membered ring in **3** has a crown conformation like that in previously studied $MeN(CH_2CH_2O)_2Ge(2\text{-thienyl})_2$, a germocane with a weak Ge←N interaction.[11] Thus, the variation of the substituents at nitrogen atoms in spirobis-(germocanes) easily leads to a decrease or increase of the effective charge on the Ge atom.

DFT Calculations. As shown above hexacoordinate germanium derivatives of dialkanolamines may exist as three different isomers (see Chart 1). One can expect that these compounds may even possess a structure with a penta- or tetracoordinated Ge atom. To determine the structures of all possible compounds discussed above and to estimate their comparative stability, we have carried out DFT calculations on these isomers up to the PBE level of theory. The most important calculated geometry parameters of the compounds, relative energies, as well as topological properties of Ge←N and Ge−O bonds, are listed in Tables 3−5. The possible calculated structures of **1** are presented in Figures 3−6. There is a satisfactory agreement between main geometry parameters of *cis*-**2** and *cis*-**3** for the solid phase (crystal structures) and for the free molecules (calculation data). However, the calculated structure of *cis*-**2** in contrast to the solid-state data possesses two different Ge←N bonds. The explanation of this disagreement may consist in the weakness of the

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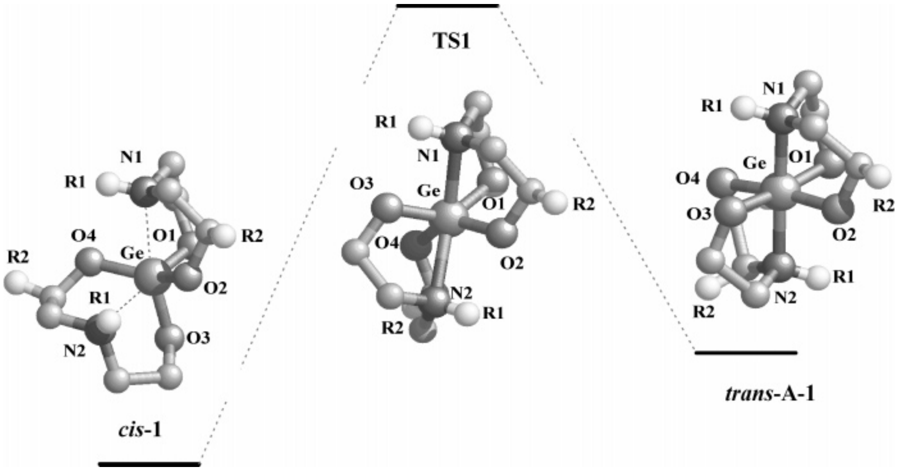

Figure 3. DFT-calculated structures of *cis*-**1** and *trans*-**A-1** as well as a structure of a transition state (**TS1**). Hydrogen atoms are omitted for clarity.

Table 3. Calculated Main Geometrical Parameters and the Ge←N and Ge−O Bond Properties for Hexacoordinated Cis- and Trans-Isomers as Well as Tetra- and Pentacoordinated Species of **1**−**3** and for **TS**s

	Ge←N, Å	Ge−O, Å
cis-**1**	2.627[a]	1.820−1.835
trans-**A-1**	2.122[a]	1.900−1.910
trans-**B-1**	2.185[a]	1.868−1.914
penta-**1**	2.380 4.110	1.805−1.831
tetra-**1**	3.986[a]	1.779−1.794
cis-**2**	2.355 2.774	1.822−1.850
trans-**A-2**	2.118[a]	1.900−1.907
trans-**B-2**[b]	2.148 2.155	1.872−1.933
trans-**B-2**[b]	2.147 2.153	1.876−1.926
penta-**2**	2.341 4.102	1.808−1.832
tetra-**2**	3.969 3.975	1.778−1.794
cis-**3**	3.007 3.025	1.794−1.799
trans-**A-3**	2.237[a]	1.872−1.909
trans-**B-3**	3.324[a]	1.778−1.799
TS-1	2.503[a]	1.847−1.871
TS-2	2.486 2.544	1.845−1.870
TS-3	2.445 2.618	1.839−1.873

[a] Two identical Ge−N distances were found in this compound. [b] Two different structures were found due to different positions of phenyl groups.

Table 4. Relative Energies (kcal·mol^{-1}) of All Calculated Isomers of **1**−**3** as Well as Calculated Activation Barrier (kcal·mol^{-1}) of the Rearengements *trans*-**A** → *cis*-**A** and *cis*-**A** → *trans*-**A**

	1	**2**	**3**
cis-	0	0	0
trans-**A**-	3.883	0.863	14.821
trans-**B**-	8.753	5.102[a] 6.220	9.804
penta-	7.565	7.515	*b*
tetra-	21.468	23.042	*b*, *c*
E_{act}(*trans*-**A**- → *cis*-**A**)	12.129	12.511	6.514
E_{act}(*cis*-**A**- → *trans*-**A**-)	16.012	13.374	21.335

[a] Two different structures were found due to different positions of phenyl groups. [b] No stable compounds were found for this structure type. [c] *trans*-**B-3** isomer may be considered as *tetra*-**3**.

Table 5. Calculated Ge←N and Ge−O Bond Properties for Cis-Isomers of **1**−**3**

	Ge←N			Ge−O		
	$\rho(\mathbf{r})$, au	$\nabla^2\lambda(\mathrm{r})$, au	$\|\lambda1\|/\lambda3$	$\rho(\mathbf{r})$, au	$\nabla^2\rho(\mathbf{r})$, au	$\|\lambda1\|/\lambda3$
cis-**1**	0.031	0.058	0.235	0.126−0.130	0.419−0.456	0.237−0.241
cis-**2**	0.023 0.051	0.048 0.086	0.209 0.274	0.121−0.129	0.398−0.458	0.235−0.241
cis-**3**	0.014	0.035	0.197	0.137	0.494-0.510	0.233−0.235

transannular bond in hexacoordinated compounds **1**−**3** and in the absence of high symmetry in compound **2**. The latter leads to the possibility of the existence of different conformations as well as diastereomers for **2** with similar energies but different geometries.

We have found that the most stable isomer for **1**−**3** in the gas phase is the cis-isomer. However, the calculated relative energies of both possible types of trans-structures of **1**−**3** (Table 3) are higher than those for the cis-isomers, but the difference is not that large.

We have found the transition state geometry (**TS**) of *cis*-**A** ↔ *trans*-**A** rearrangement process (Figure 3, Tables 3 and 4). The computed barrier of the gas-phase interconversion of *cis*-**A** into *trans*-**A** is low (13.4−21.3 kcal mol^{-1}), and the analogous barrier for the reverse process is even lower (6.5−12.1 kcal mol^{-1}). It should be noted that these reactions proceed without cleavage of Ge←N bonds.

Besides the structures with the hexacoordinated Ge atom for **1**−**3** we have also detected two other local minima for **1** and **2** on the potential energy surface. These structures correspond to the derivatives of the pentacoordinated Ge atom (*penta*-**1**, *penta*-**2**, Figure 5) and the tetracoordinated Ge atom (*tetra*-**1**, *tetra*-**2**, Figure 6). Their main geometry and energy parameters are listed in Tables 3 and 4. The coordination polyhedron of the Ge atom in *penta*-**1** and *penta*-**2** represents a distorted trigonal bypyramid with the N atom and one O atom in apical positions while three other O atoms occupy equatorial sites. The coordination environment of the Ge atoms in *tetra*-**1** and *tetra*-**2** is formed by four O atoms and may be treated as a distorted tetrahedron. The isomers with penta- and tetracoordinated Ge atoms are less stable than the structures with hexacoordinated Ge atom discussed above. The considerable contraction of the Ge−O bonds in the range from six- to four-coordinated germanium derivatives should be pointed out; it corresponds to experi-

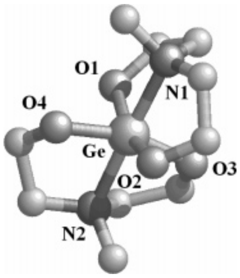

Figure 4. DFT-calculated structure of *trans*-**B**-**1**. Hydrogen atoms are omitted for clarity.

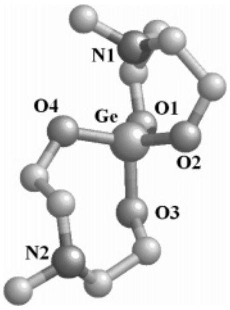

Figure 5. DFT-calculated structure of *penta*-**1**. Hydrogen atoms are omitted for clarity.

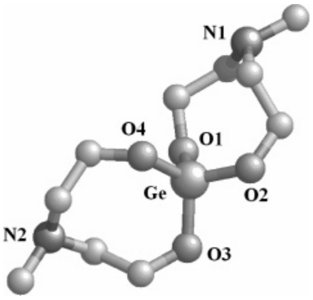

Figure 6. DFT-calculated structure of *tetra*-**1**. Hydrogen atoms are omitted for clarity.

mental data (see X-ray discussion). Also, the DFT calculations have predicted that Ge←N distances are noticeably shorter and corresponding Ge−O bonds are longer in trans-isomers in comparison with those in cis-derivatives.

To our knowledge, these are the first cases in “atrane” and “ocane” chemistry where *stable* structures with and without transannular interaction were found for the same compound by quantum chemical methods. Of interest, compound **3** does not have stable isomers with penta- and tetracoordinated Ge atoms.

On the basis of the theory of “atoms in molecules” (AIM),[51] we have analyzed properties of the Ge−O and Ge←N bonds in *cis*-**1**−**3**. We have found all anticipated BCPs in the bonding regions. According to Bader’s theory, a low value of the electron density [$\rho(\mathbf{r}_{\mathrm{bcp}})$] and the positive value of its Laplacian $\nabla^2[\rho(\mathbf{r}_{\mathrm{bcp}})]$ are the signs of closed-shell interactions (ionic bonds), while shared interactions (such as polar covalent bonds) are characterized by large value of $\rho(\mathbf{r}_{\mathrm{bcp}})$ and a negative value of the Laplacian of $\nabla^2\rho(\mathbf{r}_{\mathrm{bcp}})$. Additionally, the ratio $|\lambda1|/\lambda3$ should be below 1 for ionic bonds. Very recently, Stalke and co-workers have analyzed the closely related system of hexacoordinated silicon, $[\mathrm{Me_2N{-}N{=}C(Ph){-}O}]_2\mathrm{SiF_2}$,[52] and have found that all bonds around the Si atom in the compound possess the dominating ionic character. Our results listed in Table 5 unambiguously testify to the ionic nature of all six bonds around Ge atom in cis-isomers of **1**−**3**.

Conclusion. We have found that tetraalkoxygermanes react with dialkanolamines **4**−**6** leading to the formation of the corresponding spirobis(ocanes) $[\mathrm{RN(CH_2CHR'O)_2}]_2\mathrm{Ge}$ (**1**−**3**). The nature of the substituent R strongly affects the transannular Ge←N distance. According to DFT calculations spirobis(ocanes) may possess four-, five-, and six-coordinated Ge atoms. The derivatives with octahedrally hexacoordinated Ge atoms with the N atoms occuping cis-positions are thermodynamically the most stable.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for the structures of **2** and **3** as well as calculation details. This material is available free of charge via the Internet at http://pubs.acs.org.

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