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X-ray diffraction studies of three 1-phenylethynylgermatranes with two phenyl groups in atrane skeleton

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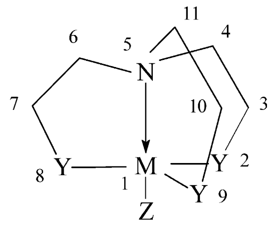
Abstract

Single crystal structures of *treo*-$N(CH_2CH_2O)_2(CHPhCHPhO)GeC{\equiv}CPh$ (**1**), *erythro*-$N(CH_2CH_2O)_2(CHPhCHPhO)GeC{\equiv}CPh$ (**2**) and $N(CH_2CH_2O)_2(CH_2CPh_2O)GeC{\equiv}CPh$ (**3**) were determined by X-ray diffraction studies. These compounds show transannular N→Ge interactions; the strength of this interaction depends on the Ph groups position in atrane skeleton (**1**, $d(N \rightarrow Ge) = 2.210(4)$ Å; **2**, $d(N \rightarrow Ge) = 2.166(4)$ Å; **3**, $d(N \rightarrow Ge) = 2.138(3)$ Å). The structures of these compounds are discussed along with performed DFT calculations data. General trends for molecular structures of the group 14 elements (Si, Ge) metallatranes containing carbon substituents in atrane framework are reviewed.

Keywords: Metallatranes; Germatranes; Hypervalent interactions; X-ray diffraction studies; DFT calculations

1. Introduction

The chemistry of metal derivatives of aminoalcohols such as triethanolamine—metallatranes (A)—has attracted considerable attention [1]. The particular interest has been shown in silatranes and germatranes due to a broad spectrum of their biological activity, which fosters the importance of these species for applications in medical science and pharmacology [4,5]. On the other side, these compounds are important from the theoretical point of view, the nature of intramolecular N→M interaction being the subject of interest [1–3]. Up to date several relationships between the nature of substituent at metal atom [both axial (Z) and three equatorial (Y=O, N–R, S, CH_2)] and the strength of N→M bond have been found for metallatranes (A). In general, stronger electron withdrawing substituent resulted in contraction of N→M distance in these compounds [6–8].



A

It should be noted that the structural chemistry of metallatranes with various substituents attached to carbon atoms of atrane cage has been studied to a very limited extent; accordingly, the influence of these substituents with different electronic and steric properties on the transannular bond strength is still unclear. Among atrane cage substituted metallatranes 3,7,10-trimethyl-substituted compounds [2–4,9] and so-called ‘tribenzometallatranes’ [derivatives of tris(2-hydroxyphenyl)amine (or 2,2′,2″-nitrilotriphenol)] [10–13] are the most known to date. There are only few reports concerning metallatranes

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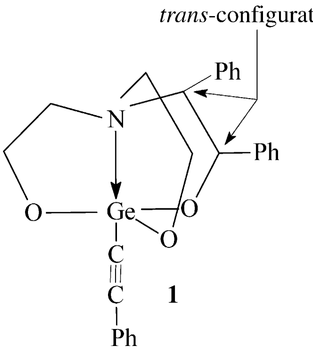
bearing other groups attached to carbon atoms of atrane fragment. The work of Herrmann and co-workers dealing with silatranes, which contain terpene moieties in one arm of triethanolamine ligand should be particularly mentioned [14]. Very recently we have reported on molecular structure of four germatranes contained phenyl group in position 3 or 4 of atrane cage [15]. Although, one phenyl group does not influence significantly N→Ge distance in three studied compounds, however, in the case of 1-trimethylsiloxy-3-phenylgermatrane the elongation of N→Ge distance in comparison with that in unsubstituted analogue was found. Here and after the terms 'substituted' and 'unsubstituted' mean metallatranes with or without any substituents at carbon atoms of atrane cage (positions 3, 4, 6, 7, 10, 11), respectively. At the same time, one could expect that the presence of two phenyl groups at 3- or 4-position of atrane skeleton may considerably influence the nature of N→Ge bond and affect the structure and properties of these molecules. To the best of our knowledge, no diphenylsubstituted main group atranes had been reported in literature when we began this study. However, it is worth to note, that Kim and Do very recently reported the preparation of (R,R,R)–Cp*Ti(OCHPhCH$_2$)$_3$N, they also found the distinction in catalytic behavior (styrene polymerization) of this compound in comparison with that for monomethyl-, dimethyl-, and trimethylsubstituted cyclopentadienyltitanatranes [16]. Nugent et al. also prepared the number of transition metals atranes with (R,R,R)–N(CH$_2$CHPhOH)$_3$ as a ligand, but no X-ray structures were reported [17–19].

Here we describe the molecular structures of three diphenylsubstituted 1-phenylacetylenyl germatranes (**1**, **2**, **3**) as well as their synthesis and spectral characterization. These complexes were synthesized as a part of our research program dedicated to the investigation of main group elements derivatives of alkanolamines (metallatranes and metallocanes) and triethylenetetramines (azametallatranes) [9,15,20–27].



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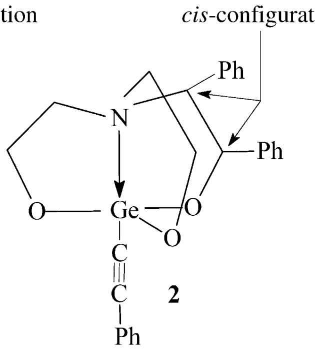

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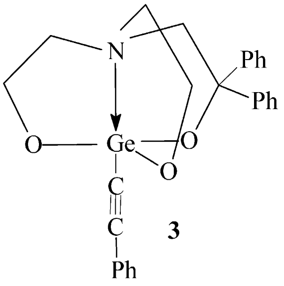

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Our motivation was: (1) to study the possible influence of two phenyl groups in different positions of atrane framework on structure of germatranes in solid state; (2) to compare our data with those previously found for other substituted group 14 elements atranes (X-ray data) and with DFT calculation results. The comparison of presented data with those for four recently studied germatranes **4**–**6**: **4**, N(CH$_2$CH$_2$O)$_3$GeC≡CPh [22]; **4**·CHCl$_3$, N(CH$_2$CH$_2$O)$_3$GeC≡CPh·CHCl$_3$ [28]; **5**, N(CH$_2$CHMeO)$_3$GeC≡CPh [9]; **6** N(CH$_2$CH$_2$O)$_2$(CH$_2$CHPhO)GeC≡CPh [15] was particularly important.

2. Experimental

2.1. Materials and procedures

All manipulations were performed under an argon atmosphere using standard Schlenk techniques. Solvents were dried by standard methods and distilled prior to use. Starting materials PhC≡CGe(OEt)$_3$ [29] and trialkanolamines [30] were prepared according to the literature. ^{1}H and ^{13}C NMR spectra were recorded on a Varian VXR 400 spectrometer (in CDCl$_3$); chemical shifts (in the ^{1}H and ^{13}C NMR spectra) are given in ppm relative to internal Me$_4$Si. The IR spectra were recorded on Zeiss UR-20. Elemental analyses were carried out by the Microanalytical Laboratory of the Chemistry Department of the Moscow State University.

*2.1.1. Preparation of treo-N(CH$_2$CH$_2$O)$_2$(CHPhCHPhO)GeC≡CPh (**1**), erythro-N(CH$_2$CH$_2$O)$_2$(CHPhCHPhO)GeC≡CPh (**2**) and N(CH$_2$CH$_2$O)$_2$(CH$_2$CPh$_2$O)GeC≡CPh (**3**)*

The germatranes were synthesized by stirring of equivalent amounts of PhC≡CGe(OEt)$_3$ and the appropriate trialkanolamine using benzene as the solvent. After 24 h the reaction mixture was filtered to give the product as a white solid, which was then washed with *n*-hexane and dried in vacuo. Crystals suitable for structural analysis were obtained by slow evaporation of the *n*-hexane/chloroform solution.

treo-N(CH$_2$CH$_2$O)$_2$(CHPhCHPhO)GeC≡CPh (**1**). Anal. Calcd for C$_{26}$H$_{25}$GeNO$_3$: C 66.16, H 5.34, N 2.97. Found C 66.11, H 5.22, N 3.02. ^{1}H NMR δ 7.52–7.50, 7.32–7.10 (2m, 15H, Ph-rings protons), 5.21 (d, 1H, OCHPh), 3.73 (d, 1H, NCHPh), 4.13–4.02, 3.84–3.78, 3.36–3.29, 3.00–2.96, 2.79–2.71, 2.34–2.30 (6m, 8H $(AA'XX')_2$ system, $2NCH_2$-CH_2O). ^{13}C NMR δ 140.30, 132.52, 131.51, 130.15, 129.33, 128.84, 128.19, 128.13, 127.81, 127.77, 127.16, 123.03 (Ph-rings carbons), 99.41 (PhC≡), 90.87 (≡C–Ge), 71.61 (OCHPh), 68.61 (NCHPh), 56.64, 56.55 ($2OCH_2$), 48.22, 47.79 ($2NCH_2$). IR (Nujol): ν(C≡C) 2179 cm^{-1}. Yield 81%. M.p. > 250 °C.

erythro-$N(CH_2CH_2O)_2(CHPhCHPhO)GeC{\equiv}CPh$ (**2**). Anal. Calcd for $C_{26}H_{25}GeNO_3$: C 66.16, H 5.34, N 2.97. Found C 65.86, H 5.31, N 2.99. ^1H NMR δ 7.57–7.53, 7.34–7.13, 7.01–6.98 (3m, 15H, Ph-rings protons), 5.41 (d, 1H, OCHPh), 4.33 (d, 1H, NCHPh), 4.08–3.96, 3.80–3.75, 3.26–3.19, 2.95–2.90, 2.81–2.73, 2.54–2.49 (6m, 8H $(AA'XX')_2$ system, $2NCH_2CH_2O$). ^{13}C NMR δ 139.43, 132.47, 131.94, 131.23, 129.21, 128.33, 128.21, 127.78 (broad signal, two carbon atoms), 127.48, 127.31, 122.94 (Ph-rings carbons), 99.39 (PhC≡), 91.00 (≡CGe), 74.33 (OCHPh), 66.77 (NCHPh), 57.47, 56.73 ($2OCH_2$), 50.62 (broad signal, $2NCH_2$). IR (Nujol): ν(C≡C) 2175 cm^{-1}. Yield 80%. M.p. 238–239 °C.

$N(CH_2CH_2O)_2(CH_2CPh_2O)GeC{\equiv}CPh$ (**3**). Anal. Calcd for $C_{26}H_{25}GeNO_3$: C 66.16, H 5.34, N 2.97. Found 66.10, H 5.20, N 3.00. ^1H NMR δ 7.61–7.56, 7.34–7.17 (2m, 15H, Ph-rings protons), 3.82–3.77, 3.70–3.65 (2m, 4H, OCH_2), 3.61 (s, 2H, NCH_2CPh_2); 2.76–2.65 (m, 4H, $2NCH_2$). ^{13}C NMR δ 146.58, 132.55, 128.45, 128.19, 127.86, 127.08, 125.67, 123.23 (Ph-rings carbons), 99.15 (PhC≡), 91.41 (≡CGe), 75.56 ($OCPh_2$), 61.05 (NCH_2CPh_2), 56.93 ($2OCH_2$), 53.18 ($2NCH_2$). IR (Nujol): ν(C≡C) 2173 cm^{-1}. Yield 76%. M.p. 244–245 °C.

According to ^1H and ^{13}C NMR spectra, each of compounds **1** and **2** represents one diastereomeric pair.

2.2. X-ray crystallographic study

Crystal data, data collection, and refinement parameters for compounds **1**, **2** and **3** are listed in Table 1. The structures were solved by direct methods [31] and refined by full matrix least-squares on F^2 [32]. All non-hydrogen atoms were refined with anisotropic thermal parameters. In the structure of **1**, all hydrogen atoms were placed in calculated positions and refined using a riding model. As for compounds **2** and **3**, all hydrogen atoms were found from diff. Fourier synthesis and refined isotropically. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with

Table 1
Crystal and structure refinement data for **1**, **2** and **3**

	1	**2**	**3**
Empirical formula	$C_{26}H_{25}Ge_1N_1O_3$	$C_{26}H_{25}Ge_1N_1O_3$	$C_{26}H_{25}Ge_1N_1O_3$
Formula weight	472.06	472.06	472.06
Color, habit	Colorless block	Colorless block	Colorless plate
Crystal size (mm)	0.20×0.20×0.04	0.30×0.25×0.10	0.30×0.10×0.02
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	*P-1*	$P2_1/c$	$P2_1/c$
Cell dimensions			
a (Å)	10.385(2)	13.439(2)	11.108(1)
b (Å)	10.748(2)	8.060(2)	22.560(2)
c (Å)	11.034(2)	21.390(2)	18.259(2)
α (°)	81.504(4)	90	90
β (°)	82.899(4)	106.98(2)	106.835(2)
γ (°)	64.701(4)	90	90
V (Å^3)	1098.7(4)	2215.9(7)	4379.5(7)
Z	2	4	8
D_{calc} (g cm^{-3})	1.427	1.415	1.432
μ(Mo Kα) (mm^{-1})	1.422	1.410	1.427
F(000)	488	976	1952
Diffractometer	Bruker SMART	Nonius CAD4	Bruker SMART
Radiation, λ (Å)	Graphite monochromatized Mo Kα(0.71073)		
Temperature (K)	120	293	120
θ range (°)	1.87–27.00	1.58–24.98	1.47–27.00
Index ranges	$-10 \le h \le 13$	$-15 \le h \le 15$	$-14 \le l \le 8$
	$-13 \le k \le 13$	$0 \le k \le 9$	$-28 \le k \le 14$
	$-14 \le h \le 14$	$0 \le l \le 25$	$-23 \le l \le 23$
Refl. collected	5429	3889	28,181
Unique refl., R_{int}	4565 (0.0526)	3889(0.0634)	9561(0.0602)
Data/restr./param.	4565/0/281	3889/0/380	9561/0/760
Goof on F^2	0.976	0.947	0.819
R_1 [$I > 2\sigma(I)$]	0.0716	0.0598	0.0404
wR_2 (all data)	0.1268	0.1082	0.1238
Extinction coeff.	0.0039(8)	–	0.00061(13)
Largest diff. peak/hole (e Å^{-3})	0.942/−0.815	0.351/−0.401	1.641/−0.550

the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-240915 (**1**), CCDC-240916 (**2**) and CCDC-240917 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk].

2.3. Calculations

All calculations were performed using the program 'PRIRODA' developed by Laikov, which implements an economical computational procedure [33]. In this work, the non-empirical generalized gradient approximation (GGA) for the exchange-correlation functional of Perdew et al. (PBE) was employed [34,35]. The all electron large orbital basis sets of contracted Gaussian-type functions of the size (8s3p2d):[4s3p2d] for H (14s8p3d2f):[8s4p3d2f] for C (14s8p3d2f):[8s4p3d2f] for N (14s8p3d2f):[8s4p3d2f] for O, and (25s19p14d3f):[18s14p9d3f] for Ge were used for DFT-PBE. Full geometry optimization was performed by DFT-PBE for a number of structures followed by vibrational frequency calculation using analytical first and second derivatives. Each structure has been characterized by the vibrational analysis. The present theoretical method has been used and has given very useful results in the germanium chemistry [36–39].

3. Results and discussions

The molecular structures of **1**, **2**, and **3** are shown in Figs. 1–3. Important bond lengths and angles are summarized in Tables 2 and 3, respectively. The coordination polyhedron of the germanium atoms in studied germatranes represents as usually a distorted trigonal bipyramid with N and C atoms in the apical positions and the three oxygen atoms in equatorial sites. The germanium atom is displaced from the equatorial plane defined by three oxygen atoms by 0.21 (for **1**), 0.20 (for **2**) and 0.18, 0.19 Å (for **3**) towards phenylacetylenyl substituent. The N–Ge–C fragment is almost linear (177.1(2)–179.6(2)°) in all these compounds. All five-membered rings of the germatrane skeleton in **1–3** adopt an 'envelope'-like conformation, the carbon atoms lying in the α-positions to the N atom occupy 'flap' sites. The latter contrasts with geometry previously found for the structures of 3,7,10-trimethylsubstituted atranes [9,40–45].

As stated above, the strength of the $N \rightarrow M$ intramolecular interaction in metallatranes is the most intriguing aspect of their structure. The $N \rightarrow M$ bond length is well-known to become shorter with increasing of electron withdrawing potential of the apical substituent [1,7]. The effect of atrane cage substituent on $N \rightarrow M$ bond strength is still unexplored. However, as it was found for silatranes contained the same apical group Z (X-ray data), a formal replacement of one to three hydrogen atoms in positions 3, 7, and 10 of atrane skeleton by one to three electron donor alkyl groups (Me or Et) leads to minor alterations in $N \rightarrow Si$ transannular bond length. For example, the value of $N \rightarrow Si$ transannular bond in $N(CH_2CHMeO)_3Si$-*p*-tolyl (2.236(3) Å) is greater than that in $N(CH_2CH_2O)_3Si$-*p*-tolyl (2.169(2) Å) [40]. Of special note is the existence of three different modifications of $N(CH_2CH_2O)_3Si$–Ph, where values of $N \rightarrow Si$ bond length are 2.193(5), 2.156(4) and 2.132(4) Å [46–48], while the analogous distance in $N(CH_2CHMeO)_3Si$–Ph is 2.175(6) Å [41]. The same values of $N \rightarrow Si$ bond length (2.120 Å) were found for pair

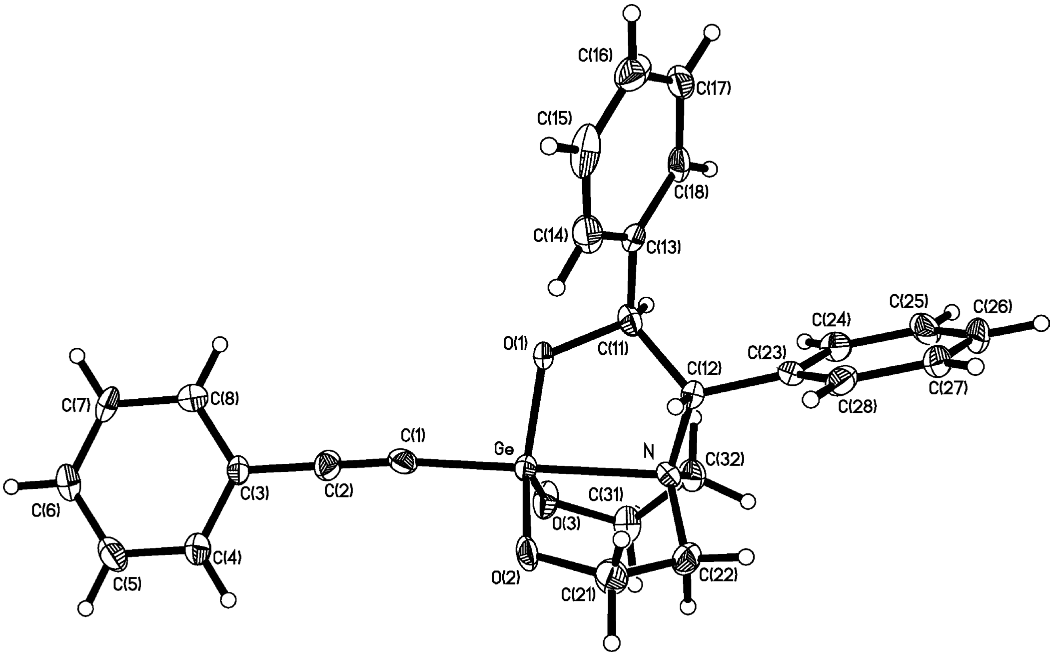

Fig. 1. Molecular structure of **1**. Displacement ellipsoids are shown at 50% probability level.

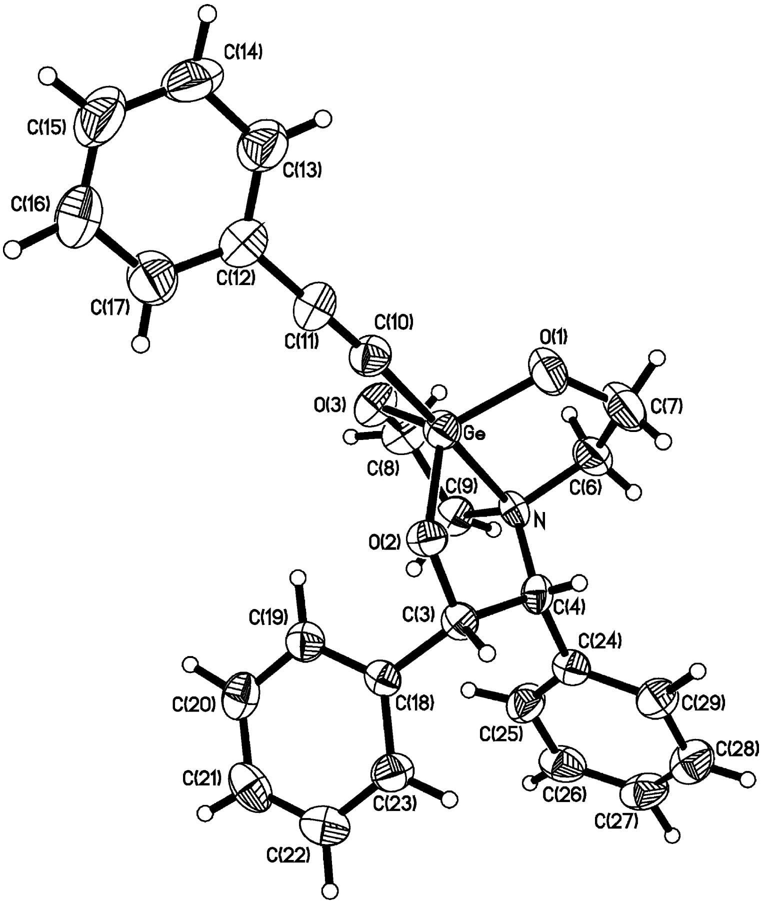

Fig. 2. Molecular structure of **2**. Displacement ellipsoids are shown at 50% probability level.

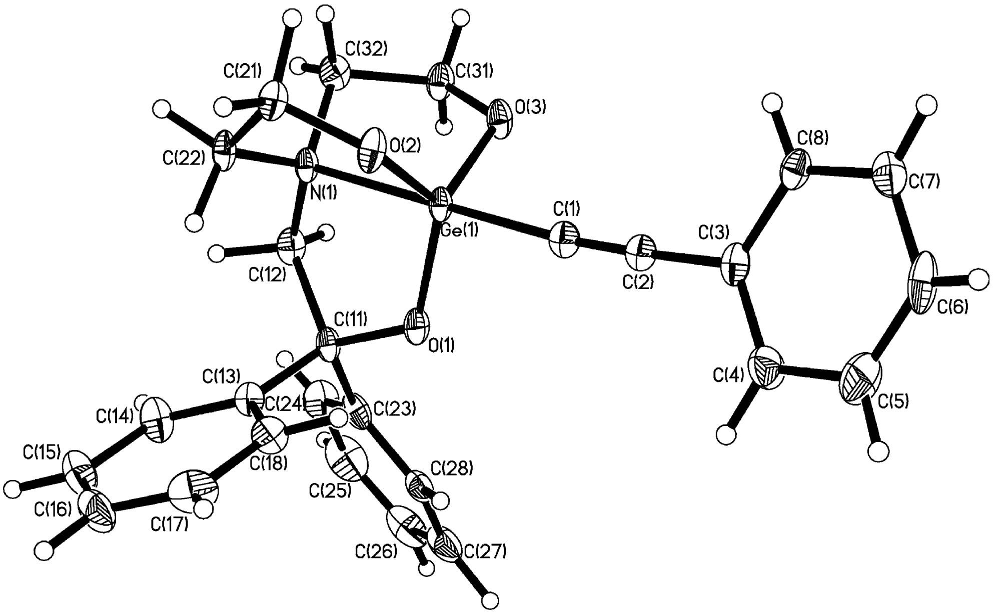

Fig. 3. Molecular structure of **3** (one independent molecule). Displacement ellipsoids are shown at 50% probability level.

Table 2
Selected bond lengths (Å) for **1**–**3**

	1	**2**	**3**	
N–Ge	2.210(4)	2.166(4)	2.138(3)	2.140(3)
C_{ax}–Ge	1.927(5)	1.898(6)	1.918(4)	1.924(4)
O_{sub}–Ge	1.791(4)	1.785(3)	1.783(3)	1.786(3)
O–Ge	1.793(4)	1.780(3)	1.796(3)	1.794(3)
	1.791(4)	1.774(4)	1.794(3)	1.788(3)
$(O–C)_{sub}$	1.429(6)	1.426(6)	1.430(5)	1.429(5)
O–C	1.429(6)	1.420(7)	1.417(5)	1.434(5)
	1.427(6)	1.416(8)	1.413(5)	1.423(5)
$(C–C)_{sub}$	1.555(7)	1.555(8)	1.545(6)	1.543(6)
C–C	1.525(7)	1.517(9)	1.527(6)	1.524(6)
	1.519(7)	1.52(1)	1.519(6)	1.506(6)
$(N–C)_{sub}$	1.477(7)	1.486(7)	1.467(5)	1.475(5)
N–C	1.496(7)	1.476(7)	1.487(5)	1.492(5)
	1.468(7)	1.468(7)	1.479(5)	1.476(5)

$N(CH_2CHMeO)_3Si-CH_2Cl$ and $N(CH_2CH_2O)_3Si-CH_2Cl$ [40] while some alterations have been noticed for $N(CH_2CH_2O)(CH_2CHMeO)_2Si-CH_2Cl$ (2.128 Å) [49] and $N(CH_2CH_2O)_2(CHEtCH_2O)Si-CH_2Cl$ (2.102 Å) [50]. Of interest, the presence of electron withdrawing group (COOH) in position 4 of atrane skeleton does not substantially change transannular N→Si distance in $N(CH_2CH_2O)_2[CH(COOH)CHMeO]Si-CH_2Cl$ (2.136(3) Å) [51] as well as in $N(CH_2CH_2O)_2[CH(COOH)CHMeO]Si-CH{=}CH_2$ (2.169(3) Å [52], unsubstituted analogue—2.150 Å [53]) and in $N(CH_2CH_2O)_2[CH(COOH)CHMeO]Si-(CH_2)_3Cl$ (2.198(3), 2.244(3) Å [51], $N(CH_2CH_2O)_2[CH(COOH)CH_2O]Si-(CH_2)_3Cl$ (2.178, 2.206 Å, two independent molecules [54], unsubstituted analogue—2.18(3) Å [55]). Analogously to above, N→Si bond length in silatran-3-ones ($[N(CH_2CH_2O)_2(CH_2COO)Si-Z$, {Z = CH_2Cl, 2.085 Å [56], unsubstituted derivative, 2.120 Å [40], Z = $(CH_2)_3Cl$, 2.149 Å [57], unsubstituted derivative, 2.18(3) Å [55], Z = CH_3, 2.134 Å [58], unsubstituted derivative, 2.1604(3) Å [59]} and in silatran-3,7-dione ($N(CH_2CH_2O)(CH_2COO)_2Si-Z$, {Z = CH_3, 2.146 Å [60], unsubstituted derivative, 2.1604(3) Å [59]} is similar to that for unsubstituted compounds.

However, there are at least two factors which lead to considerable elongation of N→Si bond in substituted silatranes: (a) the presence of one bulky substituent in position 4 or three Me groups in positions 4, 6, 11 of silatrane skeleton {$[N(CHMeCH_2O)_3Si-CH_3$—2.325 Å [61], unsubstituted analogue—2.1604(3) Å [59]; $N(CH_2CH_2O)_2[CH(i\text{-}Pr)CH_2O]Si-C_6H_5$—2.265 Å [62], 1-phenyl-3,4-terpene-substituted silatrane—2.241(1) Å [14], unsubstituted analogue—three modifications, see above [46–48])} or (b) the presence in atrane cage of one to three benzene rings (benzosilatranes, $N(CH_2CHMeO)_2(o\text{-}C_6H_4-O)Si-CH_2Cl$—2.177 Å [63], $N(o\text{-}C_6H_4-O)_3Si-CH_2Cl$—2.256 Å [64], unsubstituted analogue—2.120 Å [40]; $N(CH_2CHMeO)_2(o\text{-}C_6H_4-O)Si-C_6H_5$—2.193 Å [65]; $N(o\text{-}C_6H_4-O)_3Si-C_6H_5$—2.344(5) Å [11], unsubstituted analogue—three modifications, see above [46–48]). To our opinion, one of the significant reasons for these changes is steric crowding in these systems, such as special steric requirements of 1,2-phenylene group.

According to the previously reported data on X-ray study of substituted and unsubstituted germatranes contained the same apical group Z (Table 4), a formal replacement of three hydrogen atoms in positions 3, 7, and 10 of atrane skeleton by three electron donor methyl groups leads to minor lengthening of N→Ge bond in all cases except one. The substitution of one hydrogen atom in position 3- or 4- by one Ph or Et group does not drastically change N→Ge transannular bond length in germatranes. However, it should be noted the sufficient contraction of this bond in derivative of nitrilotriacetic acid in comparison with that in unsubstituted analogue (Table 4). Thus, according to data known to date the found alterations of N→M bond length in substituted silatranes and germatranes have rather steric than electronic nature or might be caused by crystal field effects as well as dipole–dipole interactions in the solid state [6,74,75].

Values of N→Ge bond length in **1**–**3** as well as these values for previously studied compounds **4**–**6** lie within the range of 2.138(3)–2.210(4) Å. The shortest contact has been found in compound **3** with two electron withdrawing phenyl groups in position 3 of atrane fragment. However, the analysis of values of N→Ge bond length for other structures (Table 2, **4**—2.178(6), **4** $CHCl_3$—2.160(2), **5**—2.199(4), **6**—2.166(6) Å) does not prove the conclusion about the contraction of N→Ge bond in germatranes with electron withdrawing group at carbon atoms of atrane cage.

Table 3
Selected angles (°) for **1**, **2** and **3**

	1	**2**	**3**	
N–Ge–C_{ax}	179.6(2)	177.4(2)	177.1(2)	176.0(2)
C_{ax}–Ge–O_{sub}	97.3(2)	96.8(2)	97.6(2)	97.7(2)
C_{ax}–Ge–O	97.2(2)	98.0(2)	96.6(2)	97.5(2)
	95.4(2)	94.6(2)	93.8(2)	92.3(2)
N–Ge–O_{sub}	82.4(2)	83.5(2)	83.8(1)	83.9(1)
N–Ge–O	84.5(2)	84.1(2)	85.1(1)	85.2(1)
	83.2(2)	83.0(2)	83.4(1)	83.8(1)
O–Ge–O_{sub}	120.3(2)	119.6(2)	123.4(1)	124.6(1)
	118.8(2)	118.4(2)	118.1(1)	119.9(1)
O–Ge–O	117.0(2)	118.3(2)	115.3(1)	112.6(1)
C–N–C_{sub}	116.8(4)	116.8(5)	114.7(3)	114.2(3)
	114.3(4)	112.8(5)	113.2(3)	113.3(3)
C–N–C	114.0(4)	112.2(5)	112.9(3)	112.8(3)
C_{sub}–N–Ge	103.5(3)	104.2(3)	105.9(2)	105.9(2)
C–N–Ge	104.2(3)	105.5(3)	105.6(2)	105.9(3)
	101.7(3)	103.9(4)	103.3(2)	103.5(2)
$(C–O)_{sub}$–Ge	120.9(3)	122.0(3)	121.0(2)	119.8(2)
C–O–Ge	118.9(3)	119.2(4)	119.1(3)	118.1(3)
	118.5(3)	119.1(4)	117.2(3)	116.9(2)
$(N–C–C)_{sub}$	107.6(4)	109.6(5)	109.9(3)	109.5(3)
N–C–C	109.1(4)	108.4(6)	107.7(4)	108.2(3)
	108.5(4)	107.1(5)	106.8(3)	107.1(3)
$(C–C–O)_{sub}$	106.8(4)	107.6(5)	109.9(3)	107.6(3)
C–C–O	110.4(4)	110.4(6)	110.1(4)	109.7(3)
	109.3(4)	110.1(5)	109.9(3)	109.7(4)

Table 4
Values of N–Ge bond length in substituted germatranes and unsubstituted analogues

Substituted germatrane	N–Ge (Å)	N–Ge (Å) in unsubstituted analogue, $Z–Ge(OCH_2CH_2)_3N$
$C_{13}H_8(SnMe_3)–Ge(OCHMeCH_2)_3N$	2.247(9) [43]	2.206(6) [66]
$C_{13}H_8(H)–Ge(OCHMeCH_2)_3N$	2.194(5), 2.191(5) [43][b]	2.166(2) [27]
$C_6H_5–C(Br)=C(Br)–Ge(OCHMeCH_2)_3N$	2.196(7) [8]	2.23(1) [21]
$C_6H_5–C(Cl)=C(I)–Ge(OCHMeCH_2)_3N$	2.216(8) [44]	2.213(5) [44]
$C_6H_5–C{\equiv}C–Ge(OCHMeCH_2)_3N$ (**5**)	2.199(4) [8]	**4**, 2.178(6) [21][a]
$C_6H_5–C{\equiv}C–Ge(OCH_2CH_2)_2[OCH(C_6H_5)CH_2]N$ (**6**)	2.166(6) [14]	**4**, 2.178(6) [21][a]
$Me_3SiO–Ge(OCH_2CH_2)_2[OCH(C_6H_5)CH_2]N$	2.170(4) [14]	2.128(5) [67]
$F–Ge(OCH_2CH_2)_2[OCH(C_6H_5)CH_2]N$	2.108(2) [14]	2.104(2) [68]
$HO–Ge(OCH_2CH_2)_2[OCH_2CH(C_6H_5)]N$	2.187(2) [14]	2.146(9) [69]
$HO–Ge(OCH_2CH_2)_2[OCH_2CHEt]N$	2.166(6), 2.185(6) [70][b]	2.146(9) [69]
$C_6H_5–Ge(OCH_2CH_2)_2[OC(O)CH_2]N$	2.203(3) [71]	2.212(5) [72]
$HO–Ge[OC(O)CH_2]_3N\cdot H_2O$	2.084(3) [73]	2.146(9) [69]

[a] The value of N–Ge bond length in adduct $\mathbf{4}\cdot CHCl_3$ is 2.160(2) Å [27].
[b] Two independent molecules.

Analogously, the absent of correlation between N→Ge bond length contraction and elongation of C–Ge bond length in the same compounds (Table 2, **4**—1.920(8), $\mathbf{4}\cdot CHCl_3$—1.924(2), **5**—1.919(6), **6**—1.914(7) Å) testifies also against the conclusion referred above. The other important geometrical parameters do not change significantly in the range of compounds **1**–**6**.

We also have carried out DFT calculations on germatranes **1**–**6** up to the PBE level of theory. The most important calculated geometrical parameters of these compounds are listed in Table 5. There is a good agreement between the geometry parameters of studied substances for the solid phase (X-ray data) and for the free molecules (calculated data). However, calculated values of the N→Ge distances for these compounds are somewhat longer (∼0.2 Å) than those found in the solid state. An explanation for these discrepancies is the weakness of the transannular bond in compounds **1**–**6**, which are exposed to crystal field effects and dipole–dipole interactions in the solid state [6, 74,75]. Of interest, the noticeable difference (∼0.04 Å) has been also found between calculated values of Ge–O bond length and those determined in the solid state. The latter values are smaller. It should be also noted the invariability of calculated values of C–Ge bond length for compounds **1**–**6**. The contraction of N→Ge bond length for single molecule (calculated data) is observed in the following range: $\mathbf{4}>\mathbf{5}>\mathbf{2}>\mathbf{6}>\mathbf{1}>\mathbf{3}$. It does not correspond to the same range found for solid state: $\mathbf{1}>\mathbf{5}>\mathbf{4}>\mathbf{2}=\mathbf{6}>\mathbf{4}$ $CHCl_3>\mathbf{3}$. The latter observation testifies crystal field effects and dipole–dipole interactions in the solid state being the main reason of N→Ge bond length alterations.

Table 5
The key bond distances (in Å) (calculated data) in **1**–**6**

	1	**2**	**3**	**4**	**5**	**6**
N–Ge	2.317	2.302	2.292	2.366	2.338	2.308
C_{ax}–Ge	1.913	1.914	1.916	1.912	1.915	1.914
O_{sub}–Ge	1.832	1.835	1.838	1.829	1.830	1.837
O–Ge	1.828	1.832	1.829	1.830	1.830	1.830
	1.832	1.830	1.828	1.829	1.830	1.830

In conclusion, to all appearance steric effects caused by replacement of hydrogen atoms in atrane cage by phenyl groups are the basic reason for N→Ge transannular bond alteration.

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