Structure of an oxo-bridged germatrane dimer

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Abstract

The reaction of tris(2-hydroxyphenyl)amine with Ge(OEt)$_4$ produced 1,1′-oxybis(1-germa-5-aza-2,8,9-trioxatribenzobicy-clo[3.3.3]undeca-3,6,10-triene) (**11**). This reaction proceeded via 1-ethoxy-1-germa-5-aza-2,8,9-trioxatribenzobicyclo[3.3.3]undeca-3,6,10-triene (**10a**). In oxo-bridged germatrane dimer **11**, the Ge–O–Ge moiety is bent at an angle of 131.2(4)°, and Ge–O^{bridge} distances are 1.750(7) and 1.743(6) Å. The other Ge–O distances, by comparison, averaged 1.785(7) Å. The germanium centers in **11** are nearly trigonal bipyramidal by virtue of significant interaction with transannular nitrogen: the Ge–N distances are 2.235(8) and 2.247(7) Å. Ab initio calculations on **11** and H$_3$Ge–O–GeH$_3$ predict a linear Ge–O–Ge geometry when d-orbitals are omitted from the basis set, but correctly predict a bent geometry when d-orbitals are used. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Germatrane; Oxo-bridged dimer; X-ray structures; Tris(2-hydroxyphenyl)amine

1. Introduction

As pointed out by Frye, Vincent and Hauschildt (FVH), tris(2-hydroxyphenyl)amine (or 2,2′2″-nitrilo-triphenol) (**1**) is an interesting chelating agent [1]. It reacts easily with triacetoxysilanes as shown in Eq. (1) or with trichlorosilanes to give tribenzosilatranes (**2**), with R = Ph, Me, vinyl, OAc, or Cl.

(1)
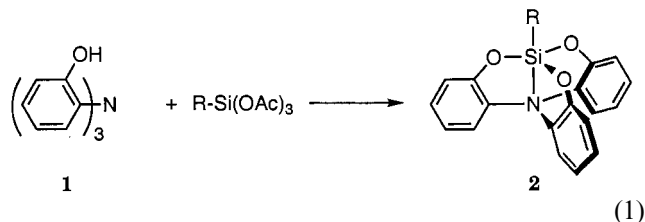
X-ray crystallography of **2** (R = Ph) revealed a Si–N distance of 2.344(5) Å which was emphasized at the time as the first direct evidence of Si–N bonding in such systems [2]. Similarly, Soulié et al. [3] obtained from the reaction of Eq. (2) the expected tribenzosilatrane **3** [4]. Other tribenzosilatranes have been reported [5].

(2)
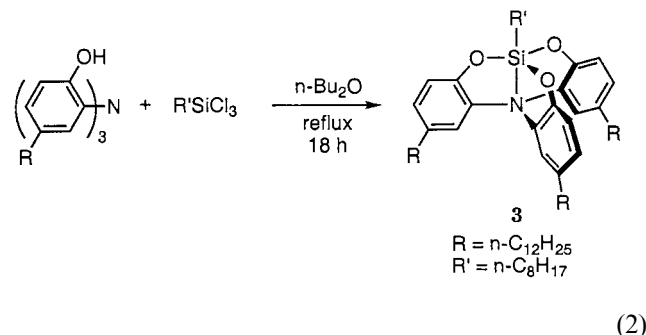
FVH also reported **4** and **5**, formed by reaction of **1** with Al(O–*iso*Pr)$_3$ and Ti(O–*iso*Pr)$_4$, respectively. Müller and Bürgi [6] re-examined the aluminate of **1**, and extended the chemistry of **1** to boron and phosphorus. Aluminate **4** was found by X-ray crystallography to be dimeric (**4**)$_2$. Also, by X-ray crystallography, the borate of **1** was found to have the structure shown for **6**, with a B–N distance of 1.681(5) Å. However, solution-phase NMR studies of Paz-Sandoval et al. gave no evidence of a B–N bond in this compound [7]. In phosphite **7**, P and N were both found to be pyramidal, with the apices of the pyramids pointing away from each other — a Verkadean football [8] with a P⋯N distance of 3.136(5) Å. Based on NMR evidence, Müller and Bürgi suggested that the phosphate ana-

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4　　　　　　　　　**5**

(4)₂
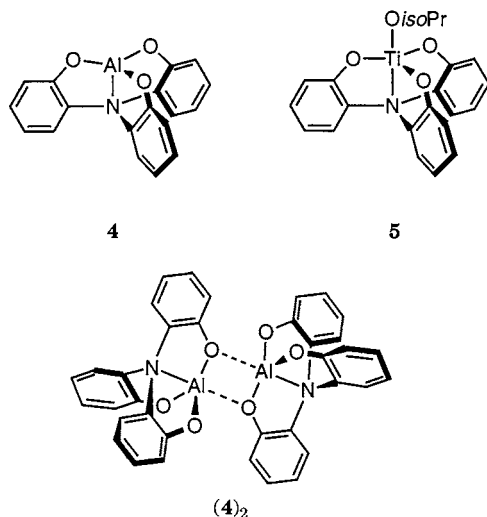
logue of **7** (P=O), also having no P–N bond, reacted with BF₃ to produce **8**, having a transannular P–N bond. Tribenzostannatranes **9** have been reported [9].

6　　　　　　　　　**7**

8　　　　**9**, R = *n*-Bu, *t*-Bu, Ph
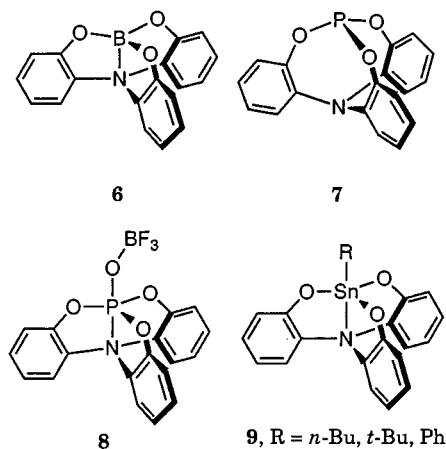
Against this background, it was of interest to us to extend the chemistry of **1** to germanium.

2. Experimental

Mass spectra were obtained on a VG7070E mass spectrometer. NMR spectra were obtained on either a Bruker AC250 spectrometer or a Bruker AM400 spectrometer. The X-ray diffractometer used was a Siemens R3m/v instrument. IR spectra were obtained using a Nicolet 5PC FT-IR spectrometer.

2.1. Solid A

2,2′,2″-Nitrilotriphenol (**1**) was prepared by the method of FVH [1]. Under nitrogen, a solution of 65 mg (0.22 mmol) of **1** in 5 ml toluene was treated with 58 mg (0.23 mmol) of Ge(OEt)₄ and the mixture brought to reflux for 12 h. After cooling, solvent was removed

at the rotary evaporator, and the solid residue was placed on the vacuum line for 3 h, to afford 60 mg of a colorless powder, solid **A**. HRMS Calc. for $C_{20}H_{17}NO_4{}^{74}Ge$ (**10a**): 409.036937. Found: 409.036682. Anal. Calc. for $C_{20}H_{17}GeNO_4$: C, 58.88; H, 4.20; N, 3.43. Found: C, 59.74; H, 4.18; N, 3.26%. EIMS (*m/z*, rel. intensity, calc. rel intensity (in italics) for Ge–C isotopic cluster normalized to most intense peak in cluster): 412 (1.4, *1.8*, M), 411 (9.2, *8.6*, M), 410 (7.6, *8.3*, M), 409 (37.2, *37.2*, M), 408 (15.3, *13.4*, M), 407 (26.4, *26.7*, M), 406 (4.4, *4.5*, M), 405 (19.9, *19.5*, M), 367 (4.6, *3.7*, M − OC₂H₅), 366 (18.1, *20.2*, M − OC₂H₅), 365 (23.0, *17.6*, M − OC₂H₅), 364 (91.0, *91.0*, M − OC₂H₅), 363 (34.0, *31.4*, M − OC₂H₅), 362 (54.0, *65.7*, M − OC₂H₅), 361 (13.2, *9.8*, M − OC₂H₅), 360 (42.8, *48.4*, M − OC₂H₅) [for remainder of the list only the most intense peak of isotopic cluster is listed] 274 (52.0), 246 (23.2), 182 (80.5), 170 (24.1), 166 (20.3), 154 (25.1), 127 (31.4), 115 (28.0), 91 (100.0), 63 (32.0). IR (KBr): 1595, 1486, 1286, 1237, 1113, 1067, 921, 859, 747, 693 cm⁻¹. ¹H-NMR showed this to be a mixture of germatranyl ethoxide **10a** (major) and a compound lacking an ethyl group (minor).

2.2. 1,1′-Oxybis(1-germa-5-aza-2,8,9-trioxatribenzobicyclo[3.3.3]undeca-3,6,10-triene) (**11**)

A sample of solid **A** was dissolved in boiling THF. The solvent was allowed to escape over several weeks through a pinhole in the cap at room temperature (r.t.) in air until the solvent had completely evaporated, affording transparent crystals of **11**, which, though of poor quality, proved minimally suitable for X-ray crystallography. A Siemens R3m/v instrument was used at ambient temperature with a source wavelength of $\lambda = 0.71073$ Å.

A $0.20 \times 0.18 \times 0.12$ mm crystal was selected; monoclinic $a = 13.278(8)$, $b = 14.324(10)$, $c = 16.916(9)$ Å, $\beta = 109.63(4)°$, $V = 3030(3)$ Å³, $Z = 4$ (C₃₆H₂₄Ge₂N₂O₇), space group $P2_1/c$. A total of 5364 reflections ($0 \leq h \leq 15$, $0 \leq k \leq 17$, $-20 \leq l \leq 18$) over a range of θ from 2.16 to 25.05° were collected; 5131 independent reflections ($R_{int} = 0.0503$). An empirical absorption correction from psi scans on three reflections was applied. Following solution of the structure using an isotropic riding hydrogen model and full-matrix least squares refinement on F^2 (data-to-parameter ratio = 12.1), goodness-of-fit = 1.030, $R_1 = 0.0764$, $wR_2 = 0.1292$ ($I > 2\sigma(I)$); $R_1 = 0.1696$, $wR_2 = 0.1681$ (all data).

A sample of solid **A** which had been stored for a number of weeks at r.t. was examined by NMR. Again a mixture of two compounds was apparent, however **11** was now the major component and **10a** was the minor component (ratio ∼ 7.3). For **11**: ¹H-NMR (250 MHz, DMSO-d_6): 8.31 (dd, $J = 8.1$, 1.4 Hz, 1H), 7.21 (ddd, $J = 8.2$, 7.3, 1.5 Hz, 1H), 6.99 (dd, $J = 8.2$, 1.5 Hz, 1H),
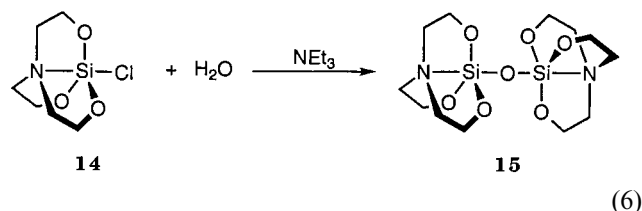
6.94 (ddd, $J = 8.0, 7.4, 1.5$ Hz, 1H). ^{13}C-NMR (63 MHz, DMSO-d_6): 152.7, 134.8, 129.4, 125.6, 120.7, 116.4. For **10a**: ^{13}C-NMR (63 MHz, DMSO-d_6): 152.4, 134.4, 129.7, 125.7, 121.2, 116.5.

3. Results and discussion
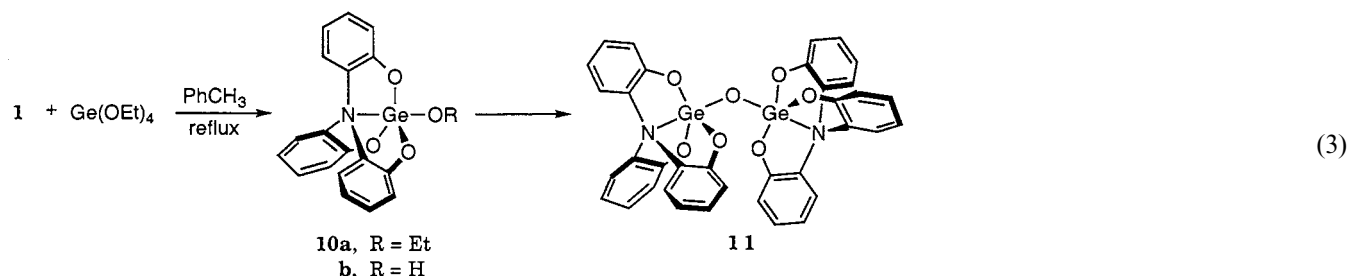
The reaction of **1** with Ge(OEt)$_4$ in refluxing toluene produced, after removal of solvent, a solid, **A**. The
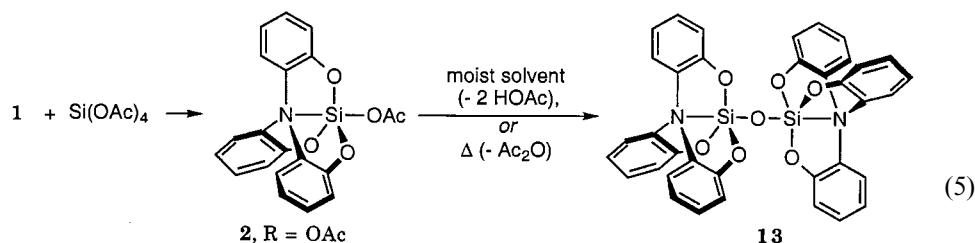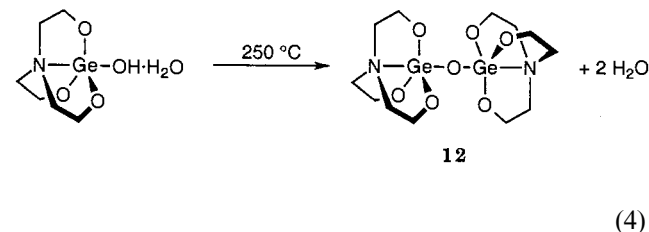
^{1}H-NMR spectrum of **A** revealed that the ratio of the area of the ethyl signals to the area of the aromatic proton signals was significantly smaller than required for the expected ethoxygermatrane **10a** (Eq. (3)). This suggested that **A** was a mixture of **10a** and a compound or compounds having no ethyl groups. Solid **A** was dissolved in boiling THF and the solvent was allowed to escape slowly at room temperature over the course of several weeks. This afforded crystalline material which was shown by X-ray crystallography (vide infra) to be dimer **11**. In solid **A**, the compound accompanying ethoxygermatrane **10a** may have been **11** or hydroxygermatrane **10b**.

To our knowledge, only one other oxo-bridged germatrane dimer has been reported in the literature, namely the parent digermatrane **12** [10]. This compound was not characterized by X-ray crystallography (Eq. (4)).

Two oxo-bridged silatrane dimers are known. The reaction of **1** with Si(OAc)$_4$ gave **2** (R = OAc), which could be transformed to oxo-bridged tribenzosilatrane dimer **13** either by refluxing **2** (R = OAc) with H$_2$O–CH$_3$CN–THF, or by strong heating (Eq. (5)) [1]. Dimer **13** was not characterized by X-ray crystallography. Dimerization of **14** led to **15** (Eq. (6)) in 89% yield [11]. The crystal structure of **15** revealed a threefold symmetric structure having a linear Si–O–Si array and Si–N distances of 2.477(5) Å.

The X-ray structural parameters of molecules like **11–13** and **15** are of interest in the context of the fascinating structural chemistry of compounds having an M–X–M backbone (M = metal or metalloid; X = O, S, C, N): the M–X–M array may be either linear or bent, seemingly capriciously. For example, R$_3$Ge–O–GeR$_3$ is bent when R = Ph [12], but linear when R = CH$_2$Ph [13]. Also, the Ge–O–Si bond in **16** is bent for $n = 0$, 1, and 2, and linear for $n = 3$ [14]. A plausible explanation for the observed geometries eluded workers for many years. Glidewell has been a major figure in this field, first providing many enigmatic examples of bent and linear M–X–M systems [15], and later suggesting a rationale for this perplexing body of data [16]. The Glidewell explanation invokes the second-order Jahn–Teller effect [17], by which

R_3M–X–MR_3 is predicted to be linear when R is electron-donating and bent when R is electron-withdrawing. A degree of mystery remains though: the same compound, μ-oxobis[iodotriphenylantimony(V)], crystallizes both as colorless crystals in which Sb–O–Sb is linear and orange crystals in which Sb–O–Sb is bent at 144.6(4)° [18].
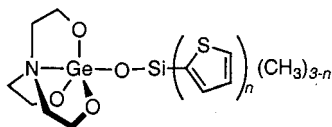
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An ORTEP diagram of **11** is given in Fig. 1 and selected geometrical parameters are presented in Table 1. Dimer **11** exhibits a Ge–O–Ge angle of 131.2(4)°. This may be compared with the sole linear Ge–O–Ge example, $(PhCH_2)_3Ge$–O–$Ge(CH_2Ph)_3$ [13], and several bent Ge–O–Ge compounds: Ph_3Ge–O–$GePh_3$, 135.2(2)° [12], $[Cp(CO)_2FeGe(CH_3)_2]_2O$, 133.9(4)° [19], H_3Ge–O–GeH_3, 125.6(4)° [20], and $(CH_3)_3Ge$–O–$Ge(CH_3)_3$, 141° [21]. A related example is $[(CH_3)_3Ge]_2OH^+$ $(C_6F_5)_4B^-$ which exhibits a Ge–O–Ge angle of 134.9(2)° [22]. Thus, the Ge–O–Ge angle of **11** is the smallest of this group, save H_3Ge–O–GeH_3. Glidewell has ranked ten groups in their electron-donating ability [23]. The methoxy group was more electron-donating than the benzyl group. Since $(PhCH_2)_3Ge$–O–$Ge(CH_2Ph)_3$ is linear, and since the Glidewell explanation posits the more electron-donating an R group is, the more likely is the R_3M–X–MR_3 system to be linear, one would expect $(CH_3O)_3Ge$–O–$Ge(OCH_3)_3$ (a model for **11**) to be linear. However, **11** is bent. Therefore, one conclusion is that $(CH_3O)_3Ge$–O–$Ge(OCH_3)_3$ with tetrahedral germaniums may be a poor model for **11**, since in **11** the germaniums are more pentacoordinate than tetracoordinate. To show this, the Ge–N distances of 2.235(8) and 2.247(7) Å may be compared to the sum of van der Waals radii of ∼ 3.5 Å [24] and to a typical Ge–N single bond distance of 1.84 Å [25], or 1.82–1.92 Å [26]. Also by adding together the angles constituting the equatorial plane of the distorted trigonal bipyramid (TBP) and comparing this sum to that for an ideal TBP
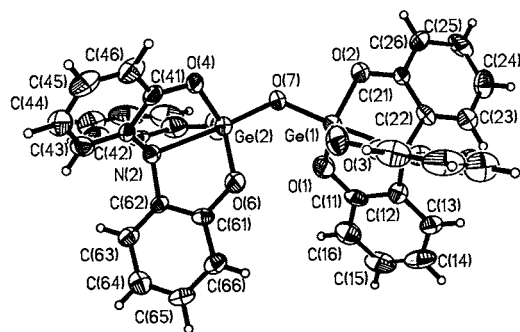
Table 1
Selected bond lengths (Å) and bond angles (°) for **11**

	Bond length (Å)		Bond angle (°)
Ge(1)–N(1)	2.235(8)	Ge(1)–O(7)–Ge(2)	131.2(4)
Ge(2)–N(2)	2.247(7)	O(7)–Ge(1)–O(1)	98.7(3)
Ge(1)–O(1)	1.784(6)	O(7)–Ge(1)–O(2)	94.8(3)
Ge(1)–O(2)	1.790(6)	O(7)–Ge(1)–O(3)	99.3(4)
Ge(1)–O(3)	1.779(7)	O(7)–Ge(2)–O(4)	95.4(3)
Ge(1)–O(7)	1.750(7)	O(7)–Ge(2)–O(5)	98.9(4)
Ge(2)–O(7)	1.743(6)	O(7)–Ge(2)–O(6)	101.5(3)
Ge(2)–O(4)	1.797(6)	C(12)–N(1)–Ge(1)	102.8(5)
Ge(2)–O(5)	1.782(8)	C(22)–N(1)–Ge(1)	102.0(6)
Ge(2)–O(6)	1.780(7)	C(32)–N(1)–Ge(1)	103.0(6)
O(1)–C(11)	1.357(12)	C(42)–N(2)–Ge(2)	102.7(5)
O(2)–C(21)	1.343(10)	C(52)–N(2)–Ge(2)	101.8(5)
O(3)–C(31)	1.362(13)	C(62)–N(2)–Ge(2)	102.2(5)
O(4)–C(41)	1.336(11)	C(11)–O(1)–Ge(1)	117.6(6)
O(5)–C(51)	1.365(13)	C(21)–O(2)–Ge(1)	118.2(6)
O(6)–C(61)	1.375(10)	C(31)–O(3)–Ge(1)	117.0(6)
N(1)–C(12)	1.455(11)	C(41)–O(4)–Ge(2)	117.3(6)
N(1)–C(22)	1.455(11)	C(51)–O(5)–Ge(2)	117.9(6)
N(1)–C(32)	1.446(11)	C(61)–O(6)–Ge(2)	116.6(6)
N(2)–C(42)	1.452(10)	C(11)–C(12)–N(1)	114.1(9)
N(2)–C(52)	1.462(12)	C(21)–C(22)–N(1)	115.2(8)
N(2)–C(62)	1.453(11)	C(31)–C(32)–N(1)	113.8(10)
		C(41)–C(42)–N(2)	113.6(8)
		C(51)–C(52)–N(2)	113.6(9)
		C(61)–C(62)–N(2)	113.7(8)

(360°) and an ideal tetrahedron (T_d; 328.4°), one may assess quantitatively to what extent a tetrahedron has progressed along the $T_d \rightarrow$ TBP coordinate [27]. In the case of **11**, this is 84% for Ge(1) and 79% for Ge(2). Another measure of progress along the $T_d \rightarrow$ TBP coordinate is the difference between the sum of equatorial angles and the sum of axial angles, which is 0° for an ideal tetrahedron and 90° for an ideal TBP [28]. In the case of **11**, Ge(1) is 69% TBP and Ge(2) is 64% TBP by this measure. In any event, the germaniums of **11** are substantially TBP and are therefore interacting in a non-trivial way with transannular nitrogen.

The Glidewell explanation with regard to M–X–M systems in which M is TBP is not well-developed, and we are unable to use it to rationalize the non-linearity of **11**. It would seem that the electron pair on nitrogen, to the extent it interacts with germanium, would tend to make germanium more electron-rich and would consequently increase the tendency toward linearity.

To explore this question further, ab initio calculations were undertaken. Results are presented in Table 2. In a simple model system, H_3Ge–O–GeH_3, a 3-21G basis with either a Hartree–Fock or B3LYP treatment predicted a linear Ge–O–Ge geometry, and Ge–O distances which were too short. Only after including d-orbitals in the basis did the predicted geometry approach the observed bent geometry. This outcome was re-

Fig. 1.

Table 2
Geometries of $H_3Ge-O-GeH_3$ and **11** calculated by various methods

Molecule	Method	Ge–O–Ge (°)	Ge–O^{bridge} (Å)	Ge–N (Å)
$H_3Ge-O-GeH_3$	HF/3-21G	180.0	1.707	
	B3LYP/3-21G	180.0	1.719	
	HF/6-311G*	143.5	1.751	
	Expt. [a]	125.6(4)	1.766(4)	
11	HF/3-21G	180.0	1.681	2.597
	B3LYP/3-21G	179.9	1.699	2.409
	HF/special [b]	136.0	1.713	2.622
				2.623
	Expt. [c]	131.2(4)	1.750(7)	2.235(8)
			1.743(6)	2.247(7)

[a] Ref. [20].

[b] For Ge, 6-311G*; for O^{bridge}, 6-31G*; for all other Os and N, 6-31G; for all Cs and Hs, 3-21G.

[c] This work.

peated exactly in the case of calculations on **11**. There, the d-orbital-containing basis set was a special basis to render the calculation slightly more economical: Ge was 6-311G*, the bridging oxygen was 6-31G*, all other oxygens and the nitrogens were 6-31G, and the carbons and hydrogens were 3-21G. The calculated Ge–O–Ge angle, 136°, was remarkably close to the experimental value of 131.2(4)°. However, the calculated Ge–O^{bridge} distance was still too short, and the calculated Ge–N distances were significantly longer than the observed Ge–N distances.

4. Conclusions

Ethoxygermatrane **10a** self-condenses under mild conditions to form oxo-bridged dimer **11**. The bridge angle (Ge–O–Ge) is 131.2(4)°. A useful conceptual framework for understanding the linearity or non-linearity of M–X–M systems appears to give the wrong prediction in the case of **11**. The quite significant Ge–N bonding interaction may be the cause of the erroneous prediction; however, we note the analogous oxo-bridged silatrane dimer **15** has a linear Si–O–Si bridge. Ab initio calculations predict the correct bridge geometry only when d-orbitals are included in the basis set for both germanium atoms and the bridge oxygen atom.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 147155 for compound **11**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: + 44-1223-336033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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