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Synthesis and molecular structure of phenyl and tolylgermatranes

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Abstract

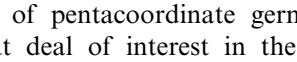
The crystals of arylgermatranes

R-C$_6$H$_4$-Ge(OCH$_2$CH$_2$)$_3$N

(R = H (**I**), 4-CH$_3$ (**II**), 3-CH$_3$ (**III**), 2-CH$_3$ (**IV**)), have been obtained to study the influence of a substituent position on coordination of the germanium atom. Compounds **I**–**IV** were prepared by the insertion of $GeBr_2$ into the carbon–bromine bond of the corresponding arylbromide, conversion of aryltribromogermanes to triethoxy derivatives by alcoholysis and their transalkoxylation with triethanolamine to germatranes; or by the condensation of halobenzene with $GeCl_4$ in the presence of copper powder followed by alcoholysis and cyclization. The crystal structure of compounds **I**–**IV** was studied via the X-ray diffraction method. The intramolecular donor–acceptor bond Ge←N in arylgermatranes (2.212–2.230 Å) is longer than that in the corresponding furyl- and thienylgermatranes. Introduction of a substituent into *o*-position of the benzene ring decreases the N–Ge–C angle value from 177.5 to 144.2°. The quantum chemical calculations were performed to investigate structures **I**–**IV** in isolated molecules. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Aryltrihalogenogermane; Germatrane; Crystal structure; MNDO calculation; Toxicity

1. Introduction

Organic derivatives of pentacoordinate germanium have attracted a great deal of interest in the recent years. Germatranes  containing an intramolecular Ge←N bond are the most intensively studied class of such compounds. The analysis of the Cambridge Crystallographic Data Bank has shown that the molecular structures of over 30 germatranes have been documented [1–27]. The germatrane structure consists of a distorted trigonal bipyramid at Ge (ΔGe is 0.095–0.37 Å) with nearly equatorial O atoms. The axial N is pyramidalized so that its lone pair points towards Ge. The transannular Ge←N bond distances for all germatranes are in the range 2.011–2.29 Å (Table 1). The general consensus is that more electronegative groups R yield shorter Ge←N bonds (2.011 Å for 1-fluorogermatrane [24], 2.081 Å for 1-isothiocyanatogermatrane [17], while 2.238 Å for 1-*t*-butylgermatrane [5]). The same tendency exists for silatranes (Si←N 1.965–2.24 Å) [28–32]. Some changes in the germatranyl groups (replacement of one CH_2 group for C=O or CH–CH_3, or CH–C_2H_5) does not significantly change the Ge←N value [33–35].

We have shown [36] that the Ge←N bond in crystals is considerably shorter than that in isolated germatrane molecules due to the crystal packing effect. Therefore, the main aim of this investigation was to study the molecular structure of tolylgermatranes in crystals as well as in the free state, to determine the influence of the position of the methyl group on the values of bond angles and on the length of intramolecular Ge←N donor–acceptor bond.

At the same time we are also interested in the study of the biological properties of this class of compounds.

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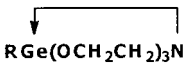
Table 1
N→Ge bond lengths (Å) in germatranes



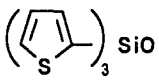
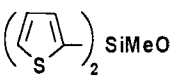
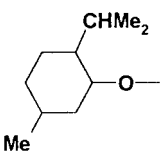
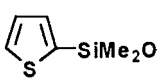
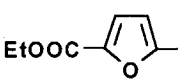
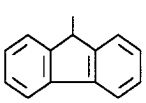
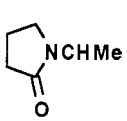
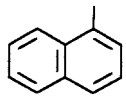
R	N→Ge (Å)	Refs.
F	2.011	[24]
NCS	2.084	[17]
Br	2.094	[6]
	2.105	[20]
Ph_3SiO	2.126	[16]
Me_3SiO	2.128	[20]
	2.144	[20]
HO	2.146	[10]
	2.15	[13]
	2.156	[20]
MeOOCCHPh	2.158	[22]
$PhC{\equiv}C(CHCl_3)$	2.160	[21]
	2.165	[7]
	2.166	[21]
$ClCH_2$	2.168	[14,15]
$4\text{-}ClC_6H_4CONHCH_2$	2.185	[11]
ICH_2	2.19	[3]
$MeOOC(CH_2)_3$	2.198	[18]
$CH_2{=}CH{-}CH_2$	2.208	[23]
$MeOOCCHSiMe_3$	2.209	[22]
$MeOOC(CH_2)_2$	2.210	[19]
Ph	2.212	This work [a]
$3\text{-}MeC_6H_4$	2.214	This work
$4\text{-}MeC_6H_4$	2.217	This work [a]
$MeOOCCMe_2$	2.22	[22]
	2.223	[9]

Table 1 (Continued)

R	N→Ge (Å)	Refs.
$2\text{-}MeC_6H_4$	2.230	This work [a]
$H_2NCOCH_2CH_2$	2.231	[8]
Me_3C	2.238	[5]
Et	2.24	[1]
	2.24	[2]
$(Me_3Si)_2N$	2.242	[27]
$N(CH_2CH_2O)_3GeCH_2$	2.29	[4]

[a] Preliminary communication [25].

It has been shown that the majority of the organogermanium compounds possess lower toxicity than the corresponding sila analogues, while the other biological properties appear to be similar. But these compounds can dramatically differ in the degree of activity. In this work, we have tested toxicity and neurotropic activity of germatranes **I** and **II**.

2. Results and discussion

Tolylgermatranes (**II**–**IV**) were obtained as a result of the following conversions: insertion of germanium dibromide into the carbon–bromine bond of the corresponding bromotoluenes, conversion of tolyltribromogermanes into triethoxy derivatives by alcoholysis, and transalkoxylation with triethanolamine to germatranes **II**–**IV** (yields 15, 25 and 14%, respectively). Phenylgermatrane (**I**) was synthesized in 67% yield by condensation of iodobenzene with $GeCl_4$ in the presence of copper followed by alcoholysis and cyclization (Scheme 1). Yields, melting points, element analysis and ^{1}H-NMR data for new compounds obtained are summarized in Table 2. After recrystallization from chloroform (**II**), chloroform–hexane (**III**, **IV**) or chloroform–pentane (**I**), they were obtained as colourless crystals suitable for an X-ray diffraction study.

To further our stereochemical investigation of atranes the crystals of germatranes **I**–**IV** were analyzed by means of X-ray diffraction. Tables 3–6 give the atomic coordinates for non-hydrogen atoms with thermal parameters for molecules **I**–**IV**. Figs. 1–4 show a perspective view of molecular structures **I**–**IV** with atomic labels. The crystal structure **I** is isomorphous to β-modification of phenylsilatrane [37]. The crystal structure **II** is also isomorphous to the corresponding silatrane structure [38]. The value of the intramolecular Ge←N donor–acceptor bond length for phenylgermatrane (**I**) is 2.212(5) Å. The

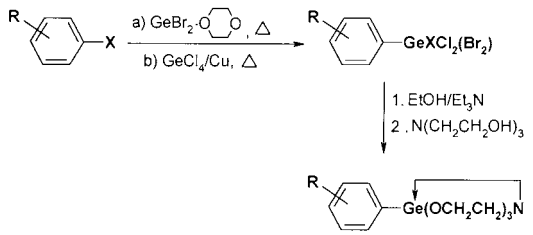
Table 2
Analytical data for arylgermatranes

R	M.p. (°C)	Molecular formula	Analysis found (calc.) (%)			^{1}H-NMR (δ ppm)	Yield (%)
			C	H	N		
C_6H_5 (**I**)	233–235	$C_{12}H_{17}NO_3Ge$	48.69(48.72)	5.72(5.79)	4.64(4.73)	2.91 (6H, t, N-CH_2), 3.89 (6H, t, O-CH_2). 7.31...7.71 (5H, m, C_6H_5)	67
4-$CH_3C_6H_4$ (**II**)	211–213	$C_{13}H_{19}NO_3Ge$	50.04(50.39)	6.30(6.18)	4.55(4.52)	2.30 (3H, s, CH_3); 2.90 (6H, t, N-CH_2); 3.88 (6H, t, O-CH_2); 7.09–7.18 (2H, d, C_6H_4); 7.57–7.66 (2H, d, C_6H_4)	15
3-$CH_3C_6H_4$ (**III**)	217–218	$C_{13}H_{19}NO_3Ge$	50.07(50.39)	6.17(6.18)	4.54(4.52)	2.31 (3H, s, CH_3); 2.89 (6H, t, N-CH_2); 3.89 (6H, t, O-CH_2); 7.11–7.56 (4H, m, C_6H_4)	25
2-$CH_3C_6H_4$ (**IV**)	192–194	$C_{13}H_{19}NO_3Ge$	50.16(50.39)	6.20(6.18)	4.49(4.52)	2.56 (3H, s, CH_3), 2.89 (6H, t, N-CH_2); 3.84 (6H, t, O-CH_2); 6.93–7.20 (3H, m, C_6H_4), 7.79–7.91 (1H, m, C_6H_4)	14

corresponding distances for tolylgermatranes are slightly longer: 2.217(4) for *p*- (**II**), 2.214(7) for *m*- (**III**) and 2.230(11) Å for the *o*-isomer (**IV**). This bond in arylgermatranes is longer than that in the corresponding furyl- and thienylgermatranes [39]. More significant changes have been found for N–Ge–C angles. For phenylgermatrane (**I**), *p*-tolyl- (**II**) and *m*-tolyl- (**III**) the N–Ge–C angle was close to linear. Introduction of a methyl group into *o*-position of the benzene ring decreases the angle value from 177.5 to 144.2°.

It has been previously shown [36] that the quantum chemical MNDO SCF molecular orbital method can be used for silatranes and germatranes. In accordance with the results obtained in the work by Belyakov et al. [36] the MNDO approximation gives more accurate data than other quantum chemical patterns. Therefore, to continue our quantum chemical study of atrane molecules the MNDO calculations for **I**–**IV** have been performed. Table 7 lists the geometrical characteristics of molecules **I**–**IV** in crystals and in the free state obtained from MNDO calculations. According to the quantum chemical calculations the Ge←N bond length is practically constant for isolated molecules **I**–**IV**. As shown in Ref. [36], the shortening of the Ge←N bond in germatrane crystal leads to the lengthening of Ge–C bonds. This is also observed for compounds **I**–**IV**. Accordingly, the bond orders of Ge←N for molecules in crystals are greater than those in the free state (see Table 7). The opposite effect is observed for the Ge–C bonds. The other bond orders for the isolated molecules almost coincide with the corresponding values for molecules in crystals. Analogously, the theoretical bond lengths (except for Ge←N and Ge–C) are near to the X-ray crystal analysis data. Thus, the lengthening of the Ge←N bond in the atrane systems for isolated molecules is realized without change of other bonds in the rings. This lengthening is achieved, mainly, due to the change of the valence and, especially, of the torsion angles in atranes. Therefore, the zigzag conformation of the atrane system in crystals differs from that in the isolated molecules. It can be seen in Fig. 5 where the projections of molecules **I** (without H atoms) on the Ge←N bond are illustrated. As the potential energy of angle changes is not significant [40], the deviation of the angles from optimum values practically does not affect the molecule energy.

With the exception of the shortening of the Ge←N bond, the deviations (ΔGe) of the Ge atom from the O2–O8–O9 plane are shorter in germatrane crystals. The values of ΔGe in crystals **I**–**IV** are 0.238–0.263 Å, while in the isolated molecules these values are



I R=H, X=I; II R=4-CH_3, X=Br;
III R=3-CH_3, X=Br; IV R=2-CH_3, X=Br

I - IV

Scheme 1.

Table 3
Atomic coordinates and equivalent isotropic thermal parameters in germatrane **I**

Atom	x	y	z	U_{eq}
Ge(1)	0.32111(2)	−0.35200(7)	0.25(0)	0.0225(2)
O(2)	0.2380(3)	−0.2298(8)	0.1733(4)	0.0389(11)
C(3)	0.1570(4)	−0.2116(13)	0.2225(6)	0.042(2)
C(4)	0.1394(4)	−0.3865(11)	0.3012(7)	0.041(2)
N(5)	0.2164(3)	−0.4259(7)	0.3668(4)	0.0279(10)
C(6)	0.2274(4)	−0.2910(14)	0.4646(6)	0.046(2)
C(7)	0.3202(4)	−0.2511(13)	0.4787(6)	0.041(2)
O(8)	0.3607(3)	−0.2249(7)	0.3739(4)	0.0365(10)
O(9)	0.3307(3)	−0.6213(6)	0.2446(9)	0.0428(12)
C(10)	0.2668(5)	−0.7394(11)	0.2916(7)	0.042(2)
C(11)	0.2289(5)	−0.6410(10)	0.3965(7)	0.046(2)
C(12)	0.4097(3)	−0.2861(9)	0.1416(5)	0.0256(11)
C(13)	0.4416(3)	−0.4304(10)	0.0660(5)	0.0319(13)
C(14)	0.4968(4)	−0.3739(13)	−0.0211(7)	0.042(2)
C(15)	0.5223(4)	−0.1786(12)	−0.0318(7)	0.045(2)
C(16)	0.4930(4)	−0.0359(11)	0.0440(7)	0.038(2)
C(17)	0.4376(4)	−0.0874(10)	0.1294(6)	0.0345(13)

0.609–0.628 Å. As follows from Table 7 the deviations (ΔN) of the N atom from the C4–C6–C11 plane, in contrast, are longer in crystals.

The lengthening of the transannular bond in isolated molecules leads to the increase of C–Ge–O valence angles. Therefore, there is a considerable difference in theoretical and X-ray values. The low values of C–Ge–O angles in crystals of compound **IV** result in shortened intramolecular contacts between the oxygen atom and hydrogens of the methyl group (distance O2···H1(C18) is 2.70 Å). That is why the N–Ge–C angle in crystals of **IV** differs from the flat angle. In isolated molecules of **IV** the distances between O and H are larger than in crystals (distance O2···H1(C18) is equal 2.92 Å), therefore, the N–Ge–C angle approaches the flat angle.

Although the Ge←N bond lengths in isolated molecules **I**–**IV** are identical, these values in crystals of the compounds are different. This fact may be explained by the influence of packing effects. Table 8 gives the packing coefficients and densities of crystals **I**–**IV**. The more dense packing promotes the shortening of the Ge←N bond. The more friable crystal structure furthers the disorder. It occurs in the crystal structures of **II** and **IV**, where the packing coefficients are less than in crystals **I** and **III**.

Previously, we discovered that many organogermatranes exhibit very low toxicity (LD_{50} for white mice more than 2000 mg kg^{-1}). The more detailed investigation allowed us to demonstrate that the acute toxicity and neurotropic activity of germatranes depend strongly on the substituent structure at the germanium atom [41].

Biological investigations have demonstrated that phenyl- (**I**) and *p*-tolylgermatranes (**II**) are highly toxic compounds (LD_{50} 35.5 and 70.0 mg kg^{-1}). Phenylgermatrane (**I**) is 100 times less toxic than the corresponding silatrane. The introduction of the methyl group into the *p*-position lowers the toxicity of germatranes (LD_{50} 70 mg kg^{-1}) but increases this parameter for *p*-tolylsilatrane (0.2 mg kg^{-1}) [42].

3. Experimental

Standard inert atmosphere techniques were used for all syntheses and sample manipulations. The solvents were dried by standard methods and distilled under argon prior use. Arylhalogenides — commercially available compounds — were distilled prior use under vacuo.

PMR spectra were conventionally recorded on a Bruker WH-90/DS spectrometer for 5–7% solutions in $CDCl_3$ with TMS as internal standard.

For X-ray crystal structure analysis of compounds **I**–**IV** a four-circle computer-controlled single-crystal Syntex $P2_1$ diffractomer with graphite-monochromated Mo–K_α ($\lambda = 0.71069$ Å) radiation was used for intensity data collection. Reflection intensities were collected at room temperature (r.t.) using the $\theta/2\theta$ scan technique. Multisolution direct method package SHELX-86 [43] was used for solution of the structures. SHELXL-93 programs [44] were used for the refinement calculations. Other crystallographic, measurement and refinement data for **I**–**IV** are given in Table 9. Earlier we reported [25] the X-ray structures **I**, **II** and **IV** without adducing the atomic coordinates. In this work the more accurate data for germatrane **IV** are given. The data of compound **III** are presented for the first time. The CCDC deposition numbers for the structures **III** and **IV** are

Table 4
Atomic coordinates and equivalent isotropic thermal parameters in germatrane **II**

Atom	Molecule A				Molecule B [a]			
	x	*y*	*z*	U_{eq}	*x*	*y*	*z*	U_{eq}
Ge(1)	0.29758(4)	0.16870(3)	0.04908(3)	0.0363(2)	0.79088(4)	0.17654(3)	0.38712(3)	0.0389(2)
O(2)	0.3804(2)	0.2524(3)	0.0070(3)	0.0567(10)	0.8662(3)	0.2716(3)	0.4432(3)	0.0675(12)
C(3)	0.3450(5)	0.3152(5)	−0.0678(5)	0.0703(19)	0.8240(5)	0.3404(6)	0.4952(6)	0.071(2)
C(4)	0.2374(5)	0.3404(5)	−0.0653(6)	0.074(2)	0.7143(6)	0.3537(6)	0.4561(7)	0.073(3)
N(5)	0.1845(3)	0.2517(3)	−0.0470(3)	0.0465(11)	0.6715(3)	0.2572(3)	0.4401(3)	0.0456(10)
C(6)	0.1048(4)	0.2694(5)	0.0087(5)	0.0637(16)	0.6489(7)	0.2055(6)	0.5200(6)	0.065(2)
C(7)	0.1503(5)	0.2759(5)	0.1110(4)	0.0608(16)	0.6703(7)	0.1007(6)	0.5086(7)	0.076(2)
O(8)	0.2238(3)	0.2058(3)	0.1355(2)	0.0572(10)	0.7529(3)	0.0858(3)	0.4617(3)	0.0659(11)
O(9)	0.2507(3)	0.0734(3)	−0.0287(3)	0.0624(11)	0.7165(3)	0.2012(3)	0.2755(3)	0.0633(11)
C(10)	0.1652(6)	0.0878(5)	−0.0959(6)	0.077(2)	0.6312(5)	0.2580(6)	0.2713(5)	0.0649(18)
C(11)	0.1556(7)	0.1891(6)	−0.1277(5)	0.079(2)	0.5886(6)	0.2569(7)	0.3584(5)	0.065(2)
C(12)	0.3991(3)	0.0966(3)	0.1303(3)	0.0356(11)	0.8955(4)	0.1042(3)	0.3405(3)	0.0417(12)
C(13)	0.4857(4)	0.0710(4)	0.0989(4)	0.0468(13)	0.9344(4)	0.0218(4)	0.3833(5)	0.0551(14)
C(14)	0.5559(4)	0.0151(4)	0.1524(4)	0.0518(15)	1.0091(4)	−0.0280(4)	0.3505(5)	0.0644(17)
C(15)	0.5448(4)	−0.0172(4)	0.2409(4)	0.0472(13)	1.0483(4)	0.0021(4)	0.2728(5)	0.0579(16)
C(16)	0.4581(4)	0.0081(4)	0.2731(4)	0.0516(14)	1.0113(4)	0.0840(5)	0.2299(4)	0.0621(17)
C(17)	0.3872(5)	0.0640(4)	0.2199(4)	0.0477(15)	0.9355(4)	0.1355(4)	0.2612(4)	0.0552(14)
C(18)	0.6219(7)	−0.0794(6)	0.2958(6)	0.077(2)	1.1315(7)	−0.0552(8)	0.2389(9)	0.100(3)
C(4′)	–	–	–	–	0.725(2)	0.310(2)	0.529(2)	0.026(6)
C(6′)	–	–	–	–	0.612(3)	0.172(2)	0.475(3)	0.043(9)
C(11’)	–	–	–	–	0.626(3)	0.317(3)	0.373(3)	0.037(9)

[a] In molecule B the *g*-factors for atoms C(4), C(6) and C(11) are 0.85 for atoms C(4′), C(6′) and C(11′) are 0.15.

118916 and 118917, respectively. The ciphers of the structures **I** and **II** in CCDB are RENWUC and RENXAJ.

The quantum chemical calculations of electronic structure for the studied systems were performed by the SCF method using the MNDO approximation analogously to work [36].

3.1. Phenylgermatrane (*I*)

Iodobenzene (10.5 g, 0.051 mol), germanium tetrachloride (12.3 g, 0.057 mol) and 10 g (0.16 g-at) copper powder were heated in a sealed ampoule for 7 h at 200°C. The content was cooled and filtered directly to a distilling apparatus under Ar. A yellow solution was distilled in vacuo and the fraction boiling at 80°C/3.5 mmHg was collected to yield phenyltrichlorogermane 1.7 g (yield 13%). To a phenyltrichlorogermane solution (1.7 g, 0.0066 mol) in abs. Et_2O (10 ml), cooled to 0°C, was added dropwise an ethanol solution (10 ml) of triethylamine (1.95 g, 0.02 mol) followed by heating to r.t. and boiling for 2 h. After cooling, pentane (15 ml) was added and the triethylamine salt was filtered off. Triethanolamine (1.0 g, 0.007 mol) in ethanol solution (15 ml) was added dropwise to the filtrate cooled to 0°C. The reaction mixture was stirred at r.t. for 10 h, cooled to 0°C and a white solid of 1-phenylgermatrane (1.31 g, 67%) was filtered off. Recrystallization from a chloroform–pentane (1:1.8) mixture was carried out. Analytical data are summarized in Table 2.

Table 5
Atomic coordinates and equivalent isotropic thermal parameters in germatrane **III**

Atom	*x*	*y*	*z*	U_{eq}
Ge(1)	0.15950(13)	0.17743(6)	0.27833(8)	0.0338(3)
O(2)	−0.0011(10)	0.0862(5)	0.2725(7)	0.061(2)
C(3)	−0.1748(15)	0.1166(8)	0.2551(12)	0.064(3)
C(4)	−0.157(2)	0.2225(11)	0.3013(17)	0.109(6)
N(5)	−0.0392(10)	0.2804(6)	0.2821(7)	0.0391(17)
C(6)	−0.154(2)	0.3271(11)	0.1695(11)	0.083(4)
C(7)	−0.0455(17)	0.3278(9)	0.1138(10)	0.062(3)
O(8)	0.0760(10)	0.2437(5)	0.1488(6)	0.0545(18)
O(9)	0.3348(10)	0.2376(5)	0.4144(6)	0.0535(17)
C(10)	0.2736(16)	0.3050(8)	0.4640(10)	0.065(3)
C(11)	0.0859(19)	0.3479(12)	0.3750(12)	0.116(7)
C(12)	0.3301(13)	0.0826(6)	0.2813(8)	0.0359(19)
C(13)	0.2851(14)	0.0388(6)	0.1745(8)	0.040(2)
C(14)	0.3902(13)	−0.0401(6)	0.1762(9)	0.042(2)
C(15)	0.5480(13)	−0.0767(7)	0.2825(8)	0.044(2)
C(16)	0.6045(13)	−0.0327(8)	0.3821(10)	0.053(3)
C(17)	0.4885(14)	0.0480(6)	0.3813(8)	0.040(2)
C(18)	0.3320(18)	−0.0871(9)	0.0642(10)	0.064(3)

Table 6
Atomic coordinates and equivalent isotropic thermal parameters in germatrane **IV**

Atom	*x*	*y*	*z*	U_{eq}
Ge(1)	0.1211(3)	0.0493(3)	0.0(0)	0.0468(10)
O(2)	0.0016(10)	−0.0564(7)	0.0166(9)	0.059(6)
C(3)	−0.1263(15)	−0.0487(9)	0.0570(15)	0.098(19)
C(4) [a]	−0.1821(28)	0.0599(21)	0.0706(27)	0.123(33)
C(4′) [a]	−0.1621(29)	0.0547(21)	0.1197(27)	0.083(32)
N(5)	−0.0643(10)	0.1324(8)	0.0690(9)	0.056(7)
C(6) [a]	−0.0254(29)	0.1459(21)	0.2026(26)	0.025(28)
C(6′) [a]	−0.0080(28)	0.1915(21)	0.1739(26)	0.092(32)
C(7)	0.1104(17)	0.1532(9)	0.2202(10)	0.086(12)
O(8)	0.1870(10)	0.0869(5)	0.1463(8)	0.079(8)
O(9)	0.1197(10)	0.1479(5)	−0.1172(8)	0.091(9)
C(10)	−0.0072(16)	0.2023(8)	−0.1207(12)	0.149(25)
C(11) [a]	−0.0612(29)	0.2349(22)	0.0041(22)	0.059(25)
C(11′) [a]	−0.1014(29)	0.2041(22)	−0.0355(22)	0.067(32)
C(12)	0.2825(19)	−0.0251(9)	0.0490(9)	0.061(9)
C(13)	0.3383(21)	−0.1143(9)	−0.0044(9)	0.077(8)
C(14)	−0.1621(23)	0.0547(9)	0.1197(9)	0.186(51)
C(15)	0.2758(23)	−0.1741(9)	−0.1090(9)	0.172(28)
C(16)	0.4610(23)	−0.1626(9)	0.0304(11)	0.105(15)
C(17)	0.3521(22)	0.0148(9)	0.1501(9)	0.084(12)
C(18)	0.4631(24)	−0.0399(9)	0.1959(14)	0.137(22)

[a] For atoms C(4), C(4′), C(6), C(6′), C(11) and C(11′) the occupation *g*-factors equal 0.5.

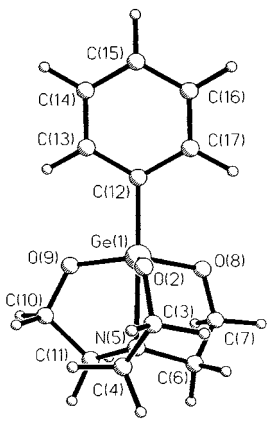


Fig. 1. Perspective view and atom numbering scheme of molecule **I**.

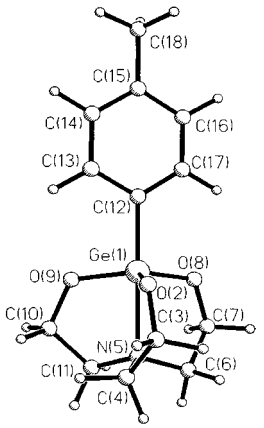


Fig. 2. Perspective view and atom numbering scheme of molecule **II**.

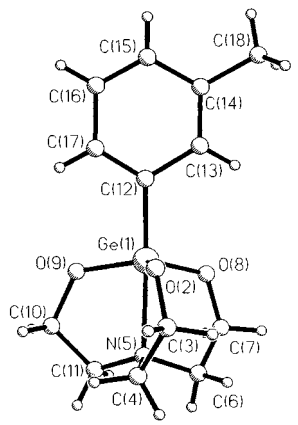


Fig. 3. Perspective view and atom numbering scheme of molecule **III**.

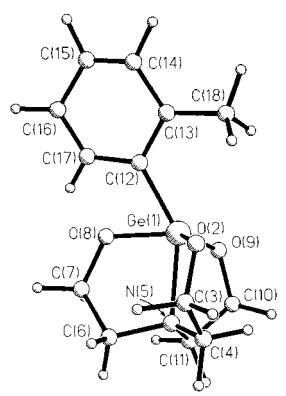


Fig. 4. Perspective view and atom numbering scheme of molecule **IV**.

3.2. *m*-Tolylgermatrane (*III*)

m-Bromotoluene (6.35 g, 0.037 mol) and a dioxane complex of germanium (**II**) dibromide (5.65 g, 0.018 mol) were heated for 30 h at 200°C in a sealed ampoule. The resultant yellow solution was distilled in vacuo, and a fraction boiling at 95–105°C/3 mmHg was collected to yield *m*-tolyltribromogermane (1.56 g, 21.5%). An ethanolic solution (10 ml) of triethylamine (1.17 g, 0.012 mol) was added dropwise to a *m*-tolyltri-

Table 7
The principal geometrical parameters of molecules **I–IV** and MNDO calculated bond orders (in square brackets); X-ray analysis results in comparison with the values for isolated molecules

	I		**II**		**III**		**IV**	
Crystal state								
N→Ge (Å)	2.212(5)	[0.221]	2.217(4)	[0.219]	2.214(7)	[0.220]	2.230(11)	[0.217]
Ge–C (Å)	1.947(6)	[0.759]	1.946(5)	[0.760]	1.947(11)	[0.760]	1.94(2)	[0.762]
Ge–$O_{(mean)}$ (Å)	1.797(4)	[0.628]	1.792(3)	[0.629]	1.792(7)	[0.629]	1.798(14)	[0.628]
O–$C_{(mean)}$ (Å)	1.404(8)	[1.024]	1.405(7)	[1.024]	1.416(16)	[1.023]	1.38(3)	[1.024]
C–$C_{(mean)}$ (Å)	1.514(9)	[0.921]	1.510(10)	[0.921]	1.51(2)	[0.921]	1.48(3)	[0.921]
C–$N_{(mean)}$ (Å)	1.475(8)	[0.931]	1.467(9)	[0.932]	1.43(2)	[0.932]	1.46(3)	[0.931]
C–Me (Å)	–		1.509(8)	[0.983]	1.503(18)	[0.983]	1.51(3)	[0.982]
N→Ge–C (°)	177.5(2)		179.0(2)		176.3(3)		144.2(8)	
C–Ge–$O_{(mean)}$ (°)	97.9(2)		97.8(2)		98.1(4)		95.2(8)	
ΔGe (Å)	0.238(1)		0.245(2)		0.253(2)		0.263(2)	
ΔN (Å)	0.371(3)		0.363(4)		0.394(9)		0.407(17)	
Free state								
N→Ge (Å)	2.759	[0.062]	2.763	[0.061]	2.758	[0.062]	2.791	[0.056]
Ge–C (Å)	1.915	[0.787]	1.918	[0.787]	1.919	[0.787]	1.932	[0.787]
Ge–$O_{(mean)}$ (Å)	1.814	[0.650]	1.814	[0.651]	1.813	[0.651]	1.815	[0.649]
O–$C_{(mean)}$ (Å)	1.380	[1.001]	1.381	[0.998]	1.380	[0.999]	1.382	[0.998]
C–$C_{(mean)}$ (Å)	1.542	[0.921]	1.542	[0.922]	1.543	[0.921]	1.540	[0.922]
C–$N_{(mean)}$ (Å)	1.478	[0.935]	1.479	[0.935]	1.478	[0.936]	1.477	[0.936]
C–Me (Å)	–		1.507	[0.983]	1.505	[0.983]	1.510	[0.981]
N→Ge–C (°)	179.8		179.6		179.5		178.4	
C–Ge–$O_{(mean)}$ (°)	110.3		109.3		109.5		110.2	
ΔGe (Å)	0.609		0.610		0.614		0.628	
ΔN (Å)	0.292		0.292		0.295		0.283	

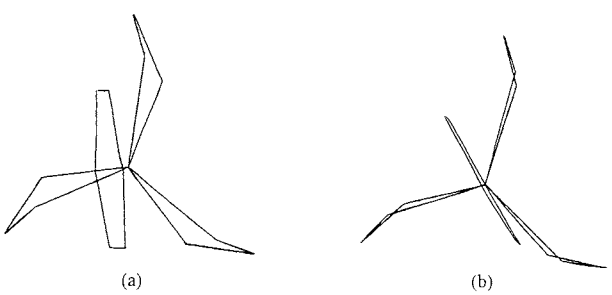


Fig. 5. Projection of molecular structure **I** along the Ge←N bond in crystals (a) and in the free state (b).

Table 8
Crystal density and packing coefficient for **I–IV**

Compound	Density (g cm^{-3})	Packing coefficient
I	1.582(1)	0.733(1)
II	1.526(1)	0.665(1)
III	1.559(1)	0.679(1)
IV	1.505(1)	0.656(1)

bromogermane solution (1.56 g, 0.004 mol) in abs. Et_2O (10 ml), cooled to 0°C, followed by heating to r.t. and boiling for 2 h. After cooling pentane (15 ml) was added and triethylamine salt was filtered off. Triethanolamine 0.57 g (0.004 mol) in an ethanol solution (15 ml) was added dropwise to the filtrate cooled to 0°C. The reaction mixture was stirred at r.t. for 8 h, cooled to 0°C and *m*-tolylgermatrane (0.3 g, 25.0%) was filtered off. Recrystallization from a chloroform–hexane (1:1) mixture was carried out. Analytical data are summarized in Table 2.

Compounds **II** and **IV** were prepared analogously. After recrystallization compound **II** (from chloroform) and compound **IV** (from chloroform–hexane (1:2)) had properties shown in Table 2.

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Table 9
Crystal data, measurement conditions and refinement results for compounds **I–IV**

	I	**II**	**III**	**IV**
Molecular weight M_r	295.86	309.88	309.88	309.88
Crystal size (mm^3)	$0.35 \times 0.30 \times 0.30$	$0.40 \times 0.25 \times 0.20$	$1.00 \times 0.50 \times 0.20$	$0.60 \times 0.30 \times 0.25$
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Orthorhombic
Space group	$Pna2_1$	$P2_1/c$	$P2_1/c$	$Pna2_1$
Cell parameters				
a (Å)	15.910(2)	13.608(3)	8.527(4)	9.759(3)
b (Å)	6.661(1)	14.012(3)	13.464(6)	12.725(3)
c (Å)	11.719(2)	14.330(2)	14.253(6)	11.015(3)
β (°)	90.0	99.13(1)	126.20(3)	90.0
Unit cell volume V ($Å^3$)	1242.0(3)	2697.8(9)	1320.4(10)	1367.9(6)
Molecular multiplicity Z	4	8	4	4
$F(000)$	608	1280	640	640
Absorption coefficient μ (mm^{-1})	2.462	2.271	2.320	2.240
Data collection				
$2\theta_{max}$ (°)	50	45	50	50
h	$0 \rightarrow 18$	$0 \rightarrow 14$	$-10 \rightarrow 8$	$0 \rightarrow 11$
k	$0 \rightarrow 7$	$0 \rightarrow 15$	$0 \rightarrow 16$	$0 \rightarrow 15$
l	$0 \rightarrow 13$	$-15 \rightarrow 15$	$0 \rightarrow 16$	$0 \rightarrow 13$
Number of measured reflections	1120	3783	2465	1261
Number of independent reflections	1120	3547	2302	1261
Number of observed reflections ($I > 2\sigma_I$)	1083	2872	1775	887
Refinement data				
R factor	0.0323	0.0458	0.0699	0.0745
$R(F)$ for all data	0.0333	0.0572	0.0804	0.1012
$wR(F^2)$ for all data	0.0841	0.1253	0.2016	0.2202
Goodness-of-fit	1.082	1.055	0.914	1.024
$(\Delta/\sigma)_{max}$	0.045	0.067	0.043	0.064
Number of parameters	222	490	163	160
Flack's x parameter	−0.01(3)	–	–	0.03(7)

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