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Molecular structure of thienylsiloxygermatranes[†]

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Summary – The molecular structures of siloxygermatranes ($R_nMe_{3-n}SiOGe(OCH_2CH_2)_3N$, R = 2-thienyl, n = 0-3) were determined by an X-ray difraction study. The value of the Si-O-Ge angle increases with the increasing number of acceptor substituents at the silicon. It equals 133.0° for trimethylsiloxygermatrane (I), 134.8° for [dimethyl(2-thienyl)siloxy]germatrane (II), 139.6° for [methyldi(2-thienyl)siloxy]germatrane (III) and 180° for [tri(2-thienyl)siloxy]germatrane (IV). The Ge $\leftarrow$ N bond shortens from 2.156 Å($n = 1$) to 2.105 Å($n = 3$) in this series of germatranes. The structure in the free state of all the siloxygermatranes studied was investigated by the quantum chemistry molecular orbital method.

siloxygermatrane / molecular structure / CNDO calculation

Introduction

A series of organosiloxanes and organogermoxanes was investigated by X-ray analysis [1-5]. It was found that the Si-O-Si angle in siloxanes is very flexible. According to the quantum-chemical calculations of Gibbs [6] only a little energy is needed to stretch the Si-O-Si angle from its optimum at 140° to 180°, while much more energy is required to reduce the angle. Indeed, it was recently demonstrated for the first time that the Si-O-Si bond angle increased from 147° to 163° when the temperature rose from −100°C to 28°C [7]. On the other hand, an increase in the Si-O-Si [1,4] and Ge-O-Ge [2,3] bond angles was observed in disiloxanes and digermoxanes with increasing numbers of aryl substituents in their molecules.

The main aim of this investigation is to determine the values of the Si-O-Ge bond angles in siloxygermatranes $R_nMe_{3-n}SiOGe(OCH_2CH_2)_3N$ (R = 2-thienyl, n = 0-3) containing a pentacoordinated germanium atom and to establish the influence of the substituents at the silicon atom on the values of this angle and intramolecular Ge $\leftarrow$ N donor-acceptor bond lengths.

Experimental section

Synthesis

(Trimethylsiloxy)germatrane (1-(trimethylsiloxy)-2,8,9-trioxa-5-aza-1-germatricyclo[3.3.3.$0^{1,5}$]undecane) (I) was prepared by the reaction of 1-hydroxygermatrane with hexamethyldisilazane [8]. The monocrystal was grown from chloroform/hexane solution. Compounds II-IV were synthesized by dehydrocondensation of thienylhydrosilanes with 1-hydroxygermatrane as described earlier [9]. The monocrystals of [dimethyl(2-thienyl)siloxy]germatrane (II) and [tri(2-thienyl)siloxy]germatrane (IV) were grown from xylene. [Methyldi(2-thienyl)siloxy]germatrane (III) was recrystallized from chloroform.

X-ray crystallographic studies

The crystals of compound I are orthorhombic, space group $Pna2_1$; the lattice constants are as follows : a = 19.966(4), b = 6.741(1), c = 10.089(2) Å, Z = 4, V = 1 358.1(7) Å^3, $F(000)$ = 640. The crystals of compound II are monoclinic, space group $P2_1$; the lattice parameters are as follows : a = 6.7745(7), b = 17.241(2), c = 14.042(1) Å, β = 93.368(7)°, Z = 4, V = 1 637.3(5) Å^3, $F(000)$ = 776. The crystals of III are monoclinic, space group $P2_1/c$; the lattice parameters are as follows : a = 8.168(1), b = 27.270(4), c = 8.613(1) Å, β = 100.14(1)°, Z = 4, V = 1 888.5(8) Å^3, $F(000)$ = 912. The crystals of the compound IV are trigonal, space group $R\overline{3}$; the lattice parameters are as follows : a = 9.4706(9), c = 42.908(4) Å, Z = 6, V = 3 332.9(9) Å^3, $F(000)$ = 1 572 in hexagonal axes, and a = 15.312(1) Å, α = 36.028(8)°, Z = 2, V = 1 111.0(3) Å^3, $F(000)$ = 524 in rhombohedral axes.

A four-circle computer-controlled single-crystal Syntex $P2_1$ diffractometer with graphite-monochromated Mo$K\alpha$ (λ = 0.71069 Å) radiation was used for intensity data collection. Reflection intensities were collected at room temperature using the $\theta/2\theta$-scan technique. Other crystallographic and intensity collection data for compounds I-IV are given in table I.

The positions of germanium atoms in the structure I were determined from the three-dimensional Patterson function. The other non-H atoms were found by the following two Fourier syntheses. Full matrix least squares were used for structure refinement. All hydrogen atoms were located from difference synthesis. The Ge, Si, O, N and C atoms were refined isotropically. All calculations were executed using the SHELXL-93 programs [10]. The coordinates of non-hydrogen atoms with thermal parameters are listed in table II.

[†] Dedicated to Professor R Calas in recognition of his outstanding contribution to organosilicon chemistry.

Table I. Crystallographic data for structures I-IV.

Parameter	compound I	compound II	compound III	compound IV
Molecular formula	$C_9H_{21}GeNO_4Si$	$C_{12}H_{21}GeNO_4SSi$	$C_{15}H_{21}GeNO_4S_2Si$	$C_{18}H_{21}GeNO_4S_3Si$
M_r	307.99	376.08	444.17	512.26
d_{calc}, g · cm^{-3}	1.506(1)	1.526(1)	1.562(1)	1.531(1)
μ, mm^{-1}	2.34	2.08	1.93	1.74
Crystal dimension, mm^3	0.50×0.20×01.10	0.40×0.20×0.20	0.50×0.25×0.15	0.40×0.40×0.10
$2\theta_{\max}$, deg	53.0	50.0	55.0	50.0
Number of unique reflections	1 502	2 722	4 337	1 313
Restrictions	$F(hkl) > 4.0 \cdot \sigma(F)$	$F(hkl) > 2.0 \cdot \sigma(F)$	$F(hkl) > 4.0 \cdot \sigma(F)$	$F(hkl) > 4.0 \cdot \sigma(F)$
Number of used reflections	1 004	2 355	3 079	1 015
Weighting scheme	$1/\sigma(F)^2$	unit	$1/[\sigma(F)^2 + 0.01 \cdot F^2]$	$1/[\sigma(F)^2 + 0.01 \cdot F^2]$
R Rw	0.0459 0.0470	0.0463 0.0463	0.0562 0.0669	0.0512 0.0631
Goodness of fit	0.959	0.883	0.770	0.770

Table II. Coordinates and equivalent isotropic thermal parameters (in Å^2) of the non-hydrogen atoms for structure I.

Atom	x	y	z	B(eq)
Ge	0.57520(5)	0.7416(1)	0.7584(1)	2.48(2)
O2	0.4947(2)	0.6380(8)	0.7936(4)	4.0(2)
C3	0.4413(3)	0.7061(12)	0.7121(7)	4.8(4)
C4	0.4650(4)	0.7511(16)	0.5742(7)	5.2(4)
N5	0.5286(3)	0.8585(8)	0.5855(5)	3.1(3)
C6	0.5754(4)	0.8083(12)	0.4775(6)	4.9(4)
C7	0.6095(4)	0.6235(14)	0.5134(7)	5.2(5)
O8	0.6299(2)	0.6213(9)	0.6505(4)	3.4(3)
O9	0.5872(3)	0.9973(6)	0.8010(4)	4.3(3)
C10	0.5788(4)	1.1342(10)	0.6982(8)	4.8(4)
C11	0.5222(4)	1.0695(11)	0.6090(7)	4.8(4)
C12	0.7131(4)	0.3847(10)	0.9825(8)	4.6(4)
C13	0.6847(4)	0.7664(14)	1.1360(7)	5.5(5)
C14	0.7488(4)	0.7804(17)	0.8644(8)	6.4(6)
O1	0.6114(3)	0.6435(9)	0.9092(5)	3.7(3)
Si	0.6870(1)	0.6431(3)	0.9687(2)	3.19(8)

The structure II was solved in $P2_1/c$ space group. For structure solution, the initial phases of 10 strong reflections were determined by the maximum determinant method [11]. The phase values obtained were introduced into the starting set of the MULTAN program [12]. Two variants were calculated, one of them yielding the model. The structure was refined by least squares in the block-diagonal approximation with anisotropic temperature factors. The hydrogen atoms of methyl groups were found from difference synthesis. All the other H atoms coordinates were calculated geometrically. Hydrogen atoms were refined isotropically. The programs AREN [13] were used for the calculations. The final coordinates and thermal parameters for non-hydrogen atoms are listed in table III.

Multisolution direct methods package SHELX-86 [14] was used for determination of the structure III. The positions of most non-hydrogen atoms were obtained from the first 20 peaks in the E-map. The other non-hydrogen atoms were found from difference Fourier map. The structure was refined by full matrix least squares in the anisotropic approximation. The hydrogen atoms of methyl group were located from difference synthesis. The other H-atoms were placed in the calculated positions. H atoms were refined isotropically. SHELXL-93 programs [10] were used for calculations. Non-hydrogen atoms coordinates and thermal parameters are given in table IV.

The structure IV was solved by heavy atoms method. The coordinates of germanium and silicon atoms were calculated from the one-dimensional Patterson function. All the other non-hydrogen atoms were located by the following Fourier synthesis. The structure was refined by full matrix least squares with anisotropic temperature factors. The coordinates of H-atoms were calculated geometrically and refined in isotropic approximation. All calculations were carried out with the help of AREN complex of programs [13]. Final coordinates and thermal parameters for non-hydrogen atoms are listed in table V.

The correction for absorption was carried out for all four structures by DIFABS program [15].

Quantum chemical study

The quantum chemical calculations of electronic structure for the studied systems were performed by the SCF method using the CNDO approximation. The *s,p,d*-basis of the Slater's orbitals for valence electrons was used. The calculations were carried out using the modified program* (its original text is given in reference [16]). The molecular integrals were calculated directly : the one-center integrals in polar spheric coordinates and the two-center integrals in spheroidal coordinates. The two-center integrals of electron repulsion were obtained by applying the Ohno's relationship [17].

The geometrical parameters were partially optimized. Equilibrium geometries on potential surfaces are located by the Davidon-Fletcher-Powell algorithm [18]. The initial geometrical parameters for quantum chemical calculation were taken from X-ray structure analysis data.

Results and discussion

Figure 1 shows a perspective view of the molecular structure with the labels on atoms for the compounds I-IV in accordance with X-ray analysis data. Table VI lists the bond lengths in the molecules I-IV, and table VII gives the values of the principal valence angles.

Figure 2 illustrates the packing of compound IV molecules in the unit cell in rhombohedral axes. There is the hindered orientation of the molecules. The molecules have the third order axis in accordance with crystal symmetry. This is why the value of the va-

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* The listing of the modified program may be received from the authors.

Table III. Coordinates and equivalent isotropic thermal parameters (in Å^2) of the non-hydrogen atoms for structure II.

	Molecule A				Molecule B			
Atom	x	y	z	B(eq)	x	y	z	B(eq)
Ge	−0.3588(1)	−0.1801(1)	0.0597(1)	3.07(1)	0.3587(1)	0.1801(1)	0.4403(1)	3.08(1)
O2	−0.4809(7)	−0.2327(3)	−0.0345(3)	4.30(10)	0.4808(7)	0.2323(3)	0.5344(3)	4.41(10)
C3	−0.6654(13)	−0.2673(6)	−0.0187(6)	4.9(2)	0.6655(13)	0.2674(5)	0.5186(6)	5.0(2)
C4	−0.6933(15)	−0.2808(6)	0.0847(8)	6.4(2)	0.6934(15)	0.2809(6)	0.4154(8)	6.5(2)
N5	−0.5938(8)	−0.2236(4)	0.1420(4)	3.85(11)	0.5939(8)	0.2235(4)	0.3581(4)	3.97(12)
C6	−0.4920(17)	−0.2486(8)	0.2319(8)	7.4(2)	0.4919(17)	0.2487(8)	0.2682(8)	7.5(2)
C7	−0.2884(13)	−0.2778(5)	0.2118(6)	5.2(2)	0.2885(13)	0.2779(5)	0.2881(6)	5.5(2)
O8	−0.2004(7)	−0.2297(4)	0.1445(4)	5.02(10)	0.2005(7)	0.2298(4)	0.3554(4)	5.04(11)
O9	−0.4516(8)	−0.0878(3)	0.0903(5)	5.17(10)	0.4515(8)	0.0879(3)	0.4098(5)	5.17(10)
C10	−0.5956(13)	−0.0840(5)	0.1558(7)	4.9(2)	0.5955(13)	0.0839(5)	0.3443(7)	5.0(2)
C11	−0.7185(14)	−0.1545(6)	0.1563(8)	6.5(2)	0.7186(14)	0.1544(6)	0.3436(8)	6.6(2)
C12	0.0767(13)	−0.0870(5)	−0.1498(6)	4.9(2)	−0.0766(13)	0.0871(5)	0.6497(6)	4.8(2)
C13	−0.3502(12)	−0.0296(5)	−0.1323(6)	5.3(2)	0.3503(12)	0.0295(5)	0.6324(6)	5.4(2)
C14	−0.0257(10)	0.0126(4)	0.0154(6)	3.8(2)	0.0256(10)	−0,0125(4)	0.4845(6)	3.9(2)
C15	−0.0690(14)	0.0365(6)	0.1118(8)	6.2(2)	−0.1269(14)	−0.0713(6)	0.5075(8)	10.7(3)
C16	0.0593(13)	0.0980(5)	0.1464(7)	5.2(2)	−0.1643(13)	−0.1230(5)	0.4232(7)	5.7(2)
C17	0.1664(14)	0.1249(6)	0.0769(8)	5.6(2)	−0.0594(14)	−0.0980(6)	0.3536(8)	5.3(2)
O1	−0.1629(7)	−0.1446(3)	−0.0066(4)	4.21(10)	0.1628(7)	0.1445(3)	0.5067(4)	4.23(12)
Si	−0.1244(3)	−0.0655(1)	−0.0660(1)	3.61(4)	0.1243(3)	0.0654(1)	0.5661(1)	3.58(4)
S1	0.1335(4)	0.0787(1)	−0.0243(2)	5.12(5)	0.0888(4)	−0.0239(1)	0.3718(1)	4.65(5)

Table IV. Coordinates, equivalent isotropic thermal parameters (in Å^2) and occupation g-factors of the non-hydrogen atoms for structure III.

Atom	x	y	z	B(eq)	g
Ge	0.18793(6)	0.01563(2)	0.29106(6)	2.56(1)	1.00
O2	0.3496(5)	0.0127(1)	0.1773(5)	3.48(10)	1.00
C3	0.3907(9)	−0.0341(3)	0.1237(9)	5.1(2)	1.00
C4	0.3571(10)	−0.0740(3)	0.2342(10)	5.4(2)	1.00
N5	0.2001(6)	−0.0629(6)	0.2901(6)	3.56(12)	1.00
C6	0.1899(9)	−0.0767(2)	0.4518(8)	4.5(2)	1.00
C7	0.2821(8)	−0.0374(3)	0.5605(7)	4.5(2)	1.00
O8	0.2422(6)	0.0098(2)	0.4996(5)	4.37(12)	1.00
O9	−0.0211(5)	0.0077(1)	0.1954(5)	3.70(10)	1.00
C10	−0.0849(7)	−0.0406(3)	0.1827(8)	4.4(2)	1.00
C11	0.0495(9)	−0.0765(3)	0.1730(8)	4.7(2)	1.00
C12	0.4206(8)	0.1282(3)	0.1389(8)	4.8(2)	1.00
C13	0.0810(7)	0.1694(2)	0.1521(7)	3.37(13)	1.00
C14	0.0941(13)	0.2141(4)	0.0668(10)	5.5(3)	0.75
C14′	−0.089(4)	0.1696(12)	0.133(4)	5.7(6)	0.25
C15	−0.0815(11)	0.2262(3)	−0.0122(11)	6.9(3)	1.00
C16	−0.1928(9)	0.2005(3)	0.0377(10)	6.0(2)	1.00
C17	0.3440(7)	0.1612(2)	0.4491(7)	3.65(14)	1.00
C18	0.4866(12)	0.1950(3)	0.4906(11)	4.9(2)	0.75
C18′	0.265(4)	0.1654(12)	0.567(4)	5.8(6)	0.25
C19	0.5102(13)	0.2078(3)	0.6476(10)	6.1(2)	1.00
C20	0.3892(13)	0.1945(3)	0.7168(9)	6.4(3)	1.00
O1	0.1630(6)	0.0802(2)	0.3018(6)	4.92(14)	1.00
Si	0.2547(2)	0.13149(5)	0.2576(2)	3.05(4)	1.00
S1	−0.1202(3)	0.15605(8)	0.1646(3)	4.34(5)	0.75
S1′	0.1087(10)	0.2126(3)	0.0159(10)	5.9(2)	0.25
S2	0.2468(3)	0.1590(1)	0.6097(3)	5.27(7)	0.75
S2′	0.5138(10)	0.1903(3)	0.4714(9)	5.5(2)	0.25

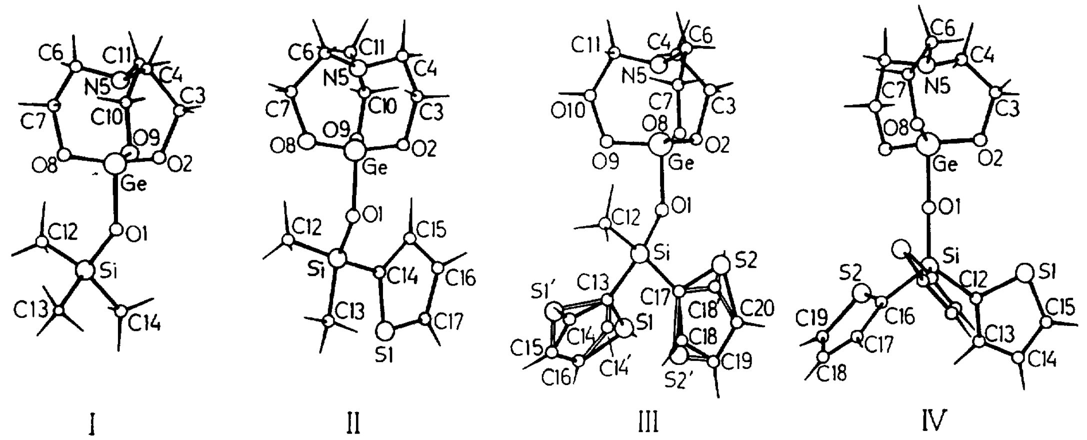
Table V. Coordinates and equivalent isotropic thermal parameters (in Å^2) of the non-hydrogen atoms for structure IV (hexagonal axes).

Atom	x	y	z	B(eq)
Ge	0.0	0.0	0.84455(2)	2.90(3)
O2	0.2015(5)	0.1681(5)	0.8412(1)	3.82(13)
C3	0.2688(8)	0.2026(8)	0.8113(1)	4.5(2)
C4	0.1378(8)	0.1621(8)	0.7876(1)	4.4(2)
N5	0.0	0.0	0.7955(1)	3.3(2)
O1	0.0	0.0	0.8855(1)	6.3(3)
Si	0.0	0.0	0.92221(5)	2.98(5)
C12	0.1750(7)	0.1876(7)	0.9383(1)	3.7(2)
C13	0.1858(7)	0.2883(6)	0.9615(1)	3.5(2)
C14	0.3304(12)	0.4172(10)	0.9696(1)	6.5(3)
C15	0.4436(11)	0.4175(10)	0.9519(1)	7.0(3)
S1	0.3682(2)	0.2639(3)	0.9248(1)	6.82(9)

lence angle Ge-O1-Si is 180°, the oxygen O1 has *sp*-hybridation and its lone electron pairs are delocalized. Therefore, the O1-Ge and O1-Si bonds are shorter than the standard values (1.79 Å and 1.62 Å). All the other bond lengths in IV are near to these [19]. The Si-O-Ge group in (triphenylsiloxy)germatrane was also found to be linear [20].

The linear configuration of the oxygen atom occurs in the crystalline state. The quantum chemical conformation analysis shows that there is generalized force 0.32 kJ · mol^{-1}· deg^{-1} that corresponds to the flat angle Ge-O1-Si. However, the minimum of its energy equals 137.9° for Ge-O1-Si angle and 1.780 Å and 1.651 Å for O1-Ge and O1-Si bonds, respectively. The map of the conformational energy of molecule IV is given in figure 3, figure 4 shows a view of molecule IV in the free state.

There are two molecular forms for compound III in the crystal. They are shown in figure 5. The main form (form A) occupies 75%, while form B or its mirror-image form occupies 25%. Because the A and B molecules exist in the same crystallographic position, structure III may be described with the help of the occupation g-factors of the corresponding atoms. The g-factors of the atoms and their coordinates are given in table IV.



I II III IV

Fig 1. Numbering scheme of molecules I-IV.

Table VI. Bond lenghts (in Å) (esds in parentheses) for structures I-IV.

Bond	I	II	III	IV
Ge-O1	1.810(5)	1.774(5)	1.776(5)	1.757(4)
Ge-O2	1.788(5)	1.769(6)	1.779(5)	1.777(3)
Ge-O8	1.742(5)	1.775(6)	1.780(4)	1.777(3)
Ge-O9	1.793(4)	1.772(6)	1.774(4)	1.777(3)
Ge-N5	2.128(5)	2.156(6)	2.144(5)	2.105(4)
O2-C3	1.423(8)	1.414(10)	1.417(9)	1.398(6)
C3-C4	1.501(10)	1.493(14)	1.502(12)	1.498(9)
C4-N5	1.466(11)	1.418(12)	1.478(10)	1.474(5)
N5-C6	1.475(9)	1.468(13)	1.459(9)	1.474(5)
N5-C11	1.448(9)	1.481(12)	1.494(8)	1.474(5)
C6-C7	1.465(12)	1.511(15)	1.531(9)	1.498(9)
C7-O8	1.442(8)	1.416(11)	1.406(9)	1.398(6)
O9-C10	1.398(9)	1.381(12)	1.414(8)	1.398(6)
C10-C11	1.509(11)	1.474(13)	1.484(11)	1.498(9)
Si-O1	1.624(6)	1.628(6)	1.663(6)	1.571(5)
Si-C12	1.823(7)	1.888(9)	1.838(7)	1.855(5)
Si-C13	1.882(8)	1.850(8)	1.858(6)	
Si-C14	1.867(9)	1.866(8)	-	-
Si-C17	-	-	1.867(6)	
C12-S1	-		-	1.698(6)
C13-S1	-		1.705(6)	
C14-S1	-	1.686(8)	-	
C15-S1	-		-	1.714(7)
C16-S1	-		1.670(8)	-
C17-S1	-	1.633(11)	-	
C12-C13	-		-	1.347(8)
C13-C14	-	-	1.437(12)	1.347(9)
C14-C15	-	1.461(14)	1.512(13)	1.313(14)
C15-C16	-	1.438(13)	1.281(12)	-
C17-S2	-		1.713(7)	
C20-S2	-		1.662(9)	
C17-C18	-	-	1.479(11)	1.347(9)
C18-C19	-		1.377(13)	1.313(14)
C19-C20	-	-	1.293(15)	

Table VII. Bond angles in degrees (esds in parentheses) for structures I-IV.

Angle	I	II	III	IV
O2-Ge-O8	120.4(2)	119.5(3)	118.3(2)	119.4(2)
O2-Ge-O9	116.6(3)	118.9(3)	119.1(2)	119.4(2)
O2-Ge-O1	92.8(3)	96.6(2)	100.2(2)	94.6(1)
O8-Ge-O9	120.9(3)	118.6(3)	120.4(2)	119.4(2)
O8-Ge-O1	96.0(2)	94.4(2)	92.6(2)	94.6(1)
O9-Ge-O1	95.5(2)	96.0(3)	92.0(1)	94.6(1)
Ge-O2-C3	115.7(4)	118.5(4)	117.5(4)	116.3(3)
Ge-O8-C7	114.7(4)	117.9(5)	117.3(4)	116.3(3)
Ge-O9-C10	116.1(4)	118.6(5)	117.5(3)	116.3(3)
Ge-O1-Si	133.0(4)	134.8(3)	139.6(3)	180.0(0)
O2-C3-C4	111.4(5)	112.5(7)	111.4(7)	110.0(5)
C3-C4-N5	107.5(6)	111.1(8)	108.9(6)	107.4(5)
C4-N5-C6	112.2(6)	117.8(8)	117.2(5)	114.9(4)
C4-N5-C11	114.9(6)	112.4(7)	112.8(5)	114.9(4)
N5-C6-C7	107.9(6)	109.0(8)	107.4(5)	107.4(5)
C6-N5-C11	113.7(6)	111.2(8)	113.7(5)	114.9(4)
N5-C11-C10	108.4(6)	109.6(7)	109.1(6)	107.4(5)
C6-C7-O8	112.2(7)	110.7(8)	110.8(5)	110.0(5)
O9-C10-C11	110.0(6)	112.7(8)	110.7(5)	110.0(5)
O1-Si-C12	107.2(3)	107.3(3)	119.5(3)	112.0(1)
O1-Si-C13	107.9(3)	112.7(3)	104.1(3)	-
O1-Si-C14	113.9(3)	110.7(3)	-	-
O1-Si-C17	-	-	106.5(3)	-
C12-Si-C13	111.1(4)	111.0(4)	109.2(3)	-
C12-Si-C14	109.1(4)	106.1(4)	-	-
C12-Si-C16	-	-	-	106.8(3)
C12-Si-C17	-	-	107.5(3)	-
C13-Si-C14	107.6(4)	108.8(4)	-	-

The conformational analysis shows that the form A and B in the crystalline state correspond to the two global minima of energy of the molecule in free state. Due to repulsion between the sulfur (S1) and hydrogen (H(C18)) atoms the energy of the B form increases by 3.12 kJ · mol^{-1}compared with that of the A form. The calculated value of Ge-O1-Si angle is 136.5° (value from X-ray data is equal 139.6(3)°), which is less than value of molecule IV. This difference may be explained by the fact that the electron-donor methyl group promotes the localization of electron pairs on the oxygen atom (O1); this leads to the decrease of valence angle in accordance with Gillespie's theory (VSEPR) [21].

It has been shown that the molecule II energy depends on the torsion angle O1-Si-C14-S1 (fig 6). The conformations with the values of torsion angles in −34° and 146° correspond to the almost identical minima of the molecule energy. Both of these conformations exist in the crystalline state. The molecules with these con-

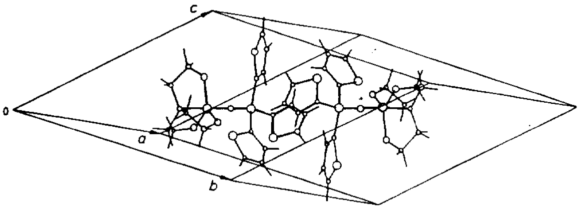


Fig 2. Unit-cell packing diagram for the structure IV (rhombohedral axes).

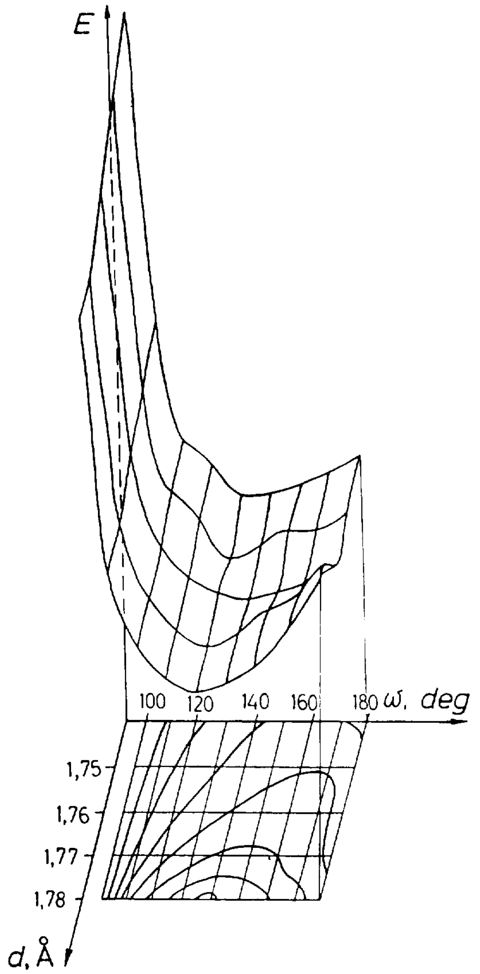


Fig 3. Dependance of molecule IV energy on the O1-Ge bond distance and on the Ge-O1-Si angle for the optimum O1-Si length (1.651 Å). The interval between lines of levels is 5 kJ · mole^{-1}.

formations are disposed in the independent parts of the unit cell and connected by the pseudosymmetry center (fig 7). The existence of two methyl groups leads to the increase of + I-effect. Therefore, the value of Ge-O1-Si angle falls to 134.8(3)° (the quantum chemical calculated value is 134.6)°.

Introduction of the third methyl group to the molecule I increase the + I-effect and the Ge-O1-Si angle is equal 133.0(4)° (the calculated value is 131.9°). The conformation with linear configuration of the O1 atom is characterized by generalized force 1.27 kJ · mol^{-1}· deg^{-1}. The crystal field is not capable of compensating this force, therefore, and this conformation is not observed in crystal where the conformation of the molecules is near to that in free state.

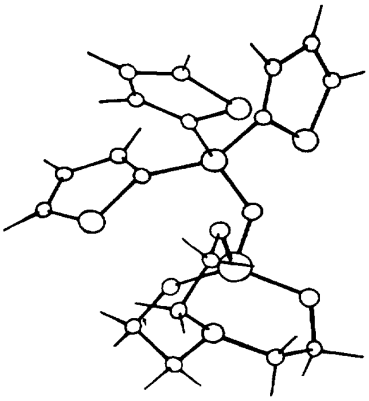


Fig 4. Perspective view of molecule IV in free state.

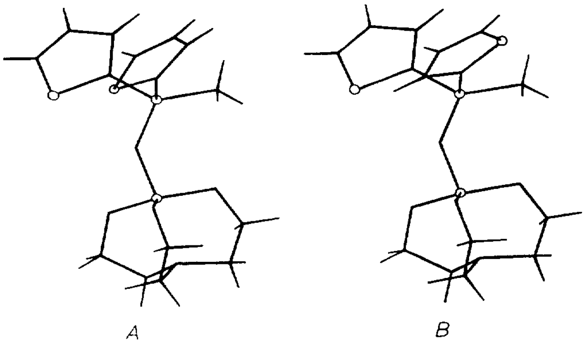


Fig 5. Molecular forms of III in the crystalline state.

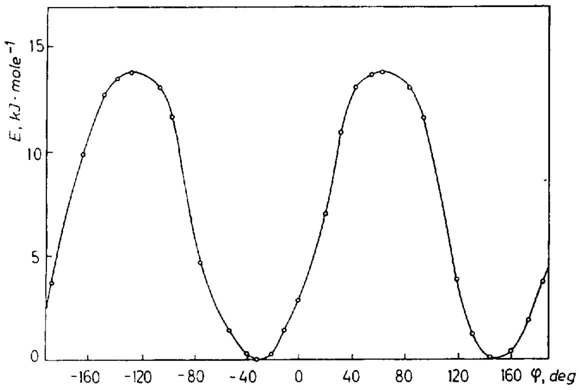


Fig 6. Variation of molecule II energy as function of the torsion angle O1-Si-C14-S1.

Generally, the following conclusion can be made. The acceptor substituents at the Si lead to the increase of Ge-O1-Si angle, while the donors cause the decrease of the valence angle. The value of this angle falls from IV to I compounds. For a comparison the values of valence angles M-O-M (where M is Ge or Si) in structures GeO_2,

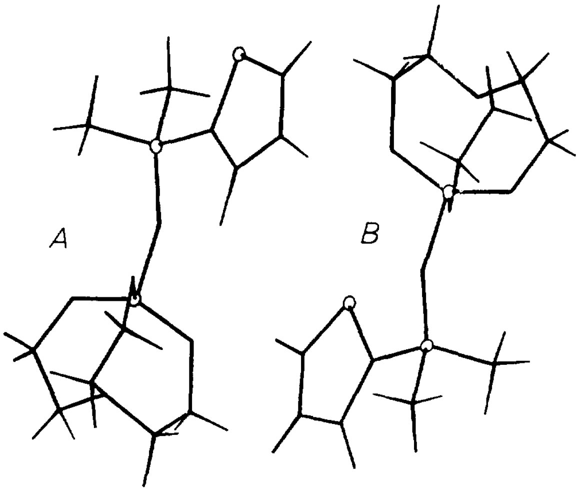


Fig 7. Disposition of molecule II in the independent part of unit cell.

SiO_2 (quartz) and solid solution of GeO_2 (14 mol%) in SiO_2 are 130.1° (in GeO_2) [22], 143.7° (in SiO_2) [23], and 142.2° (in $Si_{0.86}Ge_{0.14}O_2$) [24]. The angles in the studied compounds I-III have the intermediate values, correspondingly.

It should be noted that valence angles were always calculated as angles between the lines passing across the centers of the atoms. Figure 8 shows the schematic representation of the centers of electron density (o′ and o″) of the O1-Ge and O1-Si chemical bonds in the Ge-O1-Si plane. The centers of electron density have been determined using Boys' localization [25]. The calculated values of the o′-O1-o″ angles are smaller than the corresponding values of the valence angles. These values are equal 108.8°, 110.6°, 110.0° and 109.8° for the molecules I, II, III, IV, respectively. The values are between the corresponding values for C-O-Si and Si-O-Si bridges [26].

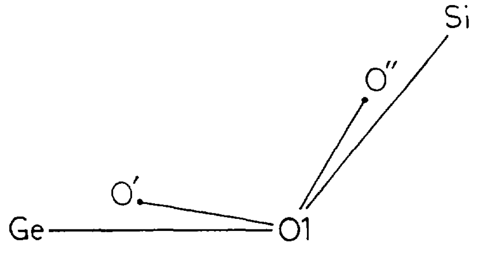


Fig 8. Centers of electron density of the O1-Ge and O1-Si chemical bonds.

The atrane system of I-IV compounds has usual geometry with approximate symmetry C_3. For the isolated molecules I-IV in accordance with quantum chemistry data, all geometrical parameters in crystals as compared with the standard values may be explained by the peculiarities of packing. For instance, the decrease of Ge-O8 bond length in I (1.742(5)°) results from the intermolecular contacts of O8-C10 and O8-H(C10). Their lengths are equal 3.472(8)° and 2.78(6)°. The intermolecular contacts in I-IV generally correspond to the sums of van der Waals radii [27].

The values of intramolecular N5-Ge donor-acceptor bond lengths are 2.128(5)°, 2.156(6)°, 2.144(5)° and 2.105(4)° for the compounds I, II, III, IV, respectively. (They are shorter than in germatranes containing electron-donor alkyl groups [28] and approach that of 1-bromogermatrane (2.09 Å)).

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