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Protonated digermyl and distannyl ethers with partial germylium and stannylium ion character [☆]

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Abstract

Hydrolysis of trimethylgermylium and triethylstannylium tetrakis(pentafluorophenyl)borate produced respectively bis(trimethylgermyl)oxonium and bis(triethylstannyl)oxonium tetrakis(pentafluorophenyl)borate, that is, the protonated forms of bis(trimethylgermyl) ether and bis(triethylstannyl) ether. The crystal structures of both molecules respectively show increased Ge–O and Sn–O bond lengths and flattened tetrahedra about germanium and tin. These structural features indicate pronounced germylium and stannylium ion character.

Keywords: Germanium; Tin; Stannylium ion; Germylium ion; Tetrakis(pentafluorophenyl)borate

1. Introduction

Although digermyl and distannyl ethers (oxides), $(R_3Ge)_2O$ and $(R_3Sn)_2O$, are common materials, their conjugate acids are unknown. Protonation on oxygen must of necessity be accompanied by a counterion (X^-), which normally displaces the oxygen functionality from germanium or tin and ultimately forms the M–X bond and water according to Eq. (1) (M = Ge or Sn) [1]. As a result, no protonated oxides

$$(R_3M)_2O + 2HX \rightarrow 2R_3MX + H_2O \qquad (1)$$

of germanium or tin, $(R_3M)_2OH^+$, have been isolated and characterized to date. The same problem thwarted the study of protonated silanols, $R_3SiOH_2^+$, until recently, when Reed et al. obtained the crystal structure of $(\text{tert-butyl})_3SiOH_2^+$ with the very low coordinating anion $Br_6CB_{11}H_6^-$ [2]. We have used the same strategy to isolate the first protonated digermyl and distannyl ethers, whose crystal structures have now been solved. The counterion is tetrakis(pentafluorophenyl)borate ($TPFPB^-$), which we used previously to obtain the crystal structure of a silyl cation loosely coordinated to toluene solvent [3].

2. Results and discussion

2.1. Preparation

Trimethylgermane and triethylstannane were prepared by reduction of the corresponding bromides with lithium aluminum hydride. The hydrides were allowed to react with trityl^+ $TPFPB^-$ to form the putative cations (R_3M^+), presumably coordinated to some extent with the solvent (benzene or toluene), according to Eq. (2). Hydrolysis

$$R_3M\text{–}H + Ph_3C^+TPFPB^- \rightarrow Ph_3C\text{–}H + R_3M^+TPFPB^- \qquad (2)$$

of the germyl and stannyl cations by water present in the solvent produced the protonated digermyl and distannyl ethers by the overall reaction of Eq. (3). The

$$2R_3M^+TPFPB^- + H_2O \rightarrow (R_3M)_2OH^+TPFPB^- + H^+TPFPB^- \qquad (3)$$

equivalent of $H(\text{solvent})^+$ $TPFPB^-$ remained in solution during the recrystallization process, which is described in Section 4.

[☆] Dedicated to Professor Hideki Sakurai on the occasion of his retirement from Tohoku University.

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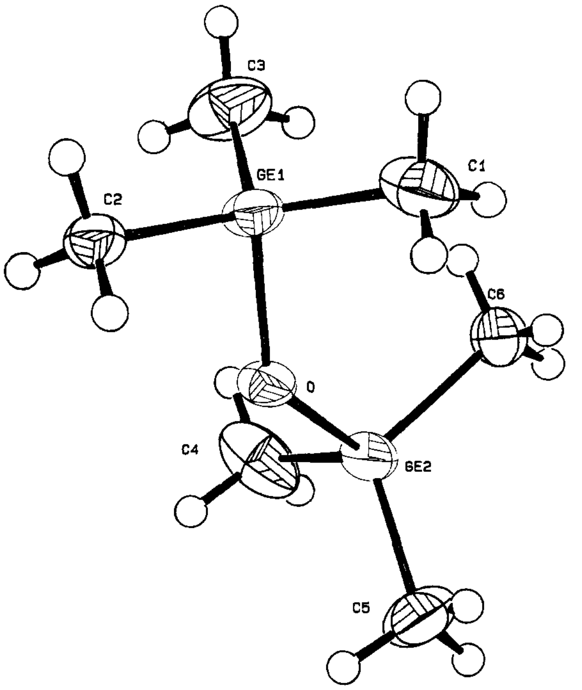
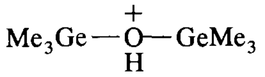


Fig. 1. Perspective view of the cationic portion of bis(trimethylgermyl)oxonium tetrakis(pentafluorophenyl)borate.

2.2. *Crystal structure of protonated bis(trimethylgermyl) ether*

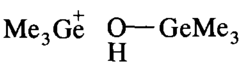
Figs. 1 and 2 display, respectively, the cationic and anionic portions, which are well separated from each other. Table 1 gives the atomic coordinates for the heavy atoms, and Table 2 gives bond lengths and angles. The structure of the anion is unremarkable. Hydrogen atoms were not observable, so that the proton on oxygen is hypothetical although required by the anion for electrical neutrality. There clearly is no third heavy atom attached to oxygen.

The Ge–O and Ge–C bond lengths respectively average about 1.90 and 1.91 Å. The Ge–O–Ge angle is 134.9°, the O–Ge–C angle averages 101.6°, and the C–Ge–C angle averages 116.0°. Although the Ge–C bond length is normal (comparable to 1.94 Å in $(\mathrm{Ph_3Ge})_2\mathrm{O}$ [4]), the Ge–O length is 0.13 Å longer than normal (ca. 1.77 Å in $(\mathrm{Ph_3Ge})_2\mathrm{O}$ [4]), indicating that some positive charge resides on germanium as well as oxygen. As a result, the geometry around germanium is a flattened pyramid, with the C–Ge–C angles increased and O–Ge–C angles decreased, as would be expected for a molecule with germylium cation character (see resonance structures **1** and **2**). In the extreme of a full germylium cation, the pyramid would flatten to a trigonal geometry in which germanium and the three methyl carbons lie in a single plane. The sum of the C–Ge–C angles in such a structure would be 360°, compared with the observed average



$$\mathrm{Me_3Ge}-\overset{+}{\underset{\mathrm{H}}{\mathrm{O}}}-\mathrm{GeMe_3}$$

1



$$\mathrm{Me_3}\overset{+}{\mathrm{Ge}}\;\underset{\mathrm{H}}{\mathrm{O}}-\mathrm{GeMe_3}$$

2

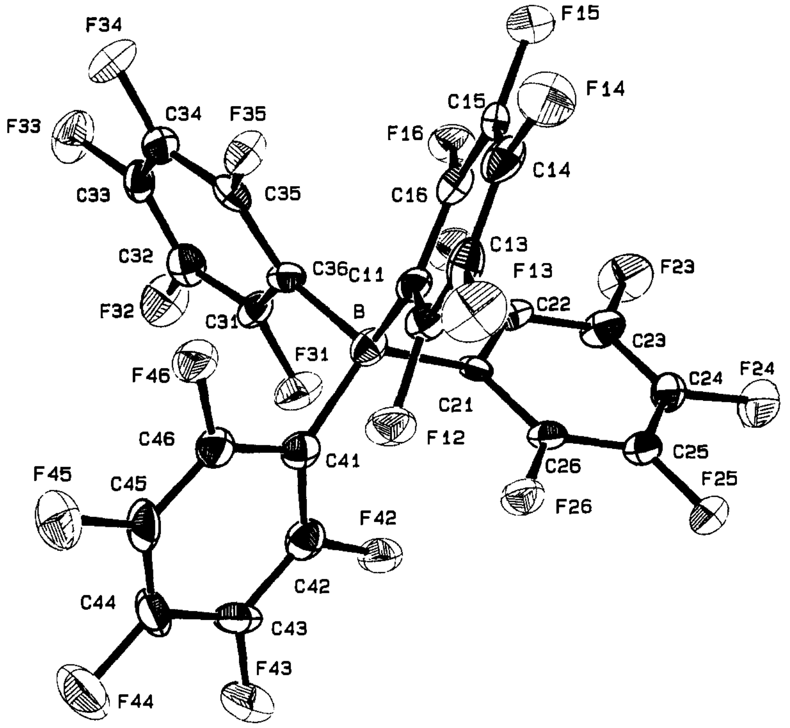


Fig. 2. Perspective view of the anionic portion of bis(trimethylgermyl)oxonium tetrakis(pentafluorophenyl)borate.

Table 1
Atomic coordinates for protonated bis(trimethylgermyl)oxonium tetrakis(pentafluorophenyl)borate

Atom	*x*	*y*	*z*
Ge(1)	0.14520(7)	0.14627(4)	0.21248(6)
Ge(2)	−0.09512(7)	0.03765(4)	0.24564(6)
O	0.0680(4)	0.0649(2)	0.2459(3)
F(12)	0.7687(3)	0.0471(2)	0.7000(2)
F(13)	0.9161(3)	0.0836(2)	0.5949(3)
F(14)	0.8851(3)	0.2062(2)	0.5060(3)
F(15)	0.6975(3)	0.2905(2)	0.5256(2)
F(16)	0.5449(3)	0.2541(2)	0.6291(2)
F(22)	0.3176(3)	0.2182(2)	0.6786(2)
F(23)	0.1504(3)	0.1852(2)	0.5497(3)
F(24)	0.1671(3)	0.0669(2)	0.4582(3)
F(25)	0.3530(3)	−0.0216(2)	0.5053(2)
F(26)	0.5211(3)	0.0069(2)	0.6382(2)
F(31)	0.3574(3)	0.1451(2)	0.8351(2)
F(32)	0.3225(3)	0.2440(2)	0.9453(3)
F(33)	0.4738(3)	0.3556(2)	0.9706(2)
F(34)	0.6647(3)	0.3632(2)	0.8863(3)
F(35)	0.7070(3)	0.2640(2)	0.7817(2)
F(42)	0.4064(3)	0.0078(2)	0.7866(2)
F(43)	0.4721(4)	−0.0744(2)	0.9182(3)
F(44)	0.6912(4)	−0.0601(2)	1.0167(3)
F(45)	0.8458(4)	0.0389(2)	0.9766(3)
F(46)	0.7790(3)	0.1257(2)	0.8478(2)
C(1)	0.1003(7)	0.1481(4)	0.0929(5)
C(2)	0.3084(6)	0.1186(4)	0.2535(5)
C(3)	0.0805(7)	0.2199(4)	0.2752(6)
C(4)	−0.1106(7)	0.0474(5)	0.3614(6)
C(5)	−0.0950(8)	−0.0556(4)	0.2004(7)
C(6)	−0.1807(6)	0.1052(4)	0.1719(5)
C(11)	0.6504(5)	0.1505(3)	0.6743(4)
C(12)	0.7460(5)	0.1099(3)	0.6583(4)
C(13)	0.8249(6)	0.1267(4)	0.6061(4)
C(14)	0.8101(6)	0.1887(4)	0.5596(4)
C(15)	0.7142(6)	0.2305(3)	0.5706(4)
C(16)	0.6373(5)	0.2104(3)	0.6240(4)
C(21)	0.4307(5)	0.1135(3)	0.6674(4)
C(22)	0.3320(6)	0.1566(3)	0.6390(4)
C(23)	0.2424(5)	0.1403(4)	0.5722(5)
C(24)	0.2489(6)	0.0817(4)	0.5270(4)
C(25)	0.3452(6)	0.0366(4)	0.5503(4)
C(26)	0.4297(5)	0.0538(3)	0.6186(4)
C(31)	0.4382(5)	0.1988(3)	0.8465(4)
C(32)	0.4160(6)	0.2482(4)	0.9033(4)
C(33)	0.4938(6)	0.3046(3)	0.9165(4)
C(34)	0.5880(6)	0.3081(3)	0.8743(4)
C(35)	0.6073(5)	0.2564(3)	0.8178(4)
C(36)	0.5319(5)	0.1998(3)	0.7980(4)
C(41)	0.5911(6)	0.0712(3)	0.8078(4)
C(42)	0.5174(6)	0.0192(3)	0.8321(4)
C(43)	0.5490(6)	−0.0248(3)	0.8992(5)
C(44)	0.6601(7)	−0.0179(4)	0.9500(4)
C(45)	0.7355(6)	0.0325(4)	0.9287(4)
C(46)	0.6992(6)	0.0754(4)	0.8613(4)
B	0.5500(6)	0.1326(4)	0.7370(5)

(over the two germanium centers) of 348° and the value of 328.5° for a perfect tetrahedron. In (Ph$_3$Ge)$_2$O, lacking the proton on oxygen, the Ge–O–Ge angle at 135.2° is essentially the same as in the present case [4], but the O–Ge–C angle at 107.6° and the C–Ge–C angle at 111.2° are much closer to tetrahedral (the sum of the three C–Ge–C angles is 333.7°). Thus there is a clear distortion of the present molecule toward the germylium cation, with a lengthened Ge–O bond and a more trigonal-like geometry about germanium. The Ge–O bond order may be calculated from the Pauling equation [3] to be ca. 0.61 from the comparison of the observed length (1.90 Å) with the value for a bond order of 1.0 (1.77 Å).

The average C–Ge–C angle of 116.0° is essentially the same as the C–Si–C angle in tert-(Bu^t)$_3$Si–O$^+$H$_2$ [2] or (Pr^i)$_3$Si–N$^+$C–CH$_3$ [5]. Reed suggested that the Si–O bond in the protonated silanol is better termed a Lewis acid–base dative bond (R$_3$Si$^+$ ← B) than a covalent bond (R$_3$Si–B$^+$, in which B represents the Lewis base), and went on to assert that "the geometry and bond length data suggest a predominance of silyl cation character over onium (covalent bond) character". Similar inferences may be made with the present geometry.

The torsional arrangements around the two germanium centers are not equivalent. The dihedral angles from Ge2 via O and Ge1 to the methyl carbons are 67.2° to C1, 173.8° to C2, and 54.5° to C3 (Fig. 1). These are normal *gauche* and *anti* geometries. The dihedral angles from Ge1 via O and Ge2 to the other methyl carbons are 103.5° to C4, 134.8° to C5, and 15.5° to C6. Perfect 60° and 180° dihedral angles in any four-atom sequence of course result in eclipsing between the 1,5 substituents on the first and third atoms, as in 1,3-diaxial interactions in cyclohexane. The open chain can relieve these interactions by torsional adjustments. It is interesting that most of the adjustments are made in half of the molecule.

2.3. *Crystal structure of protonated bis(triethylstannyl) ether*

Figs. 3 and 4 and Tables 3 and 4 provide information analogous to that in Figs. 1 and 2 and Tables 1 and 2 on

Table 2
Bond lengths (Å) and angles (°) for protonated bis(trimethylgermyl)oxonium tetrakis(pentafluorophenyl)borate with e.s.d. values in parentheses

Bond	Distance	Bonds	Angle
Ge1–O	1.897(4)	O–Ge1–C1	103.6(3)
Ge1–C1	1.889(9)	O–Ge1–C2	97.7(2)
Ge1–C2	1.920(7)	O–Ge1–C3	103.1(3)
Ge1–C3	1.931(8)	C1–Ge1–C2	115.8(3)
Ge2–O	1.903(4)	C1–Ge1–C3	116.4(4)
Ge2–C4	1.884(9)	C2–Ge1–C3	116.2(3)
Ge2–C5	1.922(9)	O–Ge1–C4	102.1(3)
Ge2–C6	1.899(8)	O–Ge2–C5	101.3(3)
		O–Ge2–C6	102.0(3)
		C4–Ge2–C5	117.5(4)
		C4–Ge2–C6	114.8(4)
		C5–Ge2–C6	115.4(4)
		Ge1–O–Ge2	134.9(2)

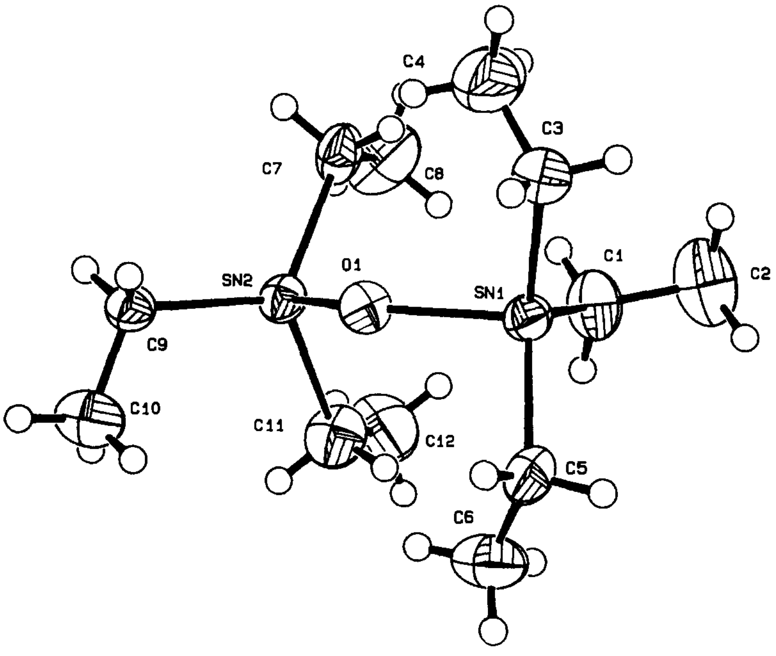


Fig. 3. Perspective view of the cationic portion of bis(triethylstannyl)oxonium tetrakis(pentafluorophenyl)borate.

the tin structure. Again, the anion and cation are noninteracting. The Sn–O and Sn–C bond lengths both average 2.12 Å. The O–Sn–O angle is 135.8°, the O–Sn–C angle averages 98.9°, and the C–Sn–C angle averages 117.6°. The Sn–C bond length is normal (comparable to 2.14 Å in $(Ph_3Sn)_2O$ [6]), but the Sn–O bond is substantially lengthened (from 1.96 Å in $(Ph_3Sn)_2O$ [6]). Thus, the protonated distannyl ether has more stan-

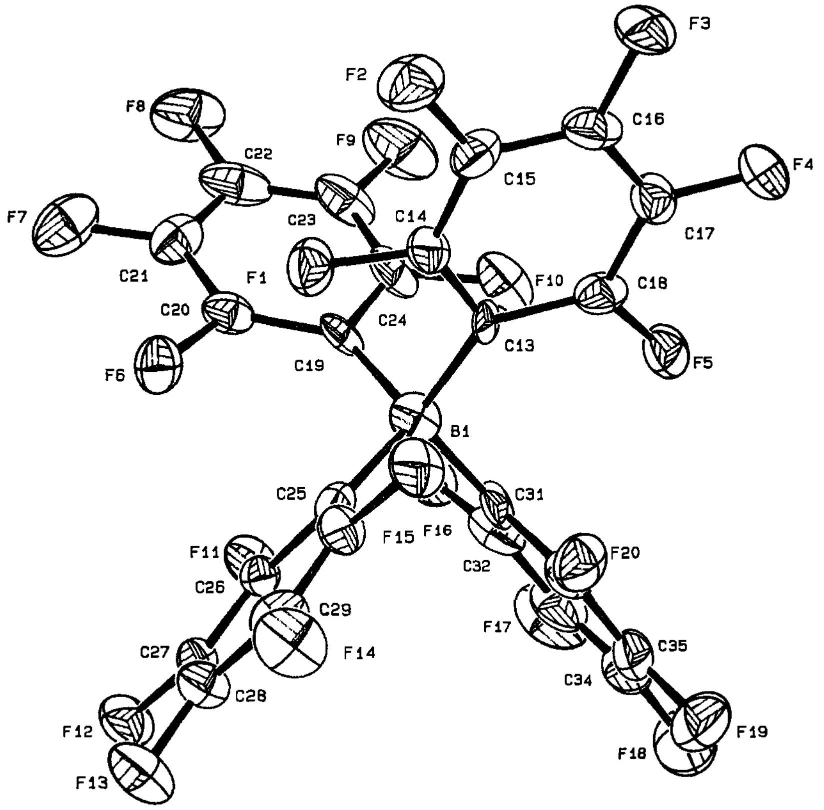


Fig. 4. Perspective view of the anionic portion of bis(triethylstannyl)oxonium tetrakis(pentafluorophenyl)borate.

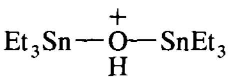
Table 3
Atomic coordinates for protonated bis(triethylstannyl)oxonium tetrakis(pentafluorophenyl)borate with e.s.d. values in parenthesis

Atom	*x*	*y*	*z*
Sn(1)	0.15184(5)	0.22333(3)	0.80193(2)
Sn(2)	0.34962(5)	0.26010(3)	0.66708(2)
O(1)	0.1941(4)	0.2245(3)	0.7127(2)
F(1)	0.7674(3)	0.3202(2)	0.3975(2)
F(2)	0.5926(4)	0.4292(2)	0.3652(2)
F(3)	0.4140(3)	0.4684(2)	0.4387(2)
F(4)	0.4120(3)	0.3911(2)	0.5444(2)
F(5)	0.5772(3)	0.2778(2)	0.5760(2)
F(6)	1.0241(3)	0.2708(2)	0.4339(2)
F(7)	1.1887(4)	0.3861(3)	0.4568(2)
F(8)	1.1742(4)	0.4863(3)	0.5509(2)
F(9)	0.9913(4)	0.4621(3)	0.6242(2)
F(10)	0.8209(4)	0.3461(2)	0.6028(2)
F(11)	1.0229(3)	0.1367(2)	0.5099(2)
F(12)	1.0755(3)	0.0164(2)	0.4388(2)
F(13)	0.9048(4)	−0.0293(2)	0.3475(2)
F(14)	0.6862(4)	0.0525(3)	0.3274(2)
F(15)	0.6337(3)	0.1752(2)	0.3949(2)
F(16)	0.9633(4)	0.2108(3)	0.6271(2)
F(17)	0.9155(5)	0.1095(3)	0.7110(2)
F(18)	0.7186(5)	0.0056(3)	0.6955(2)
F(19)	0.5636(4)	0.0116(3)	0.5933(2)
F(20)	0.5991(3)	0.1204(2)	0.5103(2)
C(1)	0.3157(8)	0.2799(5)	0.8430(4)
C(2)	0.3095(8)	0.3086(6)	0.9036(4)
C(3)	−0.0151(8)	0.2927(5)	0.7940(4)
C(4)	−0.013(1)	0.3640(7)	0.7581(5)
C(5)	0.1391(8)	0.0978(5)	0.8142(3)
C(6)	0.2530(8)	0.0515(5)	0.8024(4)
C(7)	0.3502(7)	0.3853(5)	0.6861(3)
C(8)	0.474(1)	0.4180(6)	0.7134(4)
C(9)	0.2747(6)	0.2184(4)	0.5819(3)
C(10)	0.3087(7)	0.1330(5)	0.5694(4)
C(11)	0.4914(7)	0.1852(6)	0.7104(4)
C(12)	0.608(1)	0.2225(7)	0.7385(5)
C(13)	0.6813(5)	0.2911(4)	0.4874(3)
C(14)	0.6762(6)	0.3327(4)	0.4350(3)
C(15)	0.5909(7)	0.3912(4)	0.4173(3)
C(16)	0.5000(7)	0.4100(4)	0.4539(4)
C(17)	0.4982(6)	0.3704(4)	0.5065(3)
C(18)	0.5855(6)	0.3116(4)	0.5219(3)
C(19)	0.9140(6)	0.2992(4)	0.5187(3)
C(20)	1.0106(6)	0.3150(4)	0.4836(3)
C(21)	1.0982(7)	0.3761(5)	0.4942(4)
C(22)	1.0913(8)	0.4261(5)	0.5408(4)
C(23)	0.9984(8)	0.4142(5)	0.5774(4)
C(24)	0.9135(6)	0.3530(5)	0.5644(4)
C(25)	0.8277(6)	0.1645(4)	0.4554(3)
C(26)	0.9389(6)	0.1191(4)	0.4640(3)
C(27)	0.9650(6)	0.0562(4)	0.4286(3)
C(28)	0.8819(7)	0.0335(4)	0.3821(3)
C(29)	0.7703(7)	0.0751(5)	0.3727(3)
C(30)	0.7475(6)	0.1388(4)	0.4082(3)
C(31)	0.7796(6)	0.1742(4)	0.5639(3)
C(32)	0.8551(7)	0.1642(5)	0.6166(4)
C(33)	0.8361(9)	0.1109(5)	0.6607(4)
C(34)	0.737(1)	0.0592(5)	0.6530(4)
C(35)	0.6595(8)	0.0634(5)	0.6018(4)
C(36)	0.6813(7)	0.1199(5)	0.5595(3)
B(1)	0.8006(8)	0.2315(5)	0.5068(4)

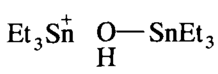
Table 4
Bond lengths (Å) and angles (°) for protonated bis(triethylstannyl)oxonium tetrakis(pentafluorophenyl)borate

Bond	Distance	Bonds	Angle
Sn1–O1	2.109(5)	O1–Sn1–C1	99.9(3)
Sn1–C1	2.122(8)	O1–Sn1–C3	99.8(3)
Sn1–C3	2.118(8)	O1–Sn1–C5	99.0(2)
Sn1–C5	2.113(8)	C1–Sn1–C3	116.6(4)
Sn2–O1	2.123(4)	C1–Sn1–C5	116.2(3)
Sn2–C7	2.127(8)	C3–Sn1–C5	119.0(3)
Sn2–C9	2.130(8)	O1–Sn2–C7	99.3(2)
Sn2–C11	2.128(8)	O1–Sn2–C9	96.0(2)
C1–C2	1.46(1)	O1–Sn2–C11	99.7(3)
C3–C4	1.44(1)	C7–Sn2–C9	119.7(3)
C5–C6	1.49(1)	C7–Sn2–C11	119.5(3)
C7–C8	1.50(1)	C9–Sn2–C11	114.5(3)
C9–C10	1.50(1)	Sn1–O1–Sn2	135.8(2)
C11–C12	1.48(1)	Sn1–C1–C2	116.6(6)
		Sn1–C3–C4	116.0(7)
		Sn1–C5–C6	115.1(6)
		Sn2–C7–C8	115.0(6)
		Sn2–C9–C10	113.7(5)
		Sn2–C11–C12	119.0(7)

nylium character than the above germanium system has germylium character. Indeed, the pyramid around tin is much more flattened. The sum of the C–Sn–C angles averages 352.8°, marginally closer to 360° than the 351° observed by Reed et al. in their structure of $(^{i}Pr)_3Si^+$ coordinated to a carborane anion [7], which represents the closest geometric approach to date to a planar silylium cation. In the present molecule the oxygen atom therefore connects two nearly planar triethyltin fragments. From the Pauling equation, the 0.16 Å lengthening of the Sn–O bond corresponds to a bond order of 0.54, or about equal contributions of covalent and ionic resonance forms, **3** and **4**. It is not surprising that the more electropositive,


$Et_3Sn-\overset{+}{\underset{H}{O}}-SnEt_3$

3


$Et_3\overset{+}{Sn}\ \underset{H}{O}-SnEt_3$

4

more polarizable, larger tin atom can sustain a larger positive charge than germanium.

As in the germanium compound, the tin compound shows dihedral deviations from pure *anti* and *gauche* geometries. The dihedral angles from Sn1 via O and Sn2 to the methylene carbons are 63.8° to C7, 174.7° to C9, and 58.5° to C11 (Fig. 3). The dihedral angles from Sn2 via O and Sn1 to the other methylene carbons are 3.8° to C1, 123.3° to C3, and 115.0° to C5. These latter deviations from *gauche* and *anti* again relieve 1,5-interactions. It also is the case that the arrangements of the ethyl groups are quite different within the two triethylstannyl groups. Around Sn2 two methyl groups are approximately *anti* to the Sn2–C9 bond (and the

C10 methyl is *gauche* to Sn1–O), whereas around Sn1 the analogous pair of methyl groups are approximately *gauche* to the Sn1–C1 bond (and the C2 methyl is *anti* to Sn1–O). These arrangements presumably minimize interactions among the ethyl groups.

3. Conclusions

The protonated forms of bis(trimethylgermyl) ether and bis(triethylstannyl) ether have flattened geometries about germanium or tin and lengthened Ge–O or Sn–O bonds that indicate considerable development of positive charge on the metal and high germylium or stannylium character. In the germanium case, the sum of the C–Ge–C bond angles is 348° whereas in the tin case the sum of the C–Sn–C bond angles is 352.8°, well advanced toward the value of 360° for the fully tricoordinate, planar cations. These molecules represent the respective closest approaches to date to germylium and stannylium ions based on solid state structural parameters.

4. Experimental section

4.1. Synthesis of bis(trimethylgermyl)oxonium tetrakis(pentafluorophenyl)borate

Bromotrimethylgermane (5 g, 0.025 mol) in 20 ml of dimethoxyethane was added to a suspension of 1 g (0.026 mol) of $LiAlH_4$ in dimethoxyethane. The product was distilled directly from the reaction mixture as it formed, to yield 0.55 g (18%) of trimethylgermane in the fraction boiling at 25–30°C. The yield was considerably reduced by the high volatility of the product. Subsequent yields ranged up to 60%. The germane was allowed to react in a 5 mm NMR tube with trityl tetrakis(pentafluorophenyl)borate in toluene in the manner described in detail for silanes in the literature [3]. The solvent was removed at low pressure and the residue washed under N_2 with hexane to remove the by-product triphenylmethane. The hexane was removed by cannulation and replaced with a 3/1 mixture of wet 1,2-dichloroethane and hexane. The crystals that were formed were of good quality for X-ray crystallography.

4.2. Synthesis of bis(triethylstannyl)oxonium tetrakis(pentafluorophenyl)borate

Bromotriethylstannane (1.95 g, 0.68 mol) in dry diethyl ether was added to 0.3 g (0.79 mol) of $LiAlH_4$ in 30 ml of ether. After workup, removal of solvent by rotary evaporation, and distillation of the residue, 0.589 g (42%) of triethylstannane was obtained. The stannane was allowed to react with trityl tetrakis(pentafluorophenyl)borate in a 5 mm NMR tube in toluene in the manner described in the literature for silanes [3]. Evaporation of the solvent and washing with hexane removed the by-product triphenylmethane. The species $Et_3SnB(C_6F_5)_4$ had a ^{119}Sn shift at δ 250.8 in C_6D_6 and δ 251.0 in $C_6D_5CD_3$. The small difference indicates only very weak coordination with solvent. Subsequent recrystallization from a mixture of wet toluene and hexane yielded crystals of sufficient quality for X-ray crystallography.

4.3. Crystal structure of bis(trimethylgermyl)oxonium tetrakis(pentafluorophenyl)borate

Crystal data: $C_{30}H_{18}BF_{20}Ge_2O$; M = 930.43; monoclinic, space group $P2_1/c$, a = 11.231(4), b = 19.107(4), c = 15.896(6) Å, β = 99.11(3)°, V = 3368(3) Å^3 (by least-squares refinement for 25 carefully centered reflections in the range $18.1 < 2\theta < 21.8°$, λ = 0.71069 Å, Z = 4, D_c = 1.835 g cm^{-2}. The transparent, colorless, plate-like crystal had approximate dimensions 0.31 × 0.26 × 0.08 mm, μ(Mo Kα) = 18.93 cm^{-1}.

Data collection and processing: Enraf-Nonius CAD-4 diffractometer, −120°C, ω/θ technique to a maximum 2θ value of 48.0°, scan rate 3.0–16.0° min^{-1} in ω, scan width $(1.00 + 0.35\tan\theta)$; 5769 reflections measured ($0 \le h \le 12$, $0 \le k \le 21$, $-18 \le l \le 18$), 5 466 unique, 2753 with $I > 3\sigma(I)$; Lorentz, polarization and absorption corrections were applied (DIFABS) with transmission factors ranging from 0.61 to 0.86. The intensity of three representative reflections were measured after every 90 min of X-ray exposure and remained constant throughout data collection.

Structure solution and refinement. The structure was solved by direct methods with the program SHELXS-86 [8]. Nonhydrogen atoms were refined anisotropically. Hydrogen atoms were fixed at idealized positions. The final cycle of full-matrix least-squares refinement based on 2 753 observed reflections and 487 variable parameters converged with an unweighted agreement factor of R = 0.044 and a weighted agreement factor of R_w = 0.043. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.44 and −0.65 e Å^{-3}, respectively. Neutral atom scattering factors were taken from Cromer and Weber [9]. All calculations were performed with the TEXSAN crystallographic software package of Molecular Structure Corporation (1985 version). Full tables of parameters have been deposited at the Cambridge Crystallographic Data Centre.

4.4. Crystal structure of bis(triethylstannyl)oxonium tetrakis(pentafluorophenyl)borate

Crystal data: $C_{36}H_{30}BF_{20}Sn_2O$; M = 1106.79; monoclinic, space group $P2_1/c$, a = 10.689(3), b = 16.639(4), c = 22.612(4) Å, β = 95.49(2)°, V = 4003(3)

Å^3 (by least-squares refinement for 25 carefully centered reflections in the range $18.1 < 2\theta < 21.8°$, $\lambda = 0.71069$ Å, $Z = 4$, $D_c = 1.835$ g cm^{-2}. The colorless, prismatic crystal had approximate dimensions $0.3 \times 0.3 \times 0.4$ mm, μ(Mo Kα) = 13.72 cm^{-1}.

Data collection and processing: Enraf-Nonius CAD-4 diffractometer, −120°C, ω/θ technique to a maximum 2θ value of 40.0°, scan rate 3.0°–16.0° min^{-1} in ω, scan width $(1.00 + 0.35\tan\theta)$; 4169 reflections measured ($0 \le h \le 10$, $-15 \le k \le 0$, $-21 \le l \le 21$), 3896 unique, 3106 with $I > 3\sigma(I)$; Lorentz, polarization, and absorption corrections were applied (DIFABS) with transmission factors ranging from 0.92 to 1.09. The intensity of three representative reflections were measured after every 90 min of X-ray exposure and remained constant throughout data collection.

Structure solution and refinement. The structure was solved by direct methods with the program SHELXS-86 [8]. Nonhydrogen atoms were refined anisotropically. Hydrogen atoms were fixed at idealized positions. The final cycle of full-matrix least-squares refinement based on 3106 observed reflections and 541 variable parameters converged with an unweighted agreement factor of $R = 0.030$ and a weighted agreement factor of $R_w = 0.043$. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.38 and −0.38 e Å^{-3}, respectively. Neutral atom scattering factors were taken from Cromer and Weber [9]. All calculations were performed with the TEXSAN crystallographic software package of Molecular Structure Corporation (1985 version). Full tables of parameters have been deposited at the Cambridge Crystallographic Data Centre.

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