Syntheses and Solid State Structures of Et₂SbTeEt and Et₂BiTeEt

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Abstract: Diethylstibanyl- and diethylbismuthanyltelluranes Et₂MTeEt (M = Sb **1**, Bi **2**) as well as *t*-Bu₃Sb (**3**) were structurally characterized by single crystal X-ray diffraction. Single crystals of **1** - **3** were grown using an IR-laser-assisted technique. **1** and **2** form short intermolecular E...Te interactions in the solid state, which were further investigated with dispersion-corrected density functional theory.

Introduction

The interest in heavier main group element compounds is largely based on their tendency to form intermolecular interactions, which is very well known in group 15 and group 16 chemistry of the heavier elements, Sb, Bi, and Te, respectively. The intermolecular interactions are largely influenced by the organic substituents. Compounds containing sterically less demanding substituents often form one- or two-dimensional polymeric networks, whereas sterically demanding substituents typically hamper the formation of intermolecular contacts between the metal centers of neighboring molecules. In addition, electron withdrawing substituents tend to suppress the formation of intermolecular contacts as can be seen by comparing dimethylditellurane Te₂Me₂ and bis(trifluoromethyl)ditellurane Te₂(CF₃)₂. Te₂Me₂ forms a chain-like structure in the solid state,[1] whereas the intermolecular distances as observed for Te₂(CF₃)₂ clearly exceed the sum of the *van-der-Waals* radii of the metal atoms.[2] Comparable intermolecular interactions were reported for homonuclear tetraalkyldistibines and -dibismuthines of the type E₂R₄ (E = Sb, Bi) such as Sb₂Me₄ and Bi₂Me₄,[3] which were originally synthesized by reaction of an Sb/Bi-mirror with methyl radicals.[4] Several distibines and dibismuthines were structurally characterized since then,[5] and they often showed weak intermolecular E...E interactions, leading to chain-like structures in the solid state with E...E bond lengths below the sum of the *van-der-Waals* radii (4.12 Å).[6] The intermolecular metal-metal interactions in the solid state are typically weak and are often interrupted upon melting, resulting in a bathochromic shift between fluid and solid phases, the so-called "*thermochromic*" behavior.[3a]

Heteronuclear group 15-16 compounds are also well known. As a result of the weak Sb-Sb bond,[7] elemental chalcogens easily react with distibines with insertion into the Sb-Sb bond and

subsequent formation of the corresponding bis(dialkylstibanyl)chalcogenanes (R₂Sb)₂E (E = S, Se, Te).[8] Comparable bis(dialkylbismuthanyl)chalcogenanes (R₂Bi)₂E (E = S, Se, Te) were obtained from analogous reactions of dibismuthines[9] and by salt elimination reaction.[10] Very recently, we reported on the solid state structures of three bis(dialkylstibanyl)chalcogenanes (Et₂Sb)₂S, (Et₂Sb)₂Te, and (Me₂Sb)₂Te as well as three bis(dialkylbismuthanyl)chalcogenanes (Et₂Bi)₂S, (Et₂Bi)₂Te, and (Et₂Bi)₂Te,[11] which showed different intermolecular interactions. The organic substituents were found to play a crucial role on the resulting packing mode in the solid state.

Distibines and dibismuthines are also known to react with dichalcogenanes E'₂R₂ (E' = S, Se, Te).[8b,9a,12] Compounds of the general type R₂SbER' (E = S, Se, Te; R = Me, Et, R' = Me, Ph) were prepared by reaction of distibines Sb₂R₄ and dichalcogenanes E'₂R'₂ at ambient temperature (Sb₂Me₄) and -40 °C (Sb₂Et₄), respectively,[13] by salt elimination reactions[14] and were reported as intermediates in reactions of BiR₃ with Te.[15] R₂SbTeMe (R = Me, Et), which decompose upon heating with formation of the corresponding trialkylstibine SbR₃ and RSb(ER')₂,[13] were reported to be thermochromic. Me₂SbTeMe is a red liquid at room temperature that solidifies at -52 °C with formation of a red solid, which turns yellow-orange at -80 °C. A similar color change was observed when the compound was dissolved in CDCl₃. Et₂SbTeMe is an orange liquid at room temperature which solidified at -80 °C to give a green-yellow solid. Freezing a solution of this substance in CDCl₃ produced a similar change in color.

Even though these types of complexes are well known for years, only limited structural information is available. A few antimony and bismuth alkoxides and sulfides have been structurally characterized by single crystal X-ray diffraction, and they typically show strong intermolecular interactions in the solid state. To the best of our knowledge, Ph₂BiSePh represents the only structurally characterized compound containing a heavier chalcogen atom.[12e] Surprisingly, no intermolecular contacts were discussed for Ph₂BiSePh, even though the closest intermolecular Bi...Se distances (3.897 Å) are below the sum of the *van-der-Waals* radii (3.97 Å). In addition, reactions of donor-stabilized low-valent organoantimony and -bismuth compounds MR (M = Sb, Bi), in which the metal centers adopt the formal oxidation state +I, with diaryldichalcogenanes E'₂Ar₂ (E' = S, Se, Te) were reported to yield compounds of the general types RM(E'Ar)₂ and R₂ME'Ar.[16] These compounds either adopt monomeric structures in the solid state or form weakly bonded dimers due to the presence of weak intermolecular interactions. Our long-term interest in the structure and reactivity of (low-valent) organometallic complexes containing the heavier group 15 elements, Sb and Bi,[6a,6b,11,17] as well as in the development of novel low-temperature precursors for the solution based [18] and gas phase based synthesis (MOCVD

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process,[19] ALD process[20]) of group 15/16 nanomaterials prompted our interest to dialkylstibanyl- and dialkylbismanylchalcogenanes of the general type R_2MTeR' ($M = Sb, Bi$) containing sterically less demanding alkyl substituents. Herein, we report on the single-crystal X-ray structures of $Et_2SbTeEt$ (**1**) and $Et_2BiTeEt$ (**2**) as well as of $t\text{-Bu}_3Sb$ (**3**). In addition, DFT calculations of **1** and **2** were performed in order to investigate the intramolecular $M\cdots Te$ and intermolecular $M\cdots Te$ bonding in these compounds.

Results and Discussion

$Et_2SbTeEt$ **1** and $Et_2BiTeEt$ **2** were synthesized by reaction of M_2Et_4 ($M = Sb, Bi$) and Et_2Te_2 [13a,b] whereas $t\text{-Bu}_3Sb$ (**3**) was prepared according to a literature method[13c] by a standard salt elimination reaction between $SbCl_3$ and $t\text{-BuLi}$ at -100°C .

Scheme 1. Synthesis of **1**, **2**, and **3**.

Single crystals of **1** - **3** were grown directly on the diffractometer using an IR-laser-assisted technique in a closed quartz glass capillary under an inert argon atmosphere. The IR-laser allowed a very controlled and focused heating of the sample, which is frozen in a nitrogen steam, hence resulting in optimized growth conditions, in which the sample re-crystallizes without decomposition.[21] Figures 1 and 2 show the crystal structures of **1** and **2**, while that of **3** is given in the SI.

Figure 1. Solid state structure of **1** (a) and **2** (b), thermal ellipsoids are shown at 50% probability levels.

1 and **2** crystallize in the monoclinic space group $P2_1/c$ as dark red crystals, whereas **3** crystallizes in $P2_1/n$ and forms colorless crystals. Table 1 summarizes the central structural parameters

of **1** - **3**. The average Sb-C (2.177(2) Å **1**, 2.228(2) Å **3**) and Bi-C (2.263(15) Å **2**) as well as the Te-C (2.163(3) Å **1**; 2.168(7) Å **2**) bond lengths are comparable to those available from the CSD for ER_3 ($E = Sb$ 2.154/2.183 Å; Bi 2.31(3) Å[22]) and $Te(CX_3)_2$ compounds ($X = H$ or C ; av. value 2.158 Å).[23] **3** was prepared in order to compare the structural parameters such as the Sb-C bond lengths and the bond angular sum at the Sb atom of **1** with those of pure trialkylstibines, for which structural data are almost unknown. Unfortunately, any attempt to grow single crystals of Et_3Sb failed. We recently reported on the solid state structures of $BiMe_3$ and $Bi(i\text{-Pr})_3$, whose average Bi-C bond length (2.259(17) Å; 2.287(9) Å) as well as bond angular sums ($276.6(24)^\circ$, $290.6(9)^\circ$) are comparable to those observed for **2**. [24]

Figure 2. Conformation of **1** (a) and **2** (b). View along the E-Te bond (thermal ellipsoids are shown at 50% probability levels).

The Sb-Te bond length in **1** (2.7834(4) Å) is shorter than the Bi-Te bond length in **2** (2.9116(5) Å) as was expected. These values are only slightly elongated compared to the sum of the covalent radii as reported by Pyykkö *et al.* (Sb-Te 2.76 Å, Bi-Te 2.87 Å).[25] The Sb-Te bond length of **1** is comparable to those reported for bis(dialkylstibanyl)telluranes ($R_2Sb)_2Te$ ($R = Me$ 2.791(1); 2.763(1) Å; Et 2.783(1), 2.770(1) Å)[11a] and the telluradistibirane Bbt_2Sb_2Te ($Bbt = 2,6\text{-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl}$; Sb-Te 2.7607(7), 2.7719(6) Å).[26] The Bi-Te bond length in **2** is slightly elongated compared to the Bi-Te bond distances as reported for $\{[(Me_3Si)_2CH]_2Bi\}_2Te$ (2.872(3) Å, 2.889(2) Å).[10] $\{[(Me_3Si)_3SiTe]_2BiR\}$ ($R = CH(SiMe_3)_2$: 2.8378(8), 2.8617(8) Å; $C(SiMe_3)_3$: 2.8638(11), 2.8826(14) Å).[27] as well as $R_2Bi(TePh)_2$ ($R = o\text{-C}_6\text{H}_4(CH=NC_6H_3(i\text{-Pr})_2-2,6)$) 2.9084(4) Å and $RBi(TePh)_2$ (2.8949(3), 2.9545(3) Å).[16a] In contrast, the Bi-Te bond length of **2** is slightly shorter than those found in $(Et_2Bi)_2Te$ (2.9778(4) Å)[11b] and as the shortest Bi-Te distance observed in the crystal of Bi_2Te_3 (3.066(2) Å).[28]

The sum of the bond angles at the Sb atom of **1** ($286.0(3)^\circ$) is slightly bigger compared to that at the Bi atom in **2** ($282.3(8)^\circ$), which points to a slightly higher p-character of the bonding electron pairs in **2** compared to **1**. In contrast, the sum of the bond angles at the Sb atom of **3** is slightly smaller ($280.4(3)^\circ$), reflecting the increased steric demand of the bulky *tert*-butyl substituents. Concerning the conformation of the molecules the most noticeable difference are the torsion angles about the E-Te bond. The orientation of the ethyl groups in **1** is T-shaped,

whereas it is Y-shaped in **2** (figure 2, table 1). Furthermore the SbEt₂ group of **1** is arranged in a *transoid* W-shaped manner (C-Sb-C-C 176.8(3)°, 150.6(3)°), whereas the BiEt₂ group in **2** shows a *cisoid* conformation (C-Bi-C-C 165.5(7)°, 45.0(9)°). Whether the different conformations of **1** and **2** are a result of or the reason for the different packing mode of the molecules (see below) could not be settled by crystallographic analysis of the packing.

Table 1. Central bond lengths (Å) and bond angles (°) of **1** - **3**.

	Et ₂ SbTeEt 1	Et ₂ BiTeEt 2	<i>t</i> -Bu ₃ Sb 3
M-Te	2.7834(4)	2.9116(5)	
M...Te	3.5599(4)	3.6217(6)	
Te-C	2.163(3)	2.168(7)	
M-C	2.176(3)	2.244(8)	2.228(3)
	2.178(3)	2.282(9)	2.229(3)
			2.229(3)
C-M-C	92.93(12)	96.6(4)	103.49(10)
			103.75(10)
			103.15(11)
M-Te-C	94.94(11)	92.9(2)	
Σ∠C-M-C/Te	286.0(3)	282.3(8)	280.4(3)
M-Te...M	160.50(1)	110.04(2)	
Te-M...Te	160.50(1)	173.19(1)	
C-M-Te-C	106.82(13)	129.2(4)	
	159.65(12)	134.0(3)	

Density Functional Theory Calculations on gas phase molecules. Gas phase structures **1a** and **2a** of the monomers were determined in dispersion-corrected density functional theory calculations (DFT+D3) employing the B-P86 functional [29] and a third generation dispersion [30] correction in conjunction with a quadruple-zeta basis set,[31] relativistic effective core potentials for the metal atoms,[32] and the resolution of the identity approximation,[33] as implemented in the TURBOMOLE program package.[34] Table 2 summarizes the most relevant structure parameters from the geometry optimizations using monomers from the crystal structure as starting points. The calculated Sb-Te bond length of **1a** is 2.796 Å, i.e. 0.013 Å longer than the value observed in the solid state crystal structure, whereas the calculated Bi-Te bond length of **2a** (2.890 Å) is 0.022 Å shorter than the value found in the crystal structure. The calculated average Sb-C and Bi-C as well as the Te-C bond lengths are all about 0.03-0.04 Å longer than the values observed in the solid state structures. The sum of the

bond angles at the Sb center (287.1°) agrees within 0.2° with the crystal structure, while the corresponding calculated sum of bond angles at the Bi center is 286.0°, deviating by nearly 4° from the crystal structure (*vide infra*).

Table 2. Central bond lengths (Å) and bond angles (°) of the geometry optimized structures **1a**, **2a**, and **4** - **7**.

	1a	2a	4	5	6	7
M-Te	2.796	2.890	2.811 ^a	2.909 ^a	2.805 ^a	2.904 ^a
			2.827 ^b	2.943 ^b	2.840 ^b	2.931 ^b
M...Te			3.566	3.679	3.691	3.580
Te-C	2.196	2.197	2.193 ^a	2.195 ^a	2.196 ^a	2.195 ^a
			2.197 ^b	2.199 ^b	2.197 ^b	2.198 ^b
M-C	2.205	2.309		2.311 ^a	2.205 ^a	2.304 ^a
	2.204	2.305	2.204 ^a			
			2.204 ^a	2.304 ^a	2.203 ^a	2.304 ^a
			2.202 ^b	2.314 ^b	2.213 ^b	2.303 ^b
			2.201 ^b	2.319 ^b	2.211 ^b	2.301 ^b
C-M-C	94.26	95.11	94.19 ^a	93.75 ^a	93.95 ^a	93.07 ^a
			94.41 ^b	96.07 ^b	99.29 ^b	93.25 ^b
M-Te-C	92.97	92.60	94.60 ^a	96.36 ^a	91.73 ^a	95.07 ^a
			91.64 ^b	91.23 ^b	92.00 ^b	91.73 ^b
Σ∠C-M-C/Te	287.05	285.95	284.68 ^a	283.35 ^a	290.35 ^a	280.63 ^a
			286.09 ^b	281.98 ^b	287.36 ^b	281.83 ^b
M-Te...M	---	---	130.48	81.69	103.92	128.39
Te-M...Te	---	---	172.35	175.00	170.89	173.33
C-M-Te-C	115.59	150.15	110.16 ^a	139.54 ^a	129.93 ^a	106.89 ^a
	149.38	114.18	155.15 ^a	126.31 ^a	134.94 ^a	159.82 ^a
			115.50 ^b	149.41 ^b	147.17 ^b	113.59 ^b
			149.46 ^b	114.35 ^b	113.23 ^b	152.82 ^b

[a] For monomer A in figures S5-S8 of the supplementary material. [b] For monomer B in figures S5-S8 of the SM.

In order to investigate the conformational flexibility of the monomers of **1** and **2** we generated further starting structures through replacing Bi in **2** with Sb, resulting in an optimized structure **1b** which is 0.8 kJ/mol higher in energy than **1a** (a harmonic zero point energy correction increases this to 0.9 kJ/mol). On the other hand replacing the Sb atom in **1** with Bi

and optimizing leads to conformer **2b** which is 0.6 kJ/mol lower in energy than **2a** (zero point energy correction reduces the difference to 0.5 kJ/mol). This energy difference is sufficiently small to be overcome by crystal packing effects.

Vibrational spectroscopy. The IR spectra of R_2SbER' ($R, R' = Me, Et; E = S, Se$) exhibited strong bands at 340 or 345 cm^{-1} for the Sb-S stretching vibration and a medium or strong band at 220 or 238 cm^{-1} for the Sb-Se stretching vibration, whereas no IR band was assigned to the Sb-Te bond.[13] We also could not assign any band in the Raman spectra of **1** and **2** to a Sb-Te and Bi-Te stretching vibration. However, the line at 480 cm^{-1} observed in the experimental Raman spectrum of **2** can be assigned to a Te-C stretch vibration according to the calculated Raman spectrum of **2a** which yields it at 474 cm^{-1} . The calculated wavenumbers of the Bi-C stretch vibrations were 424 and 439 cm^{-1} , respectively, also in good agreement with the experimental line at 427 cm^{-1} . Though we did not calculate Raman intensities, it should be noted that this assignment is simplified by the fact that there are no further lines in the range 270 – 650 cm^{-1} . Similarly the band at 480 cm^{-1} of the experimental Raman spectrum of **1** can be assigned to derive from a superposition of the Te-C stretch vibration (calculated at 475 cm^{-1} for **1a**) and the Sb-C stretch vibrations (calculated at 464 and 481 cm^{-1} , respectively). Note also that close inspection of the experimental band indeed reveals a shoulder at low wave numbers. In contrast, the bands at 253 cm^{-1} in **1** and at 238 cm^{-1} in **2** cannot be uniquely assigned from our calculations: For both in the range of 210 – 270 cm^{-1} we find 6 lines corresponding to ethyl-group torsion and metal-C-C bend vibrations. The Bi-Te stretch vibration in **2a** was calculated at 146 cm^{-1} and the Sb-Te stretch vibration of **1a** at 173 cm^{-1} , respectively, and thus unfortunately out of our experimental operation window (exp. Raman spectra and calculated vibration bands are given in the SI).

Figure 3. Chains in the packing of **1** (a: formed by translation parallel to a , linear) and **2** (b: formed by 2_1 -axis parallel to b , zig-zag). H atoms omitted for clarity, #1: $1+x, y, z$; #2: $2-x, \frac{1}{2}+y, \frac{1}{2}-z$.

Packing analysis. **1** and **2** both form chains via intermolecular $E \cdots Te$ interactions (see figure 3). Displaying contact distances well below the sum of the van der Waals radii (**1** 3.5599(4) Å; **2** 3.6217(6) Å) they are to be considered attractive from a crystallographic point of view. The adjacent molecules of these chains are generated by translational symmetry parallel to a (**1**) and a two-fold screw axis parallel to b (**2**), respectively. The different symmetry of the chains leads to a different orientations of the EEt_2 ($E = Sb, Bi$) groups. Owing to the screw axis in **2** the groups need to alternate, while in **1** they are “*syn-tactic*”. This necessarily influences the shape of the cross-section of the chains and their arrangement in the packing (figure 4). However, since the volumes of the elemental cells of **1** and **2** are approximately equal, the difference in the packing density seems to be negligible. Despite the obvious differences in the packing of **1** and **2**, based on the crystallographic it is not possible data to elucidate why which structure is preferred.

Figure 4. Cross-section of the chains in **1** (a) and **2** (b, two molecules of one chain are high-lighted in different bond colours to show the alternating orientation of the $BiEt_2$ group).

Density Functional Theory Calculations on solid state packing. The structural differences as observed in the crystals structures of **1** and **2** (linear vs. zig-zag chain orientation) prompted us to carry out DFT+D3 calculations for dimeric systems employing the same functionals, basis sets, etc. as stated above. For this purpose, first two neighboring molecules of the linear chain of the crystal of **1** were selected and used as a starting structure for geometry optimization, resulting in dimer **4**. An analogous procedure for two neighboring molecules of the zig-zag chain of the crystal of **2** results in dimer **5**. Replacing the Bi atoms in **5** with Sb atoms followed by geometry optimizing gives the dimer **6**, while the reverse dodge in **4** leads to the dimer **7**. Based on the energies of **4** - **7** the stabilization energies of dimerization were calculated as the difference between the energy of the optimized dimer and two times the energy of the lowest optimized monomer **1a** and **2b**, respectively. For **4** the resulting stabilization energy is -45.0 kJ/mol and that for **5** is -52.6 kJ/mol. The “linear” dimer **4** is 2.2 kJ/mol more stable than the corresponding “zig-zag” dimer **6** (-42.8 kJ/mol), indicating a slight intrinsic preference of the linear chain motif in the crystal structure of $Et_2Sb-TeEt$. On the other hand, for $Et_2Bi-TeEt$ an intrinsic preference of the zig-zag chain motif is suggested by the finding that the “linear” dimer **7** (-45.6 kJ/mol) is 7 kJ/mol less stable than the “zig-zag” dimer **5**. One might assume that

the preference of linear chains in **1** and of zig-zag chains in **2** is related to different orbital interactions between the metal centers of neighboring molecules. Yet, for both species $\text{Et}_2\text{Sb-TeEt}$ and $\text{Et}_2\text{Bi-TeEt}$ the highest occupied molecular orbital (HOMO) is essentially a pure 5p orbital of energy -474.7 and -464.9 kJ/mol, respectively, while the lowest unoccupied molecular orbital (LUMO) in both cases is essentially an antibonding linear combination of a 5p orbital of Te with a 5p orbital of Sb or a 6p orbital of Bi (figures 5 and 6), with similar energies of -193.6 and -196.5 kJ/mol, respectively.

Figure 5. HOMO (a) and LUMO (b) of Et_2SbTeEt .

Figure 6. HOMO (a) and LUMO (b) of Et_2BiTeEt .

Furthermore, differences in the partial charges as obtained from a natural population analysis (NPA) are hardly significant,[35] with the charge on the Te atom being close to zero and differing by less than 0.03 e between both compounds and virtually identical charges on Sb and Bi (Table 3). Thus the aforementioned structural differences of the dimeric systems cannot be ascribed to different HOMO-LUMO interactions between neighboring molecules or electrostatic interactions, but rather point to interplay of several factors, where not only metal-metal interactions but also interactions involving the ethyl-substituents play a role. This assumption is supported by the flexibility of the sum of the bond angles of the group 15 atoms (cf. Table 2): while in the monomer **1a** this was 287.1° , in the dimer **4** it now amounts to 286.1° for the Sb atom, which is involved in the intermolecular $\text{Sb}\cdots\text{Te}$ contact, and to 284.7° for the other Sb atom. The corresponding changes for Et_2BiTeEt are more significant, since the sum of the bond angles around the Bi atom in **2a** is 286.0° , whereas in **5** we obtain 282.0° for the Bi atom

which is not involved in the intermolecular contact and 283.4° for the other one. One should note that the values for Sb and Bi involved in the intermolecular metal-metal contacts thus agree very well with the crystal structure values of 286.9° for **1** and 282.3° for **2**.

Table 3. Calculated NPA charges of **1** and **2**.

	1a	2a
M	0.718	0.719
Te	-0.027	0.025

Conclusions

Single crystals of Et_2SbTeEt (**1**), Et_2BiTeEt (**2**) and $t\text{-Bu}_3\text{Sb}$ (**3**) were grown by a laser-assisted technique directly on the diffractometer. **1** and **2** show different intermolecular interactions, resulting in the formation of almost linear chains (**1**) or zig-zag chains (**2**). According to computational calculations, the small dimeric molecules $(\text{Et}_2\text{SbTeEt})_2$ and $(\text{Et}_2\text{BiTeEt})_2$ also prefer linear and zig-zag arrangements in the gas phase, respectively.

Experimental Section

General procedure for the synthesis of **1** and **2**.

1 and **2** were synthesized under an Ar atmosphere according to a literature procedure by reaction of Te_2Et_2 (1.74 g, 5.56 mmol) with Sb_2Et_4 (2.00 g, 5.56 mmol) and Bi_2Et_4 (2.97 g, 5.56 mmol), respectively. The analytical data correspond to those reported by Dickson et al.[13b] $t\text{-Bu}_3\text{Sb}$ (**3**) was prepared according to a literature method[13c] by a standard salt elimination reaction between SbCl_3 and $t\text{-BuLi}$ at -100°C . Raman spectra were recorded on a Witec Alpha 300 R microscope with a CCD camera (DU401) from Andor Newton. The exciting wavelength was 785nm with an optical grid of 600 lines/mm. A Bruker DMX 300 was used for NMR spectroscopy. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were referenced to THF-d_8 (^1H : $\delta = 3.580$; ^{13}C : $\delta = 25.31$) and C_6D_6 (^1H : $\delta = 7.159$; ^{13}C : $\delta = 128.06$).

1: Yield: 3.56 g (95%), $^1\text{H-NMR}$ (300 MHz, C_6D_6 , 25°C): δ 1.30 (t, $^3J_{\text{HH}} = 7.72$ Hz, 6 H, SbCH_2CH_3), 1.41 – 1.55 (m, 2 H, SbCH_2CH_3), 1.54 (t, $^3J_{\text{HH}} = 7.52$ Hz, 3 H, TeCH_2CH_3), 1.60 – 1.74 (m, 2 H, SbCH_2CH_3), 2.56 (q, $^3J_{\text{HH}} = 7.60$ Hz, 2 H, TeCH_2CH_3). $^{13}\text{C-NMR}$ (75 MHz, C_6D_6 , 25°C): δ -10.97 (TeCH_2CH_3), 5.26 (SbCH_2CH_3), 13.50 (SbCH_2CH_3), 20.97 (TeCH_2CH_3). Raman (ν , cm^{-1} , 200 – 1900 cm^{-1}): 253 (s), 480 (s), 666 (w), 944 (w), 1010 (w), 1175 (s), 1360 (w), 1408 (w), 1441 (w).

2: Yield: 4.43 g (94%), $^1\text{H-NMR}$ (300 MHz, THF-d_8 , 25°C): δ 1.62 (t, $^3J_{\text{HH}} = 7.61$ Hz, 3 H, TeCH_2CH_3), 2.30 (s (br), 10 H, BiEt_2), 2.96 (q, $^3J_{\text{HH}} = 7.60$ Hz, 2 H, TeCH_2CH_3). $^{13}\text{C-NMR}$ (75 MHz, THF-d_8 , 0°C): δ -15.10 (TeCH_2CH_3), 13.70 (BiCH_2CH_3), 15.54 ($\text{Bi-CH}_2\text{CH}_3$), 23.21 (TeCH_2CH_3). Raman (ν , cm^{-1} , 200 – 1900 cm^{-1}): 238 (s), 427 (s), 480 (s), 646 (w), 943 (w), 1003 (w), 1138 (s), 1174 (m), 1357 (w), 1409 (w), 1438 (w).

3: Yield: 26.50 g (82%), ¹H-NMR (300 MHz, C₆D₆, 25 °C): δ 1.32 (s, 27 H, CH₃). ¹³C-NMR (75 MHz, C₆D₆, 25 °C): δ 31.39 (SbC(CH₃)₃), 32.73 (SbC(CH₃)₃).

Single crystal X-ray analyses. Crystallographic data of **1** - **3**, which were collected on a Bruker AXS SMART diffractometer (MoK α radiation, λ = 0.71073 Å) at 100(1) K (**1**, **2**) and 188(1) K (**3**) are summarized in Table S1 (SI). The solid-state structures of **1** and **2** are shown in Figures 1 and 2, that of **3** in the SI. The structures were solved by Direct Methods (SHELXS-97) and refined anisotropically by full-matrix least-squares on F² (SHELXL-97/SHELXL-2013).^[36,37] Absorption corrections were performed semi-empirically from equivalent reflections on basis of multi-scans (Bruker AXS APEX2). Hydrogen atoms were refined using a riding model or rigid methyl groups. **3** was refined as non-merohedral twin using HKLF5 data. Single crystals of **1** - **3** were formed by an *in-situ* zone melting process inside a quartz capillary using an IR-laser.^[20] The experimental setup does only allow for ω scans with χ set to 0°. Any other orientation would have partially removed the capillary from the cooling stream and thus led to a melting of the crystals. This limits the completeness of the data to 65% to 90% depending on the crystal system. The crystallographic data of **1** - **3** (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-991433 (**1**), CCDC-991434 (**2**) and CCDC-991432 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB21EZ (fax: (+44) 1223/336033; e-mail: deposit@ccdc.cam.ac.uk).

Supporting Information. A CIF file giving X-ray crystallographic data of **1** - **3**. In addition, the crystallographic details of **1** - **3**, experimental Raman spectra of **1** and **2** and Bi₂Et₄, ¹H and ¹³C NMR data of **1** - **3** as well as computational details (gas phase structures, vibrational bands) of **1** and **2** are given. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Keywords: Antimony • Bismuth • Laser-Assisted Crystallization • Intermolecular Interactions

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Entry for the Table of Contents

FULL PAPER

Single crystals of $\text{Et}_2\text{M}-\text{TeEt}$ ($\text{M} = \text{Sb}$ **1**, Bi **2**) as well as $t\text{-Bu}_3\text{Sb}$ (**3**) were grown using an IR-laser-assisted technique. **1** and **2** form short intermolecular $\text{E}\cdots\text{Te}$ interactions in the solid state, which were further investigated with dispersion-corrected density functional theory

Stefan Heimann, Andreas Kuczkowski,
Dieter Bläser, Christoph Wölper,
Rebekka Haack, Georg Jansen and
Stephan Schulz*

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Syntheses and Solid State Structures
of Et_2SbTeEt and Et_2BiTeEt

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