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Syntheses and Solid State Structures of Bis(dialkylstibanyl)Sulfanes and Telluranes

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Dedicated to Prof. Werner Uhl on the occasion of his 60th birthday

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Distibines Sb_2R_4 ($\text{R} = \text{Me}, \text{Et}$) react with elemental chalcogenes ($\text{E} = \text{S}, \text{Se}, \text{Te}$) with insertion into the $\text{Sb}-\text{Sb}$ bond and formation of the corresponding bis(dialkylstibanyl)sulfanes, -selenanes and -telluranes $(\text{R}_2\text{Sb})_2\text{E}$. The structures of $(\text{Et}_2\text{Sb})_2\text{S}$ (**1**), $(\text{Et}_2\text{Sb})_2\text{Te}$ (**3**), and $(\text{Me}_2\text{Sb})_2\text{Te}$ (**4**) were determined by single crystal X-ray diff-

raction. The complexes either adopt a *syn-syn* (**1**, **4**) or *syn-anti* conformation (**3**) in the solid state. In addition, different intermolecular interactions modes were observed, depending on the bridging chalcogen and the organic substituent bound to the Sb atoms.

Introduction

Tetraalkylstibines R_4Sb_2 such as Me_4Sb_2 and Et_4Sb_2 are long known low-valent organoantimony compounds. Me_4Sb_2 for instance was synthesized for the first time almost eighty years ago by reaction of an Sb -mirror with methyl radicals.^[1,2] Since then, alternative synthetic pathways were established and their structures were investigated, in detail.^[3-9] They often show weak intermolecular $\text{Sb}\cdots\text{Sb}$ interactions, leading to endless Sb -chains with $\text{Sb}\cdots\text{Sb}$ bond lengths below the sum of the van-der-Waals radii (4.12 Å).^[10] The weak interactions are interrupted upon melting, leading to bathochromic shift between fluid and solid phases, the so-called "thermochromic" behaviour. For instance, Me_4Sb_2 is yellow in the solid state in liquid nitrogen, red close to its melting point of 17 °C, again yellow in the fluid state but colourless in the gas phase.^[11] The organic substituents typically determine whether the complexes are thermochromic or non-thermochromic.^[12]

Aside from their interesting structural features, distibines are also interesting due to their versatile reactivity. Even though their thermal stability is rather low as a result of the weak $\text{Sb}-\text{Sb}$ bond,^[13] they undergo different kind of reactions. Distibines are weak Lewis bases, which react with Lewis-acidic main group and transition metal complexes with subsequent formation of the corresponding Lewis acid-base adducts.^[14,15] In addition, insertion reactions into the $\text{Sb}-\text{Sb}$ bond with subsequent oxidation of the Sb atoms to the formal oxidation state +3 are known, i.e. reactions with elemental chalcogenes yield the corresponding bis(dialkylstibanyl)oxanes, -sulfanes, -selenanes and -telluranes of the type $\text{R}_2\text{Sb}-\text{E}-\text{SbR}_2$ ($\text{E} = \text{S}, \text{Se}, \text{Te}$), respectively.^[16] Some of as-prepared chalcogen-bridged complexes also show thermochromic behavior.^[17] Unfortunately, the solid state structures of bis(dialkylstibanyl)chalcogenanes containing sterically less demanding organic substituents such as methyl or ethyl groups, which are typically liquid at ambient temperature, are unknown except for $(\text{Me}_2\text{Sb})_2\text{E}$ ($\text{E} = \text{O}, \text{S}$).^[18,19] As a consequence, the question whether weak $\text{Sb}-\text{Sb}$ interactions in the solid state are responsible for their thermochromic behaviour, is still unclear. In

contrast, the gas phase structures of $(\text{Me}_2\text{Sb})_2\text{E}$ ($\text{E} = \text{O}, \text{S}, \text{Se}, \text{Te}$) were investigated by gas phase electron diffraction (GED) and computational calculations,^[20] whereas to the best of our knowledge, structural data of the corresponding ethyl-substituted derivatives $(\text{Et}_2\text{Sb})_2\text{E}$ ($\text{E} = \text{O}, \text{S}, \text{Se}, \text{Te}$) have not yet been reported.

Our long-term interest in the chemistry of low-valent organometallic complexes containing the heavier group 15 elements, Sb and Bi ,^[14,21] including their weak intermolecular interactions,^[9] as well as our increasing interest in novel precursors for solution-based nanoparticles synthesis and gas phase based film deposition prompted our interest on chalcogen-bridged bis(dialkylstibanyl)chalcogenanes.^[22,23] Herein, we report on the single-crystal X-ray structures of $(\text{Et}_2\text{Sb})_2\text{S}$ (**1**), $(\text{Et}_2\text{Sb})_2\text{Te}$ (**3**), and $(\text{Me}_2\text{Sb})_2\text{Te}$ (**4**) and compare them with those of $(\text{Me}_2\text{Sb})_2\text{O}$ and $(\text{Me}_2\text{Sb})_2\text{S}$.

Results and Discussion

$(\text{Et}_2\text{Sb})_2\text{S}$ (**1**), $(\text{Et}_2\text{Sb})_2\text{Se}$ (**2**), $(\text{Et}_2\text{Sb})_2\text{Te}$ (**3**) and $(\text{Me}_2\text{Sb})_2\text{Te}$ (**4**) were prepared in almost quantitative yields according to literature methods by reaction of elemental S , Se and Te , respectively, with the corresponding distibines R_4Sb_2 ($\text{R} = \text{Me}, \text{Et}$). Single-crystals of **1**, **3** and **4** were grown on the diffractometer using an IR-laser-assisted technique in a closed quartz glass capillary under an argon atmosphere,^[24] whereas several attempts to grow single crystals of **2** in solution or directly on the diffractometer failed. The IR-laser allowed a very controlled and focused melting of the sample, which is frozen in a nitrogen steam, hence resulting in optimized growth conditions, in which the sample re-crystallizes without decomposition. Figures 1 - 3 show the crystal structures of **1**, **3** and **4**, which were determined by single-crystal X-ray diffraction.

Table 1. Crystallographic details of **1**, **3** and **4**.

	1	3	4
Empirical formula	$\text{C}_8\text{H}_{20}\text{SSb}_2$	$\text{C}_8\text{H}_{20}\text{Sb}_2\text{Te}$	$\text{C}_4\text{H}_{12}\text{Sb}_2\text{Te}$

Molecular mass	391.80	487.34	431.24
Crystal system	triclinic	monoclinic	monoclinic
Space group	<i>P</i> -1	<i>I</i> 2/a	<i>P</i> 2 ₁ /c
a [Å]	8.9237(6)	12.337(2)	15.0267(4)
b [Å]	10.3432(8)	15.653(3)	10.8396(2)
c [Å]	14.9283(11)	15.240(4)	6.3935(2)
α [°]	85.972(2)	90	90
β [°]	80.666(8)	103.322(2)	96.3912(12)
γ [°]	88.619(7)	90	90
V [Å ³]	1356.16(17)	2863.9(11)	1034.92(5)
Z	4	8	4
T [K]	180(1)	163(1)	173(1)
μ [mm ⁻¹]	4.093	5.728	7.905
D _{calcd.} [g cm ⁻³]	1.919	2.261	2.768
2θ _{max} [°]	50.0	49.4	61.2
Crystal dim. [mm]	0.3 x 0.3 x 0.3	0.3 x 0.3 x 0.3	0.3 x 0.3 x 0.3
No. of reflections	29614	10875	38395
No. of unique reflections	3757	2131	2705
R _{int}	0.1117	0.0290	0.0367
No. param. refined / restraints	119 / 0	100 / 0	65 / 0
R1 ^[a]	0.0924	0.0257	0.0306
wR2 ^[b]	0.2432	0.0662	0.0792
Goodness of fit ^[c]	1.063	1.110	1.195
Max./min.	0.75 / 0.49	0.75 / 0.48	0.75 / 0.62
Transmission			
Final max/min.	3.193 (1.19Å	0.638 / -1.099	1.878 (0.69 Å
Δρ, e Å ⁻³	from Sb(1)) / -1.228		from Te(1)) / -1.315

[a] $R1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ (for $I > 2\sigma(I)$). - [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. - [c] Goodness of fit = $\{\Sigma[w(F_o^2 - F_c^2)^2]/(N_{\text{obs}} - N_{\text{params}})\}^{1/2}$. $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$ with $P = [F_o^2 + 2F_c^2]/3$, a and b are constants chosen by the programme.

Table 2. Central bond lengths [Å] and angles [°] of **1**, **2** and **4**.

	1 ^[a]	3	4
Sb-E	2.429(5); 2.462(7)	2.783(1); 2.770(1)	2.791(1); 2.763(1)
Sb-C	2.14(2); 2.15(2)	2.163(5); 2.165(5)	2.16(2); 2.150(5)
	2.13(2); 2.14(2)	2.161(5); 2.162(5)	2.155(6); 2.156(6)
C-Sb-C	98.8(10); 95.0(10)	95.2(2); 94.2(2)	93.6(2); 94.1(3)
C-Sb-E	93.3(8); 96.4(8)	96.2(2); 95.5(2)	97.3(2); 94.8(2)
		98.1(2)	96.9(2); 96.1(2)
Sb-E-Sb	101.1(2)	96.95(2)	91.88(2)
Sb...E	3.501(6); 3.571(6)	3.718(1)	3.625(1)
E-Sb...E	-	-	4.298(1)
E-Sb-Sb	4.952(3)	3.686(1)	3.673(1)

[a] Structural parameter are given only for one independent molecule.

1 crystallizes with two independent molecules in the asymmetric unit in the triclinic space group *P*-1, **3** in the monoclinic space group *I*2/a and **4** in the monoclinic space group *P*2₁/c. The central structural parameters of **1**, **3** and **4** are summarized in Table 2. The average Sb-C bond lengths and C-Sb-C bond angles of **1**, **3** and **4**

are almost identical to those reported for the distibines Sb₂Me₄ (Sb-C 2.15 Å; C-Sb-C 93.5°)^[11] and Sb₂Et₄ (2.170 Å; 95.8°)^[9] as well as the corresponding bis(dimethylstibanyl)oxane (2.148 Å; 97.1°) and -sulfane (2.148 Å; 95.9°),^[18] respectively.

Figure 1. Solid state structure of **1** (thermal ellipsoids are shown at 50% probability levels, C atom isotropic due to poor data); H atoms are omitted for clarity.

The average Sb-S length observed for **1** (2.446 Å), which agrees very well with the sum of the covalent radii (Sb-S 2.43 Å),^[25] is comparable to those previously reported for antimony(III) thiolate complexes.^[26,27] In addition, the tricationic cluster [Sb₇S₈Br₂]³⁺ shows comparable Sb-S bond lengths (2.44 – 2.58 Å) of the threefold and fourfold-coordinated Sb atoms.^[30a] (Me₂Sb)₂S showed slightly elongated Sb-S bond lengths in the solid state (2.4983(12) Å), whereas those observed in the gas phase were comparable (2.414(4) Å).^[18,20] In addition, the carbonylchromium complexes [Me₂SbSSbMe₂Cr(CO)₄]₂ (2.4239(19), 2.4209(15) Å) and Ph₂SbSSbPh₂Cr(CO)₅ (Sb-S 2.402(1), 2.446(1) Å) also showed comparable values.^[28] The Sb-S-Sb bond angles of **1** (101.1(2)°, 100.4(2)°) are significantly enlarged compared to that observed in the single crystal X-ray structure of (Me₂Sb)₂S (92.35(5)°),^[18] pointing to different intermolecular interactions in the solid state structures of **1** and (Me₂Sb)₂S. In contrast, the bond angles observed for the *syn-syn* conformer of (Me₂Sb)₂S in the gas phase (98.7(5)°) and the calculated distance using density functional theory (101.4°) agreed very well.^[20]

Figure 2. Solid state structure of **3** (thermal ellipsoids are shown at 50% probability levels); H atoms are omitted for clarity.

The average Sb-Te lengths observed for **3** (2.777 Å) and **4** (2.777 Å) agree almost perfectly with the sum of the covalent radii

(Sb-Te 2.76 Å).^[25] In addition, the telluradistibirane Bbt₂Sb₂Te (Bbt = 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl; Sb-Te 2.7607(7), 2.7719(6) Å),^[29] to date the only structurally characterized metal organic complex containing a direct Sb-Te bond. Moreover, comparable Sb-Te bond lengths were reported for Zintl-ions such as [SbTe₃]³⁻ (2.7831(7) Å), [SbTe₄]³⁻ (2.691(3) – 2.834(3) Å), [Sb₂Te₅]⁴⁺ (2.695(7) – 2.816(7) Å), [Sb₄Te₄]⁴⁺ (2.722(4)–2.761(4) Å), [Sb₆Te₉]⁴⁺ (2.702(5) – 2.984(5) Å), [Sb₉Te₆]³⁻ (2.664(5) - 2.994(5) Å), [Sb₇Te₈]⁵⁺ (2.80(1) - 2.91(1) Å), [Sb₂Te₂Br]⁻ (2.865(1) – 2.896(1) Å) as well as the one-dimensional polymeric [Sb₂Te₂]⁺ chain (2.801(2) – 3.057(2) Å).^[30] The Sb-Te-Sb bond angles (**3** 96.95(2)°, **4** 91.88(2)°) are significantly smaller than the Sb-S-Sb bond angle observed for **1** as was expected due to the increasing p-character of the bonding electron pairs, hence leading to an increasing s-character of the electron lone pairs with increasing atomic number of the bridging chalcogenide. However, the large difference between **3** and **4** was rather unexpected and also indicates different intermolecular interaction in **3** and **4**.

Figure 3. Solid state structure of **4** (thermal ellipsoids are shown at 50% probability levels); H atoms are omitted for clarity.

Probably the most noticeable difference in the solid state structures of **1**, **3** and **4** are their different conformations. **1** and **4** adopt *syn-syn* orientations in the solid state (Sb-S-Sb-C: 147.9(7), 139.6(7) and 156.7(8), 158.1(8) (**1**), 166.8(1), 140.9(2) (**4**)), whereas **3** crystallizes as *syn-anti* conformer (Sb-S-Sb-C: 131.3(1), 42.1(2)). Comparable findings were observed in the solid state structures of bis(dimethylstibanyl)oxane (Me₂Sb)₂O (*syn-anti* conformer) and -sulfane (Me₂Sb)₂S (*syn-syn* conformer).^[18] Moreover, GED studies by Haaland et al. showed that bis(dimethylstibanyl)oxane and -sulfane (Me₂Sb)₂E exist as *syn-syn* and *syn-anti* conformers in the gas phase (*syn-anti* concentrations: E = O 51(7)%; E = S 48(4)%), whereas the presence of *syn-anti* conformers for the heavier homologues (E = Se, Te) was uncertain.^[20] DFT calculations revealed that the *syn-syn* conformers are about 4 kJ/mol (E = O, S, Se) less in energy than the *syn-anti* conformers, whereas the energy difference for the (Me₂Sb)₂Te conformers is roughly 1 kJ/mol.^[20] These energies are low enough to be (over-) compensated by the energy gain in case of a more close packing (or intermolecular interactions) of the energetically less favored conformer. Detailed computational calculations concerning the energy differences between the *syn-syn* and *syn-anti* conformers of bis(dialkylstibanyl)chalcogenanes (R₂Sb)₂E (E = S, Se, Te; R = Me, Et) are currently performed. Moreover, the gas phase structures of bis(diethylstibanyl)chalcogenanes (Et₂Sb)₂E (E = S, Se, Te) will be studied by GED.

Table 3. Comparison of the central bond lengths [Å] and angles [°] of **4** (*syn-syn* conformation) as obtained in the gas phase and solid state as well as by computational calculation.

	DFT ^{[20b][a]}	GED ^[20b]	XRD ^[b]
Sb-Te	2.843	2.781(3)	2.791(1); 2.763(1)
Sb-C	2.201	2.172(5)	2.16(2); 2.150(5); 2.155(6); 2.156(6)
C-Sb-C	94.3	108(6)	93.6(2); 94.1(3)
C-Sb-Te	96.1	93.7(11)	97.3(2); 94.8(2) 96.9(2); 96.1(2)
Sb-Te-Sb	94.8	91(2)	91.9(1)
Sb...Te	-	-	3.625(1); 4.298
Te-Sb...Sb	-	-	3.673

[a] Standard deviations were not presented in the literature. [b] This work.

1, **3**, and **4** show different intermolecular interactions in the solid state. A chain-like structure is observed for **1** through the formation of Sb...S interactions, in which only one SbEt₂ group (Sb1, Sb11) of each independent molecule of **1** is involved. The chain is constituted via translational symmetry parallel to *b* with an alternate arrangement of the independent molecules. The sulfur atoms adopt a trigonal planar (2+1) coordination sphere (S1: 0.347(6) Å above the Sb/Sb/Sb plane, Sb-S-Sb: 121.95(18)°, 132.1(2)°, 101.1(2)°; S11: 0.209(6) Å above the Sb/Sb/Sb plane, Sb-S-Sb: 123.0(2)°, 134.8(2)°, 100.4(2)°). The intermolecular Sb...S distances (3.501(6); 3.571(6) Å) are clearly shorter than the sum of the van-der-Waals radii (3.86 Å).^[10] Comparable intermolecular Sb...S interactions have been reported for antimony(III) thiolates Sb(SR)₃,^[31] whereas those in sterically encumbered thiolate complexes as well as in thione complexes were rather larger.^[32] The shortest intermolecular distance between the chains is that between two SbEt₂ moieties (Sb12-Sb12'(1-x, -y, 1-z) 4.952(3) Å), but that clearly exceeds the sum of the van-der-Waals radii (4.12 Å).

Figure 4. Intermolecular interactions in the solid state structure of **1** (H atoms are omitted for clarity: #1: x, y+1, z).

A comparable structural motif was reported for bis(dimethylstibanyl)oxane (Me₂Sb)₂O, also forming endless zigzag chains along [010] due to intermolecular O...Sb interactions.^[18] In contrast, bis(dimethylstibanyl)sulfane (Me₂Sb)₂S, which adopts a *syn-syn* conformation, shows a completely different coordination mode. The sulphur atoms adopt a (2+2) coordination mode and the antimony atom of every dimethylstibanyl group is linked to two sulphur atoms, rather leading to a three-dimensional network instead of a one-dimensional chain. The authors stated that

the *syn-anti* conformation of the oxane complex helps to reduce repulsive interactions between the methyl groups, which then strengthen the Sb...O interaction within the chain. We herein demonstrate that the *syn-syn* conformation as observed for **1** also allows the formation of strongly bound chain structures. However, the formation of a three-dimensional network as-observed for (Me₂Sb)₂S is most likely hampered by repulsive interactions between the somewhat larger Et substituents in **1**.

Figure 5. Intermolecular interactions in the solid state structure of **3** (H atoms are omitted for clarity).

Figure 6. Intermolecular interactions in the solid state structure of **4** (H atoms are omitted for clarity).

Te1 adopts a 2+1 planar T-shaped coordination mode in **3** (Te1: 0.845(1) Å above the Sb/Sb/Sb plane, Sb-Te-Sb: 148.0(1)°, 81.4(1)°, 97.0(1)°). The fundamental structural motif found in the packing of **3** is a slightly corrugated ladder-like arrangement. The "beams" of the ladder are constituted by Sb...Te (3.718(1) Å) interactions formed via *a*-glide-plane symmetry. The two "beams" are connected via 2-fold axes with Sb...Sb (3.686(1) Å) contacts forming the "spokes". These contacts are considerably shorter than the sum of the van-der-Waals-radii (4.12 Å).^[10] The corrugation of the ladder-like structure can best be described by the angle between the best planes of two neighbouring rings in the ladder. These are 10-membered and comprise two "spokes" and the "beam" in between them. The angle between those planes is 28.3(1)°. The ladders are stacked along the *b*-axis in a brick wall-like arrangement with the ethyl groups separating the metal atoms from each other. Thus, no intermolecular metal-metal contacts below 5 Å are observed.

The structure of **4** is fairly similar to that of **3** in respect to the coordination mode of the Te atoms (2+1, T-shaped: Te1: 0.210(1) Å above the Sb/Sb/Sb plane, Sb-Te-Sb: 170.4(1)°, 92.8(1)°, 91.9(1)°) and the packing. **4** also forms ladder-like chains, which are topologically identical to those of **3**, however they are not corrugated. The intermolecular Sb...Sb distance (3.673(1) Å) is almost identical to that of **3**, whereas the intermolecular Sb...Te distance (3.625(1) Å) is significantly shortened (≈ 10 pm). Due to the symmetry equivalence (by translation) of the neighbouring 10-membered rings, the angle between their best planes is 0°, i.e. the ladder is perfectly flat. The ladder-like structure is formed via translational symmetry parallel to *c* ("beams") and inversion ("spokes"), respectively. The packing of the chains, however, differs from that observed for **3**. The somewhat sterically less demanding methyl groups allow closer distances between the metal atoms of the polymer. However, the shortest contact (Sb...Te 4.298(1) Å) is longer than the sum of the van der Waals radii and thus should from a crystallographic point of view not be considered to be attractive.

Figure 7. Packing of the ladder-like structure of **3** (view approx. parallel to *c*; #1: *x*, *-y*+3/2, *z*-1/2; H atoms are omitted for clarity). The shortest distances between two ladders (Sb1...Te1#1: 4.298 Å) are too long to be considered attractive interactions.

The intermolecular interactions in **1**, **3** and **4** might be also discussed in terms of a noncovalent interaction between a covalently-bonded electropositive Sb atom and the lone pair of the Lewis basic chalcogen atom (S, Te).^[33] A positive electrostatic potential, referred to as a σ -hole, is created on the extension of the covalent bonds at the Sb center, resulting from the anisotropy of the atom's charge distribution. The σ -hole is expected to be rather high at Sb due to its low tendency towards *sp*-hybridization and its high polarizability. Murray et al have shown that R₃X molecules containing N, P and as are able to interact noncovalently with nucleophiles according to the σ -hole concept. The strengths of these interactions increase with increasing atomic number of the pnictogen atom and was predicted to be even more pronounced for Sb.^[33a] Computational studies are currently performed in order to clarify (and quantify) if such noncovalent interactions are generally important in compounds **1** – **4** as well as their analogous Bi-complexes.

Figure 8. Packing of the ladder-like structure in **4** (view approx. parallel to *a*; H atoms are omitted for clarity).

Thermochromic distibines Sb_2R_4 typically exhibit short intermolecular $\text{Sb}\cdots\text{Sb}$ distances, which range from 3.6 to 3.7 Å, leading to the formation of endless Sb-chains in the solid state. $(\text{Me}_2\text{Sb})_2\text{Se}$ and $(\text{Me}_2\text{Sb})_2\text{Te}$ **4** were also described as thermochromic compounds. $(\text{Me}_2\text{Sb})_2\text{Se}$ was reported to be an orange liquid in the liquid state, which turns red upon solidification and becomes finally purple at temperatures below -20°C , whereas $(\text{Me}_2\text{Sb})_2\text{Te}$ was described as a purple solid, which melts at 8°C to a red liquid. We carefully investigated the colours of liquid and solid $(\text{Et}_2\text{Sb})_2\text{S}$ **1**, $(\text{Et}_2\text{Sb})_2\text{Se}$ **2** and $(\text{Et}_2\text{Sb})_2\text{Te}$ **3** and could not observe any colour change upon melting or freezing, hence these compounds are non-thermochromic (Table 4). In case of **4**, we observed a slight bathochromic shift upon solidification from dark-orange to light red in liquid nitrogen. This colour change may be attributed to the breaking of either the shorter $\text{Sb}\cdots\text{Te}$ distance (3.625(1) Å) within the chain or the intermolecular $\text{Sb}\cdots\text{Te}$ contacts (4.298(1) Å), even though these contacts are slightly longer than the van der Waals radii. Computational studies are in progress in order to address this problem in more detail.

Conclusions

The solid structures of three bis(dialkylstibanyl)chalcogenanes $(\text{Et}_2\text{Sb})_2\text{S}$ (**1**), $(\text{Et}_2\text{Sb})_2\text{Te}$ (**3**), and $(\text{Me}_2\text{Sb})_2\text{Te}$ (**4**) were determined by single crystal X-ray diffraction. The compounds, which adopt either *syn-syn* or *syn-anti* conformations, show different intermolecular interactions. The organic substituents play a crucial role on the resulting packing mode in the solid state as was shown by comparing **3** and **4**.

Experimental Section

1–4 were synthesized under an Ar atmosphere by reaction of the distibine Sb_2R_4 with an excess of the corresponding elemental chalcogen (S, Se, Te) in *n*-hexane according to literature procedures.^[16a] Solvents were carefully dried over Na/K and degassed prior to use. A Bruker DMX 300 was used

for NMR spectroscopy. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were referenced to internal $\text{C}_6\text{D}_5\text{H}$ (^1H : $\delta = 7.154$; ^{13}C : $\delta = 128.0$).

Table 4. Colors (liquid, solid) and NMR data of **1–4**.

	liquid	solid	^1H NMR ^[a]	^{13}C NMR ^[a]
1	light yellow	light yellow	1.30 (t, 12 H, $^3J_{\text{H-H}} = 7.6$ Hz, CH_3), 1.36–1.49 (m, 4 H, CH_2), 1.50–1.65 (m, 4 H, CH_2)	11.30 (s, CH_2), 15.49 (s, CH_3)
2	yellow	yellow (glass)	1.30 (t, 12 H, $^3J_{\text{H-H}} = 7.7$ Hz, CH_3), 1.42–1.58 (m, 4 H, CH_2), 1.58–1.75 (m, 4 H, CH_2)	12.18 (s, CH_2), 12.87 (s, CH_3)
3	dark orange	dark orange	1.31 (t, 12 H, $^3J_{\text{H-H}} = 7.7$ Hz, CH_3), 1.54–1.65 (m, 4 H, CH_2), 1.72–1.84 (m, 4 H, CH_2)	8.11 (s, CH_2), 13.97 (s, CH_3)
4	dark orange	light red	1.23 (s, 12 H, CH_3)	–2.49 (s, CH_3)

[a] δ (25 $^\circ\text{C}$, C_6D_6 , TMS)

Single crystal X-ray analyses. Crystallographic data of **1**, **3** and **4**, which were collected on a Bruker AXS SMART diffractometer ($\text{MoK}\alpha$ radiation, $\lambda = 0.71073$ Å), are summarized in Table 1. Figures 1–4 show diagrams of the solid-state structures of **1**, **3** and **4**. Data were collected at 180(1) K (**1**), 163(1) K (**3**) and 173(1) K (**4**), respectively. The structures were solved by Direct Methods (SHELXS-97) and refined anisotropically by full-matrix least-squares on F^2 (SHELXL-97) except for the carbon atoms of **1**.^{34,35} Due to the rather poor quality of the crystal the data quality was not sufficient to give a realistic anisotropic description of the respective atoms. Thus quantitative data from the structure model should be interpreted cautiously. 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. In both cases only ω scans with χ set to 0° were performed. Any other orientation would have partially removed the capillary from the cooling stream and thus led to a melting of the crystals.

The crystallographic data of **1**, **3** and **4** (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-933640 (**1**), CCDC-933639 (**3**) and CCDC-933641 (**4**). 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: The crystallographic data of **1**, **3** and **4**.

Acknowledgments

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Entry for the Table of Contents (Please choose one layout)

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Key Topic

Bis(dialkylstibanyl)sulfanes, -selenanes and -telluranes ($R_2Sb)_2E$ were synthesized by reaction of Sb_2R_4 ($R = Me, Et$) with elemental chalcogenes ($E = S, Se, Te$) and structurally characterized by single crystal X-ray diffraction. The roles of the bridging chalcogen atom and the organic substituents on the packing of the molecules and their intermolecular interactions are discussed.

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Syntheses and Solid State Structures of
Bis(dialkylstibanyl)Sulfanes and
Telluranes

Keywords: Antimony / Laser-Assisted
Crystallization / Intermolecular
Interactions

Supporting Information

Syntheses and Solid State Structures of Bis(dialkylstibanyl)Sulfanes and Telluranes

Stefan Heimann, Stephan Schulz, Dieter Bläser, Christoph Wölper*

Table 1. Crystal data and structure refinement for **1**.

Identification code	she_sb2s	
Empirical formula	C ₈ H ₂₀ S Sb ₂	
Formula weight	391.80 Da	
Density (calculated)	1.919 g cm ⁻³	
F(000)	744	
Temperature	180(1) K	
Crystal size	0.3 x 0.3 x 0.3 mm	
Crystal color	colourless	
Crystal description	cylindric	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	<i>P</i> $\bar{1}$	
Unit cell dimensions	<i>a</i> = 8.9237(6) Å	α = 85.972(2)°
	<i>b</i> = 10.3432(8) Å	β = 80.666(8)°
	<i>c</i> = 14.9283(11) Å	γ = 88.619(7)°
Volume	1356.16(17) Å ³	
Z	4	
Cell measurement reflections used	8305	
Cell measurement theta min/max	2.31° to 28.06°	
Diffractometer control software	Bruker AXS APEX 2 Vers.3.0/2009	
Diffractometer measurement device	Siemens SMART three axis goniometer with APEX II area detector system	
Diffractometer measurement method	Data collection strategy APEX 2/COSMO, χ +/- 10°	
Theta range for data collection	1.97° to 24.99°	
Completeness to theta = 24.99°	78.5 %	
	The compound is liquid at RT. The single crystal is formed by an in-situ zone melting process inside a quartz capillary using an IR-laser. The experimental setup does only allow for a omega scan of the single crystal. This limits the completeness to 65% to 95% depending on the crystal system.	
Index ranges	-10<= <i>h</i> <=10, -9<= <i>k</i> <=7, 0<= <i>l</i> <=17	
Computing data reduction	Bruker AXS APEX 2 Vers.3/2009	
Absorption coefficient	4.093 mm ⁻¹	
Absorption correction	Semi-empirical from equivalents	

Empirical absorption correction	Bruker AXS APEX 2 Vers.3/2009
Max. / min. transmission	0.75 / 0.49
R(merg) before/after correction	0.1598 / 0.0687
Computing structure solution	Bruker AXS SHELXTL Vers. 2008/4/(c) 2008
Computing structure refinement	Bruker AXS SHELXTL Vers. 2008/4/(c) 2008
Refinement method	Full-matrix least-squares on F^2
Reflections collected	29614
Independent reflections	3757 [$R(\text{int}) = 0.1117$]
Data / restraints / parameters	3129 / 0 / 119
Goodness-of-fit on F^2	1.063
Weighting details	$w = 1/[\sigma^2(\text{Fo}^2) + (0.1207 \cdot P)^2 + 54.7824 \cdot P]$ where $P = (\text{Fo}^2 + 2\text{Fc}^2)/3$
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0924$, $wR2 = 0.2341$
R indices (all data)	$R1 = 0.1063$, $wR2 = 0.2432$
Largest diff. peak and hole	3.193 and $-1.228 \text{ e}\text{\AA}^{-3}$
Treatment of hydrogen atoms	Riding model on idealized geometries with the 1.2 fold isotropic displacement parameters of the equivalent U_{ij} of the corresponding carbon atom. The methyl groups are idealized with tetrahedral angles in a combined rotating and rigid group refinement with the 1.5 fold isotropic displacement parameters of the equivalent U_{ij} of the corresponding carbon atom.
Comment	The crystallization was performed on the diffractometer at a temperature of 198 K with a miniature zone melting procedure using focused infrared-laser-radiation according to: R. Boese, M.Nussbaumer, "In Situ crystallisation Techniques", in: "Organic Crystal Chemistry", Ed. D.W. Jones, Oxford University Press, Oxford, England, (1994) 20-37 The crystal was non-merohedrally twinned. Data reduction with two independent crystals after matrix determination with cell_now

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **1**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U(\text{eq})$
Sb(1)	684(1)	3444(2)	2385(1)	40(1)
Sb(2)	4397(1)	5220(2)	1775(1)	42(1)
S(1)	1679(6)	5649(6)	2010(4)	52(2)
C(1)	-1300(30)	3860(30)	1778(16)	58(6)
C(2)	-1190(30)	3470(30)	837(18)	72(7)
C(3)	-270(30)	3730(30)	3779(17)	63(7)
C(4)	-1440(40)	4780(40)	3920(20)	90(9)
C(5)	4890(30)	6500(30)	2741(15)	55(6)
C(6)	4360(30)	6010(30)	3723(18)	71(7)
C(7)	4980(30)	6560(30)	622(16)	56(6)
C(8)	6610(30)	6840(30)	332(17)	64(6)
Sb(11)	9475(1)	-1542(2)	2659(1)	41(1)
Sb(12)	5785(1)	239(2)	3329(1)	44(1)
S(11)	8488(5)	659(6)	2963(4)	47(1)
C(11)	11480(30)	-810(30)	1846(19)	77(8)
C(12)	11280(40)	-380(30)	910(20)	81(8)
C(13)	10370(30)	-1840(30)	3956(18)	68(7)
C(14)	11400(30)	-930(30)	4129(17)	63(6)
C(15)	5310(30)	1960(30)	4072(18)	66(7)
C(16)	3590(30)	2250(30)	4382(18)	69(7)
C(17)	5200(20)	1160(20)	2105(13)	46(5)
C(18)	5780(30)	390(30)	1231(18)	73(8)

Table 3. Bond lengths [Å] and angles [°] for **1**.

Sb(1)-C(1)	2.14(2)	C(13)-Sb(11)-S(11)	94.1(8)
Sb(1)-C(3)	2.15(2)	C(17)-Sb(12)-C(15)	93.4(10)
Sb(1)-S(1)	2.462(7)	C(17)-Sb(12)-S(11)	96.3(6)
Sb(2)-C(5)	2.13(2)	C(15)-Sb(12)-S(11)	93.6(7)
Sb(2)-C(7)	2.14(2)	Sb(12)-S(11)-Sb(11)	100.4(2)
Sb(2)-S(1)	2.429(5)	C(12)-C(11)-Sb(11)	113(2)
C(1)-C(2)	1.48(3)	C(14)-C(13)-Sb(11)	117(2)
C(3)-C(4)	1.49(4)	C(16)-C(15)-Sb(12)	115.0(19)
C(5)-C(6)	1.52(3)	C(18)-C(17)-Sb(12)	113.6(17)
C(7)-C(8)	1.47(3)		
Sb(11)-C(11)	2.12(3)		
Sb(11)-C(13)	2.21(3)		
Sb(11)-S(11)	2.467(6)		
Sb(12)-C(17)	2.14(2)		
Sb(12)-C(15)	2.16(3)		
Sb(12)-S(11)	2.427(5)		
C(11)-C(12)	1.48(4)		
C(13)-C(14)	1.39(4)		
C(15)-C(16)	1.55(4)		
C(17)-C(18)	1.58(3)		
C(1)-Sb(1)-C(3)	98.8(10)		
C(1)-Sb(1)-S(1)	93.3(8)		
C(3)-Sb(1)-S(1)	96.4(8)		
C(5)-Sb(2)-C(7)	95.0(10)		
C(5)-Sb(2)-S(1)	95.8(7)		
C(7)-Sb(2)-S(1)	97.1(7)		
Sb(2)-S(1)-Sb(1)	101.1(2)		
C(2)-C(1)-Sb(1)	114.7(18)		
C(4)-C(3)-Sb(1)	116(2)		
C(6)-C(5)-Sb(2)	113.5(19)		
C(8)-C(7)-Sb(2)	117.1(18)		
C(11)-Sb(11)-C(13)	97.6(11)		
C(11)-Sb(11)-S(11)	92.2(9)		

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **1**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Sb(1)	28(1)	46(1)	46(1)	-5(1)	-8(1)	-1(1)
Sb(2)	29(1)	48(1)	49(1)	-8(1)	-4(1)	-1(1)
S(1)	31(3)	47(5)	74(4)	-3(3)	-1(2)	-4(2)
Sb(11)	28(1)	46(1)	50(1)	-4(1)	-8(1)	-1(1)
Sb(12)	29(1)	52(1)	49(1)	-4(1)	-1(1)	-2(1)
S(11)	28(2)	45(5)	69(3)	-7(3)	-11(2)	1(2)

Table 5. Hydrogen coordinates ($\times 10^4$) and i displacement parameters ($\text{\AA}^2 \times 10^3$) for **1**.

	x	y	z	U(eq)
H(1A)	-2178	3445	2176	70
H(1B)	-1489	4809	1766	70
H(2A)	-777	4171	394	108
H(2B)	-2226	3284	749	108
H(2C)	-552	2695	752	108
H(3A)	-735	2901	4052	76
H(3B)	569	3906	4112	76
H(4A)	-1090	5552	3528	135
H(4B)	-1586	4990	4558	135
H(4C)	-2398	4493	3768	135
H(5A)	6002	6645	2652	66
H(5B)	4387	7346	2633	66
H(6A)	3371	5603	3765	107
H(6B)	4275	6723	4128	107
H(6C)	5099	5365	3904	107
H(7A)	4615	6219	96	68
H(7B)	4431	7389	748	68

H(8A)	7027	7087	862	95
H(8B)	6732	7556	-139	95
H(8C)	7151	6070	93	95
H(11A)	11801	-50	2129	93
H(11B)	12307	-1473	1839	93
H(12A)	12062	-816	491	121
H(12B)	11384	559	801	121
H(12C)	10272	-633	804	121
H(13A)	9500	-1896	4462	82
H(13B)	10903	-2690	3955	82
H(14A)	11574	-282	3616	95
H(14B)	12369	-1350	4218	95
H(14C)	10955	-517	4682	95
H(15A)	5795	1844	4623	79
H(15B)	5784	2705	3693	79
H(16A)	3201	2736	3880	103
H(16B)	3468	2772	4913	103
H(16C)	3032	1441	4539	103
H(17A)	4076	1234	2174	56
H(17B)	5612	2044	2015	56
H(18A)	6869	211	1202	110
H(18B)	5607	918	685	110
H(18C)	5236	-428	1266	110

Table 1. Crystal data and structure refinement for **3**.

Identification code	she_079m	
Empirical formula	C ₈ H ₂₀ Sb ₂ Te	
Formula weight	487.34 Da	
Density (calculated)	2.261 g cm ⁻³	
F(000)	1776	
Temperature	163(1) K	
Crystal size	0.3 x 0.3 x 0.3 mm	
Crystal color	dark red	
Crystal description	cylindric	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	<i>I</i> 2/a	
Unit cell dimensions	<i>a</i> = 12.337(2) Å	$\alpha = 90^\circ$
	<i>b</i> = 15.653(3) Å	$\beta = 103.322(2)^\circ$
	<i>c</i> = 15.240(4) Å	$\gamma = 90^\circ$
Volume	2863.9(11) Å ³	
Z	8	
Cell measurement reflections used	6842	
Cell measurement theta min/max	2.61° to 24.72°	
Diffractometer control software	Bruker AXS APEX 2 Vers.3.0/2009	
Diffractometer measurement device	Siemens SMART three axis goniometer with APEX II area detector system	
Diffractometer measurement method	Data collection strategy APEX 2/COSMO chi = 0°	
Theta range for data collection	1.89° to 24.73°	
Completeness to theta = 24.73°	86.6 %	
	The compounds are liquids at RT. The single crystals are formed by an in-situ zone melting process inside a quartz capillary using an IR-laser. The experimental setup does only allow for a omega scan of the single crystal. This limits the completeness to 75% to 95% depending on the crystal system.	
Index ranges	-12 ≤ <i>h</i> ≤ 13, -8 ≤ <i>k</i> ≤ 18, -17 ≤ <i>l</i> ≤ 17	
Computing data reduction	Bruker AXS APEX 2 Vers.3/2009	
Absorption coefficient	5.728 mm ⁻¹	

Absorption correction	Semi-empirical from equivalents
Empirical absorption correction	Bruker AXS APEX 2 Vers.3/2009
Max. / min. transmission	0.75 / 0.48
R(merg) before/after correction	0.1269 / 0.0395
Computing structure solution	Bruker AXS SHELXTL Vers. 2008/4/(c) 2008
Computing structure refinement	Bruker AXS SHELXTL Vers. 2008/4/(c) 2008
Refinement method	Full-matrix least-squares on F^2
Reflections collected	10875
Independent reflections	2131 [$R(\text{int}) = 0.0290$]
Data / restraints / parameters	1965 / 0 / 100
Goodness-of-fit on F^2	1.110
Weighting details	$w = 1/[\sigma^2(F_o^2) + (0.0396 \cdot P)^2 + 5.0214 \cdot P]$ where $P = (F_o^2 + 2F_c^2)/3$
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0257$, $wR2 = 0.0635$
R indices (all data)	$R1 = 0.0292$, $wR2 = 0.0662$
Largest diff. peak and hole	0.638 and -1.099 $\text{e}\text{\AA}^{-3}$
Treatment of hydrogen atoms	Riding model on idealized geometries with the 1.2 fold isotropic displacement parameters of the equivalent U_{ij} of the corresponding carbon atom. The methyl groups are idealized with tetrahedral angles in a combined rotating and rigid group refinement with the 1.5 fold isotropic displacement parameters of the equivalent U_{ij} of the corresponding carbon atom.
Comment	The crystallization was performed on the diffractometer at a temperature of 193 K with a miniature zone melting procedure using focused infrared-laser-radiation according to: R. Boese, M.Nussbaumer, "In Situ crystallisation Techniques", in: "Organic Crystal Chemistry", Ed. D.W. Jones, Oxford University Press, Oxford, England, (1994) 20-37

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **3**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Sb(1)	4463(1)	4669(1)	1909(1)	28(1)
Sb(2)	2500(1)	4666(1)	3791(1)	30(1)
Te(1)	2248(1)	4399(1)	1958(1)	33(1)
C(1)	4634(5)	3532(3)	1146(4)	42(1)
C(2)	4578(6)	2700(3)	1660(4)	54(2)
C(3)	4102(4)	5512(3)	752(3)	30(1)
C(4)	3702(6)	6386(3)	982(4)	51(2)
C(5)	3297(5)	5903(3)	3877(4)	43(1)
C(6)	2498(6)	6613(4)	3462(5)	63(2)
C(7)	4045(5)	3978(3)	4254(3)	42(1)
C(8)	3881(6)	3006(4)	4175(5)	67(2)

Table 3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for **3**.

Sb(1)-C(1)	2.163(5)	C(7)-Sb(2)-Te(1)	98.05(14)
Sb(1)-C(3)	2.165(5)	C(5)-Sb(2)-Te(1)	98.07(15)
Sb(1)-Te(1)	2.7833(7)	Sb(2)-Te(1)-Sb(1)	96.948(13)
Sb(2)-C(7)	2.161(5)	C(2)-C(1)-Sb(1)	113.9(4)
Sb(2)-C(5)	2.162(5)	C(4)-C(3)-Sb(1)	112.1(3)
Sb(2)-Te(1)	2.7695(9)	C(6)-C(5)-Sb(2)	112.7(4)
C(1)-C(2)	1.529(7)	C(8)-C(7)-Sb(2)	112.2(4)
C(3)-C(4)	1.522(7)		
C(5)-C(6)	1.523(8)		
C(7)-C(8)	1.535(8)		
C(1)-Sb(1)-C(3)	95.23(19)		
C(1)-Sb(1)-Te(1)	96.18(17)		
C(3)-Sb(1)-Te(1)	95.51(14)		
C(7)-Sb(2)-C(5)	94.2(2)		

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **3**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Sb(1)	21(1)	37(1)	26(1)	-1(1)	8(1)	1(1)
Sb(2)	28(1)	34(1)	32(1)	3(1)	13(1)	4(1)
Te(1)	21(1)	46(1)	32(1)	-3(1)	6(1)	-3(1)
C(1)	52(4)	34(3)	45(3)	-1(2)	21(3)	15(2)
C(2)	68(5)	36(3)	63(4)	11(3)	24(3)	11(3)
C(3)	28(3)	34(2)	29(2)	-1(2)	7(2)	0(2)
C(4)	64(4)	32(3)	59(3)	-2(2)	21(3)	5(3)
C(5)	44(4)	33(3)	49(3)	-9(2)	9(3)	0(2)
C(6)	72(5)	33(3)	85(4)	0(3)	22(4)	9(3)
C(7)	40(4)	53(3)	32(2)	11(2)	9(2)	14(3)
C(8)	83(5)	45(3)	74(4)	21(3)	21(4)	32(3)

Table 5. Hydrogen coordinates ($\times 10^4$) and i displacement parameters ($\text{\AA}^2 \times 10^3$) for **3**.

	x	y	z	U(eq)
H(1A)	4039	3528	586	50
H(1B)	5358	3555	971	50
H(2A)	5132	2713	2235	81
H(2B)	4731	2215	1299	81
H(2C)	3832	2638	1774	81
H(3A)	4783	5585	521	36
H(3B)	3524	5248	269	36
H(4A)	2976	6326	1134	76
H(4B)	3631	6768	463	76
H(4C)	4240	6626	1499	76
H(5A)	3620	6039	4518	51
H(5B)	3915	5879	3563	51

H(6A)	2231	6511	2813	94
H(6B)	2885	7164	3558	94
H(6C)	1864	6621	3748	94
H(7A)	4580	4156	3896	50
H(7B)	4367	4127	4892	50
H(8A)	3351	2826	4529	101
H(8B)	4597	2720	4404	101
H(8C)	3591	2853	3541	101

Table 1. Crystal data and structure refinement for 4.

Identification code	tesb2me4	
Empirical formula	C ₄ H ₁₂ Sb ₂ Te	
Formula weight	431.24 Da	
Density (calculated)	2.768 g cm ⁻³	
F(000)	760	
Temperature	173(1) K	
Crystal size	0.3 x 0.3 x 0.3 mm	
Crystal color	yellow	
Crystal description	cylindric	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	<i>P</i> 2 ₁ / <i>c</i>	
Unit cell dimensions	<i>a</i> = 15.0267(4) Å	<i>α</i> = 90°
	<i>b</i> = 10.8396(2) Å	<i>β</i> = 96.3912(12)°
	<i>c</i> = 6.3935(2) Å	<i>γ</i> = 90°
Volume	1034.92(5) Å ³	
Z	4	
Cell measurement reflections used	12232	
Cell measurement theta min/max	2.32° to 30.58°	
Diffractometer control software	Bruker AXS APEX 2 Vers.3.0/2009	
Diffractometer measurement device	Siemens SMART three axis goniometer with APEX II area detector system	
Diffractometer measurement method	Data collection strategy APEX 2/COSMO chi = 0°	
Theta range for data collection	1.36° to 30.61°	
Completeness to theta = 30.61°	84.9 %	
	The compound is liquid at RT. The single crystal is formed by an in-situ zone melting process inside a quartz capillary using an IR-laser. The experimental setup does only allow for a omega scan of the single crystal. This limits the completeness to 65% to 95% depending on the crystal system.	
Index ranges	0 ≤ <i>h</i> ≤ 21, -15 ≤ <i>k</i> ≤ 0, -7 ≤ <i>l</i> ≤ 6	
Computing data reduction	Bruker AXS APEX 2 Vers.3/2009 Data reduction with three independent crystals after	

Absorption coefficient	matrix determination with cell_now 7.905 mm ⁻¹
Absorption correction	Semi-empirical from equivalents
Empirical absorption correction	TWINABS - Bruker AXS scaling for twinned crystals – Version 2008/4
Max. / min. transmission	0.75 / 0.62
R(merg) before/after correction	0.072 / 0.055
Computing structure solution	Bruker AXS SHELXTL Vers. 2008/4/(c) 2008
Computing structure refinement	Bruker AXS SHELXTL Vers. 2008/4/(c) 2008
Refinement method	Full-matrix least-squares on F ²
Reflections collected	38395
Independent reflections	2705 [R(int) = 0.0367]
Data / restraints / parameters	2531 / 0 / 65
Goodness-of-fit on F ²	1.195
Weighting details	$w = 1/[\sigma^2(\text{Fo}^2) + (0.0365 \cdot P)^2 + 2.6465 \cdot P]$ where $P = (\text{Fo}^2 + 2\text{Fc}^2)/3$
Final R indices [I>2sigma(I)]	R1 = 0.0306, wR2 = 0.0776
R indices (all data)	R1 = 0.0333, wR2 = 0.0792
Extinction coefficient	0.0064(3)
Largest diff. peak and hole	1.878 and -1.315 eÅ ⁻³
Treatment of hydrogen atoms	The methyl groups are idealized with tetrahedral angles in a combined rotating and rigid group refinement with the 1.5 fold isotropic displacement parameters of the equivalent Uij of the corresponding carbon atom.
Comment	The crystallization was performed on the diffractometer at a temperature of 265 K with a miniature zone melting procedure using focused infrared-laser-radiation according to: R. Boese, M.Nussbaumer, "In Situ crystallisation Techniques", in: "Organic Crystal Chemistry", Ed. D.W. Jones, Oxford University Press, Oxford, England, (1994) 20-37

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **4**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Sb(1)	3130(1)	9566(1)	2108(1)	26(1)
Te(1)	3018(1)	9378(1)	6424(1)	32(1)
Sb(2)	1199(1)	9845(1)	5892(1)	33(1)
C(1)	4456(3)	8772(5)	2259(10)	39(1)
C(2)	3617(5)	11431(5)	2108(10)	48(1)
C(3)	1222(4)	11401(5)	7996(11)	50(2)
C(4)	853(4)	8540(6)	8213(10)	49(2)

Table 3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for **4**.

Sb(1)-C(2)	2.150(5)
Sb(1)-C(1)	2.162(5)
Sb(1)-Te(1)	2.7907(5)
Te(1)-Sb(2)	2.7630(4)
Sb(2)-C(3)	2.155(6)
Sb(2)-C(4)	2.156(6)
C(2)-Sb(1)-C(1)	93.6(2)
C(2)-Sb(1)-Te(1)	97.26(17)
C(1)-Sb(1)-Te(1)	94.81(16)
Sb(2)-Te(1)-Sb(1)	91.875(14)
C(3)-Sb(2)-C(4)	94.1(3)
C(3)-Sb(2)-Te(1)	96.88(17)
C(4)-Sb(2)-Te(1)	96.10(16)

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **4**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Sb(1)	24(1)	35(1)	17(1)	-1(1)	2(1)	1(1)
Te(1)	26(1)	55(1)	17(1)	2(1)	3(1)	6(1)
Sb(2)	25(1)	52(1)	23(1)	2(1)	2(1)	3(1)
C(1)	30(2)	46(3)	41(4)	-6(2)	10(2)	3(2)
C(2)	72(4)	31(2)	40(4)	2(2)	8(3)	-1(2)
C(3)	51(3)	48(3)	53(4)	-5(3)	10(3)	16(2)
C(4)	39(3)	65(3)	45(4)	4(3)	8(2)	-22(2)

Table 5. Hydrogen coordinates ($\times 10^4$) and i displacement parameters ($\text{\AA}^2 \times 10^3$) for **4**.

	x	y	z	U(eq)
H(1A)	4676	8836	876	58
H(1B)	4431	7902	2665	58
H(1C)	4861	9218	3303	58
H(2A)	4135	11516	3173	71
H(2B)	3143	11997	2435	71
H(2C)	3795	11630	719	71
H(3A)	607	11632	8199	75
H(3B)	1520	12098	7390	75
H(3C)	1550	11179	9356	75
H(4A)	1228	8685	9544	74
H(4B)	952	7699	7724	74
H(4C)	221	8641	8429	74

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