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The Origin of Thermochromic Behaviour in Distibines – Still an open Question

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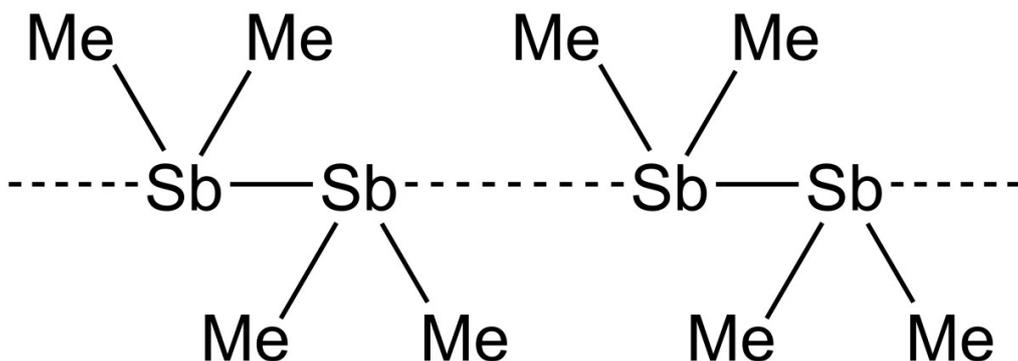
ABSTRACT. A detailed structural investigation of Sb_2Et_4 using an *in situ* crystallization technique clearly shows, that thermochromic behavior of distibines cannot be solely attributed to the formation of intermolecular $\text{Sb}\cdots\text{Sb}$ interactions in the solid state. Both the yellow and the red phase of Sb_2Et_4 showed almost identical bond lengths and angles including rather short intermolecular $\text{Sb}\cdots\text{Sb}$ bond distances.

Introduction

Group 15 metalorganics of the general type R_2E-ER_2 ($E = P, As, Sb, Bi$) have a long standing history in main group element chemistry. In fact, Me_4As_2 ("*fuming arsenical liquid*" or "*Cacodyl*"), which was initially reported by Louis Cadet de Gassicourt in 1760 and whose composition was later identified by Robert Bunsen, represents the first organometallic compound ever.^[1] Even though Me_4Sb_2 and Me_4Bi_2 ^[2] were already synthesized eighty years ago, efficient syntheses for distibines and dibismuthines R_4E_2 were developed not before the early eighties of the last century.^[3] This finding most likely results from the limited thermal and/or photochemical stability of the E-E bond. In particular distibines and dibismuthines tend to undergo homolytic E-E bond breakage reactions.

Some distibines and dibismuthines show an interesting color change upon melting/freezing. Me_4Bi_2 for instance is an orange liquid, but crystallizes as violet solid at low temperature.^[4] In contrast, Me_4Sb_2 changes its color upon melting from red to pale yellow.^[2] This so-called thermochromic behavior was reported for distibines and dibismuthines containing sterically less demanding organic substituents such as Me or Et groups, which allow the formation of close intermolecular metal...metal contacts in the solid state,^[5] as well as MMe_3 substituents ($M = Si, Ge, Sn$).^[6] Computational calculations were performed in order to reveal the bonding situation in thermochromic distibines and dibismuthines and the origin of thermochromicity.^[7] The bathochromic shift from the yellow or orange fluid phase to the violet, blue or green solid phase was assigned to the formation of intermolecular $E \cdots E$ contacts,^[8] leading to extended antimony and bismuth chain-like structures in the solid state.^[9] The intermolecular $E \cdots E$ distances are longer than the intramolecular E-E single bonds of distibines and dibismuthines R_4E_2 (Sb: 2.827 – 2.883 Å; Bi: 2.983 – 3.209 Å)^[10] and the calculated E-E single-bond covalent radii (Sb: 2.80

Å; Bi: 3.02 Å),^[11] but shorter than the sum of the van-der-Waals radii (Sb: 4.12 Å; Bi: 4.14 Å).^[12] The chains are almost linear and the E-E⋯E bond angles range from 170 -180°. Unfortunately, the number of thermochromic distibines and dibismuthines, which have been structurally characterized by single crystal X-ray diffraction, is rather limited.^[13]



Scheme 1. Intermolecular Sb⋯Sb interactions typically observed in thermochromic Sb₂Me₄.

Our general interest in organoantimony and -bismuth chemistry prompted us to study reactions of distibines and dibismuthines with group 13 metal trialkyls in detail.^[14] Moreover, we became interested in the solid state structures of the pure distibines and dibismuthines and reported very recently on the solid state structures of Et₄Sb₂ (red phase, **1b**) and Et₄Bi₂, respectively.^[15] Single crystals of these complexes were obtained by use of an IR-laser-assisted in situ crystallization technique directly on the diffractometer.^[16] Herein, we report on the solid state structure of the yellow phase of Et₄Sb₂ (**1a**) which we had previously observed but not yet structurally characterized.^[15]

Results and Discussion

Sb₂Et₄ **1** was prepared according to literature methods and purified by vacuum distillation. A single crystal of the yellow phase (**1a**) suitable for an X-ray diffraction study was obtained by

slow *in situ* crystallization. Figure 1 shows the molecular structure of Et₄Sb₂ (**1a**) in the solid state and table 1 summarizes the central structural parameters of **1a** and the low-temperature red phase **1b**.^[17,18]

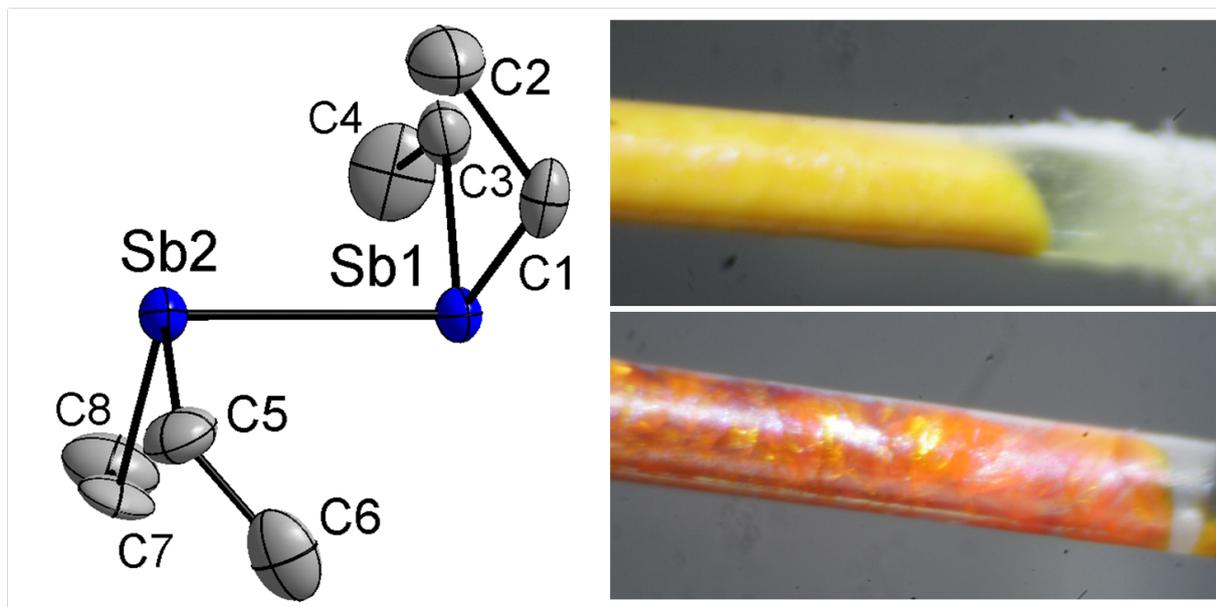


Figure 1. Solid state structure of **1a** and photographs of the yellow phase (**1a**) at -80 °C and red phase (**1b**) at -100 °C.

Table 1. Comparison of central bond lengths (Å) and angles (°) of **1a** and **1b**.

	1a	1b
Sb-Sb	2.8425(10)	2.8381(5)
Sb⋯Sb	3.7030(11)	3.6883(5)
Sb-C	2.210(15), 2.172(18), 2.161(15), 2.164(17)	2.157(7), 2.174(6), 2.166(7), 2.182(7)
Sb-Sb⋯Sb	177.92(5)	177.94(2)
C-Sb-Sb	95.0(4), 97.7(3), 9 5.5(5), 95.7(4)	95.18(18), 97.20(17), 95.36(18), 96.61(19)

1a crystallizes in the monoclinic space group $P2_1/c$ and **1b** in the triclinic space group $P-1$. The intramolecular Sb-Sb bond lengths in **1a** and **1b** as well as the C-Sb-C, C-Sb-Sb and Sb-Sb \cdots Sb bond angles are very similar. Comparable intramolecular Sb-Sb single bond lengths were observed in Me_4Sb_2 (2.838(1),^[13b] 2.862(2) Å^[13a]), Ph_4Sb_2 (2.837(1),^[19] 2.844(1) Å^[5a,11]) and $[(\text{Me}_3\text{Si})_2\text{CHSb}(\text{H})]_2$ (2.8304(8) Å^[20]), respectively.

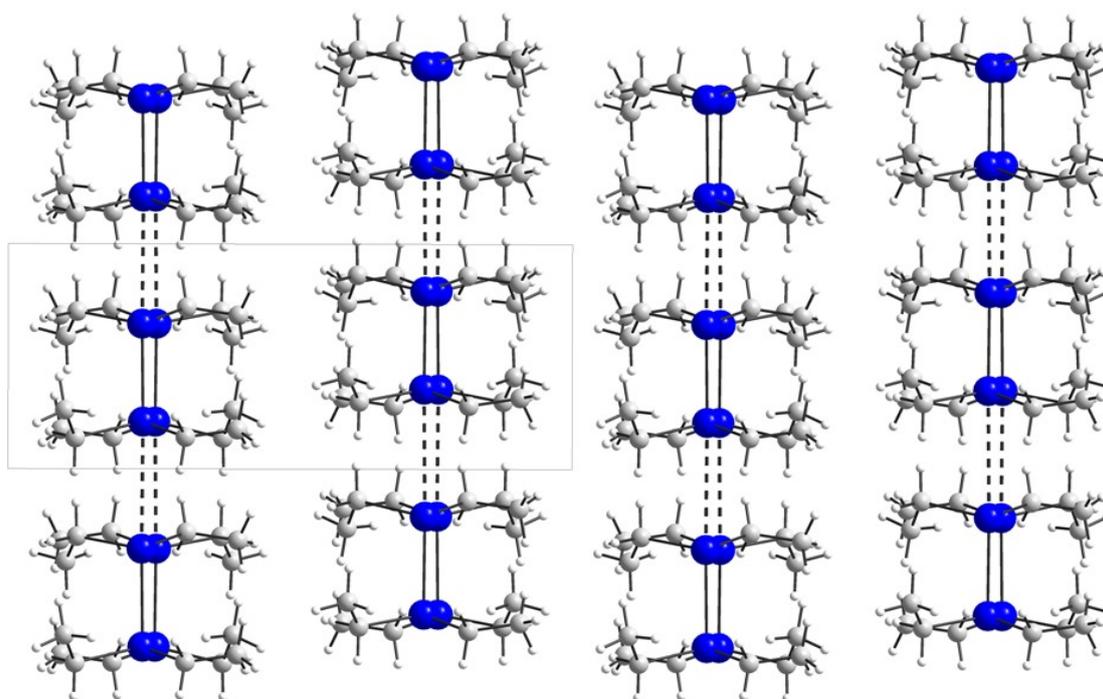


Figure 2. Packing of **1a**. View along c . The alternating offset of the layers in a -direction results in a zig-zag arrangement (in this projection) of the Sb atoms in b direction.

Figures 2 and 3 show the intermolecular Sb \cdots Sb interactions as observed in the yellow phase (**1a**) and the red phase (**1b**) of Et_4Sb_2 as well as the resulting constitution of the packing in the solid state. The intermolecular Sb-Sb bond lengths in **1a** and **1b** are again almost identical and correspond very well with those reported for Me_4Sb_2 (3.645,^[13a] 3.678 Å^[13b]) and

$[(\text{HC}=\text{CMe})_2]_2\text{Sb}_2$ (3.63 Å),^[13c] respectively. The same is true for the Sb-Sb \cdots Sb bond angles (117.92(5) **1a**, 177.94(2) **1b**), which are close to 180° as is typically observed.^[13] In contrast, the packing in (**1a**) and (**1b**) slightly differ. Both packings are constituted by layers parallel to (010) and (0-11), respectively. These layer are formed by chains parallel to *a* (both **1a** and **1b**) resulting from the Sb \cdots Sb interactions. Due to the nearly identical conformation of the distibine molecule in **1a** and **1b** in both structures, the layers are approximately 8 Å thick. The only difference between the structures is the arrangement of the layers. In **1a** the offset in *a* direction from one Sb to another in the neighboring layer is alternating whereas in **1b** the offset is always in the same direction (see fig. 2 and 3).

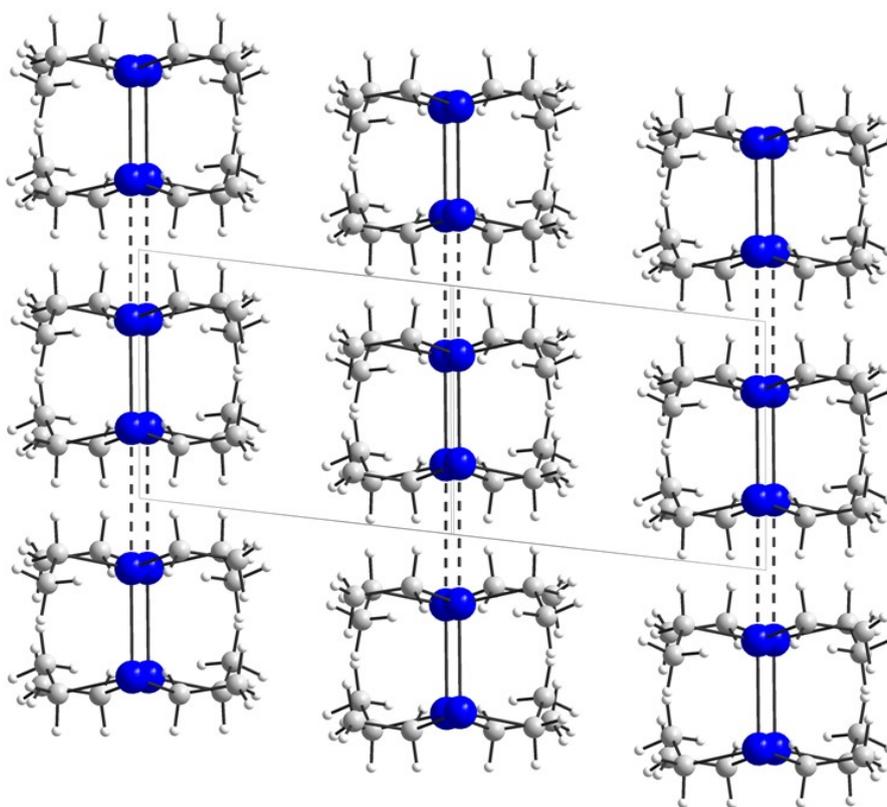


Figure 3. Packing of **1b**. View along [0-11]. The unidirectional offset parallel to *a* of the layers leads to a linear arrangement of the Sb atoms (in this projection) in [011] direction.

Thermochromic distibines typically exhibit short intermolecular Sb \cdots Sb interactions, leading to the formation of endless chains in the solid state. Upon melting, these intermolecular Sb \cdots Sb contacts are disrupted, resulting in a bathochromic shift in the melt. Interestingly, Et₄Sb₂ **1** already shows a bathochromic shift from red to yellow in the solid state at about -80 °C, and the yellow color remains upon melting.^[15] The structural characterization of both phases now clearly proved, that the color change in the solid state *can not* be assigned to the breakage of the intermolecular Sb \cdots Sb contacts, since both the yellow (**1a**) and the red (**1b**) phases of Et₄Sb₂ show comparable short intermolecular Sb \cdots Sb distances of roughly 3.7 Å.

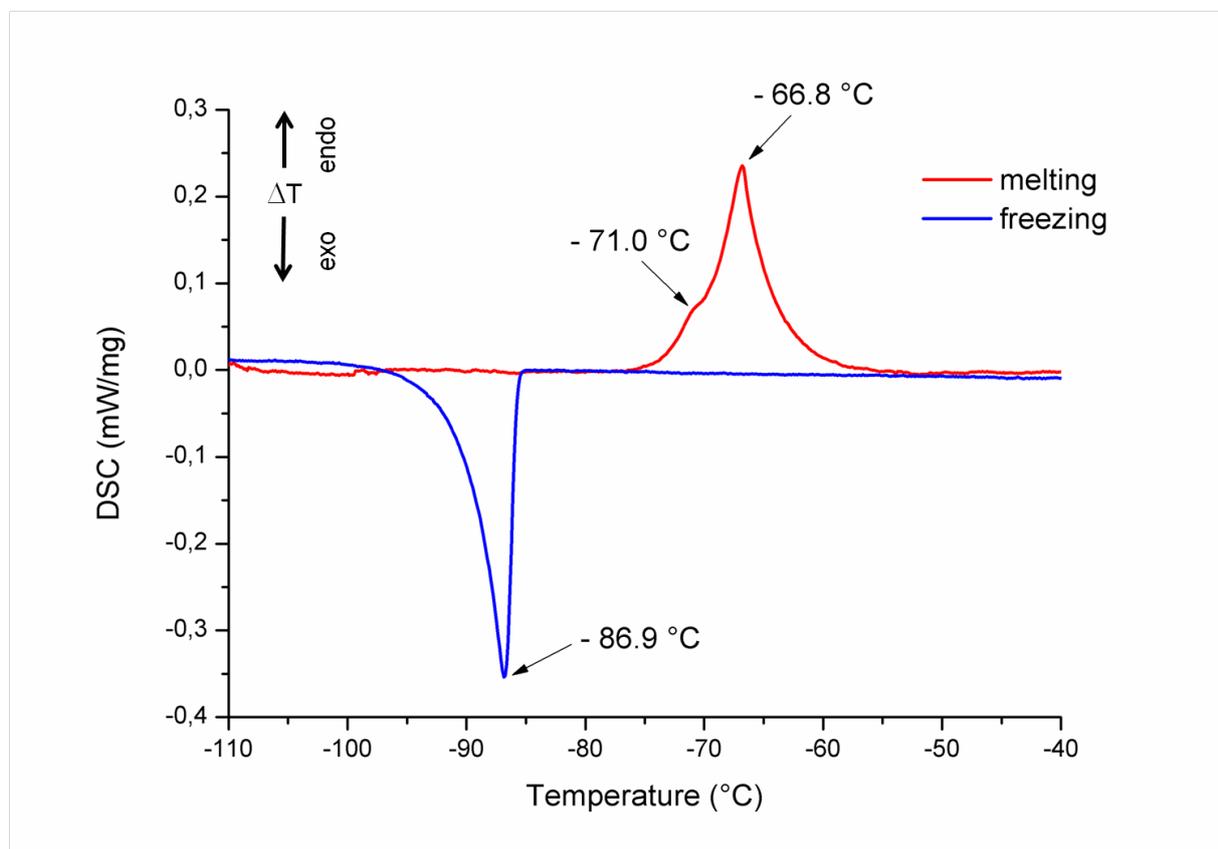


Figure 4. DSC experiment performed between -40 and -100 °C. Both the heating (red) and the cooling curve (blue) are shown.

A DSC experiment was performed in order to investigate which polymorph is the most stable one. For this purpose, a sample of Sb_2Et_4 was slowly cooled down to $-100\text{ }^\circ\text{C}$ (1 K/min) and then slowly heated back to ambient temperature (1 K/min). Figure 4 shows both DSC curves. The cooling curve (blue curve) clearly shows an exothermic peak due to the freezing of **1** at $-86.9\text{ }^\circ\text{C}$. In contrast, the heating curve (red curve) shows a broad endothermic peak due to the melting of **1** at $-66.8\text{ }^\circ\text{C}$ with an endothermic shoulder at $-71\text{ }^\circ\text{C}$. We attribute this shoulder to the phase transition from the red phase (**1b**) to the yellow phase (**1a**), indicating **1b** to be thermodynamically more stable than **1a**. The much lower freezing point results from the formation of a supercooled liquid.

Conclusions. The solid state structure of the yellow phase of Sb_2Et_4 (**1a**) is described and compared to that of the red phase (**1b**). A single crystal of **1a** was grown by a laser-assisted technique on the diffractometer. The central structural parameters of **1a** and **1b** are almost identical. As a consequence, the color change in the solid state from red (**1b**) to yellow (**1a**) upon heating from $-150\text{ }^\circ\text{C}$ to $-80\text{ }^\circ\text{C}$ cannot be assigned to the disruption of these intermolecular $\text{Sb}\cdots\text{Sb}$ interactions within the chain-type structure of both **1a** and **1b** in the solid state. Additional studies are necessary in order to clarify the origin of the thermochromic behavior of Sb_2Et_4 .

Experimental Details. **1** was synthesized under an Ar atmosphere by reaction of SbEt_3 with sodium in liquid ammonia. The resulting sodium stibide was then reacted with 1,2-dichloroethane, yielding Sb_2Et_4 in high yield.

Single crystal X-ray analyses. Crystallographic data of **1a** were collected on a Bruker AXS SMART diffractometer ($\text{MoK}\alpha$ radiation, $\lambda = 0.71073\text{ \AA}$) at $193(1)\text{K}$. Figure 1 shows the diagram of the solid-state structures of **1a**. The structure was solved by Direct Methods

(SHELXS-97)^[17] and refined anisotropically by full-matrix least-squares on F^2 (SHELXL-97).^[18] Absorption correction was 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. 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 crystal.

1a: $C_8H_{20}Sb_2$, $M = 359.74$, yellow crystal (0.5 x 0.3 x 0.3 mm); monoclinic, space group $P2_1/c$; $a = 6.5444(6)$, $b = 16.0574(18)$, $c = 12.0939(19)$ Å; $\beta = 99.452(7)$, $V = 1253.6(3)$ Å³; $Z = 4$; $\mu = 4.258$ mm⁻¹; $\rho_{ber.} = 1.906$ g cm⁻³; 4772 reflexes ($2\theta_{max} = 60^\circ$), 2322 unique ($R_{int} = 0.0686$); 91 parameters, 0 restraints; largest max./min. in the final difference Fourier synthesis 4.042 eÅ⁻³ (1.10 Å from Sb2)/-1.217 eÅ⁻³; goodness-of-fit 0.953; max./min. transmission 0.75/0.25; $R_1 = 0.0596$ ($I > 2\sigma(I)$), wR_2 (all data) = 0.1706.

The crystallographic data of **1a** (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 874708 (**1a**). 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-ak.uk).

Supporting Information. Electronic Supplementary Information (ESI) available: Experimental procedure and structural characterization of **1a**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

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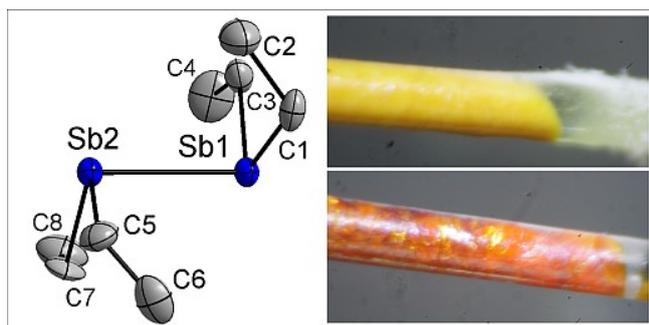
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Graphic for Table of Content.

The breakage of intermolecular Sb \cdots Sb interactions as origin of thermochromicity in Sb $_2$ Et $_4$ can be ruled out based on a structural comparison of the low-temperature red phase (**1b**) and the high temperature yellow phase (**1a**) of solid Sb $_2$ Et $_4$. Both crystalline phases show almost identical bond lengths and angles including short intermolecular Sb \cdots Sb bond distances.



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