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Tetrahedron Letters 47 (2006) 8937–8941
Tetrahedron Letters

The first methyl antimony linked dimeric tetrathiafulvalene and tetraselenafulvalenes

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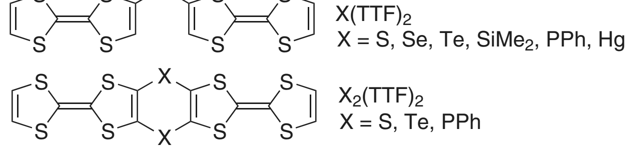
Received 9 August 2006; revised 5 October 2006; accepted 6 October 2006
Available online 31 October 2006

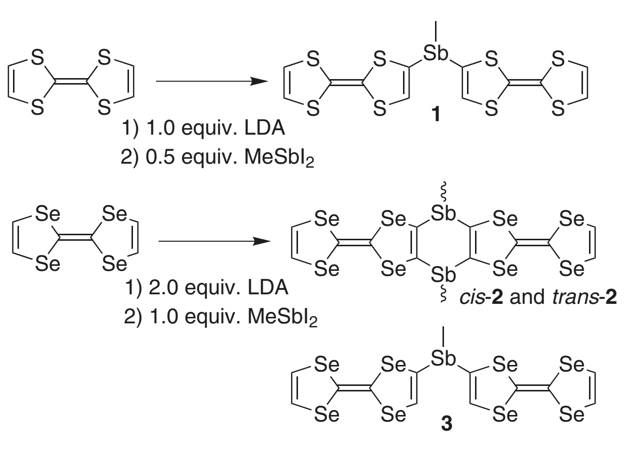
Abstract—In quest of novel organic donors, dimeric tetrathiafulvalene (TTF) and tetraselenafulvalenes (TSFs) linked by a single or double methyl antimony bridge, MeSb(TTF)$_2$ (**1**), (MeSb)$_2$(TSF)$_2$ (*cis*-**2** and *trans*-**2**), and MeSb(TSF)$_2$ (**3**), have been synthesized. Singly bridged **1** and **3** show three pairs of redox waves, whereas doubly bridged *cis*-**2** and *trans*-**2** show two pairs of redox waves similarly to TSF. The X-ray structural analyses of neutral crystals, **1**, *cis*-**2** and *trans*-**2**, have succeeded. In their structures, antimony and chalcogen atoms form close intermolecular contacts useful in constructing supramolecular networks.

Many chemical modifications of TTF (tetrathiafulvalene) have been carried out with the aim of exploring new metallic and superconducting cation radical salts.[1] Among them, dimeric TTF molecules[2] are expected to display a multiredox character by through-bond or through-space interactions between two TTF units and enhance the intermolecular interactions by the extended π-conjugation. For this purpose, main group elements such as sulfur,[3] selenium,[3] tellurium,[4] silicon,[5] phosphorus,[5] and mercury[5] have been employed to link two TTF units (Scheme 1). Recently, doubly bridged dimeric TTF with phenyl phosphorus linkage was reported.[6] These heteroatoms are expected to form supramolecular networks in the crystals of their cation radical salts.

From the viewpoint of conducting materials, these dimeric systems have not been so suitable for the cooperation between supramolecular interactions and conducting pathways. Intermolecular interactions are of essential importance in delocalizing conduction electrons and stabilizing a metallic state. For this reason, we focus on the dimeric TTF system linked by methyl antimony(III) bridge(s). The antimony atom offers a possibility for electronic delocalization through intermolecular Sb···Sb and Sb···S contacts.[7] Compared with the bulky aryl group, the small methyl group is suitable for the formation of intermolecular interactions. Moreover, antimony(III) atom is useful for electrocrystallization due to its more positive potential to antimony(V) species compared with other homologous elements. In addition, replacement of sulfur atoms with selenium atoms, which is a powerful method for the



Scheme 1. Dimeric TTF systems.



Scheme 2. Synthesis of dimeric T*C*Fs.

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doi:10.1016/j.tetlet.2006.10.025

enhancement of intermolecular interactions, has been performed.[8] In the present letter, we report synthesis, redox properties, and crystal structures of methyl antimony(III)-linked dimeric T*C*F (tetrachalcogenafulvalene) derivatives, MeSb(TTF)$_2$ (**1**), (MeSb)$_2$(TSF)$_2$ (*cis*-**2** and *trans*-**2**) and MeSb(TSF)$_2$ (**3**).

The one-pot synthesis of the present compounds is outlined in Scheme 2. Methylantimonydiiodide (MeSbI$_2$)[9] was used for the linkage of two T*C*F units. Compound **1** was obtained by the monolithiation of TTF with 1 equiv of LDA followed by a reaction with 0.5 equiv of MeSbI$_2$.[10] Similarly, the treatment of selectively bislithiated TSF[11] with 1 equiv of MeSbI$_2$ afforded compounds **2** (a *cis*/*trans* mixture) together with compound **3**.[12] It should be noted that the treatment of TSF with 1 equiv of LDA followed by a reaction with 0.5 equiv of MeSbI$_2$ also afforded **2** (a *cis*/*trans* mixture) as a main product. This result suggests the predominant formation of 2,3-bislithiated TSF even if the reaction is carried out under the monolithiation condition.[10] Subsequently, *cis* and *trans* isomers **2** were completely separated into each isomer by a gel-permeation chromatography eluted with CS$_2$ by a 6 time recycle. The *cis*/*trans* ratio was nearly 1/5 from the isolated yields. The subtle change of the peak height detected with 278 nm absorption, when *cis*/*trans* mixture had been stored in CS$_2$ solution for a long period at room temperature during the separation, would indicate the interconversion between *cis*-**2** and *trans*-**2**. The *cis*/*trans* separation was only successful by the use of CS$_2$ as the eluent. In the absence of light, *cis*-**2** and *trans*-**2** which had been stored in CS$_2$ solution for several days afforded the crystals of *cis*-**2** and *trans*-**2**, respectively. In comparison with **1**, selenium compounds *cis*-**2**, *trans*-**2** and **3** are less soluble in common organic solvents. However, it is not problematic for the study of electrochemical behaviour and electrocrystallization for preparing cation radical salts.

Redox properties of **1**–**3** and their parent TTF and TSF are presented in Table 1 and Figure 1. Singly linked compounds **1** and **3** show three pairs of reversible redox waves and the first and second stages are successive. In addition, compounds **1** and **3** show the first wave slightly more negative than those of the parent TTF and TSF, respectively, exhibiting an improved electron donor character. It is difficult for the present results to provide further information about each redox steps. This behaviour, however, is similar to those of bis(tetrathiafulvalenyl)sulfide [(TTF)$_2$S] and its selenium analogue [(TTF)$_2$Se], except that the third one is irreversible in the case of [(TTF)$_2$S] and [(TTF)$_2$Se].[3] The first and second couples of [(TTF)$_2$S] and [(TTF)$_2$Se] correspond to reversible one-electron processes to mono- and di-cationic species (TTF-*C*-TTF$^+$ and TTF$^+$-*C*-TTF$^+$: $C =$ chalcogen) and the third step is an irreversible two-electron process up to tetracation $C(\mathrm{TTF})_2^{4+}$. If taking account of this explanation, a very small separation between the first and second steps in **1** and **3** suggests that the bridging antimony atom in **1** and **3** brings about an electronic coupling between two T*C*F units in **1** and **3** to some extent.

Table 1. Redox potentials/*V*[a]

Compounds	$E^1_{1/2}$	$E^2_{1/2}$	$E^3_{1/2}$	$E^2_{1/2} - E^1_{1/2}$
TTF	−0.05	0.48		0.53
TSF	0.09	0.49		0.40
1	−0.11	0.01	0.40	0.12
cis-**2**	0.10	0.44		0.36
trans-**2**	0.11	0.47		0.36
2	0.05	0.17	0.49	0.12

[a] Versus Ag/AgNO$_3$ in PhCN with 0.1 M *n*-Bu$_4$NPF$_6$, grassy carbon working electrode, scan rate 25, 50, 100 mV s^{-1}. The potentials of TTF and TSF were measured for comparison under the identical condition. The listed values are average for the three scan rates.

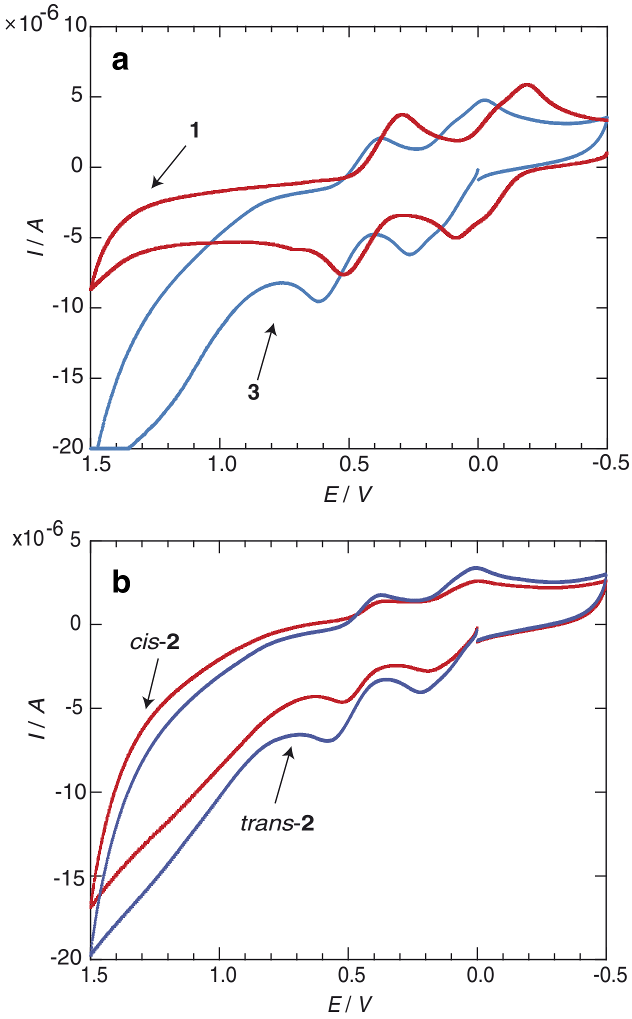

Figure 1. Cyclic voltammograms for (a) **1** and **3** and (b) *cis*-**2** and *trans*-**2**: *V* versus Ag/AgNO$_3$, 0.1 M TBAPF$_6$ in PhCN, 100 mV s^{-1}.

In contrast, the doubly bridged compounds *cis*-**2** and *trans*-**2** exhibit two pairs of reversible waves like parent TSF, and their electron donating abilities are inheritable from TSF. These two steps are quite similar to those of X$_2$(MeS$_2$TTF)$_2$ (X = Te),[4b] and contrastive to the case of X$_2$(*o*-Me$_2$TTF)$_2$ (X = PPh) that exhibits strictly separated four oxidation waves indicating the interaction between two TTF units.[6] Compared with **1** and **3**, the absence of further oxidation stages of *cis*-**2** and *trans*-**2** would suggest that the coupling of two T*C*F units in **1** and **3** comes from not the interactions via methyl antimony linkage but the approach of two T*C*F units by the bent of single methyl antimony linkage. In the case of *cis*-**2** and *trans*-**2**, the rigid central diantimony ring would prevent the approach of two TSF units, and divide the molecule into two nearly independent halves.

Recrystallization of **1**, *cis*-**2**, and *trans*-**2** from some organic solvents afforded single crystals suitable for X-ray structure analysis.[10,12,13] Compound **1** crystallizes in the monoclinic system with the space group *P*c. The molecular and crystal structures of **1** are shown in Figure 2. The whole molecule is crystallographically independent and the unit cell consists of two molecules. In contrast to a chair conformation of the neutral TTF,[14] each TTF unit of **1** is almost planar and these two TTF planes is nearly perpendicular to each other [95.31(4)°]. The angles around the pyramidal antimony atom are 95.1(2)° for C(3)–Sb(1)–C(13), 94.7(2)° for C(9)–Sb(1)–C(13), and 94.3(2)° for C(3)–Sb(1)–C(9), whose values are slightly smaller than those reported for the tertiary stibine Ph$_3$Sb [95.1(3)–98.0(3)°].[15] In the crystal, the antimony atom constructs two Sb···S intermolecular interactions within the sum of the van der Waals radii Sb···S (3.80 Å); the one is Sb(1)···S(3) [3.589(2) Å] and the other is Sb(1)···S(7) [3.730(2) Å]. Similarly, there are other remarkable interactions; short S···S contacts [3.573(3) Å for S(4)···S(6)] and some (C)H···S contacts shorter than the sum of the van der Waals radii. As a result, these interactions form the three-dimensional network in the crystal.

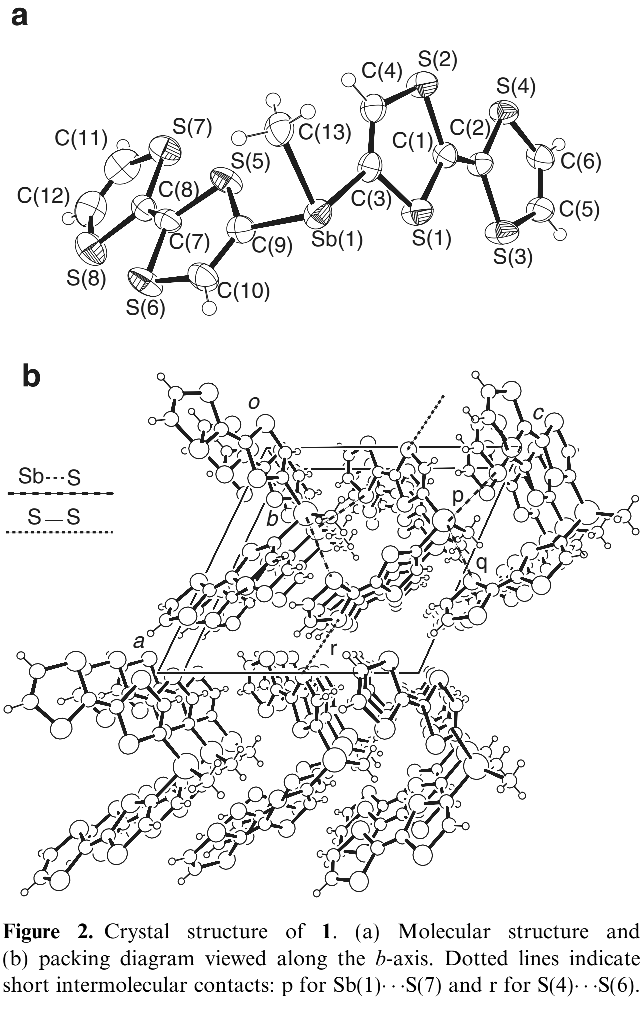

Figure 2. Crystal structure of **1**. (a) Molecular structure and (b) packing diagram viewed along the *b*-axis. Dotted lines indicate short intermolecular contacts: p for Sb(1)···S(7) and r for S(4)···S(6).

Two geometrical isomers *cis*-**2** and *trans*-**2** show entirely different types of crystal structures: the orthorhombic system with the space group *P*nma for *cis*-**2** and the triclinic system with the space group $P\bar{1}$ for *trans*-**2**. The molecular and crystal structures of *cis*-**2** are shown in Figure 3. A mirror plane passes through the molecule along the molecular long axis and the half moiety is crystallographically independent. The central diantimony ring is much distorted into a boat conformation with the dihedral angle of 67.1(2)° between the Sb(1)–C(3)=C(3′)–Sb(1′) and Sb(1)–C(7)=C(7′)–Sb(1′) planes. This conformation more resembles that in X$_2$(Me$_2$-TTF)$_2$ (X = Te, 67.8 °) than that in X$_2$(*o*-Me$_2$TTF)$_2$

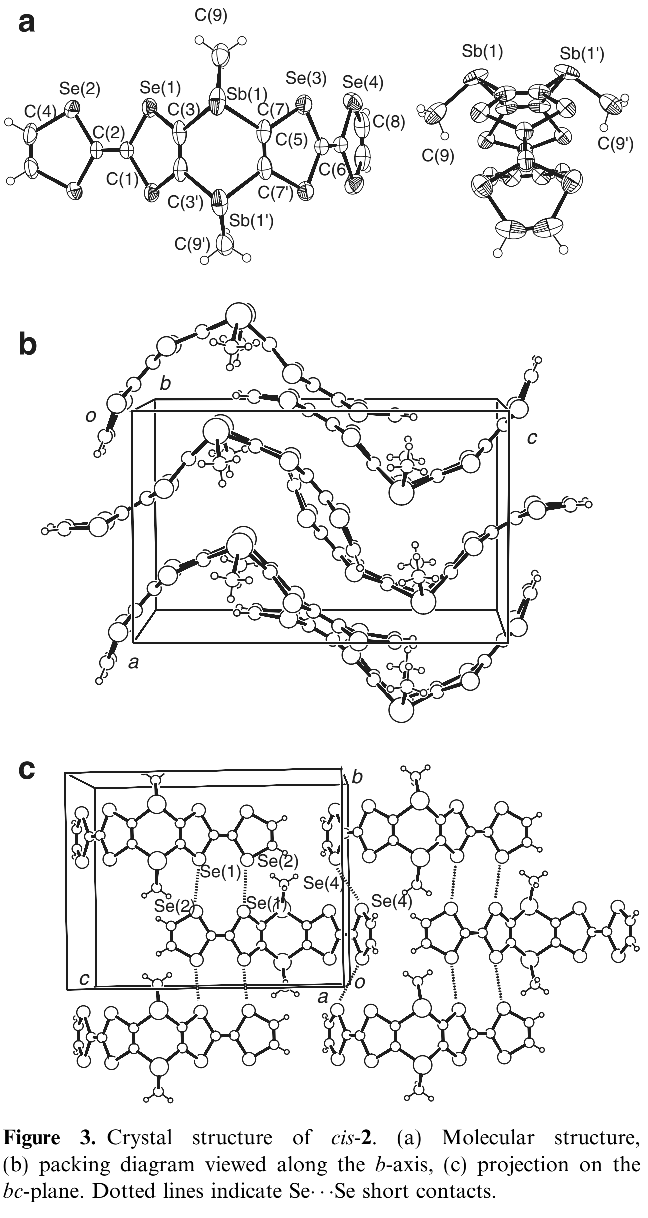

Figure 3. Crystal structure of *cis*-**2**. (a) Molecular structure, (b) packing diagram viewed along the *b*-axis, (c) projection on the *bc*-plane. Dotted lines indicate Se···Se short contacts.

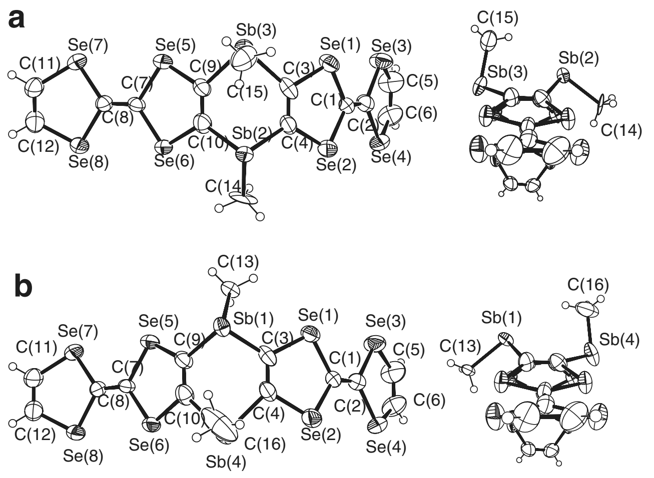

Figure 4. Molecular structure of *trans*-**2**. Perspective view perpendicular to the molecular plane and along the molecular long axis. (a) [C(14)–Sb(2) and Sb(3)–C(15)] and (b) [C(13)–Sb(1) and Sb(4)–C(16)] represent the positional disorder.

(X = PPh, 30.4(1)°).[4c,6] The marked distortion, coming from sizable atoms such as Sb and Te, appears to restrict an intramolecular interaction between two TSF units and might be responsible for the observed simple two redox steps. Both of the TSF units are held into boat conformations with their curvatures reverse to each other. The molecules concerning the *n*-glide operation form a stack along the *a*-axis. There are side-by-side intermolecular Se···Se contacts [3.6965(8) Å for Se(1)···Se(2) and 3.778(1) Å for Se(4)···Se(4)] that are considerably shorter than the van der Waals distance. Figure 4 shows the molecular structure of *trans*-**2**. The whole molecule and the half of CS_2 coming from the solvent of recrystallization are crystallographically independent and two molecules and one CS_2 molecule exist in the unit cell. Similarly to *cis*-**2**, the central diantimony ring of *trans*-**2** is distorted into a boat conformation. The doubly bridged methyl antimony atoms are disordered, showing two possible conformations: C(14)–Sb(2) and Sb(3)–C(15) with the occupancy 0.59 and C(13)–Sb(1) and Sb(4)–C(16) with the occupancy 0.41. The TSF units are distorted as shown in the *cis*-**2**. However, the planarity of the TSF skeleton should be recovered by the oxidation to the charged state as generally seen in T*C*F derivatives. The molecular arrangement in the crystal of *trans*-**2** is quite different from that in the crystal of *cis*-**2**. There are no stacks but the side-by-side Se(2)···Se(4) contact is present. The disorder in *trans*-**2** seems to prevent the effective molecular stacking.

In conclusion, we have developed the methyl antimony-linked dimeric T*C*F systems for the first time. The redox properties and crystal structures of the present molecules have been successfully confirmed. The present molecules show the favourable donating character for preparing cation radical salts and have strong tendency to form intermolecular interactions useful for the construction of the higher dimensional supramolecular network. The distortion of the TSF units in *cis*-**2** and *trans*-**2** would be suppressed by the oxidation in cation radical salts, and molecular stacks with extended intermolecular interactions through chalcogen–chalcogen or chalcogen–antimony contacts are expected. The present molecules are the most fundamental and some peripheral modifications of the T*C*F core are possible. We propose the methyl antimony-bridged T*C*F systems are promising candidates to open the next generation in molecular conductors. The preparation of conducting cation radical salts with various inorganic anions is currently in progress.

Acknowledgements

This work was partially supported by a Grant-in-Aid for Scientific Research (No. 16GS0219) from the Ministry of Education, Culture, Sports, Science, and Technology of Japan.

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10. To a solution of TTF (0.51 g, 2.5 mmol) in dry THF (12 ml) was slowly added a freshly prepared solution of LDA (2.7 mmol) in THF–hexane (5 ml) at −78 °C, and the resulting solution was stirred for 4 h at the same temperature. Then $MeSbI_2$ (0.52 g, 1.3 mmol) in dry THF (5 ml) was added dropwise to the solution and the

resulting mixture was allowed to warm up to room temperature. The mixture was filtered through Celite and extracted with toluene (100 ml). After removal of the solvent, the resulting residue was subjected to a gel-permeation chromatography (JAI polystylene-gel columns 1H + 2H, eluted with CS_2, detected with 278 nm absorption) to afford **1** (0.19 g, 29%) as yellow solids. Slow evaporation of the CS_2–$CDCl_3$ (1:1, v/v) solution of **1** gave yellow needles suitable for X-ray analysis. Mp. 177–178 °C; ^1H NMR (300 MHz; $CDCl_3/CS_2 = 1/1$), δ 6.38 (s, 2H), 6.24 (d, 4H), 1.31 (s, 3H); m/z (FAB-MS), 544 (M^+); Anal. Calcd for $C_{13}H_9S_8Sb$: C, 28.73; H, 1.67. Found: C, 29.02, H, 1.49.

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12. To a solution of TSF (0.4 g, 1.0 mmol) in dry THF (8 ml) was slowly added a solution of freshly prepared LDA (2.0 mmol) in THF–hexane (4.0 ml) at −90 °C, and the temperature was allowed to rise up to −78 °C and the resulting solution was stirred for 1 h at −78 °C. Then the mixture was cooled again to −100 °C, and $MeSbI_2$ (0.43 g, 1.1 mmol) in dry THF (3.0 ml) was added rapidly, and the reaction mixture was allowed to warm up to room temperature. After the addition of MeOH (5.0 ml), the solvent was evaporated, and the resulting residue was extracted with CS_2 (200 ml) and filtered through Celite. The solvent was removed from the filtrate and the residue was roughly separated by flash column chromatography on silica gel with CS_2. At this stage, compound **3** (0.015 g) was isolated as pink solids. The crude products **2** containing unidentified by-products were purified by a gel-permeation chromatography eluted with CS_2–THF (1:1, v/v) to give *cis* and *trans* mixture **2** (0.074 g, 14%) as orange solids. Subsequently, the small amounts of *cis* and *trans* isomers **2** were separated by a gel-permeation chromatography eluted with CS_2 after a 6 time recycle for the characterization of its basic properties. The *cis*/*trans* ratio was nearly 1/5 from the isolated yields. Slow evaporation of the CS_2–hexane (1:1, v/v) solution of *cis*-**2** and the CS_2–CH_2Cl_2 (1:1, v/v) solution of *trans*-**2** gave orange block and orange plate suitable for X-ray analysis, respectively. Selected data: *cis*-**2**, Mp. 257–270 °C (decomp.); ^1H NMR (300 MHz; $CDCl_3/CS_2 = 1/1$), δ 7.15 (s, 4H), 1.44 (s, 6H); m/z (FAB-MS), 1056 (M^+); Anal. Calcd for $C_{14}H_{10}Sb_2Se_8{\cdot}0.7THF$, *cis* and *trans* mixture: C, 18.28; H, 1.41. Found: C, 18.24, H, 1.45. *trans*-**2**, mp. 163–170 °C (decomp.); ^1H NMR (300 MHz; $CDCl_3/CS_2 = 1/1$), δ 7.16 (s, 4H), 1.40 (s, 6H); m/z (FAB-MS), 1056 (M^+). Compound **3**, mp. 167–168 °C (decomp.); ^1H NMR ($CDCl_3/CS_2 = 1/1$, 300 MHz), δ 7.36 (s, 2H), 7.14 (d, 4H), 1.32 (s, 3H); m/z (FAB-MS), 919 (M^+); Anal. Calcd for $C_{13}H_9SbSe_8$: C, 17.00; H, 0.99; Se, 68.76. Found: C, 17.01, H, 0.97; Se, 68.53.
13. Crystal data for **1**: $C_{13}H_9S_8Sb$, MW = 543.44, monoclinic, space group *P*c, $a = 13.233(10)$, $b = 5.648(4)$, $c = 13.663(10)$ Å, $\beta = 114.70(1)°$, $V = 927(1)$ Å^3, $T = 297$ K, $\mu = 2.376$ mm^{-1}, $Z = 2$, 7601 reflections measured, 3797 unique ($R_{\text{int}} = 0.036$). Final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0335$, $wR_2 = 0.0880$. For *cis*-**2**: $C_{14}H_{10}Sb_2Se_8$, MW = 1053.41, orthorhombic, space group *P*nma, $a = 10.321(5)$, $b = 13.085(7)$, $c = 16.696(9)$ Å, $V = 2254(2)$ Å^3, $T = 297$ K, $\mu = 15.306$ mm^{-1}, $Z = 4$, 18 441 reflections measured, 2687 unique ($R_{\text{int}} = 0.0404$). Final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0275$, $wR_2 = 0.0796$. For *trans*-**2**: $C_{28}H_{20}Sb_4Se_{16}{\cdot}CS_2$, MW = 2182.96, triclinic, space group $P\bar{1}$, $a = 8.990(3)$, $b = 11.611(4)$, $c = 11.839(4)$ Å, $\alpha = 97.738(6)°$, $\beta = 90.959(5)°$, $\gamma = 96.954(4)°$, $V = 1214.9(6)$ Å^3, $T = 297$ K, $\mu = 14.293$ mm^{-1}, $Z = 1$, 9892 reflections measured, 5491 unique ($R_{\text{int}} = 0.0494$). Final R indices [$I > 2\sigma(I)$]: $R_1 = 0.0759$, $wR_2 = 0.2154$. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and deposition numbers CCDC 280850–280852.
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