

A Second Crystal Modification of Bis[2,4,6-Tris(trifluoromethyl)phenyl]stannylene: A Stannylene (Stannanediyl) Dimer with Weak Tin–Tin Interactions

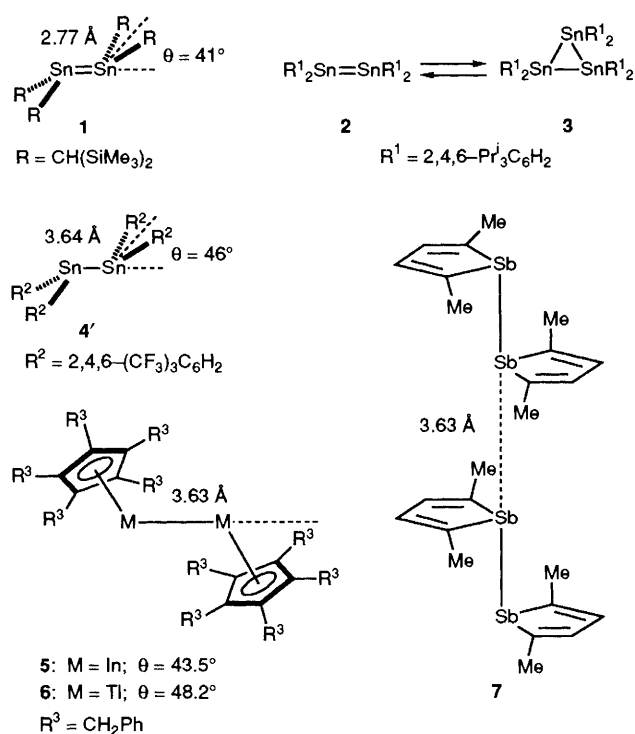
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In a second crystal modification **4'** the stannylene $[2,3,5-(\text{CF}_3)_3\text{C}_6\text{H}_2]_2\text{Sn}$ forms a weakly associated dimer with a long tin–tin distance of 3.639(1) Å; this structure is compared with the known dimeric structures of the species $[(\text{PhCH}_2)_5\text{C}_5\text{In}]_2$ **5**, $[(\text{PhCH}_2)_5\text{C}_5\text{Tl}]_2$ **6** and 2,2',5,5'-tetramethylbistibole **7** with an s^2 electronic configuration.

In 1973 Lappert and Davidson described the first dialkylstannylene **1**, a milestone in the history of low-coordinated main group element compounds.¹ In the solid state it consists of a *trans*-bent dimer with a tin–tin distance of 2.768 Å.² The nature of bonding³ in this 'distannene' and its rich chemistry⁴

have attracted much interest throughout the years. In solution **1** easily dissociates into the monomers ($\Delta H = 12.8 \text{ kcal mol}^{-1}$, $\Delta S = 33 \text{ cal K}^{-1} \text{ mol}^{-1}$; 1 cal = 4.184 J) as indicated by NMR spectroscopy.⁵ In 1985 Masamune and Sita described the synthesis of the tetraaryl-distannene **2** which was charac-



Scheme 1

terized in solution by UV and NMR spectroscopy.⁶ This dimer does not dissociate into the monomeric stannylenes and is in thermal equilibrium with the cyclotristannane **3**.

Recently we have described the stannylene [2,4,6-(CF₃)₃C₆H₂]₂Sn **4** which crystallizes from cold *n*-hexane solution as bright yellow needles. Even in the solid state it is a monomer stabilized by weak tin-fluorine interactions.⁷ We have now found a second crystal modification **4'** of **4** (**4** indicates the yellow crystal modification throughout) which is obtained pure upon slow sublimation at 0.01 Torr (1 Torr = 133.322 Pa) and 40 °C in the form of large sparkling red crystals. Alternatively, **4'** is obtained cocrystallized with the yellow modification from *n*-hexane-toluene (2 : 1 v/v) solution at -30 °C. This new modification melts sharply at 66 °C, quite different from the melting point of the yellow modification containing the monomer (76 °C).[†] We could not detect any phase transitions for **4** or **4'** by differential scanning calorimetry (DSC) between -30 and +100 °C. Above 150 °C the compound **4-4'** decomposes. The yellow modification is stable at ambient temperature under an inert gas atmosphere in carefully cleaned glassware but it slowly converts to the red modification if impurities like silicone are present. These findings suggest that the red modification **4'** is formed under thermodynamic control while the yellow one is obtained under kinetic control. Parallels for this behaviour are found in the literature for the indium and thallium compounds **5** and **6** (*vide infra*^{8,9}).

The result of an X-ray analysis of the red modification **4'** is shown in Fig. 1.[‡] Two stannylene units are linked by a very

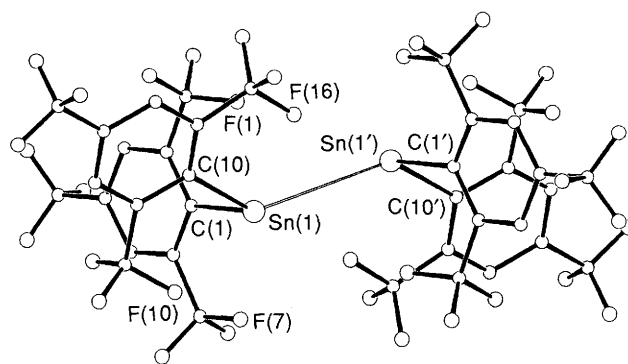


Fig. 1 Molecular structure of **4'**; selected bond lengths or separations (Å) and angles (°): Sn(1)-Sn(1') 3.639(1), C(10)-Sn(1) 2.284(3), F(1)-Sn(1) 2.711(2), F(7)-Sn(1) 2.803(3), F(10)-Sn(1) 2.689(2), F(16)-Sn(1) 2.826(2); C(10)-Sn(1)-C(1) 95.1(1), C(1)-Sn(1)-Sn(1') 102.8(2), C(10)-Sn(1)-Sn(1') 135.1(2)

long tin-tin interaction of 3.639(1) Å which is 0.83 Å longer than tin-tin bonds in α -tin (2.81 Å) and 0.62/0.46 Å longer than tin-tin contacts in β -tin (3.02/3.18 Å).¹⁰ Despite this very long tin-tin distance in **4'** compared to **1** the orientation of the stannylene units defined by the angle θ is almost the same (46° vs. 41°, Scheme 1). Bond length and angles within the stannylene fragments in **4'** do not vary significantly from those in monomeric **4**.

It is instructive to compare the stannylene 'dimer' **4'** with the solid state structures of pentabenzylcyclopentadienylindium **5**⁸ and -thallium **6**⁹ as well as that of 2,2',5,5'-tetramethylbistibole **7**¹¹ (Scheme 1). Interestingly, **5** and **6** are obtained in two different crystal modifications as well which were both characterized by means of X-ray analysis in the case of the thallium compound **6**. Comparable to the observations made for **4/4'**, the deeper coloured modification obtained by thermodynamic controlled crystallisation consists of the dimer shown in Scheme 1. In each compound **4'**, **5**, **6** and **7** intermolecular distances in the region of 3.6 Å are observed. The tilt angle θ amounts in every case roughly 45°. Calculations performed for H₂Tl₂,^{12,13} (C₅H₅)₂In₂¹⁴ and (C₄H₄Sb)₂¹⁵ at various levels of sophistication indicate that there are bonding interactions in the bent dimers. However, these are very weak and due to correlation effects as shown by Schwerdtfeger using configuration interaction calculations including relativistic spin-orbit corrections.¹³ In the case of H₂Tl₂ the bent structure ($\theta = 65^\circ$) lies 14 kcal mol⁻¹ below the dissociation limit and does not correspond to the global minimum on the potential hypersurface. A second deeper minimum was found at a tilt angle θ of 141.5°.

Whatever is the exact nature of the 'bonding' between the monomeric 5s² species RIn, R₂Sn and R₃Sb the finding of the structure of **4'** has completed a series of compounds of groups 13 to 15 in which similar electronic effects may be assumed based on the experimental facts: (i) the dimerisation is clearly a solid-state phenomenon accompanied by a bathochromic shift in the electronic absorption. § In the case of **4'**, **5** and **6** the modifications containing the dimers are obtained by crystallisation under thermodynamic control. (ii) The distance of approximately 3.6 Å between the monomeric fragments seems to be a predominant value, as does (iii) the tilt angle θ of 45°. A change of ligands in the stannylenes **1**, **2** and **4** influences the stability of the dimers, **2** being the most stable. Intramolecular fluorine-tin contacts which saturate the low-coordinated tin centres to some extent prevent stronger association in **4'**. The orientation of the stannylene units found

[†] The originally reported⁷ m.p. is 73 °C in a sealed capillary. The m.p. we report now was determined by DSC.

[‡] *Crystal data*: **4'**: triclinic, $\bar{P}1$, $a = 8.702(6)$, $b = 10.939(8)$, $c = 12.892(10)$ Å, $\alpha = 68.286(6)$, $\beta = 87.12(6)$, $\gamma = 71.04(6)^\circ$, $Z = 2$, four-circle diffractometer (Mo-K α radiation, ω scan, $2\theta = 3\text{--}60^\circ$), 6173 measured reflections, 4450 observed [$I > 2\sigma(I)$]. Nonhydrogen atoms anisotropic, hydrogen atoms isotropic, the *para*-CF₃ groups are disordered; 416 parameters, $R = 0.038$, $R_w = 0.047$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ Attempts to obtain solid-state UV spectra failed owing to the sensitivity of **4'**.

from molecular models of **4'** leads to no severe repulsive fluorine–fluorine contacts even if the tin–tin distance is diminished to 2.78 Å.

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