The Structure of Tetramethyldistibine

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Summary: The thermochromic tetramethyldistibine forms orthorhombic red crystals in which the molecules adopt a staggered trans conformation. The antimony atoms are aligned in chains with close (3.645 Å) intermolecular contacts. In the yellow liquid phase the distibine populates other conformations.

Fifty years ago Paneth reported that tetramethyldistibine (**1**) showed remarkable thermochromic behavior.[1] The distibine is a bright red solid (λ_{max} = 530 nm by diffuse reflectance) which melts reversibly at 17 °C to a pale yellow liquid. Solutions of **1** in pentane are also pale yellow (λ_{max} < 220 nm, weak end absorption to 450 nm). Recently several other thermochromic distibines have been prepared.[2-7] Crystal structures of two of them, tetramethylbistibolyl (**2**)[2] and tetrakis(trimethylsilyl)distibine (**3**),[3] show similar packing in which the antimony atoms are aligned in chains with close intermolecular Sb···Sb contacts. It has been suggested that the solid-phase colors are due to electronic interaction along these Sb–Sb···Sb–Sb chains.[2,8] We now wish to report on the crystal structure of tetramethyldistibine and on data which bear on its molecular structure in solution.

Me₄Sb₂   [structure]   (Me₃Si)₄Sb₂

1   **3**

2
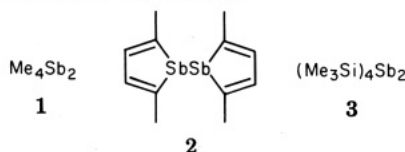
A 0.050 × 0.080 × 0.080 mm crystal grown from cooled liquid sealed in a thin walled capillary was used for data collection. The crystal was cooled to −160 °C and characterized by a reciprocal lattice search technique.[9] The space group and cell data are as follows: orthorhombic,

Figure 1. Crystal packing drawing of the solid-state structure of tetramethyldistibine. Six molecules are illustrated in two chains. The bond distances are as follows: Sb–Sb = 2.862 (2), 3.645 (1) Å; mean SbC = 2.15 (2) Å. The bond angles are as follows: mean SbSbC = 93.6 (6)°; mean CSbC = 93.5 (15)°.

space group *Pmnb* with a = 11.314 (6) Å, b = 11.507 (6) Å, c = 6.507 (2) Å, V = 847.1 Å³, d = 2.381 g/cm³, and Z = 4. A total of 1769 independent reflections with 6° < 2θ (Mo Kᾱ) < 45° were collected by using a Picker four-circle goniostat equipped with a Furnas Monochromator (HOG crystal) and Picker X-ray ϕ generator interfaced to a TI980 minicomputer. The data were reduced by procedures previously described, and the structure was solved by inspection of a Patterson synthesis.[10] Hydrogen atoms were included in the final refinement as fixed atom contributors. Final residuals were as follows: $R(F)$ = 0.059 and $R_w(F)$ = 0.070.[11]

The crystal packing structure of tetramethyldistibine is illustrated in Figure 1. The SbSb and SbC bond lengths and the bond angles about the Sb atoms are very similar to those reported for **2**,[2] **3**,[3] and tetraphenyldistibine (**4**).[12] All four distibines adopt a staggered trans conformation about the Sb–Sb axis.

However, tetramethyldistibine must adopt a different molecular structure in the liquid phase and in solution. The Raman spectrum of the solid shows an intense band at 179 cm⁻¹ assigned to the trans Sb–Sb stretch, while the liquid has two Sb–Sb bands (175 and 143 cm⁻¹), indicating population of a second (probably gauche) conformer.[13] The C NMR of **1** in solution has a resonance at δ (C_4D_8O) −10.6, while in the solid it is shifted to δ −6.4.[14] Tetramethyldistibine shows a dipole moment of 0.95 ± 0.04 D in benzene. Since the symmetrical trans conformation can have no dipole moment, a significant fraction of the tetramethyldistibine molecules must adopt another conformation.

It is particularly interesting to note that the crystal packing structure of **1** is nearly identical with that of **2**. The chains of Sb atoms are completely colinear with alternating intramolecular and short "intermolecular" separations. The intermolecular Sb···Sb separations at 3.645 (2) Å for **1** and 3.625 (1) Å for **2** are only about 25% longer than the intramolecular bond length. In the more sterically congested tetrakis(trimethylsilyl)distibine (**3**), the chains of Sb atoms are not linear and the Sb···Sb separation is greater at 3.99 Å.

The antimony atoms of distibines use primarily p orbitals for bonding since the bond angles about antimony

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(3) Becker, G.; Freudenblum, H.; Witthauer, C. *Z. Anorg. Allg. Chem.* **1982**, *492*, 37.
(4) Breunig, H. J.; Breunig-Lyriti, V. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1979**, *34B*, 926.
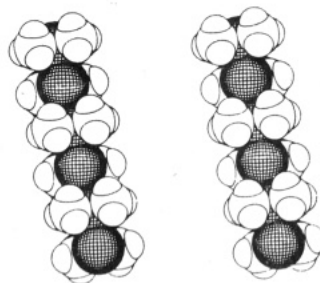(5) Meinema, H. A.; Martens, H. F.; Noltes, J. G.; Bertazzi, N.; Barbieri, R. *J. Organomet. Chem.* **1977**, *136*, 173.
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(7) Ashe, A. J., III; Ludwig, E. G., Jr.; Pommerening, H. *Organometallics* **1983**, *2*, 1573.
(8) Hughbanks, T.; Hoffmann, R.; Whangbo, M.-H.; Stewart, K. R.; Eisenstein, O.; Canadell, E. *J. Am. Chem. Soc.* **1982**, *104*, 3876.
(9) Huffman, J. C. Ph.D. Thesis, Indiana University, Bloomington, IN 1974.

(10) Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 2755.
(11) $R(F) = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$. $R_w(F) = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.
(12) von Deuten, K.; Rehder, D. *Cryst. Struct. Commun.* **1980**, *9*, 167.
(13) (a) Breunig, H. J.; Breunig-Lyriti, V.; Fichtner, W. *Z. Anorg. Allg. Chem.* **1982**, *487*, 111. (b) However, see: Bürger, H.; Eujen, R.; Becker, G.; Mundt, O.; Westerhaussen, M.; Witthauer, C. *J. Mol. Struct.* **1983**, *98*, 265.
(14) The solid C NMR spectrum was recorded by the Colorado State University Regional NMR Center funded by the National Science Foundation Grant No. CHE 78-18581.

are close to 90°. The Sb 5_{p_z} orbitals must be directed along the intermolecular chain of Sb atoms, and there is likely to be a σ-type overlap along the chains of 1, 2, and 3. The intermolecular $Sb(5_{p_z})Sb(5_{p_z})$ overlap integrals of 1, 2, and 3 are 0.168, 0.172, and 0.103, respectively, while the intramolecular overlap integrals are close to 0.37 in all cases.[15] A MO treatment by Hoffmann et al.[8] suggested that the blue (λ_{max} = 605 nm) color of solid 2 is due to a $\sigma \rightarrow \pi^*$ excitation. The structurally similar tetramethyldistibine is not expected to have low-lying π^* orbitals. Thus the blue shift between 2 and 1 corresponding to a 0.3-eV smaller band gap is consistent with the Hoffmann model. On the other hand, the much greater Sb···Sb separation in 3

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(15) Calculated for the appropriate distances from tables of Roothaen, Hartree-Fock atomic wave functions. Clementi, E.; Roetti, C. *At. Data Nucl. Data Tables* **1974**, *14*, 177.

suggests a much weaker interaction. However, the color (λ_{max} = 520 nm)[16] and hence the band gap of 3 are virtually identical with that of 1. Clearly, a more detailed theoretical study of the thermochromic distibines is desirable.

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Supplementary Material Available: Tables of atomic positional parameters, thermal parameters, bonded distances and angles, and structure factors for 1 (7 pages). Ordering information is given on any current masthead page.

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(16) Unlike 1 the reflectance spectrum of 3 does show a higher intensity absorption maximum at 300 nm.

Additions and Corrections

Adrian G. Brook, Fereydon Abdesaken, Gerhard Gutekunst, and Nicholas Plavac: ¹³C and ²⁹Si Chemical Shifts and Coupling Constants Involving Tris(trimethylsilyl)silyl Systems. **1982**, *1*, 994–998.

In Table IV an erroneous assignment of signals for the R = *adamantyl* carbons was made, chemical shifts for C^E and C^F having been exchanged, as were those for C^e and C^f. In addition, the value of 38.4 ppm (originally assigned to C^F) should be 28.4 ppm, now assigned to C^E, as confirmed by analysis of multiplicities in the coupled spectra.

James M. Burlitch, Susan E. Hayes, and George E. Whitwell II: Synthesis of (Transition metal carbonyl)zinc Alkoxides and the Crystal Structure of Tetrameric (Dicarbonyl(η^5-cyclopentadienyl)iron)zinc Methoxide. **1982**, *1*, 1074–1083.

In Table III the z coordinates of all atoms and the y coordinates of Fe(2), C(21), C(22), O(22), C(23), C(24), C(25), C(26), and C(27) should have a negative sign.

In Table II the calculated density should be 1.85 g/cm³.

Alan Cameron, Vedene H. Smith, and Michael C. Baird: Oxidatively Induced Migration of Hydrogen from Metal to Carbon Monoxide. **1983**, *2*, 465–467.

We must unfortunately retract the claim that oxidation of $CpFe(CO)_2H$ in an alcohol by copper(II) salts results in formation of a formate ester. While the detection of

methyl formate (from oxidation in methanol) had seemed unequivocal—the GC analyses were carried out by experienced operators on an HP 5880A equipped with a capillary column—we eventually realized that the product detected was, surprisingly, cyclopentadiene, which has a retention time almost identical with that of methyl formate. The identities of the misattributed products from reactions in ethanol and *n*-propanol are not known. Errors arose in these cases because the product mixtures were studied by GC using a packed column that was found later not to have the separating powers expected of it. On the other hand ceric oxidation of $CpMo(CO)_3H$ in methanol did yield methyl formate but, via a low-yield oxidation of the solvent, a reaction not anticipated from reading of the literature.

Thus the evidence for formyl intermediates is not valid.

C. Chatgialoglu, K. U. Ingold, J. Lusztyk, A. S. Nazran, and J. C. Scaiano: Formation, Decay, and Spectral Characterization of Some Alkyl- and Aryl-Substituted Carbon-, Silicon-, Germanium-, and Tin-Centered Radicals. **1983**, *2*, 1332–1335.

Figure 1 refers to reaction 1, not to reaction 4 as indicated in the text. Its caption should read as follows: Effect of Ph_3SiH on the pseudo-first-order rate constant (k_{exptl}) for the formation of Ph_3Si, monitored at 325 nm (see insert for a representative trace). Full details are given in Table VII (supplementary material).