Gas-Phase Molecular Structure of Tetramethyldistibine, 
\((\text{CH}_3)_2\text{Sb} = \text{Sb}(\text{CH}_3)_2\)

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The structure of tetramethyldistibine has been investigated in the gas at 74 °C by electron diffraction. Although gauche and anti forms of the molecule probably exist, it was not possible to determine the rotameric composition because of the small relative scattering from the torsion-sensitive distances. The results for the more important distances \((r_a)\), bond angles \((\lambda)\), and amplitudes of vibration \((l)\) with estimated 2a uncertainties are \(r(\text{Sb}-\text{Sb}) = 281.8 (4) \text{ pm}\), \(r(\text{Sb}-\text{C}) = 216.6 (4) \text{ pm}\), \(r(\text{C}-\text{H}) = 109.5 (10) \text{ pm}\), \(\angle(\text{Sb}-\text{Sb}-\text{C}) = 95.5 (7)\), \(\angle(\text{C}-\text{Sb}-\text{C}) = 102.7 (23)\), \(\angle(\text{Sb}-\text{C}-\text{H}) = 5.5 (6)\) pm, and \(\angle(\text{C}-\text{H}) = 5.9 (11)\) pm. The \(\text{Sb}-\text{Sb}\) bond length is definitely shorter than its in the crystal. The longer bonds in the crystal probably result from electron delocalization along chains of \(\text{Sb}\) atoms which results in a decrease of the bond order of the \(\text{Sb}-\text{Sb}\) bonds.

Tetramethyldistibine (hereafter TMDS) has long been known to undergo a striking color change on melting: the crystals are deep red; the liquid is pale yellow. The color of TMDS vapor could be associated with a change in molecular structure from which it appears that there may exist more than one conformation in the latter. It seemed possible that the color change on melting was the length of the \(\text{Sb}-\text{Sb}\) bond for comparison with that large enough to measure. Since the color of TMDS vapor was the intermolecular \(\text{Sb}-\text{Sb}\) distances are about 70 pm shorter than a van der Waals contact. The vibrational spectra of the solid and liquid have also been investigated from which it appears that there may exist more than one conformation in the latter.

It seemed possible that the color change on melting could be associated with a change in molecular structure large enough to measure. Since the color of TMDS vapor is similar to that of the liquid, an electron diffraction investigation of the gas was indicated. Our main interest was the length of the \(\text{Sb}-\text{Sb}\) bond for comparison with that in the crystal. We were also interested in a possible determination of the temperature dependence of the conformational composition of the gas and ultimately of the thermodynamics of the conformational equilibrium. As it turned out, the composition could be measured only very imprecisely, and we therefore limited our work to the data gathered at a single temperature.

Experimental Section

Material. The sample of TMDS was prepared at the University of Michigan as described elsewhere. Although the purity of our particular sample was not checked, past experience suggests the more important distances (\(r_a\)), bond angles (\(\lambda\)), and amplitudes of vibration (\(l\)) with estimated 2a uncertainties are \(r(\text{Sb}-\text{Sb}) = 281.8 (4)\) pm, \(r(\text{Sb}-\text{C}) = 216.6 (4)\) pm, \(r(\text{C}-\text{H}) = 109.5 (10)\) pm, \(\angle(\text{Sb}-\text{Sb}-\text{C}) = 95.5 (7)\), \(\angle(\text{C}-\text{Sb}-\text{C}) = 102.7 (23)\), \(\angle(\text{Sb}-\text{C}-\text{H}) = 5.5 (6)\) pm, and \(\angle(\text{C}-\text{H}) = 5.9 (11)\) pm. The \(\text{Sb}-\text{Sb}\) bond length is definitely shorter than in the crystal. The longer bonds in the crystal probably result from electron delocalization along chains of \(\text{Sb}\) atoms which results in a decrease of the bond order of the \(\text{Sb}-\text{Sb}\) bonds.

Other structural parameters were the mole fractions of the possible impurities mentioned earlier. Vibrational amplitude parameters were formed in the usual way following tests that indicated which one could be refined alone and which ones were likely candidates for refinement in groups. For amplitudes involving \(\text{H}\), we estimated uncertainties of 2a. Amplitudes in parentheses were calculated from an approximate force field (for details see text); quantities in brackets were assumed. The first seven parameters were used to define the geometry. Range of distances and amplitudes in free rotation model. Mole fractions.

\[ R^2 = \frac{\sum w \Delta \rho^2}{\sum w (s_j (\text{obsd}) - s_j (\text{calc})^2}} \]

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\[ R^2 = \frac{\sum w \Delta \rho^2}{\sum w (s_j (\text{obsd}) - s_j (\text{calc})^2}} \]
Table II. Correlation Matrix (×100) for TMDS Model A

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*Standard deviations from least squares. Distances (r) and amplitudes (l) in picometers; angles (L) in degrees.

Figure 1. Intensity curves. The s²I(s) curves from each plate are shown superimposed on the final backgrounds and are magnified 8 times relative to the backgrounds. The theoretical curve is for model A of Table I. The difference curves are experimental minus theoretical.

Figure 2. Radial distribution curves. The experimental curve was calculated from I(s) = I₀(s)/[Z₁Z₂A₁A₂s² exp(-25s²)], where s² = s/s₋₀, is a composite of the average curves of Figure 1 with addition of theoretical data from model A for s ≤ 0.02 pm⁻¹, and the A's are modified electron scattering amplitudes.

Results and Discussion

The results for two of the many models tested are summarized in Table I. Model A, which gives the best fit to our data, comprises anti and gauche conformers of TMDS in equal amounts, a small amount of the possible impurity C₂H₅Br₂ (the structure of which was taken from the literature[10]), and a representation[11] of free rotation for the methyl groups. Model B has the anti and gauche conformers in 0.95:0.05 mole ratio, lacks the impurity, and treats the methyl groups as nonrotating entities. An important conclusion illustrated by the results for these models, but drawn from consideration of results from a much larger group, is that the values of the main parameters (the Sb-Sb, Sb-C, and C-H bond lengths and amplitudes and the Sb-Sb-C, C-Sb-C, and Sb-C-H bond angles) are essentially independent of model, i.e., independent of uncertainties about the amount of impurity, the rotomeric composition, the nature of the methyl group torsional motion, and values assumed for certain of the amplitudes of vibration. The values of these parameters may thus be accepted with confidence.

There is nothing unusual about the structure of TMDS. Although the bond distances are somewhat longer than the sum of the Pauling covalent single bond radii (Sb-C = 213 pm; Sb-Sb = 272 pm), the Sb-C bond length and the

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C–Sb–C bond angle are very close to those found in Sb-(CH₃)₃ (216.3 (3) pm and 94.1 (5)°). Perhaps the most interesting of the parameter values is the Sb–Sb bond length. At 281.8 (4) pm in the gas, this bond is certainly shorter than in the crystal (286.2 (2) pm and 283.1 (1) pm). Presumably electron delocalization occurs in the crystal along the linear chains of Sb–Sb-related Sb atoms, thereby lengthening the Sb–Sb bond relative to that in the monomeric gas and at the same time leading to a rather short intermolecular Sb–Sb contact. One supposes that relative to the crystal, a similar bond shortening occurs in the liquid where the rupture of the chains of Sb atoms by the melting process is consistent with the accompanying color change. We had hoped to learn something about the rotomeric composition and then, by measurement of the temperature effect of the composition, to estimate the energy and entropy difference of the conformers. However, the difference between the scattering from the C–C terms in the anti and gauche forms of the molecule proved to be too small to measure. The reason is partly that this scattering is only a small part (less than 3%) of the total, but also that the two forms are otherwise distinguishable only by the fact that the anti form has two syn and two anti C–C distances, while the gauche form has three syn and one anti.

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Registry No. TMDs, 41422-43-9.

Supplementary Material Available: Tables of the total scattered intensity, the final backgrounds, and the average molecular intensities (11 pages). Ordering information is given on any current masthead page.

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Unprecedented nucleophilic activation of coordinated carbon monoxide in [CpCo(dppe)CO]²⁺. The synthesis of this and closely related dications is reported along with the crystal structure of [CpCo(dppe)CO](PF₆)₂·(CH₃)₂CO. Crystal data: monoclinic, C2/c, a = 20.266 (8) Å; b = 16.102 (2) Å; c = 22.658 (6) Å; β = 106.92 (2)°; V = 3903 (2) Å³; Z = 4; R = 7.5%, R_w = 7.2%. The unusual reactivity of CO is demonstrated by direct attack on CO by relatively unreactive nucleophiles, such as aniline and higher alcohols. The arylcarbamoyl complex from aniline, (CpCo(dppe)CO)⁺, whose molecular structure is reported as the PF₆⁻·CH₃CO(O)OC₄H₉ salt, is the first synthesized by direct attack on CO. Crystal data: monoclinic, C2/c, a = 22.553 (5) Å; b = 23.345 (6) Å; c = 19.035 (6) Å; β = 111.20 (2)°; V = 9475 (4) Å³; Z = 8; R = 10.5%, R_w = 10.9%. An unusual type of angular disorder of the Cp ring is present in this complex. Soft nucleophiles displace CO from [CpCo(dppe)CO]²⁺. The product of the reaction with C₃H₅SH produces a Co–S bond which was structurally characterized in the case of [CpCo(dppe)SC₂H₅]⁺·(PF₆)·(CH₃)₂CO. Crystal data: monoclinic, C2/c, a = 14.701 (3) Å; b = 16.276 (6) Å; c = 19.373 (3) Å; β = 105.24 (1)°; V = 4072 (2) Å³; Z = 4; R = 5.2%, R_w = 5.4%.

**Introduction**

Activation of CO toward nucleophilic attack by attachment to a metal center (eq 1) is an important step in the reaction mechanism of the Fischer–Tropsch process,¹ the water-gas shift reaction,² and selected organic syntheses involving homogeneous catalysis.₃ The nucleophilicity of CO should be enhanced by association with metals having a high formal oxidation state and/or by incorporating CO into complexes with a net positive charge. Both of these features reduce the M–C=O back-bonding and thereby mitigate against stability of the complex to the point that mononuclear, dicaticonic, metal–carbonyl complexes have been frequently isolated.₄–⁶

The pursuit of uncharacteristic reactions involving nucleophilic attack on coordinated ligands attached to Co(III)⁷ led us to attempt the preparation of an unusually reactive Co(III)–CO bond. This paper describes several

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**Notes:**


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