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Gas-Phase Molecular Structure of Tetramethyldistibine, (CH₃)₂Sb–Sb(CH₃)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 rotomeric composition because of the small relative scattering from the torsion-sensitive distances. The results for the more important distances (r_a), bond angles ($\angle$), and amplitudes of vibration (l) with estimated 2σ uncertainties are r(Sb–Sb) = 281.8 (4) pm, r(Sb–C) = 216.6 (4) pm, r(C–H) = 109.8 (10) pm, $\angle$(SbSbC) = 95.5 (7)°, $\angle$(CSbC) = 102.7 (65)°, $\angle$(SbCH) = 114.3 (23)°, l(Sb–Sb) = 6.9 (4) pm, l(Sb–C) = 5.4 (5) pm, and l(C–H) = 5.9 (11) pm. The Sb–Sb bond length is definitely shorter than it is in the crystal. The longer bonds in the crystal probably result from electron delocalization along chains of Sb atoms which results in a decrease of the bond order of the Sb–Sb bonds.

Tetramethyldistibine (hereafter TMDS) has long been known[1] to undergo a striking color change on melting: the crystals are deep red; the liquid is pale yellow. The molecules in the crystal exist in the anti conformation with the antimony atoms arranged in linear chains;[2] at 367.8 (1) pm the intermolecular Sb⋯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[3,4] from which it appears that there may exist more than one conformer 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 Sb–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.[5] Although the purity of our particular sample was not checked, past experience suggests at most only a few percent impurity, most likely trimethylstibine and/or 1,2-dibromoethane.

Experiments. The electron diffraction patterns were made in the Oregon State apparatus at two camera distances (long and intermediate, nominally 75 and 30 cm) with an accelerating voltage of about 44 kV, exposure times of 70–110 s (long camera) and 165–180 s (intermediate camera), and beam currents of 0.20–0.30 μA; the nozzle temperature was 74 °C. Four plates from the long and five from the intermediate distance were selected for analysis. The procedures for obtaining the refined molecular structure have been described.[6,7] The electron scattering amplitudes and phases were obtained from tables.[8] Figure 1 shows the final intensity curves and Figure 2 the experimental radial distribution curve.

Structure Analysis. Structural parameters for the TMDS system were taken to be the bond lengths Sb–Sb, Sb–C, and C–H, the bond angles Sb–Sb–C, C–Sb–C, and Sb–C–H, the torsion angles C–Sb–Sb–C and Sb–Sb–C–H, and the anti-gauche composition represented by the mole fraction of the gauche conformer.

Table I. Structural Results for Tetramethyldistibine[a,b]

	model A		model B	
	r_a, $\angle_a$	l	r_a, $\angle_a$	l
r(Sb–Sb)	281.8 (4)	6.9 (4)	281.8 (4)	6.9 (4)
r(Sb–C)	216.6 (4)	5.4 (5)	216.3 (5)	5.6 (5)
r(C–H)	109.8 (10)	5.9 (11)	109.6 (10)	5.9 (11)
$\angle$(SbSbC)	95.5 (7)		95.3 (15)	
$\angle$(CSbC)	102.7 (65)		102.5 (102)	
$\angle$(SbCH)	114.3 (23)		114.6 (23)	
τ(SbSbCH)			29.7 (219)	
r(Sb·C)	371.6 (21)	{15.3}	370.7 (44)	{15.3}
r(C·C)	338.2 (154)	{15.0}	337.4 (240)	{15.0}
r(Sb·H)	280.2 (29)	12.4 (46)	280.3 (29)	11.8 (49)
r(Sb⋯H)			472.3 (52)	[18.0]
r(Sb⋯H)	}341–477[c]	}10–20[c]	356.2 (124)	[21.0]
r(Sb⋯H)			406.0 (272)	[21.0]
r(C⋯C)	419.8 (111)	{26.0}	418.6 (139)	{26.0}
r(C⋯C)	539.1 (30)	{14.8}	537.7 (61)	{14.8}
r(C⋯C)	374.2 (90)	{26.0}	372.3 (179)	{26.0}
r(C⋯C)	531.0 (84)	{14.8}	529.3 (158)	{14.8}
χ_{anti}:χ_{gauche}[d]	[0.46:0.46]		[0.95:0.05]	
χ(C₂H₄Br₂)[d]	[0.08]			
R[e]	0.079		0.084	

[a] Distances (r) and amplitudes (l) in picometers; angles ($\angle$) in degrees. Quantities in parentheses are estimated 2σ. Amplitudes in braces were calculated from an approximate force field (for details see text); quantities in brackets were assumed. [b] The first seven parameters were used to define the geometry. [c] Range of distances and amplitudes in free rotation model. [d] Mole fractions. [e] $R = [\sum_i w_i \Delta_i^2 / \sum_i w_i (s_i I_i(\text{obsd}))^2]^{1/2}$ where $\Delta_i = s_i I_i(\text{obsd}) - s_i I_i(\text{calcd})$.

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 ones could be refined alone and which ones were likely candidates for refinement in groups. For amplitudes involving H, we esti-

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Table II. Correlation Matrix (×100) for TMDS Model A

		σ^a	r_1	r_2	r_3	$\angle_4$	$\angle_5$	$\angle_6$	l_7	l_8	l_9	l_{10}
1	r(Sb–Sb)	0.09	100	-3	9	-16	-21	-49	17	4	10	10
2	r(Sb–C)	0.14		100	-9	-6	-3	-19	2	-2	-4	-8
3	r(C–H)	0.35			100	4	3	-26	2	2	-6	4
4	$\angle$(SbSbC)	0.26				100	49	-9	-5	-6	-1	5
5	$\angle$(CSbC)	2.30					100	1	-8	-8	<1	21
6	$\angle$(SbCH)	0.80						100	-33	-14	-12	-34
7	l(Sb–Sb)	0.10							100	38	23	57
8	l(Sb–C)	0.15								100	6	31
9	l(C–H)	0.36									100	26
10	l(Sb·H)	1.62										100

^{a} Standard deviations from least squares. Distances (r) and amplitudes (l) in picometers; angles ($\angle$) in degrees.
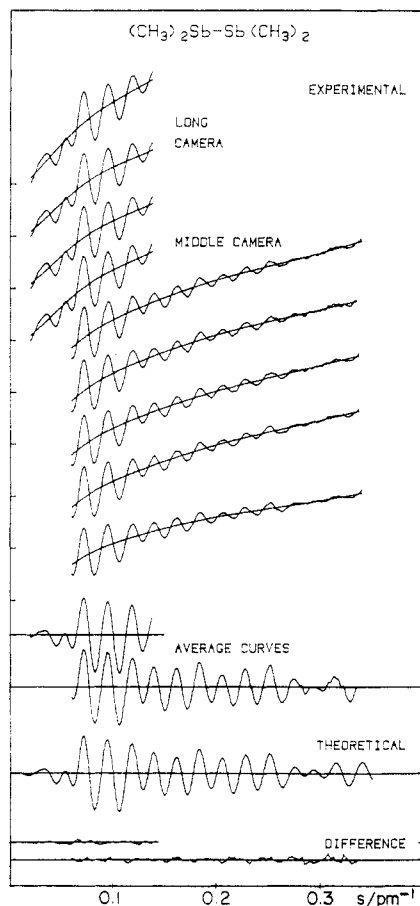

Figure 1. Intensity curves. The $s^4I_t(s)$ curves from each plate are shown superimposed on the final backgrounds and are magnified 8 times relative to the backgrounds. The theoretical curve is for model A of Table I. The difference curves are experimental minus theoretical.

mated reasonable initial values for group members, as well as values we chose not to refine, from experience with other molecules. Values for the nonrefinable, torsion-sensitive C···C amplitudes were estimated from a rough normal coordinate analysis of a pseudo TMDS—a molecule in which each methyl group was replaced by a pseudo atom of mass 15. The force constants were essentially those of Burger et al.[4]

The refinements were carried out in the usual way.[6,7] All terms were included in the calculations except H···H and nonbonded C···H, which were ignored as of no importance compared to scattering from other atomic pairs. Tests showed that no improvement to the fits was obtained by inclusion of the hypothetical impurity Sb(CH$_3$)$_3$,[9] and it was disregarded in the final calculations. Models that included C$_2$H$_4$Br$_2$ as an impurity were found to give a slightly better fit than those without it, although the amounts of the impurity were always small and the associated
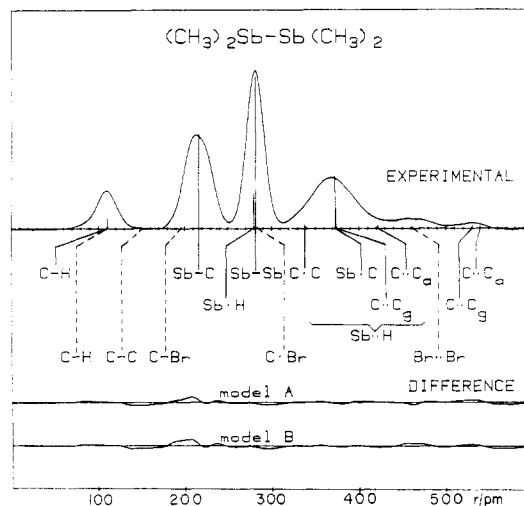

Figure 2. Radial distribution curves. The experimental curve was calculated from $I'(s) = sI_m(s)[Z_{Sb}Z_C/A_{Sb}A_C] \exp(-25s^2)$, where sI_m is a composite of the average curves of Figure 1 with addition of theoretical data from model A for $s \leq 0.02$ pm^{-1}, and the A's are modified electron scattering amplitudes.

uncertainties large enough to make them of marginal significance.

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 C$_2$H$_4$Br$_2$ (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-(CH$_3$)$_3$ (216.3 (3) pm and 94.1 (5)°).[9] 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[12] than in the crystal (286.2 (2)[2a] and 283.1 (1) pm[2b]). Presumably electron delocalization occurs in the crystal along the linear chains of Sb–Sb⋯Sb–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.[2a]

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.

(12) In principle the types of distances in the crystal and gas should not be compared without taking into account the effects of thermal motion. Conversion of our electron diffraction r_g to r_a, a distance type more comparable to the uncorrected X-ray values, would increase the apparent difference by about 0.2 pm. It appears as if one of the reported X-ray values[2a] does not have the thermal motion corrections; these corrections may have been made in the other.

Extreme Electrophilicity of Coordinated Carbon Monoxide in [CpCo(dppe)CO]$^{2+}$

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Unprecedented nucleophilic activation of coordinated carbon monoxide is achieved with [CpCo(dppe)CO]$^{2+}$. The synthesis of this and closely related dications is reported along with the crystal structure of [CpCo(dppe)CO](PF$_6$)$_2$·(CH$_3$)$_2$CO. Crystal data: monoclinic, $P2_1/c$; $a = 13.308$ (3) Å, $b = 15.129$ (4) Å, $c = 20.266$ (8) Å; $\beta = 106.92$ (2)°; $V = 3903$ (2) Å^3; $Z = 4$; $R_F = 7.5\%$, $R_{wF} = 7.2\%$. 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)[C(O)NHC$_6$H$_5$]}$^+$, whose molecular structure is reported as the PF$_6$$^-$·CH$_3$C(O)OC$_2H_5$ 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, $c = 19.303$ (6) Å; $\beta = 111.20$ (2)°; $V = 9475$ (4) Å^3; $Z = 8$; $R_F = 10.5\%$ $R_{wF} = 10.9\%$. 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 C$_6$H$_5$SH produces a Co–S bond which was structurally characterized in the case of [CpCo(dppp)(SC$_6$H$_5$)]PF$_6$·C$_6$H$_6$·(CH$_3$)$_2$CO. Crystal data: monoclinic, $P2_1/c$; $a = 14.701$ (3) Å, $b = 16.276$ (6) Å, $c = 19.373$ (3) Å; $\beta = 105.24$ (1)°; $V = 4472$ (2) Å^3; $Z = 4$; $R_F = 5.2\%$, $R_{wF} = 5.4\%$.

Introduction

Activation of CO toward nucleophilic attack by attachment to a metal center (eq 1) is an important step in the

$$M—C≡O + nuc \longrightarrow M—\overset{\overset{\textstyle O}{\|}}{C}—nuc \qquad (1)$$

$$nuc = H^-, R^-, OR^-, NHRR', \text{ etc}$$
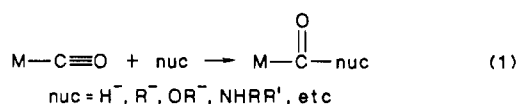
Fischer–Tropsch process,[1] the water-gas shift reaction,[2] and selected organic syntheses involving homogeneous catalysis.[3] The electrophilicity of CO should be enhanced by

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, dicationic, metal–carbonyl complexes have been infrequently 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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