Preliminary communication

The molecular structure of tetrakis(trimethylstannyl)methane by gas electron diffraction

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Abstract

The gas phase electron diffraction data of $C^*(SnMe_3)_4$ recorded with a nozzle temperature of about 120°C are consistent with a molecular model of T symmetry; the bond distances (r_a) are $C^*-Sn = 217.7(3)$, $Sn-C = 216.2(4)$, and $C-H = 112.2(6)$ pm; the valence angles $\angle C^*SnC = 112.3(4)°$ and $\angle SnCH = 111.5(6)°$.

Keywords: Tin; Alkyl; Gas electron diffraction

As our recent attempt to determine the molecular structure of $C(SnMe_3)_4$ by X-ray crystallography was thwarted by disorder of both Sn atoms and methyl groups [1], we now report a structure determination by gas electron diffraction.

The sample was synthesised as previously described [1]. Gas electron diffraction data were recorded with a Balzers Eldigraph KDG-2 unit [2] with a conventional metal inlet system at about 120°C. Exposures were made at nozzle to photographic plate distances of about 50 and 25 cm. Five plates from the first set and six plates from the second were photometered on a modified Joyce-Loebl microdensitometer and the data processed with a program system written by T.G. Strand [3]. Atomic scattering factors were taken from Ref. [4]. Backgrounds were drawn as least-squares adjusted sixth (50 cm plates) or eight (25 cm plates) degree polynomials to the difference between total experimental and calculated molecular intensities. The resulting modified molecular intensity curves are shown in Fig. 1. Structure refinements were carried out with the program KCED26 written by G. Gundersen, S. Samdal, H.M. Seip and T.G. Strand.

Structure refinements were based on a molecular model of T symmetry, see Fig. 2. In the following we shall denote the central carbon atom by C^*. The structure is determined by seven independent parameters, e.g. the C^*-Sn, $Sn-C$ and $C-H$ bond distances, the valence angles $\angle C^*SnC$ and $\angle SnCH$, and the dihedral

angles $\tau(SnC^*SnC)$ and $\tau(C^*SnCH)$. The latter parameter could not be refined and was fixed at 60°, corresponding to a staggered orientation of the methyl groups. The remaining six independent parameters were refined by least-squares calculations on the intensity data along with ten r.m.s. vibrational amplitudes, l. The vibrational amplitudes of the C^*-Sn and $Sn-C$ bond distances were assumened equal. The amplitudes of the nonbonded distances C^*--C and $C--C$ within a $C^*Sn(CH_3)_3$ fragment were strongly correlated with the amplitudes of the nonbonded $Sn--Sn$ distances and were therefore fixed at the amplitudes observed in
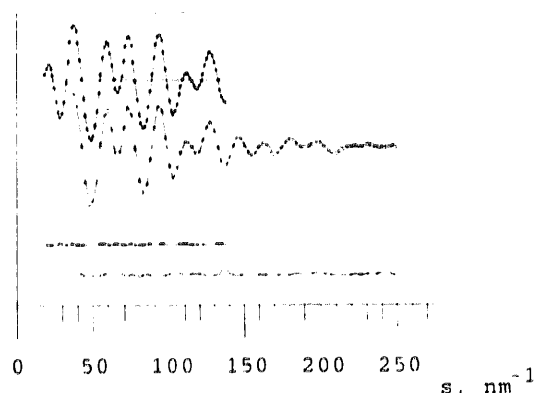

Fig. 1. Experimental (dots) and calculated (lines) modified molecular intensity curves for $C(SnMe_3)_4$. The vertical scale is arbitrary. Below: difference curves.
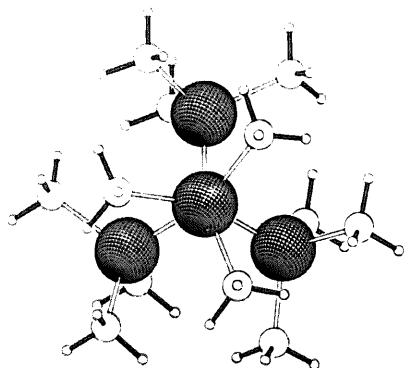
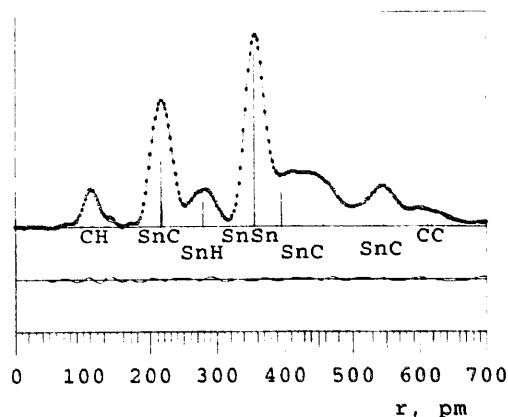Fig. 2. Molecular model of C(SnMe₃)₄, symmetry T, viewed down a threefold symmetry axis (Pluton [5]).

Fig. 3. Experimental (dots) and calculated (line) radial distribution curves for C(SnMe₃)₄. The vertical scale is arbitrary. Below: difference curves. Artificial damping constant $k = 25$ pm².

(CH₃)₄Sn after correction for the temperature differences in the two studies using $\omega_2 = \omega_4 = 150$ cm⁻¹ [6]. The refinements converged to give the best values listed in Table 1. As refinements were carried out with diagonal weight matrices, the e.s.d.s have been doubled to reflect the added uncertainty due to data correlation and further expanded to include an estimated scale uncetainty of 0.1%. Experimental and calculated intensity curves are compared in Fig. 1, experimental and calculated radial distribution curves in Fig. 3. We find the agreement satisfactory.

Table 1
Interatomic distances (r_a), root mean square vibrational amplitudes (l), valence angles and torsional angles in C⁺(Sn(CH₃)₃)₄, molecular symmetry T [a]

	r_a	l
Bond distances		
C⁺−Sn	217.7(3)	7.0(4) [b]
Sn=C	216.2(4)	7.0(4) [b]
C=H	112.2(6)	7.2(8)
Nonbonded distances		
Sn⋯Sn	355.5(4)	11.8(2)
Sn⋯C	395.7(5)	26.4(9)
	456.3(5)	17.4(10)
	545.2(6)	13.2(9)
C⁺⋯C	360.3	[15.9] [c]
C⋯C [d]	346.6	[15.9] [c]
C⋯C [e]	398 to 719	26 to 13
Valence angles		
∠C⁺SnC	112.3(4)	
∠SnCH	111.5(6)	
Torsional angles		
τ(SnC⁺SnC)	38.7(6)	
τ(C⁺SnCH)	[60]	
R-factors [f]	0.029 (50 cm); 0.110 (25 cm);	
	0.042 (total)	

[a] Interatomic distances and root mean square vibrational amplitudes in pm, angles in degrees. Estimated standard deviations in parentheses in units of the last digit.
[b] These amplitudes which were assumed equal.
[c] Transferred from (CH₃)₄Sn after correction for the temperature difference.
[d] Within a Sn(CH₃)₃ fragment.
[e] Between different Sn(CH₃)₃ fragments. $R = [\Sigma W(I_{obs} - I_{calc})²/\Sigma W(I_{obs})²]^{1/2}$.

The peripheral Sn–C(Me) bond distance in C⁺(SnMe₃)₄ is indistinguishable from the Sn–C bond distance in Sn₂(CH₃)₆; 216.5(3) pm [7]. Both may be slightly longer than in Sn(CH₃)₄; 214.3(3) pm [6].

Beagley and coworkers have determined the molecular structure of C⁺(SiMe₃)₄ by gas electron diffraction and found the central C⁺−Si bond to be 3.5 pm longer than the peripheral Si–C(Me) bond [8]. The elongation was attributed to steric repulsion between SiMe₃ groups. The C⁺−Sn bond in C⁺(SnMe₃)₄ is only slightly longer than the peripheral Sn–C(Me) bond; the difference between the two is 1.5(3) pm. Part of the elongation may be due to repulsion between Sn atoms; the Sn⋯Sn distance is 356 pm as compared with an across-angle repulsion diameter of 364 pm [9].

Otherwise the molecule appears to be relatively free from strain. In particular the shortest approach between C atoms in different SnMe₃ groups is 396 pm as compared to the methyl group van der Waals diameter of 360 pm.

The dihedral angle τ(SnC⁺SnC) = 38.7(6)° represents a thermal average, the equilibrium value may well be 60° corresponding to perfect staggering.

The C⁺−Sn bond distance obtained by refinement of a disordered crystal structure, 216.2 pm, is in good agreement with the gas phase value, but the Sn–C(Me) bond distance was found to be some 10 pm shorter than in the gas phase [1]. We believe the discrepancy to be due to the disorder in the crystalline phase which did not permit independent refinement of the positions of primary carbon atoms.

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