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Electron-diffraction Investigation of the Molecular Structure of Tetramethyltin

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The structure parameters of tetramethyltin have been determined by gas-phase electron diffraction to be as follows: $r_g(\text{Sn–C})=2.143_6\pm0.003_0$ Å, $r_g(\text{Sn}\cdots\text{H})=2.764_2\pm0.012_5$ Å, $r_g(\text{C–H})=1.117_9\pm0.009_0$ Å, $l(\text{Sn–C})=0.049_6\pm0.009_8$ Å, and $l(\text{Sn}\cdots\text{H})=0.153_2\pm0.013_2$ Å. The experimental molecular intensity has been well reproduced by the molecular model in which the methyl groups are rotating freely, or nearly freely. The scattering factors, based upon the relativistic Hartree-Fock-Slater or the Hartree-Fock atomic potential, have given a theoretical background in better agreement with the experimental one and have led to a more reasonable Sn–C mean amplitude than did the scattering factors based upon the Thomas-Fermi-Dirac or the Thomas-Fermi atomic potential.

The molecular structures of alkyltin-hydrides,[1] and chlorides[2] in the gas state have recently been investigated by the sector-microphotometer method of electron diffraction. Though tetramethyltin is one of this series, its molecular structure has, however, thus far been determined only by the visual method.[3] The main purpose of the present report is to present a structure determined more accurately by the sector-microphotometer method of electron diffraction and to complete the structural data for organotin compounds.[4]

The second purpose of the present study is concerned with the scattering factors. In a previous study,[5] the small angle scattering of electrons from molecules containing heavy atoms, including $Sn(CH_3)_4$, was observed by a counting technique and the results compared with theory, calculated from a set of the elastic scattering factors based upon the relativistic Hartree-Fock-Slater atomic potentials[6] and the inelastic scattering factors based upon the Hartree-Fock atomic potentials[7] (RHFS, HF), and from a set of the elastic and inelastic scattering factors based upon Thomas-Fermi-Dirac[8] and Thomas-Fermi atomic potentials[9] (TFD, TF) respectively. The (RHFS, HF) scattering factors reproduced the experimental intensities better at small scattering angles, particularly in the range below $s=6$, than did the (TFD,TF) scattering factors. This fitting was in line with the results of the diffraction studies of dimethylmercury[10] and mercury(II) chlorides,[11] where the experimental background agreed better with the (RHFS, HF)-based theoretical background than with the (TFD, TF)-based one. In view of the better agreement of the experimental and theoretical backgrounds, as well as the theoretical sophistication of the atomic potentials, we adopted the (RHFS, HF) scattering factors in the previous structure determinations. The scattering intensities from tetramethyltin, as measured by a photographic method, are expected to provide information on the scattering factors at larger scattering angles, which the counting technique does not cover efficiently. Thus, the present study has been performed under the best possible experimental conditions, particularly with a minimum of extraneous scattering.

Experimental

The diffraction unit used in the present study has been described elsewhere.[12] Photographs were taken with an r^3-sector under the following experimental conditions: accelerating voltage, about 42 kV; camera length; 24.43 cm; sample pressure, 10—25 Torr; exposure time, 40—60 s; beam current, 0.09 μA; and room temperature, 17 °C. The scale factor was determined with reference to the diffraction patterns of carbon disulfide taken in the same sequence. The photographs of carbon disulfide were also used for judging if

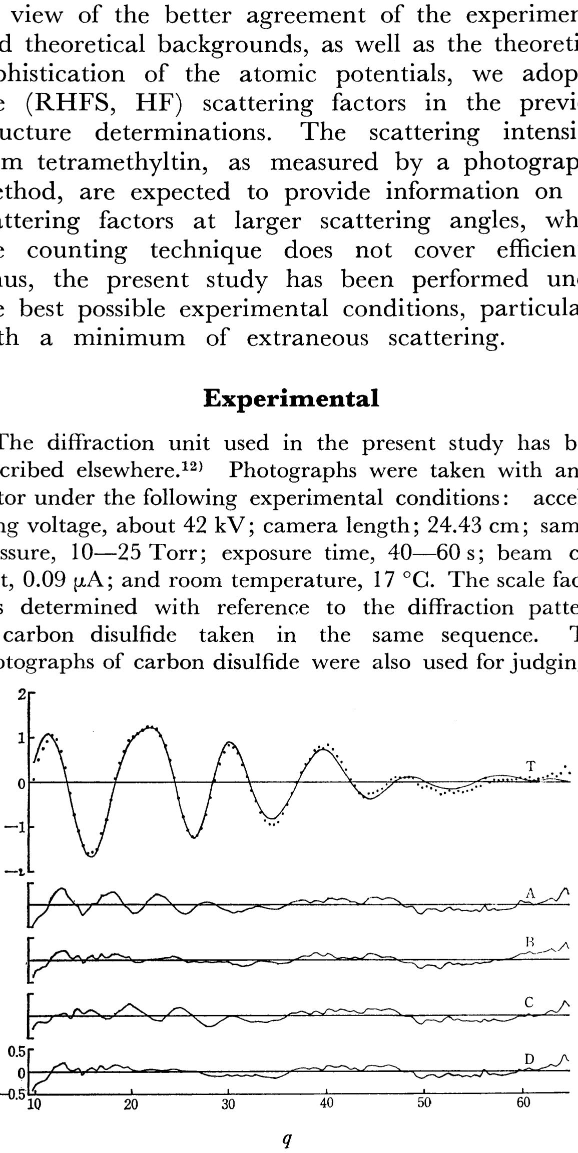

Fig. 1. Experimental molecular intensities (dotts), the best-fit theoretical intensity curve (T), and the difference correspond to the models with rotational angles of the methyl groups, 0° (eclipsed), 30° (intermediate), 60° (staggered) and the free-rotation model, respectively.

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the apparatus was in sufficiently good condition. Thus it was confirmed that no significant extraneous scattering was involved in the present experiment.[13] Four plates for the sample and four for the reference were selected and used for the structure analysis. The molecular intensities, $qM(q)$, were reduced following our conventional procedure.[2a] In this and the succeeding procedures for structure determination, the (RHFS,HF) scattering factors were employed. A comparison between the two sets of the scattering factors will be presented later. The molecular intensities obtained from one of the four plates are plotted in Fig. 1. The data covered the range of $10 \leq q \leq 60$.[14]

Structure Analysis

Least-squares Refinement. The molecular structure was determined by the least-squares method applied to the molecular intensity.[15] The SnC_4 frame and the methyl group were assumed to have the T_d symmetry and the C_{3v} symmetry respectively. With this frame symmetry, four molecular models were taken into account: three hindered-rotation models, staggered (rotational angle 60°), eclipsed (0°), and intermediate (30°) with regard to the relative positions of the methyl groups to the opposite SnC_3 frame, and a free-rotation model. The free-rotation model was approximated by mixing the three hindered-rotation models weighted equally. The independent parameters for each model were chosen to be r_a(Sn–C), r_a(Sn···H), r_a(C–H), l(Sn–C), and l(Sn···H). The other non-bonded distances were constrained in the r_a distances. The l(C–H) was assumed to be 0.08 Å, and the other non-bonded C···H and the H···H mean amplitudes were transferred from those of propane.[16] The parallel and perpendicular mean amplitudes of the SnC_4 system were estimated by solving a five-body problem in which the methyl groups were regarded as mass points. In this calculation, the Urey-Bradley force field was used with the assumption that $F' = -F/10$. The results of the vibrational analysis for the SnC_4 system are shown in Table 1, along with the mean amplitudes determined in the present study. The asymmetry parameters, κ, were estimated by a diatomic approximation[18] to be 9.0×10^{-6} Å^3 for Sn–C and 10.0×10^{-6} Å^3 for C–H; they were assumed to be zero for all the other non-bonded distances.

Table 1. Vibrational data for $Sn(CH_3)_4$

	Frequency (in cm^{-1})		Force constant (in md/Å)	
	Obsd[a]	Calcd		
A_1	507	507	K	2.10
E	145	145	H	0.049
F_2	532	532	F	0.044
	160	160		

	Mean-amplitudes (in Å) parallel	perpendicular	Stretchings (in Å) $r_a - r_\alpha$
Sn-Me	0.0529	0.0209	0.0036
Me-Me	0.1370	0.0144	−0.0033

a) Raman data. Ref. 17.

The results are listed in Columns (A), (B), (C), and (D) of Table 2, while the differences between the theoretical and observed molecular intensities are shown by Curves (A), (B), (C), and (D) in Fig. 1. As may be seen in Table 2, the r_a(Sn–C) distance converges to a constant value, irrespective of the selected models. As for the other parameters, on the other hand, the results for the hindered-rotation models are slightly different from one model to another, although they agree within their standard deviations. The results for the free-rotation model coincide with those for the intermediate model. The differences between the theoretical and observed molecular intensities all seem within the range of estimated experimental uncertainties in the intensity measurements. On a closer examination, however, the difference curves for the staggered and eclipsed models are seen to oscillate in the $10 < q < 30$ range. This oscillation in the difference curves appears consistently in all the data with phases approximately opposite to each other for the staggered and eclipsed models. The contributors to this oscillation are confirmed to be the non-bonded C···H distances, not the Sn···H distances, which also depend slightly on the selected models. Such oscillations disappear in the difference curves for the intermediate and free-

Table 2. The results of the least-squares refinement

Parameter	(A) 0°	(B) 30°	(C) 60°	(D) free rotation
k	0.931±0.035	0.944±0.022	0.907±0.029	0.942±0.023
r_a (Sn–C)	2.1435±0.0034	2.1423±0.0022	2.1432±0.0029	2.1424±0.0023
l (Sn–C)	0.0438±0.0133	0.0498±0.0073	0.0406±0.0119	0.0496±0.0076
r_a (Sn···H)	2.7397±0.0144	2.7534±0.0093	2.7667±0.0134	2.7557±0.0096
l (Sn···H)	0.1492±0.0157	0.1534±0.0100	0.1616±0.0140	0.1532±0.0101
r_a (C–H)	1.1120±0.0097	1.1196±0.0062	1.1105±0.0084	1.1121±0.0064
l (C–H)	0.08 (assumed)	0.08 (assumed)	0.08 (assumed)	0.08 (assumed)

a) Distances and mean-amplitudes in Å units, and the index of resolution, k, is dimensionless. The errors are the standard deviations.

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[14] Numerical experimental data of the leveled total intensity have been deposited with the Chemical Society of Japan, (Document No. 7317)

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rotation models, where the non-bonded C···H distances are intermediate between (or are composed of) those for the eclipsed and staggered models. The standard deviations are also much smaller for the intermediate and free-rotation models. The free-rotation model adopted in the present study is not a rigorous one, but, in the light of the finding mentioned above, the nearly free rotation of the methyl groups is acceptable and the diffraction pattern can be interpreted satisfactorily by a nearly free rotation. No further investigation was made of the rotational states of the methyl groups, for the contribution from the C···H and H···H non-bonded distances to the total intensities was not sufficiently large to distinguish more precisely various conformations, or the rotational states of the methyl groups. The intermediate conformation cannot be rejected on the basis of the electron-diffraction data alone, although it is unlikely for a reason to be described later. The possibility of the eclipsed or the staggered conformation as a stable one can, however, be ruled out.

Molecular Structure. The final parameter values were determined from the results yielded for the free-rotation model. Table 3 shows the r_g distances and the mean-amplitudes obtained from four plates, along with the limits of error, which include 2.58 times the standard deviations and the error in the scale factor.

TABLE 3. MOLECULAR STRUCTURE OF $Sn(CH_3)_4$[a] (IN Å UNITS)

	r_g	l
Sn-C	2.144±0.003	0.050±0.010
Sn···H	2.764±0.013	0.153±0.013
C-H	1.118±0.009	0.08 (fixed)
φ_g (Sn-C-H)	112.0±1.6°	

a) The uncertainties represent estimated limits of error.

Scattering Factors

The (RHFS, HF) and (TFD, TF) scattering factors differ from each other in their absolute values and phase factors. Figures 2 and 3 show the ratio of the backgrounds calculated from the two sets of scattering factors, and the leveled intensity curves, respectively. As may be seen in Fig. 2, the two backgrounds are greatly different around $q=20$, making a strong undulation in the ratio curve. The leveled intensity based upon the (TFD, TF) is higher and deviates farther from the baseline around $q=20$ than that based upon the (RHFS, HF). This indicates that the (RHFS, HF)-based background reproduces the experimental one better, in conformity with the conclusion drawn from the small-angle scattering experiment, where stress was laid on relatively small scattering angles, $q<15$.[4]

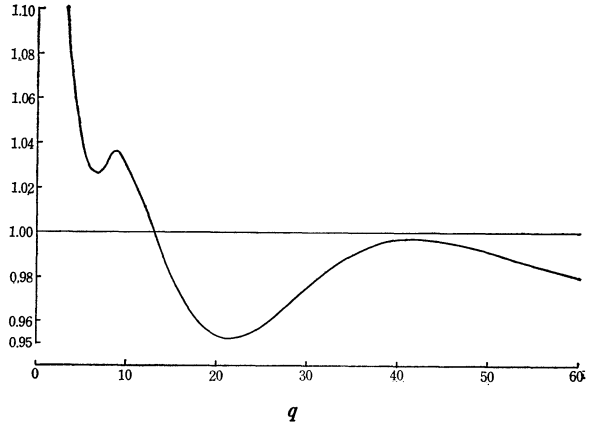

Fig. 2. Comparison of the theoretical backgrounds for $Sn(CH_3)_4$, $(I_B^{TF,DTF}/I_B^{RHFS,HF})$ vs. q.

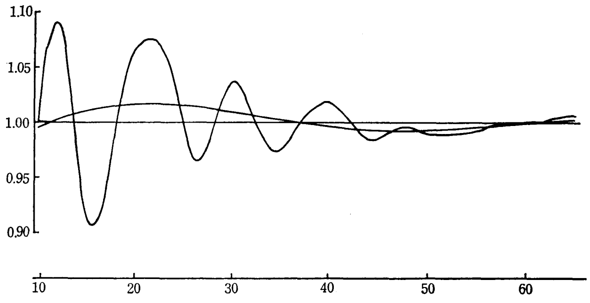

Fig. 3. The total intensity and the experimental background leveled by the use of the theoretical background calculated from the (RHFS, HF) potentials.

In order to investigate the influence of the scattering factors chosen for structure determination, the whole analytical process was repeated using the (TFD, TF) scattering factors, and the results were compared with those obtained by the (RHFS, HF)-based analysis. The Sn–C distances agreed within the standard deviations, while the Sn–C mean amplitude was increased to about 0.07 Å. This value is much larger than the experimental value obtained by the (RHFS, HF)-based analysis. Two origins for such a large mean amplitude may be considered. The first is that the cut-off in the TFD scattering factors is at a larger angle. Since the cut-off points for the Sn–C are at $q=63$ and 60 in the TFD and RHFS scattering factors respectively, the use of the (TFD, TF) scattering factors gives a larger Sn–C mean amplitude. In order to observe this effect, the structure parameters were refined by using the (RHFS, HF)-based molecular intensities employed for the present structure determination and the (TFD, TF) scattering factors. Only the l(Sn–C) amplitude was thus changed, to 0.063 Å, a value which is 0.013 Å larger than the value determined in the last section. The second, less definite but still probable, origin is the peculiar background in the (TFD, TF)-based leveled intensity described in the preceding paragraph. An initial background curve is generally drawn flat, whereas the (TFD, TF)-based leveled intensity has a strong swelling near $q=20$. As a result, the molecular intensity in the smaller q region might have been amplified falsely, leading to an apparently large mean-amplitude.

In the light of the facts mentioned above, together with those derived from the studies of $Hg(CH_3)_2$[10] and $HgCl_2$[11] and from the small-angle scattering from molecules containing heavy atoms,[5] it may be concluded that the (RHFS, HF) scattering factors are the best of all the available scattering factors for structure analysis. Recently, Beagley and McAloon[19] discussed the scattering factors for Sn in conjunction with the electron diffraction studies of organotin hydrides. They stated that the Cox and Bonham scattering factors[20] for Sn resulted in anomalously small mean amplitudes for the Sn–C and Sn–H distances, while the scattering factors calculated independently by them and by one of the present authors (M.K.) and his co-workers on the basis of the TFD potential led to a definite improvement in the mean amplitudes, *i.e.*, $l(\text{Sn–C})=0.071\pm0.009$ Å in $(CH_3)_3SnH$ and $l(\text{Sn–H})=0.098\pm0.015$ Å in $(CH_3)_2SnH_2$. It is probable that the l(Sn–C) value proposed by Beagley and McAloon becomes rather small and approaches a theoretical estimate of about 0.05 Å if the (RHFS, HF) scattering factors are used.

Methyl Torsion and Sn-C Distance

The present analysis has ruled out a hindered rotation about the staggered or the eclipsed position with C···H mean amplitudes similar to those in propane. According to NMR[21] and spectroscopic studies,[22] the barriers to hindered rotation in solid $Sn(CH_3)_4$ are 0.46 and 0.8 kcal/mol respectively. There is no available experimental value on the barrier hindering methyl torsion in gaseous $Sn(CH_3)_4$. However, in the discussion of the thermodynamic properties of tetramethyl compounds of the Group IV elements, Staveley *et al.*[23] concluded that the observed rise in the entropy of fusion with an increase in the size of the central atom was due to the release from molecular interlocking when the crystal melted and, consequently, the gain of a greater degree of rotational freedom by the methyl group in the bulky molecule than in the more compact molecules. This suggests that the hindering barrier in gaseous $Sn(CH_3)_4$ is probably lower than the values found in the solid state. Thus, the methyl groups in $Sn(CH_3)_4$ are considered to undergo oscillation with a very low hindering barrier, or a nearly free rotation.

The Sn–C distance determined in the present study, 2.144 ± 0.003 Å, is nearly the same as those observed in alkyltin hydrides, *e.g.*, 2.150 ± 0.003 Å for $Sn(CH_3)_2H_2$ and 2.147 ± 0.003 Å for $Sn(CH_3)_3H$. The Sn–C distances in the $Sn(CH_3)_nH_{4-n}$ molecules (n=1—3) are equal to each other. They are, however, longer than the corresponding distances in the $Sn(CH_3)_nCl_{4-n}$ molecules (n=1—3), 2.104—2.108 Å,[2] and become shorter in the solid state.[24] These experimental facts pose an interesting problem for the future.

We wish to thank Professor Takao Iijima and Dr. Shigehiro Konaka for their helpful suggestions and discussions throughout this work. The calculations were performed on a FACOM 230—60 of the Computing Center of Hokkaido University and also on a FACOM 270—20 electronic computer in the laboratory of Professor Kimio Ohno, to whom our thanks are also due.

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