Molecular Structure of Dimethyltin Dichloride as Studied by Gas-electron Diffraction

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The molecular structure of dimethyltin dichloride was determined by the sector-microphotometer method of electron diffraction to be as follows: r_g(Sn-Cl)$=2.327\pm0.003$ Å, r_g(Sn-C)$=2.108\pm0.007$ Å, and r_g(C-H)$=1.113\pm0.020$ Å, and all the valency angles were near 109.5°. In comparison with the Sn-Cl distances in the series of $Sn(CH_3)_{4-n}Cl_n$, as determined previously by the same method, a regular bond contraction in going from $Sn(CH_3)_3Cl$ to $SnCl_4$, as pointed out previously by Skinner and Sutton, was ascertained.

Many structural studies have recently been published of a series of molecules, $Sn(CH_3)_{4-n}Cl_n (n=0, 1, 2, 3, 4)$, by various experimental techniques, *e.g.*, dipole moment measurements,[2,3] NMR,[2,4] Mössbauer effects,[5] NQR,[6] X-ray crystal analysis,[7] and studies of the vibrational spectra[8–11] and electron diffraction.[12–14] In these studies, relations between bond lengths and other physical quantities have often been discussed.

As for the interatomic distances in these molecules in the gaseous state, Skinner and Sutton once determined tin-chlorine bond lengths by the visual method and found that the magnitude of bond contraction from the sum of the covalent radii increased with an increase in the number of halogen atoms.[12] However, these data involve large uncertainties inherent in the visual method and may even be incorrect owing to the ignorance of phase differences between Sn and Cl, and Sn and C, atoms.[15]

In order to get a more profound insight into the molecular structures of this series of molecules, it is essential to have more precise, up-to-date information regarding the bond lengths in free molecules. Recently, the present authors have determined the Sn-Cl bond length in $SnCl_4$ to be 2.281 ± 0.004 Å,[13] a value which was 0.03 Å shorter than the value determined by the visual method.[14] In the present paper we will report on the bond lengths of dimethyltin dichloride as determined by the sector-microphotometer method.

Experimental

A pure sample of dimethyltin dichloride (mp 108°C) was kindly provided by Professor Toshio Tanaka of the Osaka University. Photographs were taken by the apparatus in our laboratory equipped with an r^3-sector[16] and a high-temperature nozzle[17] at two camera lengths, 258.90 cm (long camera length) and 123.90 cm (short camera length). The accelerating voltage was about 42.25 kV. The sample was sublimed by maintaining the nozzle temperature at 85—88°C. The scale factors were determined by reference to the diffraction patterns of carbon disulfide taken under the same experimental conditions.[13] The photographs were recorded on Fuji Process Hard Plates with exposure times of 40 to 70 sec and a beam current of 0.3 μA, and were developed at 20°C for 5 min with a FD-131 developer diluted twice. Seven plates from the long camera length and four plates from the short camera length were selected, and their optical densities were measured as reported previously;[13] the observed points covered the range of $q=8$—60 and $q=25$—110 for the respective camera lengths. Because of the damping effects due to intramolecular vibrations and the phase differences of scattered beams from the Sn, Cl, and C atoms, the molecular scattering in a range of q beyond about 80 falls in amplitude down to the order of random fluctuations of the observed total intensities. Therefore, the structure parameters were determined by employing the optical densities of the plates from the long camera length.

Analysis and Results

The reductions of the molecular intensities, $qM(q)^{exptl}$, were done following the method described in our previous paper, unless otherwise stated.[13] The experimental leveled intensity, I_T, and the experimental background, I_B, curve, the $qM(q)^{exptl}$ and the difference curve of the experimental and theore-

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[2] J. Lorberth and H. Nöth, *Chem. Ber.*, **98**, 969 (1965).

[3] E. V. Van Den Berghe and G. P. Van der Kelen, *J. Organometal. Chem.*, **6**, 515 (1966).

[4] J. R. Holmes and H. D. Kaesz, *J. Amer. Chem. Soc.*, **83**, 3903 (1961).

[5] N. N. Greenwood, P. G. Perkins, and D. H. Wall, *Symposia of the Faraday Society*, **1**, 51 (1967).

[6] P. J. Green and J. D. Graybeal, *J. Amer. Chem. Soc.*, **89**, 4305 (1967).

[7] J. D. Graybeal and D. A. Berta, *Nat. Bur. Stand. Spec. Publ.*, No 301, 393 (1967).

[8] W. F. Edgell and C. H. Ward, *J. Mol. Spectrosc.*, **8**, 343 (1962).

[9] a) P. Taimsalu and J. L. Wood, *Spectrochim. Acta*, **20**, 1043 (1964); b) *ibid.*, **20**, 1357 (1964).

[10] F. K. Butcher, W. Gerrard, E. F. Mooney, R. G. Rees, H. A. Willis, A. Anderson, and H. A. Gebbie, *J. Organometal. Chem.*, **1**, 431 (1964).

[11] a) R. J. H. Clark and C. S. Williams, *Spectrochim. Acta*, **21**, 1861 (1965); b) R. J. H. Clark, A. G. Davies, R. J. Puddephatt, W. Ramsay, and R. Forster Laboratories, *J. Chem. Soc., A*, **1968**, 1828.

[12] H. A. Skinner and L. E. Sutton, *Trans. Faraday. Soc.*, **40**, 164 (1944).

[13] H. Fujii and M. Kimura, This Bulletin, **43**, 1933 (1970).

[14] R. L. Livingston and C. N. R. Rao, *J. Chem. Phys.*, **30**, 339 (1959).

[15] Critical importance of the consideration of the phase difference has been pointed out by the present authors in their study of $SnCl_4$.[13]

[16] Y. Murata, K. Kuchitsu, and M. Kimura, *Jap. J. Appl. Phys.*, **9**, 591 (1970).

[17] M. Ogasawara and M. Kimura, Symposium on Molecular Structure, Chemical Society of Japan, October, 1967.

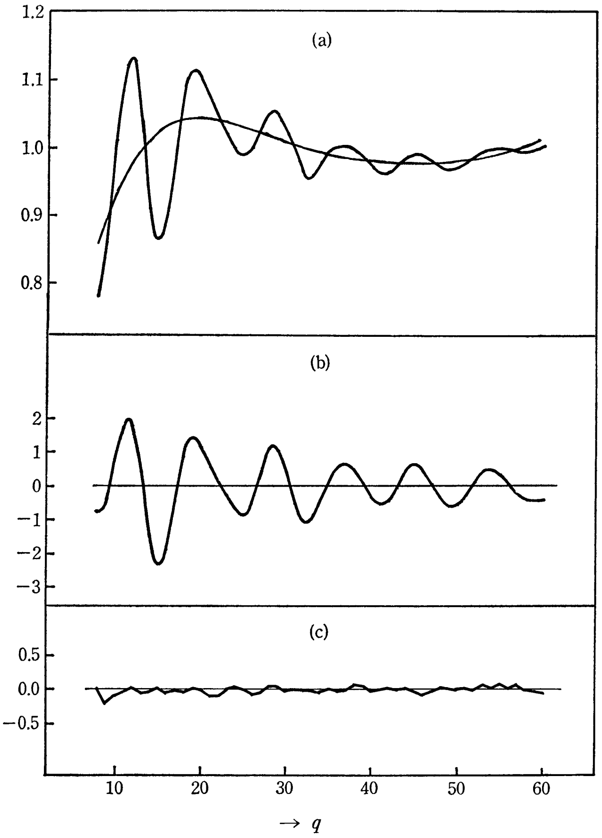

Fig. 1. (a) The experimental leveled intensity and the background curve; (b) The observed molecular intensities $qM(q)^{exptl}$; and (c) The difference curve of the experimental and theoretical molecular intensities.

tical $qM(q)$ values for an arbitrarily selected plate are shown in Figs. 1(a), (b), and (c) respectively.[18] The elastic and inelastic scattering factors used were taken from the references.[19-23]

The radial distributions, $f(r)$, were calculated by the use of the correction term for the non-nuclear scattering:[13]

$$\varDelta qM(q) = \sum_{i,j}{}' A_{ij} \sin\left(\frac{\pi}{10} q r_{ij}\right) \exp(-a_{ij} q^2)$$
$$\times \{\chi_{ij} - \mu_{ij} \cos(\varDelta\eta_{ij})\},$$

with the following correction functions, χ_{ij}:

$$\chi_{\mathrm{HH}} = 1.20 + 1.65 \exp(-0.00017\,q^2)$$
$$+ 3.1 \exp(-0.0015\,q^2),$$
$$\chi_{\mathrm{HC}} = 1.08 + 1.10 \exp(-0.00013\,q^2)$$
$$+ 2.5 \exp(-0.0020\,q^2),$$
$$\chi_{\mathrm{HCl}} = 0.20 + 2.80 \exp(-0.0002\,q^2),$$
$$\chi_{\mathrm{HSn}} = 0.88 \cos(0.3206\,q) + 0.8 \exp(-0.0020\,q^2),$$
$$\chi_{\mathrm{CC}} = 1.32 + 1.78 \exp(-0.0006\,q^2),$$
$$\chi_{\mathrm{CCl}} = 0.90 + 1.40 \exp(-0.00034\,q^2)$$
$$\chi_{\mathrm{CSn}} = 0.90 \cos(0.02523\,q) + 0.5 \exp(-0.0014\,q^2),$$
$$\chi_{\mathrm{ClCl}} = 1.40$$

and

$$\chi_{\mathrm{ClSn}} = \cos(0.01415\,q).$$

A trial background was revised after Karles' non-negativity criterion by the Fourier inverse transformation of the difference between the observed and calculated radial distributions, $\varDelta f(r)$, below $r=1.10$ Å. In these calculations, it was assumed that the molecule has C_{2v} symmetry, that each methyl group has a three-

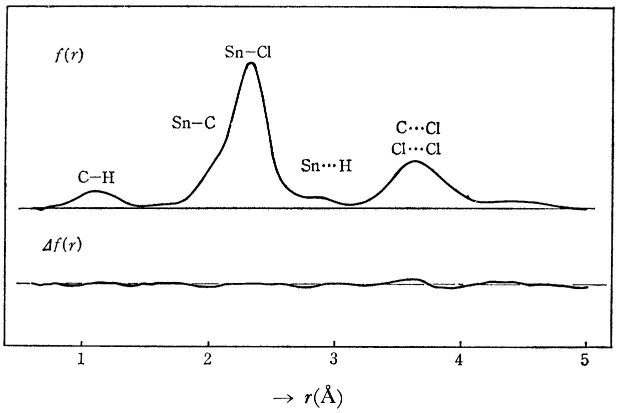

Fig. 2. The experimental radical distribution, $f(r)$, and the difference between the calculated and the experimental radial distributions, $\varDelta f(r)$.

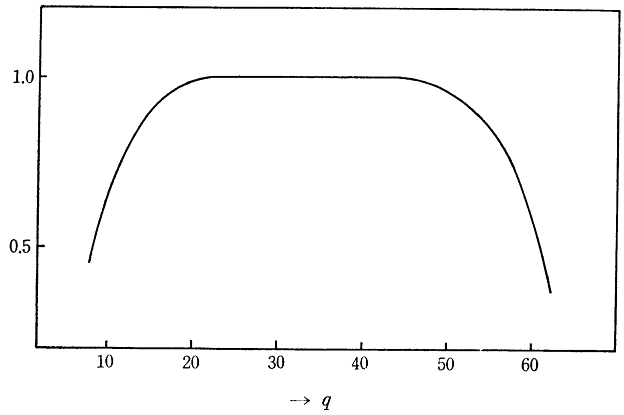

Fig. 3. The weight function used for the least-squares adjustments.

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[18] The experimental data of the leveled total intensities have been filed with the Chemical Society of Japan (Document Number 7114). A copy may be secured by citing the Document Number and by remitting, in advance, ¥400 for photoprints. Pay by check or money order payable to: Chemical Society of Japan.

[19] a) M. Kimura, S. Konaka, and M. Ogasawara, *J. Chem. Phys.*, **46**, 2559 (1967); b) M. Ogasawara, S. Konaka, and M. Kimura, *ibid.*, **50**, 1488 (1969).

[20] C. Tavard, D. Nicolas, and M. Rouault, *J. Chim Phys.*, **64**, 540 (1967).

[21] L. Bewilogua, *Physik. Z.*, **32**, 740 (1931).

[22] R. F. Pohler and H. P. Hanson, *J. Chem. Phys.*, **42**, 2347 (1965).

[23] Elastic scattering factors have been calculated by Cox and Bonham on the bases of relativistic wave functions (*J. Chem. Phys.*, **47**, 2599 (1967)). As far as the Sn atom is concerned, these scattering factors are significantly larger than those used by us[19] and also by the Manchester group, and consequently, give a larger phase difference for the Sn–Cl atom pair. However, new scattering factors based upon relativistic wave functions, which are to be published by Schäffer, Yates, and Bonham in the Journal of Chemical Physics. The authors are indebted to Professor Bonham for making use of their table for a comparative purpose.

fold symmetry about the bond joining the methyl group to the Sn atom and is staggered to the opposite Sn–Cl bond, and that all the valence angles are 109.5°. On these assumptions, the molecular parameters were evaluated appropriately from the observed $f(r)$ curve and the results of the least-squares adjustments. The final $f(r)$ and $\Delta f(r)$ values obtained from the I_T's shown in Fig. 1 are depicted in Fig. 2.

The structural parameters were determined by the least-squares method applied to the observed molecular intensities with a diagonal weight matrix (Fig. 3). The asymmetry parameters, κ, for the H···H, C···H, and Cl···H pairs were set equal to zero, while the others were fixed at the following values:

κ_{CH}	122,	κ_{ClCl}	178,
κ_{SnC}	26,	κ_{ClC}	257,
κ_{SnCl}	18,	κ_{SnH}	313, (in 10^{-7} Å^3);
κ_{CC}	281,		

These values were estimated by the method applied to $SiCl_4$ by Morino and Murata.[24,25] The interatomic distances for the non-bonded H···H, C···H, Cl···H, and C···C pairs, which make very little contributions to the scattering intensity, were constrained in the r_a structure, and their mean amplitudes were fixed at values roughly estimated from those in analogous compounds. Least-squares adjustments were then performed for the thirteen parameters listed in Table 1. The fluctuations of the adjusted values during least-squares iterations were the largest for r(Cl···Cl) or l(Cl···Cl). Therefore, the iterations were terminated when the fluctuations of the adjusted r(Cl···Cl) and l(Cl···Cl) values became less than 1.5 percent and when the parameter values for the C–H, Sn–C, and Sn–Cl atom pairs converged within 10, 4, and 1×10^{-4} Å respectively.

Table 1. Results of the least-squares adjustments[a)]

Parameter	Average[b)]	σ_1[b)]	σ_2[b)]
k	0.967	0.018	0.019
r_g(C-H)	1.1119	0.0068	0.0088
l (C-H)	0.0792	0.0077	0.0058
r_g(Sn···H)	2.6703	0.0303	0.0120
l (Sn···H)	0.1701	0.0166	0.0085
r_g(C···Cl)	3.6314	0.0101	0.0034
l (C···Cl)	0.1223	0.0062	0.0014
r_g(Sn-C)	2.1089	0.0034	0.0031
l (Sn-C)	0.0748	0.0073	0.0079
r_g(Cl···Cl)	3.7549	0.0366	0.0146
l (Cl···Cl)	0.2248	0.0325	0.0109
r_g(Sn-Cl)	2.3266	0.0010	0.0014
l (Sn-Cl)	0.0607	0.0025	0.0018

∠ClSnCl = 107.5±3.9°[c)]
∠ClSnC = 109.8±1.2°[c)]

a) Index of resolution k is dimentionless; r_g and l in Å.
b) The definitions of σ_1 and σ_2 were given in Ref. 13.
c) Estimated from the r_g values.

The value for each parameter was obtained by averaging the results from the seven plates. The parameter values thus obtained and their estimated standard deviations, σ_1 and σ_2, are shown in Table 1, where the interatomic distances are given in terms of r_g and where the σ_1 and σ_2 have the same significances as in our previous paper.[13)]

As may be seen in Table 1, the non-bonded interatomic distances could not be determined with satisfactory accuracy. If the valence angles are evaluated from the r_g values in Table 1, we get the values of 107.5±3.9° for ∠ClSnCl and 109.8±1.2° for ∠ClSnC; hence, they are indistinguishable from the tetrahedral angle. The most probable bonded interatomic distances and mean amplitudes are reproduced in Table 2, together with their limits of error, which include the random errors and the errors due to the uncertainty of the scale factor. The former errors were taken as 2.5 times the larger of σ_1 and σ_2, while the latter were estimated to be 0.1% of the interatomic distances.

Table 2. Bond distances and mean-amplitudes (in Å)

	r_g	l
C-H	1.112±0.022	0.079±0.019
Sn-C	2.109±0.009	0.075±0.020
Sn-Cl	2.327±0.004	0.061±0.006

Calculation of the Mean-square Amplitudes

Since the low-lying fundamental frequencies and their assignments were uncertain,[8–11)] the Nujol-mull spectra were measured in the region below 400 cm^{-1}. Some of them are reproduced in Table 3. Edgell and Ward[8)] assigned the Raman lines at 344 cm^{-1} and 135 cm^{-1} to accidentally degenerate Sn–Cl stretching modes and skeletal bending modes respectively. However, such degeneracies seem unlikely. Taimsalu and Wood[9b)] studied the effect of the environment on the vibrational frequencies of the $Sn(CH_3)_{4-n}Cl_n$ series and concluded that dimethyltin dichloride associated strongly in the solid state and that its Sn–Cl stretching frequencies shifted markedly towards the lower-frequency side. On the contrary, our solid spectra in this range displayed an intense band at 357 cm^{-1} with a shoulder near 349 cm^{-1} and broad, weak bands at 306 and 325 cm^{-1}. It seems that the strong band and its shoulder at 357 and 349 cm^{-1} are to be assigned to the Sn–Cl stretching frequencies, and that the two weak bands at the lower frequencies are overtone and combination bands. The assignment of the $SnCl_2$ deformation mode is also ambiguous. Taimsalu and Wood assigned bands at 124 cm^{-1} and 129 cm^{-1} to the bending and rocking modes respectively,[9a)] whereas Butcher *et al.* assigned a band at 121 cm^{-1} to the bending mode.[10)] If one follows the assignment made by Taimsalu and Wood, the observed frequencies in our spectra may be assigned as is shown in the last column of Table 3. The general

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[24)] Y. Morino and Y. Murata, This Bulletin, **38**, 104 (1965).

[25)] The κ values for non-bonded pairs are possibly smaller than the listed values. However, the use of smaller values does not change the results of the present least-squares adjustment substantially.

Table 3. The observed skeletal vibrational frequencies of $Sn(CH_3)_2Cl_2$ (in cm^{-1})

			Edgell[a] and Ward. R. L.	Taimsalu[b] and Wood. IR. Nm.	Butcher[c] *et al.* IR. Sol.[e]	Present[d] study. IR. Nm.
A_1	Sn-C	stretch	521	515 s	524	
	Sn-Cl	stretch	344	307 vs	356 sh	349 sh
	$Sn-Cl_2$	bending	135	124w	121	116
	SnC_2	bending	135	158w		158
B_1	Sn-C	stretch	566	567 s	560	
	$SnCl_2$	rocking	135	129 m		126
B_2	Sn-Cl	stretch	344	332 vs	361 s	357 s
	$SnCl_2$	rocking	135	146 s		143

R: Raman; IR: Infrared; L: liquid; Nm: Nujol mull; Sol: solution; vs: very strong; s: strong; m: medium

a) Ref. 8. b) Ref. 9a. c) Ref. 10.

d) In addition to the bands listed in this column, two weak, broad bands were observed at 325 and 306 cm^{-1}. See text.

e) Cyclohexane solutions were used except for the band at 560 cm^{-1}, which was observed in carbondisulfide solution.

pattern of our frequencies is similar to that assigned by Clark *et al.*[11b)] Although the frequencies and their assignments of the low-lying fundamental vibrations remain questionable, the mean-square amplitudes were calculated with rigid CH_3 groups and by the use of the Urey-Bradley force field. The results are listed in Table 4. It was necessary to introduce a non-zero force constant, G(SnC.SnC), in order to fit the calculated Sn–C stretching frequencies to the observed ones to the extent shown in Table 4. In spite of some uncertainties in the vibrational spectra and in spite of the approximations involved in the present calculations, the mean amplitudes thus obtained may be considered to have sufficient accuracy for comparative use. The experimental and theoretical values listed in Table 2 and 4 have similar orders of magnitude.

Table 4. The Urey-Bradley force constants, the calculated skeletal vibrational frequencies and the calculated mean amplitudes

Force constants (md/Å)		Frequencies[a] (cm^{-1})			Mean Amplitudes (Å)	
K(Sn-CH_3)	2.188	A_1	515	(515)	Sn-Cl	0.054
K(Sn-Cl)	1.866		116	(116)	Sn-C	0.054
H(ClSnCH_3)	0.036		158	(158)	C···C	0.147
H(CH_3SnCH_3)	0.062		345	(349)	Cl···Cl	0.133
H(ClSnCl)	0.049	B_1	567	(567)	C···Cl	0.146
F(CH_3-Cl)	0.086		123	(126)		
F(CH_3-CH_3)	0.038	B_2	360	(357)		
F(Cl-Cl)	0.109		146	(143)		
κ	0.044					
G(SnC SnC)	−0.168					

a) Values in parentheses are observed frequencies.

Contraction of the Sn–Cl Bonds

Table 5 presents the molecular structures of the $Sn(CH_3)_{4-n}Cl_n$ series (n=0,1,2,3,4) as determined by electron diffraction.

It is evident in Table 5 that there is a regular contraction of Sn-Cl bond lengths from $Sn(CH_3)_3Cl$ to $SnCl_4$; that is, the magnitudes of the contractions of r(Sn-Cl) from the sum of the single-bond covalent radii, 2.39 Å, are 0.04, 0.06, 0.09, and 0.11 Å for the molecules of n=1,2,3, and 4 respectively. The values of the Sn-C distances, except for $Sn(CH_3)_4$, are equal in their marginal errors, while the Sn-C distance in $Sn(CH_3)_4$ is close to those in methyl stannanes, *e.g.*, r_g(Sn-C)=2.150±0.003 Å for $Sn(CH_3)_2H_2$ and 2.147±0.004 Å for $Sn(CH_3)_3H$.[26)] The relations between the bond lengths and other physical properties for these compounds present interesting problems which will have to be solved in the future.

Table 5. The bond distances of $Sn(CH_3)_{4-n}Cl_n$ as determined by electron diffraction

Compound	Visual method			Sector-microphotometer method		
	Sn-C (Å)	Sn-Cl (Å)	Ref.	Sn-C (Å)	Sn-Cl (Å)	Ref.
$Sn(CH_3)_4$				2.134±0.007		27
$Sn(CH_3)_3Cl$	2.19±0.03	2.37±0.03	12	2·106±0.006	2.351±0.007	26
$Sn(CH_3)_2Cl_2$		2.34±0.03	12	2.108±0.007	2.327±0.003	present study
$Sn(CH_3)Cl_3$	2.19±0.05	2.32±0.03	12	2.104±0.016	2.304±0.003	26
$SnCl_4$		$2.31±0.01_5$	14		2.281±0.004	13

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26) K. McAloon, private communication. The authors wish to thank Dr. K. McAloon for permission to quote his results prior to publication.

27) A preliminary result by the present authors.

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