Journal of Molecular Structure, 66 (1980) 149—158
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

MOLECULAR STRUCTURES OF ACETYLENE DERIVATIVES OF TIN

Part IV. Gas-phase electron-diffraction study of tetraethynyltin, $Sn(C{\equiv}CH)_4$, and triethynyltin iodide, $ISn(C{\equiv}CH)_3$

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(Received 18 July 1979)

ABSTRACT

The geometrical parameters of tetraethynyltin and triethynyltin iodide have been determined by gas-phase electron diffraction. Triethynyltin iodide was present as an admixture in both the tetraethynyltin samples studied. Because the samples differed significantly in percentage of the iodide (17.4 ± 4.0 and 47.1 ± 3.5 mol %, in samples A and B, respectively), it was possible to determine the structures of both molecules to a sufficient degree of accuracy.

The r_α structures were solved by the least-squares treatment of the molecular intensities, using mean amplitudes and shrinkage corrections calculated from the force fields of a number of tin derivatives.

The T_d-symmetry model of $Sn(C{\equiv}CH)_4$ was refined to give the following parameters: $Sn{-}C{\equiv}$, 2.068(5); $C{\equiv}C$, 1.228(8); CH, 1.079(51). The structural parameters for $ISn(C{\equiv}CH)_3$ (on the basis of the C_{3v} model with linear $Sn{-}C{\equiv}C{-}H$ fragments) are as follows: Sn—I, 2.646(4); $Sn{-}C{\equiv}$, 2.062(17); $C{\equiv}C$, 1.226(6); ∠ISnC 108.0(2.8). (The thermal average bond distances, r_g, are given in Å, and the valence angle, r_α, in degrees; the values in parentheses are three times the standard deviations, 3σ.)

The $Sn{-}C{\equiv}$ bonds in $Sn(C{\equiv}CH)_4$ and $ISn(C{\equiv}CH)_3$ are shorter than the corresponding bonds in the monoethynyltin derivatives, $Me_3SnC{\equiv}CH$ and $Me_3SnC{\equiv}CSnMe_3$. The SnI bond in $ISn(C{\equiv}CH)_3$ is noticeably shorter than those in stannane iodide and trimethylstannane iodide.

INTRODUCTION

To further our studies of the stereochemical patterns exhibited by the stannylacetylenes [1—3], we decided to investigate the structure of tetraethynyltin. The compound is highly explosive, and, for this reason, it was unable to record its Raman spectrum (only the IR data are available) [4]. There are, however, some indications that the explosive tendency of tetraethynyltin depends to a certain extent on the synthetic procedure used. Apart from the preparative technique referred to in ref. 4, another route to $Sn(C{\equiv}CH)_4$ may be suggested which radically reduces its tendency to explode. This alternative procedure may, however, lead to contamination of the product with triethynyltin iodide. The study of this new method for the synthesis of $Sn(C{\equiv}CH)_4$ was one of the purposes of the present work, and, in particular, we wished to verify that a second compound was present and to identify it.

EXPERIMENTAL

Synthesis of tetraethynyltin

The general procedure for the synthesis of Si, Ge, and Sn tetraethynyl derivatives (see e.g., ref. 4 and references cited therein) is as follows

$$MCl_4 + 4\ NaC{\equiv}CH \rightarrow M(C{\equiv}CH)_4 + 4\ NaCl$$

and it is probable that the reaction medium is responsible for the strong explosions which frequently occur during the synthesis. We now suggest the following alternative route

$$SnI_4 + 4\ (n\text{-}Bu)_3SnC{\equiv}CH \rightarrow Sn(C{\equiv}CH)_4 + 4\ (n\text{-}Bu)_3SnI$$

Tris(n-butyl)stannylacetylene (0.425 mol) and tin tetraiodide (0.1 mol) were heated together at 150°C under vacuum (4 mm Hg). The products were collected in a trap cooled with solid CO_2. Because of the higher volatility of $Sn(C{\equiv}CH)_4$, this was isolated by sublimation under vacuum (1 mm Hg). Under the same conditions $(n\text{-}Bu)_3SnI$ remained unsublimed, as evidenced by NMR spectra of the sublimate. The synthetic route described here is far less dangerous than the classic procedure. However, as mentioned earlier, the products from this procedure may contain triethynyltin iodide.

Electron-diffraction procedure

Two samples (samples A and B) of tetraethynyltin, obtained as described above, were studied. These were found to differ significantly in the amounts of $ISn(C{\equiv}CH)_3$ present. For sample A, the major contribution to scattering was from tetraethynyltin, whereas for sample B, the diffraction pattern was determined by scattering from triethynyltin iodide. Comparison of the results obtained for samples A and B provided sufficient data for a reliable determination of the structures of both molecules.

The electron-diffraction patterns were obtained using a modified EG-100A instrument [5], at an accelerating voltage of 40 keV. The experimental conditions and intensity characteristics have been deposited with BLLD*. The electron-beam wavelength was determined from gaseous benzene patterns

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registered under the same conditions as those used for the tetraethynyltin samples. We estimate that the scale error was not larger than 0.1%. The nozzle temperature during exposures was 50—65°C. The intensity data for samples A and B were compiled from 4 and 2 photoplates, respectively. Data processing was carried out according to the standard procedure [6]. The experimental total intensity curves, $I^{T}(s)$, and the final versions of the background lines, $I^{B}(s)$, have also been deposited with BLLD (SUP 26150). As the experimental intensities fell within rather narrow ranges of scattering angles, we thought it reasonable to apply spectral data to the solution of the structures. The mean amplitude values, u_{ij}, and the values of perpendicular amplitude-correction coefficients, K_{ij} [7] were calculated using the data on the force fields of a number of tin derivatives (see below).

To obtain geometrically consistent r_α structures [8], the experimental molecular intensity curves (Fig. 1) were treated by the least-squares method. The theoretical molecular intensities were represented by

$$sM(s) = k\,\{sM'(s)\ [\mathrm{Sn(C{\equiv}CH)_4}] + n\ sM''(s)\ [\mathrm{ISn(C{\equiv}CH)_3}]\,\}$$

where n is the factor characterizing the amount of $\mathrm{ISn(C{\equiv}CH)_3}$ per mol of $\mathrm{Sn(C{\equiv}CH)_4}$. The scattering factors were taken from ref. 9, and anharmonicity parameters were introduced according to ref. 10.

STRUCTURE ANALYSIS

Molecular models and the choice of starting approximations

The experimental radial-distribution curves, $f(r)$, (Fig. 2) show peaks at ~2.65 and 3.80 Å, indicative of the presence of $\mathrm{ISn(C{\equiv}CH)_3}$ in the samples

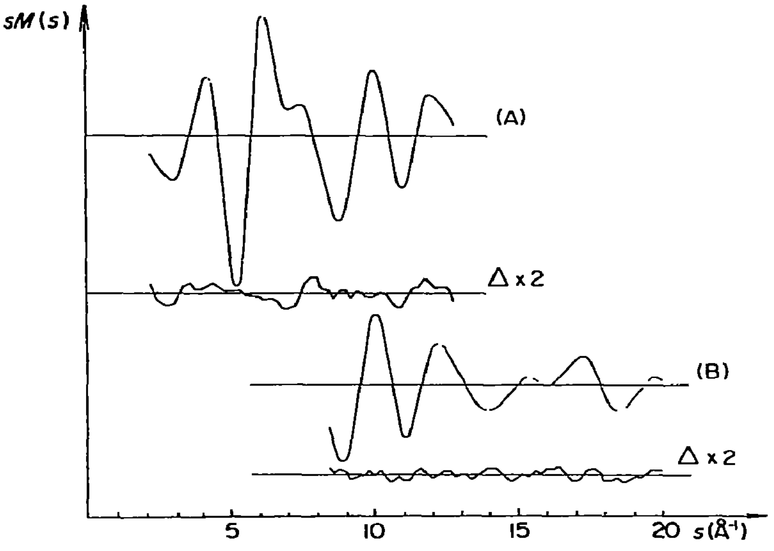

Fig. 1. The experimental $sM^{\mathrm{exp}}(s)$ curves and residuals (Δ) for refined molecular models for samples A and B.

of tetraethynyltin studied. These were assigned to the SnI bond and I · · · C nonbonded distances, respectively (cf. the electron-diffraction data on tin tetraiodide and methyltin iodides [11, 12]). The intensities of the peaks depended on the amounts of $ISn(C{\equiv}CH)_3$ present in the samples; this amount was obviously larger in sample B. No other pronounced features that did not correspond to the internuclear separations in $Sn(C{\equiv}CH)_4$ were detected in the $f(r)$ curves. The absence of any contributions from the I · · · I distances ($\sim$4.35 Å) in both the samples was interpreted as evidence against the presence of any ethynyltin iodides other than $ISn(C{\equiv}CH)_3$.

The experimental data were analyzed on the assumption of T_d symmetry for $Sn(C{\equiv}CH)_4$ and C_{3v} symmetry (with linear Sn—C≡C—H fragments) for $ISn(C{\equiv}CH)_3$. The starting approximations for $(C{\equiv}C)_{av.}$ and $(CH)_{av.}$ (weighted average bond lengths for the two molecules) were the same as those used in our previous work [1—3]. The average $(Sn{-}C{\equiv})_{av.}$ bond lengths were estimated from the $f(r)$ curves. Because sample A contained a relatively small amount of $ISn(C{\equiv}CH)_3$, this estimate was considered a good approximation to the Sn—C≡ bond length in $Sn(C{\equiv}CH)_4$. This value was then fixed in the treatment of the diffraction pattern from sample B in order to estimate the Sn—C≡ bond length in $ISn(C{\equiv}CH)_3$. The latter value was in its turn fixed in the further treatment of the pattern from sample A. This iterative procedure converged rapidly for both the parameters. The starting approximations for the SnI bond length and the ISnC bond angle were determined from $f(r)$ curves (see above).

Calculation of mean amplitudes and shrinkage corrections

The estimates for the force constants in $Sn(C{\equiv}CH)_4$ used in calculations of the mean amplitudes, u_{ij}, and shrinkage corrections, $D_{ij} = u_{ij}^2/r_{ij} - K_{ij}$,

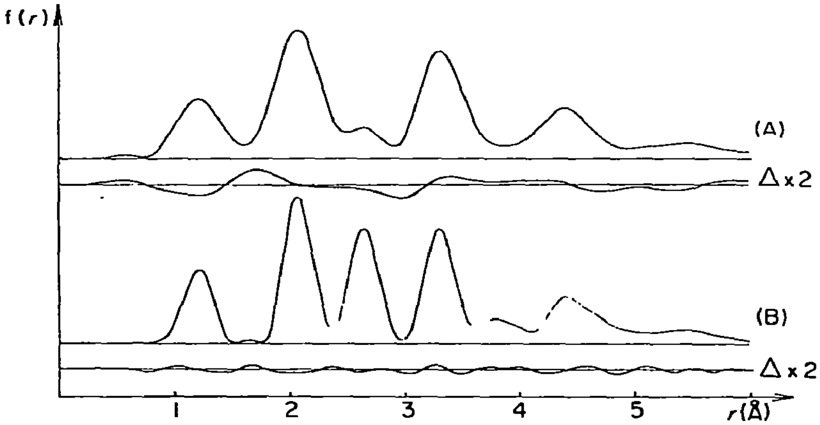

Fig. 2. The experimental $f(r)$ curves corrected for non-nuclear scattering and residuals (Δ) for the refined molecular models, samples A (damping constant 0.014 Å^2) and B (damping constant 0.0058 Å^2). The curves $f(r)$ were calculated using theoretical intensities to extrapolate to small scattering angles. The dependent internuclear distances that gave considerable contributions to scattering appear in Table 1.

have been deposited with BLLD (SUP 26150). These estimates were based on the GVFF calculations for $C_2H_5Sn(C{\equiv}CH)_3$ [13]. The value cited in that work for the CSnC bending-force constant, K_{CSnC} = 0.147 mdyn Å, however, seems to be an underestimate; the C · · · C nonbonded amplitudes calculated using that value are unusually large (~0.3 Å). This is probably due to the incorrect assignment of the CSnC bending frequency*. For this reason we have used the UBFF K_{CSnC} value of 0.275 mdyn Å, reported for $(CH_3)_2SnCl_2$ and calculated for the five-mass model [14]. As shown in ref. 15, the "point-mass" approximation leads to a lowering of the stretching and bending force constants by 20—40%. After the corresponding correction was introduced, the calculated ν_{14} frequency became 87 cm^{-1}. We also used the data on acetylene [16, 17] in our calculations. On average, the calculated frequencies differed from those observed in the spectrum of $Sn(C{\equiv}CH)_4$ [4] by ± 40 cm^{-1}.

The u_{ij} and K_{ij} values for the tetraethynyltin molecule have been calculated for t = 50°C by the normal-coordinate treatment, based on mass-weighted Cartesian displacement coordinates [18] and using the subroutine written by Stølevik et al. [19]. The program described in ref. 18 is somewhat different from Gwinn's program [20]; certain weak points in Gwinn's program have been discussed in ref. 21. Thus, the analytical expressions for the vectors determining the matrix that transforms Cartesian coordinates to internal coordinates (s-vectors) [22—24] are used in the calculations of the potential-energy matrix, instead of the numerical differentiation suggested by Gwinn. Further, certain shortcomings in the calculations for molecules containing linear fragments, such as those present in $Sn(C{\equiv}CH)_4$, have been removed. The calculated results for tetraethynyltin have been deposited with BLLD (SUP 26150). These data, together with the literature data on SnI_4 [25] were also used in treatment of the $ISn(C{\equiv}CH)_3$ molecule**. The mean amplitude values for the distances that give rise to considerable contributions to scattering are listed in Table 1 (see below).

Preliminary analysis

As the first step, the relative amounts of $Sn(C{\equiv}CH)_4$ and $ISn(C{\equiv}CH)_3$ in samples A and B were determined. The mean amplitudes were fixed at the values calculated and no shrinkage corrections were introduced.

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*Gastilovich et al. [13] considered two possible assignments for the CSnC bending modes (ν_{14}) in $Sn(C{\equiv}CH)_4$ [4], namely 97 and 45 cm^{-1}; they used the lower frequency in their calculations.

**The u_{ij} and D_{ij} values for the SnI bond distance in $ISn(C{\equiv}CH)_3$ were calculated from the mean-square parallel and perpendicular amplitudes of SnI_4 at 25°C [25]. The u_{ij} values for the I · · · C and I · · · H distances were estimated from parameter variations during the refinement; the D_{ij} values were obtained by interpolation, using the data cited in ref. 25, and the results obtained for tetraethynyltin in this work.

The percentage of $ISn(C\equiv CH)_3$ was fixed at a number of possible values, and, for each of these values, the independent parameters were varied. For sample A, the set of independent parameters included the Sn—C≡ bond length of $Sn(C\equiv CH)_4$ and $(C\equiv C)_{av.}$; for sample B, the parameters were the Sn—C≡ and SnI bond lengths and the ISnC bond angle of $ISn(C\equiv CH)_3$, and $(C\equiv C)_{av.}$. All the other independent parameters were fixed at the values estimated as described above.

The R-factor vs. composition curves for samples A and B are given in Fig. 3, where n is the mole ratio of $ISn(C\equiv CH)_3$ to $Sn(C\equiv CH)_4$. The results for samples A and B are 17.4 ± 4.0 and 47.1 ± 3.5 mol % of $ISn(C\equiv CH)_3$, respectively. The errors were estimated using the Hamilton criterion [26] (as half the range of the variation of n at a 99.5% confidence level, $\sim 3\sigma$).

Refinement

After the compositions of samples A and B had been established, the geometric parameters of $Sn(C\equiv CH)_4$ and $ISn(C\equiv CH)_3$ were subjected to r_α refinement. The mean amplitudes were fixed at the calculated values* and the sets of variables were broadened at this stage.

As before (see the section on molecular models and the choice of starting approximations), an iterative procedure was applied to determine the difference in the Sn—C≡ bond lengths between $Sn(C\equiv CH)_4$ and $ISn(C\equiv CH)_3$. A good agreement with experiment was obtained at nearly the same values

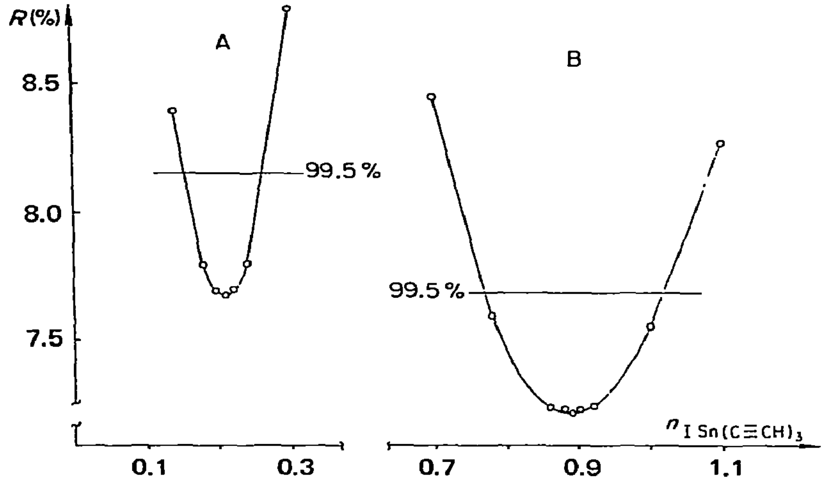

Fig. 3. R-factor curves vs. the molar ratio (n) of $ISn(C\equiv CH)_3$ to $Sn(C\equiv CH)_4$, for samples A and B and 99.5% confidence levels. The tables of Hamilton [26] give test value $\mathcal{R}_{1,60,0.005}$ = 1.068 at that level. R-factors were calculated using the formula

$$R = 100\,[\Sigma_j w_{jj}\Delta_j^2 / \Sigma_j w_{jj}(s_j M^{\exp}(s_j))^2]^{1/2}$$

where $\Delta_j = s_j M^{\exp}(s_j) - k\, s_j M^{\mathrm{theor}}(s_j)$; a unit weight matrix was used in the calculations.

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*Except the SnI mean amplitude for sample B. See also footnote** on p. 153.

for the parameters $(C{\equiv}C)_{av.}$, $(C{-}H)_{av.}$, SnI and ISnC for sample A and sample B. At the final stage, the $(CH)_{av.}$ value for sample B was fixed.

The coincidence of the $(C{\equiv}C)_{av.}$ values for samples A and B, with the uncertainties being rather small, deserves further attention. The fact that $(C{\equiv}C)_{av.}$ is independent of the sample composition shows that the C≡C bond length remains practically the same on going from $Sn(C{\equiv}CH)_4$ to $ISn(C{\equiv}CH)_3$.

The *R*-factor values for samples A and B were 7.17 and 6.67%, respectively. The correlation matrix elements did not exceed ± 0.4 for sample A and ± 0.5 for sample B. The results of the r_α refinement are listed in Table 1.

DISCUSSION

The experimental data on group IVB element acetylenides obtained by various spectroscopic methods have been analyzed in detail in ref. 27. Such parameters as ionization potentials, appearance potentials, proton-NMR chemical shifts, and characteristic stretching frequencies vary with the value of n, within rather wide ranges, along the series $(CH_3)_nM(C{\equiv}CH)_{4-n}$ $(n = 0\text{–}3)$.

TABLE 1

The results of r_α refinement of structure parameters for $Sn(C{\equiv}CH)_4$ and $ISn(C{\equiv}CH)_3$[a, b, c]

Parameters	Distances (r_α, in Å) and valence angles (r_α, in degrees)		Mean amplitudes (Å)[d]
	$Sn(C{\equiv}CH)_4$	$ISn(C{\equiv}CH)_3$	
Independent parameters			
Sn—C≡	2.067(5)	2.060(17)	0.052
C≡C	1.227(8)	1.225(6)	0.037
CH	1.074(51)	1.074 fixed	0.073
SnI	—	2.645(4)	0.054(6)
ISnC	—	108.0(2.8)	—
Dependent distances			
$Sn \cdots C_2$	3.292(8)	3.285(16)	0.054
$Sn \cdots H$	4.366(50)	4.361(16)	0.088
$C_1 \cdots C_1'$	3.376(10)	3.39(7)	0.132
$C_1 \cdots C_2'$	4.433(10)	4.46(8)	0.166
$C_2 \cdots C_2'$	5.376(13)	5.41(10)	0.225
$I \cdots C_1$	—	3.82(6)	0.076
$I \cdots C_2$	—	4.81(8)	0.131
$I \cdots H$	—	5.76(9)	0.200

[a] The refinement was performed for a T_d-symmetry model of $Sn(C{\equiv}CH)_4$, and for a C_{3v}-symmetry model of $ISn(C{\equiv}CH)_3$ comprising linear Sn—C≡CH fragments. [b] The parenthesized values are three times the standard deviations (3σ). [c] The carbon atoms are numbered as follows: $Sn{-}C_1{\equiv}C_2{-}H$. The primes indicate that the atoms belong to different groups. [d] See text (sections on: calculations of mean amplitudes and shrinkage corrections; preliminary analysis; and refinement).

MacLean and Sacher [27] do not give an unambiguous interpretation of the data available from the point of view of possible mechanisms of intramolecular interactions. On the whole, they point to a strengthening of the M—C≡ bonds with increase in the number of acetylene substituents. This was attributed to a combination of substituent-electronegativity effects and interactions of acetylene-bond π-electrons with vacant metal d-orbitals (p_π—d_π bonding, the so-called back donation of π-electrons).

The data in Table 1 show that the Sn—C≡ bond in $Sn(C{\equiv}CH)_4$ is probably shorter than those in $(CH_3)_3SnC{\equiv}CH$ (2.082(20) Å [1]) and $(CH_3)_3SnC{\equiv}CSn(CH_3)_3$ (2.095(10) Å [2]), although the accuracy of the value reported in ref. 1 is rather low. This shortening may be due to the higher electronegativity of the acetylene substituent compared with the methyl group [28, 29]. A similar electronegativity effect in tin derivatives was observed earlier [30] for methylstannanes and chloromethylstannanes.

The presence of iodine at the tin atom in $ISn(C{\equiv}CH)_3$ (Table 1) does not lead to a shortening of the Sn—C≡ bonds (within experimental error). Similarly, the Sn—C≡ bond length in $Sn(C{\equiv}C{-}CF_3)_4$ (2.070(7) Å [3]) is practically the same as that in $Sn(C{\equiv}CH)_4$, despite the presence of the electronegative CF_3 substituents in the former compound.

Variations in SnI bond lengths depending on other substituents at Sn are illustrated by the data in Table 2. The electron-diffraction data for tin tetraiodide and methyliodostannanes obtained by visual techniques involve large errors [11, 12]. For that reason we have also included data on Sn—Cl bond lengths obtained by the more up-to-date sector-microphotometric technique. On the whole, the electronegativity effect discussed by Beagley et al. [30] is observed in both series. It manifests itself, in particular, by a shortening of the SnI bond in $ISn(C{\equiv}CH)_3$ from the corresponding lengths in iodostannane [31] and trimethyliodostannane [12].

The microwave data for H_3SnI and H_3SnCl, however, do not fit the electronegativity concept so well as the data for other compounds listed in Table 2.

TABLE 2

The variation of SnI and SnCl bond lengths, depending on the effects of other substituents at Sn

Molecule	Method[a]	r(SnI) Å	Ref.	Molecule	Method[a]	r(SnCl) Å	Ref.
$ISn(C{\equiv}CH)_3$	ED	2.645(4)	This work				
H_3SnI	MW	2.674(2)	[31]	H_3SnCl	MW	2.327(1)	[32]
Me_3SnI	ED[b]	2.72(3)	[12]	Me_3SnCl	ED	2.351(7)	[30]
Me_2SnI_2	ED[b]	2.69(3)	[12]	Me_2SnCl_2	ED	2.325(3)	[14]
$MeSnI_3$	ED[b]	2.68(2)	[12]	$MeSnCl_3$	ED	2.304(3)	[30]
SnI_4	ED[b]	2.64(4)	[11]	$SnCl_4$	ED	2.280(4)	[33]

[a] ED, electron diffraction (r_a parameters); MW, microwave spectroscopy (r_s parameters).
[b] The visual technique was used for these studies; all the other ED data were obtained using the sector-microphotometric technique.

In both the molecules, the tin—halogen bonds are shorter than the corresponding bonds in Me_3SnI and Me_3SnCl, which is contrary to what might be expected, and the magnitudes of the decreases in bond length can hardly be explained by experimental errors or attributed to the difference between microwave (r_s) and electron-diffraction (r_a) operating parameters [8]. Moreover, the phenomenon seems to be of a general nature. According to the electron-diffraction data, a similar shortening of GeBr bonds occurs in H_2GeBr_2 (2.277(3) Å [34]) from Me_2GeBr_2 (2.303(3) Å [35]). Durig and co-workers [36, 37] have also pointed to the fact that element—halogen bonds in methyl, silyl and germyl halides are consistently shorter than in the corresponding trimethyl derivatives (from microwave data).

REFERENCES

1 L. S. Khaikin, V. P. Novikov, L. V. Vilkov, V. S. Zavgorodnii and A. A. Petrov, J. Mol. Struct., 39 (1977) 91.
2 L. S. Khaikin, V. P. Novikov and L. V. Vilkov, J. Mol. Struct., 42 (1977) 129.
3 V. P. Novikov, L. S. Khaikin and L. V. Vilkov, J. Mol. Struct., 42 (1977) 139.
4 R. E. Sacher, D. H. Lemmon and F. A. Miller, Spectrochim. Acta, Part A, 23 (1967) 1169.
5 A. V. Golubinskii, L. V. Vilkov, V. S. Mastryukov and V. P. Novikov, Vestn. Mosk. Univ., Ser. Khim., 20 (1979) 99.
6 V. P. Novikov, J. Mol. Struct., 55 (1979) 215.
7 S. J. Cyvin, Molecular Vibrations and Mean Square Amplitudes, Universitetsforlaget, Oslo, and Elsevier, Amsterdam, 1968.
8 K. Kuchitsu and S. J. Cyvin, in S. J. Cyvin (Ed.), Molecular Structure and Vibrations, Elsevier, Amsterdam, 1972, Chap. 12.
9 L. Schäfer and R. A. Bonham, International Tables for X-Ray Crystallography, Vol. IV, Kynoch Press, Birmingham, 1973, Chap. 2.5.
10 K. Kuchitsu, Bull. Chem. Soc. Jpn., 40 (1967) 498, 505.
11 M. W. Lister and L. E. Sutton, Trans. Faraday Soc., 37 (1941) 393.
12 H. A. Skinner and L. E. Sutton, Trans. Faraday Soc., 40 (1944) 164.
13 E. A. Gastilovich, D. N. Shigorin, K. V. Zhukova and A. M. Sklyanova, Opt. Spektrosk., 28 (1970) 889.
14 H. Fujii and M. Kimura, Bull. Chem. Soc. Jpn., 44 (1971) 2643.
15 V. P. Pantel'kin and G. S. Koptev, Vestn. Mosk. Univ., Ser. Khim., 18 (1977) 175.
16 M. V. Vol'kenshtein, L. A. Gribov, M. A. El'yashevich and B. I. Stepanov, Kolebaniya Molekul (Molecular Vibrations), Nauka, Moscow, 1972.
17 Yu. N. Panchenko, G. S. Koptev and V. M. Tatevskii, Vestn. Mosk. Univ., Ser. Mat. Mekh. Astron. Fiz. Khim., (1967) 106.
18 A. V. Belyakov and L. S. Khaikin, available from VINITI (All-Union Institute of Scientific and Technical Information), Dep. No. 1909-78, 12 June, 1978.
19 R. Stølevik, H. M. Seip and S. J. Cyvin, Chem. Phys. Lett., 15 (1972) 263.
20 W. D. Gwinn, J. Chem. Phys., 55 (1971) 477.
21 H. L. Sellers, L. B. Sims, L. Schäfer and D. E. Lewis, J. Mol. Struct., 41 (1977) 149.
22 E. B. Wilson, J. C. Decius and P. C. Cross, Molecular Vibrations, McGraw-Hill, New York, 1955.
23 D. F. McIntosh, K. H. Michaelian and M. R. Peterson, Can. J. Chem., 56 (1978) 1289.
24 I. H. Williams, J. Mol. Spectrosc., 66 (1977) 288.
25 S. J. Cyvin, J. Brunvoll, B. N. Cyvin and E. Meisingseth, Bull. Soc. Chim. Belg., 73 (1964) 5.

26 W. C. Hamilton, Acta Crystallogr., 18 (1965) 502.
27 D. I. MacLean and R. E. Sacher, J. Organometal. Chem., 74 (1974) 197.
28 J. E. Huheey, J. Phys. Chem., 69 (1965) 3284.
29 J. E. Huheey, J. Phys. Chem., 70 (1966) 2086.
30 B. Beagley, K. McAloon and J. M. Freeman, Acta Crystallogr., Sect. B, 30 (1974) 444.
31 S. N. Wolf, L. S. Krisher and R. A. Gsell, J. Chem. Phys., 55 (1971) 2106.
32 L. S. Krisher, R. A. Gsell and J. M. Bellama, J. Chem. Phys., 54 (1971) 2287.
33 H. Fujii and M. Kimura, Bull. Soc. Chem. Jpn., 43 (1970) 1933.
34 B. Beagley, D. P. Brown and J. M. Freeman, J. Mol. Struct., 18 (1973) 335.
35 J. E. Drake, R. T. Hemmings, J. L. Hencher, F. M. Mustoe and Quang Sen, J. Chem. Soc., Dalton Trans., (1976) 811.
36 Y. S. Li and J. R. Durig, Inorg. Chem., 12 (1973) 306.
37 J. R. Durig, Y. S. Li and J. B. Turner, Inorg. Chem., 13 (1974) 1495.