Molecular structures of acetylene derivatives of tin
7.* Bis(trimethylstannyl)acetylene: analysis of electron diffraction data taking into account nonlinear relations between Cartesian and internal vibrational coordinates

L. S. Khaikin,[a]* O. E. Grikina,[a] V. A. Sipachev,[a] A. V. Belyakov,[b] and E. T. Bogoradovskii[b]

[a] Department of Chemistry, M. V. Lomonosov Moscow State University,
Leninskie Gory, 119899 Moscow, Russian Federation.
Fax: +7 (095) 932 8846
[b] Department of Organic Chemistry, Technological Institute,
26 Moskovskii prosp., 198013 St. Petersburg, Russian Federation.
Fax: +7 (812) 526 1037

The electron diffraction data on bis(trimethylstannyl)acetylene, $Me_3SnC{\equiv}CSnMe_3$, were analyzed in the framework of the one-dimensional dynamic model of free internal rotation of the $SnMe_3$ group about the axis of the Sn—C≡C—Sn linear fragment. The root-mean-square amplitudes and harmonic shrinkage corrections used in the analysis were calculated from the scaled quantum-chemical force field (i) taking into account nonlinear relations between Cartesian and internal vibrational coordinates at the first-order level of perturbation theory ($h1$) and (ii) using a conventional approach ($h0$). The r_{h1} parameters of internuclear distances describe the equilibrium geometry of the $Me_3SnC{\equiv}CSnMe_3$ molecule much better than the commonly accepted parameters $r_\alpha \equiv r_{h0}$. Substituent effects on the geometry of the acetylene fragment are discussed.

Key words: bis(trimethylstannyl)acetylene; gas-phase electron diffraction; molecular structure; molecular vibrations.

Our recent investigations on bis(trimethylsilyl)acetylene (**1**)[2,3] have shown that the use of the moments of the probability density function of internuclear distances r_{ij} (the first absolute moments, δ_{ij}, or harmonic shrinkage corrections and the second central moments, which give the root-mean-square (RMS) vibrational amplitudes, u_{ij}) calculated on the basis of the scaled quantum-chemical force field appeared to be highly efficient in the analysis of electron diffraction data. This made it possible to reduce the number of varied parameters of the molecular scattering intensity $sM(s)$ and to improve reliability of the molecular structure determination. Such additional information is of the particular importance in the case of organotin compounds, for which a "short" diffraction pattern is usually recorded (for the scattering angle (s) range no greater than 20 Å^{-1}) because of its rapid damping.[4]

We have also shown[2,3] the limited possibilities of the traditional scheme of spectroscopic calculations of the u_{ij} and δ_{ij} parameters in the harmonic small-amplitude vibration approximation,[5,6] which implies linear relations between Cartesian atomic displacements $\boldsymbol{x}$ and internal vibrational coordinates $\boldsymbol{q}$. (Hereafter, this approach is denoted as $h0$, which means a zero-order harmonic approximation with respect to atomic displacements from equilibrium positions.) The problem of taking into account nonlinear relations between Cartesian and internal vibrational coordinates has been solved previously[7,8] for harmonic potentials at the first-order level of perturbation theory with respect to atomic displacements. This new approach to calculations of vibrational characteristics (hereafter, it is denoted as $h1$) has been realized using an efficient algorithm. The use of the improved procedure for calculations of Cartesian atomic displacements and scaled quantum-chemical force fields, which allows reliable determination of vibrational modes, made it possible to achieve a complete correspondence of the $u_{ij,h1}$ and $\delta_{ij,h1}$ parameters obtained from spectroscopic calculations with the electron diffraction data on molecule **1**.[2,3]

Further testing of the new approach for (i) applicability to calculations of vibrational characteristics and (ii) its advantages as compared to the traditional approach was one of the main goals of this work. We carried out an electron diffraction study of the bis(trimethylstannyl)acetylene (**2**) molecule. The u_{ij} and δ_{ij} parameters were calculated using scaled quantum-chemical force fields obtained previously[1] by the RHF and MP2(fc) methods (here, fc means the "frozen" core approximation) with the standard 6-311G** basis set for C and H atoms and the Stevens—Basch—Krauss effective core potential (SBK ECP) with the optimized 31G**

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valence basis set for Sn atoms. The discrepancies between the results of structural analysis obtained using the traditional and new schemes of calculations of vibrational characteristics are to a great extent reduced to differing interpretation of the refined parameters of internuclear distances ($r_{ij,h0} \equiv r_{ij,\alpha}$ and $r_{ij,h1}$) in terms of their closeness to the equilibrium structure parameters. The $r_{ij,h1}$ parameters are the best estimates of the equilibrium structure parameters calculated using harmonic potentials. As will be shown below, in the case of chemical bonds they are nearly equivalent to experimental thermally average $r_{ij,g}$ values (we ignore centrifugal distortions). Therefore, the question how does the interaction of the acetylene group with substituents affect the molecular structure was answered using the $r_{ij,g}$ distance parameters reported for ethynyl derivatives of Group IV and VII elements rather than the traditionally used $r_{ij,\alpha}$ values.

Experimental

Procedures for the synthesis of compound **2** and determination of the purity of the product, as well as the equipment used in the electron diffraction experiment carried out at T ~353 K, have been reported earlier.[9]

In this work, the electron diffraction patterns of compound **2** and benzene, used as gaseous standard, were re-recorded photometrically and the electron beam wavelength (λ) was refined (according to the data obtained for benzene in the scattering angle range $1.4 \le s \le 8.2$ Å^{-1}, $\lambda = 0.049028$ Å at a convergence factor $R = 5\%$). The optical density distributions were measured on an MD-100 automated microdensitometer and the results were processed using the known procedure.[10]

The averaged curve of the total scattering intensity, $I^{T}(s)$, was calculated using three electron diffraction patterns of compound **2** obtained at a nozzle—plate distance of 49.48 cm for scattering angles in the range $1.5 \le s \le 14.875$ Å^{-1} with an increment $\Delta s = 0.125$ Å^{-1}. This curve was used in the structural analysis. The background line, $I^{B}(s)$, was plotted using an approximating spline function. The experimental $I^{T}(s)$ curve and final version of the $I^{B}(s)$ line are presented in Fig. 1.

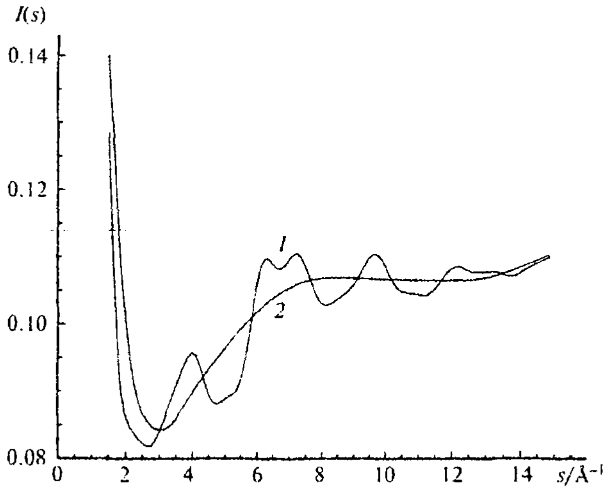


Fig. 1. Experimental total scattering intensity (*1*) and background intensity (*2*) curves for bis(trimethylstannyl)acetylene.

Structural parameters were refined by least-squares processing of the experimental molecular scattering intensity curve $sM^{\rm exp}(s)$ (Fig. 2). The theoretical molecular scattering intensities $sM^{\rm theor}(s)$ were calculated using complex scattering factors.[11] Anharmonic parameters $a_3(ij)$ for bonds were set equal to their values for diatomic molecules (2.131, 1.980, and 1.65 Å^{-1} for the C≡C, C—H, and Sn—C≡ (or Sn—C(H$_3$)) bonds, respectively).[12] For the distances between nonbonded atoms, these parameters were set to zero.

We used the KCED25 program[13] adapted for IBM-compatible PC by the Electron Diffraction Team of L. Eotvos Budapest University (Hungary) and modified at M. V. Lomonosov Moscow State University (Russian Federation). The u_{ij} and δ_{ij} parameters for internuclear distances were calculated using the SHRINK program.[7,8]

Molecular model for structural analysis of electron diffraction experiment

The results of quantum-chemical and spectroscopic study[1] have shown that molecule **2** is a nonrigid system with several large-amplitude torsional and bending motions. Internal rotations of the Me$_3$Sn groups about the Sn—C≡C—Sn fragment, which is linear in the equilibrium conformation, should be virtually free since the force constant of the motion is close to zero[1] and the possibility for steric interactions to occur between the groups in the acetylene fragment is ruled out because of large separation between them. According to the data of vibrational spectroscopy,[14] elastic, and quasi-elastic neutron scattering,[15,16] the height of the barrier to internal rotation of Me groups is more than halved on going from SiMe$_4$ to SnMe$_4$, for which it becomes equal to 0.80(5) kcal mol^{-1} only. Nearly the same barrier height

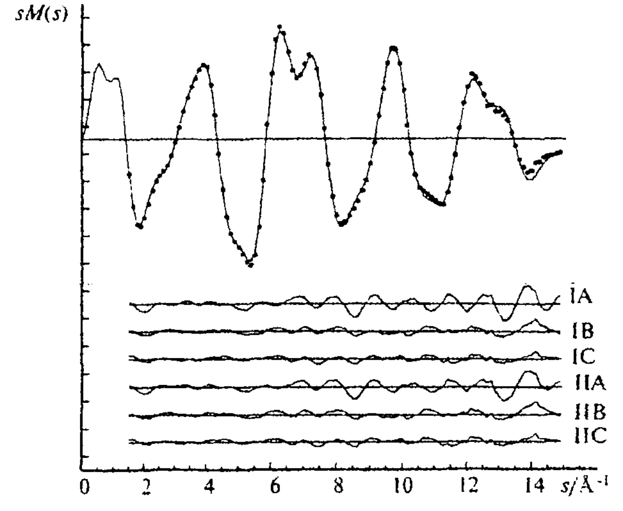


Fig. 2. Experimental points, theoretical curve of the molecular scattering intensity *sM*(*s*) for version IIB, and the difference curves for each version of structural analysis for bis(trimethylstannyl)acetylene (see text).

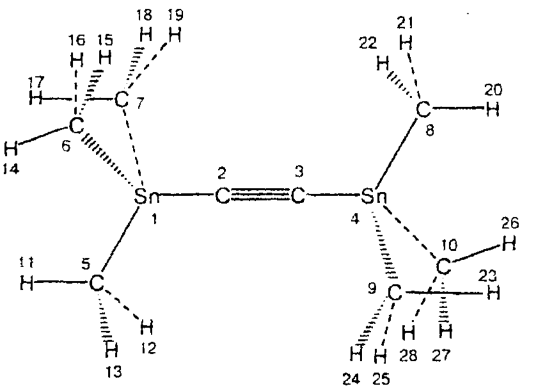
should also be expected for molecule **2**, for which the potential function will have a rather flattened shape in the range of angles of rotation of ~60° between its minimum and maximum. Finally, the results of ^{13}C NMR studies of stannylacetylenes suggest a flattened shape of the potential function and, hence, a large amplitude of linear bending vibrations in these molecules.[17,18]

In the studies of molecule **1** [3] the use of the one-dimensional dynamic model,[13,19] which takes into account only free rotations of the Me_3Si groups, has proved itself. Therefore, we used an analogous approach in the analysis of electron diffraction data on molecule **2**. The contributions of large-amplitude torsional vibrations of the Me groups affect only the distances between the pairs of atoms that include H atoms and have therefore virtually no effect on the scattering intensity in this electron diffraction experiment. When considering the linear bendings of the Sn—C≡C—Sn fragment, the incompleteness of the spectral data[20] for the low-frequency region complicates the problem of adequacy of the harmonic small-amplitude vibration approximation used in the calculations. Reliable estimates of the positions of all spectral bands corresponding to bendings of the linear fragment appeared to be impossible.[1] We will return to this problem in the section concerned with the refinement of the structural parameters of molecule **2**.

According to the dynamic model,[13,19] the probability distribution density $P_{ij}(r)$ for an internuclear distance in a molecular system characterized by a large-amplitude motion along coordinate q is approximated as

$$P_{ij}(r) \approx \int P_{ij}{}^{\mathrm{fr}}(r,q)P(q)\mathrm{d}q,$$

where $P(q)$ is the Boltzmann probability distribution density for coordinate q, which depends on the potential function $V(q)$ of the large-amplitude motion, and $P_{ij}{}^{\mathrm{fr}}(r,q)$ is the Gaussian probability distribution density for internuclear distance r_{ij} in a hypothetical molecular form which has a fixed q value and is involved in $3N - 7$ small-amplitude "framework" vibrations. Since the A_{2u} torsional mode of the Me_3Sn groups, which is inactive in vibrational spectra of **2**, is virtually pure,[1] exclusion of this mode and the corresponding degree of freedom from the solution of the spectral problem introduces no significant errors in the calculations of vibrational parameters for internuclear distances on the basis of other $3N - 7$ degrees of freedom. Within small intervals between successive q values, the $u_{ij}{}^{\mathrm{fr}}(q)$ and $r_{ij}(q)$ "framework" parameters of the $P_{ij}{}^{\mathrm{fr}}(r,q)$ function as well as harmonic corrections $\delta_{ij}{}^{\mathrm{fr}}(q)$ can be considered constant. In this work, the range of changes in the coordinate q of internal rotations of the Me_3Sn group (60° between the staggered conformation with D_{3d} symmetry and eclipsed conformation with D_{3h} symmetry) was divided into five equal intervals, and the total molecular scattering intensity was obtained as the sum of the contributions of all intervals calculated in this approximation.



2 (D_{3d})

In accord with the results of quantum-chemical calculations,[1] the Me_3Sn and Me groups were assumed to have a C_{3v} local symmetry, the Me groups being in a staggered conformation. By analogy with **1**,[2,3] it was assumed that internal rotation in molecule **2** is not accompanied by relaxational changes of other geometric parameters.

Calculations of mean vibrational amplitudes and shrinkage corrections for internuclear distances

Taking into account nonlinear relations between Cartesian and internal vibrational coordinates

The new approach[7,8] presupposes that the matrix B used in the matrix transformation $\boldsymbol{q} = B\boldsymbol{x}$ should be considered as a function of $\boldsymbol{q}$, *i.e.*, that one should take into account the dependence of B on the instantaneous configuration of the system in order to more correctly calculate Cartesian atomic displacements using internal vibrational coordinates. Correct to second-order terms in vibrational amplitudes, we can get

$$\boldsymbol{q} = B(\boldsymbol{q})\boldsymbol{x} \approx (B_0 + 1/2\Delta B)\boldsymbol{x}. \qquad (1)$$

Here, B_0 corresponds to the transformation matrix $B(\boldsymbol{q})$ for the equilibrium molecular configuration and ΔB is the matrix with the elements $\Delta b_{ij} = \sum_k q_k(t)(\partial b_{ij}/\partial q_k)|_{q=0}$. Assuming

$$q_k(t) = \sum_\alpha \bar{q}_k{}^{(\alpha)}\cos(\omega_\alpha t + \theta_\alpha),$$

where $\bar{q}_k{}^{(\alpha)}$ is the kth component of the αth eigenvector in internal vibrational coordinates, the summation is performed over all $3N - 6(5)$ vibrational modes, ω_α and θ_α are the frequency and phase of the corresponding normal vibration, and t is time, we can write

$$\Delta B = \sum_\alpha \Delta B_\alpha\cos(\omega_\alpha t + \theta_\alpha). \qquad (2)$$

Solving the spectral problem formulated using the new approach at the first-order level of perturbation theory gives (ignoring centrifugal distortions)[7,8]

$$\omega_\alpha = \omega_\alpha{}^0,$$

$$\boldsymbol{q}_\alpha(t) = \bar{\boldsymbol{q}}_\alpha{}^0\cos(\omega_\alpha t + \theta_\alpha) + \\ + \sum_\beta \chi_\beta^\pm \bar{\boldsymbol{q}}_\alpha{}^0\cos[(\omega_\alpha \pm \omega_\beta)t + (\theta_\alpha \pm \theta_\beta)], \qquad (3)$$

where superscript "0" labels the values obtained by solving the unperturbed problem, $\chi_\beta{}^\pm$ is the matrix coefficient equal to zero at $\beta = \alpha$, β runs from 1 to $3N - 6(5)$, and the summation is performed over both signs.[7,8] By applying the transformation

$$\boldsymbol{x} = B^{-1}\sum_\alpha \boldsymbol{q}_\alpha(t) \approx (E - 0.5B_0{}^{-1}\Delta B)B_0{}^{-1}\sum_\alpha \boldsymbol{q}_\alpha(t),$$

where E is the unit matrix, to Eq. (3) and by averaging the result over time and ensemble at a specified temperature, we get

$$\langle \boldsymbol{x} \rangle = -0.5B_0{}^{-1}\sum_\alpha \sigma_\alpha \Delta B_\alpha B_0{}^{-1}\bar{\boldsymbol{q}}_\alpha{}^0 = \\ = -0.5B_0{}^{-1}\sum_\alpha \sigma_\alpha \Delta B_\alpha \bar{\xi}_\alpha, \qquad (4)$$

where $\bar{\xi}_\alpha = B_0{}^{-1}\bar{\boldsymbol{q}}_\alpha{}^0$ is the αth eigenvector for the unperturbed spectral problem in Cartesian coordinates and

$$\sigma_\alpha = \langle Q_\alpha{}^2 \rangle = [h/(8\pi^2 c\nu_\alpha)]\coth[(hc\nu_\alpha/(2kT)]$$

is the so-called frequency factor corresponding to the temperature T and frequency ν_α of the αth normal mode.

Analytical expressions for u_{ij} and δ_{ij} obtained in the new approximation contain additional terms that are due to the configuration-dependent part of matrix $B(\boldsymbol{q})$. Traditional approach takes into account only the first term of the expression for the mean-square amplitudes

$$u^2{}_{ij,h1} = \sum_\alpha \sigma_\alpha(\boldsymbol{e}_{ij,e}\cdot\xi_{ij,\alpha})^2 + 0.5\delta_{ij}{}^2 + \ldots = \\ = \sum_\alpha \sigma_\alpha(\boldsymbol{e}_{ij,e}\cdot\xi_{ij,\alpha})^2 + \text{DELT}, \qquad (5)$$

where $\boldsymbol{e}_{ij,e}$ is the unit vector directed from atom i to atom j in the equilibrium state, $\xi_{ij,\alpha}$ is the vector obtained by subtracting the components corresponding to atom i from vector $\bar{\xi}_\alpha$, and DELT is the contribution due to nonlinear relations between Cartesian and internal vibrational coordinates.

In the case of linear fragment bendings and nonplanar vibrations of planar systems, the $\xi_{ij,\alpha}$ vectors are orthogonal to $\boldsymbol{e}_{ij,e}$ vectors for all internuclear distances in the fragments, so the contributions of these vibrations to the first term of Eq. (5) are equal to zero. The effect of these vibrations on the amplitude value is taken into account by the DELT terms. It is clear that in some instances the $\xi_{ij,\alpha}$ and $\boldsymbol{e}_{ij,e}$ vectors can also be orthogonal or nearly orthogonal in systems with arbitrary geometry. The fact that the frequency factor σ_α increases exponentially as frequency decreases also indicates the necessity of taking into account the DELT contribution. For this reason, the contributions of low-frequency vibrations (*e.g.*, linear fragment bendings) to the DELT value can become comparable with the contributions of high-frequency vibrations to the first term. Moreover, the contribution of linear fragment bendings can even be predominant if the frequency of these vibrations is much lower than other frequencies affecting the amplitude u_{ij}.

Comparison of the results of calculations of vibrational effects in the traditional and new approximations

The $u_{ij}{}^{\text{fr}}$ and $\delta_{ij}{}^{\text{fr}}$ values as well as the linear shrinkage effect values δ for internuclear distances in molecule **2** calculated in the traditional (*h*0) and new (*h*1) approximations for different temperatures are presented in Table 1 and in Fig. 3. The values obtained exceed those

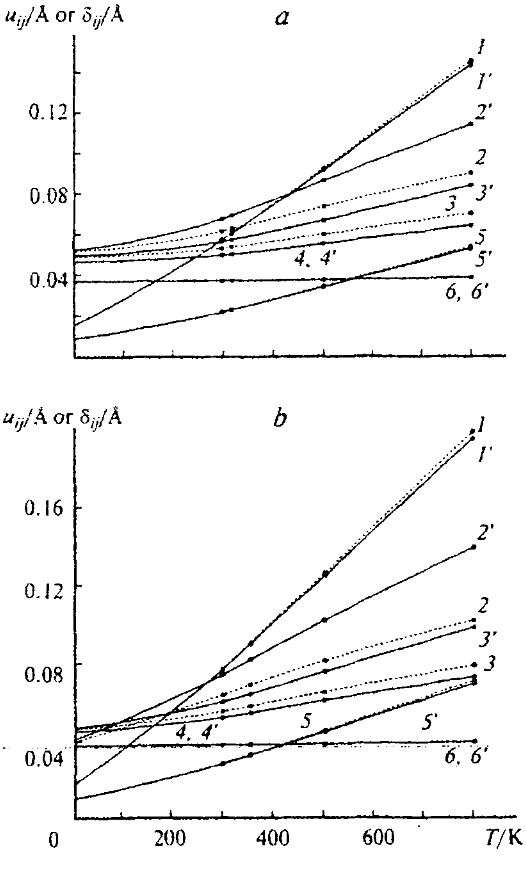


Fig. 3. Temperature dependences of the RMS amplitudes (*u*) and shrinkage effects (δ) in linear fragments of bis(trimethylsilyl)acetylene (*a*, E = Si) and bis(trimethylstannyl)acetylene (*b*, E = Sn) molecules calculated by the traditional scheme (*1—6*) and taking into account nonlinear relations between Cartesian and internal vibrational coordinates (*1′—6′*): δ(E...E) (*1*, *1′*); *u*(E...E) (*2*, *2′*); *u*(E...≡C) (*3*, *3′*); *u*(E—C≡) (*4*, *4′*); δ(E...≡C) (*5*, *5′*); and *u*(C≡C) (*6*, *6′*).

Table 1. Root-mean-square amplitudes (u_{ij}/Å) and harmonic shrinkage corrections (δ_{ij}/Å) for internuclear distances calculated for the D_{3d} conformer of the $Me_3SnC{\equiv}CSnMe_3$ molecule at $T = 0$ and 298 K using the set of $3N - 7$ internal vibrational coordinates (the internal rotation coordinate of the $SnMe_3$ group was excluded) by the traditional scheme (I) and taking into account nonlinear relations between Cartesian and internal vibrational coordinates (II)

Distance[a]	r_e/Å[b]	I				II			
		0 K		298 K		0 K		298 K	
		u_{h0}	$-\delta_{h0} \equiv K_0$	u_{h0}	$-\delta_{h0} \equiv K_T$	u_{h1}	$-\delta_{h1}$	u_{h1}	$-\delta_{h1}$
$Sn-C(H_3)$	2.1395	0.0506	0.0046	0.0543	0.0303	0.0506	0.0000	0.0543	0.0000
$Sn-C{\equiv}$	2.0991	0.0444	0.0045	0.0514	0.0292	0.0444	0.0000	0.0514	0.0000
$C{\equiv}C$	1.2038	0.0370	0.0084	0.0373	0.0185	0.0370	0.0000	0.0373	0.0000
C—H (av.)	1.0855	0.0780	0.0406	0.0780	0.1303	0.0780	0.0000	0.0781	0.0000
Sn...Sn	5.4019	0.0393	0.0001	0.0630	0.0006	0.0403	−0.0173	0.0733	−0.0758
$Sn...{\equiv}C$	3.3029	0.0457	0.0031	0.0545	0.0199	0.0463	−0.0099	0.0595	−0.0276
Sn...H (av.)	2.7166	0.1227	0.0190	0.1290	0.0834	0.1235	−0.0085	0.1315	−0.0087
$Sn...C(H_3)$	6.3917	0.1047	0.0008	0.2754	0.0043	0.1051	−0.0191	0.2789	−0.0914
Sn...H′(i.p.)	7.4411	0.1213	0.0070	0.2526	0.0295	0.1255	−0.0516	0.2748	−0.1908
Sn...H′(o.p.)	6.2995	0.2417	0.0045	0.5114	0.0147	0.2433	−0.0108	0.5183	−0.0554
$(H_3)C...C{\equiv}$	3.4265	0.0830	0.0059	0.1232	0.0468	0.0831	−0.0019	0.1232	−0.0053
$(H_3)C...{\equiv}C$	4.4525	0.0958	0.0041	0.1858	0.0332	0.0961	−0.0111	0.1877	−0.0352
$(H_3)C...C(H_3)$	3.5268	0.0884	0.0050	0.1307	0.0402	0.0885	−0.0021	0.1308	−0.0060

[a] Notations: av. is average; atoms labeled by "i.p." and "o.p." are situated in and out of the molecular symmetry plane, respectively.

[b] Obtained from quantum-chemical calculations[1] in the RHF/6-311G** approximation (Sn: SBK ECP).

found previously for molecule **1**[2] (see Fig. 3). This is first of all due to an increase in the corresponding internuclear distances by 0.3—0.6 Å.

The largest differences between the RMS vibrational amplitudes calculated in the traditional and new approximations are observed for the distances between nonbonded atoms in the $Sn-C{\equiv}C-Sn$ linear fragment and for other distances for which the contributions of bending coordinates of the linear fragment cannot be taken into account because of linearization of the problem in the traditional approximation (see Table 1). At $T =$ 298 K, the contributions of nonlinear terms to the RMS amplitudes for the Sn...Sn and $Sn...{\equiv}C$ distances amount to 0.010 and 0.005 Å, respectively, which is about twice as large as the analogous contributions for molecule **1**.[2] This can be due to a more flattened shape of the potential function of linear fragment bendings in molecule **2**. It should also be emphasized that the values of the amplitudes (and corrections) for distances between the atoms of the $Sn-C{\equiv}C-Sn$ linear fragment whose Cartesian displacements are independent of the torsional coordinate, coincide with those calculated for the complete set of $3N - 6$ internal vibrational coordinates. For other internuclear distances, which are "external" distances with respect to the rotating group, the effect of torsional motion on the vibrational parameters depends on how many atoms (one or two) are not in line with the axis of rotation. In the latter case, this effect is much more pronounced.

As can be seen in Table 1, the traditional scheme of calculations of harmonic shrinkage corrections $\delta_{ij,h0}$, which take into account only spectroscopic values of "perpendicular" amplitudes K_{ij}, gives greater correction values for the bonds than for long nonbonded distances. It has also been reported[21,22] that the corrections obtained from traditional calculations seem to be too large in the former and too small in the latter case. The new approach gives zero shrinkage corrections $\delta_{ij,h1}$ for the bonds (see above). As can be seen in Table 1, harmonic corrections $\delta_{ij,h1}$ substantially differ from zero only for the distances between nonbonded atoms.

According to calculations of molecules **1**[2] and **2** (this work), the estimates of linear shrinkage effects δ determined from the r_α- and r_{h1}-structural parameters virtually coincide. The minimum differences increase only slightly as temperature increases and do not exceed 0.001—0.002 Å for **1**[2] and 0.004 Å for **2** at 800 K (see Table 1 and Fig. 3). Hence the r_a (r_g) parameters determined from the electron diffraction experiment should be independent of the methods of calculations of shrinkage corrections (at least, for internuclear distances in the linear fragment). Substantial increase in the δ(Sn...Sn) shrinkage effect compared to the δ(Si...Si) one (see Fig. 3) confirms the conclusion drawn above that the $Sn-C{\equiv}C-Sn$ fragment is much more flexible than the $Si-C{\equiv}C-Si$ fragment, *i.e.*, that the linear fragment flexibility increases on going to heavier Group IV element. Therefore, the small-amplitude harmonic-potential approximation can appear to be insufficient for adequate description of the linear fragment bendings in molecule **2**.

Correspondence between spectroscopic values of vibrational parameters and electron diffraction data

Two series of the results obtained by refining the geometry of molecule **2** using vibrational characteristics of the internuclear distances calculated in the traditional (I) and new (II) approximations are presented in Tables 2—4. Structural analysis was carried out with

RMS amplitudes that were either fixed at the spectroscopic values or used as variables. The *R*-factor values show that the refinements performed using fixed values of all RMS amplitudes (versions IA and IIA) give insufficient agreement between theory and experiment, especially if the contributions of nonlinear relations between Cartesian and internal vibrational coordinates were not taken into account in spectroscopic calculations. In these cases, the $sM^{\exp}(s) - sM^{\text{theor}}(s)$ difference curves (see Fig. 2) demonstrate insufficiently rapid dumping of theoretical functions and the calculated $f(r)$ radial distribution curves (Fig. 4) display particularly large discrepancies between theory and experiment in the region of the peak at $r \approx 5.4$ Å, corresponding to the Sn...Sn distance in the linear fragment of molecule **2**. The use of vibrational parameters calculated in the *h*1 approximation taking into account the contributions of linear bending modes of the Sn—C≡C—Sn chain to the RMS amplitudes of the Sn...Sn and Sn...≡C distances improves agreement with the experiment by about 2% (*cf.* versions IA and IIA).

The inclusion of the RMS amplitudes as independent variables decreases the *R*-factors by an additional 3%, mainly due to further increase in the *u*(Sn...Sn) RMS amplitude, which much exceeds the experimental errors (versions IB and IIB, see Figs. 2 and 4). Changes in other amplitudes that were varied as compared to the results of spectroscopic calculations lie within the limits of experimental errors with the only exception being for *u*(Sn...H(av.)). Noteworthy is that refinement of versions IB and IIB gave virtually coinciding values of the RMS amplitudes.

Variation of the RMS amplitudes for the Sn—C(H$_3$) and Sn—C≡ bonds resulted in unrealistic values that exceed, in particular, the RMS amplitude for the Sn...≡C nonbonded distance (versions IC and IIC). In addition, the Sn—C≡ and C≡C bond lengths changed substantially because of strong correlations. The difference between the Sn—C≡ and Sn—C(H$_3$) bond lengths decreased down to 0.015 Å, which contradicts the results of MP2(fc) quantum-chemical calculations,[1] according to which the Sn—C≡ bond should be 0.04—0.05 Å shorter than the Sn—C(H$_3$) bond. Changes in other RMS amplitudes compared to those obtained for versions IB and IIB were insignificant and the *R*-factor value decreased by ~1% only.

Discrepancies between the *u*(Sn...Sn) amplitude found from electron diffraction data and the corresponding values obtained from spectroscopic calculations in the small-amplitude harmonic potential approximation can be explained by inadequacy of the force constants of linear bending vibrations, which were obtained by scaling the quantum-chemical force field, as well as by insufficiency of the small-amplitude approximation in the case of these vibrations. The former is associated with ambiguous assignment of linear bending vibrations of the Sn—C≡C—Sn fragment[1] due to incompleteness of the experimental spectra of the light and perdeuterated isotopomers of compound **2**.[20] Reproduction of the experimental u_{h1}(Sn...Sn) value obtained from electron diffraction data (0.114(5) Å) by spectroscopic calculations carried out taking into account nonlinear relations between Cartesian and internal coordinates required substantial reduction of the scale factor corresponding to the linear bending vibrations as compared to the previously obtained value (~0.3 *vs.* 0.69,[1] respectively), which has proved to be well transferable on a similar quantum-chemical force field calculated in the RHF approximation for molecule **1**.[2] As a result, several other RMS amplitudes increased appreciably in addition to the u_{h1}(Sn...Sn) amplitude. First of all was the amplitude for the Sn...≡C distance in the linear fragment, which increased from 0.0635 to ~0.085 Å. Their agreement with the amplitudes determined from the electron diffraction experiment became much poorer. Refinement of electron diffraction data using the vibrational characteristics obtained from this version of spectroscopic calculations and a fixed u_{h1}(Sn...≡C) value of 0.085 Å did not change the geometric parameters significantly as compared to version IIB (see Table 3), whereas the *R*-factor increased by ~1%.

At the same time, the *u*(Sn...Sn) value refined in both versions IB and IIB can be considered as an effective parameter; the increase in this parameter compared to the results of spectroscopic calculations is explained by insufficiency of the harmonic approximation due to the flattened shape of the potential function

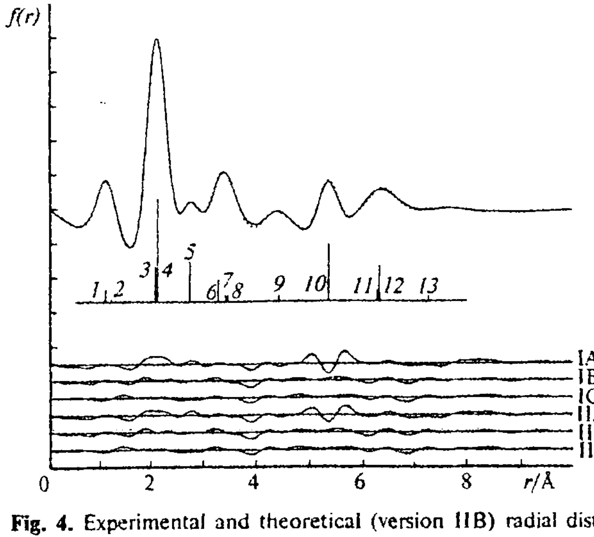


Fig. 4. Experimental and theoretical (version IIB) radial distribution curves (dashed and solid line, respectively) and the difference curves ($\Delta \times 2$) for each version of structural analysis of bis(trimethylstannyl)acetylene (see Tables 2 and 3). The damping constant $b = 0.0104$ Å^2. Shown are the principal contributions of internuclear distances independent of internal rotation of the SnMe$_3$ group: C—H (av.) (*1*), C≡C (*2*), Sn—C≡ (*3*), Sn—C(H$_3$) (*4*), Sn1...H11 (*5*), Sn1...C3 (*6*), C2...C5 (*7*), C5...C6 (*8*), C3...C5 (*9*), Sn1...Sn4 (*10*), Sn1...H21 (*11*), Sn1...C8 (*12*), and Sn1...H20 (*13*).

Table 2. Results of analysis of electron diffraction data for bis(trimethylstannyl)acetylene (T = 353 K) using the free internal rotation model in terms of the traditional approach (I, r_α-structure)

Parameter	IA		IB		IC	
	r_α	u_{h0}	r_α	u_{h0}	r_α	u_{h0}
Independent distance^a						
Sn—C(H$_3$)	2.093(7)	0.0563	2.099(5)	0.0563	2.093(5)	0.070(3)^b
Sn—C≡	2.076(13)	0.0541	2.061(8)	0.0541	2.078(8)	0.068^b
C≡C	1.192(24)	0.0373	1.216(14)	0.0373	1.185(13)	0.0373
C—H (av.)	0.951(11)	0.0782	0.947(5)	0.0782	0.950(5)	0.0782
Dependent distance^a						
Sn...Sn	5.343(12)	0.0686	5.339(12)	0.114(5)	5.342(11)	0.117(4)
Sn...≡C	3.268(14)	0.0576	3.278(10)	0.062(9)^c	3.264(9)	0.062(7)^d
Sn...H (av.)	2.651(12)	0.1324	2.652(8)	0.121(6)	2.653(7)	0.114(5)
Sn... C(H$_3$)	6.34(3)	0.2993	6.32(2)	0.320(19)^e	6.329(18)	0.321(15)^f
Sn...H′(i.p.)	7.28(3)	0.2724	7.26(2)	0.55(25)	7.273(19)	0.50(16)
Sn...H′(o.p.)	6.31(4)	0.5537	6.29(2)	0.575^e	6.31(2)	0.575^f
(H$_3$)C...C≡	3.39(3)	0.1320	3.370(15)	0.137^c	3.388(13)	0.137^d
(H$_3$)C...≡C	4.42(3)	0.2009	4.409(17)	0.22(3)	4.404(15)	0.23(2)
(H$_3$)C...C(H$_3$)	3.43(3)	0.1400	3.454(15)	0.145^c	3.435(13)	0.145^d
Bond angle/deg						
(H$_3$)C—Sn—C(H$_3$)	110.0(10)		110.7(5)		110.3(4)	
(H$_3$)C—Sn—C≡	108.9(11)		108.2(6)		108.6(4)	
Sn—C—H (av.)	115.4(11)		115.3(5)		115.7(4)	
H—C—H (av.)	103.0(13)		103.1(6)		102.6(5)	
Scale factor	1.544(23)		1.592(15)		1.645(16)	
R-factor (%)	10.13		5.11		3.97	

[a] Listed are the interatomic distances (r_α/Å) and their mean amplitudes (u_{ij}/Å). The estimates of experimental errors given in parentheses include the least-squares standard deviation values and the scale errors.[23] In the least-squares correlation matrices, the largest interaction coefficients (up to 0.8—0.96 in absolute values) were found for the Sn—C(H$_3$), Sn—C≡, and C≡C bond lengths. For notations "av.," "i.p.," and "o.p.," see note[a] to Table 1.

[b,c,d,e,f] The RMS amplitudes labeled by the same letter were refined by group; in each group, the differences between the amplitudes obtained from spectroscopic calculations were retained.

Table 3. Results of analysis of electron diffraction data for bis(trimethylstannyl)acetylene (T = 353 K) using the free internal rotation model taking into account nonlinear relations between Cartesian and internal vibrational coordinates (II, r_{h1}-structure) and comparison with the data of MP2(fc)/6-311G** (Sn: SBK ECP) calculations

Parameter	IIA		IIB		IIC		MP2,[1]
	r_{h1}	u_{h1}	r_{h1}	u_{h1}	r_{h1}	u_{h1}	r_e
Independent distance^a							
Sn—C(H$_3$)	2.131(6)	0.0563	2.135(5)	0.0563	2.129(5)	0.070(3)^b	2.1389
Sn—C≡	2.104(11)	0.0541	2.095(9)	0.0541	2.113(8)	0.068^b	2.0947
C≡C	1.224(20)	0.0373	1.239(14)	0.0373	1.206(13)	0.0373	1.2421
C—H (av.)	1.110(9)	0.0784	1.108(6)	0.0784	1.111(5)	0.0784	1.0926
Dependent distance^a							
Sn...Sn	5.433(12)	0.0816	5.429(12)	0.114(5)	5.432(11)	0.117(4)	5.4316
Sn...≡C	3.329(12)	0.0639	3.334(10)	0.065(9)^c	3.319(9)	0.066(7)^d	3.3369
Sn...H (av.)	2.769(11)	0.1361	2.770(8)	0.122(7)	2.771(7)	0.114(5)	2.7190
Sn... C(H$_3$)	6.44(3)	0.3037	6.42(2)	0.322(19)^c	6.436(18)	0.322(15)^f	6.4215
Sn...H′(i.p.)	7.52(3)	0.3001	7.51(2)	0.56(26)	7.523(19)	0.52(17)	7.4782
Sn...H′(o.p.)	6.39(4)	0.5622	6.37(3)	0.580^e	6.40(2)	0.580^f	6.3233
(H$_3$)C...C≡	3.44(2)	0.1320	3.425(15)	0.133^c	3.446(13)	0.134^d	3.4240
(H$_3$)C...≡C	4.49(2)	0.2033	4.484(17)	0.21(3)	4.479(15)	0.22(2)	4.4841
(H$_3$)C...C(H$_3$)	3.50(2)	0.1403	3.514(15)	0.142^c	3.493(13)	0.142^d	3.5245
Bond angle/deg							
(H$_3$)C—Sn—C(H$_3$)	110.3(8)		110.8(5)		110.3(4)		110.95
(H$_3$)C—Sn—C≡	108.6(9)		108.1(6)		108.7(4)		107.94
Sn—C—H (av.)	113.6(8)		113.5(5)		113.8(3)		110.24
H—C—H (av.)	105.1(9)		105.2(5)		104.8(4)		108.69
Scale factor	1.563(20)		1.594(16)		1.650(16)		—
R-factor (%)	8.30		5.24		4.01		—

[a,b,c,d,e,f] See the corresponding notes to Table 2.

Table 4. Experimental internuclear distances (r_a), harmonic vibrational corrections calculated for $T = 353$ K (the temperature of the experiment) and $T = 0$ K, and the r_α^0 and r_{h1}^0 parameters for the bond lengths in the ground vibrational state of the $Me_3SnC{\equiv}CSnMe_3$ molecule (in Å)

Distance	IB (R = 5.11%, see Table 2)[a]				IIB (R = 5.24%, see Table 3)[a]				r_a (see Ref. 9)[b]
	r_a	$r_\alpha - r_a$	$r_\alpha^0 - r_a$	r_α^0	r_a	$r_{h1} - r_a$	$r_{h1}^0 - r_a$	r_{h1}^0	
Sn—C(H$_3$)	2.1331	−0.0343	−0.0046	2.129(5)	2.1333	0.0015	0.0000	2.133(5)	2.127(5)
Sn—C≡	2.0944	−0.0330	−0.0054	2.089(8)	2.0936	0.0014	−0.0009	2.092(9)	2.095(10)
C≡C	1.2366	−0.0202	−0.0073	1.230(14)	1.2379	0.0012	0.0011	1.239(14)	1.21[c]
C—H (av.)	1.1023	−0.1553	−0.0350	1.067(5)	1.1023	0.0057	0.0055	1.108(6)	1.108(14)
Sn...Sn	5.3389	0.0002			5.3389	0.0900			5.341(9)
Sn...≡C	3.3002	−0.0224			3.3008	0.0332			3.295(8)
Sn...H (av.)	2.7543	−0.1022			2.7546	0.0152			2.781(19)
Sn...C(H$_3$)	6.3082	0.0090			6.3004	0.1216			6.01—6.45
Sn...H′(i.p.)	7.2818	−0.0245			7.2718	0.2339			6.12——7.48
Sn...H′(o.p.)	6.2540	0.0317			6.2574	0.1150			
(H$_3$)C...C≡	3.4199	−0.0502			3.4135	0.0113			3.41(5)
(H$_3$)C...≡C	4.4396	−0.0302			4.4333	0.0502			4.33—4.47
(H$_3$)C...C(H$_3$)	3.4957	−0.0420			3.5013	0.0126			3.51(5)

[a] See note[a] to Table 2.

[b] Results of r_a-analysis with inclusion of effective nonlinearity of the Sn—C≡C—Sn fragment.

[c] Fixed.

of linear bending vibrations in molecule **2**. Agreement between the values of the u(Sn...≡C) RMS amplitude obtained from electron diffraction experiment and by spectroscopic calculations (versions IIA and IIB, see Table 3) indicates that the contribution of this vibration to u(Sn...≡C) is much smaller than its contribution to the u(Sn...Sn) amplitude. Therefore the small-amplitude harmonic-potential approximation is more appropriate.

Interpretation of experimental values of structural parameters

The data presented in Table 4 confirm the conclusion drawn above that the $r_{ij,a}$ parameters of the molecular scattering intensity function determined directly from the electron diffraction data are virtually independent of the approximation used in spectroscopic calculations of the vibrational characteristics of internuclear distances. Apparently, the same is also valid for the thermally average internuclear distances $r_{ij,g}$, which are related to $r_{ij,a}$ simply through the mean-square amplitude ($r_{ij,g} = r_{ij,a} + u^2_{ij}/r_{ij}$) in the case of Gaussian probability distribution.[6]

As was mentioned above, the discrepancies between the results of structural analyses performed using the standard and new scheme of calculations of u_{ij} and δ_{ij} values (versions I and II, respectively) are determined by the closeness of the obtained estimates of the $r_{ij,h0} \equiv r_{ij,\alpha}$ and $r_{ij,h1}$ parameters to the equilibrium values. If we ignore the contribution of centrifugal distortion, then, correct to third-order terms, the general equation for the thermally average value of internuclear distance

$$r_{ij,g} \approx r_{ij,e} + \langle \Delta z_{ij} \rangle + [(\langle \Delta x_{ij}^2 \rangle + \langle \Delta y_{ij}^2 \rangle)/2r_{ij,e}] =$$
$$= r_{ij,e} + \langle \Delta z_{ij} \rangle + K_{ij}$$

can be rewritten at the first-order level of perturbation theory as

$$r_{ij,g} \approx r_{ij,e} + \langle \Delta z_{ij} \rangle_{\mathrm{anharm}} + \langle \Delta z_{ij} \rangle_{\mathrm{harm}} + K_{ij}, \qquad (6)$$

since first-order harmonic and anharmonic corrections are additive. The last term in Eq. (6) should be positive, whereas the preceding term, which is also of the second order in vibrational amplitudes, is most often negative. Its absolute value is larger than or nearly equal to (for bonds) K_{ij}.[7,8] The commonly accepted $r_{ij,\alpha} \equiv r_{ij,h0}$ parameters are obtained by subtracting the last term from both sides of Eq. (6)

$$r_{ij,\alpha} = r_{ij,g} - K_{ij} = r_{ij,e} + \langle \Delta z_{ij} \rangle_{\mathrm{anharm}} + \langle \Delta z_{ij} \rangle_{\mathrm{harm}}.$$

The standard approach[5,6] presupposes that the mean-square "perpendicular" amplitude K_{ij} is the only harmonic vibrational contribution to the thermally average internuclear distance and that the $\langle \Delta z_{ij} \rangle$ correction is completely determined by anharmonic terms of the potential energy function. If so, harmonic vibrational effects $\delta_{ij,\alpha} = \delta_{ij,h0}$ lengthen chemical bonds. In this approximation, the $r_{ij,g}$ and, as a rule, $r_{ij,a}$ parameters are larger than corresponding $r_{ij,\alpha}$ values or analogous estimates for the ground vibrational state, r_α^0 (see Tables 1, 2, and 4), which would coincide with the data for the equilibrium structure correct to anharmonic corrections.

Taking into account nonlinear relations between Cartesian and internal vibrational coordinates, we determine that the total harmonic shrinkage corrections $\delta_{ij,h1}$ for bonds are nearly equal to zero (if centrifugal distortions are ignored).[7,8] In other words, the assumption that the harmonic component of $\langle \Delta z_{ij} \rangle$ is equal to zero immediately gives $K_{ij} \cong 0$. This means that we cannot take into account the contribution of "perpendicular" amplitudes and simultaneously ignore $\langle\Delta z_{ij}\rangle_{\rm harm}$. Though the algorithm developed to assess the $r_{ij,h1}$ parameters does not include separate calculations of K_{ij} and $\langle\Delta z_{ij}\rangle_{\rm harm}$ values,[8] we will write its key expression for comparison

$$r_{ij,h1} = r_{ij,g} - \langle\Delta z_{ij}\rangle_{\rm harm} - K_{ij} = r_{ij,e} + \langle\Delta z_{ij}\rangle_{\rm anharm}, \qquad (7)$$

whence it follows that the $r_{ij,h1}$ parameters do differ from $r_{ij,e}$ by the anharmonic contribution and are nearly equal to $r_{ij,g}$ for bonds. Physically, the $\boldsymbol{r}_{h1}$ coordinate vector corresponds to the minimum of the harmonic potential function which best describes both electron diffraction and spectroscopic data for the molecule and is temperature-dependent because of the second term in the right side of expression (7). We believe that the r_{h1}-structure is the closest approximation to the equilibrium structure that can be obtained using harmonic potentials. This is confirmed by very good agreement between the results of the MP2 quantum-chemical calculations of the equilibrium structure of molecule **2** and the $r_{ij,h1}$ parameters (see Table 3), which is not observed for the $r_{ij,h0} \equiv r_{ij,\alpha}$ parameters (see Table 2). The physical meaning of the r_α-structure remains unclear. At best, the $r_{ij,\alpha}$ parameters can serve as intermediate values in the course of calculations because, as was discussed above, the procedure for calculations of shrinkage corrections has no significant effect on the $r_{ij,a}$ ($r_{ij,g}$) parameters, which are arguments of the $sM(s)$ function. Since the corrections calculated at the first-order level of perturbation theory are additive, the use of the r_{h1}-structure makes it possible to allow for anharmonic effects with ease. It should also be emphasized that the estimates of the $r_{ij,h1}{}^0$ parameters for bonds obtained by introducing partial anharmonic corrections in the diatomic approximation, $r_g - r_g{}^0 \approx 1.5a_3(u_T{}^2 - u_0{}^2)$,[6] and the $\delta_{ij,h1}$ corrections calculated for $T = 0$ K virtually coincide with the $r_{ij,h1}$ parameters, whereas the estimates of the $r_{ij,\alpha}$ and $r_{ij,\alpha}{}^0$ values differ significantly (see Tables 2—4).

The C≡C and Sn—C≡ bond lengths in mono- and polyethynyl tin derivatives

In Table 5, we compare the C≡C and Sn—C≡ bond lengths in molecule **2** obtained in this work with corresponding values in other stannylacetylenes studied by electron diffraction.[24—27] Since the $r_{ij,h1}$ parameters, which are the best estimates of the equilibrium structure in the harmonic approximation, can be considered nearly equal to the $r_{ij,g}$ values in the case of bonds, the use of the latter rather than the traditional $r_{ij,\alpha}$ parameters for comparison is more justified.

According to quantum-chemical calculations,[1,2] the C≡C bond in molecule **2** must be nearly as long as that in molecule **1** (only 0.003 Å longer). This has been confirmed by comparing the results obtained in the electron diffraction study of molecule **1** [3] and in this work (see Table 5). The effect of asymmetrical substitution in the acetylene fragment of the $Me_3SnC{\equiv}CH$ molecule could not be determined because of large experimental errors.[24,25] However, compared to asymmetrically substituted polyethynyl derivatives of tin, the C≡C bond in molecule **2** is somewhat lengthened. Recently,[2,3] our analysis of the data for ethynyl derivatives of silicon has led to an analogous conclusion.

It has been accepted for long that the C≡C acetylene bond length is only slightly sensitive to substituent effects. Lengthening of the C≡C bond in acyclic hydrocarbons was first observed in electron diffraction studies of the simplest acetylene derivatives.[28,29] In the diacetylene molecule, the r_g(C≡C) value appeared to be ~0.005 Å larger than in the acetylene molecule.[30] However, the effect of heteroatoms has been little studied as yet. In Table 6, we compare the spectroscopic (r_s) and electron diffraction (r_g) data for acetylene and ethynyl derivatives of Group IV and VII elements and the experimental estimates of the r_e(C≡C) equilibrium parameters. Usually, the $r_g - r_s$ difference is estimated at 0.01±0.01 Å.[6] According to the electron diffraction data (see Table 6),

Table 5. Estimates of the r_g parameters (in Å) and linear shrinkage effects δ (Å) for stannylacetylenes (the experiments were carried out at temperatures between 295 and 360 K)

Molecule	r_g		δ		Ref.
[version]	C≡C	Sn—C≡	Sn...≡C	Sn...Sn	
$Me_3SnC{\equiv}CH$	1.22(5)	2.09(6)	0.0[a]	—	24
	1.23(2)	2.13(3)	0.02	—	25
$Me_3SnC{\equiv}CSnMe_3$	1.21[a]	2.096(10)	0.04[b]	0.06[b]	9
[I]	1.238(14)	2.096(8)	0.032	0.089	This work
[II]	1.239(14).	2.095(9)	0.032	0.089	
$Sn(C{\equiv}CH)_4$	1.228(8)	2.068(5)	—	—	26
$ISn(C{\equiv}CH)_3$	1.226(6)	2.062(17)	—	—	26
$Sn(C{\equiv}CCF_3)_4$	1.216(6)	2.072(7)	0.0[a]	—	27

[a] Fixed.

[b] Obtained from the r_a-analysis carried out using the model with a nonlinear acetylene fragment (the Sn—C≡C angle was 170.4(15)°).

Table 6. Comparison of the $C{\equiv}C$ bond lengths (r/Å) in the acetylene molecule and in the molecules of ethynyl derivatives of Group IV and VII elements obtained from spectroscopic calculations and electron diffraction data[a]

Molecule	Spectroscopic calculations		Electron diffraction data,
	r_e	r_s	r_g
$H-C{\equiv}C-H$	1.2024(3),[31] 1.2026(3)[32]	1.207(5)[33]	1.212(1)[30]
$Me-C{\equiv}C-H$	—	1.2066(3)[34]	1.210(4)[35]
$Me-C{\equiv}C-Me$	—	—	1.2135(13)[28]
$Me_3C-C{\equiv}CH$	—	1.209(2)[36]	1.211(8)[37]
$H_3Si-C{\equiv}C-H$	—	1.2076(20)[38,39]	1.223(2)[40]
$Me_3Si-C{\equiv}C-SiMe_3$	—	—	1.239(3)[3]
$H_3Ge-C{\equiv}C-H$	—	1.208(2)[41]	—
$Sn(C{\equiv}C-H)_4$	—	—	1.228(8)[26]
$Me_3Sn-C{\equiv}C-SnMe_3$	—	—	1.239(14)[b]
$F-C{\equiv}C-H$	1.1962(8)[42,43]	1.198(3)[44]	—
$Cl-C{\equiv}C-H$	—	1.2033(5)[45]	—
$Br-C{\equiv}C-H$	—	1.2038(30)[46]	—
$F_3C-C{\equiv}C-H$	—	1.201(2)[47]	—
$F_3C-C{\equiv}C-CF_3$	—	—	1.205(4)[48]

[a] Experimental errors are given in parentheses.

[b] This work.

the interaction of stannyl and silyl groups with the acetylene fragment causes lengthening of the $C{\equiv}C$ bond by 0.01—0.03 Å as compared to acetylene and its alkyl derivatives. The results of spectroscopic studies indicate that the presence of electronegative substituents (Hal and CF_3 group) causes shortening of the $C{\equiv}C$ bond.

The equilibrium $C{\equiv}C$ bond length in the acetylene molecule found from the data of high-resolution rovibrational IR and Raman spectra (1.2025(3) Å)[31,32] appeared to be smaller than the $r_g(C{\equiv}C)$ parameter obtained from electron diffraction data (1.212(1) Å).[29] Therefore, anharmonic vibrational effects cause a lengthening of this bond by ~0.01 Å. Quantum-chemical calculations of the acetylene molecule in the MP2/6-31G* approximation gave an exaggerated estimate of the equilibrium $C{\equiv}C$ bond length (1.2177 Å).[49] Our calculations in the (11s7p1sp3d2f1g/6s3p1d)/[5s3p1sp3d2f1g/4s3p1d] extended basis set reduced the estimate down to 1.2080 and 1.2001 Å at the MP2 and MP4(SDQ) levels of theory, respectively. Therefore, the anharmonic contribution to the experimental value of the $C{\equiv}C$ bond length and the systematic error of MP2 calculations of this bond length in ethynyl derivatives of Si and Sn with basis sets of the 6-311G** type (see Refs. 2 and 1, respectively) should be nearly equal and have the same sign.

The $Sn-C{\equiv}$ bond in monoethynyl derivatives of Sn is 0.02—0.03 Å longer than in polyethynyl ones (see Table 5). This can be due to higher electronegativities of ethynyl substituents compared to those of methyl substituents.[50,51] Analogous changes are also observed for other molecular systems (*e.g.*, methylchlorostannanes[52—54]) in which the bonds of the central atom with electronegative substituents are shortened as the number of these substituents increases. By and large, the results of detailed analysis[55] of changes in the ionization potentials, chemical shifts in the ^1H NMR spectra, and characteristic vibrational frequencies of the ethynyl derivatives of Group IV elements (E), $Me_nE(C{\equiv}CH)_{4-n}$, also indicate that the $E-C{\equiv}$ bond strengthens as the number of ethynyl groups increases. This was explained by the joint effect of electronegativity of the substituents and $p_\pi-d_\pi$-interaction.

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