

Structures of Vinylstannane (Ethenylstannane) and Allylstannane (2-Propenylstannane) Determined by Gas-Phase Electron Diffraction and Quantum Chemical Calculations

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Vinylstannane ($\text{H}_2\text{C}=\text{CHSnH}_3$) and allylstannane ($\text{H}_2\text{C}=\text{CHCH}_2\text{SnH}_3$) have been synthesized, and their structures and conformational properties have been determined by ab initio and density functional theory calculations and gas electron diffraction. There is only one stable conformation of vinylstannane, where one of the Sn–H bonds is *synperiplanar* to the double bond. The most important structural parameter is the $\text{C}(\text{sp}^2)\text{--Sn(IV)}$ bond length, which is $r_a = 215.1(6)$ pm ($r_e = 214.1(6)$ pm). The CCSn bond angle is $121.6(4)^\circ$. Uncertainties are estimated errors equal to 2.5 times the least-squares standard deviation and include uncertainty in the electron wavelength. Theoretical calculations indicate that there are two stable rotameric forms of allylstannane. The $\text{C}=\text{C}\text{--C--Sn}$ chain of atoms is *synperiplanar* (dihedral angle $= 0^\circ$) in the less stable form and *anticlinal* (dihedral angle $\approx 106^\circ$ from *synperiplanar*) in the more stable rotamer. Theoretical calculations predict an energy difference between the two conformations of about 10 kJ mol^{-1} . There is no indication of the presence of the *synperiplanar* conformation in the gas phase at room temperature. The final analysis was therefore carried out assuming that only the *anticlinal* conformer was present. The $\text{C}=\text{C}\text{--C--Sn}$ dihedral angle was found to be $102.9(19)^\circ$ from the *synperiplanar* conformer, which is the smallest value found for this angle in the $\text{C}=\text{C}\text{--C--X}$ ($\text{X} = \text{C}, \text{Si}, \text{Ge}, \text{Sn}$) series of compounds. The $\text{C}(\text{sp}^3)\text{--Sn(IV)}$ bond length is $r_a = 218.9(8)$ pm ($r_e = 217.6(8)$ pm), and the CCSn bond angle is $110.9(6)^\circ$. The B3LYP calculations using the cc-pVTZ basis set for C and H and the cc-pVTZ-PP basis set for Sn reproduce the experimental $r_e(\text{C--Sn})$ bond distances very well, while the MP2(FC) calculations underestimate the $r_e(\text{C--Sn})$ bond distances by 3–4 pm.

Introduction

Progress made in the last decade toward the synthesis of primary α,β - and β,γ -unsaturated stannanes (e.g., allenylstannane,¹ 1-alkynylstannane,¹ and propargylstannane²) makes it possible to study the molecular properties of the smallest members of these compounds. The geometrical structures of these smallest stannanes are important because they will serve as prototypes for this family of molecules and act as reference structures when the molecular structures of larger stannanes are discussed. Moreover, it will also be important to know the molecular structure in the gas phase when comparisons are made with the structures in the condensed phase in order to assess the influence of intermolecular forces. Accurate molecular geometries of these prototypes are useful for quantum chemists exploring computational methods and basis sets.

Vinylstannane ($\text{H}_2\text{C}=\text{CHSnH}_3$) is the smallest stannane with a double bond and is therefore of special interest. Recently, a first determination of a $\text{Sn--C}(\text{sp}^2)$ bond distance³ has been determined in the gas phase for a free allenylstannane ($\text{H}_2\text{C}=\text{C}=\text{CHSnH}_3$) molecule. A comparison of the $\text{Sn--C}(\text{sp}^2)$ bond

distances in vinylstannane and allenylstannane would be interesting to see if the $\text{C}=\text{C}=\text{C}$ group will have any effect on the $\text{Sn--C}(\text{sp}^2)$ bond distance.

Allylstannane ($\text{H}_2\text{C}=\text{CH--CH}_2\text{SnH}_3$) is the smallest unsaturated stannane that can exist as a conformational mixture. To our knowledge, very little information is available about the conformational behavior of these molecules. The present study of allylstannane should therefore be of interest.

Gas electron diffraction (GED) is a well-suited method to investigate the conformational and structural problems presented by vinyl- and allylstannane. The scarcity of information concerning the molecular structures and conformational properties of unsaturated organostannanes in general was the motivation to undertake the present investigation.

Synthesis of Vinyl- and Allylstannane

The preparation of several 1-alkenylstannanes has already been reported.^{4,5} In 1959, Brinckman and Stone⁴ reported the first synthesis of the unsubstituted derivative, vinylstannane **1**, by addition of lithium aluminum hydride (LAH) to trichloroethenylstannane **2**.^{6,7} Compound **1** was obtained in a low yield

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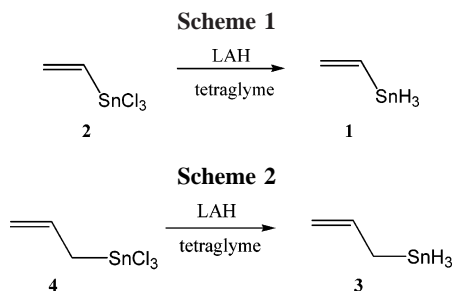
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after a difficult purification. This approach was then optimized and generalized to substituted derivatives (Scheme 1).⁵

Only one allylic stannane with Sn–H bonds, the (*E*)-but-2-enyldimethylstannane, has so far been prepared.⁸ The unsubstituted derivative, 2-propenylstannane **3**, was synthesized in Rennes by reduction of trichloro-2-propenylstannane **4** with LAH. Allylstannane **3** was obtained in a 34% yield and characterized by infrared and ¹H, ¹³C, and ¹¹⁹Sn NMR spectroscopy and high-resolution mass spectrometry (HRMS). The ¹H NMR chemical shifts and coupling constants are typical for allylstannane, and the ¹¹⁹Sn NMR chemical shift (δ –328.9 ppm) is comparable to that of phenylstannane (δ –320 ppm) and the low-frequency shift relative to those of primary alkylstannanes (EtSnH₃: δ –282 ppm).⁵ The half-life time of a 5% sample diluted in deuterotoluene or CD₂Cl₂ is about 6 h, and it increases to 1 day in the presence of duroquinone, a radical inhibitor. Brown, unidentified oligomeric compounds were obtained on standing at room temperature.

Experimental Section

Materials. Tetraglyme, lithium aluminum hydride, 2-propenyltri-*n*-butylstannane, and tin tetrachloride were purchased from Aldrich and used without further purification. Trichloroethenylstannane **2** has been prepared as previously reported.^{6,7}

Preparation of Ethenylstannane 1. The apparatus previously described for the reduction of phosphonates⁹ was used. A 250 mL flask containing the reducing mixture (1.6 g, 40 mmol of LiAlH₄ in 60 mL of tetraglyme) was attached to the vacuum line, cooled to –10 °C, and degassed. The trichloroethenylstannane **2** (5.0 g, 20 mmol in 20 mL of tetraglyme) was slowly added with a flex-needle through the septum. During and after the addition, the high-boiling compounds were removed in a trap cooled at –80 °C, and ethenylstannane **1** was condensed in a second trap cooled at –130 °C. When the reaction was complete (30 min), the second trap was disconnected from the vacuum line by stopcocks, attached to the spectrometer, and kept at a low temperature (–80 °C) before analysis. Ethenylstannane **1** was obtained in 63% yield (1.9 g, 12.6 mmol).

2-Propenyltrichlorostannane 4.^{10–13} Into a 50 mL two-necked flask immersed in a cold bath (–30 °C) and equipped with a magnetic stirring bar and through a nitrogen inlet was introduced tin tetrachloride (13.1 g, 50 mmol). 2-Propenyltri-*n*-butylstannane (16.5 g, 50 mmol) was added dropwise for about 5 min. The mixture was allowed to warm to 30 °C and stirred for 20 min at this

temperature. The product purified by distillation (bp 51 °C (0.1 mm of Hg)) was obtained in a 67% yield (8.9 g, 33 mmol).

2-Propenylstannane 3. The apparatus used for ethenylstannane **1** was employed. A 250 mL flask containing the reducing mixture (1.6 g, 40 mmol of LiAlH₄ in 60 mL of tetraglyme) was attached to the vacuum line, cooled to –10 °C, and degassed. The 2-propenyltrichlorostannane **4** (2.66 g, 10 mmol in 20 mL of tetraglyme) was then slowly added (10 min) via a flex-needle through a septum. During and after the addition, the 2-propenylstannane **3** was distilled off in vacuo from the reaction mixture. A cold trap (–80 °C) selectively removed the less volatile products, and stannane **3** was condensed into a cell cooled at –120 °C. After being disconnected from the vacuum line by stopcocks, the cell was connected to the spectrometer and kept at low temperature (< –80 °C) before analysis. Bp_{0.1} ≈ –90 °C. Yield: 34%. $\tau_{1/2}$ (5% diluted in C₇D₈ or CD₂Cl₂, room temperature): 6 h. ¹H NMR (C₇D₈): δ 1.61 (d, 2H, ³J_{HH} = 8.3 Hz, ²J₁₁₉SnH = 74.0 Hz, CH₂Sn); 4.36 (t, 3H, ³J_{HH} = 2.0 Hz, ¹J₁₁₉SnH = 1855 Hz, SnH₃); 4.63 (d, 1H, ³J_{HHcis} = 9.9 Hz, ⁴J₁₁₉SnH = 28.0 Hz, C=CH(H)); 4.74 (d, 1H, ³J_{HHtrans} = 16.7 Hz, ⁴J₁₁₉SnH = 29.0 Hz, C=CH(H)); 5.68 (ddt, 1H, ³J_{HHtrans} = 16.7 Hz, ³J_{HHcis} = 9.9 Hz, ³J_{HH} = 8.3 Hz, CH). ¹³C NMR (C₆D₆): δ 11.6 (t, ¹J_{CH} = 133.3 Hz, ¹J₁₁₉SnC = 354.2 Hz (d)); 112.1 (dd, ¹J_{CH} = 153.4 Hz, ¹J_{CH} = 160.6 Hz, ³J₁₁₉SnC = 61.8 Hz (d)); 137.4 (d, ¹J_{CH} = 151.8 Hz, ²J₁₁₉SnC = 55.4 Hz (d)). ¹¹⁹Sn NMR (C₆D₆–C₇H₈, rt): δ –328.9 (¹J₁₁₉SnH = 1855 Hz). Gas-phase IR ($\nu_{cm^{-1}}$): 3091 (m, $\nu_{C=CH}$), 2983 (m), 2928 (m), 1904 (vs, ν_{Sn-H}), 1634 (m, $\nu_{C=C}$), 1194 (w), 1027 (w), 901 (m), 682 (s). HRMS: calcd for C₃H₈¹²⁰Sn 163.9648, found 163.964.

Microwave Experiment. Attempts were also made to observe the microwave spectrum of vinylstannane in the 26–62 GHz spectral interval using the Oslo Stark spectrometer.¹⁴ However, no signals that could be attributed to vinylstannane were observed. Since the intensities of the spectral transitions are proportional to the square of the dipole moment, the failure to observe a spectrum is assumed to indicate that the dipole moment of this compound is too small. This is consistent with the quantum chemical predictions described below.

Electron-Diffraction Experiment. Vinylstannane and allylstannane were synthesized in Rennes as described above, and the purity was determined by ¹H NMR spectroscopy to be 97 and 92%, respectively. The same syntheses were performed in Oslo without any further checking of the purity. The compounds were pumped on before exposure to remove the most volatile components. Both compounds were distilled directly into the apparatus. The estimated purity should therefore be better than stated above. The sample bulb was partially in liquid N₂ and adjusted to give a steady gas flow through the nozzle in order to get optimum scattering conditions. Neither the vapor pressure nor the temperature inside the sample bulb was monitored during the experiment.

GED data were recorded using a Balzers KD-G2 unit.¹⁵ The experimental data were recorded on BAS-III image plates, which were scanned using a BAS-1800II scanner. Both the image plates and the scanner are manufactured by FujiFilm.

Each image plate was divided into four sectors, two in the *x*-direction (left and right) and two in the *y*-direction (up and down). Data for each sector were treated separately, and the two sectors in the *x*-direction were averaged to give one modified intensity curve in the *x*-direction and, similarly, one modified intensity curve in the *y*-direction. The data range in *x*- and *y*-direction is slightly different, as a consequence of the rectangular shape of the image plate. This procedure applies for both camera distances and gave four curves as shown in Figures 4 and 6. These four curves were

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Table 1. Experimental Conditions of the GED Investigation

	vinylstannane		allylstannane	
camera distance/mm	498.65	248.88	498.65	248.88
electron wavelength/pm	5.820	5.820	5.820	5.820
nozzle temperature/°C	22	22	22	22
s ranges/nm ⁻¹ : x-direction	20.00–145.00	40.00–270.00	22.25–148.75	50.00–290.00
y-direction	20.00–131.25	40.00–250.00	20.00–130.00	50.00–240.00
$\Delta s/\text{nm}^{-1}$	1.25	2.50	1.25	2.50

Table 2. Calculated Structure^a of Vinylstannane (C_s-symmetry)

	HF ^b		B3LYP ^b		MP2 ^b (FC)
	<i>sp</i>	<i>ap</i>	<i>sp</i>	<i>ac</i>	<i>sp</i>
Bond Lengths					
Sn ₁ –C ₂	213.8	214.2	214.6	215.1	211.2
C ₂ =C ₃	132.0	131.9	132.8	132.8	133.9
Sn ₁ –H ₇	171.2	171.2	171.5	171.5	169.0
Sn ₁ –H ₈	171.3	171.2	171.7	171.6	169.1
C ₂ –H ₆	107.8	107.8	108.6	108.6	108.4
C ₃ –H ₄	107.7	107.7	108.6	108.6	108.4
C ₃ –H ₅	107.6	107.7	108.4	108.5	108.3
Bond Angles					
∠Sn ₁ C ₂ C ₃	123.4	124.4	123.4	124.4	122.3
∠C ₃ C ₂ H ₆	117.9	117.8	118.8	118.6	117.6
∠C ₂ C ₃ H ₄	121.9	121.9	121.8	121.8	121.7
∠C ₂ C ₃ H ₅	122.5	122.7	122.5	122.8	121.9
∠C ₂ Sn ₁ H ₇	108.3	108.8	108.0	109.0	107.3
∠C ₂ Sn ₁ H ₈	110.4	110.4	110.4	110.4	110.7
∠H ₇ Sn ₁ H ₈	109.7	109.3	109.8	109.2	109.8
Dihedral Angles					
∠C ₃ C ₂ Sn ₁ H ₇	0.0	180.0	0.0	180.0	0.0
∠C ₃ C ₂ Sn ₁ H ₈	–120.2	60.1	–120.1	60.0	–119.8
Energy ^c					
<i>E</i> ₀	–292.48425	–292.48302	–294.10866	–294.10750	–293.03862
Relative Energy ^d					
Δ <i>E</i>	0.0	3.23	0.0	3.04	

^a Distances in pm, angles in deg, energy in hartree, rotational barrier, Δ*E*, in kJ mol^{–1}. ^b The following basis sets were used: cc-pVTZ for C and H atoms and cc-pVTZ-PP for the Sn atom. The frozen-core procedure was employed. ^c In hartree and corrected for zero-point vibrational energies. ^d Relative to the *sp* form.

used in the least-squares structure analysis. The raw data were further processed as described elsewhere.¹⁶

The necessary modification and scattering functions were computed from tabulated atomic scattering factors¹⁷ for the proper wavelength and *s*-values. The experimental backgrounds were computed using the program KCED12,¹⁸ where the coefficients of a chosen degree of a polynomial function are determined by the least-squares method by minimizing the differences between the total experimental intensity and the molecular intensity calculated from the current best geometrical model. The average experimental intensities were modified by $s/|f'_{\text{C}}f'_{\text{Ge}}|$, where f' denotes the coherent scattering factors. The experimental conditions employed in the GED experiments are given in Table 1.

Quantum Chemical Calculations

Procedure. Quantum chemical calculations were performed for vinyl- and allylstannane using the GAUSSIAN03 suite of programs¹⁹ running on the HP “superdome” facilities in Oslo. Full geometry optimizations were carried out for the *sp* and *ap* forms of vinylstannane (Figure 1) and of each of the *sp*, *ap*, and *ac* forms of allylstannane (Figure 2) at the ab initio Hartree–Fock (HF) level of theory, followed by density functional theory calculations at the B3LYP level.^{20,21} Dunning’s correlation-

consistent polarized valence triple- ζ (cc-pVTZ) basis set²² was employed for the carbon and hydrogen atoms, whereas the cc-pVTZ-PP basis set²³ was used for the tin atom. This basis set includes a small-core relativistic pseudopotential to replace 28 core electrons ([Ar] + 3d).²⁴ Vibrational frequencies were calculated in each case.

It has been claimed that Møller–Plesset second-order perturbation calculations (MP2) using a comparatively large basis set will predict structures that are close to the equilibrium structures.²⁵ MP2 frozen core (FC) calculations using the same

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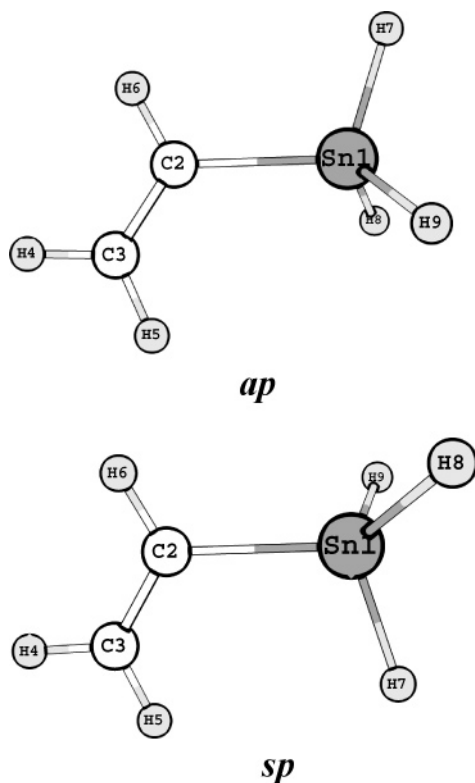


Figure 1. The *antiperiplanar* (*ap*) and *synperiplanar* (*sp*) rotamers of vinylstannane. The *sp* rotamer is the only stable form of this molecule.

basis sets were performed for the most stable rotamers of vinyl- and allylstannane only, owing to restrictions on computer time.

Selected results are listed in Tables 2 and 3. The energies shown in these tables are total electronic energies, which have been corrected for zero-point vibrational energies. The B3LYP and MP2 vibrational frequencies and their assignments are shown in Tables 4 and 5. Vibrational frequencies have been reported for the gas-phase infrared spectrum of vinylstannane.^{4,5} They are included in Table 4. The gas-phase spectrum of allylstannane is listed in Table 5. This spectrum was obtained at room temperature and a pressure of 50 mbar using a Nicolet Avatar 320 FT-IR spectrometer having a resolution of 0.5 cm⁻¹.

Vinylstannane. Some comments are warranted. The *sp* form of vinylstannane was found to be more stable than the *ap* conformation. The HF energy difference between *sp* and the *ap* form is 3.2 kJ mol⁻¹, and nearly the same value, 3.0 kJ mol⁻¹, is found in the B3LYP calculations. No imaginary vibrational frequencies were computed for the *sp* form as opposed to the *ap* rotamer, which was found to have one imaginary frequency associated with rotation of the SnH₃ group around the Sn₁–C₂ bond. The *sp* form is therefore a minimum on the energy hypersurface, whereas the *ap* form is a first-order transition state.²⁶ The energy difference of the two forms (about 3 kJ mol⁻¹) corresponds to the rotational barrier of the stannyl group.

It should be noted that the MP2 structural parameters of the *sp* isomer are close to those computed using the B3LYP or HF procedures, apart from the Sn₁–C₂ bond length, which is predicted to be significantly shorter (2–4 pm) in the MP2 calculations than in the HF or the B3LYP calculations.

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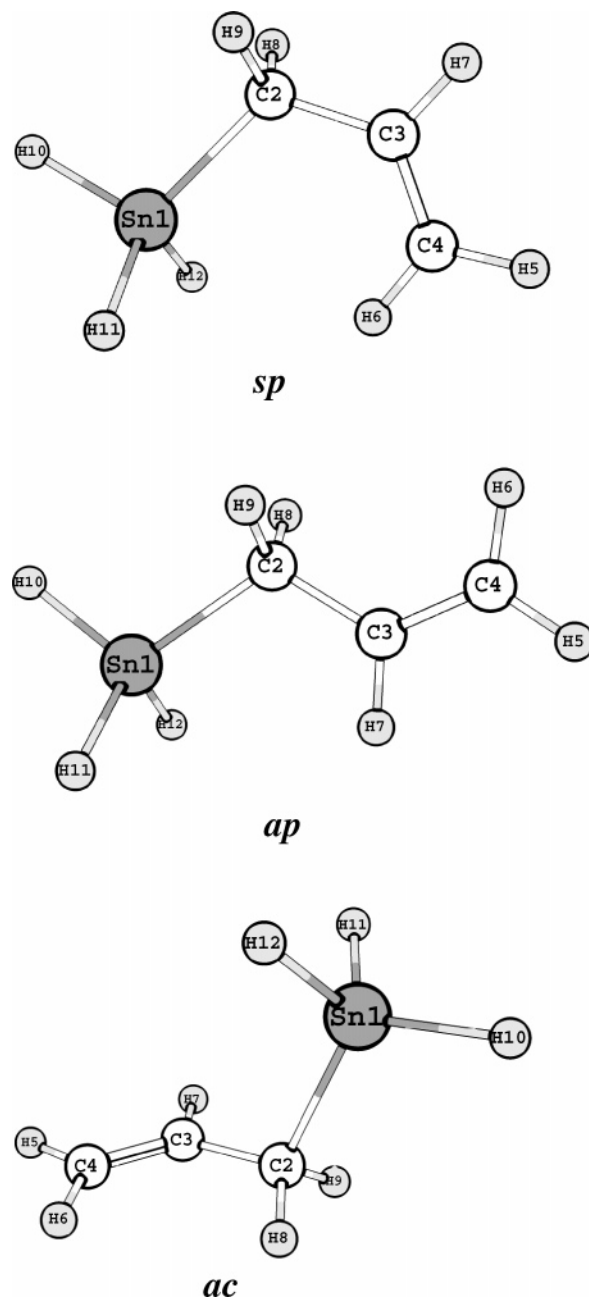


Figure 2. The *synperiplanar* (*sp*), *antiperiplanar* (*ap*), and *anticlinal* (*ac*) conformers of allylstannane with atom numbering. The gas phase consists almost exclusively of *ac* at room temperature.

The principal inertial axis dipole moment components of the *sp* rotamer were calculated to be $\mu_a = 0.11$, $\mu_b = 0.63$, and $\mu_c = 0.0$ D (by symmetry) by the MP2 procedure. Similar results were obtained in the HF and B3LYP calculations. The comparatively small calculated dipole moment components are consistent with the failure to observe a microwave spectrum (see above), taking into consideration that the calculated dipole moments are normally larger than their experimental counterparts.

Allylstannane. The *ac* isomer was determined to be the global energy minimum in the case of allylstannane. No imaginary vibrational frequencies were calculated in this case. A different situation was found for the *ap* form. One imaginary frequency associated with the rotation around the C₂–C₃ bond was obtained for this conformation, which is therefore a transition state. The *sp* rotamer is another stable conformation, since no

Table 3. Calculated Structure^a of Allylstannane

	HF ^b			B3LYP ^b			MP2(FC) ^b
	C _s <i>sp</i>	C _s <i>ap</i>	C ₁ <i>ac</i>	C _s <i>sp</i>	C _s <i>ap</i>	C ₁ <i>ac</i>	C ₁ <i>ac</i>
Bond Lengths							
Sn ₁ –C ₂	216.4	216.2	217.3	217.8	217.5	219.3	214.7
C ₂ –C ₃	150.4	151.5	149.4	149.8	151.1	148.6	148.8
C ₃ =C ₄	131.6	131.6	131.8	132.7	132.7	133.1	133.7
Sn ₁ –H ₁₀	171.5	171.3	171.5	171.8	171.6	171.9	169.3
Sn ₁ –H ₁₁	171.3	171.5	171.4	171.6	171.8	171.7	169.2
Sn ₁ –H ₁₂	171.3	171.5	171.2	171.6	171.8	171.5	169.0
C ₂ –H ₈	108.6	108.4	108.4	109.3	109.1	108.9	108.9
C ₂ –H ₉	108.6	108.4	108.3	109.3	109.1	109.0	108.9
C ₃ –H ₇	107.9	107.7	107.8	108.9	108.6	108.7	108.6
C ₄ –H ₅	107.4	107.4	107.3	108.2	108.2	108.1	108.0
C ₄ –H ₆	107.4	107.4	107.5	108.2	108.2	108.4	108.2
Bond Angles							
∠Sn ₁ C ₂ C ₃	118.6	115.2	112.5	118.0	115.0	111.8	109.8
∠C ₂ C ₃ C ₄	127.9	124.4	125.8	127.8	124.3	125.8	125.1
∠C ₃ C ₂ H ₈	109.2	110.2	110.7	109.9	110.8	112.0	111.3
∠C ₃ C ₂ H ₉	109.2	110.2	111.2	109.9	110.8	111.8	111.6
∠C ₃ C ₄ H ₅	121.0	121.2	121.2	121.2	121.4	121.4	121.2
∠C ₃ C ₄ H ₆	121.0	121.2	121.8	121.2	121.4	121.7	121.1
∠C ₄ C ₃ H ₇	117.5	117.5	118.3	117.6	117.6	118.4	118.4
∠Sn ₁ C ₂ H ₈	106.8	107.2	106.9	106.4	106.7	106.8	108.0
∠Sn ₁ C ₂ H ₉	106.8	107.2	107.5	106.4	106.7	105.7	107.6
∠C ₂ Sn ₁ H ₁₀	107.5	109.7	109.7	107.5	109.8	110.1	111.1
∠C ₂ Sn ₁ H ₁₁	111.4	110.1	109.8	111.4	110.0	109.6	108.9
∠C ₂ Sn ₁ H ₁₂	111.4	110.1	109.7	111.4	110.0	109.3	108.4
∠H ₁₀ Sn ₁ H ₁₁	108.8	109.2	109.0	108.7	109.2	109.1	109.3
∠H ₁₀ Sn ₁ H ₁₂	108.8	109.2	109.3	108.7	109.2	109.5	109.7
∠H ₁₁ Sn ₁ H ₁₂	108.9	108.6	109.3	108.9	108.6	109.3	109.5
∠H ₈ C ₃ H ₉	105.3	106.4	107.8	105.3	106.4	108.5	108.4
Dihedral Angles							
∠C ₄ C ₃ C ₂ Sn ₁	0.0	180.0	106.8	0.0	180.0	105.7	103.7
∠C ₃ C ₂ Sn ₁ H ₁₀	180.0	180.0	171.9	180.0	180.0	171.9	172.3
∠C ₃ C ₂ Sn ₁ H ₁₁	60.9	59.9	52.1	60.9	59.8	52.0	52.0
∠C ₃ C ₂ Sn ₁ H ₁₂	–60.9	–59.9	–68.1	–60.9	–59.8	–67.8	–67.1
∠C ₂ C ₃ C ₄ H ₅	180.0	180.0	–178.9	180.0	180.0	–178.9	–178.1
∠C ₂ C ₃ C ₄ H ₆	0.0	0.0	1.2	0.0	0.0	1.2	2.0
∠H ₅ C ₄ C ₃ H ₇	0.0	0.0	0.0	0.0	0.0	–0.1	–0.3
Energy ^c							
E ₀	–331.50187	–331.49913	–331.50567	–333.41036	–333.40751	–333.41431	–332.23750
Relative Energy ^d							
ΔE	10.0	17.2	0.0	10.4	17.2	0.0	0.0
ΔG ⁰	9.0	<i>e</i>	0.0	6.1	<i>e</i>	0.0	0.0

^a Distances in pm, angles in deg, energy in hartree, rotational barrier, ΔE, in kJ mol^{–1}. ^b The following basis sets were used: cc-pVTZ for C and H atoms and cc-pVTZ-PP for Sn atoms. The frozen-core procedure was employed. ^c Corrected for vibrational ZPE. ^d Relative to the energy of the *ac* conformer. Dimension: kJ/mol. ^e Not calculated.

imaginary frequencies were predicted for it. However, its total energy is significantly *higher* than that of the *ac* form. It is seen in Table 3 that the *ac* form is predicted by both HF and B3LYP calculations to be more stable than the *sp* by about 10 kJ/mol, whereas the *ap* transition state is predicted to be about 17 kJ/mol above the *ac* conformer.

The Gibbs energy differences between the *ap* and *ac* rotamers, ΔG⁰, which are given in the same table, were calculated to be 9.9 and 6.1 kJ/mol, respectively. The difference between these two numbers (9.9 and 6.1) is mainly due to a vibrational entropy effect. The lowest torsional frequency is predicted to be 18 cm^{–1} for the *sp* rotamer and 81 cm^{–1} for the *ac* rotamer in the B3LYP calculations, while 66 cm^{–1} for the *sp* rotamer and 84 cm^{–1} for the *ac* rotamer were computed for the HF calculations.

The potential energy function for internal rotation about the C–Sn bond, which was calculated at the B3LYP level of theory, is sketched in Figure 3. The energy of the *ac* conformer has been arbitrarily taken to be zero. Calculations were performed at intervals of 15°, with full optimization of all the other structural parameters.

It is noted that the Sn₁–C₂ bond length is considerably shorter in the MP2 calculations than in the HF and B3LYP calculations, just as found for vinylstannane. Moreover, the ∠C₂C₃C₄ and ∠Sn₁C₂C₃ bond angles in the *sp* conformation are calculated to be about 2° and 6° larger than in the *ac* conformation. This may reflect steric strain arising when the vinyl and stannyl groups are brought into close proximity.

Structure Refinement

Vinylstannane. It was found in the quantum chemical calculations above that the *sp* isomer with a symmetry plane (C_s symmetry) is the only stable form of this compound. Fifteen independent parameters were chosen to describe its molecular structure. These parameters are the bond distances *r*(Sn₁C₂), *r*(C₂C₃), *r*(C₂H₆), *r*(C₃H₄), *r*(C₃H₅), *r*(Sn₁H₇), and *r*(Sn₁H₈) = *r*(Sn₁H₉) and the bond angles ∠Sn₁C₂C₃, ∠C₂C₃H₄, ∠C₂C₃H₅, ∠C₃C₂H₆, ∠C₂Sn₁H₇, ∠C₂Sn₁H₈ = ∠C₂Sn₁H₉, and ∠H₇Sn₁H₈ = ∠H₇Sn₁H₉. In addition, the ∠C₃C₂Sn₁H₇ dihedral angle was allowed to vary in order to test whether the rotational barrier of the stannyl group could be determined by electron diffraction.

Table 4. Calculated Fundamental Frequencies and Tentative Assignments^a for the *sp* Rotamer of Vinylstannane

symmetry		B3LYP	MP2(FC)	IR (gas)
A''	C–SnH ₃ <i>tor</i>	90	110	
A'	SnCC <i>b</i>	225	228	
A''	SnH ₃ <i>r</i>	364	379	
A'	Sn–C <i>st</i>	439	469	
A'	SnH ₃ <i>r</i>	548	577	
A''	CH <i>w</i>	562	580	
A'	SH ₃ <i>s b</i>	689	726	683 ^b
A''	SH ₃ <i>as b</i>	717	760	693 ^b
A'	SH ₃ <i>as b</i>	727	771	717 ^b
A''	CH ₂ <i>w</i>	993	995	953 ^b
A'	CH ₂ <i>r</i>	1016	1017	1002 ^b
A''	CH <i>w</i>	1043	1060	1008 ^b
A'	CH <i>r</i>	1283	1288	1250 ^c
A'	CH ₂ <i>sc</i>	1440	1446	
A'	C=C <i>st</i>	1650	1637	ca. 1600 ^b
A'	SnH ₃ <i>s st</i>	1893	2034	1865 ^c
A''	SnH ₃ <i>as st</i>	1893	2038	
A'	SnH ₃ <i>as st</i>	1902	2040	
A'	CH ₂ <i>s st</i>	3100	3152	2938 ^c
A'	CH <i>st</i>	3127	3183	2980 ^c
A'	CH ₂ <i>as st</i>	3177	3243	3042 ^c

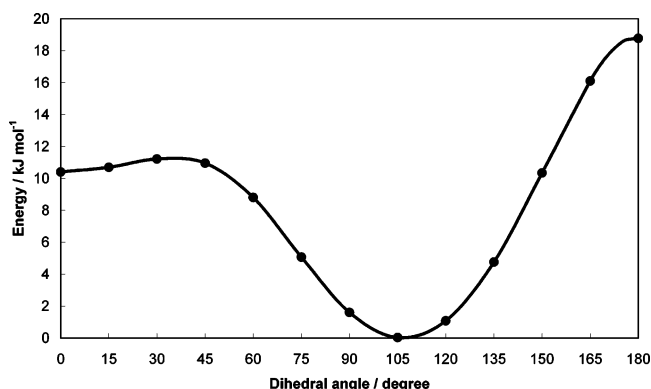
^a Frequencies in cm^{−1}; *tor*, torsion; *b*, bending; *st*, stretching; *w*, wagging; *tw*, twist; *sc*, scissoring; *r*, rock; *s*, symmetric; *as*, asymmetric. ^b Ref 4. ^c Ref 5.

Table 5. Calculated Fundamental Frequencies and Tentative Assignments for the *ac* Rotamer of Allylstannane^a

assignment	B3LYP	MP2(FC)	IR (gas) ^b
C–Sn <i>tor</i>	81	79	
C–C <i>tor</i>	96	95	
C–C–Sn <i>b</i>	194	194	
C=C–C <i>b</i>	377	388	
SnH ₃ <i>r</i>	412	418	
SnH ₃ <i>r</i>	433	450	
Sn–C <i>st</i>	491	521	
SnH ₃ <i>s b</i>	685	708	677
=CH ₂ <i>tw</i>	702	718	
SnH ₃ <i>as b</i>	720	755	
SnH ₃ <i>as b</i>	727	762	
=CH ₂ <i>r</i>	786	784	
=CH ₂ <i>w</i>	928	916	901
C–C <i>st</i>	945	954	991
=CH ₂ <i>r</i>	1023	1024	1027
=CH <i>w</i>	1060	1058	
CH ₂ <i>w</i>	1136	1142	1018
CH ₂ <i>w</i>	1219	1224	1194
=CH <i>b</i>	1335	1327	
=CH ₂ <i>sc</i>	1444	1441	
CH ₂ <i>sc</i>	1474	1473	
C=C <i>st</i>	1690	1685	1634
SnH ₃ <i>s st</i>	1881	2027	1904
SnH ₃ <i>as st</i>	1895	2034	
SnH ₃ <i>as st</i>	1905	2039	
CH ₂ <i>s st</i>	3049	3094	3091
CH ₂ <i>as st</i>	3098	3156	
=CH <i>st</i>	3123	3174	
=CH ₂ <i>s st</i>	3131	3183	
=CH ₂ <i>as st</i>	3215	3279	

^a See Table 4 for abbreviations. ^b See text.

The low scattering power of the hydrogen atoms was the reason for using constraints as follows: $r(\text{C}_3\text{H}_4) = r(\text{C}_2\text{H}_6) + \Delta 1$, where $\Delta 1$ is the difference between the bond lengths $r(\text{C}_3\text{H}_4)$ and $r(\text{C}_2\text{H}_6)$. Similarly, $r(\text{C}_3\text{H}_5) = r(\text{C}_2\text{H}_6) + \Delta 2$, $r(\text{Sn}_1\text{H}_8) = r(\text{Sn}_1\text{H}_9) = r(\text{Sn}_1\text{H}_7) + \Delta 3$, $\angle \text{C}_2\text{C}_3\text{H}_4 = \angle \text{C}_3\text{C}_2\text{H}_6 + \Delta 4$, $\angle \text{C}_2\text{C}_3\text{H}_5 = \angle \text{C}_3\text{C}_2\text{H}_6 + \Delta 5$, $\angle \text{C}_2\text{Sn}_1\text{H}_8 = \angle \text{C}_2\text{Sn}_1\text{H}_9 = \angle \text{C}_2\text{Sn}_1\text{H}_7 + \Delta 6$, $\angle \text{H}_7\text{Sn}_1\text{H}_8 = \angle \text{H}_7\text{Sn}_1\text{H}_9 = \angle \text{C}_2\text{Sn}_1\text{H}_7 + \Delta 7$. The differences, $\Delta 1$ – $\Delta 7$, were taken from the quantum chemical calculation (B3LYP/cc-pVTZ-PP(Sn)/cc-pVTZ(C,H)). They are 0.02, −0.13, and 0.14 pm and 3.08°, 3.77°, 2.39°,

**Figure 3.** B3LYP potential energy function for rotation about the C–Sn bond in allylstannane. Calculations were performed at intervals of 15°, shown as dots in the figure. 0° corresponds to the *sp* conformer and 106° to the *ac* conformer.**Table 6.** Structure and *u*-Values of Vinylstannane^{a,b}

	<i>r</i> _a	<i>u</i> _{calc}	<i>u</i> _{exp}
Bond Lengths			
Sn ₁ –C ₂	215.1(6)	5.1	6.3(6)
C ₂ =C ₃	133.7(5)	4.0	4.0
Sn ₁ –H ₇	180.4(9)	9.2	10.7(10)
Sn ₁ –H ₈ ^c	180.5(9)	9.2	10.7(10)
C ₂ –H ₆	108.4(8)	7.5	7.5
C ₃ –H ₄ ^c	108.4(8)	7.4	7.4
C ₃ –H ₅ ^c	108.2(8)	7.4	7.4
Bond Angles			
∠Sn ₁ C ₂ C ₃	121.6(4)		
∠C ₃ C ₂ H ₆ ^d	118.8		
∠C ₂ C ₃ H ₄ ^c	121.8		
∠C ₂ C ₃ H ₅ ^c	122.5		
∠C ₂ Sn ₁ H ₇	106.3(24)		
∠C ₂ Sn ₁ H ₈ ^c	108.7		
∠H ₇ Sn ₁ H ₈ ^c	108.1		
Dihedral Angle			
∠C ₃ C ₂ Sn ₁ H ₇	9(31)		
<i>R</i> _f , %	9.91 ^e		

^a Distances and *u*-values in pm, angles and dihedral angles in deg. Parenthesized values are estimated error limits given as $2.5(\sigma^2_{\text{lsq}} + (0.001r)^2)^{1/2}$ for bond distances where σ_{lsq} is one standard deviation obtained from the least-squares refinements using a diagonal weight matrix and the second term represent 0.1% uncertainty in the electron wavelength. For angles and *u*-values the estimated error limits are $2.5\sigma_{\text{lsq}}$. The error estimates are in units of the last digits. ^b The B3LYP structure that was used as the starting point in least-squares analysis; see text. ^c These parameters were calculated according to the constraints discussed in the text. ^d Fixed. ^e Goodness of fit defined as $\sum_s w(I_s^{\text{obs}} - I_s^{\text{calc}})^2 / \sum_s w(I_s^{\text{obs}})^2$, where *w* is a weight function usually equal to 1.

and 1.78°, respectively. It was not possible to determine $\angle \text{C}_3\text{C}_2\text{H}_6$. This angle was therefore fixed at the value shown in Table 6.

An attempt was made to determine the barrier to internal rotation of the SnH₃ group. The C₃C₂Sn₁H₇ dihedral angle was refined for this purpose. A value of 9° with one standard deviation of 13° was found in this refinement. Clearly, the scattering from C₃...H_{Sn} pairs of atoms is not sufficient to obtain an accurate value for the barrier to internal rotation of the stannyl group. Fixing this dihedral angle at 0.0° did not influence the values of the other structural parameters.

The root-mean-square vibrational amplitudes (*u*-values) and perpendicular correction coefficients (*D*-values) were calculated employing the ASYM program^{27,28} using the B3LYP/cc-pVTZ-PP(Sn)/cc-pVTZ(C,H) force fields. Vibrational amplitudes for

(27) Hedberg, L.; Mills, I. M. *J. Mol. Spectrosc.* **1993**, *160*, 117.

(28) Hedberg, L.; Mills, I. M. *J. Mol. Spectrosc.* **2000**, *203*, 82.

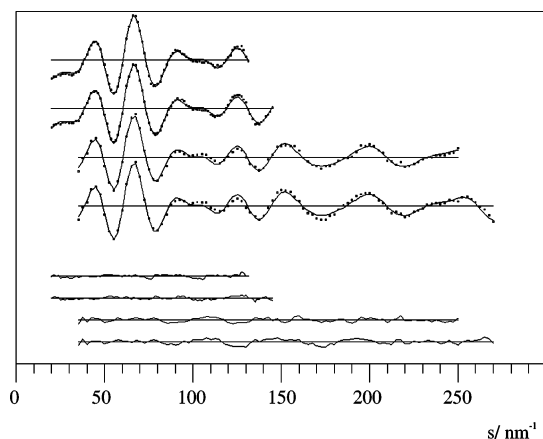


Figure 4. Intensity curves for vinylstannane. The two upper curves are for the *y*- and *x*-directions of the long camera distance, respectively. The two next curves are for the *y*- and *x*-directions of the middle camera distance. The four lower curves are difference curves. Camera distances are found in Table 1.

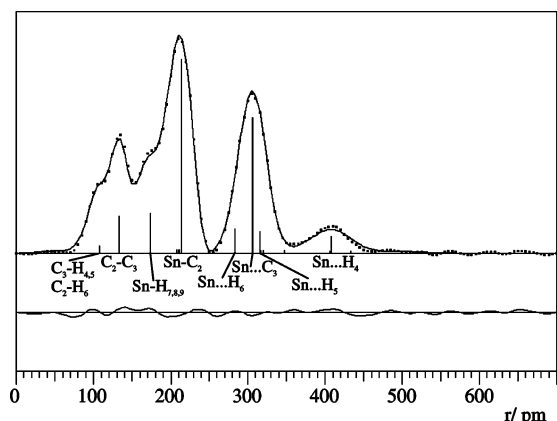


Figure 5. Radial distribution curve for vinylstannane (upper curve) and difference curve (lower curve).

distances with small contributions to the total molecular scattering were kept at the theoretical values, whereas the other *u*-values were refined with the result shown in Table 6. The B3LYP structure was used as the starting point in the structure refinement. The KCED25 least-squares fitting program²⁹ was used. The intensity and radial distribution curves are shown in Figures 5 and 7, while the experimental structure is shown in Table 6.

Allylstannane. The gas phase was initially assumed to contain a mixture of the *ac* and *sp* forms. However, the first analysis revealed that the *sp* form could not be detected in the gas at room temperature. A crude estimate of the composition of the gas phase was therefore calculated using the theoretical Gibbs energy difference, ΔG° , between the *sp* and *ac* forms shown in Table 3. Considering the equilibrium $ac \leftrightarrow sp$, the equilibrium constant $K = N_{sp}/N_{ac} = \sigma_{sp}X_{sp}/\sigma_{ac}X_{ac} = X_{sp}/2X_{ac}$ where σ is the statistical weight and *X* is the mole fraction. $\Delta G^\circ = -RT \ln K$ at equilibrium, where *R* is the universal gas constant and *T* the absolute temperature. The statistical weight of *ac* has been assumed to be twice the statistical weight of *sp*. The mole fraction of the *ac* conformer was calculated to be 0.97 at room temperature using the HF results and 0.86 employing the B3LYP calculations. The final structural analysis was performed assuming that only the *ac* rotamer is present in the gas at room

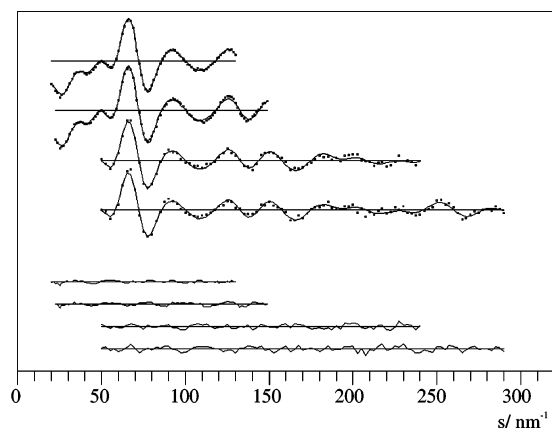


Figure 6. Intensity curves for allylstannane. Same definitions as for vinylstannane; see Figure 4.

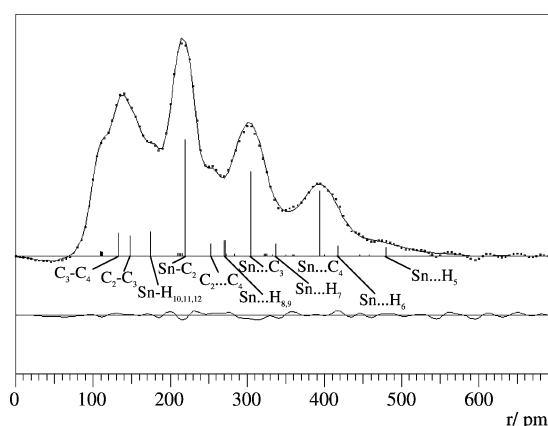


Figure 7. Radial distribution (upper) and difference (lower) curves for allylstannane.

temperature. The possible existence of a small fraction of the *sp* form is not expected to have any influence on the results.

The following structural parameters were chosen as independent: the bond lengths $r(\text{Sn}_1\text{C}_2)$, $r(\text{C}_2\text{C}_3)$, $r(\text{C}_3\text{C}_4)$, $r(\text{C}_4\text{H}_5)$, $r(\text{C}_4\text{H}_6)$, $r(\text{C}_3\text{H}_7)$, $r(\text{C}_2\text{H}_8)$, $r(\text{C}_2\text{H}_9)$, $r(\text{Sn}_1\text{H}_{10})$, $r(\text{Sn}_1\text{H}_{11})$, and $r(\text{Sn}_1\text{H}_{12})$, the bond angles $\angle\text{Sn}_1\text{C}_2\text{C}_3$, $\angle\text{C}_2\text{C}_3\text{C}_4$, $\angle\text{C}_4\text{C}_3\text{H}_7$, $\angle\text{C}_3\text{C}_4\text{H}_5$, $\angle\text{C}_3\text{C}_4\text{H}_6$, $\angle\text{C}_3\text{C}_2\text{H}_8$, $\angle\text{C}_3\text{C}_2\text{H}_9$, $\angle\text{Sn}_1\text{C}_2\text{H}_8$, $\angle\text{Sn}_1\text{C}_2\text{H}_9$, $\angle\text{C}_2\text{Sn}_1\text{H}_{10}$, $\angle\text{C}_2\text{Sn}_1\text{H}_{11}$, $\angle\text{C}_2\text{Sn}_1\text{H}_{12}$, $\angle\text{H}_{10}\text{Sn}_1\text{H}_{11}$, and $\angle\text{H}_{10}\text{Sn}_1\text{H}_{12}$, and the dihedral angles $\angle\text{C}_4\text{C}_3\text{C}_2\text{Sn}_1$, $\angle\text{C}_2\text{C}_3\text{C}_4\text{H}_5$, $\angle\text{C}_2\text{C}_3\text{C}_4\text{H}_6$, $\angle\text{H}_6\text{C}_4\text{C}_3\text{H}_7$, and $\angle\text{C}_3\text{C}_2\text{Sn}_1\text{H}_{10}$. The last three dihedral angles were fixed at 0° or 180° (see Figure 2), while the first was refined. The following constraints were used in the structure determination: $r(\text{C}_4\text{H}_6) = r(\text{C}_4\text{H}_5) + \Delta 1$, $r(\text{C}_3\text{H}_7) = r(\text{C}_4\text{H}_5) + \Delta 2$, $r(\text{C}_2\text{H}_8) = r(\text{C}_4\text{H}_5) + \Delta 3$, $r(\text{C}_2\text{H}_9) = r(\text{C}_4\text{H}_5) + \Delta 4$, $r(\text{Sn}_1\text{H}_{11}) = r(\text{Sn}_1\text{H}_{10}) + \Delta 5$, $r(\text{Sn}_1\text{H}_{12}) = r(\text{Sn}_1\text{H}_{10}) + \Delta 6$, $\angle\text{C}_3\text{C}_4\text{H}_6 = \angle\text{C}_3\text{C}_4\text{H}_5 + \Delta 7$, $\angle\text{C}_4\text{C}_3\text{H}_7 = \angle\text{C}_3\text{C}_4\text{H}_5 + \Delta 8$, $\angle\text{C}_3\text{C}_2\text{H}_9 = \angle\text{C}_3\text{C}_2\text{H}_8 + \Delta 9$, $\angle\text{Sn}_1\text{C}_2\text{H}_9 = \angle\text{Sn}_1\text{C}_2\text{H}_8 + \Delta 10$, $\angle\text{C}_2\text{Sn}_1\text{H}_{11} = \angle\text{C}_2\text{Sn}_1\text{H}_{10} + \Delta 11$, $\angle\text{C}_2\text{Sn}_1\text{H}_{12} = \angle\text{C}_2\text{Sn}_1\text{H}_{10} + \Delta 12$, $\angle\text{H}_{10}\text{Sn}_1\text{H}_{11} = \angle\text{C}_2\text{Sn}_1\text{H}_{10} + \Delta 13$, $\angle\text{H}_{10}\text{Sn}_1\text{H}_{12} = \angle\text{C}_2\text{Sn}_1\text{H}_{10} + \Delta 14$. The differences (the Δ 's) were those calculated by the B3LYP//cc-pVTZ-PP(Sn)/cc-pVTZ(C,H) procedure. They are 0.25, 0.54, 0.82, 0.91, -0.22 , and -0.40 pm and 0.30° , -3.06° , -0.19° , -1.05° , -0.51° , -0.83° , -1.04° , and -0.63° , respectively.

The *u*- and *D*-values were derived in the same way as that described previously for vinylstannane. The refinements were carried out in the same manner as for vinylstannane. The

(29) Gundersen, G.; Samdal, S.; Seip, H.-M.; Strand, T. G. Annual Report 1977, 1980, 1981 from the Norwegian Gas Electron Diffraction Group.

Table 7. Structure and u -Values of Allylstannane^{a,b}

	r_a	u_{calc}	u_{exp}
Bond Lengths			
Sn ₁ –C ₂	218.9(8)	5.8	6.0(8)
C ₂ –C ₃	148.1(10)	5.0	5.8(11)
C ₃ –C ₄	132.9(7)	4.1	4.0(9)
Sn ₁ –H ₁₀	174.9(13)	9.5	11.5(14)
Sn ₁ –H ₁₁ ^c	174.7(13)	9.5	11.4(14)
Sn ₁ –H ₁₂ ^c	174.5(13)	9.4	11.4(14)
C ₂ –H ₈ ^c	111.4(6)	7.7	7.7
C ₂ –H ₉ ^c	111.5(6)	7.7	7.7
C ₃ –H ₇ ^c	109.6(6)	7.6	7.6
C ₄ –H ₅	110.5(6)	7.6	7.6
C ₄ –H ₆ ^c	110.8(6)	7.6	7.6
Bond Angles			
∠Sn ₁ C ₂ C ₃	110.9(6)		
∠C ₂ C ₃ C ₄	128.5(16)		
∠C ₃ C ₂ H ₈	112.0		
∠C ₃ C ₂ H ₉ ^c	111.8		
∠C ₃ C ₄ H ₅	121.4		
∠C ₃ C ₄ H ₆ ^c	121.7		
∠C ₄ C ₃ H ₇ ^c	118.4		
∠Sn ₁ C ₂ H ₈	106.8		
∠Sn ₁ C ₂ H ₉	105.7		
∠C ₂ Sn ₁ H ₁₀	111.8(35)		
∠C ₂ Sn ₁ H ₁₁ ^c	111.3		
∠C ₂ Sn ₁ H ₁₂ ^c	111.0		
∠H ₁₀ Sn ₁ H ₁₁ ^c	110.7		
∠H ₁₀ Sn ₁ H ₁₂ ^c	111.2		
Dihedral Angle			
∠C ₄ C ₃ C ₂ Sn ₁	102.9(19)		
	$R_f = 12.6\%$		

^{a–c} Same comments as for Table 6.

intensity and radial distribution curves for the final model are shown in Figures 5 and 7. The experimental structure is given in Table 7.

Discussion

The r_a value of the prototype C(sp²)–Sn(IV) bond length in vinylstannane is 215.1(6) pm (Table 6). The equilibrium bond length, r_e , can be estimated using $r_e \approx r_a + u^2/r_a - K - \delta r - 1.5au$,^{2,30,31} where u is the root-mean-square amplitude of vibration, K is the perpendicular correction coefficient, δr is the centrifugal stretching, and a is the Morse anharmonicity parameter. Using the SHRINK program,^{32,33} the anharmonicity parameter was calculated by Sipachev³⁴ to be $a = 0.0162 \text{ pm}^{-1}$ for a C–Sn bond. The centrifugal stretching, δr , which usually is very small, is calculated to be 0.13 pm. In this manner, the equilibrium C–Sn bond length is estimated to be $r_e \approx 214.1$ –(6) pm in vinylstannane ($K = 0.34 \text{ pm}$), which should be compared to the MP2(FC) value of 211.2 pm and the B3LYP value of 214.6 pm. The C(sp³)–Sn(IV) bond length in allylstannane ($K = 0.48 \text{ pm}$) is $r_a = 218.9(8) \text{ pm}$, and r_e is estimated to be 217.6(8) pm, which should be compared with the MP2-(FC) value of 214.7 pm and the B3LYP value of 219.3 pm. The estimated error in r_e is the experimental error, and since

no error related to theory is included, these errors should be considered as lower limits. The C(sp²)–Sn(IV) bond length in allenylstannane³ (CH₂=C=CHSnH₃) is $r_a = 213.2(7) \text{ pm}$ and $r_e = 212.7(7) \text{ pm}$, while the MP2(FC) value is 211.7 pm and the B3LYP value is 215.3 pm. The MP2(FC) calculations underestimate the C–Sn bond length, and B3LYP is the preferable method for vinylstannane and allylstannane, but for allenylstannane it is not obvious which method is the best.

Another noticeable feature is that the C(sp²)–Sn(IV) bond length is about 1.9 pm shorter in allenylstannane compared to vinylstannane. A shortening is expected if there is a conjugation in the C=C=C group. However, there is not expected to be any conjugation in the C=C=C group since the two π -bonds are perpendicular to each other. Actually, both MP2(FC) and B3LYP predict a small increase in the bond length. We do not have a good explanation for this observed shortening. It is also noticeable that the C(sp³)–Sn(IV) bond length is influenced by the substituents to a remarkable degree. The r_g bond length is 214.36(30) pm in tetramethyltin,³⁵ which is nearly 5 pm shorter than in allylstannane.

Another structural feature of allylstannane is worth noting, viz., the Sn₁C₂C₃C₄ dihedral angle, which is 102.9(8)° from *synperiplanar* (0°) in the *ac* conformer. The corresponding X₁C₂C₃C₄ dihedral angles, where X₁ = C, Si, or Ge, are 119.9–(3)°,³⁶ 106.8(11)°,³⁷ and 106.2°,³⁸ respectively. The X₁C₂C₃C₄ dihedral angle thus diminishes by as much as 13–17° when the terminal carbon atom in 1-butene (H₂C=CHCH₂CH₃) is substituted by a heteroatom.

The gaseous composition of this series of allylic compounds is also noticeable. In 1-butene, the *ac* conformation is 0.63(63) kJ mol^{−1} more stable than the *sp* conformation.³⁶ No *sp* conformation has been found experimentally for the corresponding allylic compounds with heteroatoms (H₂C=CHCH₂XH₃, X = Si, Ge, Sn).^{36–38} The present high-level quantum chemical calculations as well as other recent calculations³⁸ indicate that the *sp* rotamer in these compounds is 5–8 kJ mol^{−1} less stable than the *ac* conformer.

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