Structures of 1,2-Propadienylgermane (Allenylgermane) and 1,2-Propadienylstannane (Allenylstannane) Determined by Gas-Phase Electron Diffraction and Quantum Chemical Calculations

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Allenylgermane and allenylstannane ($H_2C_{(4)}{=}C_{(3)}{=}C_{(2)}HM_{(1)}H_3$, M = Ge, Sn) have been synthesized, and their structures have been determined by ab initio and density functional theory calculations and gas electron diffraction. The only stable conformation of the MH_3 group has one of the M−H bonds *synperiplanar* to the double bond. The most important structural parameters (r_a/pm and ∠/degree) are as follows (Ge/Sn): $M_1{-}C_2$ = 194.2(5)/213.2(7), $C_2{=}C_3$ = 131.2(3)/130.7(4), $\angle M_1C_2C_3$ = 120.7(3)/121.0(7). The C_4 atom is bent slightly toward the M atom, making the $C_2{=}C_3{=}C_4$ bond angles 178.3(8)°/177.4(18)°. The difference between the two bond lengths $C_3{=}C_4$ and $C_2{=}C_3$ is kept constant at the values obtained from the theoretical calculations. Uncertainties are estimated error essentially equal to 2.5 times one standard deviation from the least-squares refinement. The corresponding MP2 values using a cc-pVTZ basis set for all atoms, except for Sn, where the basis set is cc-pVTZ-PP, are as follows (Ge/Sn): $M_1{-}C_2$ = 193.0/211.7, $C_2{=}C_3$ = 130.8/130.6, $\Delta CC = C_3{=}C_4 - C_2{=}C_3$ = 0.2/0.6, $\angle M_1C_2C_3$ = 120.7/120.1 and $\angle C_2C_3C_4$ = 178.1/177.8. The r_a(C−Sn) in vinylstannane is 215.1(6) pm, a decrease of 1.9 pm compared to allenylstannane, while the MP2 calculations predict an increase of 0.4 pm. The calculated rotational barrier for the MH_3 group is 2.2 and 1.1 kJ mol^{-1}, respectively, for allenylgermane and allenylstannane.

Introduction

Few primary allenic heterocompounds have been synthesized. Allenic alcohols[1,2] and amines[1,2] have been described twenty years ago. The first allenylphosphines,[3] arsines,[4] stibines,[5] and stannanes[6] have been reported a decade ago. There is not much information about the structure of primary allenylgermanes, allenylthiols, and allenylselenols to be found in the literature. Primary allenic derivatives are an interesting group of compounds because of the presence of an allenyl function connected to a heteroatom MH_n group. It has been demonstrated that for some of them they rearrange into the corresponding 1-heterodienes.[5]

Considerable progress has been made in the last decade toward the synthesis of primary α,*β*- and *β*,*γ*-unsaturated germanes and stannanes.[6,7] Some experimental gas-phase structures of organogermanes such as germane and halogenated germanes,[8−13] ethynylgermane,[14] methylgermane,[15] ethylgermane,[16] ethylchlorogermane,[17] cyclopropylgermane,[18] vinylgermane,[19] (halomethyl)germane,[20,21] and propargylgermane[22] and organostannanes such as stannane,[8] trimethylstannylacetylene,[23,24] methylstannane[25] bis(trimethylstannyl)acetylene,[26] tetramethyltin,[27] and tetraethynyltin[28] have been determined. The

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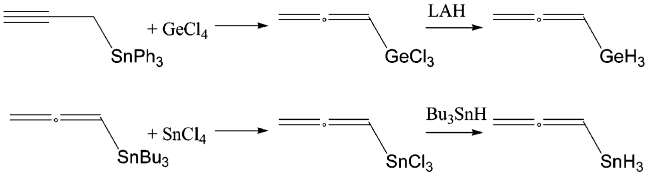
first structural studies of vinylstannane and allylstannane[29] will be published shortly.

In this work, a structural study is devoted to allenylgermane and allenylstannane ($H_2C{=}C{=}CHMH_3$, M = Ge, Sn), the simplest propadienyl heterocompounds with group 14 elements. To our knowledge, no experimental structural investigations either by electron diffraction, microwave spectroscopy, or quantum chemical calculations have previously been reported for the two title compounds as well as for any primary allenic heterocompound except allenylphosphine.[30] Gas electron diffraction (GED) and modern quantum chemical calculations are well suited to investigate structural features presented by these two compounds. The scarcity of information concerning the molecular structure of organostannanes and organogermanes was the motivation to undertake the present study. Moreover, so far only one experimental $C(sp^2){-}Ge$ bond length for a free molecule has been determined (vinylgermane)[19] by microwave spectroscopy, and a comparison would be interesting. We also want to focus on the linearity of the C=C=C group. Due to the molecular symmetry (C_s), the C=C=C group is not expected to be completely linear, and it would be of interest to examine any deviation from linearity and in which direction the deviation appears, toward or away from the metal atom. Finally, it would also be of interest to examine the influence that a vinyl and allenyl group would have on the C−Ge,Sn bond length and in particular if the perpendicular π-system in the allenyl group would have any pronounced influence on the bond distance.

Experimental Section

Synthesis of Allenylgermane and Allenylstannane. Allenylgermane has been synthesized in a two-step sequence starting from the reaction of propargyltriphenylstannane with germanium tetrachloride followed by chemoselective reduction of the formed allenyltrichlorogermane[7] with LAH. Allenylstannane was prepared by reduction of the allenyltrichlorostannane[6] with tin hydride in the presence of a radical inhibitor. Both reactions were performed using a vacuum line. Yields were determined by ^1H NMR spectroscopy using an internal reference (C_6H_6). Propadienylgermane is kinetically much more stable than the corresponding tin derivative. Similar observations have already been reported for vinyl, ethynyl, allyl, and propargyl derivatives.[6,7,14,31−34]



Caution: *Allenylgermane and Allenylstannane are pyrophoric and potentially toxic. All reactions and handling should be carried out in a well-ventilated hood.*

Synthesis of Allenylgermane. General Procedure. The apparatus used for both reductions was similar to the one described for the preparation of 2-propynylphosphine.[35] In a 100 mL two-necked flask equipped with a stirring bar and a septum were introduced the reducing agent ($LiAlH_4$, 0.38 g, 10 mmol) and tetraglyme (30 mL). The flask was attached to the vacuum line equipped with two traps, immersed in a cold bath (0 °C), and degassed. The allenyltrichlorogermane (654 mg, 3.0 mmol) diluted in tetraglyme (10 mL) was slowly added with a flex-needle through the septum for about 5 min. During and after addition the formed allenylgermane was distilled off in vacuo from the reaction mixture. The first cold trap (−80 °C) removed less volatile products, and the allenylgermane was condensed in the second cold trap (−120 °C) to remove the most volatile products (mainly GeH_4). After disconnection from the vacuum line by stopcocks, the product was kept at a low temperature (<−50 °C) before analysis. The allenylgermane was thus obtained in a 78% yield (268 mg). $\tau_{1/2}$ (5% in CD_2Cl_2, 293 K): 2 days. ^1H NMR (400 MHz, CD_2Cl_2, 293 K): δ 3.97 (dt, 3H, $^3J_{HH} = 2.9$ Hz, $^5J_{HH} = 1.5$ Hz, GeH_3); 4.42 (dq, 2H, $^4J_{HH} = 7.1$ Hz, $^5J_{HH} = 1.5$ Hz, CH_2); 4.96 (tq, 1H, $^4J_{HH} = 7.1$ Hz, $^3J_{HH} = 2.9$ Hz, CH). ^{13}C NMR (100 MHz, CD_2Cl_2, 293 K): δ 67.6 (t, $^1J_{CH} = 167.9$ Hz, CH_2); 70.5 (d, $^1J_{CH} = 166.2$ Hz, CH); 212.8 (s, C=*C*=C). HRMS: calcd for $C_3H_5{}^{74}Ge$ $[M - H]^+$ 114.9603; found 114.959.

Synthesis of Allenylstannane.[6] The general procedure has been used with allenyltrichlorostannane (1.33 g, 5 mmol) and, as reducing agent, tributyltin hydride (8.7 g, 30 mmol) with small amounts of duroquinone. The allenylstannane was thus obtained in a 63% yield (510 mg). It was stabilized in diethylene glycol dibutyl ether with small amounts duroquinone and stored at dry ice temperature. $\tau_{1/2}$ (5% in CD_2Cl_2, 293 K): 6 h. ^1H NMR (400 MHz, CD_2Cl_2, 293 K): δ 4.32 (d, 2H, $^4J_{HH} = 7.1$ Hz, $^4J_{SnH} = 57.9$ Hz (d), CH_2); 4.95 (dt, 3H, $^3J_{HH} = 1.8$ Hz, $^5J_{HH} = 0.9$ Hz, $^1J_{SnH} = 1967$ Hz (d), SnH_3); 5.01 (tq, 1H, $^4J_{HH} = 7.1$ Hz, $^3J_{HH} = 1.8$ Hz, $^2J_{SnH} = 169.2$ Hz (d), CH). ^{13}C NMR (100 MHz, CD_2Cl_2, 293 K): δ 65.2 (t, $^1J_{CH} = 167.8$ Hz, $^3J_{SnC} = 58.8$ Hz (d), CH_2); 67.4 (d, $^1J_{CH} = 169.5$ Hz, $^1J_{SnC} = 489$ Hz (d), CH); 212.6 (s, C=*C*=C). ^{119}Sn NMR (111 MHz, C_6D_6/C_7H_8, 243 K): δ −338.4. HRMS: calcd for $[M - H]^+$ $(C_3H_5{}^{120}Sn)^+$ 160.9413; found 160.942.

Microwave Experiment. Attempts were made to observe the microwave spectrum of the title compounds in the 26−62 GHz spectral interval using the Oslo Stark spectrometer.[36] However, no signals that could be attributed to these molecules 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 the compounds is too small. This is consistent with the quantum chemical predictions described below.

Electron Diffraction Experiment. Both compounds were synthesized in Oslo as described in the section above and stored at dry ice temperature. The purity of allenylgermane and allenylstannane determined by ^1H NMR spectroscopy was about 92% and 90%, respectively. Allenylstannane is unstable in pure form at a temperature higher than −100 °C. So only a sample diluted in a high-boiling glyme was used to record the GED data. Both compounds were distilled directly into the apparatus. The sample bulb was kept at dry ice temperature and the nozzle at room temperature. The vapor pressure of the sample was not monitored during the experiment. After the recording of the electron diffraction

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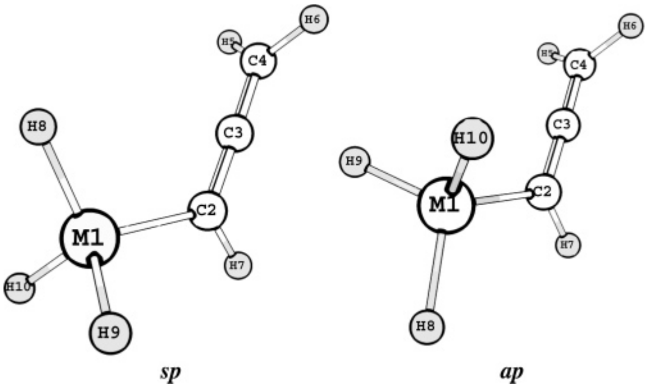

Figure 1. The *antiperiplanar* (*ap*) and *synperiplanar* (*sp*) rotamers of allenylgermane (M1 = Ge) and allenylstannane (M1 = Sn).

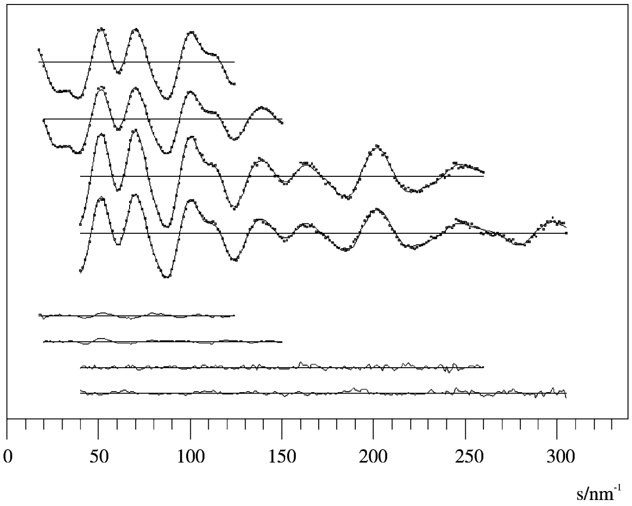

Figure 2. Intensity curves for allenylgermane. The two upper curves are for the *y*- and *x*-directions of the long camera distance, respectively. The next two curves are for the *y*- and *x*-directions of the middle camera distance. The four lower curves are difference curves. Camera distances are found in Table 1.

data a sample bulb exploded and destroyed a Dewar and several synthesized compounds. The quality of the allenylstannane electron diffraction data is not as good as usually achieved, because repetition of the experiment could not be performed.

The GED data were recorded using a Balzers KD-G2 unit.[37] 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. The image plates are more sensitive and have a higher resolution, a much higher linear response, and a higher dynamic range than photographic plates. Owing to the high linear response of the image plates, no blackness correction is needed.

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 the *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 Figure 2 and Figure 4. These four curves were used in the least-squares structure analysis. The raw data were further processed as described elsewhere.[38]

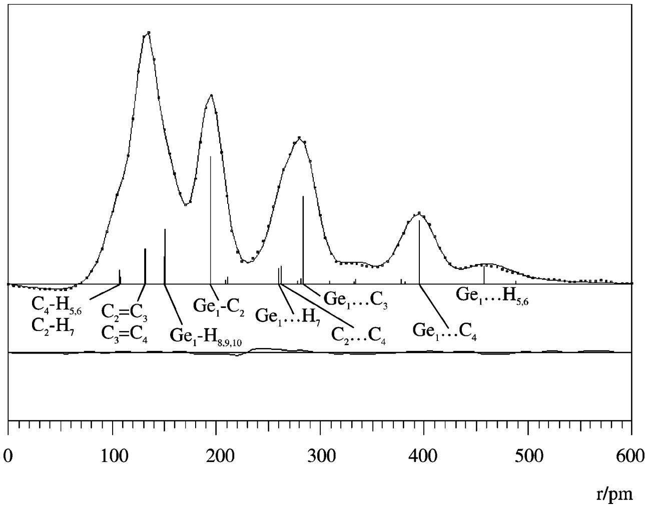

Figure 3. Radial distribution (upper) and difference (lower) curves for allenylgermane.

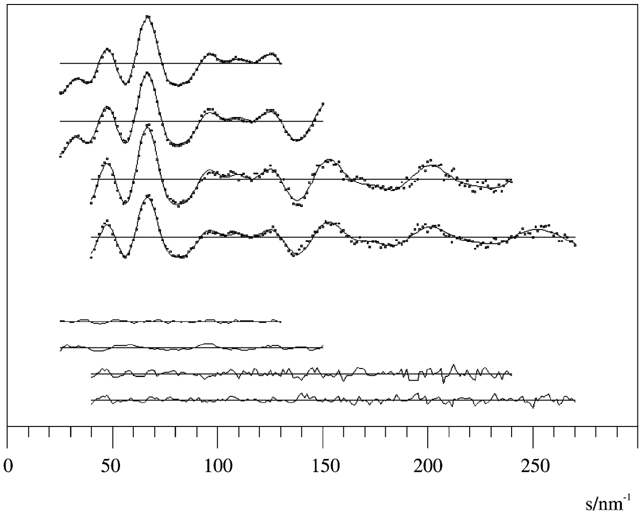

Figure 4. Intensity curves for allenylstannane. The two upper curves are for the *y*- and *x*-directions of the long camera distance, respectively. The two next curves are for the *y*- and *x*-directions of the middle camera distance. The four lower curves are difference curves. Camera distances are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

The necessary modification and scattering functions were computed from tabulated atomic scattering factors[39] for the proper wavelength and *s*-values. The experimental backgrounds were computed using the program KCED12,[40] 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 $s/|f'_C\, f'_M|$, (M = Ge, Sn), where f' denotes the coherent scattering factors. The experimental conditions employed in the GED experiments are given in Table 1.

Quantum Chemical Calculations. Quantum chemical calculations were performed for the title compounds using the GAUSSIAN03 suite of programs[41] running on the HP "superdome" facilities

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Table 1. Experimental Conditions of the GED Investigation.

	allenylgermane		allenylstannane	
camera distance/mm	248.77	498.74	248.78	498.86
electron wavelength/pm	5.813	5.813	5.820	5.820
nozzle temperature/°C	23	23	23	23
s ranges/nm^{-1}				
x-direction	40.00−305.00	20.00−150.00	40.00−270.00	25.00−150.00
y-direction	40.00−260.00	17.50−126.25	40.00−240.00	25.00−130.00
Δs/nm^{-1}	1.25	1.25	1.25	1.25

in Oslo. Full geometry optimizations were carried out for the *sp* and *ap* forms (Figure 1) by density functional theory calculations at the B3LYP level.[42,43] Dunning's correlation-consistent polarized valence triple-ζ (cc-pVTZ) basis set[44] was employed for the germanium, carbon, and hydrogen atoms, whereas the cc-pVTZ-PP basis set[45] was used for the tin atom. This basis set includes a small-core relativistic pseudopotential to replace 28 core electrons ([Ar] + 3d).[46] 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;[47] therefore MP2 frozen core (FC) calculations using the same basis sets were also performed.

The calculated molecular structures of the most stable *sp* conformation are listed in Table 2. The structure of the *ap* form is also calculated, and it is found to be very similar to the *sp* form. The vibrational frequencies and their assignments are given in Table 3. No experimental vibrational frequencies have been reported for these molecules.

The *sp* form was found to be more stable than the *ap* conformation for both molecules. The B3LYP energy difference is 2.2 and 1.1 kJ/mol respectively for allenylgermane and allenylstannane. 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 MH_3 group about the M_1-C_2 bond. The *sp* form is therefore a minimum on the energy hypersurface, whereas the *ap* form is a first-order transition state.[48] The energy difference of the two forms corresponds to the rotational barrier of the MH_3 group.

It should be noted that the MP2 structural parameters are close to those computed using the B3LYP procedures, apart from the M_1-C_2 bond length, which is predicted to be significantly shorter by about 3 pm in the MP2 calculations than in the B3LYP calculations.

The principal inertial axis dipole moment components of the *sp* rotamer for allenylgermane and allenylstannane were calculated to be $\mu_a = 0.13/0.17$ and 0.11/0.11, $\mu_b = 0.25/0.27$ and 0.14/0.16, and $\mu_c = 0.0$ D (by symmetry), respectively, by the B3LYP/MP2 procedure. 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.

Table 2. Calculated Structure[a,b] for the *sp* Form of Allenylgermane and Allenylstannane (C_s-symmetry)

	allenylgermane		allenylstannane	
	B3LYP	MP2	B3LYP	MP2
		Bond Lengths		
M_1-C_2	195.7	193.0	215.3	211.7
$C_2=C_3$	129.8	130.8	129.6	130.6
$C_3=C_4$	130.2	131.0	130.4	131.2
M_1-H_8	153.4	151.5	171.1	168.6
M_1-H_9	153.9	152.0	171.7	169.1
C_2-H_7	108.6	108.4	108.5	108.4
C_4-H_5	108.3	108.1	108.3	108.1
		Bond Angles		
$\angle M_1C_2C_3$	122.4	120.7	121.6	120.1
$\angle C_2C_3C_4$	178.5	178.1	178.1	177.8
$\angle C_3C_4H_5$	121.3	120.7	121.3	120.7
$\angle C_3C_2H_7$	119.4	118.7	120.2	118.9
$\angle C_2M_1H_8$	109.0	108.1	108.3	107.5
$\angle C_2M_1H_9$	109.7	109.9	109.4	109.7
$\angle H_8M_1H_9$	110.0	110.2	110.5	110.5
$\angle H_9M_1H_{10}$	108.2	108.6	108.7	108.8
		Dihedral Angles		
$\angle C_3C_2M_1H_8$	0.0	0.0	0.0	0.0
$\angle C_3C_2M_1H_9$	120.6	120.3	120.5	120.3
$\angle C_2C_3C_4H_6$	90.2	90.3	90.3	90.4

[a] Distances in pm, angles in deg. [b] The following basis sets were used: cc-pVTZ for allenylgermane, cc-pVTZ for C and H atoms, and cc-pVTZ-PP for the Sn atom in allenylstannane. The frozen-core procedure was employed for MP2.

Table 3. Calculated Fundamental Frequencies (cm^{-1}) and Assignments for the *sp* Rotamer of Allenylgermane and Allenylstannane

	Ge-B3LYP	Ge-MP2	Sn-B3LYP	Sn-MP2
1 A″ CH_2 as str	3199	3271	3201	3272
2 A′ CH str	3127	3185	3134	3187
3 A′ CH_2 sym str	3124	3181	3128	3181
4 A′ C=C=C as str	2027	2021	2019	2057
5 A′ MH_3 as str	2153	2291	1920	2039
6 A″ MH_3 as str	2125	2266	1895	2035
7 A′ MH_3 s str	2123	2263	1893	2012
8 A′ CH_2 scis	1460	1462	1458	1460
9 A′ C=C=C sym str	1244	1239	1214	1211
10 A′ CH rock	1094	1080	1082	1073
11 A″ CH_2 rock	1015	1009	1015	1009
12 A″ CH_2 twist	868	887	874	888
13 A′ CH_2 wag	834	835	840	826
14 A′ MH_3 as bend	889	938	725	766
15 A″ MH_3 as bend	889	928	713	754
16 A′ MH_3 sym bend	850	874	685	721
17 A′ MC str	704	725	636	654
18 A″ MH_3 rock	626	645	531	547
19 A′ MH_3 rock	521	546	432	458
20 A′ C=C=C bend	429	436	396	412
21 A″ C=C=C bend	420	417	391	393
22 A″ CH_2 twist	339	342	323	332
23 A′ MCC bend	139	135	122	120
24 A″ MH_3 tors	76	91	60	65

Structure Refinement. The quantum chemical calculations above predict that the *sp* isomer with a symmetry plane (C_s

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Table 4. Structure and *u*- and *D*-Values of Allenylgermane[a]

	rectilinear[b]					curvilinear[b]				
parameter	r_a	r_g[c]	u_{exp}	u_{calc}	D_{calc}	r_a	r_g[c]	u_{exp}	u_{calc}	D_{calc}
Bond Lengths										
$Ge_1{-}C_2$	194.2(5)	194.3	4.9(2)	5.0	−0.30	194.2(5)	194.3	5.0(2)	5.0	0.15
$C_2{=}C_3$	131.2(3)	131.3	4.1(2)	4.0	−0.46	131.2(3)	131.3	4.1(2)	4.0	0.05
$C_3{=}C_4$[d]	131.6(3)	131.7	4.1(2)	4.0	−0.89	131.6(3)	131.7	4.1(2)	4.0	0.09
$Ge_1{-}H_8$	150.4(6)	150.9	11.7(5)	9.0	−6.10	150.4(6)	150.9	11.7(5)	9.0	0.17
$Ge_1{-}H_9$[d]	150.9(6)	151.4	11.7(5)	9.0	−7.00	150.9(6)	151.4	11.8(5)	9.1	0.17
$C_2{-}H_7$	107.5(6)	108.0	7.6[e]	7.6	−1.90	107.5(6)	108.0	7.6[e]	7.6	0.20
$C_4{-}H_5$[d]	107.2(6)	107.7	7.5[e]	7.5	−2.20	107.2(6)	107.7	7.5[e]	7.5	0.21
Bond Angles										
$\angle Ge_1C_2C_3$	120.7(3)					120.3(3)				
$\angle C_2C_3C_4$	178.3(8)					173.1(7)				
$\angle C_3C_4H_5$[d]	124.7					124.8				
$\angle C_3C_2H_7$	122.8(13)					122.9(13)				
$\angle C_2Ge_1H_8$	108.7(21)					108.3(21)				
$\angle C_2Ge_1H_9$[d]	109.3					108.8				
$\angle H_8Ge_1H_9$[d]	109.8					109.3				
$\angle H_9Ge_1H_{10}$	109.6					112.5				
Dihedral Angles										
$\angle C_3C_2Ge_1H_8$	0.0[e]					0.0[e]				
$\angle C_3C_2Ge_1H_9$	119.5					118.1				
$\angle C_2C_3C_4H_6$	90.2[e]					90.2[e]				
$R_{f\%}$[f]	8.0					8.0				

[a] Distances and *u*-and *D*-values in pm, angles and dihedral angles in deg. Parenthesized values are estimated error limits given as $2.5(\sigma^2_{lsq} + (0.001r)^2)^{1/2}$ 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 represents 0.1% uncertainty in the electron wavelength. For angles and *u*-values the estimated error limits are $2.5\sigma_{lsq}$. The error estimates are in units of the last digits. [b] See text. [c] The r_g-values listed in this table were calculated from $r_g = r_a + u_{calc}^2/r_a$. [d] These parameters were calculated according to the constraints discussed in the text. [e] Fixed. [f] Goodness of fit: $R = [\sum_s w(I_s^{obs} - I_s^{calc})^2]/[\sum_s w(I_s^{obs})^2]$, where w is a weight function usually equal to 1, and I is the molecular modified intensity.

symmetry) is the only stable form of this compound. Seventeen independent parameters were chosen to describe its molecular structure. These parameters are the bond distances $r(M_1C_2)$, $r(C_2C_3)$, $r(C_3C_4)$, $r(C_4H_5) = r(C_4H_5)$, $r(C_2H_7)$, $r(M_1H_8)$ and $r(M_1H_9) = r(M_1H_{10})$ and the bond angles $\angle M_1C_2C_3$, $\angle C_2C_3C_4$, $\angle C_3C_4H_5 = \angle C_3C_4H_6$, $\angle C_3C_2H_7$, $\angle C_2M_1H_8$, $\angle C_2M_1H_9 = \angle C_2M_1H_{10}$, and $\angle H_8M_1H_9 = \angle H_8M_1H_{10}$. In addition, the two dihedral angles $\angle M_1C_2C_3C_4$ and $\angle M_1C_2C_4H_5$ and the dihedral angle $\angle H_8M_1C_2C_3$ were used in order to test whether the rotational barrier of the MH_3 group could be determined by electron diffraction.

It is difficult to determine accurate structure parameters by ED where H atoms are involved owing to the low scattering power of the hydrogen atoms. It is also difficult to determine accurately the difference between bond lengths if the bond type and bond lengths are similar. This is the reason for introducing the following constraints: $r(C_3C_4) = r(C_2C_3) + \Delta 1$, where $\Delta 1$ is the difference between $r(C_3C_4)$ and $r(C_2C_3)$. Similarly, $r(M_1H_9) = r(M_1H_{10}) = r(M_1H_8) + \Delta 2$, $r(C_4H_5) = r(C_4H_6) = r(C_2H_7) + \Delta 3$, $\angle C_2M_1H_9 = \angle C_2M_1H_{10} = \angle C_2M_1H_8 + \Delta 4$, $\angle H_8M_1H_9 = \angle H_8M_1H_{10} = \angle C_2M_1H_8 + \Delta 5$, and $\angle C_3C_4H_5 = \angle C_3C_4H_6 = \angle C_3C_4H_7 + \Delta 6$. The differences, $\Delta 1{-}6$, were taken from the quantum chemical calculation B3LYP//cc-pVTZ-PP(Sn)/cc-pVTZ(C,H) for allenylstannane, and they are 0.82, 0.60, and −0.22 pm and 1.15°, 2.17°, and 1.04°, respectively. The differences $\Delta 1{-}6$ for allenylgermane were taken from the quantum chemical calculation B3LYP//cc-pVTZ, and they are 0.40, 0.50, and −0.30 pm and 0.63°, 0.90°, and 1.90°, respectively. As can be seen, the trend in the calculated differences is very similar for the two compounds.

It was explored if the barrier to internal rotation of the MH_3 group could be determined. The $C_3C_2M_1H_8$ dihedral angle was refined for this purpose. As expected, the uncertainty in the dihedral angle was very large. For allenylgermane the dihedral angle refined to 23(19)° and the *R*-factor did not change compared to when the dihedral angle was fixed to 0°. For allenylstannane it was even worse; the dihedral angle refined to 17(65)°. This shows that introduction of a dynamic model does not serve any purpose. Clearly, the scattering from $C_3,C_4\cdots H_M$ pairs of atoms is not sufficient to obtain any useful information about the barrier to internal rotation. 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 shrinkage correction terms (*D*-values) were calculated employing the SHRINK program[49,50] using the B3LYP//cc-pVTZ-PP(Sn)/cc-pVTZ(C,H) force field for allenylstannane and the B3LYP/cc-pVTZ force field for allenylgermane. The SHRINK program calculates these parameters using two different approaches. The first approach is based on a rectilinear movement of the atoms, which most programs are based on. The second is based on a curvilinear movement of the atoms. The latter approach is generally considered to be best. An appropriate warning should be given here for those using the SHRINK program on molecules having close to linear groups. Great care should be taken and several models should be tested. There exist two auxiliary programs that automatically generate an input in the SHRINK program. Both fail to generate a correct input; however one of them gives an explicit warning if linear groups are present. We have tested three models. In one model the proper dummy atoms have been introduced but the $C{=}C{=}C$ group is slightly bent. This model is recommended by Sipachev, and the results are given in Tables 4 and 5. In a second model the $C{=}C{=}C$ group was made linear by changing the Cartesian coordinates of the middle C atom, and in a third model a force field was obtained forcing the $C{=}C{=}C$ group to be linear. The rectilinear approach gives essentially the same parameters for all three models, while the curvilinear approach gives rather different values for the *D*-values far more different than expected. According to Sipachev, this can be traced back to the perturbation treatment used in the program to calculate the *D*-values.

Vibrational amplitudes for distances with small contributions to the total molecular scattering were kept at their calculated values, while some *u*-values were refined in groups, and the final results are shown in Tables 4 and 5. The KCED25 least-squares fitting program[51] was used. The intensity and radial distribution curves

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Table 5. Structure and *u*- and *D*-Values of Allenylstannane[a]

parameter	rectilinear[b] r_a	r_g[c]	u_{exp}	u_{calc}	D_{calc}	curvilinear[b] r_a	r_g[c]	u_{exp}	u_{calc}	D_{calc}
Bond Lengths										
Sn_1-C_2	213.2(7)	213.3	5.8(10)	5.5	−0.52	213.3(7)	213.4	5.8(10)	5.5	0.18
$C_2=C_3$	130.7(4)	130.9	4.9(5)	4.0	−0.80	130.7(4)	130.9	4.9(5)	4.0	0.04
$C_3=C_4$[d]	131.5(4)	131.7	4.9(5)	4.0	−1.28	131.6(4)	131.8	4.9(5)	4.0	0.10
Sn_1-H_8	172.8(10)	173.3	9.0(11)	9.4	−14.73	172.8(10)	173.3	9.0(11)	9.4	0.19
Sn_1-H_9[d]	173.4(10)	173.9	9.1(11)	9.5	−16.57	173.4(10)	173.9	9.0(11)	9.5	0.19
C_2-H_7	108.4(13)	108.9	7.6[e]	7.6	−2.84	108.5(13)	109.0	7.6[e]	7.6	0.20
C_4-H_5[d]	108.2(13)	108.7	7.6[e]	7.6	−3.00	108.2(13)	108.7	7.6[e]	7.6	0.21
Bond Angles										
$\angle Sn_1C_2C_3$	121.0(7)					119.9(7)				
$\angle C_2C_3C_4$	177.4(18)					168.2(14)				
$\angle C_3C_4H_5$[d]	123.5					122.5				
$\angle C_3C_2H_7$	122.5(25)					121.5(30)				
$\angle C_2Sn_1H_8$	108.3[e]					108.3[e]				
$\angle C_2Sn_1H_9$[d]	109.4					109.4				
$\angle H_8Sn_1H_9$[d]	110.5					110.5				
$\angle H_9Sn_1H_{10}$	108.7					108.7				
Dihedral Angles										
$\angle C_3C_2Sn_1H_8$	0.0[e]					0.0[e]				
$\angle C_3C_2Sn_1H_9$	120.5					120.5				
$\angle C_2C_3C_4H_6$	90.3[e]					90.3[e]				
$R_{f,\%}$[f]	17.6					17.8				

[a] Distances and *u*-and *D*-values in pm, angles and dihedral angles in deg. Parenthesized values are estimated error limits given as $2.5(\sigma^2_{lsq} + (0.001r)^2)^{1/2}$ 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 represents 0.1% uncertainty in the electron wavelength. For angles and *u*-values the estimated error limits are $2.5\sigma_{lsq}$. The error estimates are in units of the last digits. [b] See text. [c] The r_g-values listed in this table were calculated from $r_g = r_a + u_{calc}^2/r_a$. [d] These parameters were calculated according to the constraints discussed in the text. [e] Fixed. [f] Goodness of fit: $R = [\sum_s w(I_s^{obs} - I_s^{calc})^2]/[\sum_s w(I_s^{obs})^2]$, where w is a weight function usually equal to 1, and I is the molecular modified intensity.

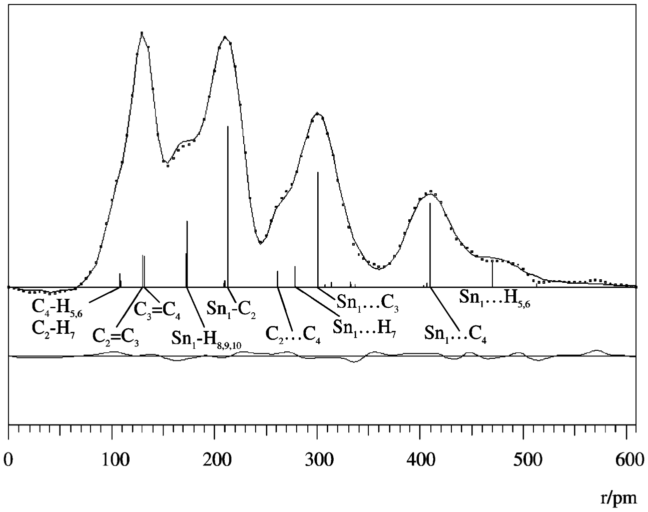

Figure 5. Radial distribution (upper) and difference (lower) curves for allenylstannane.

are shown in Figures 2 and 3 for allenylgermane and in Figures 4 and 5 for allenylstannane.

Table 6. M−C Bond Length in Some Germane and Stannane Compounds

	Ge exp	Ge calc[a]	Sn exp	Sn calc[b]
$H_3M-C\equiv C-H$	189.6(1)[14]	188.9	209.6(17)[c,24]	207.3
$H_3M-CH=CH_2$	192.6(12)[19]	192.5	215.1(1)[29]	211.2
$H_3M-CH=C=CH_2$	194.2(5)	193.0	213.2(7)	211.7
H_3M-CH_3	194.53(5)[15]	193.9	214.0(1)[25]	212.7

[a] MP2(FC)/cc-pVTZ. [b] MP2(FC)/ cc-pVTZ for C and H and cc-pVTZ-PP for Sn. [c] $(CH_3)_3Sn-C\equiv C-H$.

Results and Discussion

The equilibrium bond length, r_e, was estimated[52,53] using $r_e \approx r_a + u^2/r_a - \delta r - K - 1.5au^2$, where u is the root-mean-square vibrational amplitude, δr the centrifugal stretching, K is the perpendicular correction coefficients, and a the Morse anharmonicity parameter, which can be calculated employing the SHRINK program[49,50] as described by Sipachev.[54] The centrifugal stretching, δr, is usually very small and can be neglected. Using $a = 0.0162$ pm^{-1}, the experimental equilibrium distance, r_e, for C−Sn is estimated to be 212.7(7) pm^{-1}, just between the B3LYP (215.3 pm) and MP2 (211.7 pm) calculations. The same tendency was found for vinylstannane. Using $a = 0.0175$ pm^{-1} gives an experimental r_e of 193.7(5) for C−Ge.

Recently, the first C(sp^2)−Sn(IV) bond length for a free molecule has been determined for vinylstannane,[29] and its r_a-value is 215.1(6) pm. Comparison with the corresponding value of 213.2(7) pm in allenylstannane should therefore be of interest. A shortening is expected if there is a conjugation through the allenyl fragment. However, this expected shortening is not predicted in the ab initio MP2 calculations, where actually a lengthening of 0.4 pm is predicted using the same basis set. In Table 6, the experimental and theoretical M−C bond lengths for some selected germane and stannane compounds are given. As can be seen (Table 6), the calculated Ge−C bond length is predicted to increase by 0.5 pm from vinylgermane to allenylgermane, and this increase is actually supported by experimental values. Further, it seems that the Sn−C bond length in

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vinylstannane is unusually long compared to the other Sn−C bond lengths, and at the moment we do not have a good explanation of this finding.

As mentioned in the previous section, some problems were encountered using the SHRINK program. We have tested[55] the rectilinear and curvilinear approaches before, and so far we have always obtained the same structure parameters within the error limits and the same fit to the experimental data. This is the first time where we have obtained significantly different structure parameters, i.e., the C═C═C angle. The rectilinear approach gives the same results for all three models and C═C═C bond angles of 178.3(8)° and 177.4(18)° for allenylgermane and allenylstannane, which should be compared to the ab initio values of 178.5/178.1° and 178.1/177.8° (B3LYP/MP2). The curvilinear approach gives C═C═C bond angles of 173.1(7)° and 168.2(14)°. Due to the excellent agreement with the high-level ab initio calculations and that the rectilinear approach gives the same results for the three models tested, we choose to select the rectilinear approach to be the best for this molecule. It seems that the curvilinear approach, in this case, overestimates the shrinkage correction. High-level ab initio calculations on allenylphosphine[30] give a C═C═C bond angle of 178.6°. It is interesting to notice that the calculated C═C═C bending in allenylphosphine of 178.6° is the same for both the *syn* and *gauche* conformation independent of the orientation of the electron lone pair on the P atom. Moreover, in progargylgermane[22] the C−C≡C bond angle is bent toward the metal atom, where the experimental value is 178.3(10)° compared to the ab initio result of 177.3°.

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