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Structural and Conformational Properties of 2-Propenylgermane (Allylgermane) Studied by Microwave and Infrared Spectroscopy and Quantum Chemical Calculations

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The structural and conformational properties of allylgermane have been investigated using Stark and Fourier transform microwave spectroscopies, infrared spectroscopy, and high-level quantum chemical calculations. The parent species $H_2C{=}CHCH_2GeH_3$ was investigated by microwave spectroscopy and infrared spectroscopy, while three deuterated species, namely, $H_2C{=}CDCH_2GeH_3$, $H_2C{=}CHCHDGeH_3$, and $H_2C{=}CHCH_2GeD_3$, were studied only by infrared spectroscopy. The microwave spectra of the ground vibrational state as well as of the first excited state of the torsion vibration around the sp^2-sp^3 carbon−carbon bond were assigned for the ^{70}Ge, ^{72}Ge, and ^{74}Ge isotopomers of one conformer. This rotamer has an *anticlinal* arrangement for the C═C−C−Ge chain of atoms. The infrared spectrum of the gas in the 500−4000 cm^{-1} range has been assigned. No evidence of additional rotameric forms other than *anticlinal* was seen in the microwave and infrared spectra. Several different high-level ab initio and density functional theory calculations have been performed. These calculations indicate that a less stable form, having a *synperiplanar* conformation of the C═C−C−Ge link of atoms, may coexist with the *anticlinal* form. The energy differences between the *synperiplanar* and *anticlinal* forms were calculated to be 5.6−9.2 kJ/mol depending on the computational procedure. The best approximation of the equilibrium structure of the *anticlinal* rotamer was found in the MP2/aug-cc-pVTZ calculations. The barrier to internal rotation of the germyl group was found to be 6.561(17) kJ/mol, from measurements of the splitting of microwave transitions caused by tunneling of the germyl group through its threefold barrier.

Introduction

The literature dealing with structural, conformational, and dynamical properties of compounds possessing the germyl (GeH_3) group is rather limited. Accurate structures are known in some cases, for example, germane (GeH_4),[1,2] the germyl halides (GeH_3X, X = F,[3] Cl,[4,5] Br,[5,6] and I[5,6]), germylacetylene ($GeH_3C{\equiv}C{-}H$),[7] methylgermane (H_3GeCH_3),[8] ethylgermane ($H_3GeCH_2CH_3$),[9] and cyclopropylgermane ($C_3H_5GeH_3$).[10] Some structural information is available for vinylgermane ($H_2C{=}CHGeH_3$),[11] (fluoromethyl)germane (H_3GeCH_2F[12]), and (chloromethyl)germane (H_3GeCH_2Cl).[13] A review of germane and the germyl halides has been given by Bürger and Rahner.[14]

The barrier to internal rotation of the GeH_3 group has been determined in some cases. This threefold barrier is typically 5−7.3 kJ/mol when the germyl group is attached to a sp^3-hybridized carbon atom. Examples are H_3GeCH_3 (5.19),[8] H_3GeCH_2F (5.81(17)),[12] H_3GeCH_2Cl (7.28(17)),[13] $H_3GeCH_2CH_3$ (5.98(12)),[9] and cyclopropylgermane (5.58(20) kJ/mol).[10] The barrier is generally found to be lower than for corresponding silyl (SiH_3) and methyl (CH_3) containing compounds.[9]

Gas-phase studies of the conformational properties of molecules containing the germyl group are rare. This was one motivation to conduct this first study of 2-propenylgermane (allylgermane), $H_2C{=}CHCH_2GeH_3$.

Allylgermane is an allylic compound. These molecules normally exist as a mixture of two rotamers. In the first of these, the C═C−C−Ge chain of atoms takes a *synperiplanar* conformation (dihedral angle ≈ 0°), while the second rotamer has an *anticlinal* conformation (dihedral angle ≈ 120° from *synperiplanar*). These two forms of allylgermane are denoted **sp** and **ac**, respectively, and are drawn in Figure 1, where atom numbering is also indicated.

A variety of methods, including Stark and Fourier transform microwave (MW) spectroscopy, advanced quantum chemical calculations, and infrared (IR) spectroscopy, have been employed in this work to investigate a series of physical properties of the title compound. While the parent species was studied by MW and IR methods, three additional deuterated isotopomers, $H_2C{=}CDCH_2GeH_3$, $H_2C{=}CHCHDGeH_3$, and $H_2C{=}CHCH_2GeD_3$, were investigated exclusively by IR spectroscopy to assign vibrational modes and at the same time investigate the conformational composition of this compound.

The MW methods are characterized by their extremely high resolution and specificity, making them ideal techniques for conformational studies. IR spectroscopy is also a sensitive

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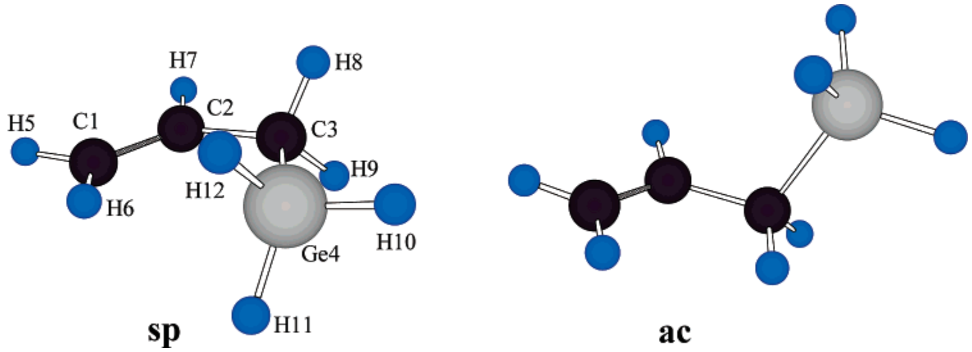

Figure 1. Two stable rotameric forms of allenylgermane. The C1═C2─C3─Ge skeleton is *synperiplanar* in the **sp** conformer and *anticlinal* in the **ac** conformer. Atom numbering is indicated on the **sp** rotamer.

method for the study of conformational composition. Modern quantum chemical calculations are now able to provide useful predictions of molecular properties, even in compounds containing electron-rich elements such as germanium (32 electrons). These calculations are, therefore, a useful supplement to the experimental work.

Experimental Section

Materials. Lithium aluminum hydride, lithium aluminum deuteride, tetraethylene glycol dimethyl ether (tetraglyme), bis(cyclopentadienyl)zirconium chloride deuteride (deuterated Schwartz reagent), and 2-propenyltributylstannane were purchased from Aldrich and used without further purification. 2-Propynyltriphenylstannane[15] and (*Z*)-3-deutero-2-propenyltriphenylstannane[16] were prepared as previously reported.

Synthesis of 2-Propenylgermanes. Allylgermane was synthesized in two steps. Reaction of 2-propenyltributylstannane with germanium tetrachloride led to the 2-propenyltrichlorogermane, which was then reduced with $LiAlH_4$ to give the expected product. The same approach was employed to synthesize the three deuterated allylgermanes using a deuterated stannane or $LiAlD_4$ as the reducing agent.

2-Propenyltrichlorogermane.[17] To a 50-mL two-necked flask equipped with a magnetic stirring bar and a nitrogen inlet was introduced germanium tetrachloride (4.28 g, 20 mmol). 2-Propenyltributylstannane (6.62 g, 20 mmol) was added dropwise at room temperature for about 5 min. The mixture was stirred at 40 °C for 3 h. The flask was then attached to a vacuum line equipped with a trap, which was cooled at −50 °C to condense the 2-propenyltrichlorogermane selectively. The product was distilled by heating the reaction mixture up to 40 °C. At the end of the distillation, the trap was disconnected from the vacuum line by stopcocks and allowed to warm to room temperature. 2-Propenyltrichlorogermane (4.05 g, 18.4 mmol) was obtained in a 92% yield. ^{1}H NMR ($CDCl_3$): δ 2.90 (d, 2H, $^3J_{HH} = 7.9$ Hz, CH_2─Ge), 5.38 (d, 1H, $^3J_{HHcis} = 10.2$ Hz, CH(*H*)═C), 5.38 (d, 1H, $^3J_{HHtrans} = 16.3$ Hz, C*H*(H)═C), 5.87 (ddt, 1H, $^3J_{HHtrans} = 16.3$ Hz, $^3J_{HHcis} = 10.2$ Hz, $^3J_{HH} = 7.9$ Hz, CH═C). ^{13}C NMR ($CDCl_3$): δ 37.0 (t, $^1J_{CH} = 136.5$ Hz, CH_2─Ge), 121.6 (dd, $^1J_{CH} = 163.0$ Hz, $^1J_{CH} = 155.8$ Hz, CH_2), 125.8 (d, $^1J_{CH} = 159.8$ Hz, CH).

Synthesis of 2-Propenylgermane.[18] Caution: *Allylgermane is pyrophoric and potentially toxic. All reactions and handling should be carried out in a well-ventilated hood.*

The apparatus used here was similar to the one described for the preparation of 2-propynylphosphine.[19] To a 250-mL two-necked flask were introduced the reducing agent ($LiAlH_4$, 0.76 g, 20 mmol) and tetraglyme (50 mL). The flask was connected to a vacuum line, immersed in a cold bath (0 °C), and degassed. 2-Propenyltrichlorogermane (2.2 g, 10 mmol) in tetraglyme (10 mL) was slowly added with a flex needle through the septum for about 5 min. During and after addition, 2-propenylgermane was distilled off in vacuo from the reaction mixture. A cold trap (−80 °C) selectively removed less volatile products, and 2-propenylgermane was condensed in a second cold trap (−120 °C) to remove the most volatile products (mainly GeH_4). After disconnecting from the vacuum line by stopcocks, the product was kept at low temperature (<−50 °C) before analysis. Yield: 88% (1.03 g). ^{1}H NMR ($CDCl_3$): δ 1.94 (dq, 2H, $^3J_{HH} = 7.6$ Hz, $^3J_{HH} = 3.1$ Hz, CH_2─Ge), 3.61 (t, 3H, $^3J_{HH} = 3.1$ Hz, GeH_3), 4.88 (d, 1H, $^3J_{HHcis} = 9.8$ Hz, CH(*H*)═C), 4.99 (d, 1H, $^3J_{HHtrans} = 15.8$ Hz, C*H*(H)═C), 5.91 (ddt, 1H, $^3J_{HHtrans} = 15.8$ Hz, $^3J_{HHcis} = 9.8$ Hz, $^3J_{HH} = 7.6$ Hz, CH═C). ^{13}C NMR ($CDCl_3$): δ 14.1 (t, $^1J_{CH} = 130.1$ Hz, CH_2─Ge), 113.3 (dd, $^1J_{CH} = 160.6$ Hz, $^1J_{CH} = 152.4$ Hz, CH_2), 136.2 (d, $^1J_{CH} = 152.6$ Hz, CH).

Synthesis of 1-Deutero-2-propenylgermane. 1-Deutero-2-propenyltrichlorogermane was prepared starting from (*Z*)-3-deutero-2-propenyltriphenylstannane and germanium tetrachloride using the experimental procedure reported above. The reaction occurs via an allylic transposition and only the 1-deutero-2-propenylgermane was obtained. Yield: 71%. Isotopic purity: >96%. ^{1}H NMR ($CDCl_3$): δ 2.89 (dm, 1H, $^3J_{HH} = 7.9$ Hz, $^2J_{HD} = 0.8$ Hz, CHD─Ge), 5.38 (dm, 1H, $^3J_{HHcis} = 10.2$ Hz, CH(*H*)═C), 5.38 (dm, 1H, $^3J_{HHtrans} = 16.3$ Hz, C*H*(H)═C), 5.87 (dddt, 1H, $^3J_{HHtrans} = 16.3$ Hz, $^3J_{HHcis} = 10.2$ Hz, $^3J_{HH} = 7.9$ Hz, $^3J_{HD} = 1.0$ Hz, CH═C). ^{13}C NMR ($CDCl_3$): δ 36.8 ($^1J_{CD} = 20.8$ Hz), 121.6, 125.9.

1-Deutero-2-propenylgermane was prepared starting from 1-deutero-2-propenyltrichlorogermane and $LiAlH_4$ using the experimental procedure reported above. Yield: 88%. Isotopic purity: >95%. ^{1}H NMR ($CDCl_3$): δ 1.94 (m, 2H, $^3J_{HH} = 7.6$ Hz, $^3J_{HH} = 3.3$ Hz, CHD─Ge), 3.61 (d, 3H, $^3J_{HH} = 3.3$ Hz, GeH_3), 4.88 (dm, 1H, $^3J_{HHcis} = 9.8$ Hz, CH(*H*)═C), 4.99 (dm, 1H, $^3J_{HHtrans} = 15.8$ Hz, C*H*(H)═C), 5.91 (dddq, 1H, $^3J_{HHtrans} = 15.8$ Hz, $^3J_{HHcis} = 9.8$ Hz, $^3J_{HH} = 7.6$ Hz, $^3J_{HD} = 1.0$ Hz, CH═C). ^{13}C NMR ($CDCl_3$): δ 13.8 ($^1J_{CD} = 20.1$ Hz), 113.3, 136.2.

Synthesis of 2-Deutero-2-propenylgermane. 2-Deutero-2-propenyltriphenylstannane was first prepared as follows: To a dried Schlenk flask protected from the light by aluminum foil and equipped with a stirring bar were introduced under argon the deuterated Schwartz reagent (517 mg, 2 mmol) and tetrahydrofuran (10 mL). Propynyltriphenylstannane (624 mg, 1.6 mmol, 0.8 equiv) was then added, and this mixture was stirred at room temperature for 1 h. Pure water (1.0 mL) was then quickly added, and the mixture was stirred for 10 min. Diethyl ether (20 mL) was added, and the mixture was dried with $MgSO_4$. The product was purified by chromatography using alumina. Yield: 92%. Isotopic purity: >97%. ^{1}H NMR ($CDCl_3$): δ 2.48 (s, 2H, $^2J_{SnH} = 70.9$ Hz, CH_2—Sn), 4.81 (s, 1H, $^4J_{SnH} = 21.9$ Hz, C*H*(H)═C), 4.99 (s, 1H, $^4J_{SnH} = 22.4$ Hz, CH(*H*)═C), 7.39 (m, 9H, $SnPh_3$); 7.56 (m, 6H, $^3J_{SnH} = 49.8$ Hz, $SnPh_3$). ^{13}C NMR ($CDCl_3$): δ 17.4, 112.0, 128.3, 128.8, 135.3 ($^1J_{CD} = 23.3$ Hz), 136.8, 138.1. HRMS (LSIMS with cesium gun, positive mode, matrix: mNBA) *m*/*z*: $[M - H]^+$ calcd for $C_{21}H_{16}D^{120}Sn$, 390.0415; found, 390.042.

2-Deutero-2-propenyltrichlorogermane was prepared starting from 2-deutero-2-propenyltriphenylstannane and germanium tetrachloride using the experimental procedure reported above. Yield: 72%. Isotopic purity: 96%. ^{1}H NMR ($CDCl_3$): δ 2.89 (s, 2H, CH_2—Ge); 5.39 (s, 2H, CH_2═C). ^{13}C NMR ($CDCl_3$): δ 37.0, 121.4, 125.7 ($^1J_{CD} = 24.5$ Hz).

2-Deutero-2-propenylgermane was prepared starting from 2-deutero-2-propenyltrichlorogermane and $LiAlH_4$ using the experimental procedure reported above. Yield: 88%. Isotopic purity: 96%. ^{1}H NMR ($CDCl_3$): δ 1.93 (m, 2H, $^3J_{HH} = 3.1$ Hz, $^3J_{HD} = 1.0$ Hz, CH_2—Ge), 3.61 (t, 3H, $^3J_{HH} = 3.1$ Hz, GeH_3), 4.88 (s, 1H, CH(*H*)═C), 4.99 (s, 1H, C*H*(H)═C). ^{13}C NMR ($CDCl_3$): δ 14.0, 113.1, 135.9 ($^1J_{CD} = 23.3$ Hz).

Synthesis of 2-Propenylgermane-*d*$_3$.[18] 2-Propenylgermane-*d*$_3$ was prepared starting from the 2-propenyltrichlorogermane and $LiAlD_4$ using the experimental procedure reported above. Yield: 88%. Isotopic purity: >94%. ^{1}H NMR ($CDCl_3$): δ 1.94 (d, 2H, $^3J_{HH} = 7.6$ Hz, CH_2—Ge), 4.88 (dm, 1H, $^3J_{HHcis} = 9.8$ Hz, CH(*H*)═C), 4.99 (dm, 1H, $^3J_{HHtrans} = 15.8$ Hz, C*H*(H)═C); 5.91 (ddt, 1H, $^3J_{HHtrans} = 15.8$ Hz, $^3J_{HHcis} = 9.8$ Hz, $^3J_{HH} = 7.6$ Hz, CH═C). ^{13}C NMR ($CDCl_3$): δ 13.8, 113.3, 136.2.

MW Stark Spectrometer Experiment. The MW spectrum of the title compound was studied using the Oslo Stark spectrometer, which is described briefly in ref 20. A 2 m brass Stark cell was utilized. The 11.5−51 GHz spectral region was investigated, with the cell cooled to dry ice temperature (−78 °C). The pressure was a few pascals when the spectra were recorded using a program by Grønås.[21] The accuracy of the spectral measurements was better than ±0.10 MHz, and the maximum resolution was about 0.4 MHz.

The compound was kept for several months in a refrigerator at about −30 °C or in a Dewar flask at dry ice temperature when not in use. The compound was found to polymerize easily. In fact, polymerization occurred even when the compound was kept under these conditions. However, gaseous allylgermane held at a pressure of about 10 Pa showed no signs of decomposition or polymerization in the brass MW cell over the course of 6−8 h. The spectra were taken at a pressure of a few pascals. No impurities were noted in the MW spectrum.

Fourier Transform MW Spectrometer Experiments. Rotational spectra were recorded for the parent species in the 6−20 GHz spectral range using the Lille Fourier transform MW spectrometer.[22] A gas mixture formed from 3 mbar of allylgermane with neon as the carrier gas to a total pressure of 1 bar was prepared. Gas pulses were then expanded into the vacuum chamber through a pulsed nozzle to create a supersonic jet. As the nozzle is inserted in the center of the fixed mirror of the Fabry−Perot cavity, the supersonic expansion is parallel to the optical axis of the cavity. Each transition is divided into two Doppler components.

Large spectral region surveys were conducted from 11.5 to 16.5 GHz, using the fast (low-resolution) scan mode facilities of the spectrometer.[22] In this operating mode, about 10 free induction decays were averaged and Fourier transformed at a repetition rate of 1.5 Hz. This operation is then automatically repeated every 0.4 MHz, which corresponds to the bandwidth of the Fabry−Perot cavity, to cover the desired frequency region. Molecular transitions observed during this initial search were subsequently recorded using a higher resolution. The central frequencies of the lines are determined by averaging the frequencies of the two Doppler components after transformation of 4096 data points of the time domain signal, leading to a resolution of 2.4 kHz per point. The accuracy of frequency measurements is estimated to be better than 3 kHz. The line width for a typical well-resolved line is 10 kHz.

μ_a- and μ_b-type transitions were observed for the ^{70}Ge, ^{72}Ge, and ^{74}Ge isotopomers. These were readily assigned to the **ac** conformer using the results from the assigned Stark spectrum discussed below. The optimal MW power required to polarize the molecules was found to be around 40 mW for μ_a-type transitions and 4 mW for μ_b-type transitions, which indicates that $\mu_b > \mu_a$ as predicted by the quantum chemical calculations below. All the observed *b*-type transitions were split into two components. The splittings are a few tens of kilohertz (see Table 6).

IR Experiment. The IR spectra were recorded in the 500−4000 cm^{-1} range using a 120HR Bruker Fourier transform interferometer equipped with a KBr beam splitter, a Globar source, and a liquid nitrogen-cooled mercury cadmium telluride detector. A gas cell equipped with 3 mm ZnSe windows and a multiple-pass optical system[23] was used. The total optical path length was adjusted to 10 m when recording the spectra. The gas-phase spectrum of allylgermane is shown in Figure 2. The corresponding spectra of the deuterated species CH_2═CH—CHD—GeH_3, CH_2═CH—CH_2—GeD_3, and CH_2═CD—CH_2—GeH_3 are shown in Supporting Information, Figures 1S−4S. All spectra were taken at −40 °C. The resolution is 0.5 cm^{-1} in each case. The pressure of these species was 0.340 mbar for the parent species, 0.405 mbar for CH_2═CH—CHD—GeH_3, 0.280 mbar for CH_2═CH—CH_2—GeD_3, and 0.432 mbar for CH_2═CD—CH_2—GeH_3, respectively.

Results

Computational Methods. The quantum chemical calculations were made in Lille with the MolPro2000[24] and Gaussian 03 programs[25] and in Oslo using the latter program.

It is known that ab initio electronic structure calculations employing a large basis set and the second-order Møller−Plesset (MP2) perturbation treatment for electron correlation[26] yield fairly accurate structures and consequently predict rotational constants that are rather close to the experimentally determined ones.[27] This will of course facilitate the assignments of the MW spectra.

With this in mind, calculations were performed at the MP2 level of theory to get the best possible starting point. The structures of the **ac** and the **sp** conformers were fully optimized, with no geometrical restrictions imposed. Three different basis sets were used. The first one is Dunning's correlation consistent basis set with polarized valence electrons and diffuse functions at the triple-ζ level.[28,29] The other two are the standard cc-pVTZ for H and C. For Ge, two different small-core relativistic pseudopotential correlation consistent basis sets called cc-pVTZ-PP[30] and SDB-cc-pVTZ[31] were employed.

These three basis sets give almost identical results, except for the Ge—H and Ge—C bond lengths. The SDB-cc-pVTZ gives the largest values and the cc-pVTZ-PP the smallest ones. For instance, for the Ge4—H10 bond length (Figure 1), the results are for the **ac** form (in pm): 150.5 (cc-p-VTZ-PP); 151.9 (aug-cc-pVTZ); and 153.5 (SDB-cc-pVTZ). The equilibrium

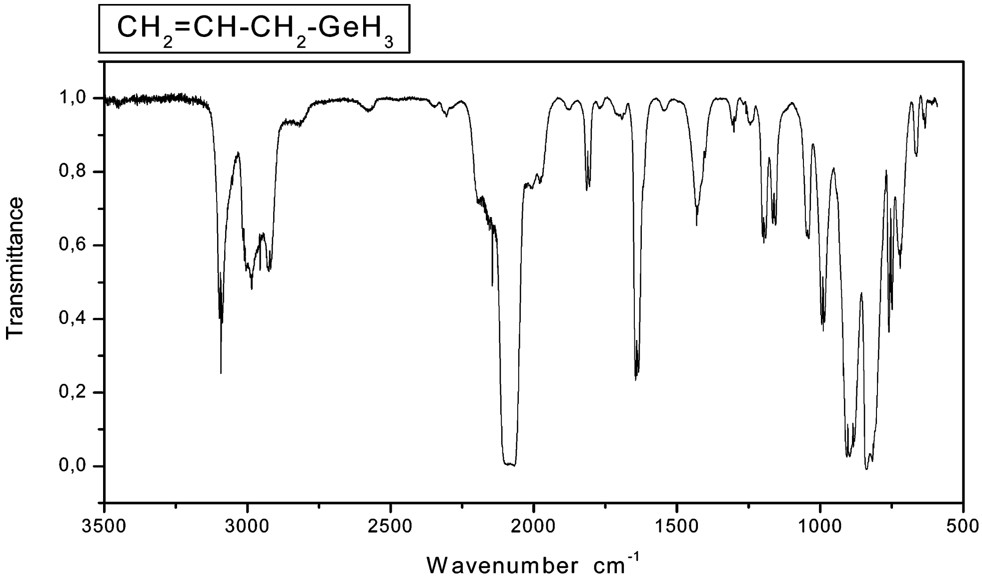

Figure 2. Gas-phase IR spectrum of $H_2C{=}CHCH_2GeH_3$ taken at a pressure of 0.340 mbar and a temperature of −40 °C.

Ge—H bond length has been accurately determined for three germyl compounds: GeH_4 (151.6),[14] GeH_3F (151.5),[4] and GeH_3Cl (151.6).[3] These values are extremely close and indicate that the Ge—H bond length in the **ac** conformer should be close to 151.6 pm too. To confirm this statement, we performed ab initio calculations for GeH_4 using the same basis sets. The results are (in pm): 149.9 (cc-p-VTZ-PP); 151.2 (aug-cc-pVTZ); and 153.0 (SDB-cc-pVTZ). This indicates that the equilibrium value of Ge—H should be close to 152.0 pm.

To estimate the error of the Ge—C bond length, it is possible to use methylgermane where r_s(Ge—C) = 194.5(5) pm.[8] The same calculations were repeated for this molecule. They give for the Ge—C bond length (in pm): 196.2 (SDB-cc-pVTZ) and 193.7 (aug-cc-pVTZ). The cc-pVTZ-PP basis set does not converge because of the excessive mixing of frozen core and valence orbitals. Thus, the equilibrium Ge—C bond length should be close to 196.0 pm in the **ac** conformer.

These results indicate that the aug-cc-pVTZ basis set gives the best results, probably by an accidental compensation of errors. This is confirmed by comparing the experimental (Table 3) and ab initio rotational constants where the smallest errors are found with the aug-cc-pVTZ basis set. For this reason, only the structure obtained at the MP2/aug-cc-pVTZ level of theory is given in Table 1. The rotational constants for the ^{74}Ge isotopomer calculated from the refined structures, dipole moment components of the same isotopomer, and energy differences are found in Table 2.

A few comments about the structures of the two rotamers are warranted. The **sp** conformer has a symmetry plane (C_s symmetry). The important C1C2C3Ge4 dihedral angle in **ac** is predicted to be 106.2°, about 14° from the idealized value (120°). The **ac** rotamer is preferred relative to **sp** by 5.6 kJ/mol. It is possible that this energy difference reflects repulsive forces in the **sp** conformer, increasing its energy. The evidence for existence of repulsive forces is seen in the C2C3Ge4 angle, which is calculated to increase from 110.3° in **ac** to 116.0 in **sp** (Table 1).

TABLE 1: Ab Initio MP2/aug-cc-pVTZ Structures[a,b] of the *Anticlinal* and *Synperiplanar* Conformers of Allylgermane

	ac conformer	**sp** conformer
	Bond Lengths	
C1═C2	133.7	133.6
C1—H5	108.1	108.1
C1—H6	108.3	108.2
C2—C3	149.0	149.8
C2—H7	108.6	108.6
C3—Ge4	195.1	194.5
C3—H8	109.1	109.3
C3—H9	109.0	109.3
Ge4—H10	151.9	151.7
Ge4—H11	151.7	151.8
Ge4—H12	151.8	151.8
	Angles	
C2C1H5	121.2	120.9
C2C1H6	121.0	121.9
C1C2C3	124.9	126.0
C1C2H7	118.6	117.9
C2C3Ge4	110.3	116.0
C2C3H8	111.1	109.6
C2C3H9	110.9	109.6
C3Ge4H10	110.6	108.7
C3Ge4H11	109.0	110.5
C3Ge4H12	109.1	110.5
	Dihedral Angles	
H5C1C2C3	178.0	180.0
H5C1C2H7	0.2	0.0
H6C1C2C3	−2.0	0.0
C1C2C3Ge4	−106.2	0.0
C1C2C3H8	134.2	−122.4
C1C2C3H9	14.1	122.4
C2C3Ge4H10	−117.4	180.0
C2C3Ge4H11	65.0	60.4
C2C3Ge4H12	−54.2	−60.4

[a] Bond lengths in picometers; angles in degrees. [b] Atom numbering is given in Figure 1.

The harmonic (or quartic) centrifugal distortion constants and vibrational frequencies are other parameters of interest in this investigation. The harmonic force field needs to be known to calculate these parameters. This force field was calculated with Becke's density functional theory procedure, B3LYP,[32] using the 6-311G(3df,2pd) basis set. The five quartic centrifugal distortion constants of the Watson *A* reduction[33] were calculated for the ^{74}Ge isotopomer and are listed in Table 2.

It should be stated that all the B3LYP vibrational frequencies were positive for both rotameric forms. This indicates that both **ac** and **sp** represent minima (i.e., are "stable") on the potential energy hypersurface.[34] The energy difference between these two rotamers was calculated to be 9.2 kJ/mol by this method, nearly twice as much at the MP2 value given above.

TABLE 2: Rotational Constants (MHz),[a] Centrifugal Distortion Constants (kHz),[b] Dipole Moments (10^{-30} C m),[c] and Relative Energies[d] of the *Anticlinal* and *Synperiplanar* Conformers of Allylgermane

	ac	sp
	Rotational Constants	
A	14 616.7	11 130.5
B	2005.0	2498.9
C	1928.3	2119.4
	Centrifugal Distortion Constants[e]	
Δ_J	1.25	1.09
Δ_{JK}	−32.4	−5.22
Δ_K	335	24.4
δ_J	0.162	0.216
δ_K	0.332	−0.755
	Dipole Moments	
μ_a	0.12	1.22
μ_b	1.69	2.24
μ_c	0.07	0.0[f]
μ_{tot}	1.70	2.55
relative energy	0.0	5.6[g]

[a] ^{74}Ge isotopomer. MP2/aug-cc-pVTZ calculations. [b] B3LYP/6-311G(3df,2pd) calculations. [c] 1 D = 3.335 64 × 10^{-30} C m. [d] In kJ/mol. Total MP2 energy of **ac**: −5 761 428.03 kJ/mol. [e] *A* reduction.[33] [f] For symmetry reasons. [g] The energy difference calculated by the G2 method was 6.6 kJ/mol, and the one calculated by the B3LYP method was 9.2 kJ/mol.

TABLE 3: Relative Energies (kJ/mol) of the *Anticlinal* and *Synperiplanar* Conformer of $H_2C{=}CHCH_2XH_3$ with X = C, Si, Ge[a]

		∠(CCCX)[a]	G3B3 method ΔE[b]	G2 method ΔE[b]
allyl-CH_3	**ac**	119.6	0.0	0.0
	sp	0.0	0.7	1.2[c]
allyl-SiH_3	**ac**	107.6	0.0	0.0
	sp	0.0	5.4	6.7
allyl-GeH_3	**ac**	105.0	*d*	0.0
	sp	0.0	*d*	6.6

[a] Dihedral angle calculated at the B3LYP/6-31G(d) level of theory. [b] Energy relative to **ac** (0.0 kJ/mol). [c] Experimental value: 0.63(63) kJ/mol. [d] Ge is not implemented in our version of the program.

The G2[35] procedure is known to give comparatively reliable energy differences, and calculations at this level of theory were, therefore, carried out next for the **ac** and **sp** rotamers. Although germanium is a rather large atom, the errors of the energies are largely systematic and would be expected to cancel to a large degree in relative energy calculations. The energy difference found in our G2 calculations was 6.6 kJ/mol with **ac** as the preferred form, close to the MP2 value (5.6 kJ/mol) but lower than the B3LYP result (9.2 kJ/mol).

This calculation was also repeated for allylsilane and 1-butene. To check the accuracy of the energies, a variant of the Gaussian-3 (G3) theory[36] was also used for the latter two molecules (the G3 theory is implemented only for atoms up to $Z = 18$ in our version of Gaussian 03). In the variant used, G3B3,[37] the geometries and zero-point energies are obtained from B3LYP density functional theory [B3LYP/6-31G(d)] instead of geometries from second-order perturbation theory [MP2/6-31G(d), all electrons being correlated], and zero-point energies are from Hartree−Fock theory. The G3B3 method is slightly more accurate than the original G3 method. Its average absolute deviation from experiment (for a total of roughly 300 molecules) is 4.1 kJ/mol, whereas it is 6.2 kJ/mol for the G2 theory. The results are gathered in Table 3.

MW Spectra and Assignment of the ac Conformer. Survey spectra taken using the Stark spectrometer revealed a rather weak and fairly dense spectrum. This was expected because the quantum chemical calculations above predict rather small dipole moments for both **sp** and **ac**. There are also several low-frequency vibrational fundamentals that will have a significant population even at −78 °C. Five of these vibrations are below 500 cm^{-1} in both rotamers according to the B3LYP calculations. Moreover, germanium has several isotopes. The most abundant ones are ^{70}Ge (20.5%), ^{72}Ge (27.4%), and ^{74}Ge (36.5%). The remaining two isotopes, ^{73}Ge and ^{76}Ge, are each present in concentrations of less than 8% of the total. This distribution of isotope concentration will lead to a further reduction of the intensities of the MW lines.

The theoretical calculations above predict that the **ac** conformer is preferred. This rotamer is seen in Table 2 to have the major component of its dipole moment along the *b*-inertial axis (1.69 × 10^{-30} C m). Searches were, therefore, first made for the ^bQ-branch $J_{1,J-1} \leftarrow J_{0,J}$ series of the most abundant (^{74}Ge) isotopomer, and these transitions were identified and assigned. The frequencies of two further *Q*-branch series ($K_{-1} = 2 \leftarrow 1$ and $K_{-1} = 3 \leftarrow 2$) could now be predicted accurately. *Q*-branch transitions with J values up to $J = 57$ were soon assigned.

Spectral lines attributable to the ^bR-branch transitions were then found after several alternative lines had been tested. *R*-branch transitions with values of J up to $J = 35$ were now assigned. The hypothetical frequencies of *a*- or *c*-type lines could now be calculated very accurately, but they were not found in the Stark spectrum, presumably because they are too weak. This is consistent with the very small dipole moment predicted for these lines (Table 2). It should also be noted that no splittings resulting from internal rotation of the germyl group were seen in the Stark spectrum. Such splittings would have been discovered if they had been larger than about 0.40 MHz.

The spectroscopic constants obtained by Stark spectroscopy were next used to predict further transitions that were subsequently measured using the Fourier transform spectrometer. Both *b*-type as well as the much weaker *a*-type lines were now assigned. All *b*-type lines were split into two components owing to tunneling of the germyl group through its threefold barrier (see Barrier to Internal Rotation section). There was no evidence of splitting for the *a*-type transitions. The full spectrum which also incorporates the transitions measured by Fourier transform spectroscopy is shown in Table 1S in Supporting Information. The average frequencies of the split *b*-type lines were used in the fitting procedure.

The spectroscopic constants (*A*-reduction I^r representation[33]) including the five quartic centrifugal distortion constants and one sextic constant (ϕ_J) are listed in Table 4. Inclusion of this sextic constant was necessary to obtain a fit with an average deviation comparable to the experimental uncertainty. The transitions were weighted according to the inverse square of their uncertainties in the fitting procedure. Sørensen's program ROTFIT[38] was utilized. The weighted root-mean-square deviation is minimized in this program.

The shifts in the rotational constants that accompany substitution of ^{74}Ge by ^{72}Ge or ^{70}Ge can be predicted well. This made it easy to assign the spectra of the corresponding isotopomers. The spectra of these species are displayed in Tables 3S and 5S in Supporting Information. The spectroscopic constants resulting from least-squares fits are listed in Table 4. Interestingly, the quartic centrifugal distortion constants in Table 4 for the most abundant species are in quite good agreement with those listed in Table 2 in all cases but δ_K, which differs from the experimental one by more than 90%.

TABLE 4: Rotational (MHz), Quartic Centrifugal Distortion (kHz), and Sextic Centrifugal Distortion Constants (Hz)[a] of the Ground Vibrational State of the ac Conformer of Allylgermane

	^{74}Ge isotopomer	^{72}Ge isotopomer	^{70}Ge isotopomer
A	14 751.0877(31)	14 759.9809(37)	147 69.3268(53)
B	1967.793 34(58)	1982.146 46(65)	1997.2145(32)
C	1895.385 76(59)	1908.848 60(65)	1922.9795(31)
Δ_J	1.586 74(59)	1.6197(16)	1.6515(93)
Δ_{JK}	−40.8215(87)	−41.138(13)	−41.305(23)
Δ_K	394.21(23)	402.3(14)	384.1(31)
δ_J	0.229 23(10)	0.233 84(10)	0.238 67(12)
δ_K	1.780(31)	1.765(35)	1.648(42)
ϕ_J[b]	0.002 631(35)	0.002 748(36)	0.002 813(36)
N[c]	167	131	115
rms[d]	2.78	2.85	2.55

[a] A-reduction I^r representation.[33] [b] Further sextic constants preset at zero. [c] Number of lines used in the fit. [d] Root-mean-square deviation from a weighted fit.

TABLE 5: Rotational (MHz), Quartic Centrifugal Distortion (kHz), and Sextic Centrifugal Distortion Constants (Hz)[a] of the First Excited State of the Torsion around the C2−C3 Bond of the ac Conformer of Allylgermane

	^{74}Ge isotopomer	^{72}Ge isotopomer	^{70}Ge isotopomer
A	14 747.096(20)	14 755.767(22)	14 764.878(25)
B	1978.0491(33)	1992.4737(38)	2007.6217(69)
C	1900.8567(33)	1914.3251(38)	1928.4653(69)
Δ_J	1.6440(85)	1.621(13)	1.645(24)
Δ_{JK}	−40.199(24)	−40.517(29)	−40.788(32)
Δ_K	398.5(48)	405.7(57)	402.0(61)
δ_J	0.246 31(11)	0.251 13(11)	0.256 42(12)
δ_K	3.477(30)	3.539(38)	3.604(43)
ϕ_J[b]	0.002 823(39)	0.002 939(34)	0.003 128(39)
N[c]	104	87	76
rms[d]	1.99	1.97	1.97

[a−d] Footnotes are the same as for Table 4.

TABLE 6: Transitions and Parameters Used To Determine the Barrier to Internal Rotation of the Germyl Group of the ^{74}Ge Isotopomer[a,b]

J'	K_{-1}'	K_{+1}'	←	J''	K_{-1}''	K_{+1}''	$\nu_A - \nu_E$ (MHz)	obs. − calc. (MHz)
4	1	3		4	0	4	0.043	0.002
5	1	4		5	0	5	0.043	0.002
6	1	5		6	0	6	0.044	0.002
7	1	6		7	0	7	0.046	0.000
1	1	1		0	0	0	0.048	−0.004
1	1	0		1	0	1	0.042	0.002
2	1	1		2	0	2	0.048	−0.004
3	1	2		3	0	3	0.044	0.000

[a] See text. [b] Parameters kept fixed: $I_\alpha = 0.630$ u nm^2, $\lambda_a = 0.6406$, $\lambda_b = -0.496\,35$, $\lambda_c = 0.083\,86$, $\beta = 0.074\,472$ rad, $\gamma = 0.161\,76$ rad. From fit $V_3 = 6561(17)$ J/mol, root-mean-square dev. = 0.0025 MHz. See Woods for the definitions of the parameters.[40] These parameters have been calculated using the structure given in Table 1.

The ground-state transitions in the Stark spectrum were accompanied by less intense lines presumably belonging to vibrationally excited states. One such state, assumed to be the first excited state of the lowest fundamental, was assigned. The spectra of the ^{74}Ge, ^{72}Ge, and ^{70}Ge isotopomers of this excited state are listed in Supporting Information, Tables 2S, 4S, and 6S. The spectroscopic constants are displayed in Table 5.

Relative intensity measurements performed as described in ref 39 yielded 92(20) cm^{-1} for this vibrational mode. The lowest fundamental vibration found in the B3LYP calculations has a frequency of 88 cm^{-1}. This mode is the torsion around the C2−C3 bond (Figure 1).

It was not possible to determine the dipole moment from the Stark effect in this case because the low-J lines normally used for this purpose were too weak to allow quantitative measurements to be made.

Structure of the ac Conformer. Comparison of the experimental (Table 4) and the MP2/aug-cc-pVTZ (Table 2) rotational constants of the ^{74}Ge isotopomer calculated from the structure of Table 1 reveals the differences between the experimental and theoretical values to be 0.9, −1.9, and −1.7% in the cases of A, B, and C, respectively. A positive difference of roughly 1% in each case would have been expected if an accurate equilibrium structure had been available.

Interestingly, the size of the second moment defined as $P_{cc} = (I_a + I_b - I_c)/2$, where I_a, I_b, and I_c are the principal moments of inertia, is sensitive to the value of the C1C2C3Ge4 dihedral angle. The value calculated for P_{cc} from the structure in Table 1 is 12.28×10^{-20} u m^2, close to 12.22×10^{-20} u m^2 calculated from the experimental rotational constants. This is evidence that the said dihedral angle is indeed close to 106°.

It was mentioned above that bond lengths involving germanium obtained in these calculations were close to the expected values. Very small changes in bond lengths, angles, and dihedral angles would produce the observed differences between the observed and the calculated rotational constants. It is, therefore, concluded that the structure presented for the **ac** rotamer in Table 1 is a good approximation of the equilibrium structure.

Searches for the sp Conformer. Extensive searches were carried out for the **sp** rotamer using both Stark and Fourier transform spectroscopy, though no assignment could be made. The same was found using IR spectroscopy (see below). It is concluded that this conformer must be a high-energy form of the molecule in agreement with the theoretical predictions above (5.6−9.2 kJ/mol), if it exists at all as a stable rotameric form of the molecule.

Barrier to Internal Rotation of the Germyl Group. Most lines measured by Fourier transform MW were found to be split into doublets as a consequence of the internal rotation of the germyl group, as already mentioned. The observed splittings (Table 6) are nearly identical for all Ge isotopic species. Only those corresponding to the main isotopic species (^{74}Ge) were, therefore, analyzed. As the number and diversity of the splittings are small, only the potential barrier could be fitted. Consequently, all the structural parameters, that is, the moment of inertia of the germyl group around the symmetry axis (I_α) and the direction cosines of the symmetry axis of the top (λ_a, λ_b, and λ_c), were calculated from the MP2/aug-cc-pVTZ structure given in Table 1. Woods' program[40] was used for the fit.

The value of the barrier to internal rotation of the germyl group found in this manner ($V_3 = 6.561(17)$ kJ/mol) should be compared to those of H_3GeCH_3 (5.19),[8] H_3GeCH_2F (5.81(17)),[12] H_3GeCH_2Cl (7.28(17)),[13] $H_3GeCH_2CH_3$ (5.98(12)),[9] and cyclopropylgermane (5.58(20) kJ/mol).[10] It is, therefore, concluded that the barrier to internal rotation of the germyl group of the title compound is rather typical for compounds where the said group is attached to a sp^3-hybridized carbon atom.

It is interesting to compare the barrier to internal rotation of the XH_3 top of the three allyl-XH_3 molecules (X = C; Si and Ge). The barrier to internal rotation of the methyl group of the **ac** form of $H_2C{=}CHCH_2CH_3$ is 13.22 kJ/mol.[41] A barrier of 8.74 kJ/mol was found for the silyl top in the corresponding rotameric form of $H_2C{=}CHCH_2SiH_3$.[42] The fact that the barrier of the germyl group is 6.561(17) kJ/mol in allylgermane is consistent with increased distance between X and the atom to which the XH_3 group is attached, reducing the interaction between the top and the frame.

IR Spectrum and Assignments. The gas-phase IR spectrum of allylgermane in the 500−4000 cm^{-1} region is given in Figure 2. It is evident from this figure that parts of the spectrum are quite complicated, sometimes making the assignments of the various bands difficult. Use has been made of the spectra of the three deuterated species $CH_2{=}CH{-}CHD{-}GeH_3$, $CH_2{=}CH{-}CH_2{-}GeD_3$, and $CH_2{=}CD{-}CH_2{-}GeH_3$ in the assignment procedure. These spectra are given in Supporting Information, Figures 1S−4S. The B3LYP predictions made for the vibrational fundamentals were also helpful, as were the IR spectra of several related compounds.[43−45]

It is seen that the spectral region between 1050 and 500 cm^{-1} is rather complicated with several overlapping absorption bands. By making use of the expected isotope effects of the $-CHD-$ methylene group in $CH_2{=}CH{-}CHD{-}GeH_3$ (Figure 1S, Supporting Information) and of the GeD_3 group in $CH_2{=}CH{-}CH_2{-}GeD_3$ (Figure 2S), the assignment of the fundamental vibrational bands is considerably simplified. The tri-deuteration of the germane group induces a significant shift of its deformation vibrations. The average ratio of $\nu_{obs}(-GeH_3)/\nu_{obs}(-GeD_3)$ is found to be 1.39.

The vibrational modes of the methylene$-CH_2$ group appearing in this same region, namely, the scissoring, wagging, twisting, and rocking, are shifted in the spectrum of $CH_2{=}CH{-}CHD{-}GeH_3$ and have been unambiguously identified. Consequently, all other vibrational bands in this region that are not sensitive to the isotopic effect are attributed to the vibrations of the vinyl group.

The 1050−2700 cm^{-1} spectral range is much less complicated than the previous region (Figure 2), allowing assignments to be made readily.

However, the region around 3000 cm^{-1} is quite complex. The isotopic shift of the C−H stretching vibration of the vinyl group produced by $CH_2{=}CD\text{-}CH_2{-}GeH_3$ (Figure 3S) was useful for making definite assignments here. The spectrum of the parent species ($CH_2{=}CH{-}CH_2{-}GeH_3$) with assignments and intensities is listed in Table 7. Similar information for the three deuterated species is listed in Table 7S in Supporting Information. The IR spectra of the parent and deuterated species are compared in Figure 4S.

The theoretical calculations above predict the existence of two stable rotameric forms of allylgermane, the **sp** and the **ac** conformers, with **ac** as the favored one. The B3LYP harmonic frequencies are nearly the same for these two forms. The close proximity of the fundamental vibrations of **sp** and **ac** makes it difficult to find **sp** provided it is present in a concentration below about 10% of the total. The IR spectrum, therefore, corroborates the MW findings and the quantum chemical calculations in that **ac** is considerably more stable than the hypothetical **sp** conformer.

TABLE 7: IR Spectrum and Assignments of $H_2C{=}CHCH_2GeH_3$

	assignment[a]	frequency	intensity[b]
ν_1	$=CH_2$ antisymmetric stretching	3092	s
ν_2	$=CH_2$ symmetric stretching	3052	m
$3\nu_{15}$	($=CH-$ bend out-of-plane)	2985	w
ν_3	$=CH-$ stretching	3010	m
ν_4	$-CH_2-$ symmetric stretching	2952	w
ν_5	$-CH_2-$ antisymmetric stretching	2922	m
ν_6	GeH_3 stretching	2111	vs
ν_7	GeH_3 stretching	2082	vs
ν_8	GeH_3 stretching	2078	vs
$2\nu_{15}$	($=CH-$ out-of-plane bending)	1973	m
$2\nu_{17}$	($=CH_2$ wagging)	1810	m
$2\nu_{18}$	(GeH_3 deformation)	1767	w
ν_9	C=C stretching	1639	s
ν_{10}	$-CH_2-$ deformation	1431	m
ν_{11}	$=CH_2$ deformation	1405	w
ν_{12}	$=CH-$ in-plane bending	1299	w
ν_{13}	$-CH_2-$ wagging	1199	m
ν_{14}	$-CH_2-$ twisting	1159	m
ν_{15}	C−C stretching	1040	m
ν_{16}	$=CH-$ out-of-plane bending	989	s
ν_{17}	$=CH_2$ rocking	920	w
ν_{18}	$=CH_2$ wagging	903	vs
ν_{19}	GeH_3 deformation	883	s
ν_{20}	GeH_3 deformation	829	vs
ν_{21}	GeH_3 deformation	754	s
ν_{22}	$-CH_2-$ rocking	720	m
ν_{23}	$=CH_2$ twisting	664	w
ν_{24}	Ge−C stretching	636	vw

[a] See text. [b] vs (very strong), s (strong), m (medium), w (weak), and vw (very weak). $=CH_2$, vinyl group; $-CH_2-$, methylene group.

Discussion

It is interesting to compare the structural and conformational properties of the two related molecules 1-butene ($H_2C{=}CHCH_2\text{-}CH_3$) and allylsilane ($H_2C{=}CHCH_2SiH_3$) to the present study of allylgermane ($H_2C{=}CHCH_2GeH_3$).

1-Butene exists as a mixture of the **sp** and **ac** conformers.[41,44] The **ac** form is 0.63(63) kJ/mol more stable than **sp**[41,44] in this case. A different situation exists for allylsilane. This compound has been studied by electron diffraction,[46] MW spectroscopy,[47] IR spectroscopy,[42] and quantum chemical calculations.[42] Only the **ac** rotamer has been found in the experimental investigations.

The C=C−C−X (X = C, Si, Ge) dihedral angle determines the conformation of these three compounds. This angle is 119.9(3)° in the **ac** conformer of 1-butene,[41] rather different from 106.8(11)° in allylsilane,[47] which is nearly the same as 106.4° found for allylgermane (Table 1). The conformational properties of allylgermane are, thus, much more similar to that of allylsilane than to that of 1-butene. The reason this dihedral angle in allylsilane and allylgermane is so different from that in 1-butene is not obvious. It is possible that the *d* orbitals on Si and Ge play a role here.

There has been speculation as to whether the **sp** form of allylsilane is indeed a stable conformer of this compound (minimum on the potential energy hyper/surface) or whether it represents a maximum and is consequently a transition state.[42] $\sigma-\pi$ hyperconjugation might cause such a behavior according to this study.[42] A similar situation cannot be completely ruled out for allylgermane, although the quantum chemical calculations above indicate that the **sp** form is indeed a stable rotameric form because positive normal vibrations were always predicted in the theoretical calculations.

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Supporting Information Available: Tables 1S−6S contain the MW spectra, the IR spectra are shown in Figures 1S−4S, and Table 7S shows the comparison of observed vibrational frequencies for allylgermane and its deuterated derivatives. This material is available free of charge via the Internet at http://pubs.acs.org.

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