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Ge_6Me_{12} and Ge_6H_{12} Cyclohexagermanes: Conformer Equilibria Studied by Raman Spectroscopy and Quantum Chemical Calculations

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In the first experimental study of rotational isomerism of a compound possessing a fourth row element backbone, the totally symmetric Ge–Ge stretching mode of dodecamethylcyclohexagermane (Ge_6Me_{12}), which is the most intense Raman band in the range 200–300 cm^{-1}, was analyzed with temperature-dependent vibrational Raman spectroscopy in both the crystalline and solution states. Below 50 °C, the Raman spectrum of the solid shows a single band at 232 cm^{-1} originating from the chair conformer. Between 50 and 60 °C, a shoulder at 227 cm^{-1} appears, which is associated with a twisted conformer. In solution, the band attributed to the chair conformer displays a shoulder arising from an averaged twist/boat conformer, even at –80 °C. The intensity of the shoulder increases with temperature. By using the van't Hoff relationship, an enthalpy difference of 2.4 $kJ\,mol^{-1}$ between chair and twist/boat conformers was obtained. An improved X-ray crystal structure of Ge_6Me_{12} was also obtained, and an average Ge–Ge bond length of 242 pm was found, about 5 pm longer than previously reported. With the help of quantum chemical DFT and MP2 calculations, the geometries and energies of the conformers of Ge_6Me_{12} and of the parent Ge_6H_{12} compound were investigated thoroughly by employing 6-31+G*, D95V and aug-cc-pVTZ basis sets, as well as SDD and aug-cc-pVTZ-PP pseudopotentials on the Ge atoms. B3LYP/aug-cc-pVTZ calculations predict two conformers for Ge_6H_{12}, chair and twist, with zero-point vibrational energy (ZPVE) corrected relative energies of 0.0 and 5.7 $kJ\,mol^{-1}$, respectively. They predict three conformers, chair (0.0), twist (5.2) and boat (9.2), for Ge_6Me_{12}. They also give reasonable geometry parameters, relative energies and barriers for the conformer interconversion.

Introduction

In the early days of stereochemistry, which at the time was essentially carbon chemistry, it was assumed that rotation about single bonds was free. Yet by the middle of the third decade of the twentieth century, the idea that rotation around the C–C bond in ethane and related carbon compounds was not free had been widely accepted. In 1936, Kemp and Pitzer[1] calculated the barrier for the internal rotation in ethane to be 13.2 $kJ\,mol^{-1}$ from entropy data, a value which is very similar ($\pm 10\%$) to the most recent results (12.1–12.3 $kJ\,mol^{-1}$).[2] About forty years later, the barrier for disilane, Si_2H_6, was determined to be 5.1 $kJ\,mol^{-1}$.[3] The barrier for Ge_2H_6 was estimated with the aid of vibrational spectroscopy to be about 6 $kJ\,mol^{-1}$.[4] However, no experimental data for Sn_2H_6 and Pb_2H_6 are available as they have not even been prepared.

With the availability of quantum chemical calculations, the origin of these barriers could be investigated. Schleyer et al. analyzed the barriers for X_2H_6 (X = C, Si, Ge, Sn and Pb) in detail.[5] In the natural bond orbital (NBO) picture, the stabilizing vicinal $\sigma(XH)\rightarrow\sigma^*(XH)$ delocalization is responsible for the more stable staggered rather than eclipsed conformation, and decreased overlap due to longer X–X bonds is responsible for the smaller rotational barriers of the heavier species.[5] These results contradict the long and widely held belief that the steric repulsion of X–H bonds is responsible for hindered rotation. The debate is ongoing; for instance a more recent ab initio valence bond (VB) study by Mo et al. [HF/6-31G(d) and HF/6-311G(d,p)] reinstated that the barrier for ethane and its congeners is overwhelmingly dominated by steric repulsion.[2a–2d]

In disubstituted ethane-like molecules such as FH_2XXH_2F, the conformer stabilities are influenced by the relative magnitudes of $\sigma(XH)$ and $\sigma(XF)$ delocalization into the antibonding $\sigma^*(XH)$ and $\sigma^*(XF)$ orbitals. For instance, in FH_2CCH_2F, the gauche form is preferred even in the gas phase, despite the repulsive dipole–dipole interactions.

Of course, steric effects due to the increasing size of the pendant groups will increasingly dominate the conformational potential. While conformer stabilities and equilibria due to hindered rotation about C–C bonds have been determined for a huge number of compounds and various pendant groups, experimental data for Si–Si bonds remain

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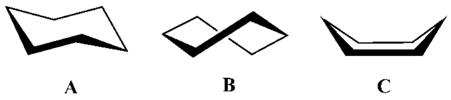
scarce.[6] Generally, not only barrier heights but also energy differences between conformers decrease from carbon- to silicon-containing molecules, and this is accompanied by a considerable decrease in the conformer mean lifetimes. The increased rate constants for conformer interconversion make NMR spectroscopy – so successful in organic chemistry – an inadequate method for the monitoring of many silicon compounds. The NMR time scale of 10^{-1} to 10^{-9} seconds demands temperatures as low as –160 °C or lower to slow down reaction rates sufficiently for conformer observation. For instance, the splitting of the ^{13}C resonances of the methyl groups of Si_6Me_{12} as a result of them being in axial and equatorial positions was observed at –165 °C, and a ring inversion barrier of ca. 20 kJ mol^{-1} was deduced. However, the signals were barely detectable due to low solubility.[7]

So far, no experimental studies of hindered rotation about Ge–Ge, Sn–Sn or Pb–Pb bonds have been reported in the literature. Surely NMR spectroscopy is not a suitable method for exploring these systems, and the question arises whether vibrational spectroscopy, possessing a time scale which on average is six orders of magnitudes smaller (about 10^{-13} seconds) than that of NMR spectroscopy, might be able to resolve these fast processes. If vibrational transitions originating from two different conformers are separated by 10 cm^{-1} or by a frequency difference $\Delta\nu$ of 3×10^{11} Hz, the lifetime of the conformers has to be longer than $\Delta\nu^{-1}$ to give resolved vibrational spectra. By using the theory of the activated complex, a barrier height of about 4 kJ mol^{-1} or larger is estimated for this to occur at 300 K.[8,9] Alternatively, it can be argued that the barrier must be noticeably larger than the Boltzmann energy *RT*, which is 2.5 kJ mol^{-1} at 300 K.

Recent ab initio calculations for digermane predict a barrier of 3.1 to 3.6 kJ mol^{-1}; this result is dependent on the methods and basis sets that were used.[2b,10] These results support the expectation that the conformer equilibria of digermanes and oligogermanes will be borderline cases as far as the use of vibrational spectroscopy is concerned. We have therefore set out to investigate some germanes that are expected to possess at least two conformational minima on the potential energy surface (PES) by employing Raman spectroscopy combined with quantum chemical ab initio calculations. Here we report on cyclohexagermane studied by quantum chemical calculations and on dodecamethylcyclohexagermane studied by both theory and Raman spectroscopy. Results for 1,2-dichlorotetramethyldigermane, tetramethyldigermane, and hexamethyldigermane will be published elsewhere.[11]

We were led to choose Ge_6Me_{12} because, by analogy with C_6Me_{12} and Si_6Me_{12}, we expected the barriers for the chair-to-chair and chair-to-twist interconversions to be larger than the barrier in digermane itself. Dynamic NMR spectroscopic studies for C_6Me_{12} and Si_6Me_{12} gave barriers for the chair-to-chair interconversion of 70 kJ mol^{-1} and 20 kJ mol^{-1}, respectively.[7,12] In two Raman spectroscopic studies of Si_6Me_{12} and $Si_6Me_{11}X$ (X = H, F, Cl, Br and I), we were able to identify chair and twist conformers and to determine their enthalpy differences.[13,14] It turned out that boat conformations also represent minima for these cyclohexasilanes, and that the boat-to-twist interconversion is fast even on the timescale of Raman spectroscopy. Therefore, a three-conformer equilibrium between chair (**A**), twist (**B**) and boat (**C**) must also be expected for Ge_6Me_{12}.



Generally, reports of experimental studies of conformer equilibria for molecules composed of fourth or higher row elements (group 14: Ge, Sn, Pb; group 15: As, Sb, Bi; group 16: Se. Te) are virtually absent from the literature. To the best of our knowledge, group 14 and group 16 elements have not been studied at all. Of the group 15 elements, tetramethyldistibane has been examined by photoelectron spectroscopy, and the existence of *gauche* and *anti* conformers in the gas phase was observed. No enthalpy data or barrier heights were given.[15] A gas-phase electron diffraction study of tetrakis(trifluoromethyl)diarsane showed quite a different behaviour: only the trans conformer was present.[16]

Results and Discussion

Cyclohexagermane, Ge_6H_{12}

Ge_6Me_{12} was prepared by known methods.[17] It is now well established by extensive calculations on Ge_2H_6 (and also SiH_3GeH_3) that experimental geometrical parameters are reproduced well at correlated levels by employing triple-zeta basis sets augmented with f polarization functions on the heavy atoms.[10b,18] The calculated Ge–Ge distance was 0.013 Å longer than the experimental value at the CISD/TZP(f) level. MP2 and DFT calculations, which may be used for larger molecules, performed satisfactorily in computing geometries and vibrational spectra. The Ge–Ge distances were longer than the experimental value by about 0.030–0.035 Å, and consequently, the barriers were generally about 10% too small.

DFT calculations for Ge_6H_{12} employing the B3LYP functional and all-electron basis set 6-31+G* predict three conformers, chair, twist and boat, with relative energies of 0.0, 10.2 and 12.1 kJ mol^{-1}, respectively. DFT and MP2 calculations with SDD predict only two conformers, chair and twist, with relative energies of 4.4 and 4.2 kJ mol^{-1}, respectively. Finally, B3LYP/aug-cc-pVTZ calculations also led to two conformers, again chair and twist, with respective energies of 0.0 and 5.7 kJ mol^{-1}. The boat turned out to be a transition structure for the twist-to-twist interconversion with a relative energy of 6.4 kJ mol^{-1}.

We know from calculations of the ring inversion barriers of cyclohexasilanes Si_6H_{12} and Si_6Me_{12} that sofa and half-chair transition structures have almost the same energy.[13]

To obtain a representative value for the barrier of Ge_6H_{12}, we calculated the energy of the sofa transition structure to be 10.0 kJ mol^{-1}, and we anticipated that it would not differ significantly from that of the half-chair. The energy profile for ring inversion at the B3LYP/aug-cc-pVTZ level is depicted in Figure 1. It is of some note that B3LYP/6-31+G* calculations gave an energy of 40 kJ mol^{-1} for the half-chair transition structure, thus predicting a ring inversion barrier that is considerably larger than that found for Si_6H_{12} (15 kJ mol^{-1}) and Si_6Me_{12} (16 kJ mol^{-1}). This large value can be explained with the shorter Ge–Ge bonds and the much larger Ge–Ge–Ge–Ge dihedral angles (up to 70°) obtained by using nonrelativistic basis sets on the Ge atoms. Even when the small SDD quasi-relativistic basis set for Ge is used, this barrier is more appropriately estimated [7.4/7.6 kJ mol^{-1} (DFT/MP2)]. However, the large-core effective core pseudopotential (ECP) in the SDD basis sets is known to result in bond lengths that are too long. The aug-cc-pVTZ basis set with the small-core ECP gives more accurate bond lengths. Nevertheless, it is obvious that relativistic effects in the Ge atom have to be taken into consideration, and to this purpose the ECP approximation seems to be satisfactory.

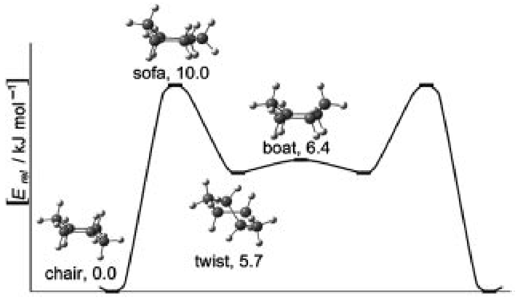


Figure 1. Calculated minima and transition structures of Ge_6H_{12} at the B3LYP/aug-cc-pVTZ level of theory. All relative energies are ZPVE-corrected.

Dodecamethylcyclohexagermane, Ge_6Me_{12}

X-ray Structure Determination

A first crystal structure of dodecamethylcyclohexagermane obtained at 298 K with R = 0.131 was published in 1975; an average Ge–Ge bond length of 2.37 Å was reported.[19] In the present work, an improved structure (R = 0.101) determined at 100(2) K is presented and is depicted in Figure 2.[20] The average Ge–Ge bond length is found to be 2.42 Å, which is 5 pm longer than that previously reported, whereas the Ge–Ge–Ge angles are the same. Other structural parameters do not differ significantly from the parameters determined for Si_6Me_{12}.[21] The average Ge–Ge–Ge–Ge dihedral angle is ±52.97°, the same as that in the silicon ring (53.4°). Further, the average Ge–Ge–Ge angle of 112.0° is only 0.1° smaller than the average Si–Si–Si angle of 111.9°.

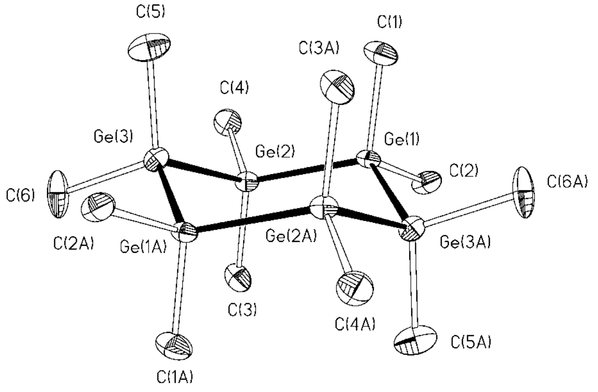


Figure 2. ORTEP plot (30% probability) of the molecular structure of Ge_6Me_{12}, including numbering of the atoms. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and bond angles [°] (with standard deviations): Ge(1)–Ge(2) 2.4094(19), Ge(1)–Ge(3A) 2.4242(17), Ge(2)–Ge(3) 2.4300(16), Ge(1)–C(1) 1.971(11), Ge(1)–C(2) 1.979(11), Ge(2)–C(3) 1.994(11), Ge(2)–C(4) 1.969(11), Ge(3)–C(5) 1.987(11), Ge(3)–C(6) 1.982(13), Ge(1)–Ge(2)–Ge(3) 111.13(6), Ge(2)–Ge(3)–Ge(1A) 111.56(6), Ge(2)–Ge(1)–Ge(3A) 113.32(6), C(1)–Ge(1)–Ge(2) 109.0(4), C(1)–Ge(1)–Ge(3A) 106.7(4), C(1)–Ge(1)–C(2) 108.4(5), C(1)–Ge(1)–Ge(2)–Ge(3) –65.2(4), C(2)–Ge(1)–Ge(2)–Ge(3) 177.0(3), Ge(3A)–Ge(1)–Ge(2)–Ge(3) 53.45(8), Ge(1)–Ge(2)–Ge(3)–Ge(1A) –52.49(8).

For comparison, the Ge–Ge bond length in Ge_6Ph_{12} was determined to be 2.466 Å, and the dihedral angles to be 49.16° and –48.92° (R = 7.1%, r.t.).[22] In Ge_2Ph_6, this bond length is 2.437 Å (R = 3.3%, r.t.).[23] A shorter Ge–Ge bond of 2.419 Å was found in $Ph_3GeGeMe_3$ (R = 3.6%, r.t.).[24] The longest Ge–Ge bond of 2.713 Å was detected in $Ge_2(t\mathrm{Bu})_6$ (R = 2.8%, r.t.).[25]

Ab Initio Calculations

As observed for Ge_6H_{12}, the optimized geometry parameters for Ge_6Me_{12} also strongly depend on the basis sets employed. We will therefore present results for B3LYP/aug-cc-pVTZ calculations only. Additional results are summarized in the Supporting Information (Figure S1, Tables S1–S4). Three minima closely related to those of Si_6Me_{12},[13] chair, twist and boat, with ZPVE-corrected relative energies of 0.0, 5.2 and 9.2 kJ mol^{-1}, respectively, were found. Table 1 summarizes the most important geometry parameters for the conformers of both Ge_6Me_{12} and Ge_6H_{12}, including the wavenumbers and Raman intensities of the symmetric ring-breathing modes. As can be seen from Table 1, the calculations overestimate Ge–Ge bond lengths by about 5 pm relative to those obtained from the X-ray results, but agree reasonably well with experimental bond angles and dihedral angles.

In order to assign the vibrational spectra, calculations of the Raman and infrared intensities were also performed. In the range expected for Ge–Ge stretching vibrations between 200 and 300 cm^{-1}, where rotational isomerism is expected to show up most clearly, the symmetric Ge–Ge stretch possessing the smallest wavenumber (henceforth denoted as the ring-breathing mode) has by far the largest Raman intensity for all the conformers. Although the absolute wavenumbers

Table 1. Calculated relative energies, wavenumbers and Raman intensities of the ring-breathing modes, and selected geometry parameters for the conformers of Ge_6H_{12} and Ge_6Me_{12} obtained at the B3LYP/aug-cc-pVTZ level.

	Ge_6H_{12}		Ge_6Me_{12}		
	Chair	Twist	Chair	Twist	Boat
E_{rel} [kJ mol^{-1}]	0.0	5.7	0.0	5.2	9.2
ν_s(Ge–Ge) [cm^{-1}]	198.4	197.8	214.7	209.4	211.5
Raman intensity [Å^4 amu^{-1}]	51	52	18	16	14
av. r(Ge–Ge) [Å]	2.450	2.453	2.473	2.475	2.477
av. ∠(Ge–Ge–Ge) [°]	111.2	111.6	112.3	113.1	113.9
av. ∠(Ge–Ge–Ge–Ge) [°]	±55.5	±63.3/±30.5	±52.2	±57.5/±27.8	±0.1/±46.7

of the modes shift depend on the basis set and method used, the wavenumber differences between the various conformers remain almost constant. Table 1 includes the most important predictions, and further details of the calculations can be retrieved from the Supporting Information. As we will show shortly, the chair conformer can be distinguished experimentally from the twist and boat conformers by a close examination of the ring-breathing mode. It is noteworthy that the calculations also show that the CH_3-group vibrations ν_s, ν_{as}, δ_s, δ_{as}, $\rho(CH_3)$ and ν_s, ν_{as}, δ, γ, τ, $\rho(GeC_2)$ cannot be used for this purpose.

To estimate the ring inversion barrier of Ge_6Me_{12}, the energy of the half-chair structure was calculated at the B3LYP/SDD level to be 10.1 kJ mol^{-1}. For cyclohexasilanes it is known that the calculated barriers are almost the same for both Si_6H_{12} (ca. 15 kJ mol^{-1}) and Si_6Me_{12} (ca. 16 kJ mol^{-1}).[13,14,26] Therefore, a calculation at the aug-cc-pVTZ level was not performed for Ge_6Me_{12} in the interest of conserving time (the barrier is 10.0 kJ mol^{-1} for Ge_6H_{12} at the B3LYP/aug-cc-pVTZ level). The predicted barrier for the twist-to-chair interconversion of about 10 kJ mol^{-1} for Ge_6Me_{12} is realistic when compared with C_6Me_{12} (70 kJ mol^{-1}) and Si_6Me_{12}. This value is considerably larger than RT (2.5 kJ mol^{-1} at 300 K) and supports the expectation that the chair and twist conformers will give separate Raman spectra.

Solid-State Raman Spectra

For Si_6Me_{12}, a phase transition in the solid state from a crystalline phase containing only the chair conformer into a plastic phase with chair and twist conformers has been reported. The transition occurs between 70 and 80 °C.[7] A similar transition was also detected for Ge_6Me_{12} between 50 and 60 °C. Figure 3 shows the ring-breathing mode of crystalline Ge_6Me_{12} for different temperatures. At 60 °C, a shoulder suddenly appears at lower wavenumbers, certainly originating from a second conformer, which can be either twist or boat in nature. However, a detailed investigation of its nature was not performed in this work.

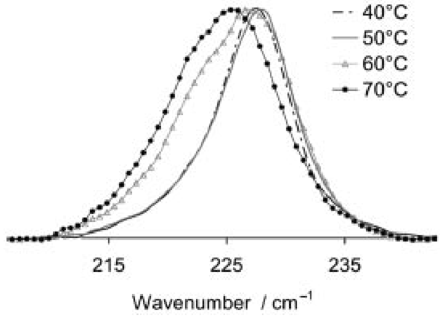


Figure 3. Shape of the ring-breathing mode of crystalline Ge_6Me_{12} for different temperatures.

Solution Raman Spectra

With a band shape closely resembling that in the solid state, a second band on the low-wavenumber side of the ring-breathing mode of the chair conformer is observed in thf solution. On the basis of quantum chemical calculations, it is identified as the signal for the twist or the averaged twist/boat conformer. At –80 °C, the band is barely observed as a small shoulder separated by about 5 cm^{-1}, and it gains intensity with increasing temperature. At room temperature, it is more intense than the band of the chair conformer. The band shapes for two temperatures as well as the relevant deconvolutions are shown in Figure 4.

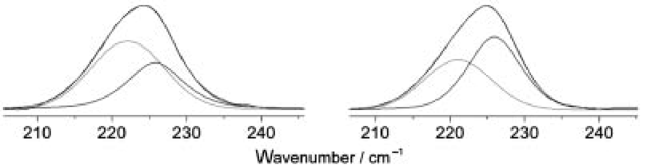


Figure 4. Appearance and deconvolution of the ring-breathing mode of Ge_6Me_{12} in the Raman spectrum of a thf solution for 0 °C (left) and –40 °C (right).

According to Boltzmann statistics, the population of two conformational states varies with temperature. To analyze temperature-dependent Raman spectra of a compound possessing two conformational minima, I and II, the van't Hoff relation is used. The simple formula, $\ln(A_I/A_{II}) = -\Delta H/RT$ + constant, can be derived by assuming that ΔH and the ratio of Raman scattering coefficients, a_I and a_{II}, are temperature independent (a_I, a_{II} and ΔS are incorporated into the constant term). A_I and A_{II} are the intensities of the lines originating from conformers I and II (either band areas or band heights resulting from deconvolution may be used). The enthalpy difference, ΔH, can then be obtained from the slope of a plot of $\ln(A_I/A_{II})$ against T^{-1}.

The calculated wavenumber difference between the chair and the averaged twist conformations is only ca. 5 cm^{-1}. To get the line intensities A, a band deconvolution was performed. First, peak positions were obtained by calculating the second derivative, which clearly indicates the presence of two overlapping peaks. Deconvolution was then achieved by free peak fitting using Lorentzian band shapes, and an enthalpy difference of 2.4 kJ mol^{-1} was obtained between the chair and the averaged twist/boat conformer. A graphical reproduction of the resulting van't Hoff plot is shown in Figure 5. The statistical errors of the experimental results are not given here because the standard deviation obtained from van't Hoff analysis certainly underestimates the actual error of the method, which originates, amongst other things, from the assumptions made in the van't Hoff analysis[27] and from ambiguities in the band deconvolution. The overall accuracy of the experimental method is estimated to be no better than ± 20 %.

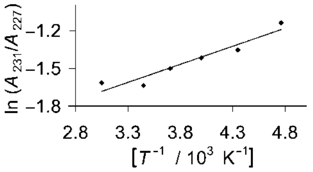


Figure 5. van't Hoff plot for the 231/227 cm^{-1} band pair of Ge_6Me_{12} in thf solution.

As the quantum chemical calculations refer to the isolated molecule in the gas phase, the calculated enthalpy values of 4–5 kJ mol^{-1}, which depend on the method and basis set used, compare fairly well with the experimental ΔH value of 2.4 kJ mol^{-1}.

Conclusions

Third and higher row E_6H_{12} and E_6Me_{12} ring systems behave somewhat differently from cyclohexanes because the ring inversion barriers and the energy differences between stable conformers are considerably larger in the cyclohexanes. By using quantum chemical calculations, two minima, belonging to chair and twist conformations, were located on the PES for Ge_6H_{12}, and three minima, belonging to chair, twist, and boat conformations, were found for Ge_6Me_{12}. Relativistic effects have to be taken into account for the Ge atoms.

As in the case for Si_6Me_{12}, an averaged twist/boat conformer was observed in the Raman spectrum of Ge_6Me_{12} in solution in addition to the most stable chair conformer, even at low temperatures. In the spectrum of the solid, a phase transition was observed between 50 and 60 °C. It should be noted though that Ge_6Me_{12} represents a borderline case for the successful application of temperature-dependent Raman spectroscopy in terms of conformational analyses. Substituted digermanes with fairly small substituents, such as H, Me or Cl, which possess smaller rotational barriers between stable conformers, cannot be detected separately in a Raman spectrum. As we will report elsewhere, they must be investigated with the faster gas-phase electron diffraction technique.

Experimental Section

Synthesis: Ge_6Me_{12} was synthesized as described by Carberry et al.[17] by a coupling reaction of dimethyldichlorogermane with excess Li granulate in thf and was purified by recrystallization from acetone. The purity of the compound was checked with ^1H NMR spectroscopy, GC-MS and Raman spectroscopy. Data were compared with literature data.[17]

Quantum Chemical Calculations: Geometry optimizations were initiated by using the previously published structures of Si_6H_{12} and Si_6Me_{12} as a starting point.[13] All geometry optimizations and minimum energy calculations, as well as the calculations of vibrational frequencies and intensities, were performed with the Gaussian03 program package at the DFT and MP2 levels of theory.[28] MP2 and B3LYP[29] density functional with the 6-31+G*[30] basis sets were employed to scan the potential energy surface, as well as the combination of D95V[31] basis sets for the C and H atoms and the quasi-relativistic Stuttgart Dresden large-core pseudopotentials (ECP28MWB[32]) for the Ge atoms. This combination is incorporated in Gaussian03 and is denoted as SDD. Geometry optimizations for located stationary points of Ge_6H_{12} and Ge_6Me_{12} were performed by using B3LYP with the aug-cc-pVTZ[33,34] basis set for the H atoms and aug-cc-pVTZ-PP,[35] a small-core relativistic pseudopotential correlation consistent basis set, for the Ge atoms. However, in the interest of reduced computational costs, the 6-31+G* basis set was used for the C and H atoms in Ge_6Me_{12}. In order to simplify the discussion, both of these methods are referred to as B3LYP/aug-cc-pVTZ.. The minima possess all real frequencies, while the transition structures have one single imaginary frequency. No symmetry restraints were employed to ensure a full investigation of the PES.

X-ray Structure Determination: For X-ray structure analyses, the crystals were mounted onto the tip of glass fibers, and data collection was performed with a BRUKER-AXS SMART APEX CCD diffractometer using graphite-monochromated Mo-K_α radiation (0.71073 Å). The data were reduced to F^2_o and corrected for absorption effects with SAINT[36] and SADABS,[37] respectively. The structures were solved by direct methods and refined by the full-matrix least-squares method (SHELXL97).[38] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in calculated positions to correspond to standard bond lengths and angles. CCDC-642005 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Raman Spectroscopy: Raman spectra were recorded with a Jobin Yvon T64000 spectrometer equipped with a triple monochromator and a CCD camera. The samples were transferred into 1-mm glass capillary tubes and irradiated with the green 532-nm line of a frequency-doubled Nd-YAG laser (Coherent DPSS model 532–20, 20 mW). Spectra were recorded for both solid samples and solutions in thf. For high-temperature measurements, a metal block of copper with filament heating, on which the capillary was mounted, and a thermocouple for temperature monitoring were used. A continuous-flow cryostat (Oxford Instruments OptistatCF™ using liquid nitrogen for cooling) was employed for the low-temperature measurements.

Supporting Information (see footnote on the first page of this article): Due to space limitations, a compilation of geometric parameters for the chair, twist and boat conformers of Ge_6H_{12} and Ge_6Me_{12} obtained with various basis sets at the MP2 and B3LYP levels is presented.

Acknowledgments

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