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Conformational energies of silacyclohexanes $C_5H_{10}SiHMe$, $C_5H_{10}SiH(CF_3)$ and $C_5H_{10}SiCl(SiCl_3)$ from variable temperature Raman spectra

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From variable temperature vibrational Raman spectra, the axial/equatorial enthalpy differences for the substituted silacyclohexanes $C_5H_{10}SiHMe$, $C_5H_{10}SiH(CF_3)$ and $C_5H_{10}SiCl(SiCl_3)$ were determined. The pure liquids and solutions in various solvents were investigated. Preferred conformations are equatorial for methylsilacyclohexane and axial for trifluoromethylsilacyclohexane, consistent with earlier results from nuclear magnetic resonance experiments and *ab initio* calculations. For $C_5H_{10}SiCl(SiCl_3)$ an enthalpy difference close to zero was found, which is supported by high-level which is supported by high-level quantum chemical calculations at the second-order Møller-Plesset (MP2) and coupled cluster with single, double, and perturbative triple excitations (CCSD(T)) levels, which employed various basis sets. A novel synthesis for $C_5H_{10}SiCl(SiCl_3)$ was developed using $ClMg(CH_2)_5MgCl$ instead of $BrMg(CH_2)_5MgBr$ as a starting material. The procedure avoids the formation of partially brominated products, facilitating the purification of the compound. ^1H, ^{13}C and ^{29}Si nuclear magnetic resonance data are reported. Copyright © 2012 John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this article.

Keywords: silacyclohexanes; conformations; Raman spectroscopy; quantum chemical calculations; synthesis

Introduction

The influence of steric and stereoelectronic effects on the axial/equatorial equilibrium of monosubstituted cyclohexanes $C_6H_{11}X$ has been the topic of numerous studies. Even today, it is an active field of research tilled by employing combinations of sophisticated experimental and theoretical methods. The conformational preference generally is for the equatorial conformer, with energy differences $\Delta E = E_{ax} - E_{eq}$ depending not only on the size of the substituent X, but also on the electronegativity. Naturally, these studies have also been extended to six-membered heterocycles composed of nitrogen, oxygen, sulfur and carbon, and a comprehensive review has been published recently by Kleinpeter.[1] The understanding of the conformational properties of these rings not only is important for basic science, but also plays a crucial role in biological and medicinal chemistry.

All these investigations have been facilitated by the observation that twist conformations need not be taken into consideration, because the chair/twist energy differences are so large that the twist conformational states are populated only to a negligible extent at moderate temperatures. For instance, the energy of twist cylohexane is higher by about 23 kJmol^{-1}, which translates to about one molecule in the twist conformation for every 10 000 molecules in the chair conformation at 25 °C.[2]

If the carbon atoms in C_6H_{12} are replaced successively by silicon, the twist-chair energy difference decreases with increasing number of Si-atoms. For instance, 1,3,5-trisilacyclohexane and cyclohexasilane have relative twist energies ($E_{twist} - E_{chair}$) of +9.2 and +7.9 kJmol^{-1}, respectively.[3] The presence of the twist form thus has to be taken into account, depending on the temperature for which the equilibrium is studied. In the series, the largest drop in relative energy occurs for silacyclohexane $C_5H_{10}SiH_2$ with the introduction of the first Si-atom. With about 16 kJmol^{-1}, the relative twist energy still is large enough so that the presence of the twist form safely can be disregarded for temperatures below ≈200–250 °C.[4] In this respect, C_6H_{12} and $C_5H_{10}SiH_2$ share a common trait, which greatly facilitates conformational analysis.

However, an important difference between cyclohexane and silacyclohexane is that the general preference of a substituent X for the equatorial position is not present in 1-substituted silacyclohexanes $C_5H_{10}SiHX$. For instance, trifluoromethylcyclohexane prefers the equatorial conformation, which is not found for 1-trifluoromethylsilacyclohexane.[5,6] Recent quantum chemical calculations predict that also in 1-trifluorosilylsilacyclohexane the axial conformer is stabilized over the equatorial by 1.88 kJ mol^{-1} (value converted from kcal mol^{-1}).[7] Moreover, a preference for axial is also predicted for 1-chloro and 1-fluorosilacyclohexane, but not for 1-trichloromethylsilacyclohexane.[8] For these molecules, the predicted energy differences have been verified experimentally just for 1-fluorosilacyclohexane, employing microwave spectroscopy,[9] low temperature nuclear magnetic

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resonance (NMR) and low temperature Raman spectroscopy and gas electron diffraction.[10]

In a joint research program, we therefore have set out to prepare the silacyclohexanes $C_5H_{10}SiH(CCl_3)$, $C_5H_{10}SiH(SiCl_3)$ and $C_5H_{10}SiH(SiF_3)$ and to investigate their conformational properties using NMR and Raman spectroscopy. In the present publication, we report on the synthesis and purification of $C_5H_{10}SiCl(SiCl_3)$, which will serve as a precursor for $C_5H_{10}SiH(SiCl_3)$ and $C_5H_{10}SiH(SiF_3)$, and its axial/equatorial equilibrium using variable temperature Raman spectroscopy and quantum chemical calculations. We also include Raman investigations for $C_5H_{10}SiH(CH_3)$ and $C_5H_{10}SiH(CF_3)$ to complement earlier experimental results.

Experimental part

Synthesis of $C_5H_{10}SiCl(SiCl_3)$: The synthesis of the compound was first described by one of the authors (IA), using the reaction between the Grignard reagent $BrMgC_5H_{10}MgBr$ and Si_2Cl_6.[11] Because of halogen exchange, a mixture of partially brominated silacyclohexanes formed, which turned out to be impossible to separate. We therefore used 1,5-dichloropentane as the starting material for the Grignard reagent, which resulted in a clean formation of $C_5H_{10}SiCl(SiCl_3)$. All manipulations employed in the synthesis were carried out under an atmosphere of dry, oxygen-free nitrogen and all solvents were dried prior to use and distilled under an N_2 atmosphere.

A suspension of $ClMg(CH_2)_5MgCl$ (19.4 g, 102.3 mmol) in 100 mL of diethylether was slowly added to $Cl_3SiSiCl_3$ (25.0 g, 93.0 mmol) dissolved in about 100 mL of diethylether at a temperature of 0 °C. After stirring overnight, about 500 mL of toluene was added and diethylether was removed by distillation. The reaction mixture was then filtered and the salts were washed twice with toluene and then discarded. After removal of the solvent, the yellowish oily residue was subjected to distillation under reduced pressure (110 °C, 5 Torr). About 15 g of $C_5H_{10}SiCl(SiCl_3)$ (55.9 mmol, 60%) was obtained as a colourless, oily liquid.

^{1}H-NMR (pure liquid, 299.953 MHz): $\delta = 0.94$ ppm (m, 4H), $\delta = 1.28$ ppm (m, 2H), $\delta = 1.60$ ppm (m, 4H).

^{29}Si-NMR (pure liquid, 59.592 MHz): $\delta = 6.4$ ppm (s), $\delta = 10.4$ ppm (m).

$^{13}C\{^1H\}$-NMR (pure liquid, 75.430 MHz): $\delta = 14.7$ ppm, $\delta = 23.3$ ppm, $\delta = 28.6$ ppm.

For recording the NMR spectra, a D_2O capillary was used as an external lock.

$C_5H_{10}SiHMe$, $C_5H_{10}SiDMe$ and $C_5H_{10}SiH(CF_3)$: All three silacyclohexanes were prepared closely following procedures described in the literature. Therefore, no further details are given here.[12,6]

Raman spectroscopy: Raman spectra were recorded with a Jobin Yvon T64000 spectrometer equipped with a triple monochromator and a charge-coupled device camera. Spectra were recorded in the subtractive mode with a resolution of 3 cm^{-1}. The samples were filled into 1 mm capillary glass tubes and irradiated by the green 532 nm line of a frequency doubled Nd-YAG Laser (Coherent, DPSS Model 532-20, 10 mW). Spectra were recorded from pure compounds and from solutions in various solvents such as toluene, *n*-pentane, CH_2Cl_2 or tetrahydrofurane (THF). A continuous flow cryostat, Oxford instruments OptistatCF™, using liquid nitrogen for cooling was employed for the low temperature measurements.

The van't Hoff relation in the form

$$\ln\left(A_{ax}/A_{eq}\right) = -\Delta H/RT + \Delta S/R + \text{constant}$$

was used for extracting enthalpy differences from the temperature-dependent Raman spectra. Here, A_{ax} and A_{eq} denote intensities of bands belonging to the axial or equatorial conformer. Band areas must be used for overlapping peaks, peak heights can be used if the bands are well separated. Provided that the ratio of the Raman scattering coefficients α_{ax} and α_{eq}, which is included in the constant, and ΔH and ΔS are independent of temperature, a linear relation is obtained by plotting the logarithm of the intensity ratio against the inverse temperature.

Quantum chemical calculations

Harmonic frequency calculations were performed on the title compounds using the Becke, three-parameter, Lee–Yang–Parr (B3LYP) and Barone's modified Perdew Wang 1991 exchange functional and Perdew Wang 1991 correlation functional (MPW1PW91) with 6-31+G* basis sets to aid the interpretation of the Raman spectra. The program Gaussian 03 was used.[13]

Single-point second-order Møller–Plesset (MP2) and CCSD(T) frozen-core calculations using various basis sets were performed on MP2/cc-pVTZ geometries of the axial and equatorial conformers of both $C_5H_{10}SiH(SiCl_3)$ and $C_5H_{10}SiCl(SiCl_3)$. These calculations were performed using Molpro 2006.1.[14]

The axial/equatorial electronic energy difference at the CCSD(T)/CBS (complete basis set limit) was then derived by the following relation.

$$\Delta E^{\text{CCSD(T)/CBS}} \approx \Delta E^{\text{MP2/CBS}} + \left(\Delta E^{\text{CCSD(T)/small basis}} - \Delta E^{\text{MP2/small basis}}\right)$$

The MP2 calculations were performed with the correlation consistent basis sets[15,16] up to the cc-pV5Z level and were extrapolated to the basis set limit by separate extrapolation of Hartree-Fock energies (T,Q,5) and MP2 correlation energies (T,Q,5) by the extrapolation scheme of Helgaker *et al.*[17] The ($\Delta E^{\text{CCSD(T)/small basis}} - \Delta E^{\text{MP2/small basis}}$) term was calculated at the CCSD(T)/cc-pVTZ and MP2/cc-pVTZ level. Thermal corrections to enthalpies were calculated from B97-1/pc-2 harmonic vibrational frequencies. This CCSD(T)/CBS protocol has been used in previous studies on silacyclohexanes.[18,12]

Results

General

A discussion of the vibrational spectra of 1-silacyclohexanes $C_5H_{10}SiHX$ in terms of stretching and bending group vibrations using the tools of symmetry and normal coordinate analysis quickly arrives at the result that not all wavenumber regions of the spectrum are equally appropriate for the investigation of the mixture of conformers. For instance, each conformer (axial or equatorial) possesses ten CH stretching vibrations (five asymmetric vibrations, $\nu_{as}CH_2$ and five symmetric ones, ν_sCH_2), which all fall into the narrow wavenumber range 2900–3000 cm^{-1}. Many of these bands therefore will overlap, making a conformational analysis virtually impossible. The same problem arises in the region of the CH_2 deformations. Because each CH_2 group has four relevant degrees of freedom (δCH_2, ρCH_2, τCH_2, γCH_2), a total of 20 bands for a single conformer is expected in the typical range 800–1500 cm^{-1}. Because of their group character, many will overlap.

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It turns out that vibrations involving the silicon atom, for instance νSiC, νSiX or δCSiX are most suitable for the task. Moreover, Raman spectroscopy has a considerable advantage over infrared spectroscopy if heavy atoms are involved. As the scattering coefficients increase with the number of electrons in the atoms participating in the vibrations process, SiC and SiX vibrations belong to the most intense bands in the spectrum.

$C_5H_{10}SiHMe$

A combined electron diffraction, low temperature NMR and quantum chemical investigation of the conformational properties of 1-methyl-1-silacyclohexane identified the equatorial conformer as the low-energy isomer, favoured by 0.96–2.5 kJmol^{-1} (values converted from kcal mol^{-1}) depending on the method. These findings contradict prior results from NMR experiments and molecular mechanics MM2 calculations, which had identified axial as being more stable. To gain further insight into the conformer equilibrium, we performed a thorough Raman spectroscopic investigation employing the neat liquid and solutions in various solvents.

We first prepared $C_5H_{10}SiHMe$ and recorded its Raman spectrum, which is displayed in Fig. S1. Much to our disappointment, the spectrum showed no doubling of bands, which could be due to the axial/equatorial equilibrium. The symmetric SiC-stretch $\nu_s SiC_2$, which gives the intense Raman signal at 600 cm^{-1} is just a single line without any asymmetry, which could have been interpreted as originating from two overlapping bands. Quantum chemical calculations (B3LYP/6-31+G*) predict a wavenumber difference of about 8 cm^{-1}, well within the resolving power of the spectrometer (3 cm^{-1}).

We therefore prepared the Si-deuterated isotopomer $C_5H_{10}SiDMe$ because calculations suggested in this case a much larger difference of about 30 cm^{-1}. The Raman spectrum presented in Fig. 1 indeed shows separate emission lines for the axial (calc.: 594 cm^{-1}, found 612 cm^{-1}) and equatorial conformer (calc.: 622 cm^{-1}, found: 635 cm^{-1}). Moreover, their intensities vary with temperature as shown in Fig. S2, with the signal of the axial conformer losing intensity upon lowering the temperature. Thus, the equatorial conformer is energetically favoured. A quantitative evaluation using van't Hoff's equation (see Experimental Part) gives a ΔH-value of 0.68 kJ mol^{-1} if peak heights are used, and 0.56 kJ mol^{-1} for peak areas. Just the van't Hoff plot for peak heights ($R^2 = 0.9943$) is presented in Fig. 2 for illustrative purposes. Using peak areas, the fit is equally good with $R^2 = 0.9954$.

Variable temperature measurements were also carried out for solutions in *n*-pentane, methylene chloride and tetrahydrofurane (THF). They all give very consistent results, which are summarized in Table S1.

$C_5H_{10}SiH(CF_3)$

In the room temperature Raman spectrum of neat 1-(trifluoromethyl)-1-silacyclohexane presented in Fig. 3, the symmetric SiC_2-stretch clearly appears as a doublet of bands located at 641 cm^{-1} (axial conformer) and 665 cm^{-1} (equatorial conformer). Calculated values (B3LYP/6-31+G*) are 626 cm^{-1} (axial) and 649 cm^{-1} (equatorial). The exocyclic Si–CF_3 stretching vibration also appears as a doublet (390/400 cm^{-1}).

Upon lowering the temperature, the band at 665 cm^{-1} eventually disappears almost completely at 130 K as shown in Fig. S3, proving that axial is the low energy conformer. The derived van't Hoff plot is presented in Fig. 4, displaying excellent linearity over the whole temperature range 293–130 K.

The band pair inspected in a solution of $C_5H_{10}SiH(CF_3)$ in methylene chloride shows essentially the same temperature dependence, giving ΔH-values of −2.6 kJmol^{-1} using peak areas

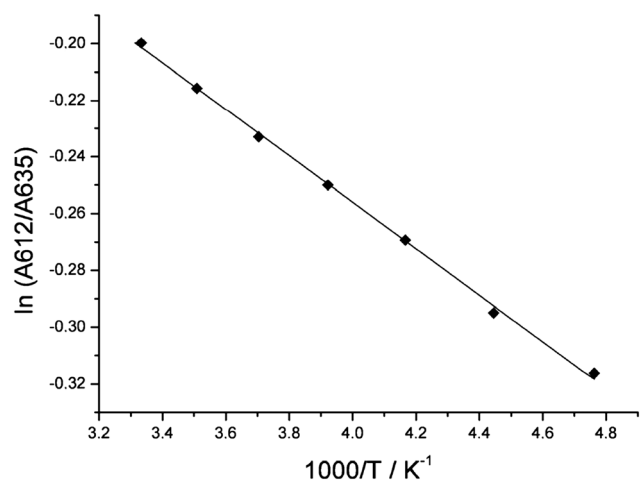

Figure 2. The van't Hoff plot for the band pair 612/635 cm^{-1} of $C_5H_{10}SiDMe$ using peak heights.

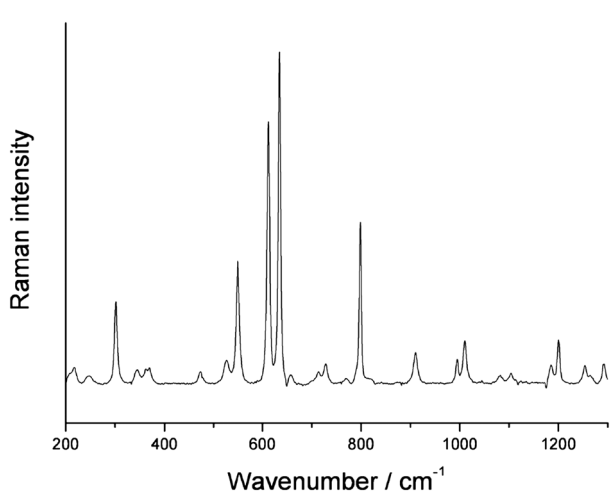

Figure 1. Room temperature Raman spectrum of pure $C_5H_{10}SiDMe$ in the wavenumber range 200–1200 cm^{-1}.

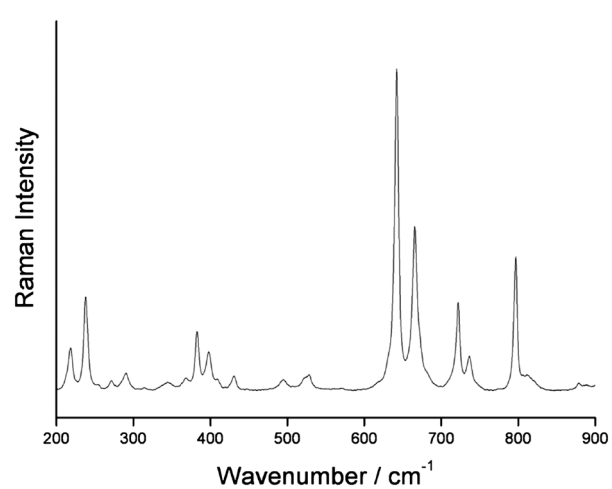

Figure 3. Room temperature Raman spectrum of neat, liquid $C_5H_{10}SiH(CF_3)$ in the wavenumber range 200–900 cm^{-1}.

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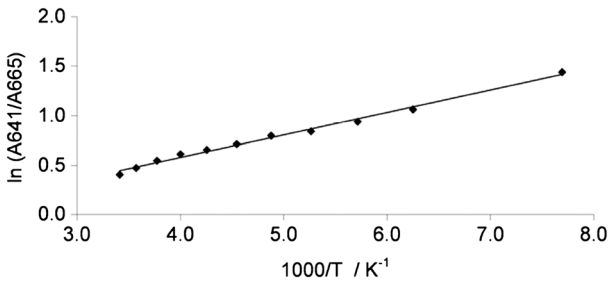

Figure 4. Van't Hoff plot for the band pair 641/665 cm^{-1} for pure $C_5H_{10}SiH(CF_3)$ from which a ΔH-value ($\Delta H = H_{ax} - H_{eq}$) of -1.9 kJ mol^{-1} is derived. Peak areas have been used in this case. Peak heights give a somewhat l value of -2.4 kJ mol^{-1}.

and -2.5 kJmol^{-1} for peak heights. Because of space limitations, no Figures referring to the solution spectra are presented here.

The Raman spectra thus confirm results from a combined *ab initio*, electron diffraction and NMR investigation concluding that the axial conformer is more stable than the equatorial. Moreover, solvent polarity has no noticeable effect on the conformational energies, which is also found for 1-methyl-1-silacyclohexane (described in this paper), 1-fluoro-1-silacyclohexane[10] and 1-silyl-1-silacyclohexane.[12]

$C_5H_{10}SiH(SiCl_3)$ and $C_5H_{10}SiCl(SiCl_3)$

The CCSD(T)/CBS energy differences between axial and equatorial conformers were derived by a protocol of single-point energy calculations on MP2/cc-pVTZ optimized geometries of both $C_5H_{10}SiH(SiCl_3)$ and $C_5H_{10}SiCl(SiCl_3)$ and are shown in Table S2.

The CCSD(T) results for $C_5H_{10}SiH(SiCl_3)$ predict the conformer with the $SiCl_3$ group in an axial position to be more stable, while for $C_5H_{10}SiCl(SiCl_3)$, the conformer with $SiCl_3$ equatorial, is the lower energy conformer.

From the MPW1PW91/6-31+G* wavenumber calculations it can be inferred that the vibrations in the range 300–700 cm^{-1}, which comprise motions of the heavy atoms, are best suited for identifying the axial and equatorial conformers of $C_5H_{10}SiCl(SiCl_3)$. For a better description of these backbone modes, a normal coordinate analysis was carried out for each conformer using the MPW1PW91 quantum chemical equilibrium geometries and Hessian matrices. Symmetry coordinates as linear combinations of internal coordinates were chosen as described previously for silylcyclohexane.[19] The Hessian matrices then were transformed into a force field defined by the symmetry coordinates, and potential energy distributions (PEDs) were calculated, which were used to assign observed frequencies to vibrational modes. The program ASYM40 was used for these calculations.[20]

According to the PEDs, strong mixing of the vibrational modes occurs for most backbone vibrations of axial and of equatorial $C_5H_{10}SiCl(SiCl_3)$. Generally, up to five symmetry coordinates can contribute to a single mode, with contributions in the range 10–50%. Therefore, the description of these vibrations is rather arbitrary and should be considered as just a convenient classification system.

Table S3 summarizes the calculated wavenumbers for axial and equatorial $C_5H_{10}SiCl(SiCl_3)$ in the range 290–700 cm^{-1}, and the observed wavenumbers for a mixture axial/equatorial (neat liquid) and for the equatorial conformer, which is present in the crystalline solid. Tabulated PEDs for the axial isomer comprise just the symmetry coordinate with the largest contribution. PEDs for equatorial $C_5H_{10}SiCl(SiCl_3)$ are not much different and are not presented here because of lack of space.

The calculations predict that the SiSi stretching vibrations for the axial and equatorial conformer differ by about 40 cm^{-1} and possess large Raman intensities. Calculated values are 365 cm^{-1} (axial) and 407 cm^{-1} (equatorial). Figure 5 presents the room temperature Raman spectrum of $C_5H_{10}SiCl(SiCl_3)$ (neat liquid), which indeed displays two intense emissions located at 373 and 413 cm^{-1} originating from the axial and equatorial conformer. Their relative intensities vary with temperature, a sure sign for the presence of a conformational equilibrium.

For room temperature, Fig. S4 presents the appearance of this band pair obtained for a toluene solution. Upon cooling to 210 K, the compound crystallizes in the form of the equatorial conformer, because the 373 cm^{-1} line is now absent almost completely as shown in Fig. S5. The small residual line still observable represents a ring deformation, predicted by the calculations as a low Raman intensity band located at 373 cm^{-1}. Noteworthy, the band at 476 cm^{-1}, representing a ring deformation of the axial conformer (Table S3) is also missing in the spectrum of the crystalline solid.

Figure 6 displays the van't Hoff plot for the band pair 373/413 cm^{-1} (toluene solution) using the peak heights. Because the line at 373 cm^{-1} contains a small contribution from the equatorial

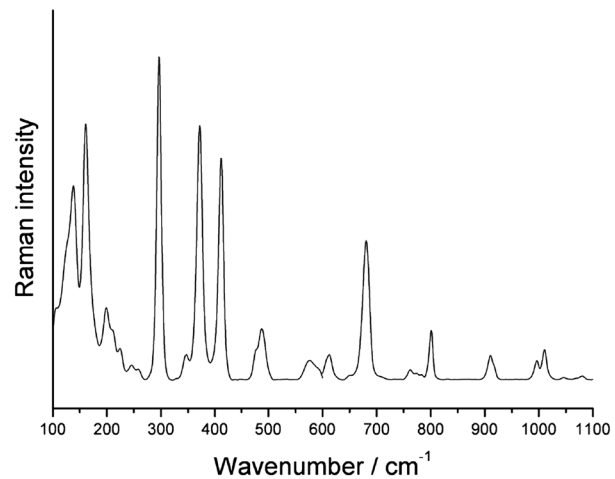

Figure 5. Room temperature Raman spectrum of neat, liquid $C_5H_{10}SiCl(SiCl_3)$ in the wavenumber range 100–1100 cm^{-1}.

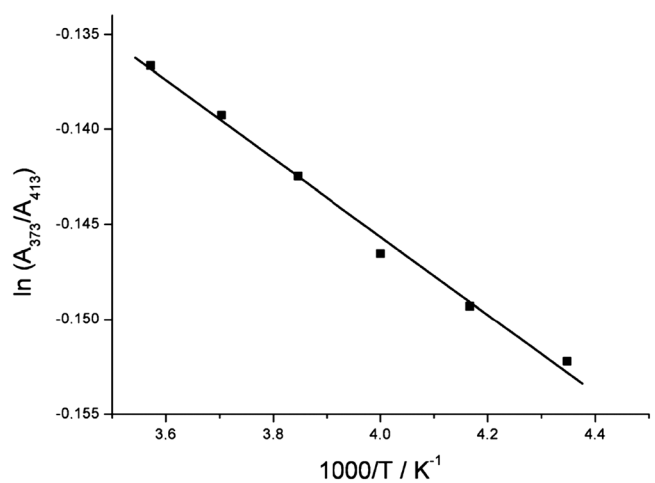

Figure 6. Van't Hoff plot for the band pair 373/413 cm^{-1} of $C_5H_{10}SiCl(SiCl_3)$ (band heights, toluene solution) in the temperature range 225–280 K.

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conformer, the peak height used for the band in the van't Hoff plot was reduced by a fraction of the intensity of the line at 413 cm^{-1}. This fraction was obtained from the intensity ratio of the two lines in the spectrum of the crystalline solid. A ΔH-value of +0.17 kJ mol^{-1} is obtained. If band areas are used, a negative value of −0.22 kJ mol^{-1} results. From the pure liquid, ΔH-values of −0.36 and −0.18 kJ mol^{-1} are deduced using band areas and band heights, respectively.

The accuracy attainable for ΔH by employing vibrational spectroscopy is limited by several factors, which have been comprehensively reviewed by Klaboe.[21] For instance, overtones with intensities that often are enhanced by Fermi resonance might overlap fundamental bands, thus reducing the accuracy, which is achievable. Moreover, fundamental bands originating from different conformers can overlap, which is the case here. An honestly estimated value for ΔH thus is -0.15 ± 0.5 kJ mol^{-1}, which certainly is close to zero. High-level CCSD(T)/CBS values predict a ΔH value of +0.58 kJ mol^{-1}, which is in quite good agreement with the experimental results, keeping in mind the uncertainties associated with both experiment and computation (Table S2).

Discussion

The conformational properties of substituted silacyclohexanes are associated with small energy differences between the axial and equatorial conformers. This distinguishes the silacyclohexanes from cyclohexanes and O-containing and N-containing six-membered heterocycles.

This feature makes the silacyclohexanes generally more favourable for high-accuracy determinations of conformational properties. The small energy differences, however, represent a challenge to quantitative agreement between the Raman experiments and theoretical calculations where the latter are associated with quantum chemical method errors, basis set errors, errors from thermal corrections and errors from neglect of environmental effects.

The CCSD(T) method is often referred to as the golden standard of quantum chemistry and should be the most suitable method (and which is feasible) for reliable conformational energy differences of organic and main group compounds. There will, however, always be errors associated with insufficient basis sets in these kinds of calculations. Thermal corrections were obtained from harmonic vibrational frequency density functional theory calculations, but errors should be of a small magnitude because entropic effects are not of concern here.

In our calculations, environmental effects have been neglected, because they are hard to reliably account for. Raman measurements for these compounds have generally indicated solvent effects to be quite small. Energy differences of substituted silacyclohexanes from Raman experiments have now been reported for seven compounds overall. As CCSD(T)/CBS estimates of all these compounds exists, we can now compare Raman determined ΔH values to high-accuracy *ab initio* ΔH values. Table 1 compares ΔH values from CCSD(T)/CBS calculations with ΔH values from Raman experiments. Overall, the difference between theory and experiment is not too bad and a linear regression analysis of the data shows a correlation coefficient of 0.92. Considering the uncertainties associated with both theory and experiment and the very small energy differences involved, we consider this a satisfactory result.

Table 1. Comparison of all available Raman data of silacyclohexanes with coupled cluster calculations. $\Delta H = H^{axial} - H^{equatorial}$ values in kJ mol^{-1}

$C_5H_{10}SiH$-X X=	CCSD(T)/ CBS + therm. corr.*	Raman experiments
Me	0.81[a,b]	0.62[a]
CF_3	−1.70[a,b]	−2.22[a]
F	−0.75[a,b]	−1.05[c]
SiH_3	0.23[d]	−1.09[d]
F/Me[e]	1.06[a,b]	2.09[b]
CF_3/Me[e]	2.02[a,b]	3.05[b]
Cl/$SiCl_3$[f]	0.58[a]	−0.15[a]
MAE[g]	0.75	
ME[g]	−0.16	
Slope[h]	0.60	
Correlation coefficient, r[h]	0.92	

*The thermal correction term is calculated at the B97-1/pc-2 level for all cases.
[a]This work
[b]From Wallevik *et al.*[18]
[c]From Ref. [10]
[d]From Ref. [12]
[e]Equilibrium defined with respect to the Me substituent.
[f]Equilibrium defined with respect to the $SiCl_3$ substituent.
[g]MAE, mean absolute errors; ME, mean errors (exp. value – calc. value).
[h]Slope and correlation coefficient refers to the regression line of CCSD(T) values (*y* axis) *versus* Raman values (*x* axis).

Conclusions

In the present publication we have shown that variable temperature vibrational Raman spectroscopy is a valuable tool for investigating axial/equatorial conformer equilibria of silacyclohexanes $C_5H_{10}SiXY$. The enthalpy differences ΔH obtained for $C_5H_{10}SiHMe$, $C_5H_{10}SiH(CF_3)$ and $C_5H_{10}SiCl(SiCl_3)$ correlate in a very satisfactory manner with results drawn from NMR and electron diffraction experiments, and with results derived from quantum chemical calculations.

Acknowledgements

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Supporting information

Supporting information may be found in the online version of this article.

References

[1] E. Kleinpeter, *Adv. Heterocycl. Chem.* **2004**, *86*, 41.
[2] See for instance: E. L. Eliel, S. H. Wilen, Stereochemistry of Organic Compounds, Wiley, New York, **1994**; K. Mislow, Introduction to Stereochemistry, Benjamin/Cummings, Reading MA, **1965**.
[3] I. Arnason, H. Oberhammer, *J. Mol. Struct.* **2001**, *598*, 245; I. Arnason, G. J. Thorarinsson, E. Matern, *J. Mol. Struct. (THEOCHEM)* **1998**, *454*, 91.

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[4] I. Arnason, G. K. Thorarinsson, E. Matern, *Z. Anorg. Allg. Chem.* **2000**, *626*, 853.
[5] E. W. Della, *J. Am. Chem. Soc.* **1967**, *89*, 5221.
[6] (a) G. V. Girichev, N. I. Giricheva, A. Bodi, P. I. Gudnason, S. Jonsdottir, A. Kvaran, I. Arnason, H. Oberhammer, *Chem. Eur. J.* **2007**, *13*, 1776. (b) G. V. Girichev, N. I. Giricheva, A. Bodi, P. I. Gudnason, S. Jonsdottir, A. Kvaran, I. Arnason, H. Oberhammer, *Chem. Eur. J.* **2009**, *15*, 8929. (b) is a corrigendum to (a).
[7] A. Bodi, R. Bjornsson, I. Arnasson, *J. Mol. Struct.* **2010**, *978*, 14.
[8] R. Bjornsson, I. Arnason, *Phys. Chem. Chem. Phys.* **2009**, *11*, 8689.
[9] L. B. Favero, B. Velino, W. Caminati, A. J. Kvaran, *J. Phys. Chem. A* **2006**, *110*, 9995.
[10] A. Bodi, A. Kvaran, S. Jonsdottir, E. Antonsson, S. O. Wallevik, I. Arnason, A. V. Belyakov, A. A. Baskakov, M. Hölbling, H. Oberhammer, *Organometallics* **2007**, *26*, 6544.
[11] R. J. West, *J. Am. Chem. Soc.***1954**, *76*, 6012.
[12] S. O. Wallevik, R. Bjornsson, A. Kvaran, S. Jonsdottir, I. Arnason, A. V. Belyakov, A. A. Baskakov, K. Hassler, H. Oberhammer, *J. Phys. Chem. A* **2010**, *114*, 2129.
[13] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, T. Vreven Jr, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. N. Scalmani Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. I. Toyota, R. Fukuda, J. Hasegawa, V. Bakken, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Will, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, A. J. Pople, Gaussian 03, Revision E.01, Gaussian, Inc., Wallingford CT, **2004**.
[14] H. J. Werner, P. J. Knowles, R. Lindh, F. R. Manby, M. Schütz, P. Celani, T. Korona, G. Rauhut, R. D. Amos, A. Bernhardsson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, A. W. L. C. Hampel, G. Hetzer, S. J. McNicholas, W. Meyer, M. E. Mura, A. Nicklass, P. Palmieri, R. Pitzer, U. Schumann, H. Stoll, A. J. Stone, R. Tarroni, T. Thorsteinsson, *MOLPRO, version 2006*.1, a package of ab initio programs, see http://www.molpro.net, **2006**.
[15] T. H. Dunning, *J. Chem. Phys.* **1989**, *90*, 1007.
[16] D. E. Woon, T. H. Dunning, *J. Chem. Phys.* **1993**, *98*, 1358.
[17] T. Helgaker, W. Klopper, H. Koch, J. Noga, *J. Chem. Phys.* **1997**, *106*, 9639.
[18] S. O. Wallevik, R. Bjornson, A. Kvaran, S. Jonsdottir, G. V. Girichev, N. I. Giricheva, K. Hassler, I. Arnason, *J. Mol. Struct.* **2010**, *978*, 209.
[19] C. Zheng, S. Subramaniam, V. F. Kalasinsky, J. R. Durig, *J. Mol. Struct.* **2006**, *785*, 143.
[20] L. Hedberg, I. M. Mills, *J. Mol. Spectrosc.* **1993**, *160*, 117.
[21] P. Klaboe, *Vib. Spectrosc.* **1995**, *9*, 3.

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