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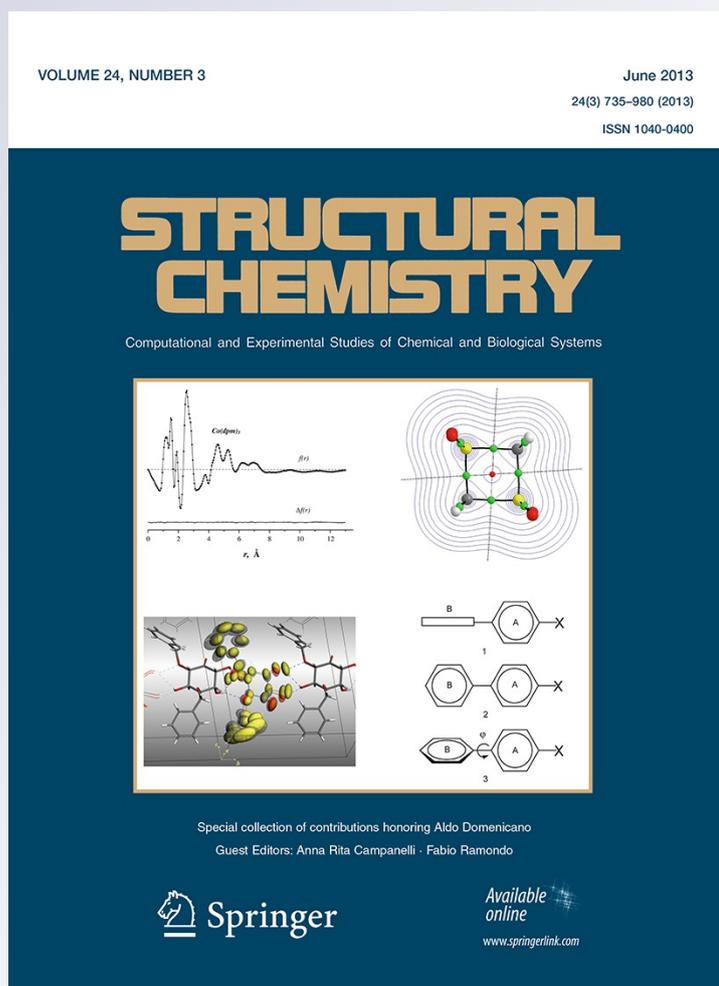
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ORIGINAL RESEARCH

Conformational properties of 1-methyl-1-germacyclohexane: low-temperature NMR and quantum chemical calculations

**Nanna Rut Jonsdottir · Ágúst Kvaran ·
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Abstract The conformational preference of the methyl group of 1-methyl-1-germacyclohexane was studied experimentally in solution (low-temperature ^{13}C NMR) and by quantum chemical calculations (CCSD(T), MP2 and DFT methods). The NMR experiment resulted in an axial/equatorial ratio of 44/56 mol% at 114 K corresponding to an A value ($A = G_{ax} - G_{eq}$) of 0.06 kcal mol^{-1}. An average value for $\Delta G^{\#}_{e \rightarrow a} = 5.0 \pm 0.1$ kcal mol^{-1} was obtained for the temperature range 106–134 K. The experimental results are very well reproduced by the calculations. CCSD(T)/CBS calculations + thermal corrections resulted in an A value of 0.02 kcal mol^{-1}, whereas a ΔE value of -0.01 kcal mol^{-1} at 0 K was obtained.

This study is dedicated to Professor Aldo Domenicano on the occasion of his 75th birthday.

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Introduction

The stereochemistry of cyclohexane is among the best explored areas in organic stereochemistry [1, 2]. The chair-to-chair inversion in cyclohexane is well understood, the Gibbs free energy of activation for the step chair → half-chair$^{\#}$ → twist is generally accepted to be 10.1–10.5 kcal mol^{-1} and the conformational equilibrium of a large number of monosubstituted cyclohexanes has been studied. Winstein and Holness defined A-values as the thermodynamic preference for the equatorial conformation over the axial one (see Scheme 1 for definition of A) [3], where a positive A value corresponds to a preference for the equatorial conformer and $\Delta G = G_{ax} - G_{eq}$. All energy differences herein will be presented as (axial–equatorial). As a rule, in monosubstituted cyclohexanes, the substituent prefers the equatorial position of the chair conformation. Rare exceptions are substituents having mercury bonded to the cyclohexane ring. When the substituent becomes bulkier its equatorial preference generally increases. The simplest alkyl groups; methyl, ethyl, isopropyl, and *t*-butyl have been used as examples. This tendency has in a classical way been ascribed to a 1,3-synaxial interaction between the substituent in axial position and axial hydrogens on the ring carbon atoms in positions 3 and 5 [4]. Towards the end of the last century, accepted A values were 1.74, 1.79, 2.21 and 4.9 kcal mol^{-1} for Me, Et, *i*-Pr and *t*-Bu, respectively [5–7]. Evidence that may question the model of 1,3-synaxial interaction are starting to appear. Wiberg et al. [8] revised the A values for the three lightest alkyl groups and reported the values of 1.80, 1.75 and 1.96 kcal mol^{-1} for Me, Et and *i*-Pr, respectively (all values reported with the error limit of ±0.02 kcal mol^{-1}) and the authors concluded that there was no evidence of a 1,3-synaxial interaction with the axial hydrogens at C(3,5). Taddei and Kleinpeter have examined the role of

$$A = -\Delta G^\circ = RT\ln(K)$$
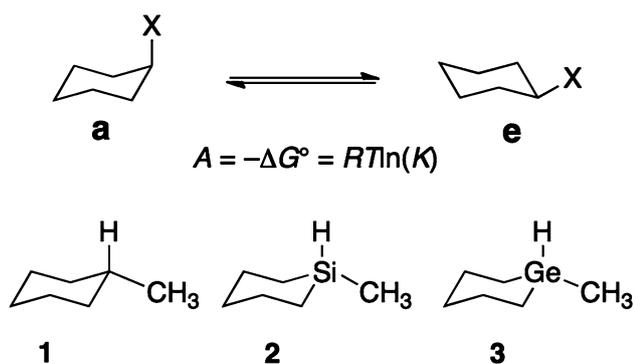
Scheme 1 .

hyperconjugation in substituted cyclohexanes [9, 10]. Cuevas et al. [11] using the theory of atoms in molecules concluded that the *t*-Bu group is more stable when it adopts the axial position in cyclohexane but produces destabilization of the cyclohexyl ring. Clearly, the conformational preferences in monosubstituted cyclohexanes are not fully understood. Far less investigations have been reported on heavier group 14 element-containing six-membered rings. In silacyclohexane the activation energy for the chair-to-chair inversion is about one-half of the value for cyclohexane [12]. In recent years *A* values for some monosubstituted derivatives of silacyclohexane have been reported. Methyl [13–15] and phenyl [16] substituents were found to have positive *A* values, albeit much lower in magnitude than the corresponding cyclohexane analogues [17–19]. Other substituents like CF_3 [20, 21], SiH_3 [22] and F [23] were found to prefer the axial position contrary to their cyclohexane analogues. Interestingly, our first case of monosubstituted silacyclohexane to study was 1-methyl-1-silacyclohexane **2**. We were suspicious about the correctness of former reports by other groups using molecular mechanics (MM) calculations [24, 25] and the Winstein–Holness equation for NMR data for dynamic systems [26]. According to those reports, the *A* value was predicted to be negative. For 1-methyl-1-germacyclohexane **3** the situation is similar. Takeuchi et al. estimated from substituent chemical shift (^{13}C and ^{73}Ge NMR) of the methyl group, and from MM calculations a conformational mixture of ca. 60/40 mol% of axial and equatorial conformers [27]. The aim of this study is to re-examine the conformational properties of the title compound using dynamic NMR experiments and high-level quantum chemical (QC) calculations.

Results and discussion

Dynamic NMR spectroscopy (DNMR)

DNMR is a powerful and frequently used method to establish a temperature dependence of conformational equilibrium.

When applied to phenomena like the chair-to-chair inversion of a monosubstituted saturated six-membered ring, it is essential to reach a temperature low enough so the NMR spectrometer can distinguish between the two conformers. In case of substituted cyclohexanes, this is no obstacle because of the relatively high energy barrier of more than 10 kcal mol^{-1}. The temperatures needed (230 K or a little lower) [28, 29] can easily be reached using commercial solvents. When dealing with Si-monosubstituted silacyclohexanes one has to reach temperatures of about 110 K to see coalescence and splitting into separate signals for the two conformers. Such measurements are not performed on a routine basis. Suitable solvents are in most cases low-boiling freons like CHF_2Cl, $CHFCl_2$ or $CBrF_3$ or mixtures of them and thus experience in handling gases on a vacuum line becomes a prerequisite. The solubility of the solute may become a limiting factor at low temperatures and in some cases this can be met by varying the solvent mixture. Modern FT-spectrometers need a deuterated solvent component like CD_2Cl_2 for locking purposes. In our experience, the loss of the lock signal at very low temperatures is in most cases the limiting factor that determines how low temperatures can be reached. In retrospect it is remarkable that Bushweller and Jensen were able to record ^1H NMR spectra down to temperatures as low as 96 K utilizing a 60 MHz fitted with a variable temperature probe designed especially for work at very low temperature. Recording the spectra on a continuous-wave spectrometer obviously has also had some advantages. The authors reported a free activation energy $\Delta G^{\#} = 5.5 \pm 0.1$ kcal mol^{-1} for 1,1-dimethyl-1-silacyclohexane [30, 31].

Takeuchi et al. attempted without success to observe directly the axial and equatorial conformers of **3** using DNMR. They reported 123 K as the lowest possible temperature and no observation of line broadening for ^{13}C signals of 1,1-dimethyl-1-germacyclohexane. No information is given on solvents for the DNMR experiment [27].

According to our DNMR experiments of the title compound **3**, ^{13}C NMR spectra above about 140 K show rapid interconversion of the two chair conformers. On cooling below 140 K, the spectra show large line broadening and gradual splitting of signals into two components, indicating a mixture of two conformers. This effect is most pronounced for the Me signal, which is shown in Fig. 1. The higher field (lower δ) component signal is the minor component. In a previous work on the related silicon analogue **2** we have shown that the ^{13}C chemical shifts of the Me group have lower δ values when the substituent is in the axial position than in the equatorial one [13]. This assignment is also supported by QC calculations (see computational part and supplementary material).

Dynamic NMR simulations of the spectra, using the software WinDNMR [32] as shown in Fig. 1, allowed
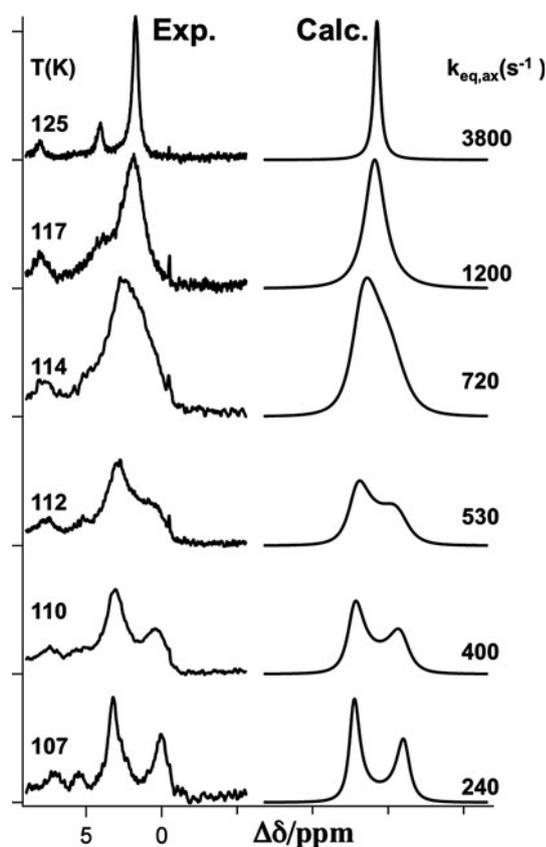
Fig. 1 Low-temperature ^{13}C NMR spectra for the methyl group of **3**. Experimental spectra are to the *left* and calculated spectra to the *right*

determination of the rate constants ($k_{e\to a}$) and the corresponding free energies of activation ($\Delta G^{\#}_{e\to a}$) as a function of temperature. There are some impurities in the sample but the agreement between experimental and calculated spectra is very good. Chemical shifts, derived from NMR spectra, which were recorded at the lowest temperatures, were assumed to represent conditions of negligible interconversions. An average value for $\Delta G^{\#}_{e\to a} = 5.0 \pm 0.1$ kcal mol^{-1} was obtained for the temperature range 106–134 K. Furthermore, the equilibrium constant ($K_{e\to a}$) and free-energy difference ($\Delta G_{e\to a} = A$), for the equatorial to axial transformations, corresponding to 114 K (a temperature close to the coalescence point) were determined from the relative signal intensities. The results ($K_{e\to a} = 0.8$ and $\Delta G_{e\to a} = 0.06$ kcal mol^{-1}) are shown in Table 1. This corresponds to about 44/56 mol% mixture of axial and equatorial conformers.

Quantum chemical calculations

The absolute ^{13}C NMR shielding constants of the carbon nuclei in both conformers were calculated with the GIAO method [33, 34] using the functional PBE1 [35–37] and a mixed basis set consisting of aug-pcS-2 [38] on carbon

atoms and def2-TZVPP [39] on all other atoms. Shielding constants were converted to chemical shifts by referencing to ^{13}C shielding constants in TMS. All geometries (including the TMS standard) were optimized at the MP2/cc-pVTZ level. The magnitude of the relative shieldings is in reasonable agreement with experiment (slight overestimation), and their sign confirms the expected assignment in which the ring carbon nuclei are more shielded in the axial conformer than in the equatorial one.

The minimum energy pathway for the chair-to-chair inversion of compound **3** was calculated in redundant internal coordinates with the STQN(Path) method as implemented in Gaussian09 [40] at the B3LYP [41, 42]/6-31G(d) [43–45] level of theory. The pathway is shown in Fig. 2. Similarly to silacyclohexanes, the inversion path starting from the axial conformer, consists of a half-chair/sofa like transition state from which the molecule can move into a twist form of relatively high energy. The molecule then goes through a boat form into a more stable twist form at the midpoint of the path. The molecule then proceeds further through a boat transition state, a twist minimum and a half-chair/sofa transition state before it ends up in the equatorial form.

High-level ab initio calculations were carried out (using the ORCA package, version 2.9) [46] on MP2/cc-pVTZ [47, 48] optimized geometries to get accurate potential energy differences between the axial and equatorial conformers as shown in Table 1.

Energy differences at the CCSD(T)/CBS (CBS = complete basis set) level were estimated by performing large basis MP2 calculations that were extrapolated to the basis set limit and then applying a CCSD(T) correction to the MP2/CBS value:

$$\Delta E^{\text{CCSD(T)/CBS}} \approx \Delta E^{\text{MP2/CBS}} + (\Delta E^{\text{CCSD(T)/smallbasis}} - \Delta E^{\text{MP2/smallbasis}})$$

The MP2 calculations were performed with the correlation consistent basis sets [47–49] up to the aug-cc-pVQZ level and extrapolated to the complete basis set (CBS) limit using an automatic two-point extrapolation [50] (as implemented in ORCA) of MP2 correlation energies (extrapolation constant $\beta = 3.00$). The ($\Delta E^{\text{CCSD(T)/small}}$

Table 1 Conformational properties of C_5H_{10}GeHCH$_3$ (**3**)

	$T = 0$ K $\Delta E = E_{\text{ax}} - E_{\text{eq}}$ (kcal mol^{-1})	$T = 114$ K $A = G_{\text{ax}} - G_{\text{eq}}$ (kcal mol^{-1})
Calculations		
CCSD(T)/CBS	–0.01	+0.02[a]
Experiment		
DNMR		+0. 06

[a] Thermal correction evaluated from B97-1/def2-TZVPP computed harmonic frequencies

Fig. 2 Minimum energy pathway of the chair-to-chair interconversion of **3**
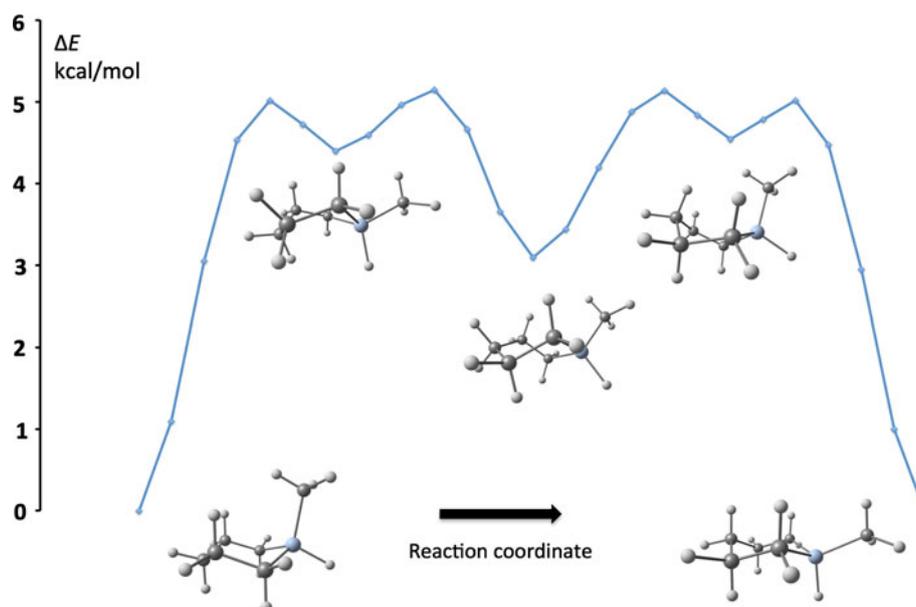
$^{\text{basis}} - \Delta E^{\text{MP2/small basis}}$) term was calculated at the CCSD(T)/aug-cc-pVTZ and MP2/aug-cc-pVTZ level. Input files for these calculations using the ORCA program are provided in the supporting information. Similar CCSD(T)/CBS protocols have been used in studies on silacyclohexanes [15, 22, 51].

The enthalpy and entropy corrections to the conformational energies were calculated at the B97-1 [52]/def2-TZVPP [39] level using Gaussian 09; this functional is known to predict good harmonic frequencies and enthalpy and entropy corrections [53] and has been used in previous studies on silacyclohexanes. A problem with harmonic frequency calculations for six-membered rings, persists, however, for the evaluation of thermal corrections to free energies. Six-membered rings include a number of low-frequency vibrations that are known to be badly predicted by the harmonic approximation. As they contribute significantly to entropy, errors in the entropy correction are to be expected. We also note that we have not attempted to take into account solvent effects in the computations as such effects are very hard to account for accurately and are in our experience small for these kinds of systems.

Shown in Table 1 are calculated relative energies with thermodynamical corrections at the NMR experimental temperature compared to the free-energy difference from the NMR experiment. The 0 K potential energy difference (ZPE exclusive) evaluated at the CCSD(T)/CBS level of theory is -0.01 kcal/mol, making the two conformers equally stable in terms of potential energy. Inclusion of free-energy corrections, evaluated from the rigid-rotor harmonic approximation and DFT-computed frequencies results in a slight preference for the equatorial conformer. Overall the agreement with experiment is very satisfactory.

Conclusions

With this report the knowledge of the conformational properties of the three homologous cyclohexane derivatives **1**, **2** and **3** has been improved. The *A* value of about 1.8 kcal mol^{-1} for **1** is well-established. The much lower *A* value for **2** (0.2–0.5 kcal mol^{-1}, depending on method) demonstrates a rather dramatic change in molecular properties when a carbon atom in cyclohexane is substituted by a silicon atom while the change due to silicon-germanium substitution is much smaller. While an understanding of what physical effects govern the conformational properties of these heterocycles is not clear at present, we for now simply note the inverse trend in the conformational energy difference with respect to endocyclic bond lengths as determined by gas electron diffraction; C–C (1.534 Å) [54], C–Si (1.867 Å) [55] and C–Ge (1.956 Å) [56]. The atomic properties of Si and Ge in group 14 are also rather similar [57]. It is therefore not surprising to observe that conformational properties change only moderately from **2** to **3**.

Experimental

Synthesis

Materials

The 1,1-dichloro-1-germacyclohexane used as the starting material for the synthesis listed below was prepared according to the general preparation of silacyclohexanes described by West [58]. GeCl$_4$ was used instead of SiCl$_4$. All solvents were dried using appropriate drying agents and

distilled before use. Standard Schlenk technique and an inert atmosphere of dry nitrogen was used for all manipulations.

Germacyclohexane

1,1-Dichloro-1-germacyclohexane (24.3 g, 114 mmol) was dissolved in 100 mL of diethylether and added dropwise to a suspension of LiAlH$_4$ (3.6 g, 95 mmol) in 100 mL of diethylether while stirring at 0 °C. After complete addition the cooling bath was removed and the reaction mixture slowly warmed up to room temperature and then refluxed for 1.5 h. The reaction mixture was stirred over night and the refluxing was continued for another 5 h. The diethylether was distilled off and replaced by pentane and then the precipitate was filtered off under nitrogen. Distillation of the reaction mixture over a column under reduced pressure (140 torr, 66–88 °C) yielded 1.8 g (19 mmol, 11 %) of pure germacyclohexane confirmed by NMR spectroscopy. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 1.02–1.09 (m, 4H, CH$_2$), 1.40–1.47 (m, 2H, CH$_2$), 1.72–1.79 (m, 4H, CH$_2$), 3.66 (bs, 2H, GeH$_2$). ^{13}C NMR (100 MHz, CDCl$_3$): δ = 9.29, 26.72, 29.81.

1-Bromo-1-germacyclohexane

A solution of bromine (1.92 g, 12.0 mmol) in 20 mL of pentane was added dropwise to a flask containing germacyclohexane (1.76 g, 12.0 mmol) and 80 mL of pentane while stirring and keeping the temperature at −50 °C. After stirring the reaction mixture over night most of the solvent was distilled off and the product was further purified by condensation. The remaining solution was confirmed by NMR spectroscopy to be an 85/15 % mixture of 1-bromo-germacyclohexane and the starting material, germacyclohexane.

1-Methyl-1-germacyclohexane

A Grignard solution of MeMgI (1.36 g, 8.69 mmol) and 40 mL diethylether was added dropwise to a solution of 1-bromo-1-germacyclohexane (1.94 g, 8.88 mmol) and 40 mL of diethylether while stirring at 0 °C. The reaction mixture turned grey with dark grey precipitate. After stirring over night at room temperature most of the solvent was distilled off and the remaining solvent was condensed off under reduced pressure to avoid heating the product too much. A final condensation in vacuum yielded 0.37 g (2.33 mmol, 27 %), NMR spectroscopy confirmed the existence of 1-methyl-1-germacyclohexane with small traces of 1,1-dimethyl-1-germacyclohexane and germacyclohexane. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 0.23 (d, 3H, $^3J_{H-H}$ = 3.30 Hz, CH$_3$), 0.76–0.85 (m, 2H, CH$_2$), 1.01–1.11 (m, 2H, CH$_2$), 1.34–1.48 (m, 2H, CH$_2$), 1.65–1.80 (m, 4H, CH$_2$), 1.75–1.81 (m, 1H, GeH). ^{13}C NMR (100 MHz, CDCl$_3$): δ = −6.56 (CH$_3$), 12.58, 26.07, 30.09.

NMR

A 400 MHz NMR spectrometer (Bruker Avance 400) was used for all NMR experiments. A solvent mixture of CD$_2$Cl$_2$, CHF$_2$Cl, and CF$_3$Br in a ratio of 1:2:2 was used for the ^{13}C DNMR experiment. The temperature of the probe was calibrated by means of a type K (Chromel/Alumel) thermocouple inserted into a dummy tube. The readings are estimated to be accurate within ± 2 K. The NMR spectra were loaded into the data-handling program IGOR (WaveMetrics) for analysis, manipulations, and graphic display. Line-shape simulations of the NMR spectra were performed using the WinDNMR program [32].

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