

Conformational Studies by Dynamic NMR. 66.¹ Ring Inversion in a Cyclic Disilane: 1,1,4,4-Tetramethyl-1,4-Disilacyclohexane.

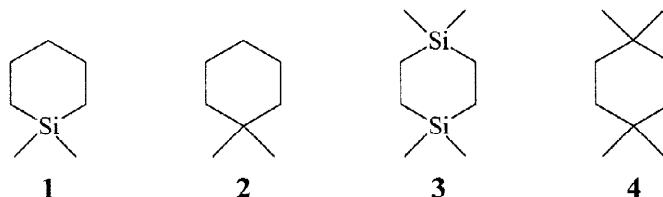
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Abstract. The barrier to ring inversion of the title compound ($\Delta G^\ddagger = 6.0 \text{ kcal mol}^{-1}$) has been found to be much lower than that ($\Delta G^\ddagger = 11.1 \text{ kcal mol}^{-1}$) of the corresponding cyclohexane derivative (1,1,4,4-tetramethylcyclohexane). © 1998 Elsevier Science Ltd. All rights reserved.

When a ring carbon in a cyclohexane derivative is substituted by a silicon atom, the chair conformation is expected to become more flexible (owing to the longer C-Si bond) and thus exhibiting a lower barrier for the ring inversion process. So far only a single measurement has been reported for such a case: the ring inversion barrier of silane **1** was found to be significantly lower ($\Delta G^\ddagger = 5.4 \text{ kcal mol}^{-1}$)³ than that ($\Delta G^\ddagger = 10.2 \text{ kcal mol}^{-1}$)⁴ of the corresponding cyclohexane **2**.



Likewise the barrier to ring inversion of the title compound **3** (1,1,4,4-tetramethyl-1,4-disilacyclohexane) is expected to be smaller than that measured ($\Delta G^\ddagger = 11.1 \text{ kcal mol}^{-1}$)⁵ for the corresponding cyclohexane **4** (1,1,4,4-tetramethylcyclohexane).

We considered it not unreasonable to predict that the difference between the barriers of the two cyclohexanes **4** and **2** (i.e. $\Delta\Delta G^\ddagger = 11.1 - 10.2 = 0.9 \text{ kcal mol}^{-1}$) should be similar to that between the corresponding cyclosilanes **3** and **1**. Consequently, addition of such a difference to the known barrier of **1** ($\Delta G^\ddagger = 5.4 \text{ kcal mol}^{-1}$) suggests a $\Delta G^\ddagger = 6.3 \text{ kcal mol}^{-1}$ for the unknown barrier of **3**, a value which, in principle, is accessible to experimental determinations by means of NMR spectroscopy.

Independent considerations based on C-C and C-Si bond lengths and on torsional barriers of acyclic compounds, had suggested that the difference between the barriers of **4** and **3** should be equal to $4.56 \text{ kcal mol}^{-1}$, thus leading to a prediction⁶ of $6.5 \text{ kcal mol}^{-1}$ for the unknown barrier of **3**: both empirical approaches anticipate, therefore, extremely similar values.

However, attempts of measuring this barrier by detecting different ^1H NMR signals for the axial and equatorial methylene or methyl hydrogens of **3** failed, since separated signals were not observed even at $-160\text{ }^\circ\text{C}$.⁶ The authors thus concluded⁶ that the ring inversion of **3** actually has a barrier lower than 6 kcal mol^{-1} .

We report here the result of a successful measurement of this barrier, which was performed by monitoring the ^{13}C NMR spectrum (75.5 MHz) of **3** dissolved in $\text{CHF}_2\text{Cl}/\text{CHFCl}_2/\text{CD}_2\text{Cl}_2$. Below $-100\text{ }^\circ\text{C}$ the single line (at -3.6 ppm) of the four methyl carbons broadens much more than that (at 9.5 ppm) of the methylene carbons, eventually decoalescing below $-135\text{ }^\circ\text{C}$. Two sharp lines (-2.2 and -5.8 ppm) were finally observed at $-155\text{ }^\circ\text{C}$ (Figure 1) for the equatorial and axial methyl groups, respectively.⁷

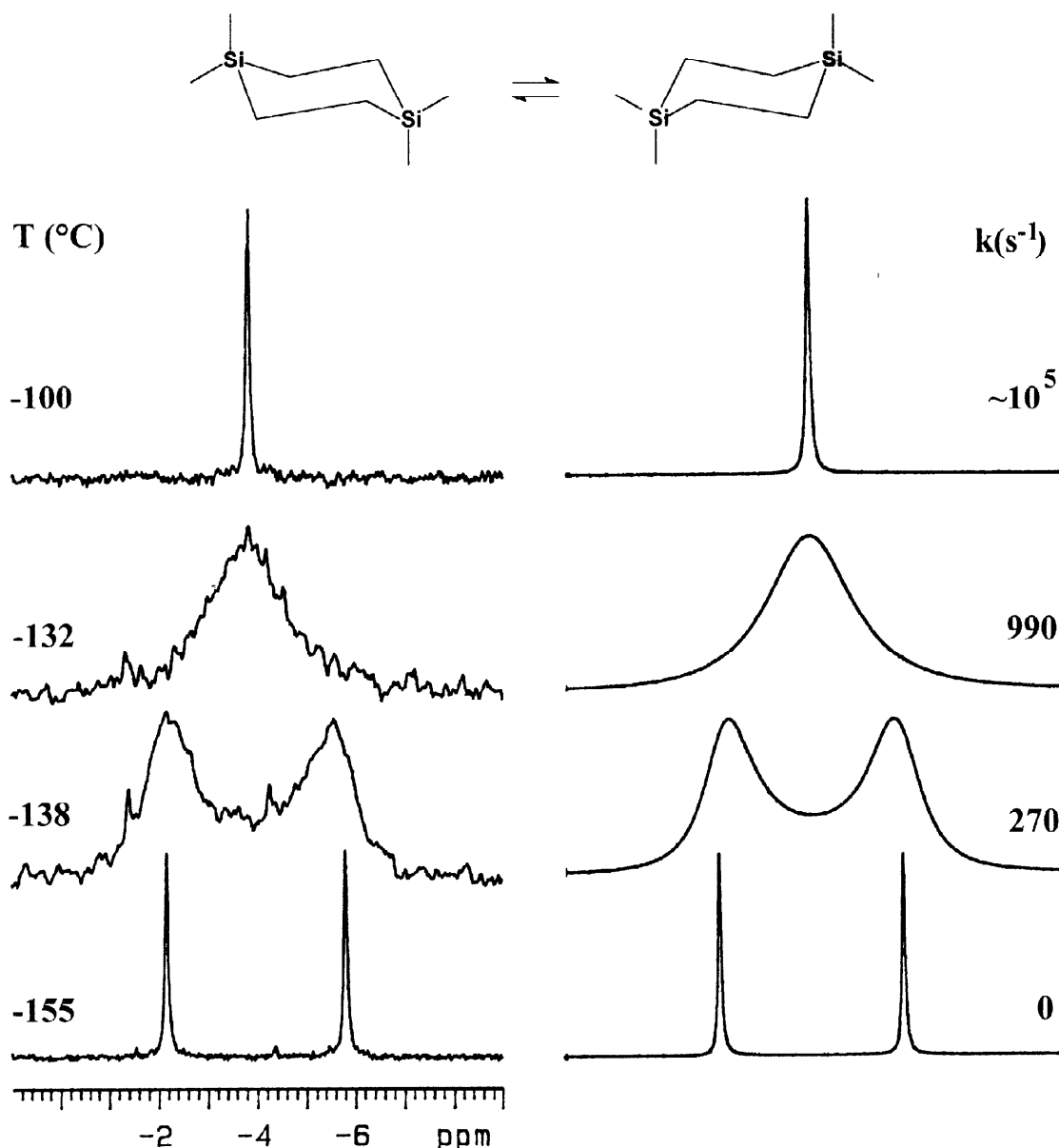


Figure 1. Temperature dependence (left) of the ^{13}C NMR signal (75.5 MHz) of the methyl groups of **3** in $\text{CHF}_2\text{Cl}/\text{CHFCl}_2/\text{CD}_2\text{Cl}_2$. On the right the simulation, with the rate constants (in s^{-1}) indicated, is reported.

Computer line shape simulation at various temperatures (a few selected examples are shown in Figure 1) yielded a set of rate constants from which a $\Delta G^\ddagger = 6.0 \pm 0.15$ kcal mol⁻¹ was derived.⁸ As often reported in conformational processes, the ΔG^\ddagger values were found independent of temperature within the experimental errors, thus indicating a negligible ΔS^\ddagger and essentially coincident values for ΔH^\ddagger and ΔG^\ddagger .^{4,9}

At 300 MHz, the ¹H NMR single signal of the methyl groups splits likewise, yielding, at -155 °C, two peaks separated by 22.5 Hz (Figure 2). At the same temperature separated signals ($\Delta\nu = 61$ Hz) were also observed for the axial and equatorial methylene hydrogens: the corresponding AA'BB'-type spectrum almost approaches (Figure 2) a simple AB pattern (apparent $J_{\text{HH}} \approx 9.0$ Hz). Computer simulation of this signal at the coalescence temperature (-143 °C) provided the same ΔG^\ddagger value (6.0 kcal mol⁻¹) obtained from the ¹³C NMR spectrum.

It is therefore gratifying to conclude that the empirical predictions have matched surprisingly well the result of the experimental measurements.

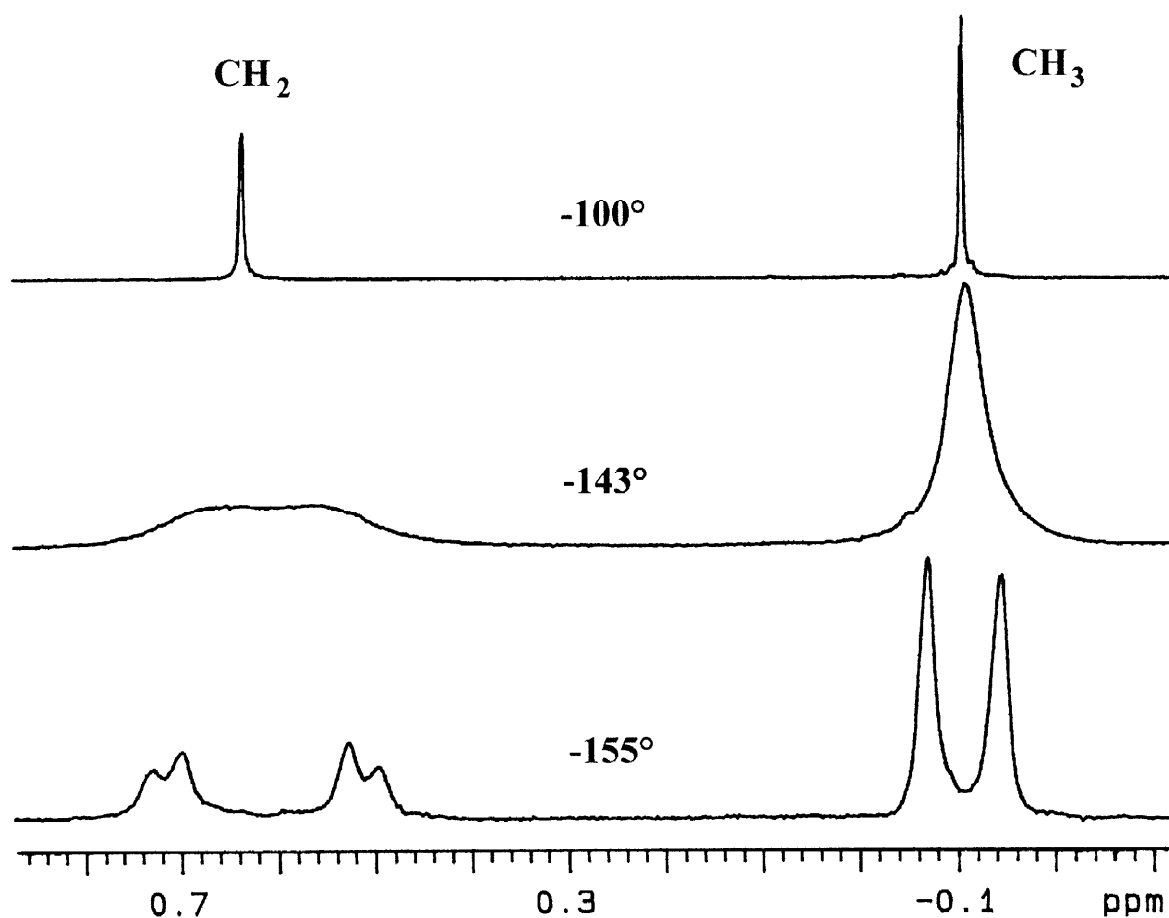


Figure 2. Temperature dependence of the ¹H NMR spectrum (300 MHz) of 3 in CHF₂Cl/CHFCl₂/CD₂Cl₂.

Experimental

The synthesis of the title compound **3** was performed as described in the literature.⁶ The reaction actually gives, as a major product, 1,1,2,3,3-pentamethyl-1,3-disilacyclopentane whose boiling point is extremely close to that of **3**: the latter thus had to be purified by vacuum distillation (bp: 43.5 °C at 4 mmHg) with a spinning band still device having about 200 plates efficiency. In this way the major product was reduced to a less than 2% impurity, barely detectable in the very low temperature NMR spectra of Figure 1.

The samples were prepared by connecting the NMR tubes, containing the title compound as well as some CD₂Cl₂ (for locking purpose), to a vacuum line and condensing the gaseous CHFCl₂ and CHF₂Cl with liquid nitrogen to obtain a 1:1:3 proportion of the three solvents. The tubes were then sealed *in vacuo* and introduced in the precooled probe of the spectrometer. The temperatures were calibrated by means of a precision Cu/Ni thermocouple inserted into the probe of the spectrometer before or after the spectral determination.

The computer simulation of the line shape was performed using a PC computer program¹⁰ based on DNMR6 routines (QCPE) and the best fit was visually judged by superimposing the plotted and experimental traces.

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References and Notes

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- (10) Courtesy of Prof. F. Gasparini, University "La Sapienza", Rome.