

**Conformational Studies by Dynamic NMR.  
67.<sup>1</sup> Ring Inversion, in Solution and in the  
Solid, of the Silane Analogue of  
Permethylcyclohexane:  
Dodecamethylcyclohexasilane**

Daniele Casarini,\* Lodovico Lunazzi,\* and  
Andrea Mazzanti

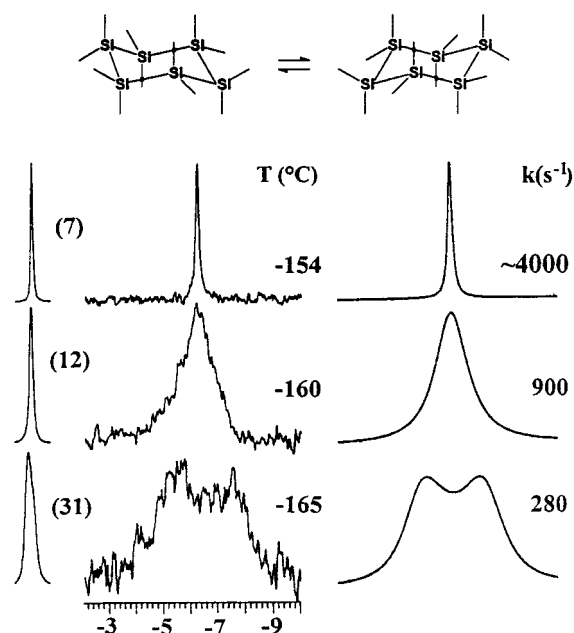
Department of Organic Chemistry "A.Mangini", University  
of Bologna, Risorgimento, 4, Bologna 40136, Italy

Received July 22, 1998

The six-membered cyclic polysilanes (i.e., the analogues of cyclohexane having six silicon atoms replacing the six carbon atoms) are expected to exhibit chair conformations that are more flexible than the corresponding cyclohexane derivatives, owing to the greater bond lengths and, possibly, also to the lower angle bending force constants. For instance, substitution of even a single ring carbon with a silicon atom lowers the ring inversion barrier<sup>3</sup> of cyclopentamethylenedimethylsilane  $\text{Me}_2\text{Si}(\text{CH}_2)_5$  significantly from that of the corresponding 1,1-dimethylcyclohexane,  $\text{Me}_2\text{C}(\text{CH}_2)_5$ <sup>4</sup> (i.e., 5.4 vs 10.2 kcal mol<sup>-1</sup>).

Dodecamethylcyclohexasilane,  $(\text{Me}_2\text{Si})_6$ , is the analogue of dodecamethylcyclohexane,  $(\text{Me}_2\text{C})_6$ : for the latter a ring inversion barrier ( $\Delta G^\ddagger$ ) as high as 17.3 kcal mol<sup>-1</sup> has been measured.<sup>5</sup> Although  $(\text{Me}_2\text{Si})_6$  was found to adopt a "normal" chair conformation in the crystal,<sup>6</sup> attempts of detecting separate <sup>1</sup>H NMR signals for the axial and equatorial methyl groups failed,<sup>7</sup> thus making impossible detection of the ring inversion process and, consequently, measurement of the corresponding barrier. Equally unsuccessful have been attempts at observing different axial and equatorial  $a_{\text{Me}}$  hyperfine splittings in the corresponding radical anion, by means of low-temperature ESR spectroscopy.<sup>7</sup>

We report here a successful outcome of this conformational problem, achieved by monitoring the high field <sup>13</sup>C spectra of  $(\text{Me}_2\text{Si})_6$  at temperatures much lower than those previously attained. The 75.5 MHz signal of the 12 equivalent methyl carbons (a single, sharp peak at -6.5 ppm) broadened steadily on cooling the sample, much in the same way as did the lines of the solvents, an effect which is the consequence of the increasing viscosity of the solution.<sup>3b</sup> Accordingly, in the range -100° to -150 °C the ratio between the line width of the solute and of the solvent signals was found to be essentially constant ( $1.6 \pm 0.3$ ). Below -155 °C, however, this relationship suddenly broke down in that the width



**Figure 1.** Temperature dependence of the <sup>13</sup>C NMR solution spectrum of  $(\text{Me}_2\text{Si})_6$  at 75.5 MHz (center). The computer simulation, obtained with the rate constants (in s<sup>-1</sup>) indicated, is shown on the right. On the left is reported, in the same scale, a typical solvent signal (central peak of  $\text{CHF}_2\text{Cl}$ ), with the corresponding line width (Hz) given in parentheses.

of the methyl carbon signals increased dramatically: at -160 °C, for instance, its value was about 100 Hz as opposed to 12 Hz for the solvent lines. This suggests that an exchange process has begun to take place, and indeed at -165 °C the typical shape of two lines just below the coalescence point<sup>8</sup> was clearly observed (Figure 1).

Such an occurrence allows determination of the ring inversion rate by computer simulation,<sup>9</sup> provided the line width in the absence of exchange is available. Although at lower temperatures the solubility of  $(\text{Me}_2\text{Si})_6$  is insufficient for detecting its <sup>13</sup>C spectrum,<sup>10</sup> the intrinsic line width nonetheless could be obtained by multiplying that of the solvent signals (31 Hz, as in Figure 1) by the mentioned 1.6 factor.<sup>11</sup> The resulting value ( $50 \pm 11$  Hz) allowed us simultaneously to compute the rate constant ( $280 \pm 30$  s<sup>-1</sup>) at -165 °C and the separation ( $210 \pm 25$  Hz)<sup>12</sup> of the axial and equatorial methyl lines. Shift differences exceeding this interval yielded unacceptable simulations in that the computed spectral shape became

(8) Jennings, W. B.; Kochanewycz, M. J.; Lunazzi, L. *J. Chem. Soc., Perkin Trans. 2* **1997**, 1525.

(9) A modified PC version of the DNMR6 program (QCPE) has been employed, courtesy of Prof. F. Gasparrini, University "La Sapienza", Rome.

(10) A weak signal is still detectable in the <sup>1</sup>H spectrum, but its line width is so broad as to exceed the shift difference for the axial and equatorial methyl substituents. Such a difference is in fact expected to be much smaller than in the <sup>13</sup>C spectrum. As an indication, in dodecamethylcyclohexane the <sup>1</sup>H signals differ only by 0.21 ppm<sup>5</sup> (corresponding to 63 Hz at 300 MHz), a value definitely smaller than the intrinsic proton line width of our sample below -165 °C.

(11) (a) Lunazzi, L.; Macciantelli, D.; Bernardi, F.; Ingold, K. U. *J. Am. Chem. Soc.* **1977**, *99*, 4573. (b) Casarini, D.; Lunazzi, L.; Mazzanti, A. *J. Org. Chem.* **1997**, *62*, 7592.

(12) This value (corresponding to 2.78 ppm) is similar to that reported for the separation of the <sup>13</sup>C signals of dodecamethylcyclohexane (2.26 ppm).<sup>5</sup>

(1) For Part 66 see: Casarini, D.; Lunazzi, L.; Mazzanti, A. *Tetrahedron* **1998**, *54*, 1381.

(2) In partial fulfillment of the Ph. D. requirements in Chemical Sciences, University of Bologna.

(3) (a) Jensen, F. R.; Bushweller, C. H. *Tetrahedron Lett.* **1968**, 2825.

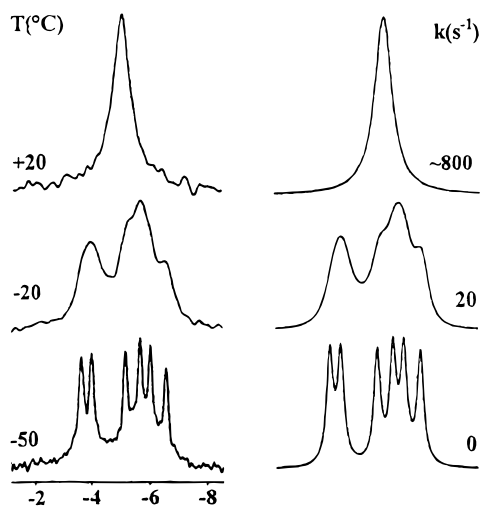
(b) Bushweller, C. H.; O'Neil, J. W.; Bilofsky, U. S. *Tetrahedron* **1971**, *27*, 3065.

(4) Dalling, D. K.; Grant, D. M.; Johnson, L. F. *J. Am. Chem. Soc.* **1971**, *93*, 3678.

(5) Wehele, D.; Scheuermann, H.-J.; Fitjer, L. *Chem. Ber.* **1986**, *119*, 3127. See also: Fitjer, L.; Scheuermann, H.-J.; Wehle, D. *Tetrahedron Lett.* **1984**, *25*, 2329.

(6) Carrell, H. L.; Donohue, J. *Acta Crystallogr.* **1972**, *B28*, 1566.

(7) Carberry, E.; West, R.; Glass, G. E. *J. Am. Chem. Soc.* **1969**, *91*, 5446.



**Figure 2.** CP-MAS solid state  $^{13}\text{C}$  NMR spectra (75.5 MHz) of  $(\text{Me}_2\text{Si})_6$  as function of temperature (left). The computer simulation, obtained with the rate constants ( $\text{s}^{-1}$ ) indicated, is shown on the right.

either narrower or broader than the experimental trace, *whatever* the rate constant employed. The free energy of activation ( $\Delta G^\ddagger$ ) for ring inversion is therefore  $4.7_5 \pm 0.2 \text{ kcal mol}^{-1}$ ,<sup>13</sup> if a transmission coefficient of 1/2 is considered, as suggested for the inversion process of cyclohexane-like derivatives.<sup>3b,4,14,15</sup>

This result was cross-checked by recording the spectrum at an even higher frequency (125.7 MHz), whereby a decoalescing signal, analogous to that of Figure 1 at  $-165^\circ\text{C}$ , was observed, as theory predicts,<sup>14</sup> at a higher temperature ( $-160^\circ\text{C}$ ). The computer simulation, carried out as mentioned above, yielded a shift difference ( $330 \pm 15 \text{ Hz}$ ) greater than the previous one by a factor equal to the ratio of the spectrometer frequencies (i.e., 500:300), a result which proves the consistency of this approach. From the same  $-160^\circ\text{C}$  spectrum<sup>16</sup> a rate constant of  $450 \pm 30 \text{ s}^{-1}$  was simultaneously derived, which corresponds to a  $\Delta G^\ddagger$  value ( $4.8_5 \pm 0.2 \text{ kcal mol}^{-1}$ ) essentially equal to that obtained at 75.5 MHz, therefore confirming the reliability of these measurements.

As anticipated, the barrier for the ring inversion of  $(\text{Me}_2\text{Si})_6$  has proved to be much lower ( $\Delta\Delta G^\ddagger = 12.5 \text{ kcal mol}^{-1}$ ) than that of the corresponding cyclohexane derivative  $(\text{Me}_2\text{C})_6$ ,<sup>5</sup> a feature which parallels that computed for the corresponding rotational processes.<sup>17</sup>

The greater flexibility of the cyclohexasilane ring is further indicated by the  $^{13}\text{C}$  solid-state NMR (CP-MAS) spectrum, in which a single line is observed for the 12 methyl carbons at ambient temperature, indicating that rapid ring inversion occurs even in the crystal. At  $-50^\circ\text{C}$ , however, this process becomes sufficiently slow to result in a six-line spectrum (Figure 2).

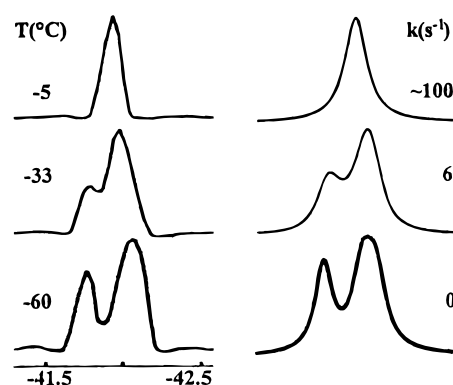
(13) The quoted error takes into account all the above-mentioned uncertainties as well as those due to the temperature determination ( $\pm 2^\circ\text{C}$ ).

(14) Sandström, J. *Dynamic NMR Spectroscopy*; Academic Press: London, 1982.

(15) Depending on the temperature range the use of a unitary coefficient would yield  $\Delta G^\ddagger$  values larger by  $0.15 \text{ kcal mol}^{-1}$  (at  $-165^\circ\text{C}$ )<sup>3b</sup> or by  $0.3 \text{ kcal mol}^{-1}$  (between  $-35^\circ\text{C}$  and  $-10^\circ\text{C}$ ).

(16) The 500 MHz spectrometer could not operate below this temperature.

(17) Schleyer, P. V. T.; Kaupp, M.; Hample, F.; Bremer, M.; Mislou, K. *J. Am. Chem. Soc.* **1992**, *116*, 6791.



**Figure 3.** CP-MAS solid state  $^{29}\text{Si}$  NMR spectra (59.6 MHz) of  $(\text{Me}_2\text{Si})_6$  as function of temperature (left). The computer simulation, obtained with the rate constants (in  $\text{s}^{-1}$ ) indicated, is shown on the right.

This is because the rigid chair conformation in the crystal not only displays, as in solution, diastereotopic axial and equatorial methyl groups but also exhibits nonequivalence for the three pairs of silicon atoms (and consequently for the methyl carbons bonded to them), as made evident also by the  $^{29}\text{Si}$  solid-state spectrum (59.6 MHz), in which the single peak observed at ambient temperature splits, at  $-60^\circ\text{C}$ , into two closely spaced lines ( $\Delta\nu = 15 \text{ Hz}$ ) with a 1:2 intensity ratio (Figure 3). Of the three expected  $^{29}\text{Si}$  lines, the two upfield are almost coincident, as indicated by the major signal (at  $-42.05 \text{ ppm}$ ) being broader than the minor one (at  $-41.8 \text{ ppm}$ ).<sup>18</sup>

X-ray diffraction<sup>6</sup> had shown in fact that site symmetry and molecular symmetry of  $(\text{Me}_2\text{Si})_6$  are not coincident (the molecules lie at positions of site symmetry  $\bar{1}$  in the  $A2/a$  space group). Thus the three silicon atoms in positions 1, 2, 3 are nonequivalent in the crystalline state. In such a situation half the molecule, containing three independent silicon and six independent carbon atoms, is symmetry related to the other half, thus accounting for the multiplicity of the low temperature  $^{13}\text{C}$  and  $^{29}\text{Si}$  solid-state spectra.

Computer simulation of the exchange-broadened  $^{13}\text{C}$  lines in the range  $-35^\circ$  to  $-10^\circ\text{C}$  (Figure 2) yielded the rate constants for the exchange process in the crystal, corresponding to a  $\Delta G^\ddagger$  value<sup>19</sup> equal to  $12.8_5 \pm 0.2 \text{ kcal mol}^{-1}$ : essentially the same value ( $12.7_5 \pm 0.2 \text{ kcal mol}^{-1}$ ) resulted from the simulation of the  $^{29}\text{Si}$  spectra<sup>15</sup> (Figure 3).

This  $\Delta G^\ddagger$  value, much larger than that determined in solution ( $\Delta\Delta G^\ddagger = 8 \text{ kcal mol}^{-1}$ ), reflects the hindrance exerted by the crystal lattice upon the molecular motions, as also observed for other types of exchange processes.<sup>20</sup> Such a difference is apparently larger than that of the only other case of ring inversion investigated in both phases.<sup>26</sup> In the much wider cyclododecane ring, in fact,

(18) Computer simulation of the trace at  $-60^\circ\text{C}$  (Figure 3, bottom right) shows that the major signal at  $-42.05 \text{ ppm}$  is actually a combination of two unresolved peaks (each having the same 8.5 Hz line width of the single line at  $-41.8 \text{ ppm}$ ) separated by 5 Hz, a feature which accounts for its apparently larger width.

(19) Within the experimental errors, the  $\Delta G^\ddagger$  values were found temperature independent, thus suggesting negligible values for  $\Delta S^\ddagger$ .

(20) Increasing of the barriers in the solid state has been reported for the degenerate Cope rearrangement of bullvalene,<sup>21</sup> for the tautomerism of imidazole,<sup>22</sup> for *tert*-butyl<sup>23</sup> and  $\text{Me}_3\text{Si}$  rotation,<sup>24</sup> and for pseudorotation of five-membered rings.<sup>25</sup>

(21) Miller, R. D.; Yannoni, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 7396.

this motion occurs in the same temperature range both in solution and in the solid state.<sup>26</sup> This seems to indicate that the two barriers are not very different, although the authors did not measure the actual  $\Delta G^\ddagger$  value for ring inversion of cyclododecane in the crystal.

Two possible explanations should be considered to account for the six <sup>13</sup>C lines (and the three <sup>29</sup>Si lines) that become a single signal on raising the temperature of crystalline (Me<sub>2</sub>Si)<sub>6</sub>.

(i) With respect to a rigid chair (molecular symmetry *D*<sub>3d</sub>), rapid ring inversion would generate additional elements of symmetry, leading to an effective *D*<sub>6h</sub> dynamic symmetry, which might then yield a molecular symmetry coincident with the site symmetry. This process would thus render equivalent not only the axial and equatorial methyl groups but also the silicon atoms in positions 1, 2, 3 and, consequently, the pairs of Si-bonded carbons. In the framework of this hypothesis only a ring inversion process would be responsible for the NMR observations in the solid state, and the corresponding greater value of the barrier would represent the resistance encountered in the crystal lattice for achieving such an equilibrium.

(ii) In addition to the ring inversion process, the molecule might undergo, in the crystal, a rotational motion about the 3-fold symmetry axis, which would make equivalent the three Si atoms and the Si-bonded pairs of carbons: such a rotation might thus contribute, in principle, to the  $\Delta G^\ddagger$  value. These types of higher level reorganizations in the solids are usually accompanied by a phase change which, on the contrary, is not expected to occur in the case of a simple ring inversion process.

A differential scanning calorimetry (DSC) determination did not show any phase change in the range  $-80$  °C to  $+65$  °C, whereas a sharp phase transition was observed at  $+68.5$  °C (lit.,<sup>27</sup>  $+74.5$  °C). Thus the high level reorganization does not occur when the exchange process is observed by NMR (i.e. between  $-35$ ° and  $+10$  °C), but at a temperature at least  $50$  °C higher. A similar behavior was reported, for instance, when the *tert*-butyl rotation of a trialkylmethanol was investigated in the solid state.<sup>23a,b</sup> In that case the authors concluded that

(22) Elguero, J.; Fruchier, A.; Pellegrin, V. *J. Chem. Soc., Chem. Commun.* **1981**, 1207.

(23) (a) Riddell, F. G.; Arumagam, S.; Anderson, J. E. *J. Chem. Soc., Chem. Commun.* **1991**, 1525. (b) Barrie, P. J.; Anderson, J. E. *J. Chem. Soc., Perkin Trans. 2* **1992**, 2031. (c) Riddell, F. G.; Arumagam, S.; Harris, K. D. M.; Rogerson, M.; Strange, J. H. *J. Am. Chem. Soc.* **1993**, *115*, 1881.

(24) Aliev, A. E.; Harris, K. D. M.; Apperley, D. C. *J. Chem. Soc., Chem. Commun.* **1993**, 251.

(25) (a) Lambert, J. B.; Xue, L.; Howton, S. C. *J. Am. Chem. Soc.* **1991**, *113*, 8958. (b) Riddell, F. G.; Cameron, K. S.; Holmes, S. A.; Strange, J. H. *J. Am. Chem. Soc.* **1997**, *119*, 7555.

(26) Möller, M.; Gronski, W.; Cantow, H.-J.; Höcker, H. *J. Am. Chem. Soc.* **1984**, *106*, 5093.

(27) Stolberg, U. G. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 150.

the large difference with respect to the solution barrier did not involve contributions related to the phase transition.

Accordingly it does not seem unreasonable, on this ground, to consider the exchange process observed in crystalline dodecamethylcyclohexasilane as due essentially to ring inversion.

## Experimental Section

Dodecamethylcyclohexasilane was prepared according to the procedure described in the literature.<sup>28</sup> The sample for the solution spectra was prepared by connecting the NMR tube, containing the title compound dissolved in CD<sub>2</sub>Cl<sub>2</sub> (for locking purpose) to a vacuum line and condensing the gaseous solvents (CHFCl<sub>2</sub> and CHF<sub>2</sub>Cl) with liquid nitrogen, in such a way as to have a 1:1:3 proportion of the three solvents. The tube was then sealed in vacuo and introduced in the precooled probe of the spectrometers, the same sample having been used for both the 75.5 and 125.7 MHz determinations. The temperatures of the probes were calibrated by means of a Ni/Cu thermocouple inserted into a dummy tube before or after the spectral measurements. The high resolution <sup>13</sup>C and <sup>29</sup>Si NMR solid-state CP-MAS spectra were obtained at 75.5 and 59.6 MHz, respectively. The sample, a white crystalline powder, was packed in a 7 mm zirconia rotor spun at the magic angle with a speed of 3300 Hz. The number of transients (8–32) varied in order to achieve good signal-to-noise ratios in the VT experiments. The chemical shifts were measured, by replacement, with respect to the lower frequency signal of adamantane (29.4 ppm) for <sup>13</sup>C and with respect to TMS (0 ppm) for <sup>29</sup>Si. Cooling was achieved by means of a flow of dry nitrogen, precooled in a heat exchanger immersed in liquid nitrogen. The temperatures of the solid-state spectra were calibrated by using the shift dependence of the <sup>13</sup>C lines of 2-chlorobutane absorbed upon solid decalite,<sup>29</sup> assuming a dependence equal to that observed in neat liquid, which had been previously calibrated by the same Ni/Cu thermocouple.

The DSC trace was obtained with a scanning rate of 10°/min, heating the sample from  $-80$  °C to the melting point ( $+249$  °C). Near the phase transition temperature ( $+68.5$  °C) the scanning rate was reduced to 0.1°/min: the process was found to be reversible, with an enthalpy change of about 3.7 kcal mol<sup>-1</sup>.

**Acknowledgment.** The authors thank I.Co.C.E.A., Bologna, for access to the solid state NMR facilities and Drs E. Hoffmann and P. Sandor (Varian GmbH, Darmstadt, Germany) for helping with the low temperature experiments at the 500 MHz spectrometer. This work has received financial support from the University of Bologna (Funds for selected research topics 1995–1997) as well as from MURST (National Project: Stereoselection in Organic Synthesis) and CNR, Rome.

JO9814400

(28) Laguerre, M.; Dunogues, J.; Calas, R. *J. Chem. Soc., Chem. Commun.* **1978**, 272.

(29) Aliev, A. E.; Harris, K. D. M. *Magn. Reson. Chem.* **1994**, *32*, 366.