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THE INTERCONVERSION BARRIER OF CYCLOPENTAMETHYLENEDIMETHYLSILANE

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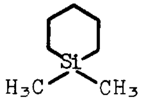
NMR spectroscopy has proven to be a valuable method for ascertaining barriers of the magnitude of 5 to 15 kcal/mole, especially for 6-ring carbocyclic (1) and heterocyclic (2) compounds. For saturated monocyclic 6-ring compounds the barriers reported thus far differ only slightly. However, the value for dimethylpentamethylenesilane (I) is very small in comparison to that of the carbon analog.



(I)

The nmr spectrum of (I) was examined in a 15% by volume solution in bromotrifluoromethane (Freon 13-Bl).* The chemical shifts were measured in reference to the $(CH_3)_2Si$ proton resonance which did not split or show any detectable kinetic broadening at the lowest temperature (-177°) at which spectra were recorded.

At -46°, the proton nmr spectrum of I (Fig. 1a) consists of the very sharp $(CH_3)_2Si$ resonance, the C-2 and C-6 proton resonances (37 Hz downfield from the reference methyl resonances), and the complex proton resonances on C-3, C-4 and C-5 (95 Hz downfield from the reference signal). The temperature was lowered and at -159° the fine structure of the $-CH_2-Si-CH_2-$ protons coalesced, and the

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*The nmr spectra were obtained utilizing a Varian HR-60 Spectrometer fitted with a variable temperature probe designed especially for work at very low temperatures.

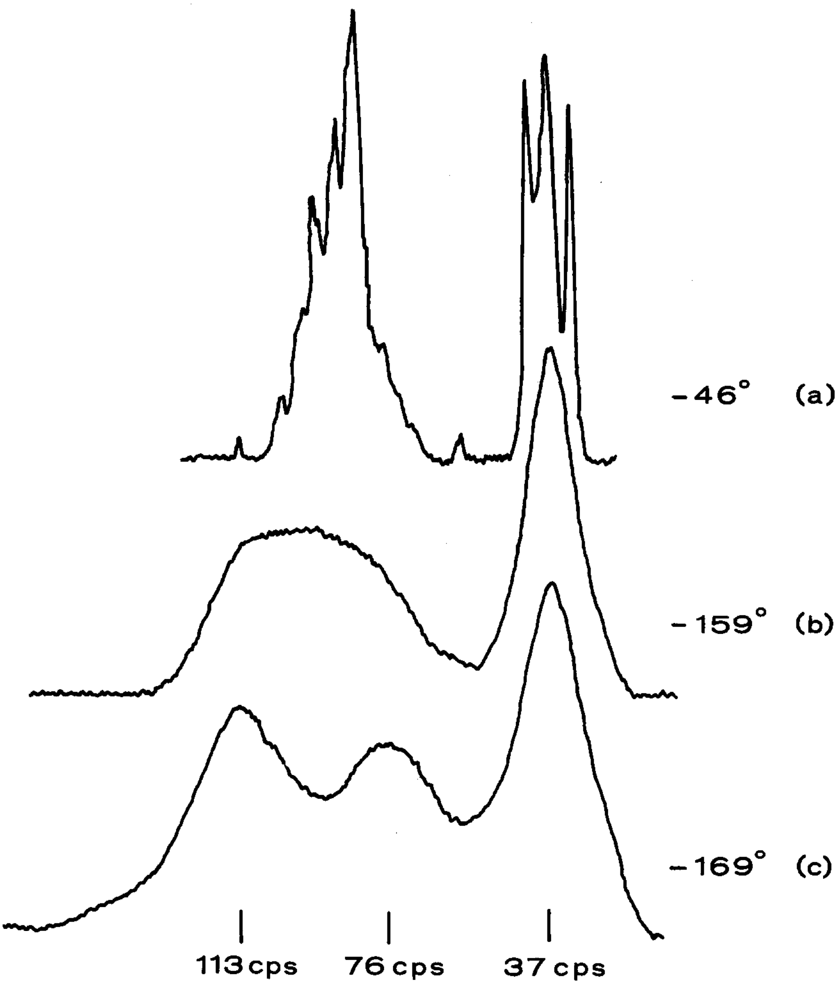

FIGURE 1. The proton nmr spectrum (60 Hz) of the ring protons of cyclopentamethylenedimethylsilane at various temperatures. (The CH_3—Si—CH_3 resonance is not shown.)

resonances of the protons on C-3, C-4 and C-5 broadened appreciably (Fig. 1b). By -169° (Fig. 1c, no further change had occurred in the $-CH_2-Si-CH_2-$ resonances but the signals of the protons on C-3, C-4 and C-5 had separated into two broad peaks centered at 76 and 113 Hz downfield from the reference (methyl) resonances.

These spectral changes are consistent with the expectation that the compound exists in the chair form. From the observed changes in spectra with temperature, and assuming a discrete intermediate is formed which has an equal probability of converting to either chair, a chair to intermediate barrier ($\Delta F^{\ddagger}$) of 5.5 ± 0.25 kcal/mole is obtained. The uncertainty reported in $\Delta F^{\ddagger}$ arises principally as a consequence of the broad nature of the peaks due to spin-spin interactions and the relatively high solution viscosity.

At -163.1°, the peaks are at 87% of their maximum observed separation. From the equation relating peak separation to rate constant (3) a rate constant of 82 sec^{-1} is calculated for the chair to twist conversion (1a). By application of the Erying equation, a $\Delta F^{\ddagger}$ of 5.25 kcal/mole is obtained. This value represents a minimum value because under these conditions with overlapping peaks the true centers of resonance are actually separated to a greater extent. At -152.2°, the peak envelope as indicated by the width at half height is about 40% separated from its maximum value. By assuming half separation a barrier of $\Delta F^{\ddagger} =$ 5.75 kcal/mole is obtained. This value represents a maximum. (For sharp peaks, at coalescence the half height width of the envelope is greater than 50% of the maximum envelope half height width. For broad peaks the width will be a greater percentage of the total (3). Therefore, this estimate is a very liberal maximum.) With the aid of a cumputer program to relate line shapes with peak separations for very broad peaks an approximate (best) value of $\Delta F^{\ddagger} = 5.4$ kcal/mole is obtained (4). From these data, a barrier for the chair to twist interconversion of $\Delta F^{\ddagger} = 5.50 \pm 0.25$ kcal/mole at -157.1° is obtained.

No exact barrier has been determined for 1,1-dimethylcyclohexane but from the observed broadening in the spectra at low temperature it is expected to be about the same as for other cyclohexane derivatives, i.e., 10-11 kcal/mole (5). The substantially smaller barrier for the silicon analog appears to be due to smaller force constants for bond deformation of silicon, and decreased eclipsing interactions and bond deformation in the transition state. As expected, because of the increased bond length, the rotational barrier in methylsilane (1.70 kcal/mole) is substantially less than in ethane (2.75 kcal/mole) (6). The effect on the conformation of the ring of the longer carbon-silicon bond, as compared to carbon-carbon, is to increase the C_2-C_6 distance and to make the atoms at the 1, 2, 3, 5, 6 positions more coplanar than in cyclohexane. In the transition state for the interconversion, at least four of the atoms must become coplanar and because of the greater coplanarity expected for the chair form of the silicon analog, less bond deformation is expected to occur in its transition state.

The maximum barrier for the reaction probably involves conversion of the chair to twisted half-chair forms, and the interconversion barrier between twisted half-chair forms is probably very low. By either of the proposed transition states, the multiplicity of the reaction would be two and hence the $\Delta S^{\ddagger} \sim R \ln 2 = 1.4$ eμ (1).

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