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ACTIVATION PARAMETERS FOR RING REVERSAL IN CYCLOPENTAMETHYLENEDIMETHYLSILANE

TOTAL NMR LINE SHAPE ANALYSIS

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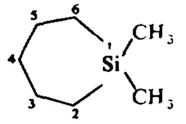
Abstract—Using variable temperature PMR spectroscopy and total PMR line shape analysis, the activation parameters for chair-chair interconversion in cyclopentamethylenedimethylsilane ($E_a = 6{\cdot}1 \pm 0{\cdot}3$ kcal/mole. $\Delta G^{\ddagger} = 5{\cdot}5 \pm 0{\cdot}1$ kcal/mole at 111°K. $\Delta S^{\ddagger} = 3{\cdot}5 \pm 2{\cdot}5$ eu) were determined indicating a dramatic $\Delta H^{\ddagger} = 5{\cdot}9 \pm 0{\cdot}3$ kcal/mole reduction in the potential barrier to ring reversal as compared to cyclohexane and a host of 6-membered heterocycles.

CONFORMATIONAL preference and the rate of stereomutation of medium rings are important in determining the chemistry of such systems. Although the potential barriers to chair-chair or chair-twist interconversions in a large number of saturated 6-rings containing nitrogen,[1] oxygen,[2] sulfur,[3] and selenium[4] are usually similar to or greater than that in cyclohexane derivatives ($\Delta H^{\ddagger} \simeq 11$ kcal/mole),[5] there is a dearth of information regarding the effect of silicon,[6] germanium, and tin on the conformational dynamics of the 6-ring.

In a previous paper,[6] we reported evidence for slowing of the chair-chair interconversion process in cyclopentamethylenedimethylsilane(I) using the dynamic nuclear magnetic resonance (DNMR) technique and in that report[6] a free energy of activation ($\Delta G^{\ddagger}$) was calculated using an approximate line shape method. This communication concerns the determination of all the activation parameters for ring reversal in I employing total PMR line shape analysis.

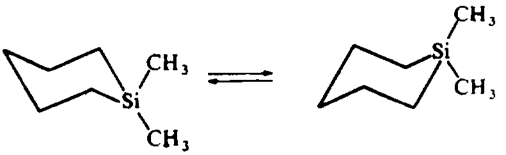


I

Examination of the PMR spectrum (60 MHz) of I (10% v/v in $CBrF_3$) at −45° revealed a sharp singlet for the $Si(CH_3)_2$ group. Although the $Si(CH_3)_2$ resonance broadened at very low temperatures (a shortened T_2) due to spin–spin relaxation mechanisms dependent on viscosity, it always remained Lorentzian and showed no indication of asymmetry or splitting even at the lowest temperature reached (−177°). Thus all calibrations (audio modulation) of spectra utilized in this study were done with reference to the $Si(CH_3)_2$ resonance. At low temperatures, the fine structure in the peak due to the protons on C-2 and C-6 at δ 0·62 (CH_2Si; Fig 1) coalesced but no evidence for peak separation was forthcoming. In Fig 1, only the C-2,6 and C-3,4,5 proton resonances are shown. The $Si(CH_3)_2$ peak is omitted.

However, the complex resonance due to the C-3,4,5 methylene groups (δ 1·58 at

−45°; Fig 1) first exhibited fine structure coalescence at about −137° and then broadened and separated into two broad overlapping peaks at δ 1·27 and δ 1·88 (Fig 1, −171·0°). Such spectral behavior is entirely consistent with a slowing of the ring reversal rate process in I (Eq. 1). Although no spin–spin splitting is evident for the peaks at δ 1·27 and δ 1·88, the broader upfield resonance at δ 1·27 reflects a greater coupling to adjacent hydrogens and can be assigned to the C-3,4,5 axial protons in the chair form of I by analogy with chemical shift trends in other 6-rings[7] and the established dihedral angular dependence of coupling constants.[7] The lowest field more narrow resonance (δ 1·88, Fig 1) is assigned to the equatorial C-3,4,5 protons (Fig 1). Implicit in the above analysis of the PMR spectrum of I under slow exchange conditions (e.g., −171·0°; Fig 1) is identical or nearly identical equatorial



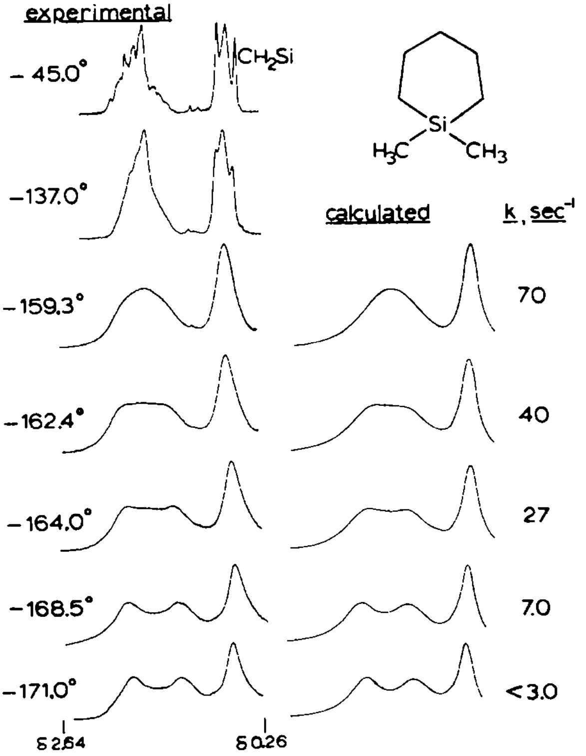


Fig 1. The experimental PMR spectrum (60 MHz) of I as a function of temperature and calculated spectra as a function of the rate of chair–chair interconversion. Only the C-2,6 methylene (CH_2Si) and C-3,4,5 methylene resonances are shown. The $Si(CH_3)_2$ resonance is omitted.

proton chemical shifts on C-3, C-4, C-5 and similar behavior for the axial hydrogens.

We have performed a total line shape analysis of the temperature dependent C-3,4,5 methylene resonance using some approximations. First, we made the assumption regarding axial and equatorial proton chemical shifts mentioned above. Second, since no spin–spin splitting is evident under conditions of slow exchange (Fig 1) the axial and equatorial proton resonances on C-3,4,5 were assumed to be broad singlet resonances of Lorentzian line shape. Obviously the unresolved spin–spin splitting in these two resonances contributes to the apparent respective T_2 values. Also assuming the CH_2Si resonance to be a singlet of Lorentzian line shape, a calculated spectrum gave an excellent fit to the experimental spectrum under conditions of slow exchange (Fig 1, −171·0°). Third, we assumed that the widths-at-half-height (or T_2) and chemical shifts of the peaks in question were independent of temperature. There is a slight but real variation in the width-at-half-height of the $(CH_3)_2Si$ resonance with temperature, e.g., 4·2 Hz at −158° and 5·1 Hz at −168°, and the same general behavior might be assumed for the C-3,4,5 proton resonances. Hence, our assumption of no variation of T_2 with temperature will lead to an apparent rate constant at higher temperatures slightly greater than the actual rate constant.

A series of theoretical spectra[8] were calculated as a function of the rate of chair–chair interconversion and matched to the experimental spectra (Fig 1). In all cases, the C-2,6 methylene protons peak was also included in the theoretical spectrum by superposition in order to account for any perturbation on the C-3,4,5 line shape by overlap of the C-2,6 peak. The derived rate constants are compiled in Table 1. An Arrhenius plot of ln k vs 1/T (correlation coefficient = 0·995) gave $E_a = 6{\cdot}1 \pm 0{\cdot}3$ kcal/mole, $\Delta H^\ddagger = 5{\cdot}9 \pm 0{\cdot}3$ kcal/mole, $\Delta G^\ddagger = 5{\cdot}5 \pm 0{\cdot}1$ kcal/mole at 111°K, and $\Delta S^\ddagger = 3{\cdot}5 \pm 2{\cdot}5$ eu. If a twist intermediate having an equal probability of going to either chair is assumed, the activation parameters are $E_a = 6{\cdot}1 \pm 0{\cdot}3$ kcal/mole, $\Delta H^\ddagger = 5{\cdot}9 \pm 0{\cdot}3$ kcal/mole, $\Delta G^\ddagger = 5{\cdot}4 \pm 0{\cdot}1$ kcal/mole at 111°K, and $\Delta S^\ddagger = 4{\cdot}4 \pm 2{\cdot}5$ eu. It should be emphasized at this point that $\Delta S^\ddagger$ was extracted from a plot of ln k versus 1/T over only a 15° range necessitated by the rapid change in rate constant with temperature at these very low temperatures.

TABLE 1. RATE CONSTANTS (k)[a] FOR CHAIR INTERCONVERSION IN I AS A FUNCTION OF TEMPERATURE

T, °K	104·7	109·2	110·8	113·9	115·8	119·4
k, sec^{-1}	7·0	27·0	40·0	70·0	139	300

[a] k = first order rate constant for the conversion of one chair to the other chair

Although the $\Delta S^\ddagger$ for ring inversion in I is not atypical of saturated 6-rings, e.g., cyclohexane (2·8 eu),[5] bromocyclohexane (3·4 eu),[9] the potential barrier to ring reversal is dramatically lower than that in cyclohexane ($\Delta H^\ddagger = 10{\cdot}8$ kcal/mole)[5] or more appropriately in 1,1-dimethylcyclohexane ($\Delta G^\ddagger = 10{\cdot}4$ kcal/mole at −60°). Such an observation is not unexpected in light of the low rotational barrier in methylsilane (1·70 kcal/mole)[11] as compared to ethane (2·90 kcal/mole).[12] Since any process equilibrating the two equivalent chair forms (Eq 1) involves necessarily rotation about certain bonds, the lower barrier is understandable. In addition, the long carbon-silicon single bonds effectively increase the distance between C-2 and C-6 tending to render the atoms at positions 1,2,3,5, and 6 (I) more coplanar than in cyclohexane. Thus the ground state conformation of I is already close to one plausible transition state for ring reversal, i.e., the semiplanar form (atoms at positions 1,2,3,5,6 all coplanar) and bond angle deformation for ring inversion in I would be expected to be less severe than in cyclohexane.

EXPERIMENTAL

The NMR spectra were obtained using a Varian HR-60A spectrometer equipped with a custom-built variable temp probe. Spectral calibrations were performed by the audio-modulation technique using a Hewlett-Packard 651A audio oscillator and 5221 electronic counter.

Temp measurement was performed using a calibrated copper-constantan thermocouple permanently in place in the probe and is done simultaneously with the recording of the spectrum. Temp measurement is accurate to ± 0·3° at the sample.

The error associated with the rate constants (± 5%) obtained by matching theoretical to experimental spectra is a maximum error established by obviously poor fits at higher and lower values of the rate constant giving the best fit. The error reported for the activation energy is a maximum error obtained by drawing another line through the Arrhenius plot which gives a reasonable though much poorer fit than the line used.

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