

Conformational Studies by Dynamic NMR, 69^[‡]

Conformation and Stereodynamics of Aliphatic Triisopropylsilanes in Solution and in the Solid State

J. Edgar Anderson,^{*,[a]} Daniele Casarini,^[b] Lodovico Lunazzi,^{*,[c]} and Andrea Mazzanti^[c]**Keywords:** Conformational analysis / Dynamic NMR / MM calculations / Solid-state NMR

A dynamic process has been detected in the solution ¹³C-NMR spectra of *t*Bu–Si(*i*Pr)₃ (**4**) in the temperature range –145 °C to –163 °C, the corresponding free energy of activation being 5.5 kcal mol^{–1}. Molecular mechanics calculations have identified three types of conformations that are markedly more stable than all the others, but the one with the highest symmetry cannot be populated, as is evident from the appearance of the spectrum at low temperature.

This spectrum can be interpreted in terms of restricted rotation of the *tert*-butyl group and of the isopropyl groups, leading to a structure centered around the (*a,g*,–*g*) conformation. In the case of the analogous (*i*Pr)₃SiCl derivative (**5**), this dynamic process was not observed in solution, but an appropriate spectrum for the same (*a,g*,–*g*) conformation was obtained by the solid-state CP-MAS NMR spectroscopy at –100 °C.

Introduction

The rotational processes shown by isopropyl groups bonded to the same sp³ atom have been investigated by Anderson and co-workers.^{[2][3]} In particular, it was found that the three isopropyl groups bonded to the CH moiety in triisopropylmethane, *i*Pr₃CH (**1**), or to the CMe moiety in 1,1,1-triisopropylethane, *i*Pr₃CMe (**2**) exist in two complicated sets of conformations, these being enantiomers of one another. Any isopropyl group conformation may be defined by the torsional relationship of its methine hydrogen atom with the central hydrogen atom (as in **1**) or methyl group (as in **2**).

<i>i</i> Pr ₃ C–R	R	
	H	1
	Me	2
<i>i</i> Pr ₃ Si–R	R	
	H	3
	<i>t</i> Bu	4
	Cl	5
	I	6

Molecules of compound **1** prefer to adopt the (*a,g,g*) conformation (point group C₁), corresponding to a structure having the isopropyl groups arranged as in conformer **4b** in

Scheme 1. This conformation equilibrates with a significant amount of the (*g,g,g*) conformation (point group C₃), having the isopropyl groups disposed as in conformer **4a** in Scheme 1. By reversing such an interconversion, the degenerate (*g,a,g*) and (*g,g,a*) conformations become accessible and so form part of the populated set. Conformations other than these were calculated to be too high in energy to be significantly populated. The molecule, however, is equally likely to adopt the enantiomeric set of conformations, i.e. (*a*,–*g*,–*g*) etc., as well as (–*g*,–*g*,–*g*), and at room temperature interconverts rapidly on the NMR time scale between these two sets of at least four conformations.

Below –127 °C, the methyl signal in the ¹³C-NMR spectrum becomes a doublet, indicating slow interconversion between the two sets (the barrier associated with this process being 6.6 kcal mol^{–1}), whereas interconversion of the degenerate forms within sets is still rapid.

Molecule **2** also prefers to adopt the (*a,g,g*) conformation in its six degenerate and enantiomeric forms, but the second most stable conformation (*a,g*,–*g*) is calculated to be just 0.86 kcal mol^{–1} less stable (in this form, the isopropyl groups are arranged as in conformer **4c** in Scheme 1). The three degenerate forms of such a conformation may therefore be populated, although there is no NMR evidence at any temperature to confirm or refute this. At low temperatures, two dynamic processes become slow on the NMR time scale, the higher barrier of 6.8 kcal mol^{–1} being attributable to interconversion of degenerate versions of the (*a,g,g*) conformation via the symmetrical (*g,g,g*) conformation, while the lower barrier corresponds to interconversion of the enantiomeric sets, presumably via the symmetrical (*a,g*,–*g*) conformation.

These two examples serve to illustrate the complexity of the conformational interchange possible for *i*Pr₃X–R compounds, and show the usefulness of calculations in interpretation of the spectral observations. We now report on

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[a] Chemistry Department, University College, Gower Street, London, WC1H 0AJ U.K. Fax: (internat.) +44 (0)171 380 7463 E-mail: j.e.anderson@ucl.ac.uk

[b] Department of Chemistry, Università della Basilicata, I-85100 Potenza, Italy

[c] Department of Organic Chemistry "A. Mangini", University of Bologna, Viale Risorgimento 4, I-40136 Bologna, Italy Fax: (internat.) + 39-051/209-3654 E-mail: lunazzi@ms.fci.unibo.it

conformational studies of some triisopropylsilyl compounds, i.e. $i\text{Pr}_3\text{Si}-\text{R}$, where $\text{R} = \text{H}$ (**3**), $t\text{Bu}$ (**4**), Cl (**5**), and I (**6**).

In these derivatives, interactions between the isopropyl groups and the group R are somewhat weaker since the silicon–carbon bonds are longer than carbon–carbon bonds (1.88 vs. 1.34 Å, conventionally). Different types of conformation are not so disparate in energy, and dynamic NMR shows that calculations of the type that proved so useful in the work described above are, in the present case, much less reliable as a guide to the interpretation of the experimental results.

Results

In contrast to the case of $i\text{Pr}_3\text{Si}-\text{H}$ (**1**), we were unable to observe any dynamic process in the corresponding triisopropylsilane $i\text{Pr}_3\text{Si}-\text{H}$ (**3**) by ^1H NMR (at 400 MHz) or ^{13}C NMR (100.6 MHz) at the lowest attainable temperature (-165°C). This was not unexpected, as substitution of carbon by silicon has, in other cases, been found to greatly reduce interconversion barriers.^{[4][5]} We thus envisaged that substitution of the Si-bonded hydrogen of **3** with a bulky *tert*-butyl group, to give *tert*-butyltriisopropylsilane $i\text{Pr}_3\text{Si}-t\text{Bu}$ (**4**) might sufficiently enhance the rotational barriers as to make them detectable by NMR.

The ^1H -NMR spectrum of **4** is not informative since it comprises only two closely spaced single lines, one due to the 9 protons of the *tert*-butyl group and the other due to the 21 protons of the three isopropyl groups. The CH and Me signals of the latter are coincidentally superimposed at all temperatures^[6] and do not display any appreciable dynamic process on cooling. The ^{13}C -NMR data (75.45 MHz) for **4** were, at first glance, somewhat puzzling. The single line due to the *tert*-butyl methyl carbon atoms broadens significantly below -140°C , eventually splitting into two signals of relative intensity 1:2, separated by as much as 490 Hz at -163°C (Figure 1), yet over the same temperature range the CH and Me carbon signals of the isopropyl groups remain as relatively sharp singlets (the same is seen at 100.6 MHz).

Computer simulation of the line shape of the *tert*-butyl Me signals (Figure 1) yielded rate constants, from which a barrier of $\Delta G^\ddagger = 5.5 \pm 0.2 \text{ kcal mol}^{-1}$ was obtained. We can envisage three possible explanations for the observed spectral changes.

(i) If the rotation of the *tert*-butyl and the isopropyl groups were to occur in a concerted manner,^[7–10] the measured barrier would be for the simultaneous rotation of all four substituents. Such tight interlocking seems unlikely where three relatively long carbon–silicon bonds are involved.

(ii) If the *tert*-butyl group rotates independently and this process has an activation energy higher than that for rotation of the isopropyl groups, the value of $5.5 \text{ kcal mol}^{-1}$ would be for the lower of the two barriers, i.e. the rotation of the three isopropyl groups. It would, however, be some-

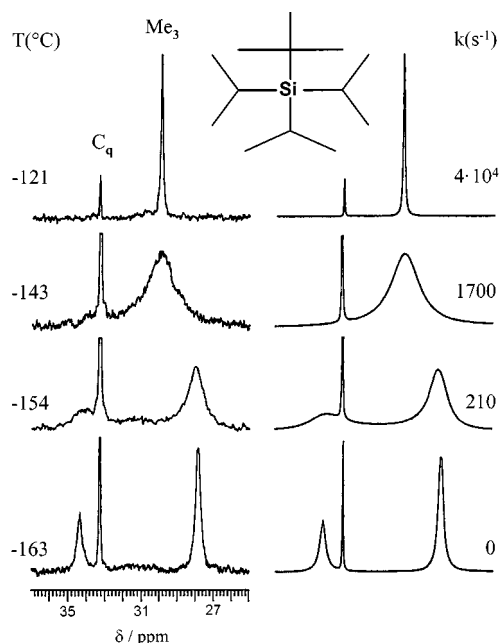


Figure 1. Experimental (left) ^{13}C -NMR spectrum (75.45 MHz) of the *tert*-butyl region of **4** in $\text{CF}_3\text{Br}/\text{CCl}_2\text{F}_2$ as a function of temperature, the sharp line being that of the quaternary carbon; on the right, the simulated spectra are reproduced, showing the calculated rate constants

how paradoxical if changes in the *tert*-butyl Me signal were to give information on the rotation of the isopropyl groups, the signals of which do not change significantly.

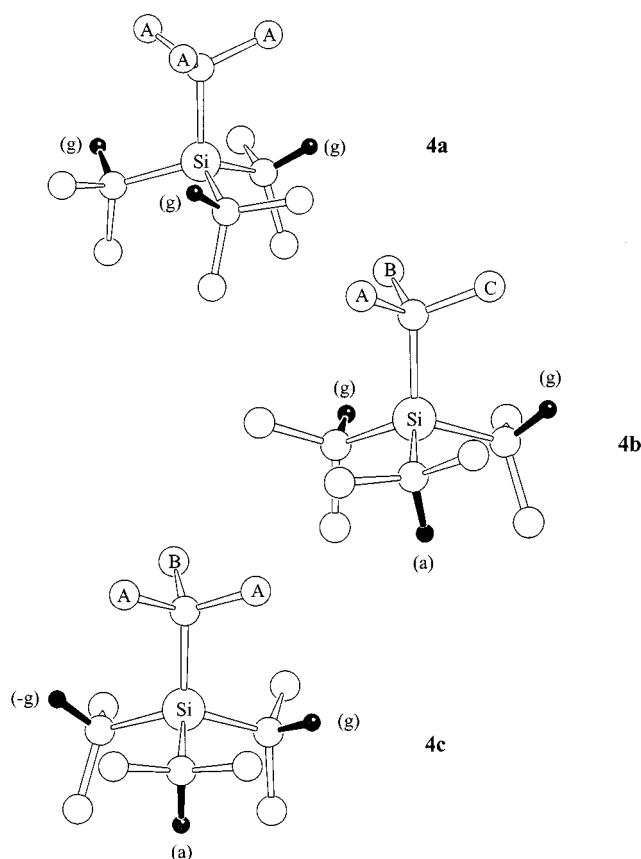
(iii) If the reverse situation were to apply, where the barrier associated with isopropyl group rotation is higher than that for *tert*-butyl group rotation, the measured barrier would then correspond to rotation of the *tert*-butyl group itself. It has to be pointed out, however, that *tert*-butyl rotations about sp^3-sp^3 bonds have been found to have barriers understandably higher than those for rotation of isopropyl groups.^[3,9,11,12]

For any of these three postulates, the coincidence of the isopropyl chemical shifts is apparently at variance with the observation of two well-spaced signals for the *tert*-butyl methyl groups.

The theory of the NMR exchange^[13] predicts that, for a given $\Delta G^\ddagger$ value, the dynamic process is detectable at a higher temperature for exchanging lines with a larger shift difference and at a lower temperature for lines with a smaller separation. Computer simulation shows that if discrete signals for the isopropyl groups have shift separations of only 15–25 Hz^[14] as opposed to the 490 Hz observed for the *tert*-butyl group and the barrier is $5.5 \text{ kcal mol}^{-1}$, such signals would not be resolved at the lowest accessible temperature of our experiments since a temperature lower than -170°C would be required.^[15] Such a small relative shift difference might imply some averaging of molecular environments and this will be considered further in discussing the calculations.

To account for the observed 1:2 intensity ratio of the anisochronous *tert*-butyl methyl signals in Figure 1, we considered the full range of possible isopropyl group confor-

mations with the aid of molecular mechanics calculations, both MMX^[16a] and MM3.^[16b] The 27 staggered arrangements accessible to three isopropyl groups attached to the same sp^3 atom, as in **4**, fall into seven categories as reported in Table 1, which also indicates the degenerate and enantiomeric conformations. From the relative energies reported, it can be seen that in the case of **4**, the three conformers (g,g,g), (a,g,g), and ($a,g,-g$) appear to be markedly more stable than the other four. These correspond to the three stable conformations, labelled **4a**, **4b**, and **4c**, respectively, in Scheme 1.



Scheme 1. MMX-computed structures of the conformers (g,g,g) **4a**, (a,g,g) **4b** and ($a,g,-g$) **4c**; the *tert*-butyl Me carbon atoms are labelled with the same upper case letter when equivalent

Table 1. MMX-, MM3-, and AM1-computed relative energies (in kcal mol⁻¹) for the conformers of derivatives **4–6**, iPr_3Si-R

Conformation ^[a]	(g,g,g) [1,1]	(a,g,g) [3,3]	($a,g,-g$) [3,0]	(a,a,g) [3,3]	(a,a,a) [1,0]	($g,g,-g$) [3,3]	($a,-g,g$) [3,0]
4 MMX	0.0	0.6	0.7	2.7	2.7	3.0	4.2
MM3	0.0	0.5	0.8	2.6	2.8	3.2	3.1
AM1	0.0	0.5	0.8	2.3	2.4	2.1	2.6
5 MMX	0.9	0.1	0.0	1.1	2.6	1.6	1.7
MM3	1.1	0.02	0.0	1.3	2.8	2.1	1.9
6 MMX	0.9	0.4	0.0	1.4	2.8	1.98	2.3
MM3	1.0	0.2	0.0	1.5	3.0	2.5	1.8

^[a] The first figure in [brackets] is the number of degenerate forms of that type, the second figure is the number of enantiomeric forms; these figures give the total of 27 mentioned in the text.

Conformer (g,g,g), **4a**, is calculated to be slightly more stable than (a,g,g), **4b**, and ($a,g,-g$), **4c**; it has a threefold symmetry axis coincident with the *t*Bu–Si bond (point group C_3), so that the three *tert*-butyl methyl groups (labelled A) will always yield a single NMR line, even when rotation about the *t*Bu–Si bond is slow on the NMR time scale. For this reason, the (g,g,g) conformer is incompatible with the experimental spectrum of Figure 1 and thus, in spite of the calculations, this conformation cannot be populated on the NMR time scale at low temperature. Conformer (a,g,g), **4b**, cannot account for the spectrum shown in Figure 1 either, since it does not have any element of symmetry (point group C_1); when rotation about the *t*Bu–Si bond is slow, three *tert*-butyl methyl signals should be seen, corresponding to the three diastereotopic methyl groups labelled A, B, and C in Scheme 1.^[17] Only the conformer ($a,g,-g$), **4c**, has the appropriate symmetry (point group C_s) to account for the low-temperature spectrum. As shown in Scheme 1, two methyl groups (labelled A) are enantiotopic, being related by a plane of symmetry, whereas the third one (labelled B) is diastereotopic. This is in agreement with the 2:1 ratio of the corresponding spectral lines seen at -163°C (Figure 1). Interconversion between two degenerate conformations having *anti* arrangements of their isopropyl groups is slow, as of course is rotation of the *tert*-butyl group.

Moving on from this very reasonable explanation in terms of a single kind of populated conformation for **4**, we now consider the possibility of a mixture of two different kinds of conformations rapidly interconverting at all temperatures, as was found for **1** and considered for **2**. Thus, the observed NMR changes may also be explained if the structure **4** is centred on the ($a,g,-g$) conformation **4c**, but is rapidly interconverting back and forth with a certain population of the remaining stable conformation type **4b**. This last type (a,g,g) and its enantiomer ($a,-g,-g$) are certainly populated in **1** and **2**. If, as before, *t*Bu–Si rotation and interconversion of **4c** with its two degenerate forms ($-g,a,g$) and ($g,-g,a$) are both slow on the NMR time scale, then, even though **4c** interconverts with **4b**, a 2:1 doublet will nonetheless be seen for the *tert*-butyl group. This second “equilibrating” picture has the advantage of not excluding a second conformation calculated to be very similar in energy and allowing a degree of averaging of the environments for the isopropyl groups, in accord with the small isopropyl chemical shift differences obtained by computer simulation as outlined above.

Any such mixture of conformations cannot, however, be extended to include the (g,g,g) conformation **4a**, calculated to be the most stable, owing, as mentioned above, to its C_3 symmetry.

Barriers to interconversion of the conformations have been calculated using the MM3 program.^[16b] The reliability of such calculations may be in doubt in view of the discrepancy concerning the relative energy observed and calculated for the (g,g,g) conformation **4a**, but nevertheless some interesting points emerge. The barrier to interconversion of conformations **4b** and **4c** is 5.1 kcal mol⁻¹. In the confor-

mations **4a–4c**, the barrier to rotation of the *tert*-butyl group is calculated to be 5.6 kcal mol^{−1} or greater (for instance, 6.1 kcal mol^{−1} in **4c**). Interconversion between degenerate forms of **4b** or **4c** is achieved by passing through the more symmetrical conformations **4a** (*g,g,g*) or **4d** (*a,g,g*); the latter pathway has an associated barrier of 6.2 kcal mol^{−1}, which is markedly lower than that (8.2 kcal mol^{−1}) associated with proceeding via the (*g,g,g*) conformation.

Overall, the calculated barriers are very similar, but the threefold rotation of the *tert*-butyl group seems to be slightly easier than attaining the higher energy symmetrical conformations **4a** or **4d** necessary for the interconversion of the degenerate stable conformations.

At this stage, we tentatively concluded that, despite the coincidence of the isopropyl group shifts, compound **4** actually adopts the (*a,g,−g*) conformation **4c** or is centred thereon, although further support for this was clearly desirable. In principle, high-resolution NMR spectra in the solid state might provide this, since the rotation of alkyl groups is known to be more hindered in the crystal than in solution.^[18] Anisochronous signals for diastereotopic carbon atoms can often be observed at much higher temperatures, thus allowing the detection of processes that are too rapid in solution. Furthermore, since the chemical environments experienced by the carbon atoms in the crystal are likely to be less varied than in solution, a splitting of the isopropyl signals in solid **4** might be observed. Since **4** is a liquid at room temperature, the ¹³C CP-MAS spectrum was recorded at about −100°C but, unfortunately, the resulting solid turned out to be quite disordered, thus yielding broad lines^[19] for the four carbon atoms (width at half-height > 200 Hz). Under these circumstances, it was impossible to identify any shift separation due to slow conformational interconversion processes.

To overcome this difficulty, we sought analogous molecules having similar symmetry, but with more polar character. This would be expected to produce more ordered solids, which might provide sharper spectral lines. Triisopropylsilyl chloride (**5**, *i*Pr₃Si-Cl) and the corresponding iodide **6** (*i*Pr₃Si-I) were investigated in this context. Both the chlorine and the iodine atoms have rather large van der Waals radii, which may make them sterically comparable with the *tert*-butyl group in **4**.^[20] The solution ¹³C-NMR spectra of **5** and **6** were found to display isochronous signals even at −165°C, although their lines were quite broad at that temperature (in both cases, the widths at half-height were 80 and 50 Hz for Me and CH, respectively, at 75.45 MHz). Thus, if the isopropyl group rotation is slow on the NMR time scale, the chemical shift separation in **5** and **6** must be smaller than the line width, which parallels the above result for **4**, in which rotation of the isopropyl groups is known to be restricted. It is not inconceivable that in **5** and **6** an insufficiently large chemical shift difference again prevents the observation of anisochronous signals, that would confirm slow rotation of the isopropyl group.

The parallel behaviour of the isopropyl group signals in **5**, **6**, and **4** at low temperature suggests that all three com-

pounds have similar stereodynamics. Indeed, calculations for **5** and **6** suggest that, as in the case of **4**, the (*g,g,g*), (*a,g,g*), and (*a,g,−g*) conformers are the most stable, having energies within about 1 kcal mol^{−1} of each other. The stability sequence is different, however, with the (*g,g,g*) conformer no longer being the most stable, but rather the (*a,g,−g*) conformer, albeit only marginally (Table 1). We then examined the NMR spectrum of compound **5** in the solid state in the hope of finding a barrier sufficiently higher than that in solution that would allow observation of the expected spectral changes.

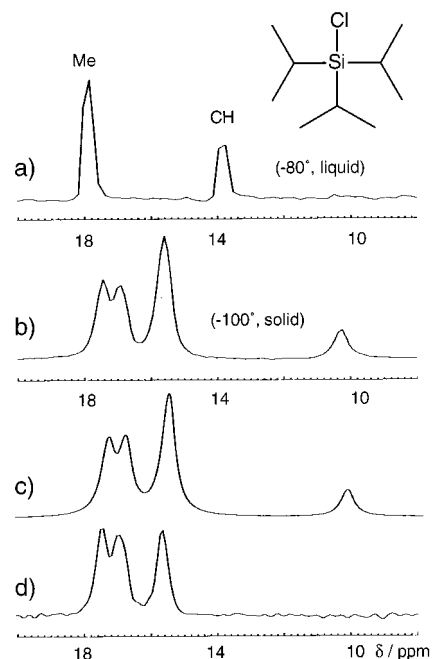
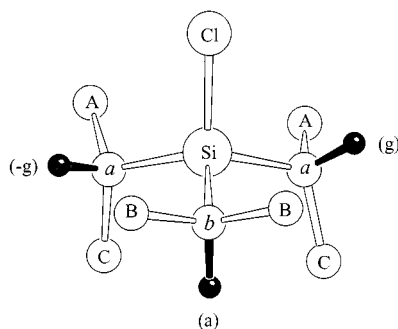


Figure 2. (a) ¹³C-NMR spectrum (75.45 MHz) of **5** as a neat liquid at −80°C; (b) CP-MAS spectrum of **5** in the solid phase at −100°C; (c) computer simulation of the previous trace (b) obtained by combining three methyl lines (ratio 2:2:2) and two CH lines (ratio 2:1); (d) CP-MAS solid-state spectrum, obtained at −100°C by means of the non-quaternary suppression pulse sequence, exhibiting only the three equally intense residual Me lines

In the neat liquid phase, we observed a pair of ¹³C lines due to the Me and CH carbon atoms ($\delta = 17.8$ and 13.9, respectively, at −80°C; Figure 2a; intensity ratio 6:3). These split into four signals (ratio 2:2:4:1) at −100°C when a solid phase was formed (Figure 2b). As shown in the computer simulation (Figure 2c), these signals are due to three Me lines with a 2:2:2 intensity ratio and two CH lines with a 2:1 intensity ratio,^[21] the upfield Me line (at $\delta = 15.7$) being superimposed on the more intense of the two CH lines. This interpretation fits with the averaged chemical shifts seen in the neat liquid spectrum (Figure 2a) and was confirmed by a spectrum obtained using the non-quaternary suppression pulse sequence (Figure 2d), which cancels out the CH signals completely, yielding three equally intense lines due to the residual Me signals. The signal equivalence observed in the low-temperature solution spectra of **5** is thus no longer seen in the solid state. Of the three calculated low-energy conformations of **5**, the (*a,g,−g*) conformation shown in Scheme 2 is the only one which fits with the peak multi-

plicity, and thus it would seem likely that only this single conformation is populated in the solid state.



Scheme 2. MMX-computed structure of conformer (*a,g,-g*) of **5**; the same letters (upper case for methyl and lower case italic for methine) are used to label symmetry-related carbon atoms

The results for both **4** and **5** thus point to structures essentially centred around the (*a,g,-g*) conformation. As a final source of information, we found twelve crystal structure reports pertaining to triisopropylsilyl groups attached to sp^3 -hybridized carbon atoms on searching the Cambridge Crystallographic Database.^[22] The isopropyl conformational set is (*a,g,-g*) in three of these structures, (*a,g,g*) in three others, (*g,g,-g*) in three more, and (*a,a,g*) in two. In only one case is the set (*g,g,g*), **4a**, the conformation so wrongly favoured by calculations. The fact that a small set of twelve reports produce examples of five of the seven conformational sets is consistent with the finding of molecular mechanics calculations that the conformations are not very different in energy.

Discussion

It is interesting to compare the contrasting low-temperature NMR results for hydrocarbons **1** and **2** with those for the silanes **4** and **5**. For **1**, there is slow interconversion of the enantiomeric sets of conformations but fast interconversion of degenerate conformations [(*a,g,g*) etc. via the (*g,g,g*) conformation]. For **2**, interconversion both within degenerate sets and between enantiomeric sets of the (*a,g,g*) type is slow. On the other hand, for **4**, and for **5** in the crystal, the stable conformation is centred around the symmetrical (*a,g,-g*) conformation with slow interconversion of degenerate sets.

The other striking result is the disagreement between experiment and calculations concerning the stability of the (*g,g,g*) conformation. The NMR observations for **4** and **5** show unequivocally that this conformation is not significantly populated and that there is a barrier of at least 5 kcal mol⁻¹ to attaining it, since otherwise the isopropyl groups could interconvert on the NMR time scale proceeding via this conformer. Calculations nevertheless predict that such a conformation should be the most stable in the case of **4** and that it should somehow be populated even in the case of **5**. It is seldom that experiment so clearly suggests, as for **4**, that calculations are not wholly reliable, unless one believes that for such a trialkylsilane this reflects a difference

between calculations on an isolated molecule (as in the gas-phase) and measurements in solution.^[23] In any case, it is not surprising that minor disagreements between an approximate theoretical model and experiment can be encountered for such relatively large molecules.^[24] The explanation lies partly in the degeneracy of conformations (see Table 1), for there are a total of nine versions of the (*a,g,-g*) and (*a,g,g*) conformations that might be populated, while there are only two versions of (*g,g,g*), and thus entropy disfavors the latter. Even so, there is no experimental evidence for this conformation of **4**, hence the low relative strain calculated for this conformation does not seem to be acceptable. The application of MM3 to silanes has been discussed by Chen and Allinger,^[25] but while a variety of quite highly substituted molecules were calculated and matched reasonably well with gas-phase structures, systems as conformationally complex as the triisopropylsilyl species investigated here were not examined.

Experimental Section

Materials

tert-Butyltriisopropylsilane (iPr₃Si^tBu, **4):** To a solution of *tert*-butyllithium (36 mmol) in anhydrous THF (20 mL) kept at -50°C was added 6.4 mL of commercially available triisopropylsilyl chloride (iPr₃SiCl, **5**), dissolved in THF (12 mL). After 1 h at low temperature, the mixture was allowed to react for an additional 2 h at ambient temperature and subsequently quenched with aqueous NH₄Cl. The resulting mixture was extracted with diethyl ether, and the combined extracts were dried and concentrated. The crude product was purified by distillation through a spinning-band device, having about 200 plates efficiency (b.p. 86°C at 2 Torr), and then subjected to column chromatography, eluting with pentane. - ¹H NMR (CDCl₃, 300 MHz): δ_H = 1.08 (s, 9 H, 3 × CH₃C), 1.25 (s, 21 H, 3 × CHCH₃ and 6 × CH₃CH). - ¹³C NMR (CDCl₃, 75.46 MHz): δ_C = 11.0 (3 × CH), 18.9 (6 × CH₃CH), 28.8 (3 × CH₃C), 33.3 (CCH₃). The carbon signals were assigned by a DEPT sequence and a HETCOR experiment showed that the isopropyl methine and methyl ¹H signals are coincidentally superimposed at δ = 1.25 through their correlations with the ¹³C signals at δ = 11.0 and δ = 18.9 (similar coincidence was also observed in the ¹H-NMR spectrum of **5**).

Triisopropylsilyl Iodide (iPr₃SiI, **6):** Prepared according to the literature.^[26]

NMR Measurements: The samples for the low-temperature measurements were prepared by connecting NMR tubes containing the desired compounds and a few drops of [D₁₂]TMS (for locking purposes) to a vacuum line and condensing therein gaseous CF₃Br and CCl₂F₂ in 1:4 proportions by means of liquid nitrogen cooling. The tubes were subsequently sealed in vacuo and introduced into the precooled probe of a 300-MHz Varian Gemini spectrometer operating at 75.45 MHz for ¹³C or a 400 MHz Varian Mercury spectrometer operating at 100.6 MHz. Temperatures were calibrated by substituting the sample with a precision Cu/Ni thermocouple before the measurements. The high-resolution solid-state CP-MAS ¹³C-NMR spectra were obtained at 75.45 MHz (Bruker CXP 300). The liquid compounds were introduced into a tightly sealed 7-mm zirconia rotor and spun at the magic angle at a speed of 3–4 kHz; on cooling, the compounds become solid, allowing attainment of cross-polarization conditions. The cooling was achieved by means

of a flow of dry nitrogen, precooled in a heat exchanger immersed in liquid nitrogen. The temperatures within the solid-state probe were calibrated from the shift dependence of the ^{13}C -NMR lines of 2-chlorobutane absorbed upon solid dicalite, assuming a dependence equal to that observed in the neat liquid, which had been previously calibrated using the aforementioned Cu/Ni thermocouple. The chemical shifts were measured, by replacement, with respect to the lower frequency signal of adamantane ($\delta = 29.4$). — Complete line-shape simulations for both the solution and solid-state spectra were achieved by using a computer program for PCs based on the Block equations. In the solution spectrum of **4**, the intrinsic line width of the *tert*-butyl methyl signal was assumed to be equal, at the same temperature, to those of the isopropyl carbon signals that do not exhibit line-broadening effects due to the exchange process. In any case, errors in these values of as much as 30% had little effect on the rate constants since the latter values are so much higher than the intrinsic line widths. Over the examined range, the $\Delta G^\ddagger$ values were found to be temperature-independent, as is often observed for conformational processes,^[27] so that they remained essentially coincident with the $\Delta H^\ddagger$ values.

Acknowledgments

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