Conformational Studies by Dynamic NMR. 71.[1] Stereodynamics of Triisopropyl(aryl)silanes in Solution and in the Solid State

J. Edgar Anderson*

Chemistry Department, University College, Gower Street, London WC1E 6BT, UK

Daniele Casarini

Chemistry Department, University of Basilicata, Potenza, Italy

Lodovico Lunazzi* and Andrea Mazzanti

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

Received October 11, 1999

A study has been carried out of the conformations of triisopropyl(aryl)silanes $(i\text{-Pr})_3$SiAr, (Ar = phenyl, 1-naphthyl, and 2-naphthyl) both as to the orientation of the three isopropyl groups and the conformation about the silicon−aromatic bonds. The report comprises dynamic NMR studies of conformational interconversions in solution and in the solid state as well as molecular mechanics calculations. The barriers for the stereomutation processes measured in the crystalline state were found significantly higher than those in solution.

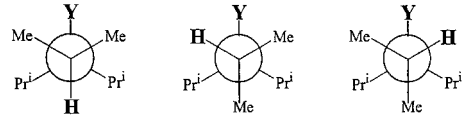
Introduction

When three secondary groups, such as isopropyl, are attached to the same tetrahedral central atom, their interaction leads to interesting ranges of conformations and interconversion processes.[2] Each isopropyl group is sterically anisotropic, resembling a methyl group on approach from the methine side and a *tert*-butyl group on approach from the side of the geminal methyl groups. In compounds such as $(i\text{-Pr})_3$X−Y, the interactions of isopropyl groups with each other and with X and Y, which largely determine the energy of conformations, should depend on the length of C−X and X−Y bonds (which can be quite different as X and Y change), on the C−X−C and C−X−Y bond angles, and on the conformations along individual *i*-Pr−X bonds, which determine the confrontation between isopropyl groups. The steric demands of group Y, if it is large, have a significant effect on conformations.

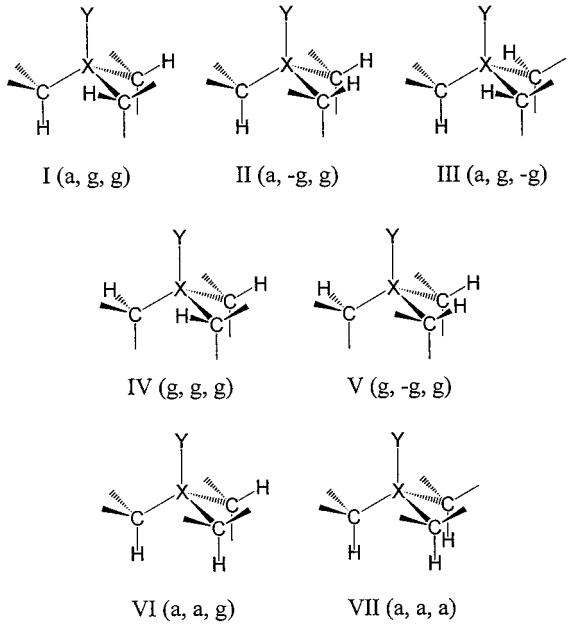
The conformation of any one isopropyl group with respect to the rest of the molecule may be one of the three kinds conveniently defined by the torsion angle of the methine proton with respect to the X−Y bond. These are *anti* "a", +*gauche* "g", and −*gauche* "−g" and are shown in Scheme 1. Torsion angles may often be quite different from 60° and 180°, if such a distortion reduces the interactions of groups. The overall molecule can then be represented as in the idealized structures I−VII (Scheme 2) which make no attempt to indicate possible distortions. The labels beneath I−VII are self-explicatory, the isopropyl group conformations being reported in the order left, central, right.

With three staggered conformations for each of three X−CH bonds there are $3^3 = 27$ conformation types for the overall molecule, but because of degenerate and enantiomeric forms, structures I−VII represent all possibilities. The (a, g, g) conformation I, for example, is found as degenerate forms (g, a, g) and (g, g, a), and also

Scheme 1. Conformation of an Isopropyl Group in $(i\text{-Pr})_3$X−Y. Torsion Angle H−C−X−Y Determines the Label



Scheme 2. Seven Conformations of $(i\text{-Pr})_3$X−Y That Are Not Degenerate nor Enantiomeric



(1) (a) Part 70: Casarini, D.; Lunazzi, L.; Mazzanti, A.; De Lucchi, O. Fabris, F. *J. Org. Chem.* **2000**, *65*, 883−888. (b) Part 69: Anderson, J. E.; Casarini, D.; Lunazzi, L.; Mazzanti, A. *Eur. J. Org. Chem.* **2000**, 479.

(2) Anderson, J. E.; Casarini, D.; Lunazzi, L. *J. Org. Chem.* **1996**, *61*, 1290.

10.1021/jo991580p CCC: $19.00
Published on Web 03/01/2000

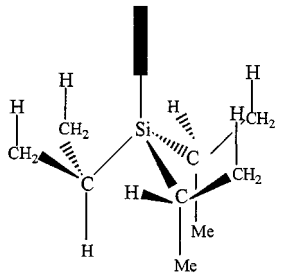
as three enantiomeric versions (a, −g, −g), (−g, a, −g) and (−g, −g, a), that is six in all, so when talking of the (a, g, g) conformation we include these other five versions if that is appropriate. Even if such conformations were so stable as to be the only kind populated, there would still be a complex dynamic equilibrium within each degenerate set or between two enantiomeric sets of conformations. Structure I, V, and VI each exist as two enantiomeric sets, each containing three degenerate forms. Structures II and III both exist as three degenerate forms; there are two enantiomeric forms of IV, whereas structure VII is unique: thus the 27 expected conformations.

It will be noted that *anti* conformations maximize parallel 1,3-interactions particularly of methyl groups, round the middle of the molecule near Y (see conformation VII) while *gauche* conformations balance such compression in the middle, and remote from Y at the bottom of the molecule (see conformations IV and V). The size of Y might therefore affect the population of such conformations for individual isopropyl groups, and of course rotation away from perfect staggering of *i*-Pr−X bonds may reduce interactions.

Triisopropylmethane (*i*-Pr)$_3$CH may be taken as a model for such compounds, and it exists[3] as a rapid equilibrium between (a, g, g) and (g, g, g) types of conformation, viz. I and IV. Vicinal coupling constants suggest that there is about three times as much of the former conformation, so allowing for its higher degeneracy, the two conformations are of very similar energy. Molecular mechanics calculations favor the former by only 0.21 (MM2) or 1.07 (MM3) kcal mol^{-1}. There is a barrier calculated to be about 3 kcal mol^{-1} to the interconversion of I and IV and thus, because of the high symmetry of the latter, to interconversion of degenerate forms of I. There is an experimentally measured (NMR) barrier of 6.6 kcal mol^{-1} to interconversion of I and IV with the [(a, −g, −g) + (−g, −g, −g)] enantiomeric set. Similar results have been reported[4] for tricyclohexylmethane for which a crystal structure confirms that (a, g, g) conformation and its enantiomer are preferred in the solid state.

Triisopropylethane (*i*-Pr)$_3$C−CH$_3$ shows behavior particularly relevant to the present work, having a group Y that is more sterically demanding.[5] The preferred conformation still appears to be (a, g, g), but now the (g, g, g) conformation, which places three methyl groups in the proximity of the substituent Y, is much less stable. As the temperature is lowered, two sets of changes were seen in the NMR spectrum, and at the lowest temperature six separate signals were detected for isopropyl methyl groups[5] in contrast to two signals for (*i*-Pr)$_3$CH.[3] The two sets of changes correspond first to slowing the interconversion of degenerate conformations [(a, g, g) to (g, a, g) to (g, g, a)] via the (g, g, g) conformation, and second to slowing the interconversion of enantiomeric conformations [(a, g, g) to (a, −g, −g) to etc.] via the (a, a, g) and (a, a, −g) conformations, with barriers of 6.8 and 6.4 kcal mol^{-1}, respectively.[5] Other compounds that were studied are triisopropylamino,[2,6,7,8] and tris(diethylamino)methane.[2]

Scheme 3. Example of a Conformation III (a, g, −g) Having the Planar Substituent Placed in a Channel Formed by Four Isopropyl Methyl Groups



We now report investigations of three triisopropyl(aryl)silane compounds:

$$(i\text{-Pr})_3\text{Si}-\text{Ar}$$

Ar = Ph (**1**); Ar = 2-naphthyl (**2**); Ar = 1-naphthyl (**3**)

All four carbon−silicon bonds are markedly longer than the corresponding carbon−carbon bonds, so the interactions of isopropyl groups with Y and with each other should be reduced. We have already reported[1b] a study of aliphatic triisopropylsilyl compounds (*i*-Pr)$_3$Si−Y, where Y = H, Cl, *t*-Bu and found that the preferred conformation is (a, g, −g). Barriers to isopropyl rotation are indeed low in these compounds so that in the case of (*i*-Pr)$_3$Si−Cl, for instance, isochronous NMR signals were observed even at −165 °C in solution. Only in the low temperature CP-MAS NMR solid state spectra could this rotation be rendered sufficiently slow for an experimental observation.

As an additional piece of information we refer to the Cambridge Crystallographic Data Base[9] where nine structures with a triisopropylsilyl group attached to an sp^2-hybridized atom were retrieved. Eight of these adopt the (a, g, −g) conformation III, with the planar system placed in a channel formed by four of the methyl groups (as shown diagramatically in Scheme 3), with only one example preferring the (a, a, g) conformation VI.

Results and Discussion

Triisopropyl(phenyl)silane (1) and Triisopropyl-(2-naphthyl)silane (2). The 75.5 MHz ^{13}C NMR spectrum of PhSi(Pr^i)$_3$ (**1**) in CF_2Cl_2/CF_3Br displays two sharp lines for the Me and CH carbons down to −130 °C. Below −150 °C these lines broaden and eventually split, at −166 °C (Figure 1), with the methyl carbons yielding three equally intense lines, and the aliphatic methine carbons yielding a pair of lines, with a 2:1 intensity ratio. The lines of the phenyl carbons, on the contrary, always remain sharp.

Computer line shape simulation of both the Me and aliphatic CH signals yields essentially the same rate constant (72 s^{-1} at −158 °C), which corresponds to a $\Delta G^{\ddagger}$ value of 5.5 kcal mol^{-1}.

(3) Anderson, J. E.; Koon, K. H.; Parkin, J. E. *Tetrahedron* **1985**, *41*, 561.
(4) Columbus, I.; Biali, S. E. *J. Org. Chem.* **1993**, *58*, 7020.
(5) Anderson, J. E.; Bettels, B. R. *Tetrahedron* **1990**, *46*, 5353.
(6) Bock, H.; Göbel, I.; Havlas, Z.; Liedle, S.; Oberhammer *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 187.
(7) Boese, R.; Bläser, D.; Antipin, M. Y.; Chaplinski, V.; de Meijere, A. *Chem. Commun.* **1998**, 781.
(8) Bock, H.; Göbel, I.; Bensch, W.; Solouki B. *Chem. Ber.* **1994**, *127*, 347.
(9) Allen, F. H.; Davies, J. E.; Galloy, J. J.; Johnson, O.; Kennard, O.; Maccrae, C. F.; Mitchell, E. M.; Smith, J. M.; Watson, D. G. *J. Chem. Inf. Comput. Sci.* **1991**, *31*, 187 ("July 1997 CSD Release").

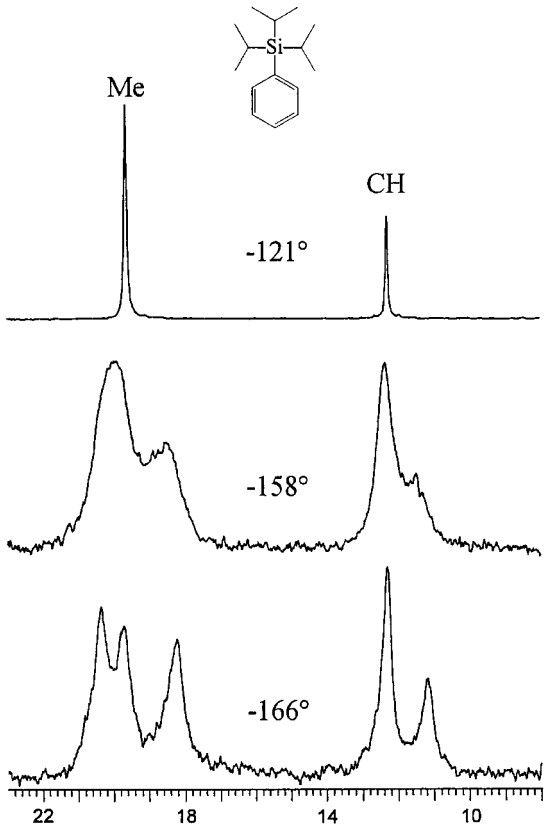


Figure 1. Temperature dependence of the ^{13}C (75.5 MHz) aliphatic signals of **1**.

Table 1. MM3 Relative Energies (E, in kcal mol^{-1}) of Ph-Si(*i*-Pr)$_3$, 1. the Dihedral Angles (ϑ) Are Those between the C−H Isopropyl and the Phenyl−Si Bonds

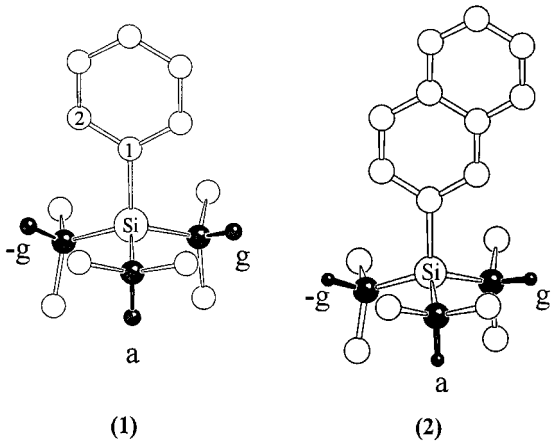
conformation	*E*	ϑ_1	ϑ_2	ϑ_3
(a, g, −g)	0	179	64	−51
(a, a, g)	1.23	−166	−153	58
(g, −g, −g)	1.67	76	−46	−48
(a, −g, g)	1.82	180	−77	76
(a, g, g)	1.95	− 179	51	90
(g, g, g)	2.81	41	53	51
(a, a, a)	6.01	−175	146	−155

To explain the spectral multiplicity of the ^{13}C spectrum at low temperature the molecule must adopt a conformation where one methine carbon is diastereotopic with respect to the remaining two enantiotopic methine carbons. A possible conformation of this type is that having one C−H bond *anti* to the Si−Ph bond, with the other two C−H bonds *gauche*, their corresponding H−C−Si−Ph dihedral angles being opposite in sign, as in conformations (a, g, −g) or (a, −g, g).

The absence of line broadening for the lines of the phenyl ring carbons can be explained in two possible ways: either the Ph−Si rotation is still fast at −166 °C, or the phenyl group is locked in a position where the ortho and meta carbons remain equivalent.

Molecular mechanics calculations (MMX[10] and MM3[11] force field) found the seven expected conformational types, which with their degenerate or enantiomeric versions make up the 27 possible staggered arrangements. As shown in Table 1 the (a, g, −g) conformation

Scheme 4. Computed MM3 Structures of the Preferred Conformers of 1 (left) and 2 (right)



(i.e., the one having the two *gauche* CH bonds pointing toward the *anti* substituent as shown in Scheme 4, left) is indeed the most stable form and also PM3 and AM1 calculations[12] confirm that. The corresponding three ϑ values in Table 1 represent the three dihedral angles C1−Si−C−H made by each of the CH bonds of the isopropyl moieties with the Si−Ph bond. In this conformation two CH carbons are in practice enantiotopic, owing to the low-energy libration processes, having an averaged angle of $|58 \pm 7°|$, i.e., the mean between $|+64|$ and $|-51°|$ (Table 1). This conformation also accounts for the existence of three pairs of methyl groups, as experimentally observed, because the methyl carbons of the isopropyl group having the CH bond in the position *anti* are obviously enantiotopic. The two methyl carbons of the isopropyl group having the C−H bond in the position +*gauche* are diastereotopic, but each of them is symmetry-related to the corresponding methyl of the isopropyl group having the CH bond in the position −*gauche*. The calculations also indicate that this (a, g, −g) conformation has the plane of the phenyl ring perpendicular to the molecular plane of symmetry (i.e., the dihedral angle C2−C1−Si−CH$_{anti}$ is about 90°, as shown in Scheme 4, left). Thus, even if the Ph−Si rotation is slow on the NMR time scale at low temperature, the ortho and meta carbons will remain enantiotopic. The other computed energy minima of Table 1 do not bear the symmetry corresponding to the experimental spectrum, with the exception of the other (a, −g, g) conformation (i.e., the one with the *gauche* C−H bonds pointing away from CH bond *anti*, as in conformer II of Scheme 2) which, however, has a relative energy much too high (1.8 kcal mol^{-1}) to be appreciably populated (in this conformation the phenyl ring is coplanar, rather than orthogonal with respect to the molecular plane of symmetry).

Two rotation pathways about the (Me)$_2$CH−Si bond are available for the two types of isopropyl groups in the most stable (a, g, −g) conformation, and the corresponding barriers were computed (in the MMX framework) by driving the C1−Si−C−H angles ϑ in steps of 10°, whereas allowing all the other parameters to relax. Two maxima of energy were computed for the rotation of the isopropyl having the CH bond in the *anti* position, their values being 4.0 (when $\vartheta = 0°$) and 5.6 kcal mol^{-1} (when $\vartheta = 115°$). The rotation process for the other two isopropyl

(10) Program PC Model, Serena Software, Bloomington, IN.
(11) Allinger, N. L.; Yu, Y. H.; Lii, J.-H. *J. Am. Chem. Soc.* **1989**, *111*, 8551.
(12) MOPAC package computer program.

groups (having the C−H bonds in the *gauche* positions) also yielded two barriers: 5.4 and 6.0 kcal mol^{-1}, when $\vartheta = 0°$ and $= 115°$, respectively. To achieve a complete rotation, the isopropyl groups have thus to overcome a barrier of 5.6 (*anti*) and of 6.0 (*gauche*) kcal mol^{-1}; these values are so close as to be indistinguishable, and their average (5.8 ± 0.2 kcal mol^{-1}) matches very well the experimental result (5.5 ± 0.2 kcal mol^{-1}).

As mentioned above, it is impossible to know whether the phenyl ring is still in rapid rotation or whether its motion is slow on the NMR time scale since, owing to the symmetry, the spectral multiplicity is the same in both cases. To decide between these two situations, we investigated the triisopropyl(2-naphthyl)silane, **2**, where the degeneracy has been eliminated by substituting the phenyl with the 2-naphthyl moiety, which has essentially the same steric requirements. MMX and MM3 calculations confirmed that the most stable form of **2** is still the (a, g, −g) conformation and that the plane of the naphthyl ring is also orthogonal to the Si−C−H$_{anti}$ plane. Thus, if the rotation of the 2-naphthyl ring becomes slow on the NMR time scale, the two *gauche* isopropyl groups would display two different signals, yielding, as a whole, three methine carbon lines. Likewise, the three methyl carbons signals of derivative **1** will become six in the case of **2** (Scheme 4, right). The aliphatic signals of the spectrum of **2** at −165 °C were essentially equal to those **1** at the same temperature, a clear indication that the aryl−Si rotations are still rapid when the *i*-Pr−Si rotation has become slow. Also the barrier for the process, which makes equivalent the isopropyl signals of **2** (5.5 ± 0.2 kcal mol^{-1}), is the same as in **1**.

The solid-state CP-MAS spectrum of crystalline **2** at room-temperature yields a single line for both the methyl and the methine carbons. On lowering the temperature the methyl line broadens and splits, at −65 °C, into two signals with an integrated intensity of 1:2 (Figure 2). As the width of the more intense signal is markedly broader than the other, the spectrum must be interpreted as due to three lines, two of which are not resolved, indicating that the preferred conformer has the same symmetry (a, g, −g) as in solution. Contrary to the methyl, the methine carbons signal remains a single line at low temperature because the expected 2:1 doublet, which was observed in solution, has, in the solid, a shift difference smaller than the line width. The absence of additional splitting with respect to the solution spectrum indicates that also in the solid state the naphthyl−Si bond rotation is still rapid in the NMR time scale, at least at −65 °C. Computer simulation of the methyl signals at about −15 °C yields a $\Delta G^{\ddagger}$ value of 13.0 ± 0.3 kcal mol^{-1}. The dynamic process of **2** in the solid state has therefore a barrier much higher than that (5.5 kcal mol^{-1}) measured in solution, this being a consequence of the resistance to molecular motions occurring in the crystal lattice, as observed in a number of other cases.[13]

Triisopropyl(1-naphthyl)silane (3). When the 2-naphthyl is replaced by the more sterically demanding

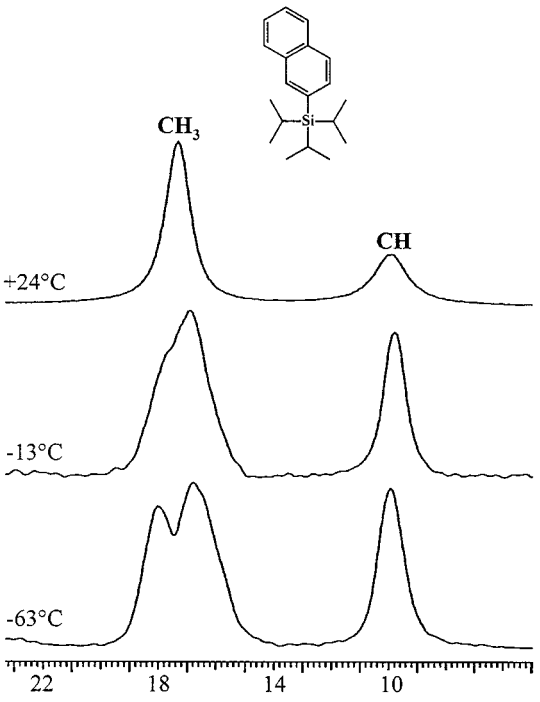


Figure 2. Aliphatic region of the solid-state CP-MAS spectrum (75.5 MHz) of **2** as function of temperature. The Me signal, which a single line at +24 °C, splits into a 1:2 pair of lines at −63 °C.

1-naphthyl group [(*i*-Pr)$_3$Si−Ar, with Ar = 1-naphthyl, **3**], the spatial requirements are greatly modified, and different conformations undergoing different stereodynamic processes are expected to occur.

Dynamic NMR in Solution. All the ^{13}C lines of **3** broaden on lowering the temperature below −120 °C and subsequently sharpen, eventually displaying two groups of signals at −165 °C, corresponding to a pair of conformers. At this temperature the isopropyl methine carbons yield a pair of 2:1 signals in the range 12−14 ppm and three 1:1:1 signals in the range 16−18 ppm (Figure 3, bottom left trace), their relative proportion being about 0.9:1, respectively.[14] The single methyl line is likewise split into a number of overlapping peaks, that appear as six signals, with a 1:1:2:3:3:2 intensity ratio as suggested by computer simulation. The presence of two almost equally populated conformers is confirmed by the spectrum of the aromatic region, where three lines are also split into pairs of nearly equally intense peaks at −165 °C.

The patterns of the aliphatic CH signals at −165 °C indicate that one of the two conformers is wholly asymmetric, thus chiral, having three equally intense lines, whereas the other conformer comprises a plane of symmetry, since it displays two lines with a 2:1 intensity ratio. Molecular mechanics calculations predicted a very large number of energy minima for **3**, due to the presence of the 1-naphthyl moiety, which allows many more possible dispositions for the isopropyl groups, with respect to the aromatic substituent, than those available in the case of **1** or **2**. A number of these forms, including all the most stable, are reported in Table 2, where they are labeled according to Scheme 5.

(13) Miller, R. D.; Yannoni, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 7396. Elguero, J.; Fruchier, A.; Pellegrin, V. *J. Chem. Soc., Chem. Commun.* **1981**, 1207. Riddell, F. G.; Arumagam, S.; Anderson, J. E. *J. Chem. Soc., Chem. Commun.* **1991**, 1525. Lambert, J. B.; Xue, L.; Howton, S. C. *J. Am. Chem. Soc.* **1991**, *113*, 8958. Barrie, P. J.; Anderson, J. E.; *J. Chem. Soc. Perkin Trans. 2* **1992**, 2031. Riddell, F. G.; Arumagam, S.; Harris, K. D. M.; Rogerson, M.; Strange, J. H. *J. Am. Chem. Soc.* **1993**, *115*, 1881. Riddell, F. G.: Cameron, K. S.; Holmes, S. A.; Strange, J. H. *J. Am. Chem. Soc.* **1997**, *119*, 7555. Casarini, D.; Lunazzi, L.; Mazzanti, A. *J. Org. Chem.* **1998**, *63*, 9125.

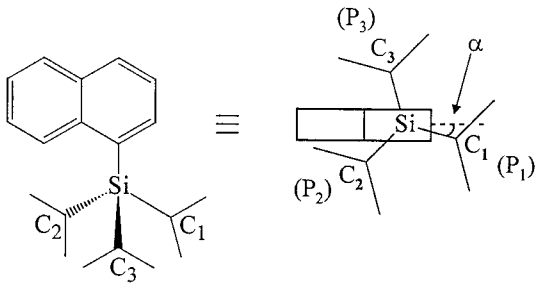
(14) The ratio changes slightly at higher temperatures, eventually becoming 1.1:1 at −143 °C.

Table 2. MM3 Relative Energies (E, in kcal mol^{-1}) for the Eight More-Stable Conformers of Ar−Si(i-Pr)$_3$ (Ar = 1-naphthyl, 3). Conformers with Energies Higher than 1.9 kcal mol^{-1} are not Reported, Except (g, g, g) and (a, a, a). The Numbering is that of Scheme 5. The Dihedral Angles (ϑ) Are Those between the C−H Isopropyl and the Naphthyl−Si Bonds

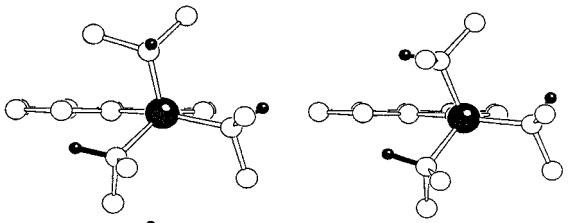
conformation	E	α[a]	ϑ_1	ϑ_2	ϑ_3
(g, −g, a) **3a**	0	−15	49	−75	−176
(g, −g, g) **3b**	0.23	−5	49	−79	44
(a, −g, g) **3c**	0.36	0	180	−80	80
(a, −g, a) **3d**	1.35	−8	−175	−79	−145
(g, a, a) **3e**	1.56	−14	54	136	177
(a, −g, −g) **3f**	1.57	−16	−169	−83	−76
(a, −g, a) **3g**	1.69	−22	−163	−74	−155
(g, −g, g) **3h**	1.86	−12	50	−80	−91
(g, g, g)	4.2	15	35	66	63
(a, a, a)	6.0	−45	−131	172	−155

[a] For the meaning of the angle α see Scheme 5.

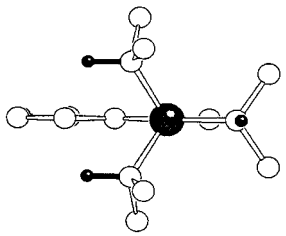
Scheme 5. Schematic View of Ar−Si(i-Pr)$_3$ (Ar = 1-naphthyl, 3) along the Ar−Si Bond. C_1, C_2, C_3 Identify the CH Carbons (see Table 2). P_1, P_2, P_3 Correspond to the Spatial Positions with Respect to a Fixed Naphthalene Ring



Scheme 6. Computed MM3 Structures of the Three More Stable Conformers of 3



3a **3b**



3c

There are three conformations (**3a**, **3b**, **3c**) with very similar energies (they lie within 0.36 kcal mol^{-1}, as reported in Table 2) that are much more stable than all the others (even the fourth next stable conformation **3d** has an energy more than 1 kcal mol^{-1} higher).

As shown in Scheme 6, conformation **3c** has a plane of symmetry so that a 2:1 doublet is expected for the corresponding methine carbons, in agreement with the signals observed at −165 °C (Figure 3, 12−14 ppm region). The corresponding methyl signals should appear as a 2:2:2 triplet, and this too is compatible with the spectrum observed at −165 °C (Figure 3). Conformers **3a** and **3b** are both asymmetric and either should give rise to a 1:1:1 CH triplet, as observed at −165 °C (Figure 2, 16−18 ppm region), or to six equally intense methyl signals, which are again compatible with the methyl signals observed at the same temperature. It is notable that **3a** and **3b** differ only in the θ_3 torsion angles (their values being −176° and 44°, respectively, as in Table 2). As a consequence their interconversion requires rotation of only isopropyl no. 3 (Scheme 5) with no significant adjustment of the other torsion angles. Indeed MM3 calculations suggest a barrier of only 4.8 kcal mol^{-1} for this process. Therefore, it is conceivable to propose that the above-mentioned aliphatic lines corresponds to the weighted average of the signals of **3a** and **3b**.[15]

The dynamic process appearing in the spectrum at temperatures higher than −165 °C shows a quite unexpected feature. The three methine carbon lines at 16−18 ppm broaden and coalesce (at −149 °C) into a single signal (17.0 ppm), and the two lines at 12−14 ppm do likewise at about the same temperature, to give a single line at 13.4 ppm. On further raising the temperature, these two single signals begin to broaden again and only above −135 °C coalesce into an unique, sharp CH line at 15.1 ppm. These features point out the presence of independent dynamic processes, each with its own energy of activation which, although quite similar, are undoubtedly distinct. One such process exchanges the isopropyl groups within the structure which gives rise to a triplet (rate constant k_a), and a second process exchanges the isopropyl groups within the structure which gives rise to a 2:1 doublet (rate constant $k_{a'}$), whereas the third process reflects exchange between those two types of structures (rate constant k_b), i.e., the triplet as a whole and the doublet as a whole. In principle k_a values are not equal to $k_{a'}$ values, and indeed slightly different sets for such values were employed in the simulation (Figure 3, right). From this interpretation a barrier with a $\Delta G^{\ddagger}$ of 5.7 kcal mol^{-1} corresponds to the rate constants k_a, a $\Delta G^{\ddagger} = 5.9$ kcal mol^{-1} corresponds to $k_{a'}$, and the highest barrier ($\Delta G^{\ddagger} = 6.25$ kcal mol^{-1}) corresponds to the rate constants k_b.

In the aromatic region each conformer only has a single line for each naphthyl carbon, so that the two nearly equally populated conformers can yield only the single barrier for their mutual interconversion, rather than the three values afforded by the much more complex aliphatic region. Of the 10 aromatic signals only three turned out to have shift differences large enough to display the line-broadening effects due to a dynamic process. The temperature dependence observed for the line of the quaternary carbon at the furthest downfield field is reported in Figure 4. It is quite evident, however, that such a signal splits in an asymmetric manner (the upfield line at 138.8 ppm is much broader than the downfield one at 140.05 ppm), yet at the lowest temperature, where the exchange process has become slow, the two lines are equally sharp. This is typical of a major species exchanging with a substantially shifted minor one and indeed in

(15) Unless the exchanging lines have an extremely high shift difference, exchange broadening cannot be detected when the barrier is as low as 5 kcal mol^{-1}. As we shall discuss later, such a large separation only occurred for a single aromatic line, so that this assumption eventually found experimental support.

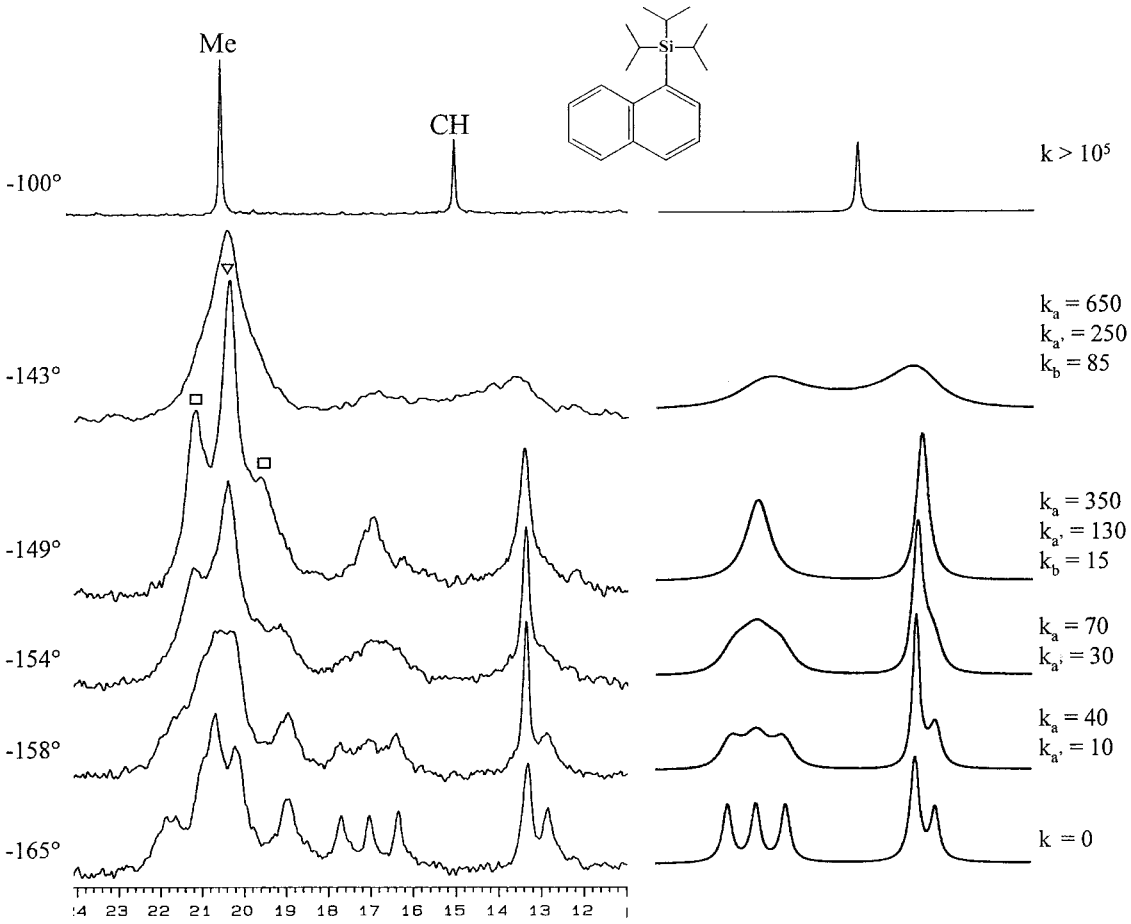


Figure 3. Left: Temperature dependence of the ^{13}C (75.5 MHz) aliphatic signals of **3**. Right: computer simulation of the methine carbon signals obtained with the rate constants (in s^{-1}) reported (see text for the meaning of k_a, $k_{a'}$, and k_b).

the spectrum at −165 °C an additional line at 133.95 ppm (relative intensity about 15%) was detected. This line disappears when the temperature is increased by a few degrees. Computer line shape simulations (Figure 4) were obtained with rate constants (k_a) corresponding to a barrier of 5.7 kcal mol^{-1} (a value which turns out to be equal to the lowest barrier determined in the aliphatic region) and with a second set of rate constants (k_c) corresponding to an even lower barrier of 5.4 kcal mol^{-1}. The latter process (which is that due to the exchange of the small line at 133.95 ppm with its major companion at 138.8 ppm) could be observed only in this case (and not in the case of the aliphatic lines, nor of other aromatic lines) owing to the fortunate occurrence of an unusually large shift separation (i.e., 366 Hz at 75.5 MHz).

It is now necessary to account for the observations that, on raising the temperature to −149 °C, the rapidly exchanging set (**3a** + **3b)** and conformer **3c** are able to make their own CH carbons dynamically equivalent (each thus giving a single CH signal) with constants k_a and $k_{a'}$ lower than that (k_b) for interchanging with each other. This requires that both the pair (**3a** + **3b)** and **3c** each scramble the CH lines without losing their conformational identity. Such a scrambling requires not only appropriate rotation of the isopropyl groups but also a change of their positions with respect to the naphthalene ring, which implies some rotation about the naphthyl−Si bond. Even in the presence of all these motions, the two conformations, nonetheless, must not interchange. In the presence of a rapidly rotating naphthyl substituent, conformer **3c** exists in three degenerate forms (a_1, $-g_2$, g_3), (g_1, a_2, $-g_3$) and ($-g_1$, g_2, a_3) which are labeled **3c**, **3c′**, and **3c″**, respectively. Likewise there are degenerate forms **3a′** and **3a″** for **3a** and **3b′** and **3b″** for **3b**. [16]

Scheme 7 shows how scrambling may be achieved in the case of **3c**. Rotation of each isopropyl group in turn, accompanied at some point by a naphthyl−Si rotation, interconverts **3c** into **3c′**, and an analogous set of rotations leads either **3c** or **3c′** to **3c″**. Even the most stable of the intermediate conformations (i.e., **3e**) is too high in energy (see Table 2) to be significantly populated; thus all of them are experimentally invisible. When such a process if fast in the NMR time scale, each carbon would spend an equal time in the *anti*, *+gauche*, *−gauche* environments, so that a single averaged signal will be seen. On this pathway, conformers **3a** or **3b** have never been visited.

Scheme 7. Possible Pathway for the Interconversion of the Three Degenerate Forms 3c, 3c′, 3c″ ($\Delta G^{\ddagger}$ = 5.9 kcal mol^{-1}). The Conformers in Square Brackets Have Too High an Energy To Be Appreciably Populated

3c, (a_1, $-g_2$, g_3) → [a_1, a_2, g_3] → [a_1, a_2, $-g_3$] → (g_1, a_2, $-g_3$), **3c′**

3c′, (g_1, a_2, $-g_3$) → [g_1, a_2, a_3] → [$-g_1$, a_2, a_3] → ($-g_1$, g_2, a_3), **3c″**

Scheme 8 shows how an analogous scrambling may be achieved in the case of **3b**. Again only a high energy, thus experimentally invisible, intermediate (g, g, g) is visited.

Since, as mentioned above, **3a** exchanges with **3b**, scrambling with **3a′** and **3a″** may also follow the same pathway. A single averaged signal can thus be obtained, without ever visiting conformer **3c**. Schemes 7 and 8 thus explain how two single signals are observed at −149 °C for the methine carbons.

Scheme 8. Possible Pathway for the Interconversion of the Three Degenerate Forms 3b, 3b′, 3b″ ($\Delta G^{\ddagger} = 5.7$ kcal mol^{-1}). The Conformer in Square Bracket Has Too High an Energy To Be Appreciably Populated

3b, $(g_1, -g_2, g_3) \rightarrow [(g_1, g_2, g_3,] \rightarrow (-g_1, g_2, g_3)$, **3b′**

3b′, $(-g_1, g_2, g_3) \rightarrow [(g_1, g_2, g_3,] \rightarrow (g_1, g_2, -g_3)$, **3b″**

Further support to this interpretation also comes form the spectrum of the methyl groups. According to the model of Scheme 7, when the three CH carbons of the conformer **3c** become equivalent, the corresponding six methyl groups must also become equivalent. In fact each isopropyl group in turn adopts the *anti* conformation, and when this motion is rapid the methyls within each isopropyl group become enantiotopic.

On the other hand the processes of Scheme 8, while they make the methine carbons equivalent, still leave the two methyls within any isopropyl group distinct, so that two methyl signals are expected. This is because the local plane of symmetry (i.e., the one bisecting the isopropyl group) never coincides, even with fast rotation, with the dynamic plane of symmetry of the molecule as a whole, contrary to the case of **3c**. The complex pattern of the signals, due to nine overlapping methyl lines observed at −165 °C, broaden and coalesce, at −149 °C, into three lines, with an integrated intensity (checked by computer simulation) of about 3:6:3 as shown in Figure 2. Thus the intense central line (indicated by a triangle) corresponds to the six equivalent methyl groups predicted by the motion of Scheme 7 for the set of conformers **3c**, **3c′**, **3c″**. The two equally intense lines (indicated by squares) each corresponds to three methyl groups, as predicted by the motion of Scheme 8 for the set of conformers **3a** + **3b** (the line on the left of the major signal, being sharper, appears taller than its equally intense broader companion on the right). Only above −149 °C the interconversion of **3c** with the pair **3a** + **3b** becomes rapid (having a barrier of 6.25 kcal mol^{-1}) eventually leading to a single line for the CH as well as for the CH_3 carbons (Figure 3).

Molecular Mechanics Calculations. MM3 calculations of bond rotations help to elucidate the conformational processes that give rise to the spectral changes of compound **3**. With four asymmetric rotors the possibilities are very complex, but a few useful conclusions emerge from these computations. Independent rotation of the naphthyl group in **3** appears to have a barrier much higher than any experimentally observed, the lowest we could find being as high as 8.6 kcal mol^{-1} in the case of conformer **3a**. We were able, however, to model a concerted rotation of the naphthyl and of one isopropyl group from various conformational minima with barriers of 5.7, 6.6, and 6.7 kcal mol^{-1} for **3c**, **3b**, and **3a**, respectively. The value for **3c** is indeed almost equal to that experimentally measured for the symmetric conformer (5.9 kcal mol^{-1}), and also the other two differ by only 1 kcal mol^{-1} from that determined for the asymmetric conformer (5.7 kcal mol^{-1}). Naphthalene rotation has its high energy point when one isopropyl passes through the plane of the naphthalene at the *peri*-position, and after examining a model of the starting conformation, the reported barriers were calculated by ensuring, quite reasonably, that the isopropyl group rotates in concert, in the sense that keeps its methine hydrogen, rather than a methyl group, near the *peri*-hydrogen. The interconversion proposed in Scheme 8 is readily modeled since it centers around the highly symmetrical (g, g, g) conformation and only two torsion angles change significantly. The barrier here is computed to be 6.8 kcal mol^{-1} without naphthyl rotation and 6.6 kcal mol^{-1} with accompanying naphthyl rotation. If a total view of all four rotors could be theoretically modeled, the calculated barrier for such interconversion could only be lower than 6.6 kcal mol^{-1}, thus becoming even closer to the experimental values of 5.7 kcal mol^{-1}.

Isopropyl rotation, without concomitant naphthyl group rotation, can be modeled straightforwardly. In the case of the **3a** into **3b** interconversion mentioned above, a simple rotation of one group achieves this smoothly with a barrier of 4.8 kcal mol^{-1}. The third dynamic process of 5.4 kcal mol^{-1} observed in the aromatic region might thus be attributed to the slowing down of this process, which would lead to separate signals of different intensities for these conformers at −165 °C. This interpretation stems from the fact that the observed barrier not only is lower than the previous ones (i.e., 5.7, 5.9, and 6.25 kcal mol^{-1}) but is also similar to the theoretically calculated value (4.8 kcal mol^{-1}) for the exchange of **3a** with **3b**. Any alternative explanation would involve conformers calculated to be much less stable.

This interpretation also requires that the highest barrier of 6.25 kcal mol^{-1} corresponds to the interchange of the pair of conformers **3a** + **3b** with conformer **3c**, with the naphthyl group still rapidly rotating *above* −150 °C. Accordingly, this same barrier of 6.25 kcal mol^{-1} should be also obtained when monitoring the aromatic signals in the same temperature range, because, in principle, they too should display different shifts, even in the presence of fast naphthyl rotation. On the other hand, the highest barrier determined from the aromatic signals could be detected only *below* −150 °C, and its value turned out to be equal to the lowest of the barriers (5.7 kcal mol^{-1}) determined from the aliphatic signals.[17] This apparent discrepancy is due to the fact that the shift difference of the aromatic signals in conformer **3c** and in the set (**3a** + **3b**) is initially quite small, being partly averaged by the fast rotation of the naphthyl group. Only when, on further cooling, the mentioned concerted process renders the naphthyl rotation sufficiently slow does the separation of some aromatic signals become large

(16) The degenerate forms are **3a** = $(g_1, -g_2, a_3)$, **3a′** = $(a_1, g_2, -g_3)$, **3a″** = $(-g_1, a_2, g_3)$, and **3b** = $(g_1, -g_2, g_3)$, **3b′** = $(-g_1, g_2, g_3)$, **3b″** = $(g_1, g_2, -g_3)$. Of course also the enantiomers **3a*** = $[-(g_1), -(-g_2), -(a_3)]$ and **3b*** = $[-(g_1), -(-g_2), -(g_3)]$ have three degenerate forms but in a nonchiral medium this distinction is immaterial.

(17) The aliphatic and aromatic spectral regions were simultaneously acquired at the same identical temperature. The differences in the free energies of activation cannot be thus attributed to differences in the determination of the relative temperatures. The only uncertainities are those on the rate constants derived from the theoretical fitting of the line shape which, given the quality of the experimental spectra, was about ±20%. Such uncertainity about the rate constants leads to an error of ±0.05 kcal mol^{-1} in the measurement of the relative $\Delta G^{\ddagger}$ values at these temperatures.

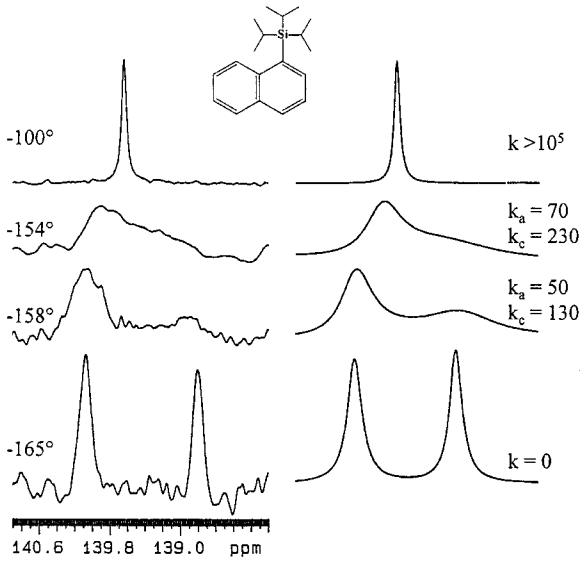


Figure 4. Left: Temperature dependence of the lowest field quaternary carbon signal of **3**. Right: computer simulation obtained with the rate constants (in s^{-1}) reported (see text for the meaning of k_a and k_c).

enough to display observable line-broadening effects (even in these conditions, however, only three, out of ten aromatic signals, have different shifts). This explains, therefore, why the higher of the two barriers measured in the aromatic region apparently corresponds to the lowest, rather than to the highest, barrier determined in the aliphatic region.

Solid-State NMR. The ambient temperature CP-MAS solid-state spectrum of **3** displays aliphatic carbon signals that broaden on cooling and eventually split, at −95 °C, into a number of peaks that, similarly to what observed in solution, belong to a pair of distinct conformers. In particular the methine carbons display a 1:1:1 triplet (indicated by the three bent arrows in Figure 5) for one conformer and a single line (at 11 ppm) for the second one, all surely identified by their disappearance in the nonquaternary suppression (NQS) sequence. The triplet can be assigned to one or the other of the asymmetric conformers **3a** and **3b**. A mixture of these two in rapid exchange, as in solution, seems less likely to occur in the crystalline state and indeed the relative shift of the three lines are different. The more intense upfield single line is assigned to conformer **3c**; the 2:1 doublet splitting observed in solution (36 Hz at 75.5 MHz) is not resolved in the solid, due to a broader (50 Hz) line width. Whereas in solution the two types of conformers were almost equally populated, in the solid state the intensity of the asymmetric conformer has increased, the ratio now being 63:37. The slightly greater dispersion of the methyl signals allowed to resolve seven out of the nine lines expected for one asymmetric and one symmetric conformer. The simulation of Figure 5 was in fact obtained by superimposing on the four mentioned CH signals the six Me peaks (one carbon each) of an asymmetric conformer and the three methyl peaks (two carbons each) of the symmetric conformer **3c,** in the mentioned proportion. The symmetry assigned to these conformers, on the basis of the multiplicity of the methine carbon signals in the solution spectrum, thus agrees with that derived from the multiplicity of the methyl carbon signals in the solid state.

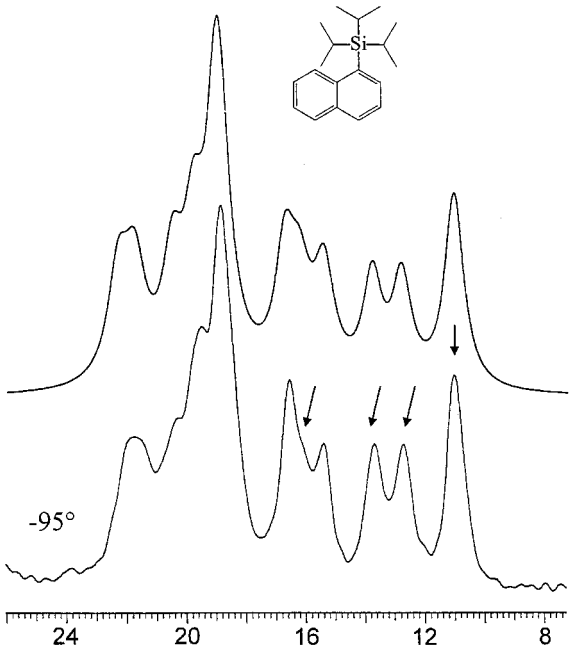


Figure 5. Experimental ^{13}C solid-state CP-MAS spectrum (75.5 MHz) of the aliphatic region of **3** at −95 °C (bottom), with the arrows identifying the CH lines. On the top is reported the computer simulation obtained with asymmetric and symmetric conformers in a 63:37 proportion (see text).

The line broadening due to the exchange process occurs at much higher temperature (range −60 °C to 0 °C) than in solution, indicating that, as for **2**, the barrier for **3** has substantially increased in the solid. The complexity of the spectral patterns did not allow us to obtain a very accurate simulation, so that it was impossible to ascertain whether the two processes described in Schemes 7 and 8 also occur in the crystal. Nonetheless at −30 °C a $\Delta G^{\ddagger}$ value of about 10.8 ± 0.5 kcal mol^{-1} could be estimated for the interconversion barrier of the two conformers in the solid state. The difference of about 5 kcal mol^{-1} with respect to solution is the consequence of the crystal lattice effects, as observed in many other instances. [13] Although quite unlikely, there is also a small possibility that lattice effects in the solid might render relatively more stable conformations calculated to be less stable according to Table 2, yet having a symmetry compatible with the multiplicity observed at low temperatures.

Whereas a X-ray determination would have been most helpful, it was impossible to obtain a structure for **3**. Despite the fact that good diffraction patterns were observed, a unit cell could not be determined. This failure is almost certainly due to the simultaneous presence of two species in the crystal, as proved by the low-temperature solid-state NMR spectrum.

Conclusions

Derivatives **1** and **2** adopt a single, symmetric conformation (a, g, −g) where the aromatic rings still rotate rapidly at any attainable temperature. The barrier for the rotation of the isopropyl groups was found, in both cases, to be 5.5 kcal mol^{-1} in solution, and 13.0 kcal mol^{-1} for **2** in the solid state. The more hindered derivative **3** displays two distinct ^{13}C spectra at low temperature. The symmetric is due to the (a, −g, g) conformation (**3c**), the asymmetric to the rapidly interconverting pair of con-

formers **3a** and **3b**, i.e., (g, −g, a) and (g, −g, g), respectively. These assignments were based upon the results of MM comparisons. Interconversion of the rapidly exchanging pair **3a** + **3b** with **3c** has a barrier of 6.25 kcal mol^{-1} in solution and 10.8 kcal mol^{-1} in the solid state. Two other dynamic processes observed in solution correspond to the concerted rotation of 1-naphthyl ring with the isopropyl groups within conformer **3c** (5.9 kcal mol^{-1}) and within the pair **3a** + **3b** (5.7 kcal mol^{-1}). A fourth dynamic process, due to the interconversion of **3a** with **3b**, was also detected in the aromatic region, with an even lower barrier of 5.4 kcal mol^{-1}. Thus all the four motions occurring in **3** have been experimentally detected and their barriers determined.

Experimental Section

Material. Triisopropyl(aryl)silanes **1**−**3** were prepared according to the following general procedure. To an aryllithium solution, prepared by adding *n*-butyllithium (16 mmol) to a solution of the appropriate aryl bromide (15 mmol in 40 mL of anydrous THF) kept at −78° was added the appropriate silyl chloride (20 mmol in 5 mL of THF) at −78 °C. The mixture was allowed to reach ambient temperature and after 1−2 h was quenched with aqueous NH_4Cl. The organic layers were extracted (Et_2O) and dried (Na_2SO_4), and the solvent was evaporated at reduced pressure. The crude product was purified by preparative TLC (SiO_2) with pentane as eluent.

Triisopropyl(phenyl)silane (1):[18] ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.08 (d, 18H, J = 7.5 Hz), 1.41 (septet, 3H, J = 7.5 Hz), 7.35 (m, 3H), 7.48 (m,2H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 10.77 (CH), 18.57 (Me), 127.44 (CH), 128.48 (CH), 133.72 (q), 135.27 (CH); MS (*m*/*z*) 234 (M^+). Anal. Calcd for $C_{15}H_{26}Si$: C, 76.84; H, 11.18; Si, 11.98. Found: C, 76.79; H, 11.23; Si, 11.95.

Triisopropyl(2-naphthyl)silane (2): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.10 (d, 18H, J = 7.4 Hz), 1.50 (septet, 3H, J = 7.4 Hz), 7.47 (m, 2H), 7.57 (dd, 1H, J = 11.5 Hz, J = 1.8 Hz), 7.83 (m, 3H), 7.99 (bs, 1H);^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 11.75 (CH), 19.30 (Me), 126.32 (CH), 126.81 (CH), 127.10 (CH), 128.30 (CH), 128.77 (CH), 132.40 (CH), 133.24 (q), 133.57 (q), 134.15 (q),136.60 (CH); MS (*m*/*z*) 284 (M^+). Anal. Calcd for $C_{19}H_{28}Si$: C, 80.21; H, 9.92; Si, 9.87. Found: C, 80.18; H, 9.93; Si, 9.95.

Triisopropyl(1-naphthyl)silane (3): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.18 (d, 18H, J = 7.6 Hz), 1.75 (septet, 3H, J = 7.6 Hz), 7.53 (m, 3H), 7.90 (m, 3H), 8.17 (m, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 13.93 (CH), 19.45 (Me), 125.85 (CH), 125.95 (CH), 126.19 (CH), 129.75 (CH), 129.82 (CH), 130.16 (CH), 134.15 (q), 135.06 (q), 136.34 (CH), 138.57 (q); MS (*m*/*z*) 284 (M^+). Anal. Calcd for $C_{19}H_{28}Si$: C, 80.21; H, 9.92; Si, 9.87. Found: C, 80.22; H, 9.90; Si, 9.84.

NMR Measurements. The samples for the low temperature determinations were prepared by connecting to a vacuum line the NMR tubes containing the desired compounds and condensing therein the gaseous CF_2Cl_2 and $CBrF_3$ in about a 3:1 proportion. A few drops of TMS-d_{12} were added for reference and lock. The tubes were subsequently sealed in vacuo and introduced into the precooled probe of the 300 MHz spectrometer operating at 75.5 MHz for ^{13}C. The temperatures were calibrated by substituting the sample with a precision Cu/Ni thermocouple before the measurements. The high resolution ^{13}C NMR solid-state CP-MAS spectra were also obtained at 75.5 MHz. The samples were packed in a zirconia rotor spun at the magic angle with a speed in the range of 3−4 kHz. The chemical shifts were measured, by replacement, with respect to the lower frequency signal of the adamantane (29.4 ppm). The cooling was achieved by means of a flow of dry nitrogen, precooled in a heat exchanger immersed in liquid nitrogen. Line shape simulations of the solution and solid-state spectra were obtained with a PC computer program based upon the DNMR 6 routines.[19]

Acknowledgment. Thanks are due to Dr. J. A. Steed (King's College, London, UK) for several attempts to obtain a crystal structure of **3** and to Dr. A. E. Aliev and Mr. J. G. Outeirinho (University College, London, UK) for helping, respectively, with the low temperature CP-MAS spectra and with retrieving structures from the Cambridge Crystallographic Data Base. Financial support has been obtained from MURST, Rome (national project "Stereoselection in Organic Synthesis") and from the University of Bologna (Finanziamento d' Ateneo 1997−1999).

JO991580P

(18) Schlosser, M.; Choi, J. H.; Takagishi, S. *Tetrahedron* **1990**, *46*, 5633.

(19) QCPE program no. 633, Indiana University.