Journal of Organometallic Chemistry, 341 (1988) 281–291
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Structure and dynamics of hindered organosilicon compounds. The conformation and enantiotopomerization of (chlorodiphenylsilyl)(methoxydimethylsilyl)-bis(trimethylsilyl)methane *

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(Received October 20th, 1987)

Abstract

At low temperatures, the ^1H and ^{13}C NMR spectra of (chlorodiphenylsilyl)(methoxydimethylsilyl)bis(trimethylsilyl)methane show resonances from nine non-equivalent methyl groups, and are consistent with the presence in solution of enantiotopomeric molecules with conformations very similar to those found in the solid state by an X-ray crystal structure determination. By means of NOESY and COSY 2D NMR experiments, the ^1H and ^{29}Si resonances have been assigned to particular sites in the molecule, and the enantiotopomerization has been shown to be of ESSS type, with free energy of activation 43.3 kJ mol^{-1}. Some aspects of the structure and chirality of hindered molecules, such as those containing $(Me_3Si)_3C$ groups, are discussed.

Introduction

During the last ten years, Eaborn and co-workers have used bulky groups such as $(Me_3Si)_3C$ ("Trisyl" denoted Tsi) and $(PhMe_2Si)_3C$ to stabilize many novel organometallic compounds and to prepare and study the unusual reactions of highly hindered organosilicon compounds [1]. X-Ray crystal structure determinations have shown that as well as providing steric protection for atoms to which it is attached, the trisyl group is itself strained internally, and the bonds from silicon to the central

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* Dedicated to Professor Colin Eaborn on the occasion of his 65th birthday and in gratitude for many (continuing) years of friendly and fruitful collaboration.

carbon atom are often long, and in TsiH they subtend unusually large angles at carbon [2]. Our investigations have shown that the internal strain in these molecules also lowers the rate of certain internal motions so that it becomes normal to observe non-equivalence between chemically identical methyl groups in the ^1H NMR spectra at low temperatures. Our first observations were reported briefly in relation to the compound $[(Me_3Si)_2C(SiMe_2ONO_2)(SiPh_2Me)]$ for which the crystal structure and the low temperature ^1H NMR spectrum in solution show the presence of nine non-equivalent methyl groups [3]. In this paper we report a more extensive study of the NMR spectra of $[(Me_3Si)_2C(SiMe_2OMe)(SiPh_2Cl)]$ (**1**). The crystal structure of this compound has been reported recently, and it is of particular interest because there is strong evidence that the oxygen atom of the methoxy group, which lies close to the silicon atom of the $SiPh_2Cl$ group, moves in the analogous bromide to form an SiOSi bridge in the course of reactions in which bromide is abstracted [4].

The NMR results indicate that the conformation of this molecule, **1**, in solution closely resembles that in the solid state, and at low temperatures the interconversion between the two enantiotopomeric forms that are also present in the crystal becomes sufficiently slow to follow using the NOESY (nuclear Overhauser effect spectroscopy) pulse sequence. Our results thus highlight the chirality of the predominant conformations of molecules containing the trisyl and related groups. Although this chirality and its origins have been recognised previously in closely related molecules [2,5], it appears that its significance in the structure of trisyl compounds may have been somewhat overlooked [6] until it re-emerged during our work. Some of the structural consequences of the chirality of trisyl groups have subsequently been discussed elsewhere [7], but it is clear that even molecules as simple as $[(Tsi)_2Hg]$ are, at least in principle, capable of existing in *d*- and *l*-forms, as well as in the known centrosymmetric (*meso*) form [8].

Since none of our results indicate that rotation of methyl groups about the C–Si bonds is sufficiently hindered to affect the NMR spectra, in the following discussion we do not discuss the possible orientations of methyl groups with respect to the rest of the molecule. With this restriction, the origin of chirality in molecules of this class is outlined in terms of the conformations of the parent molecule, $[(Me_3Si)_4C]$, as follows.

In the fully staggered conformation of $[(Me_3Si)_4C]$, in which the Me–Si–C–Si torsion angles take values +60, 180 and −60°, the twelve methyl groups can be regarded as being symmetrically located close to the corners of the equilateral triangular faces of a regular tetrahedron centred on the central carbon atom. The silicon atoms are placed on lines joining the centre to the apices of the tetrahedron and the three methyl groups close to an apex are attached to a single silicon atom. Overall, this conformation belongs to the point group T_d, and all the methyl groups are equivalent. Four methyl groups lie close to each edge of the tetrahedron and form a rectangular array. In compounds of this type, the distance between the carbon atoms of methyl groups attached to a single silicon atom is found to be shorter than that between methyl groups on different silicon atoms, so the shorter side of the rectangle lies at right angles to the mirror plane containing the edge of the tetrahedron. Although the fully staggered conformation minimizes the interactions between the methyl groups and the non-bonded silicon atoms, a calculation based on the distances and bond angles in the C(2)Si(1)C(1)Si(2)C(4) fragment of the structure of $[(Me_3Si)_2C(SiMe_2OMe)(SiPh_2Cl)]$ [4] (Fig. 1) shows that with torsion angles appropriate for the staggered conformation, the Me · · · Me distance corresponding to the long side of the rectangle would be close to 3.4 Å. This is much shorter than the Van der Waals contact distance (4 Å) between two methyl groups, so it is evident that 1,3-interactions between methyl groups would be strong in the staggered conformation of the molecule.

The Me · · · Me contact corresponding to the longer side of the rectangle can be relieved by small equal conrotatory motions of the two parent $SiMe_3$ groups that place a methyl group on one silicon atom between two groups on the other silicon. The four methyl groups would then no longer lie on a plane, but projection onto the mean plane would form a parallelogram. In $[(Me_3Si)_4C]$, the short Me · · · Me contacts would be relieved only if all four Me_3Si groups were rotated in the same sense away from the fully staggered conformation, and in $[(Me_3Si)_2C(SiMe_2OMe)(SiPh_2Cl)]$, Fig. 1, (and in many compounds containing the trisyl group [7,9]) the torsion angles are found to be close to 40, 160, and −80°. In the $(Me_3Si)_2C$ fragment of $[(Me_3Si)_2C(SiMe_2OMe)(SiPh_2Cl)]$, the methyl group C(2) on Si(1) is found to be approximately equidistant from two methyl groups on Si(2), and the distances [C(2) · · · C(5) 3.62, C(2) · · · C(6) 3.61 Å] show that considerable strain persists, but that the 1,3-contacts between methyl groups are significantly longer than the shortest such contact (3.4 Å) calculated for the fully staggered conformation.

Mislow has used the term "static gearing" to describe the conformation resulting from the minimization of 1,3-interactions of this type [5]. From the foregoing, it follows that each group attached to a silicon atom of a tetrahedral Si_4C moiety is expected to be placed between two groups on a neighbouring silicon atom, and thus to lie close to the plane formed by the third group on this silicon atom, the silicon atom itself, and the central carbon atom. For the fragment under consideration, it is therefore expected that the dihedral angle C(2)–C(1)–Si(2)–C(4) should be close to 180° (i.e. C(2) should be close to the plane containing C(1), Si(2), and C(4)). The angle calculated from the crystal structure determination is 180.0°, and the corresponding dihedral angles calculated for other sets of atoms in this molecule and in other molecules of this type typically yield values in the range 175–180°, indicating that the 1,3-interactions have a dominant effect on the conformations of all molecules of this class. The calculated value for the dihedral angle for the fully staggered conformation is 150°. Deviations from 180° for this type of dihedral angle, and unequal distances to the two neighbouring groups, are to be expected and are found when a group is engaged with groups of dissimilar size on a neighbouring silicon atom.

As indicated above, the 1,3-interactions are relieved only if all the Me_3Si groups rotate in the same sense and by about 20° away from the fully staggered conformation. For $[(Me_3Si)_4C]$, the two possible senses of rotation result in enantiotopomeric conformations of point group *T*, and the trisyl group also has enantiotopomeric conformations. Crystals of compounds containing trisyl groups normally contain both enantiotopomeric forms, which often occur in an ordered array, but the spatial requirements of the enantiotopomers are very similar and disordered arrangements are not unusual. Although the results of crystal structure determinations of trisyl compounds sometimes appear to indicate disorder between two mirror image sets of silicon atoms within a common manifold of carbon atom positions [6,10], the disorder must in fact relate to the enantiotopomeric forms of the whole trisyl group, the carbon atom manifolds of which are not exactly superimposable. Thus, it is clear from accurate determinations of the structures of ordered crystals that Me · · · Me distances within an $SiMe_3$ group (about 3.0 Å) are shorter than those between methyl groups on different silicon atoms (about 3.6 Å), so an accurate determination of the carbon manifold can be consistent only with a single set of silicon atom sites. The carbon atom positions reported for these disordered crystals must therefore be an average of the sites in the superimposed enantiotopomeric forms.

In systems as crowded as $[(Me_3Si)_4C]$, or in compounds containing trisyl or closely related groups, the correlated rotation of two or more Me_3Si groups is likely to have a lower barrier than the independent rotation of a single group. Possible motions of individual groups have been designated S or E [5]. An example of an S motion is where an initial Me–Si–C–Si torsion angle changes from 40° through a staggered transition state (torsion angle 60°) to an arrangement in which the torsion angle is 80°. Alternatively, in the corresponding E motion, the torsion angle changes from 40°, through the eclipsed transition state (torsion angle 0°), to an arrangement in which the torsion angle is −40°. Mislow has shown that systems of the type $(Me_3C)_3MX$ are expected to undergo enantiotopomerisation by an SSS mechanism in which all three Me_3C groups undergo correlated conrotation. For the alternative ESS mechanism, in which two of the pairwise interactions between Me_3C groups involve disrotation while the third involves conrotation, the activation energy is expected to be greater. These expectations have been confirmed by NMR studies of $[(Me_3C)_3PMe]^+$ at very low temperature [11], but we have found that molecules formally derived from $[(Me_3Si)_4C]$ are especially well suited to studies of this type of process.

Experimental

The $[(Me_3Si)_2C(SiMe_2OMe)(SiPh_2Cl)]$ was prepared as described in ref. [4]. The NMR spectra of the CD_2Cl_2 solutions were recorded using a Bruker WM360 instrument at 360 (^1H), 71.5 (^{29}Si), or 90.6 MHz (^{13}C). The ^1H–^{29}Si heteronuclear COSY (correlation spectroscopy) experiment was performed at 193 K using the standard pulse sequence [12]. The Δ_1 and Δ_2 delay times were set to give maximum polarization transfer for $^2J(HSi)$ 10 Hz. A 64 × 1 K data block was used. The exchange process was investigated at 183 K using the ^1H-NOESY sequence with a 64 × 256 data block [13]. The calculations of non-bonded distances, torsion and dihedral angles, etc., were performed using programs listed by Dunitz [14]; hydrogen atom coordinates for $[(Me_3Si)_2C(SiMe_2OMe)(SiPh_2Cl)]$ were supplied by Dr. P.B. Hitchcock.

Results and Discussion

Figure 1 shows a diagram of the structure of $[(Me_3Si)_2C(SiMe_2OMe)(SiPh_2Cl)]$ (**1**) derived from the recently published report of the X-ray crystal structure determination [4]. The crystal space group was found to be $P2_1/c$, with four molecules per unit cell, which comprises two molecules each of the enantiotopomers shown in Figs. 1a and 1b. For CD_2Cl_2 solutions of this compound, the experiments to be described are consistent with the presence of molecules with structures closely similar to those found in the solid state, and at low temperatures the enanti-

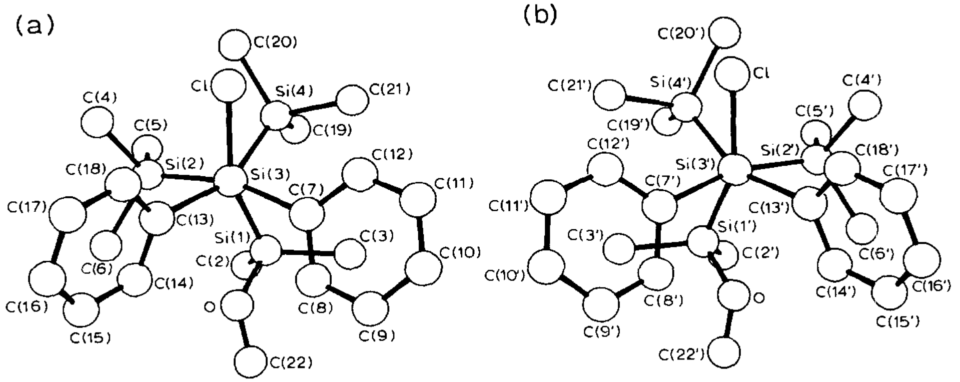

Fig. 1. Projections along the Si(3)–C(1) bond of the enantiotopomers of [$(Me_3Si)_2C(SiMe_2OMe)(SiPh_2Cl)$] (**1**) (atom C(1) lies behind Si(3)) (see ref. [4]).

otopomerisation is sufficiently slow for the rate to be determined. At higher temperatures, the spectra are affected by another rate process, which, inter alia, must involve the complete rotation of the $SiMe_3$ groups, but in the temperature range studied (209–311 K) the spectra suggest that other molecular conformations are not present in substantial proportions. Since we used non-chiral solvents, the NMR spectra of the enantiotopomers are identical; except where site interchanges are being described, the sites in both enantiotopomers will be denoted by the labels in Fig. 1a, and the site of a methyl group will be denoted by the label of the corresponding carbon atom site.

At ambient temperatures, the NMR spectra (^{1}H, 298 K; ^{13}C, 311 K; ^{29}Si, 303 K) show sharp resonances corresponding to the numbers of chemically non-equivalent nuclei implied by the molecular formula. At low temperatures, all the spectra show the larger number of lines consistent with the presence of enantiotopomers of structure implied by Figs. 1a and 1b. Each enantiotopomer has C_1 symmetry so the ^{29}Si{^{1}H} NMR spectrum comprises four resonances (labelled Si1–Si4, and the ^{1}H and ^{13}C {^{1}H} NMR spectra contain eight resonances (H1–H8, C1–C8) corresponding to the eight non-equivalent silicon methyl group sites. Resonances from ^{29}Si or methyl groups in the NMR spectra are numbered for a particular nucleus in descending order of resonance frequency. The chemical shifts and proposed site assignments are summarized in Table 1.

The ^{1}H and ^{13}C resonances of the OMe group are sharp singlets throughout the temperature ranges 289–183 K (^{1}H) and 311–183 K (^{13}C). This indicates that only one conformation (and its enantiotopomer) is present in solution at low temperatures, in contrast to related systems such as [$(Me_3Si)_2C(SiMe_2X)_2$] and [$(XMe_2Si)_4C$] ($X = Br$ or I) for which several conformational isomers have been detected at low temperatures [15].

By means of a ^{1}H–^{29}Si COSY experiment at 193 K, the two $SiMe_3$ groups have been shown to be associated with lines Si3, H4, H6, H7 and Si4, H1, H2, H5, and the $SiMe_2$ group is associated with Si1, H3, H8. Line H8 of the $SiMe_2$ group occurs at a particularly low frequency (Table 1). It is apparent from Fig. 1 that the ^{1}H resonance of the methyl group on site C(3) would experience a shift to low frequency due to its spatial relationship to the C(7)–C(12) phenyl ring. Co-ordinates

Table 1

NMR chemical shifts ^{a} and site assignments for $(Me_3Si)_2C(SiMe_2OMe)(SiPh_2Cl)$

Group	^{1}H NMR			^{29}Si NMR			^{13}C NMR ^{b}	
	289 K	183 K	Site ^{c}	303 K	193 K	Site ^{c}	311 K	183 K
		(H1) 0.436	C(21)					5.535
		(H2) 0.283	C(20)		(Si4) −1.596	Si(4)		5.228
		(H5) 0.125	C(19)					4.479
Me_3Si	0.258			−0.894			5.921	
		(H4) 0.177	C(5)					4.404
		(H6) 0.015	C(6)		(Si3) −0.156	Si(2)		3.419
		(H7) −0.111	C(4)					2.772
Me_2Si	0.077	(H3) 0.273	C(2)	16.544	(Si1) 16.833	Si(1)	2.387	1.267
		(H8) −0.421	C(3)					0.101
MeOSi	3.557	3.052	C(22)				49.103	48.648
	8.13 ^{d}	8.27 ^{e,f}		7.074	(Si2) 7.165	Si(3)	137.06 ^{f}	135.96 ^{f}
		7.89 ^{e,f}						135.7 ^{e}
$ClPh_2Si$							127.53 ^{g}	126.7 ^{g}
	7.34 ^{d}	7.36 ^{e,g,h}						126.46 ^{g}
		7.27 ^{e,g,h}					129.87 ^{h}	129.07 ^{h}
								128.79 ^{h}

^{a} In ppm from tetramethylsilane; positive shifts are to high frequency of the reference. ^{b} In the absence of ^{1}H–^{13}C COSY results, no assignment of ^{13}C resonances to sites is implied. ^{c} Silicon atom and methyl group sites are labelled in accordance with Fig. 1a and ref. 4. ^{d} Multiplet. ^{e} Broad. ^{f} 2,6-. ^{g} 3,5-. ^{h} 4-.

for methyl group carbon atoms relative to the phenyl rings have been calculated from the published X-ray crystal structure data (Table 2). Also included in Table 2 are the coordinates for the hydrogen atoms of methyl groups C(3), C(4), C(6) and C(21), which are the only methyl groups in close proximity to a phenyl ring. From the iso-shielding curves of the Johnson–Bovey ring current theory [16], it is clear that the protons of methyl group C(3) should experience the greatest mean shift to low frequency, but the shift estimated from the hydrogen atom coordinates (about 0.1 ppm) is small in comparison with the shift difference between H3 and H8 (0.69 ppm). The shift differences in the spectrum of our compound may be enhanced at low temperatures by the diminution of phenyl ring torsional vibrations, which would cause the methyl group C(3) to spend greater time on the face of the phenyl ring. This effect has been noted for the methylene hydrogens in 3-(phenylmethyl)piperazine-2,5-dione [17]. In addition, low frequency shifts of up to 1.2 ppm have been inferred for overcrowded protons [18] so it is probable that the shifts for our compound can be expected to correlate qualitatively but not quantitatively with the Johnson–Bovey theory. Following from the assignment of resonance H8 to site C(3), the COSY experiment shows H3 to be assigned to site C(2).

The assignment of the ^{1}H resonances to sites is more problematical for the $SiMe_3$ groups. The results in Table 2 indicate that methyl groups on sites C(4), C(6) and C(21) are sufficiently close to a phenyl ring to experience a ring current effect, but estimation of mean values of the shift contributions from the Johnson–Bovey theory over the three hydrogens of each methyl group gives results close to zero. It is clear from the results for the $SiMe_2$ group that strictly quantitative applications of the Johnson–Bovey theory are unlikely to fit the results for the $SiMe_3$ groups, and a

Table 2

Calculated distances (Å) [a] of atoms from phenyl ring centres (r) [b] and planes (Z) [c] for methyl groups in $[(Me_3Si)_2C(SiMe_2OMe)(SiPh_2Cl)]$

Atom [d]	Phenyl C(7)–C(12)		Phenyl C(13)–C(18)	
	r	Z	r	Z
C(2)	6.38		6.70	
C(3)	4.03	3.45	6.56	
C(4)	6.80		4.21	3.23
C(5)	7.71		6.40	
C(6)	6.79		4.29	2.83
C(19)	6.55		7.71	
C(20)	6.51		6.68	
C(21)	4.47	2.45	6.88	
H(3a)	4.53	4.05		
H(3b)	4.50	3.92		
H(3c)	3.25	2.96		
H(4a)			4.56	2.64
H(4b)			4.69	1.76
H(4c)			3.47	3.15
H(6a)			3.53	3.17
H(6b)			4.71	4.01
H(6c)			4.62	2.71
H(21a)	3.88	2.43		
H(21b)	4.30	3.58		
H(21c)	5.24	2.54		

[a] Data from ref. 4 and Dr. P.B. Hitchcock. [b] Distance from mean positions of carbon atoms C(7)–C(12) or C(13)–C(18). [c] Distance from plane of C(7), C(8) and C(12) or C(13), C(14) and C(18). [d] Hydrogen atoms are numbered according to the carbon atom to which they are attached.

more qualitative approach suggests that site C(4) should experience a shift to low frequency and site C(21) a shift to high frequency. Site C(6) should also experience some shift to low frequency, but despite the somewhat misleading impression from Fig. 1, the effect seems likely to be smaller than for C(4). We shall show later that interchange of the assignments of sites C(4) and C(6) is incompatible with other results.

On the basis that C(4) is expected to experience a shift to low frequency arising from the C(13)–C(18) ring current, resonance H7 is assigned to this site, and in consequence resonance Si3 is assigned to site Si(2), and Si4 to Si(4). The highest frequency resonance H1 is similarly assigned to site C(21) and since resonances H1 and Si4 are known to correlate this adds support to the above assignment of the resonances Si4 and Si3 to sites Si(4) and Si(2).

Resonances H4 and H5 have similar shifts near the middle of the range for the Me_3Si resonances. This suggests that the corresponding methyl groups have very closely similar environments that are relatively remote from the magnetic influence of the phenyl rings. The ^1H–^{29}Si correlation shows that these lines originate from methyl groups that belong to different $SiMe_3$ groups, and inspection of Fig. 1 and of molecular models points very clearly to sites C(5) and C(19), which then leads to the assignment of H4 to site C(5) and H5 to C(19). The similarity of the environments of sites C(5) and C(19) is also evident from the close similarity in the

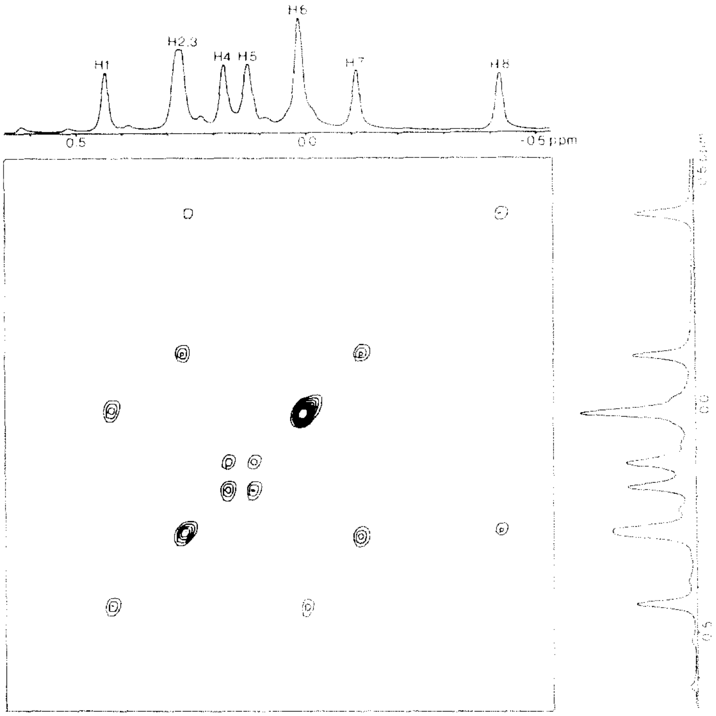

Fig. 2. ^{1}H NOESY spectrum at 183 K showing the resonance numbering scheme for the ^{1}H spectrum. An impurity resonance coincides with resonance H6.

distances C(5) ··· Si(3), 4.78, and C(19) ··· Si(3) 4.79 Å, and in the torsion angles C(5)–Si(2)–C(1)–Si(3) 159.3°, and C(19)–Si(4)–C(1)–Si(3) 161.5°.

The remaining assignments of H2 to site C(20) and H6 to site C(6) follow from the results of the ^{1}H–^{29}Si correlation experiment. It appears therefore that there is a good correspondence between the low temperature NMR spectra and the spectra to be expected from molecules of conformation very similar to that found in the solid state. The number and arrangement of methyl groups in proximity to the phenyl rings appears to correlate well with the observed form of the ^{1}H NMR spectrum. These assignments of lines to sites are also independently supported by a study of the interconversion of enantiotopomers.

The results of a ^{1}H NOESY experiment on a sample at 183 K are presented in Fig. 2. The experiment shows that even though significant line broadening in the ^{1}H NMR spectrum does not occur at this temperature, an exchange process is occurring in which magnetisation is transferred between pairs of lines as follows: H1, H6; H2, H7; H3, H8; H5, H4. This exchange process can only be enantiotopomerisation, so if the above assignment of lines and sites is correct the interchanges of sites implied by the assignments and the NOESY experiment must be feasible and plausible. Transformed into site exchanges using the assignments in Table 1, the NOESY results read as follows: C(21), C(6′); C(20), C(4′); C(2), C(3′); C(19), C(5′). This is one of three topologically feasible interchanges; in addition, there are three interchanges that would require bond breaking, for example: C(21), C(6′); C(20), C(5′); C(2), C(3′); C(19), C(4′).

The crystal structure data were used to produce projections of the structure as viewed along each of the Si–C(1) bonds. A space-filling (Corey–Pauling–Koltun) model was then constructed to conform as closely as possible with the molecular structure, with the exception that it proved more convenient to represent C(1) by a larger tetrahedral (phosphorus) atom. Rotation of individual SiX_3 groups in the model was impossible, but a relatively easy correlated rotation of all four appendages to the central atom was found to give the enantiotopic form of the original model. The atom site interchanges corresponding to this manipulation were precisely those proposed above.

The nature of the enantiotopomerisation is readily appreciated in terms of Figs. 1a and 1b, and the process in which 1a is transformed into 1b, and the internal rotations as viewed from C(1) outwards, is now described. Since C(2) must move to a final position close to the face of the C(7′)–C(12′) ring, and it is probable that the small methoxy group remains between the phenyl rings throughout, anticlockwise rotation about Si(1)–C(1) is indicated, so that C(2) moves directly to site C(3′). Calculations from the crystal data show that the torsion angles C(2)–Si(1)–C(1)–Si(2, 3 or 4) change by $-86°$, as is expected for an E-type motion in which the torsion angles in starting and finishing structures deviate from perfect staggering by 17° $\{120° - (2 \times 17)° = 86°\}$.

The methyl group C(19) on Si(4) is engaged between C(2) and C(3) of Si(1). As Si(1) rotates anticlockwise, it is clear from Fig. 1a that Si(4) is likely to be driven clockwise. After passing through a staggered orientation with respect to the $C(1)Si_3$ moiety, the first new position compatible with overall enantiotopomerisation is reached after a total rotation of approximately 42°, corresponding to an S-type motion in which the starting and finishing configurations deviate from perfect staggering by 21°. The methyl group of C(2) is engaged with methyls C(5) and C(6) on Si(2), and assuming that the relatively large angular motion of C(2) on Si(1) determines the way Si(2) moves, Si(2) is expected to rotate clockwise. In the same way as described for Si(4), Si(2) would appear to execute an S-type rotation through about 40°, and it is clear from Figs. 1a and 1b that a similar (clockwise) S-type motion of Si(3) is to be expected from the engagement of the methoxy group with the two phenyl rings (rotation by 48°, corresponding to the initial deviation of 24° of Si(3) from the staggered conformation).

With the assumption, therefore, that the motions of Si(2), Si(3) and Si(4) correlate directly with the necessary and relatively large rotation of Si(1), the following site interconversions are expected: C(21), C(6′); C(20), C(4′); C(2), C(3′); C(19), C(5′), and these agree exactly with those implied by the proposed assignment of the NMR lines to sites and the NOESY experiment. Furthermore, the overall mechanism of enantiotopomerisation may be described as ESSS, which is a highly plausible result.

As indicated at the outset of our discussion of the assignment of the ^1H resonances of the $SiMe_3$ groups to sites, the estimation of shift contributions for the methyl groups proximate to the phenyl rings leaves open the possibility that resonance H7 should be assigned site C(6). Following methods analogous to those described above then leads to the assignment: H1, C(21); H2, C(20); H5, C(19); H4, C(5); H6, C(4); H7, C(6). This assignment is incompatible with the results of the NOESY experiment since the enantiomerisation implied would require bond-breaking.

The rate of the enantiotopomerisation has been determined from the coalescence of Si3 and Si4 and from the coalescence of the ^{13}C resonances of the Si*Me*$_2$OMe group. The corresponding free energies of activation were found to be 43.5 and 43.1 kJ mol^{-1} from the two experiments.

Under conditions in which the enantiotopomerisation is fast on the NMR time scale, four resonances are expected for the Si*Me* groups in the ^1H and ^{13}C spectra, and three resonances in the ^{29}Si spectrum. Neither the ^1H nor the ^{13}C NMR spectrum conforms with this expectation in the temperature range studied; for both nuclei, the spectra broaden and coalesce before sharpening to give the high temperature limiting spectra appropriate for six equivalent $SiMe_3$ methyl groups and two equivalent $SiMe_2$ methyl groups. Evidently, an additional process (or processes), which must interchange all the methyl sites of $SiMe_3$ groups, begins to affect the spectra before the enantiotopomerisation has become rapid on the NMR timescale. However, relative to the residual proton resonances from the CD_2Cl_2 solvent, the mean positions of the $SiMe_2$, $SiMe_3$, and OMe resonances all move to lower frequencies (by 0.151, 0.104 and 0.055 ppm, respectively) as the temperature is raised. These small shifts seem more likely to derive from the effects of temperature on the chemical shifts of the enantiotopomers discussed above, rather than the significant population of other conformations at higher temperatures.

The regions of the ^1H and ^{13}C NMR spectra due to the phenyl groups in $[(Me_3Si)_2C(SiMe_2OMe)(SiPh_2Cl)]$ have not been analysed in detail, but they change with temperature in the manner expected from the foregoing discussion (Table 1). In the ^1H NMR spectrum at 303 K, the resonances from the 2,6-protons are distinguishable from the 3,5- and 4-protons, and at low temperatures further splitting is observed, but the resonances are somewhat broadened at the lowest temperatures studied. In the ^{13}C NMR spectrum at 311 K, there are three resonances from the 2,6-, 3,5-, and 4-carbon nuclei. The *ipso*-carbon resonance was not assigned, due to the presence of low intensity resonances from impurities. At 183 K, two resonances each are observed for the 2,6-, 3,5-, and 4-carbon nuclei, indicating the expected presence of non-equivalent phenyl groups. However, the non-equivalence of the 2,6- and 3,5-carbon resonances within each phenyl ring was not apparent in the spectra.

The X-ray crystal structure determination of $[(Me_3Si)_2C(SiMe_2OMe)(SiPh_2Cl)]$ showed that, in the solid state, the oxygen atom of the methoxy group was within 3.2 Å of Si(3) [4]. It was noted that the position of the oxygen was close to that expected for oxygen bridging in the silicocation intermediate indicated by the anchimeric assistance and migration of the methoxy group in reactions of the corresponding bromo compound. The NMR studies reported here provide strong support for the view that the structure in the solid state is a reliable indicator of the structure of the dominant conformer in solution, and it may be noted that if enantiotopomerization were to occur in such a way that the bond lengths and angles in the fragment O–Si(1)–C(1)–Si(3) were invariant, the oxygen atom would approach to within 2.8 Å of Si(3) during enantiotopomerisation, when the four atoms were coplanar.

Acknowledgements

We thank the Royal Society for a Research Fellowship (for P.D.L.), Dr. N.H. Buttrus for Fig. 1 and other projections of the molecular structure, and Dr. P.B. Hitchcock for helpful discussions.

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