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Solid State Dynamic Properties of Tetrakis(trimethylsilyl)methane: High-Resolution Solid State ^{13}C and ^{29}Si NMR Investigations

Abil E. Aliev and Kenneth D. M. Harris[1]
Department of Chemistry, University of St. Andrews, St. Andrews, Fife KY16 9ST, Scotland

and

David C. Apperley and Robin K. Harris
Department of Chemistry, University of Durham, Durham DH1 3LE, England

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The dynamic properties of solid tetrakis(trimethylsilyl)methane ($C(Si(CH_3)_3)_4$; TTMSM) have been determined using high-resolution solid state ^{13}C and ^{29}Si NMR spectroscopy. TTMSM is known to undergo a phase transition from a high-temperature "rotator" phase, in which there is isotropic reorientational motion of the molecule within the solid, to a low-temperature phase in which the molecular motion becomes anisotropic. In this low-temperature phase, one Si*Me*$_3$ group of the TTMSM molecule becomes inequivalent from the other three Si*Me*$_3$ groups and the molecules undergo two different types of dynamic process. These are classified as (1) exchange between the crystallographically unique Si*Me*$_3$ group and an Si*Me*$_3$ group within the set of three equivalent Si*Me*$_3$ groups, and (2) hindered rotation of each Si*Me*$_3$ group about the relevant C[central]–Si bond. The energy barriers for these dynamic processes are discussed, and the dynamic behavior of TTMSM is compared with that reported previously for solid tetrakis(trimethylsilyl)silane. The ^{13}C NMR results strongly suggest that the molecular symmetry of the TTMSM molecule in the low-temperature phase is C_3. © 1994 Academic Press, Inc.

It has been reported previously (1) that tetrakis(trimethylsilyl)methane ($C(Si(CH_3)_3)_4$; TTMSM) exists as a "rotator" phase solid at room temperature, and undergoes a solid–solid phase transition below this temperature. Differential scanning calorimetric measurements have shown that this transition is associated with significant hysteresis; the reported transition temperature is ca. 221 K on the cooling cycle and ca. 239 K on the heating cycle. (These reported transition temperatures are for measurements at cooling and heating rates of 10 K min^{-1}; it is noted in Ref. (1) that the difference between the transition temperatures for the cooling and heating cycles is reduced to ca. 8.5 K when the rates of cooling and heating are reduced to 0.625 K min^{-1}, although the actual values of transition temperature are not reported by these authors. While there is clearly some uncertainty on this issue, we are nevertheless confident that all the coalescence phenomena observed in the NMR experiments reported in this paper are occurring within the low-temperature phase of TTMSM.) Broadline ^1H NMR data (1) are consistent with the view that, in common with other highly symmetrical molecules, the high-temperature phase is a "rotator" phase solid, in which the molecules undergo essentially isotropic reorientational motion about fixed centers of mass. The (average) crystal structure of TTMSM in the high-temperature phase has been assigned (1) to the cubic crystal system, although, to our knowledge, there have been no structural studies of this material in the low-temperature phase.

In this paper, we report high-resolution solid state ^{13}C and ^{29}Si NMR investigations of TTMSM, aimed toward understanding the structural and dynamic properties of this material in both the high-temperature and low-temperature phases. A parallel study of the dynamic properties of solid tetrakis(trimethylsilyl)silane ($Si(Si(CH_3)_3)_4$; TTMSS) has been reported recently (2), and the results obtained for these structurally related systems are compared in this paper.

Solid state ^{13}C and ^1H NMR spectra of TTMSM were recorded at 125.8 and 500.13 MHz, respectively, on a Bruker MSL500 spectrometer. High-resolution solid state ^{13}C NMR spectra were recorded using the CP-MAS technique, with high power ^1H decoupling applied during acquisition. ^{29}Si CP-MAS NMR spectra were recorded at 59.58 MHz on a Varian VXR 300 spectrometer, with high power ^1H decoupling applied during acquisition. All ^{13}C,

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[1] To whom correspondence should be addressed at present address: Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, England.

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^{1}H, and ^{29}Si chemical shifts are given relative to tetramethylsilane (external standard). Temperature measurements on both instruments were calibrated via experiments on freshly recrystallized samples of samarium acetate tetrahydrate (3).

The solid state ^{1}H MAS NMR spectrum recorded at room temperature (MAS frequency 12.4 kHz) contains a single line with linewidth ca. 175 Hz; the comparative narrowness of this line suggests that direct ^{1}H–^{1}H dipole–dipole interaction is substantially averaged by molecular motion, and is consistent with the assignment that TTMSM is an isotropic "rotator" phase solid at room temperature.

In the ^{13}C CP-MAS NMR spectra of TTMSM recorded at 293 K (with ^{1}H decoupling and at several different MAS frequencies in the range 200–12,400 Hz), there are two relatively narrow peaks, which are assigned to the methyl carbons ($\delta = 6.5$ ppm; linewidth $\approx$ 13–15 Hz) and to the central carbon ($\delta = -1.1$ ppm; linewidth $\approx$ 7–10 Hz).

The ^{13}C NMR spectrum recorded for a static sample of TTMSM at 293 K had linewidth ca. 540 Hz with no ^{1}H decoupling applied, and linewidth ca. 180 Hz with ^{1}H decoupling applied. This observation is consistent with the occurrence of rapid isotropic molecular reorientation at room temperature.

Figure 1 shows ^{13}C CP-MAS NMR spectra of TTMSM recorded in the temperature range 236–177 K. There are no significant changes for the peak assigned to the central carbon on lowering the temperature, except a temperature dependence of the chemical shift ($\delta = -2.0$ ppm at 223 K; $\delta = -2.4$ ppm at 167 K). Henceforth, the discussion will consider only the region of the spectrum containing peaks due to the methyl carbons. At 231 K, an abrupt change of linewidth occurs (from ca. 20 Hz at 236 K to ca. 40 Hz at 231 K). The spectrum at 231 K (Fig. 2a) may be interpreted (using the Bruker spectral analysis program LINESIM) as a superposition of two peaks with linewidths 23 Hz (6.0 ppm) and 64 Hz (6.1 ppm) and approximately equal peak areas (Figs. 2b and 2c).

The peak at 6.0 ppm at 231 K is assigned to the methyl carbons of the high-temperature phase (metastable below 231 K). The intensity of this peak decreases on cooling, and its intensity becomes negligible at ca. 193 K (not shown in Fig. 1).

The broad peak at 6.1 ppm at 231 K is assigned to the methyl carbons of the low-temperature phase. On lowering the temperature from 231 to 225 K, this peak broadens further; below 222 K it develops into two peaks with 1 : 3 intensity ratio, and then below 213 K it develops into a set of four peaks with 1 : 1 : 1 : 1 intensity ratio (δ = 7.5, 6.2, 5.3, and 4.8 ppm at 167 K). Two-dimensional ^{13}C CP-EXSY spectra (4) were recorded at 177 K with a mixing period of 500 msec (Fig. 3). The observed cross-peaks confirm the occurrence of exchange processes between all four types of methyl sites (vide infra). (It should be noted that spin diffusion processes are another possible source of cross-peaks in such spectra, but are not important in this case.)

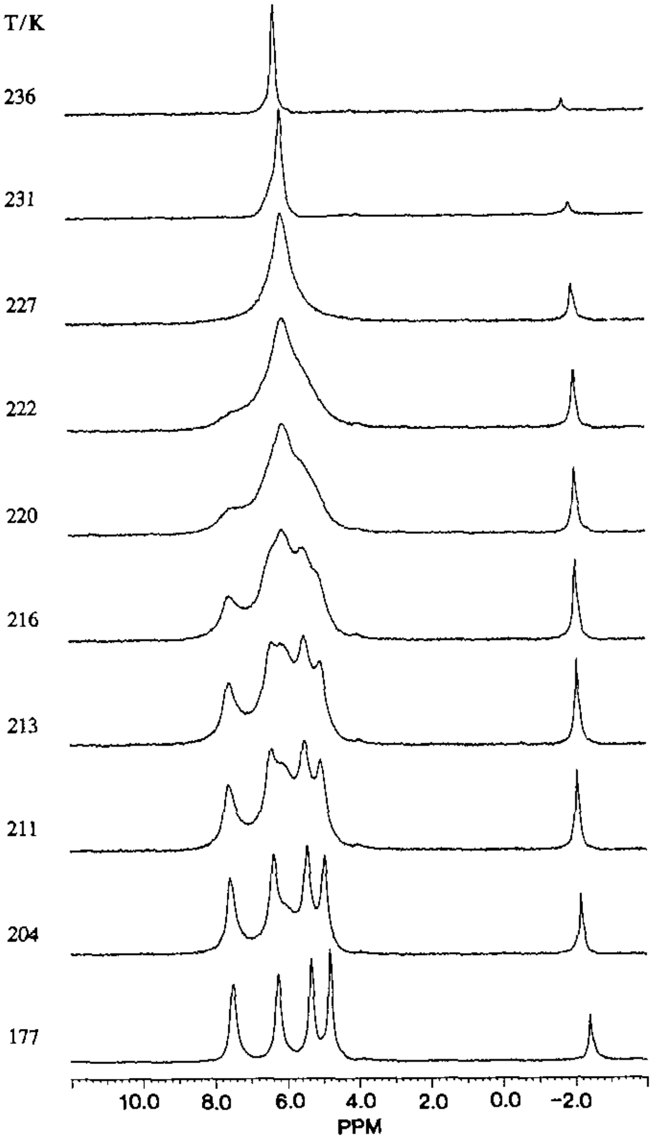

FIG. 1. ^{13}C CP-MAS NMR spectra of TTMSM recorded (at 125.8 MHz) as a function of temperature (recycle delay = 5 sec; MAS frequency = 4 kHz). Chemical shifts are given relative to tetramethylsilane.

The ^{29}Si CP-MAS NMR spectrum recorded at 304 K contains a single peak ($\delta = -1.4$ ppm; linewidth ca. 4 Hz). On cooling below the phase transition temperature, this peak broadens considerably and becomes a pair of peaks with 1 : 3 intensity ratio, representing two different SiMe_3 environments. At 144 K, the chemical shifts of the two peaks with 1 : 3 intensity ratio in the spectrum are $\delta = -0.1$ ppm and $\delta = -1.2$ ppm, respectively.

We now propose a model for the temperature dependence of the dynamic properties of solid TTMSM which

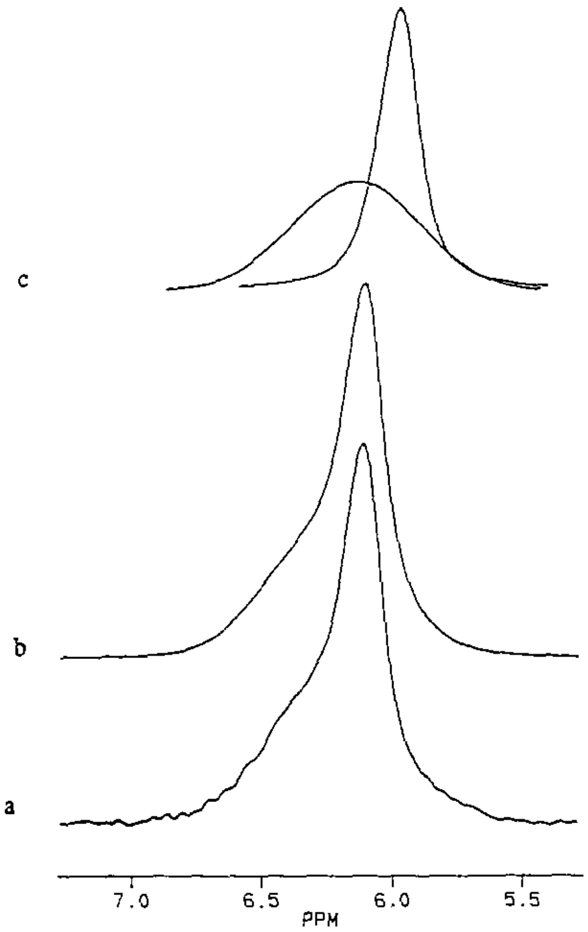

FIG. 2. (a) Experimental ^{13}C CP-MAS NMR spectrum recorded (at 125.8 MHz) for TTMSM at 231 K. (b) Simulated ^{13}C NMR spectrum consisting of the superposition of a pair of overlapping peaks centered at 6.0 ppm (linewidth 23 Hz) and 6.1 ppm (linewidth 64 Hz) and with approximately equal peak areas. (c) Individual peaks used in the simulated ^{13}C NMR spectrum shown in (b).

is consistent with the spectroscopic evidence discussed above and consistent with plausible dynamic behavior for the TTMSM molecule.

The broadening of the peak due to the methyl carbons in the ^{13}C NMR spectrum from 231 to 227 K is indicative of a gradual decrease in the motional rate of these carbons on lowering temperature. In the high-temperature phase, the motion is essentially isotropic, whereas, as discussed below, the motion in the low-temperature phase consists of the following dynamic processes: (1) exchange between a crystallographically unique Si*Me*$_3$ group and an Si*Me*$_3$ group within a set comprising the other three Si*Me*$_3$ groups (which are crystallographically equivalent); (2) reorientation of each Si*Me*$_3$ group about the relevant C[c]–Si bond (where C[c] denotes the central carbon atom); and (3) exchange between the Si*Me*$_3$ groups in the set of three equivalent Si*Me*$_3$ groups (although this will clearly have no effect on the spectrum). It is suggested that the symmetry of the TTMSM molecule in the crystal changes from *T* to C_3 on passing below the transition from the "rotator" phase, giving rise to the situation in which one Si*Me*$_3$ group becomes crystallographically inequivalent from the other three.

On lowering the temperature through the range 230–177 K, the ^{29}Si NMR spectrum (Fig. 4) changes from a single peak at high temperature to two peaks with 1 : 3 intensity ratio at low temperature (with coalescence at ca. 205 K). This is attributed to a change in molecular and/or crystal symmetry from a situation in which all four Si*Me*$_3$ groups are crystallographically equivalent (at least over the appropriate NMR timescale) to a situation in which one Si*Me*$_3$ group (denoted Si[1]*Me*$_3$) becomes inequivalent to the other three Si*Me*$_3$ groups (denoted Si[2]*Me*$_3$). In this temperature region, it is assumed that each Si*Me*$_3$ group is undergoing rapid reorientation about the relevant C[c]–Si bond, and it is probable, as in the case of tri-*tert*-butylsilane (5), that there is a high degree of correlation between the reorientational motions of these different Si*Me*$_3$ groups. It is proposed that just below the phase transition temperature, there is exchange of each Si*Me*$_3$ group between the Si[1]*Me*$_3$ and the Si[2]*Me*$_3$ sites (dynamic process (1)). (As discussed further below, dynamic process (1) *and* dynamic process (2) *both* contribute to coalescence in the ^{13}C NMR spectrum of the Si*Me*$_3$ groups in the temperature range 222–220 K (see Fig. 1).) There are no further changes in the ^{29}Si NMR spectrum upon further decreasing the temperature, suggesting that there are no further changes in crystal symmetry down to the lowest temperatures studied.

There are, however, further changes in the ^{13}C NMR spectrum, and these changes can be understood on the basis of alterations in the reorientational motions of the Si*Me*$_3$ groups around the C[c]–Si bonds (while maintaining the overall C_3 symmetry of the TTMSM molecule).

From 216 to 177 K, the ^{13}C NMR spectrum develops into a set of four peaks with 1 : 1 : 1 : 1 intensity ratio. This spectral change is a consequence of the reorientation of each Si[2]*Me*$_3$ group about the relevant C[c]–Si bond becoming increasingly hindered such that, over the timescale of the ^{13}C NMR measurement, the three methyl carbons within each Si[2]*Me*$_3$ group become inequivalent. All methyl carbons in the Si[1]*Me*$_3$ group remain equivalent to each other (and inequivalent to any of the methyl carbons in the Si[2]*Me*$_3$ groups), giving rise to one of the lines in the set of four lines.

The observation of four lines with 1 : 1 : 1 : 1 intensity ratio in the ^{13}C NMR spectrum below ca. 216 K strongly suggests that the molecular symmetry of the TTMSM molecule in this temperature region is C_3 rather than C_{3v}. If the TTMSM molecule had C_{3v} symmetry (requiring one methyl group of each Si[2]*Me*$_3$ group to lie in the Si[1]–C[c]–Si[2] plane, with the other two methyl groups

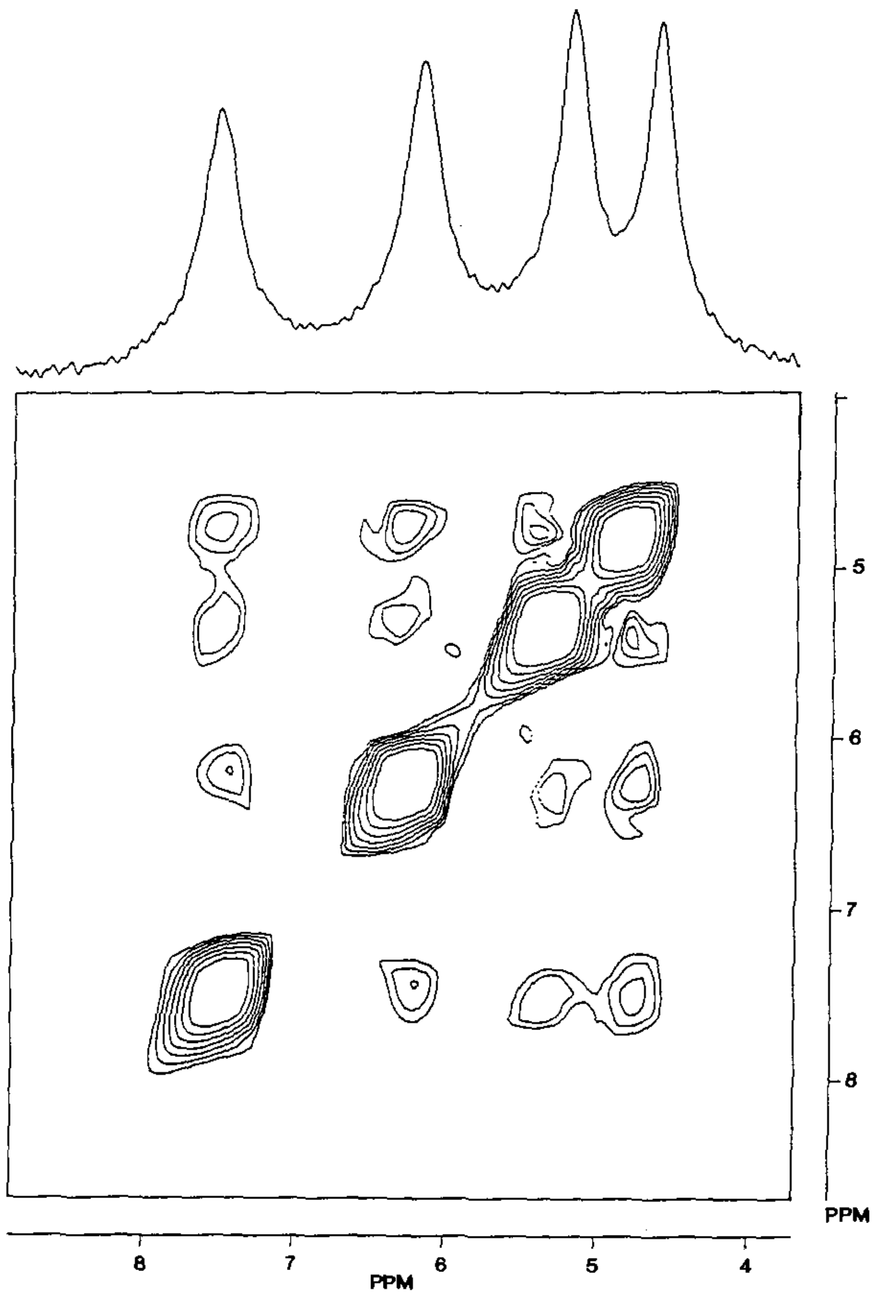

FIG. 3. Two-dimensional ^{13}C CP-EXSY spectrum recorded (at 125.8 MHz) for TTMSM at 177 K using the pulse sequence given in Ref. (4). Only the region of the spectrum containing peaks due to the methyl carbons is shown—there are no cross peaks relating the central carbon and the methyl carbons. Operating conditions: mixing time = 500 msec; CP contact time = 2.4 msec; recycle delay = 2 sec; MAS frequency = 4 kHz.

related to each other across this mirror plane), then the methyl carbons of the Si[2]*Me*$_3$ group would give rise to two lines with 1 : 2 intensity ratio in the ^{13}C NMR spectrum, rather than the three lines with 1 : 1 : 1 intensity ratio observed.

All methyl carbons of the Si[1]*Me*$_3$ group remain equivalent at all temperatures studied in the low-temperature phase, since these methyl carbons are related by the C_3 molecular symmetry. The methyl carbons of the Si[1]*Me*$_3$ group therefore give rise to a single peak in the ^{13}C NMR spectrum throughout the temperature range studied, irrespective of whether the Si[1]*Me*$_3$ group is undergoing rotation about the C[c]–Si[1] bond and irrespective of whether the whole molecule is undergoing rotation about a crystallographic axis coincident with the molecular C_3 symmetry axis.

From the similarity of the coalescence temperatures for dynamic processes (1) and (2), it can be deduced that

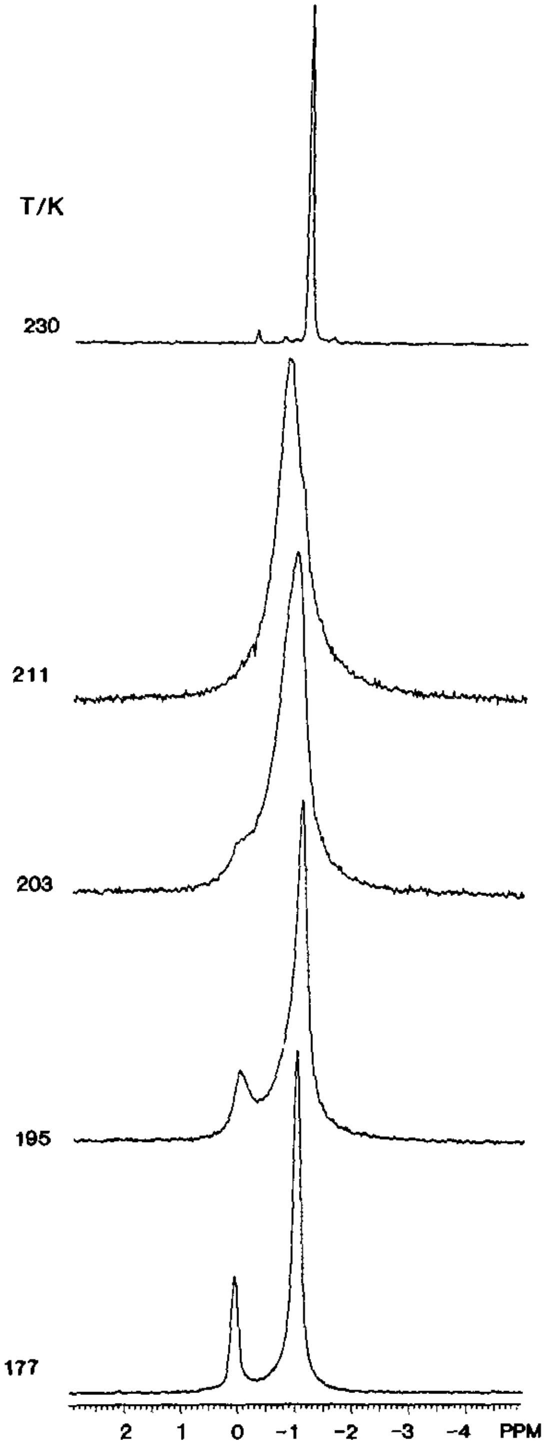

FIG. 4. ^{29}Si CP-MAS NMR spectra of TTMSM recorded (at 59.58 MHz) as a function of temperature (recycle delay = 5 sec; MAS frequency = 2.1 kHz).

the free energy of activation for the dynamic process involving exchange of Si[1]*Me*$_3$ and Si[2]*Me*$_3$ groups is substantially the same as the free energy of activation for the dynamic process involving rotation of each Si[2]*Me*$_3$ group about the relevant C[c]–Si bond. However, due to the extensive overlap of spectral lines in the coalescence region for the ^{13}C NMR spectra, and due to the presence of a signal from the metastable high-temperature phase in this temperature region, it is not considered justified to attempt to derive quantitative information on the free energies of activation from lineshape analysis of these ^{13}C NMR spectra.

Instead, the free energy of activation ($\Delta G\ddagger$) for dynamic process (1), involving exchange of Si[1]*Me*$_3$ and Si[2]*Me*$_3$ groups, has been estimated (using the method described in Ref. (6)) as $\Delta G\ddagger$ = 41 kJ mole^{-1} at the coalescence temperature (ca. 205 K) in the ^{29}Si NMR spectra. From the fact that the coalescence temperatures for dynamic processes (1) and (2) in the ^{13}C NMR spectra are close to each other, it is valid to assume that the free energies of activation for these processes will be similar. Thus, we infer that the free energy of activation for the dynamic process involving rotation of each Si[2]*Me*$_3$ group about the relevant C[c]–Si bond will be close to 41 kJ mole^{-1}.

We now compare and contrast the free energies of activation for these dynamic processes in solid TTMSM with those for the corresponding processes in the structurally related molecule TTMSS in the solid state. The values reported previously (2) for TTMSS are: process (1), $\Delta G\ddagger$ = 46 kJ mole^{-1} (228 K); process (2), $\Delta G\ddagger$ = 36–38 kJ mole^{-1} (182–193 K). (Note: comparison of $\Delta G\ddagger$ values determined at different temperatures, in the manner attempted below, is strictly valid only if $\Delta S\ddagger$ is close to zero; this fact has indeed been demonstrated (7) by lineshape analysis for reorientation of the Si[2]*Me*$_3$ groups (dynamic process (2)) in solid TTMSS ($\Delta H\ddagger$ = 34 ± 3 kJ mole^{-1}; $\Delta S\ddagger$ = 0 ± 20 J K^{-1} mole^{-1}).) The shorter bond length for C[c]–Si in TTMSM (r(C–Si) = 1.93 Å(8)) in comparison with Si[c]–Si in TTMSS (r(Si–Si) = 2.36 Å (9)) results in an increase of $\Delta G\ddagger$ for the reorientational motion of the Si[2]*Me*$_3$ groups (dynamic process (2)) in TTMSM.

In the two-dimensional ^{13}C CP-EXSY spectrum for TTMSS at 162 K (2), there are no observable cross-peaks relating to the exchange of Si*Me*$_3$ groups between the Si[1]*Me*$_3$ and the Si[2]*Me*$_3$ sites, and the only observed cross-peaks relate to the three distinguishable methyl sites of the Si[2]*Me*$_3$ groups. For TTMSM, on the other hand, four different types of cross-peaks relating the methyl carbons are observed in the two-dimensional ^{13}C CP-EXSY spectrum at 177 K, suggesting that, even at this low temperature, each methyl group still participates in *both* types of dynamic process (which, at this temperature, are in the slow exchange region for the one-dimensional ^{13}C NMR experiments). The $\Delta G\ddagger$ value for the exchange process between the Si[1]*Me*$_3$ and Si[2]*Me*$_3$ sites in TTMSS is higher than the corresponding value for TTMSM, whereas the $\Delta G\ddagger$ value for the exchange process involving reorientation of each Si[2]*Me*$_3$ group

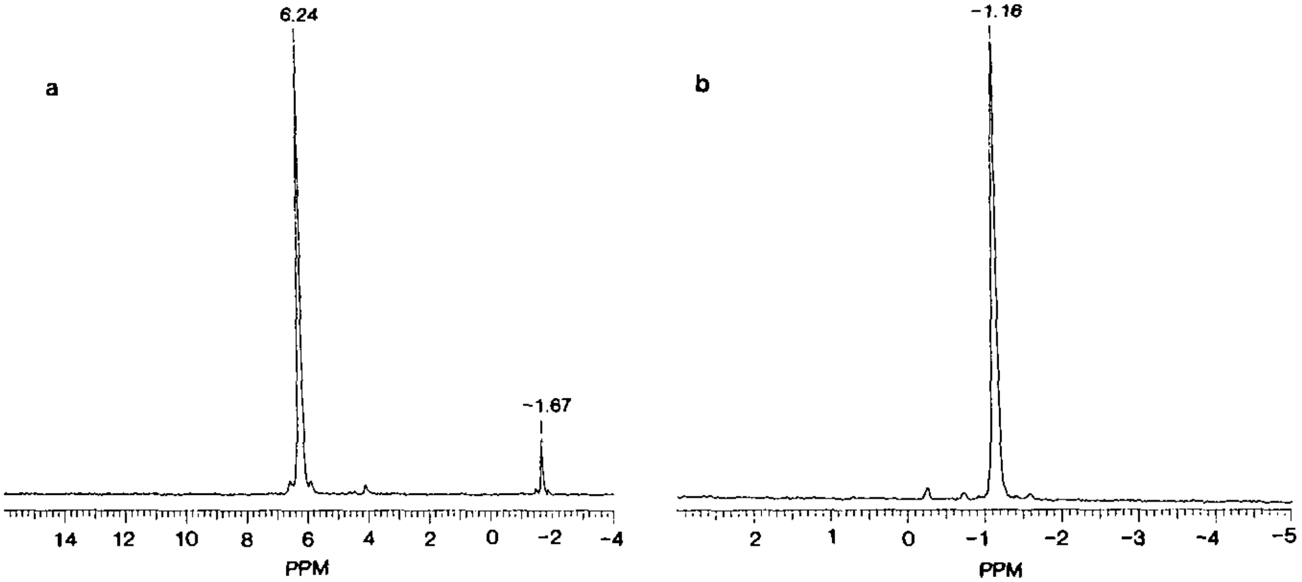

FIG. 5. (a) ^{13}C CP-MAS NMR spectrum recorded at 75.43 MHz (VXR 300 spectrometer) for TTMSM in the high-temperature phase (at 236 K) (recycle delay = 5 sec; MAS frequency = 2.1 kHz). The peak at $\delta \approx 4.2$ ppm arises from an impurity. (b) ^{29}Si CP-MAS NMR spectrum recorded at 59.58 MHz for TTMSM in the high-temperature phase (at 236 K) (recycle delay = 5 sec; MAS frequency = 2.1 kHz). The peak at $\delta \approx -0.2$ ppm arises from an impurity.

about the relevant C[c]–Si[2] bond in TTMSS is lower than the corresponding value for TTMSM. Thus, the molecular reorientation required to exchange an Si*Me*$_3$ group between the Si[1]*Me*$_3$ and Si[2]*Me*$_3$ sites is relatively *more restricted* within solid TTMSS, whereas, as discussed above, the reorientational motion of the Si[2]*Me*$_3$ groups is relatively *less restricted* in TTMSS.

The solution state ^{13}C NMR spectrum (at 125.8 MHz) for TTMSM dissolved in a mixture of $CDCl_3$ and $CFCl_3$ (1 : 2 v/v) contains two peaks at all temperatures down to 173 K. These peaks are assigned to the methyl carbons (δ = 5.47 ppm at 293 K, with small additional peaks on both sides originating from ^{29}Si–^{13}C coupling with $|^1J_{SiC}| = 51.4$ Hz) and to the central carbon atom (δ = -1.63 ppm at 293 K). The fact that only a single peak is observed for the methyl carbons even at 173 K suggests that $\Delta G‡$ for the reorientational motion of each Si*Me*$_3$ group about the relevant C[c]–Si bond is appreciably smaller in the solution state than in the solid state.

It is interesting to note that satellite peaks due to ^{29}Si–^{13}C coupling are not observed in the high-resolution solid state ^{13}C NMR spectrum recorded at 125.8 MHz (see Fig. 1), whereas such satellite peaks *are* observed in the high-resolution solid state ^{13}C NMR spectrum recorded at 75.43 MHz (see Fig. 5a) and also in the high-resolution solid state ^{29}Si NMR spectrum recorded at 59.58 MHz (see Fig. 5b). From these spectra (recorded at 236 K), the measured coupling constants are $|^1J_{SiC}|$ = 51 Hz (for the methyl carbons) and $|^1J_{SiC}|$ = 29 Hz (for the central carbon). In the ^{13}C NMR spectrum, the linewidths of the main peaks (8.6 Hz for the signal due to the methyl carbons and 5.1 Hz for the signal due to the central carbon) are narrower than those discussed above for the ^{13}C NMR spectrum recorded at 125.8 MHz.

The molecular structures of TTMSS and TTMSM have been studied by gas-phase electron diffraction and by molecular mechanics calculations (8–11) and, on the basis of these results, it is suggested that the Si*Me*$_3$ groups undergo cooperative torsional displacements and that their torsional freedom is appreciably reduced by the methyl–methyl interactions. Although considerable caution must be taken before using information derived from these approaches to understand the properties of the same molecule in the solid state, it is nevertheless interesting to recognize the underlying similarities between the results derived from the gas-phase studies and the dynamic models proposed above for TTMSM in the solid state.

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