Structure and Dynamics of Solid Tris(trimethylsilyl)amine by Deuterium Nuclear Magnetic Resonance Spectroscopy

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Deuterium NMR spectra for solid [$^2H_9$]tris(trimethylsilyl)amine were recorded at 77 K and in the region 114–353 K. At 77 K there is only fast rotation of the methyl groups. Between 122 and 171 K rotation of the trimethylsilyl groups and of the entire molecule (about its C_3 axis) affect the deuterium NMR line shape. Above 180 K both motions are fast ($> 10^5$ Hz). There is a phase transition at 227 ± 2 K. Above 227 K the molecule undergoes a fast precessional motion of increasing effective amplitude until the melting point (343 K). The only dynamic model capable of explaining the spectra at temperatures above 180 K requires the three N–Si bonds to be coplanar.

The structure of silylamines has been the subject of considerable interest,[1–6] particularly since many are planar whereas other amines are pyramidal. One of the most studied of these planar silylamines is tris(trimethylsilyl)amine.[7–9] Recently the molecular structure of $N(SiMe_3)_3$, in the gas phase, was determined by electron diffraction.[7] The results are consistent with a planar geometry at nitrogen. Solid $N(SiMe_3)_3$ is a soft waxy solid and not amenable to crystal diffraction studies, and a proton wide-line NMR study of solid $N(SiMe_3)_3$ indicated a considerable amount of rotational disorder.[8] With this in mind it seems unlikely that an X-ray diffraction study of solid $N(SiMe_3)_3$ would yield a well defined molecular structure. Such a study of $NH(SiMe_3)_2$ by Blake *et al.*[5] required the temperature to be lowered to 116 K. The internal rotation and overall molecular rotation of $N(SiMe_3)_3$ were studied by following the proton linewidth and second moment as a function of temperature.

The dominant spin interaction in the proton NMR of solids is the dipolar spin coupling between protons. When calculating the proton linewidth and second moment all possible proton spin–spin interactions must be considered. In addition to this the averaging of these interactions by motion of the C–H bonds must be taken into account. Whereas proton NMR spectroscopy benefits from excellent signal-to-noise ratios, interpretation of the motionally averaged spectra suffers from the inability to distinguish between some dynamic models. In contrast, deuterium NMR spectroscopy suffers from poor signal-to-noise ratios (at natural abundance) but displays *line shapes* that are modulated by reorientation of the C–D bond. In many cases deuterium line-shape analysis can distinguish between dynamic models whereas analysis of proton linewidth cannot. Because of the sensitivity of the line shape to the dynamic model, information on molecular structure can also be obtained from deuterium NMR line-shape analysis. We have undertaken a deuterium NMR study of solid [$^2H_9$]-tris(trimethylsilyl)amine in order to gain some insight into the dynamics and structure of the molecule in the solid state.

Deuterium NMR spectroscopy has been used for the study of molecular structure and dynamics in many solid systems.[10–12] The deuterium NMR line shape is dominated by the quadrupolar interaction between the nuclear quadrupole moment, eQ, and the electric field gradient at the nucleus, eq_{zz}. The quadrupolar coupling constant, χ, is a measure of the quadrupolar interaction and is given by equation (1). Another measureable parameter is the asymmetry, η. It is a measure of the difference in magnitude between the two smaller principal components of the electric field gradient tensor, eq_{xx} and eq_{yy}, with respect to the largest component, eq_{zz}. For methyl C–D, eq_{zz} lies along the bond and the asymmetry parameter is typically zero.

$$\chi = e^2q_{zz}Q/h \qquad (1)$$

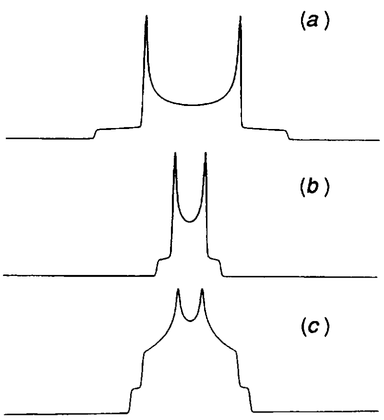

Fig. 1 (*a*) A typical deuterium powder spectrum for a methyl deuterium with no reorientation of the C–D bond. The quadrupolar coupling constant, χ, is 172 kHz yielding a splitting, $\Delta\nu$, of 127 kHz. (*b*) A spectrum of the deuterium in (*a*) when undergoing a three-site exchange with the C–D bond making an angle of 70.5° with respect to the rotational axis (tetrahedral geometry). (*c*) The line shape expected for a two-site exchange. The spectrum shown is that for a fast flip through 120° as expected for a planar tris(trimethylsilyl)amine. The spectrum must be scaled down by a factor of 9 in order to account for additional methyl and trimethylsilyl rotation

Under conditions where the C–D bonds are reorienting at a rate much smaller than the quadrupolar coupling constant the typical rigid-lattice powder spectrum is observed, as shown in Fig. 1(*a*). The spectrum is characterized by a peak-to-peak splitting $\Delta\nu$ [equation (2)] and a separation between the outer

$$\Delta\nu = \tfrac{3}{4}\chi \qquad (2)$$

shoulders which is twice $\Delta\nu$. If only fast axially symmetric motions, such as n-fold ($n \geqslant 3$) rotational jumps of the C–D bonds, are considered the line shape will not change but the linewidth will be reduced by the motion. Methyl rotation, as depicted in Fig. 2(*a*), will yield a partially averaged spectrum

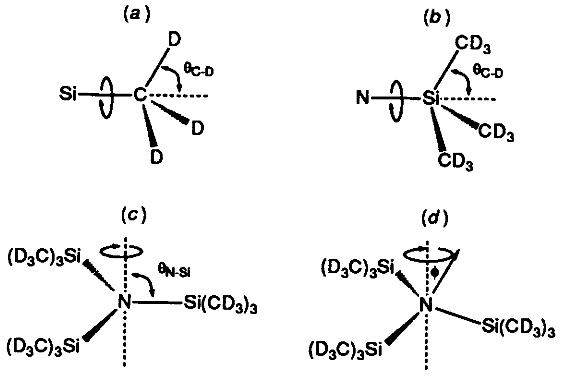

Fig. 2 (*a*) Rotation of the methyl C–D bonds about the Si–C bond axis. (*b*) Rotation of the trimethylsilyl group about the N–Si bond axis. (*c*) Rotation of the molecule about its C_3 axis. (*d*) The precessional motion of the molecule about a cone defined by half-angle φ

with a peak-to-peak splitting as given in equation (3), where

$$\Delta\nu = \tfrac{3}{8}\chi(3\cos^2\theta_{C-D} - 1) \qquad (3)$$

θ_{C-D} is the angle between the three-fold methyl axis and the C–D bonds (typically 70.5°). The effect of a three-site reorientation of the C–D bonds is shown in Fig. 1(*b*). In addition to this motion the three-fold reorientation of the trimethylsilyl groups, as shown in Fig. 2(*b*), will further reduce the splitting to that given in equation (4), where θ_{Si-C} is the angle between the three-fold

$$\Delta\nu = \tfrac{3}{16}\chi(3\cos^2\theta_{C-D} - 1)(3\cos^2\theta_{Si-C} - 1) \qquad (4)$$

axes (along the N–Si bonds) and the Si–C bonds. Finally the entire molecule may reorient; and there are a number of ways in which this may be done. First there may be a rotation of the molecule about its C_3 axis [see Fig. 2(*c*)]. This would further reduce the splitting to that given in equation (5), where θ_{N-Si} is

$$\Delta\nu = \tfrac{3}{32}\chi(3\cos^2\theta_{C-D} - 1)(3\cos^2\theta_{Si-C} - 1)(3\cos^2\theta_{N-Si} - 1) \qquad (5)$$

the angle between the C_3 axis and the N–Si bonds. The molecule may also experience two-fold flips about the N–Si bonds. If the N–Si bonds are coplanar, fast, random two-site jumps about the three equivalent N–Si bonds will give a result, on average, indistinguishable from that of a random three-site exchange. On the other hand, this type of motion would have the effect on a tetrahedral geometry (Si–N–Si 109.5°) of an exchange between four tetrahedral sites. This is known as pseudo-isotropic rotation, in that the result is a narrow resonance ($\Delta\nu = 0$) characteristic of that for isotropic motion (as observed in solution). If the molecule has a geometry with Si–N–Si angles between 120 and 109.5° the result of random jumps about each N–Si bond is that the trimethylsilyl groups sample a distribution of sites on a sphere. If this motion is sufficiently rapid the result should be the equivalent of isotropic motion. Two-site rotation about one preferred N–Si bond is not an axially symmetric mode of reorientation and would introduce an asymmetry into the deuterium powder spectrum, as shown in Fig. 1(*c*), although this would seem to be an unlikely situation. Spectra for intermediate exchange rates (10^3–10^6 s^{-1}) are more complex in appearance and the line shapes depend strongly on the exchange rates and molecular geometry.

Experimental

[$^2H_9$]Tris(trimethylsilyl)amine was synthesised by the dropwise addition of chloro[$^2H_9$]trimethylsilane (MSD isotopes) to a solution of lithium bis(trimethylsilyl)amide in tetrahydrofuran (thf) (Aldrich).[13] After evaporation of the solvent the product was sublimed. Its identity and purity was confirmed by ^{1}H, ^{13}C, ^{29}Si and ^{14}N NMR spectroscopy.[14,15]

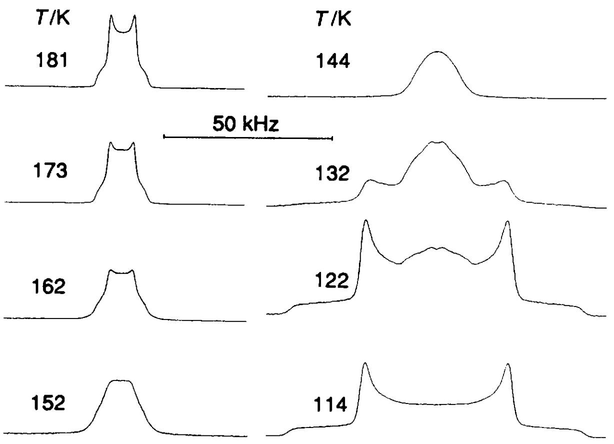

Fig. 3 Deuterium NMR spectra of [$^2H_9$]tris(trimethylsilyl)amine between 114 and 181 K

Deuterium NMR spectra were collected at temperatures ranging from 114 to 333 K in approximately 10 K intervals. The data were acquired at 41.3 MHz using a laboratory-built spectrometer and employing the quadrupolar echo pulse sequence.[16] Typically the length of a 90° pulse was 3.5 μs, and 100 scans were collected. Echo signals were collected after a delay of 40 μs and were Fourier transformed to obtain the deuterium frequency spectra. The spectrum at 77 K was obtained with a Bruker CXP-200 spectrometer operating at a frequency of 30.7 MHz and employing a laboratory-built probe.

Results and Discussion

In presenting and discussing the results we will begin with those at the lowest attainable temperature and discuss the evolution of the deuterium spectra as the temperature is increased and as contributions to the dynamic model are introduced.

At 77 K the observed quadrupolar splitting, $\Delta\nu$, is 43.0 ± 0.5 kHz. This is consistent with fast methyl rotation. Using equation (1) and assuming a tetrahedral geometry for the methyl carbons ($\theta_{C-D} = 70.5°$) we calculate a quadrupolar coupling constant, χ, of 172 ± 2 kHz. The line shape does not change until a temperature of about 122 K is reached. Levy[8] similarly interprets the proton data in terms of C_3 rotation of the methyl groups at temperatures below 114 K.

In the temperature range 122–173 K there is a gradual change in the line shape (see Fig. 3). At 181 K a typical powder spectrum with a splitting of 7.3 ± 0.2 kHz is observed. The reduction in proton linewidth and second moments for this temperature interval was interpreted by Levy[8] in terms of increasingly fast rotation of the trimethylsilyl groups. If we assume that the trimethylsilyl groups have a tetrahedral arrangement about the silicons, the splitting for rapid reorientation should be 14.3 kHz. This is about twice the observed splitting. If the reduction in $\Delta\nu$ is due solely to trimethylsilyl rotation an N–Si–C bond angle (180° − θ_{Si-C}) of 118° is implied. This is a deviation of 8.5° from a tetrahedral geometry, a *highly* unlikely situation even for a sterically hindered molecule like tris(trimethylsilyl)amine. We suggest that an additional motion of the molecule would account for the further reduction in $\Delta\nu$. Any motion of non-axial symmetry can be discounted as such a motion would result in a change of line shape. A likely motion is the additional rotation of the molecule about its C_3 axis. The only reasonable angle, θ_{N-Si}, which yields a $\Delta\nu$ value close to the observed splitting is 90° (the other being 35°). Therefore if the geometries of the methyl and trimethylsilyl groups are assumed to be tetrahedral and that at the nitrogen to be planar a calculated $\Delta\nu$ value of 7.2 ± 0.1 kHz is obtained. This is in excellent agreement with the observed splitting of

Table 1 Quadrupolar splittings and calculated precessional angles for tris(trimethylsilyl)amine

T^a/K	$\Delta\nu^b$/kHz	φ^c/°
303	1.00	49.3
292	1.20	48.2
283	1.30	47.7
273	1.40	47.1
263	1.65	45.8
253	1.75	45.3
243	2.00	43.9
233	2.20	42.9

[a] Error about ± 1 K. [b] Error about ± 0.05 kHz. [c] Error about ± 0.5°.

7.3 ± 0.2 kHz. Allowing the NSi_3 framework to deviate from a planar geometry would decrease the calculated value of $\Delta\nu$, increasing the difference between the calculated and experimental values. An increase in the N–Si–C bond angles will further decrease $\Delta\nu$, as will an increase in the Si–C–H bond angles. Allowing N–Si–C or Si–C–H to decrease, thus improving the agreement between experiment and calculation, is physically unreasonable considering the crowding of the trimethylsilyl groups. As previously noted, the only other reasonable dynamic model that would result in exchange of the trimethylsilyl groups is random two-fold jumps about all three N–Si bonds. In order for the trimethylsilyl groups to exchange between equivalent sites the N–Si bonds must be coplanar. If the N–Si bonds are not coplanar the trimethylsilyl groups will be rapidly sampling a distribution of sites on a sphere. This pseudo-isotropic motion should yield a narrow liquid-like resonance. Therefore both models require the N–Si bonds to be coplanar in order to explain a deuterium quadrupolar splitting of 7.3 kHz. Reorientation of the molecule about the C_3 axis should be a less sterically demanding process than rotation about an axis perpendicular to the C_3 axis. One might be tempted to think of the general shape of tris(trimethylsilyl)amine as spherical and argue that no axis should be preferred, but space-filling models reveal a shape more reminiscent of a fat doughnut (torus). Hence our results provide strong NMR evidence for a planar silylamine in the solid state. The spectral changes then suggest that trimethylsilyl rotation and molecular C_3 reorientation are simultaneously introduced in the temperature range 122–173 K. We are not able quantitatively to disentangle these two motions. Qualitatively the spectra show that the trimethylsilyl motion is only 'frozen out' at temperatures below 122 K, suggesting a rather low activation energy for trimethylsilyl rotation. Electron diffraction studies reveal a nearly C_{3h} molecular symmetry with the trimethylsilyl groups twisted 5.2° out of the plane of the Si–N bonds. This gearing of the trimethylsilyl groups could account for such a low activation energy.

The spectrum remains unchanged from 180 to 225 K. This is consistent with the proton wideline spectra which also show no changes until 232 K.[8] Between 225 and 228 K the splitting is further reduced to 2.2 kHz. This abrupt change suggests that there is a phase transition occurring at about 227 ± 2 K. A visual phase transition was reported at 242 ± 5 K.[8] The difference may be due to the visual nature of the latter observation. As the temperature is raised from 233 to 333 K the splitting decreases from 2.2 to 0.9 kHz. The spectra for this temperature region are shown in Fig. 4. We interpret the decrease in $\Delta\nu$ with increasing temperature as arising from a precessional motion of the whole molecule. Heyes and Dobson[17] have employed a precessional model to explain the continuous change in the deuterium NMR line shape of the deoxycholic acid-[$^2H_{10}$]ferrocene inclusion complex with temperature. The fact that the asymmetry parameter remains equal to or very near zero suggests that the precessional motion takes the form of an axially symmetric 'wobbling' of increasing effective amplitude with temperature. A precessional 'wobble' has been used to explain the decrease in $\Delta\nu$ with increasing temperature for deuteriated CH_3NH_3 cations in methylammonium salts.[18,19] A large-amplitude libration would introduce an effective non-zero asymmetry into the spectra as would an ellipsoidal type of precession (combined libration and 'wobble'). Although the motion is best described as a diffusion within a cone where the distribution of angles, φ, is governed by some function $g(\varphi)$, a simpler model may be employed in which the molecule is allowed to precess about some cone of half-angle φ. This would further reduce $\Delta\nu$ by a factor of $R = \frac{1}{2}(3\cos^2\varphi - 1)$. Strictly speaking the reduction in splitting measures the average quantity $\langle 3\cos^2\varphi - 1\rangle$.

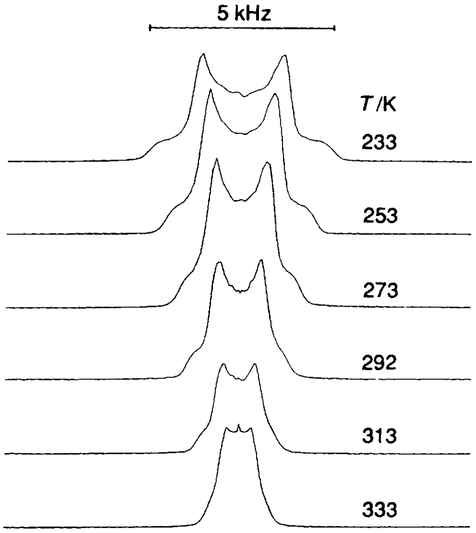

Fig. 4 Deuterium NMR spectra of [$^2H_9$]tris(trimethylsilyl)amine between 233 and 333 K

Taking into account the three aforementioned motions ($\theta_{C-D} = 70.5$, $\theta_{Si-C} = 70.5$, $\theta_{N-Si} = 90°$) in equation (5) and considering the reduction, R, due to precessional motion yields a quadrupolar splitting given by equation (6). The *effective* polar angle, φ, can then be related to the splitting, $\Delta\nu$, by equation (7).

$$\Delta\nu = \frac{\chi}{24}R \qquad (6)$$

$$\varphi = \cos^{-1}\left[\tfrac{1}{3}(2R + 1)\right]^{\frac{1}{2}} \qquad (7)$$

Values of $\Delta\nu$ and φ for temperatures between 333 and 303 K are given in Table 1. As the temperature increases $\Delta\nu$ decreases and the effective precessional angle, φ, increases. This is to be expected if the distribution of angles, $g(\varphi)$, becomes more diffuse. Due to the poor magnetic field homogeneity, line shapes above 303 K were not well defined, nevertheless it is evident that the line shape has not reached $\Delta\nu = 0$ (φ = 54.7°) before the sample melts. The sample melts at 343 K, and at temperatures above 343 K the spectrum is that of a typical liquid.

Conclusion

The various modes of rotational reorientation that can be undertaken by solid tris(trimethylsilyl)amine are summarized diagrammatically in Fig. 2. At some temperature below 77 K methyl rotation begins. Between 122 and 171 K both trimethylsilyl [Fig. 1(*b*)] rotation and rotation of the entire molecule about its C_3 axis affect the line shape. Above 180 K these motions are rapid. There is a phase transition at 227 ± 2 K, accompanied by the introduction of a fast precessional motion of the molecule. The amplitude of the precession increases with temperature until the melting point at 343 K. The deuterium NMR spectrum for temperatures between 180 and 225 K can only be explained using a model in which the N–Si bonds of tris(trimethylsilyl)amine are coplanar.

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