Molecular Dynamics in the Solid Trimethylamine-Borane Complex: A Deuterium NMR Study

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The molecular dynamics of solid $(CH_3)_3NBH_3$ is investigated by deuterium NMR spectroscopy. Variable temperature lineshape analyses yield activation energies of 27 ± 3, 19 ± 2, and 12.5 ± 2 kJ/mol for $-CH_3$, $-N(CH_3)_3$ and $-BH_3$ rotation, respectively. Analysis of the temperature dependence of the spin-lattice relaxation times, T_1, gives activation energies of 33 ± 3, 15 ± 1.5, and 14 ± 1.5 kJ/mol, respectively. Direct comparison of rotational exchange rates (from lineshape simulations) an of rotational correlation times (from T_1 analyses) for $-N(CH_3)_3$ and $-BH_3$ rotation indicate that the two motions are correlated in solid $(CH_3)_3NBH_3$ and together constitute a whole molecule reorientation about the N–B bond. This is supported by an internal rotational barrier of 18.0 kJ/mol for $-BH_3$ rotation, obtained from ab initio molecular orbital calculations at the MP2/6-31G* level.

Key words: NMR spectroscopy; Molecular dynamics; NMR relaxation.

Introduction

Nuclear magnetic resonance (NMR) spectroscopy has proven to be a powerful technique for the investigation of molecular dynamics in solids [1–3]. Spectral lineshape changes are most sensitive when the correlation time, τ_c for the molecular reorientation is approximately equal to the inhomogeneous linewidth, $\Delta\omega$ [4]. Faster motions may be studied by following the spin-lattice relaxation in the laboratory frame, T_1 [5]. The T_1 provides the greatest amount of information in the region of the T_1 minimum, when $\tau_c \approx \omega_0^{-1}$, where ω_0 is the Larmor precessional frequency. Other NMR techniques such as spin-lattice relaxation in the rotating frame, $T_{1\varrho}$, [6] and spin alignment [1, 7] have also been used to probe molecular dynamics in solids.

The motions of a large number of solid trimethyl derivatives, $(CH_3)_3M$, have been investigated by NMR spectroscopy [8, 9]. These molecules can, in principle, undergo two types of rotation: reorientation of the entire $(CH_3)_3M$ group, referred to as trimethyl rotation and denoted C_3', in addition to internal rotation of the three methyl moieties, referred to as methyl rotation and denoted C_3. These two motions are depicted in Figure 1. For many years proton NMR spectroscopy has been used in the investigation of molecular dynamics [10]. The presence of hydrogen in many molecular solids and the high receptivity of ^1H for NMR work made ^1H NMR spectroscopy an obvious choice. Unfortunately neither proton lineshapes (second moment studies) nor T_1 measurements can independently distinguish between C_3 and C_3' motion. It has been generally assumed that C_3 reorientation is less restricted and that, at a given temperature, C_3 rotation is faster than C_3' rotation [11–14]. More recently the molecular dynamics in a number of solids have been reinvestigated using deuterium (^2H or D) NMR spectroscopy [15, 16]. Both deuterium lineshape and T_1 can distinguish between C_3 and C_3' reorientation under conditions where the two motions are unequally restricted. Whereas intermolecular contributions to proton linewiths and relaxation times are significant, deuterium NMR spectroscopy is dominated by the quadrupolar interaction, which depends on the electric field gradient at the deuteron site. The principal part of the electric field gradient comes from the electronic structure of the C–D bond, as a result, the quadrupolar interaction is predominantly an intramolecular property. Deuterium NMR spectroscopy has the additional advanatage in that, with some synthetic ingenuity, specific parts of the molecule of interest can be selectively deuterated [17]. Deuterium is also a relatively inexpensive isotope source for selective enrichment (compared with ^{13}C, ^{15}N, ^{17}O etc.).

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The donor-acceptor complexes formed by trimethylamine and boranes, having the general structure $(CH_3)_3NBX_3$, are known to undergo molecular reorientation in the solid phase. Solid state ^1H, ^{19}F, and ^{11}B NMR spectroscopy have been used to study the various modes of molecular motion for those compounds with X = H, F, and Cl [11, 18–24]. In particular the borane adduct, $(CH_3)_3NBH_3$ was first studied by Yim and Gilson in 1970 [11]. They interpreted second moment results with a model in which rotation of both CH_3 and BH_3 groups was fast at 120 K; and a torsional oscillation about the B–N bond existed at higher temperatures. Merchant and Fung [18] reported a ^2H lineshape in $(CH_3)_3NBD_3$ that was consistent with rapid BD_3 rotation down to 130 K. Ang and Dunell [22] later investigated the temperature dependence of the proton T_1 between 120 K and 380 K. They attributed the T_1 minimum at 157 K to C_3 reorientation of the methyl groups and the borane group while the minimum at 259 K was ascribed to a more restricted reorientation of the entire molecule about the B–N bond. In 1986, Reynhardt [21] remeasured the proton second moments and T_1 as a function of temperature. In addition, proton $T_{1\varrho}$ and ^{11}B T_1 measurements were carried out as complementary methods. The results were explained in terms of dynamically non-equivalent molecules in the unit cell in a ratio of 2:1. The experimental results were interpreted in such a way that the C_3 motions of the methyl and borane groups had the same activation energies and that, between 120 K and 155 K, two-thirds of the molecules reoriented about the molecular B–N bond and one third performed only CH_3 and BH_3 rotation.

We have reinvestigated the dynamics of $(CH_3)_3NBH_3$ through a detailed study of deuterium NMR lineshapes and spin-lattice relaxation times in the two isotopic species $(CD_3)_3NBH_3$ and $(CH_3)_3NBD_3$. Figure 1 shows the three modes of molecular reorientation possible in solid $(CH_3)_3NBH_3$: i) C_3 rotation of each of the methyl groups about the C–N bonds (C_3^C rotation), ii) C_3 rotation of the trimethylamine group about the N–B bond (C_3^N rotation) and iii) C_3 rotation of the borane group about the N–B bond (C_3^B rotation). The two rotations about the N–B bond (C_3^N and C_3^B) constitute a single hindered rotation for the isolated (gas phase) molecule, but may be hindered differently in the solid, due to intermolecular interactions; or the two rotations may combine to yield a correlated hindered whole molecule reorientation in the solid. In addition the molecule can undergo internal rotation in both phases. The dynamic behaviour of the molecule will naturally depend on the relative magnitudes of the intermolecular and intramolecular forces experienced by the molecule in each phase.

Experimental

A sample of $(CD_3)_3NBH_3$ was prepared by the reaction between $(CD_3)_3NHCl$ (MSD isotopes) and $NaBH_4$ in tetrahydrofuran [25]. The product was sublimed to give a pure sample. A sample of $(CH_3)_3NBD_3$ was prepared by isotopic exchange between $(CH_3)_3NBH_3$ (Aldrich) and 0.5 M D_2SO_4/D_2O solution (MSD isotopes) [26]. After sublimation a high degree of deuteration was confirmed by high resolution ^{11}B NMR spectroscopy.

Deuterium NMR spectra were obtained at 44.67 MHz on a home-built spectrometer, using the quadrupolar echo pulse sequence: $[\pi/2]_x-\tau_Q-[\pi/2]_y-\tau_Q$-acquire [27]. Typically, the length of a $\pi/2$ pulse was 4.0 μs. At each temperature the echo signals were collected for a τ_Q value of 50 μs. The echo signals were Fourier transformed to obtain the deuterium NMR spectra. Approximately 250 scans were collected for a single spectrum and the repetition rate for each scan was 1–2 seconds. The T_1 data were acquired using an inversion recovery pulse sequence modified for quadrupolar nuclei: $[\pi]-\tau-[\pi/2]_x-\tau_Q-[\pi/2]_y-\tau_Q$-acquire. Typically 15–20 values of τ were used to determine T_1, at a particular temperature. The time between repetitions of the pulse sequence were always greater than $5T_1$. The temperature at the sample was controlled with a flow of N_2 gas and stabilized with a temperature control unit with a precision of roughly ± 1 °C.

Lineshape simulations of quadrupolar echo spectra, partially narrowed by molecular motion, were performed by standard methods using the program MXQET [28]. Molecular orbital calculations were performed using Gaussian 92 [29] on a Silicon Graphics Power Series 8 computer.

Results and Discussion

(a) $(CH_3)_3NBD_3$

The temperature dependence of the deuterium T_1 for $(CH_3)_3NBD_3$ is shown in Figure 2. The T_1 values were measured between 233 K and 123 K. They pass through a minimum (6.7 ms) at 158 K. If a single re-

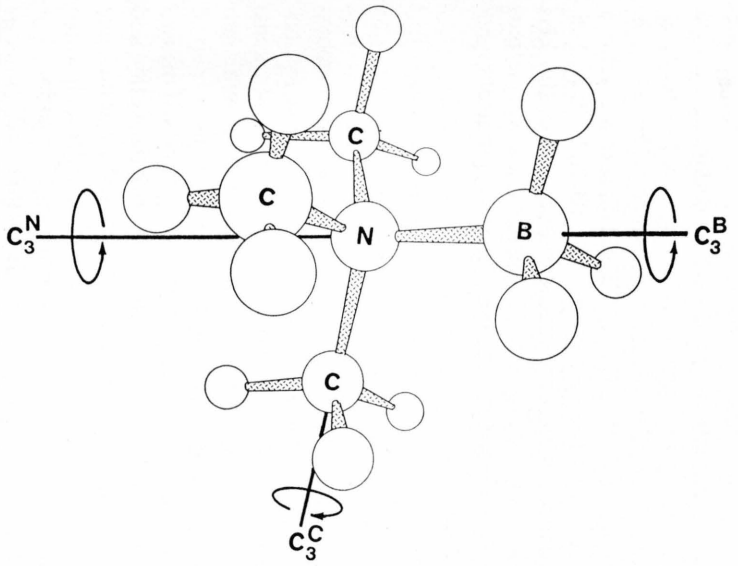

Fig. 1. Structure of $(CH_3)_3NBH_3$ showing the three internal rotational axes. The staggered conformation is depicted. The symbols C_3^N, C_3^B, and C_3^C denote trimethylamine rotation, borane rotation and methyl rotations, respectively.

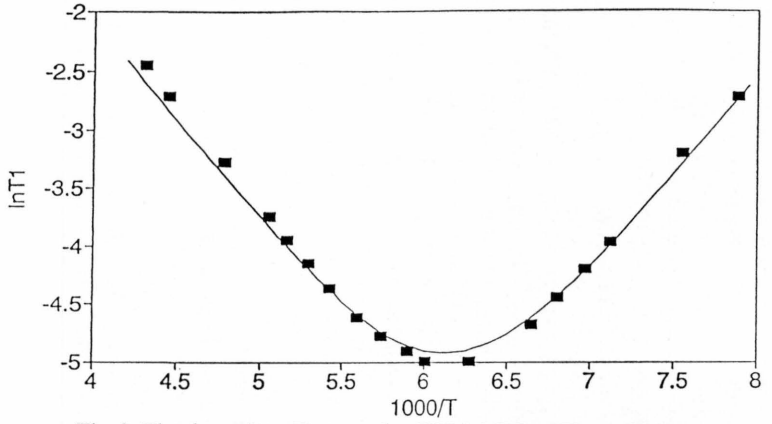

Fig. 2. The deuterium T_1 curve for $(CH_3)_3NBD_3$. The solid line corresponds to the best fit using (1) and (2).

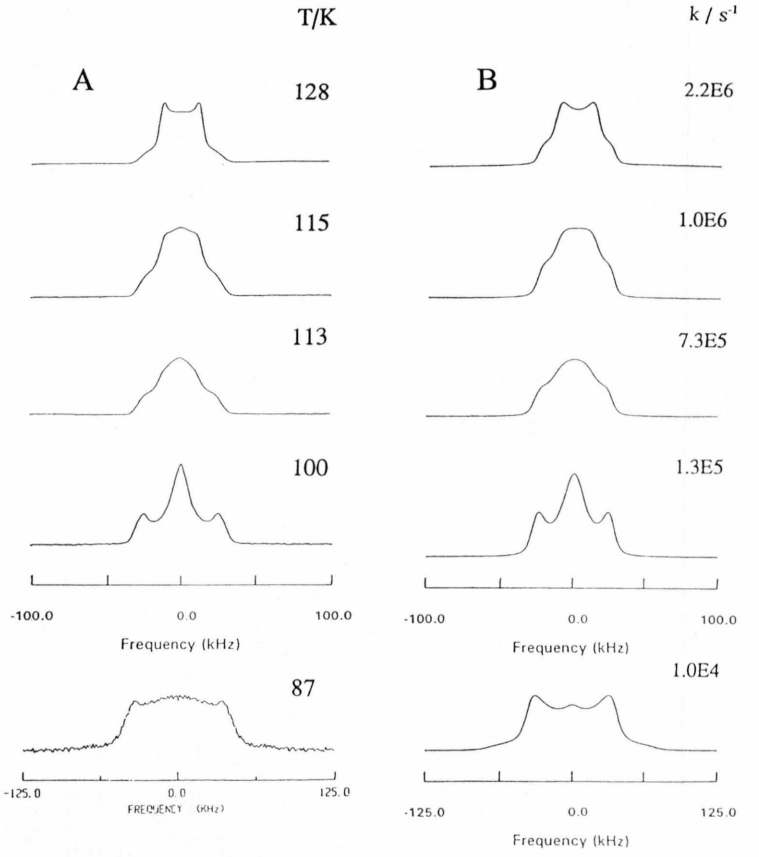

Fig. 3. Deuterium NMR spectra for $(CH_3)_3NBD_3$ at various temperatures (A) together with the best fit simulated spectra (B).

orientational motion is considered, the deuterium T_1 is related to the correlation time, τ_c, for that motion:

$$\frac{1}{T_1} = K\left\{\frac{\tau_c}{1+(\omega_0\tau_c)^2} + \frac{4\tau_c}{1+(2\omega_0\tau_c)^2}\right\}, \quad (1)$$

where K depends on the geometry of the molecular reorientation and, for a given geometry, is proportional to χ^2, where χ is the nuclear quadrupolar coupling constant. The correlation time τ_c of the motion is related to the absolute temperature by the Arrhenius equation:

$$\tau_c = \tau_\infty \exp(E_a/RT), \quad (2)$$

where E_a is the activation energy. In this case τ_c describes the rotation of the BH_3 group and, for a three-site exchange model, is related to the exchange rate, k, between the sites; $\tau_c = 1/3k$. A non-linear least squares three parameter fit of 18 experimental points yields $E_a = 14.1$ kJ/mol, $\tau_\infty = 6.5 \times 10^{-14}$ s and $K = 2.7 \times 10^{10}$ s^{-2}. The estimated uncertainty in these parameters is about 10%. If a tetrahedral geometry is assumed for the borane group one has

$$K = 8\chi^2/3, \quad (3)$$

yielding a deuterium quadrupolar coupling constant of 101 ± 10 kHz.

The ^{2}H lineshape for $(CH_3)_3NBD_3$ is a Pake doublet with a quadrupolar splitting, $\Delta\nu$, of 25.5 ± 1.0 kHz, and does not change between 138 K and 320 K. For rapid n-site ($n \geq 3$) exchange of an X–D bond between equally populated sites the observed quadrupolar splitting, $\Delta\nu$, is related to χ by the equation

$$\Delta\nu = \tfrac{3}{8}\chi(3\cos^2\theta_{X-D} - 1), \quad (4)$$

where θ_{X-D} is the angle the X–D bonds make with the rotational axis. The observed lineshape is consistent with fast BH_3 rotation and, if the geometry at the boron is assumed to be tetrahedral ($\theta_{B-D} = 70.5°$), (4) yields a χ value of 103 ± 3 kHz. This result is in excellent agreement with the value of 101 ± 10 kHz obtained from the T_1 minimum. These values are significantly smaller than the typical values of 160 kHz to 180 kHz observed for aliphatic C–D deuterons [30], suggesting that the electric field gradient along the B–D bond is significantly smaller than that along the typical C–D bond. Few $\chi(^2H)$ values have been reported for boranes and borane adducts. Two early reports give 95 kHz for BD_4^- [31] and 105 ± 1 kHz for $(CH_3)_3NBD_3$ [18], the compound examined in the present study. Recently, Penner and Custodio reported a value of 104 kHz for the cyanoborodeuteride anion, BD_3CN^- [32].

It should be noted that in [18] Merchant and Fung state that a large peak at the center of the spectrum due to rapid isotropic reorientation of the molecule obscures the quadrupole splitting at room temperature, and is still present, albeit small, at 150 K. We do not observe such a peak in our spectra at any temperature above the region of intermediate BD_3 rotation (130 K) and below the temperature at which the sample begins to sublime (320 K).

Deuterium spectral lineshapes for temperatures between 128 K and 87 K are displayed in Figure 3. As the temperature is decreased the spectral line broadens. Unfortunately the completely rigid lattice is not observed, even at the lowest temperature attainable with our equipment. The best-fit simulations of spectra for the intermediate rotational exchange rates are also shown in Figure 3. The spectra were simulated with a $\chi(^2H)$ value of 103 kHz and a tetrahedral borane geometry ($\theta_{B-D} = 70.5°$). The temperature dependence of the five exchange rates, obtained from spectral simulations, yields on activation energy of 12.5 ± 2.0 kJ/mol for C_3^B rotation. This is in good agreement with the value of 14.0 ± 1.5 kJ/mole obtained from the T_1 analysis.

It is interesting to note at this point that the lineshape simulations could only be performed with the introduction of quite large amounts of line broadening (5 kHz). This observation can be explained by the influence of ^{11}B–^2H and ^{10}B–^2H dipolar interactions. For a rigid BD_3 group the ^{11}B–^2H and ^{10}B–^2H dipolar coupling constants are estimated to be 10.7 kHz and 6.3 kHz, respectively. These values will be partially averaged by rotation of the BD_3 group at higher temperatures.

(b) $(CH_3)_3NBH_3$

The methyl deuterium T_1 as a function of temperature is shown in Figure 4. Two T_1 minima are observed: the high temperature minimum ($T_1 = 6.9$ ms) is at 286 K and the low temperature minimum ($T_1 = 4.3$ ms) is at 178 K. Reynhardt [21] also observed two minima in the proton T_1 and $T_{1\varrho}$ curves. If the two minima are associated with rotation of the methyl and trimethyl groups and if they are well separated, the ratio of the T_1 minimum values will depend on which minimum is associated with C_3^N or C_3^C rotation. For tetrahedral geometries of the methyl and trimethyl

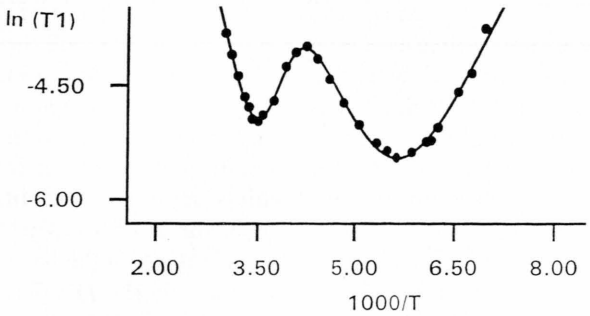

Fig. 4. The deuterium T_1 curve for $(CD_3)_3NBH_3$. The solid line corresponds to the best fit using (4) and (2).

groups, the ratio of $T_{1(\text{high temp.})}^{\min}/T_{1(\text{low temp.})}^{\min}$ is 1.5 when methyl rotation is slower than trimethyl rotation and is associated with the high temperature minimum [33]. If methyl rotation is faster than trimethyl rotation, and is associated with the low temperature minimum, the predicted ratio is 9.0. The ratio of observed deuterium T_1 minima for $(CH_3)_3NBH_3$ is 1.6 ± 0.1, strongly indicating that methyl rotation is more hindered than trimethyl rotation. The temperature dependence of the T_1 values can be fit to the equation

$$\frac{1}{T_1} = K_1 \left\{ \frac{\tau_{c1}}{1+(\omega_0 \tau_{c1})^2} + \frac{4\tau_{c1}}{1+(2\omega_0 \tau_{c1})^2} \right\} + K_2 \left\{ \frac{\tau_{c2}}{1+(\omega_0 \tau_{c2})^2} + \frac{4\tau_{c2}}{1+(2\omega_0 \tau_{c2})^2} \right\}, \quad (5)$$

where K_1 and $\tau_{\infty 1}$ correspond to methyl rotation, K_2 and $\tau_{\infty 2}$ correspond to trimethyl rotation, and the temperature dependence of τ_{c1} and τ_{c2} are described by the Arrhenius relationship (2). A non-linear least squares fitting of 26 points to the six free parameters in (5) and (2) yield $K_1 = 2.47 \times 10^{10}\ s^{-2}$, $\tau_{\infty 1} = 1.65 \times 10^{-15}$ s, $E_{a1} = 32.8$ kJ/mol, $K_2 = 4.55 \times 10^{10}\ s^{-1}$, $\tau_{\infty 2} = 8.91 \times 10^{-15}$ s and $E_{a2} = 15.0$ kJ/mol. Figure 4 shows that the agreement between theory and experiment is excellent through the entire curve (128 K to 333 K).

Deuterium NMR spectra of $(CH_3)_3NBH_3$ were obtained for a wide range of temperature (88 K to 253 K). In this temperature range, intermediate exchange rates for methyl and trimethyl rotations are fully observed. Spectra for the high temperature range are shown in Figure 5. At 232 K, a typical powder spectrum with a quadrupolar splitting of 10.5 kHz is observed. This lineshape indicates that the molecule is

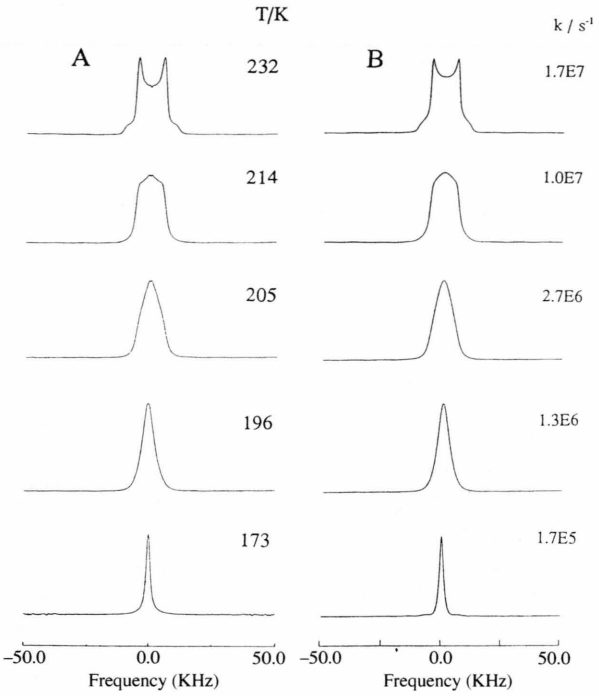

Fig. 5. Deuterium NMR spectra of $(CD_3)_3NBH_3$ for temperatures between 232 K and 173 K (A) together with the best fit simulated spectra (B).

performing predominantly fast methyl and trimethyl rotations. At temperatures between about 232 K and 353 K, the lineshape remains unchanged. If it is assumed that the trimethyl amine group and the methyl groups have tetrahedral arrangements then, using a typical χ value of approximately 170 kHz for an aliphatic C–D deuteron, the splitting under conditions of rapid methyl and trimethyl rotation is predicted to be about 14 kHz. There are two possible reasons for the reduction in the observed splitting. First, the decrease in $\Delta\nu$ may be due to further averaging of the quadrupolar interaction by a wobbling or precessional motion of the molecule. The amplitude of such a motion often decreases with decreasing temperature. This is not observed for $(CH_3)_3NBH_3$ above 232 K. Also, the spectra at lower temperatures cannot be simulated by changing the effective quadrupolar coupling constant with temperature. Furthermore, the splitting in $(CH_3)_3NBD_3$ appears not to be averaged by any wobbling motion. The second possible reason for a reduction in $\Delta\nu$ is a deviation from tetrahedral geometries. A molecular structure for $(CH_3)_3NBH_3$ in the solid state, employing diffraction methods, has not

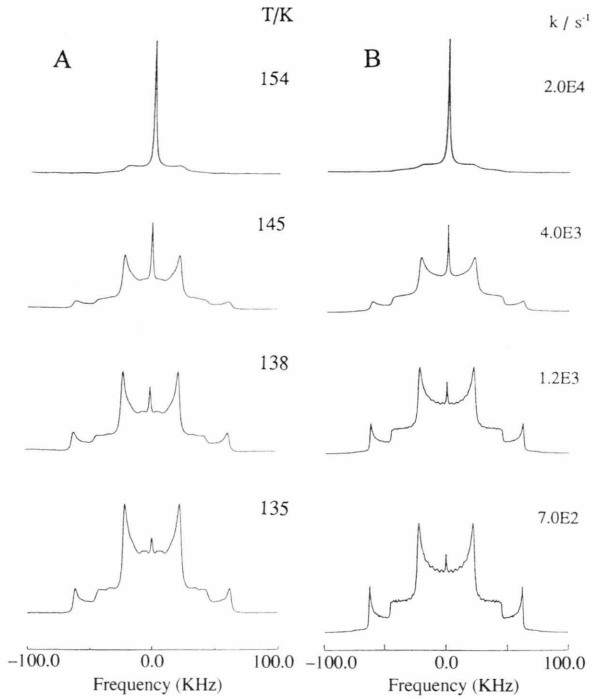

Fig. 6. Deuterium NMR spectra of $(CD_3)NBH_3$ for temperatures between 154 K and 135 K (A) together with the best fit simulated spectra (B).

been reported. This is likely due to the soft waxy nature of solid $(CH_3)_3NBH_3$ which makes growing single crystals of high quality extremely difficult. Microwave results for ten isotopimers of gaseous $(CH_3)_3NBH_3$ indicate that the methyl and trimethylamine groups do deviate from tetrahedral geometries, but the experimental geometry depends on the method of analysis used [34]. At the lowest temperature the ^2H spectrum is that of a rigid C–D deuteron and the splitting of 125 kHz gives a quadrupolar coupling constant of 167 kHz. Using this value we were able to successfully simulate all of the high and low temperature spectra if we used a B–N–C bond angle of 113°, which is 3.5° larger than the value for a tetrahedral amine nitrogen.

As the temperature is lowered, the sharp peaks of the Pake doublet become less well defined and by 205 K, the lineshape has collapsed, leaving only a smooth Lorentzian-like curve with a width at half maximum of about 10 kHz. As the temperature is further decreased the line width continues to decrease until, at about 170 K, it has reduced to approximately 2 kHz. At around 155 K a broad component, about 45 kHz wide, has increased sufficiently in intensity to become visible (see Figure 6). The intensity of the broad component continues to increases and that of the narrow peak decreases with decreasing temperature. By 145 K the broad component is recognizable as a Pake doublet with a quadrupolar splitting of 45 kHz. Another doublet with a splitting of about 125 kHz also appears. By 135 K the central narrow peak is nearly gone and the outer features of the powder spectrum have become significantly sharper. The spectrum at 135 K is typical of that expected for the deuterons of a trimethyl group where methyl rotation is slow ($k < 10^3\ s^{-1}$) and trimethyl rotation is fast ($k' > 10^6\ s^{-1}$). Figures 5 and 6 also show spectra simulated for different, intermediate, rates of methyl rotation while keeping the trimethyl rotational exchange rate in the fast limit. The spectra were simulated with a χ value of 167 kHz, a B–N–C bond angle of 113° ($\theta' = 67°$) and tetrahedral methyl groups ($\theta = 70.5°$). The fact that these spectra could only be simulated using a model with fast trimethyl exchange and slow to intermediate methyl rates is in agreement with the T_1 minimum assignment. The corresponding activation energy of 26.6 ± 3 kJ/mol for methyl rotation (ten points for a $\ln(k)$ vs. $1/T$ regression) is in reasonable agreement with the value of 32.8 ± 3 kJ/mol from the T_1 curve.

Deuterium NMR spectra for the low temperature region (below 135 K) are shown in Figure 7. The lineshapes in this temperature range are consistent with those expected for the case when methyl rotation is in the slow exchange limit and trimethyl rotation is passing through the intermediate exchange regime. At 126 K, the intensity of the broad component of the spectrum ($\Delta\nu = 125$ kHz) has increased significantly with respect to that at 135 K. As the temperature is further lowered, and the rate of trimethyl rotation decreases, the intensity of the broad component continues to increase at the expense of the central component. By 89 K the central component has disappeared, indicating that the trimethyl rotation has stopped and the molecules have become rigid on the NMR timescale (k and $k' < 10^3\ s^{-1}$). The observed quadrupolar splitting at this temperature is 125.3 kHz. This corresponds to a χ value of 167 kHz. The best-fit simulations of the low temperature spectra for the intermediate C_3^B exchange rates are also shown in Figure 7. The spectra in this temperature range can be simulated with a χ value of 167 kHz and a polar angle, θ_{N-C}, of 67° (corresponding to a bond angle, B–N–C, of 113°).

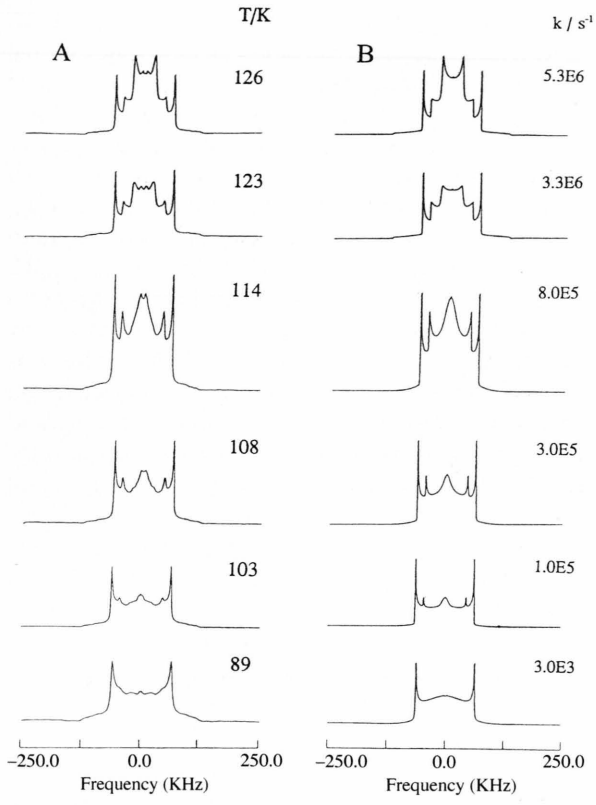

Fig. 7. Deuterium NMR spectra of $(CD_3)_3NBH_3$ for temperatures between 126 K and 89 K (A) together with the best fit simulated spectra (B).

The methyl groups were assumed to have a tetrahedral geometry and occupy a staggered low energy conformation. The five exchange rates, k', were used to obtain an activation energy for C_3^N rotation of 19 ± 2 kJ/mol. This value is in reasonable agreement with the value of 15 ± 1.5, obtained from the T_1, curve.

One consequence of the lineshape analysis performed here is that information about the geometry of the $(CH_3)_3N$ group may be obtained. That the bond angles must deviate from the tetrahedral geometries in order to successfully simulate the spectra has been noted. Furthermore, the orientation of the methyl C–H bonds, i.e. the dihedral angles H–C–N–B, in the lowest energy conformation of the molecule can be investigated. In general the trimethylamine group may be considered to have a staggered (Fig. 1) or an eclipsed conformation. The simulated lineshapes could only be matched to the experimental spectra when a staggered conformation was used. Previous investigations have assumed staggered geometries when simulating lineshapes [7, 8, 35].

In compounds of the type $(CH_3)_3M$ activation energies for methyl and trimethyl rotation can cover wide ranges. For some time trimethyl rotation as thought to be the higher energy process. More recently, many examples of the opposite behaviour have been reported. In many crystalline solids investigated to date, methyl rotation has an activation energy that is equal to or higher than that for trimethyl rotation of M is carbon or nitrogen [8, 35] (M may be part of a larger group e.g. $M = NC_6H_5^+$; phenyltrimethylammonium). In these cases the methyl reorientation is a conserted motion involving a gearing of the methyl C–H bonds. This effect is significantly reduced when the C–M bonds are longer, for example when M is silicon or phosphorus, and the activation energy for methyl rotation decreases significantly. In these cases the increase in the size of the $(CH_3)_3M$ group usually causes an increase in E_a for trimethyl rotation, due to larger intermolecular interactions in the solid. Solid $(CH_3)_3NBH_3$ falls easily into the first category, where the E_a for C_3^C rotation is significantly higher than that for C_3^N rotation.

A question that must be addressed is that of correlated rotation of the trimethylamine and borane groups about the B–N axis. The values of E_a and τ_∞ for the two motion as obtained by analysis of T_1 results are in good agreement. Hence the rotational exchange rates, k, for the two motions are close. On the other hand a comparison of the activation energies obtained from lineshape analysis are rather different. Activation energies alone are not sufficient to characterize rotational motion. In order to obtain k one must also know k_∞, which can be obtained from the intercepts ($\ln k_\infty$) of the linear regressions. The uncertainties in k_∞ are rather large and an alternative is to directly compare the exchange rates used to visually fit the lineshapes for $(CH_3)_3NBH_3$ and $(CH_3)_3NBD_3$ in the 87 K–128 K temperature region. Such a comparison (Figs. 3 and 7) reveals that, for similar temperatures, rather similar exchange rates are employed in the simulations of the ^2H spectra for $(CD_3)_3NBH_3$ and $(CH_3)_3NBD_3$. For example in the third set of spectra from the top of Figs. 3 and 7, which are in the most sensitive region for lineshape changes and where the difference in temperature between the two experiments was only 1 K, the k value for $(CD_3)_3N$ rotation in $(CD_3)_3NBH_3$ is $8.0 \times 10^5\ s^{-1}$ and the k value for BD_3 rotation in $(CH_3)_3NBD_3$ is $7.3 \times 10^5\ s^{-1}$. These

values are in excellent agreement. The only case where the agreement in k for the two rotations is poor is that of $3 \times 10^3\ s^{-1}$ for $(CD_3)_3NBH_3$ at 89 K and $1 \times 10^4\ s^{-1}$ for $(CH_3)_3NBD_3$ at 87 K. This is expected since the lineshapes are least sensitive to k in this region ($10^3\ s^{-1}$–$10^4\ s^{-1}$); and are independent of the reorientation rate for k values below $1 \times 10^3\ s^{-1}$.

A very recent study of the molecular motion in solid $(CH_3)_3NBCl_3$ using ^1H NMR and ^{35}Cl NQR demonstrated quite clearly that the molecule as a whole rotates with an activation energy of about 51–52 kJ/mol [24]. This was interpreted as being due to the predominance of intramolecular over intermolecular forces. In other words the barrier to internal rotation about the N–B bond is greater than, or comparable to, the barrier for whole molecule rotation. Previous ^1H NMR T_1 and second moment studies indicate that the intermolecular hindrance for $-N(CH_3)_3$ rotation is greater than that for $-BH_3$ rotation, and that a correlated whole molecule rotation does not occur [11, 21, 22]. In light of the present work, which correctly assigns a higher E_a for methyl rotation than for trimethyl rotation, it is apparent that $(CH_3)_3NBH_3$ does indeed undergo a correlated whole molecule rotation with an activation energy of about 15 kJ/mol. Very little work has been done on the determination of the internal rotational barrier in $(CH_3)_3NBH_3$. Durig, Li and Odom [34] deduced a lower limit of 14 kJ/mol, based on the assignment of the torsional BH_3 mode in the microwave spectrum. We have performed ab initio molecular orbital calculations on $(CH_3)_3NBH_3$ at the MP2/6-31G* level and obtain a barrier to internal rotation of 18.0 kJ/mol.

In general, high level *ab initio* calculations on borane-amine complexes yield rotational barriers that are in reasonable agreement with those observed in the gas phase [36, 37]. In cases where the two disagree, the calculated B–N bond lengths are longer than the corresponding experimental gas phase values, yielding rotational barriers that are too small [37, 38, 39]. Two interesting studies of borane-amine adducts indicate that the B–N bond length is significantly shorter in the solid state [39, 40]. This implies a higher barrier to internal rotation about the B–N bond in the solids. Hence our *ab initio* value for the internal rotational barrier should be considered a lower limit, and supports a model in which the molecule undergoes a correlated rotation.

Finally, the results reported here must be compared to previous proton T_1 studies of $(CH_3)_3NBH_3$. Ang and Dunell [22] give values of 13.8 kJ/mol and 28 kJ/mol as the activation energies for the two motional processes at temperatures below 350 K. Reynhardt [21] reports similar values of 14.4 kJ/mol and 26.8 kJ/mol. These values are in agreement with our results. On the other hand, the present study of both deuterium lineshape and spin-lattice relaxation times for selectively deuterated isotopomers of $(CH_3)_3NBH_3$ lead to an unambiguous assignment of methyl rotation to the higher energy process and combined trimethyl rotation and borane group rotation to the lower energy process. This is not in agreement with the conclusions of Ang and Dunell, who assign a lower activation energy to methyl rotation and borane rotation, and the higher activation energy to trimethylamine rotation. Our assignments also disagree with those of Reynhardt who interprets the combined $T_1(^1H)$, $T_{1\varrho}(^1H)$, and $T_1(^{11}B)$ data with a model which is similar to that of Ang and Dunell in that the CH_3 and BH_3 rotations have a lower activation energy than $(CH_3)_3N$ rotation. In addition the model had dynamically non-equivalent molecules in the unit cell where, between 120 K and 155 K, two thirds of the molecules reorient about the molecular B–N bond and one third perform only CH_3 and BH_3 rotation.

Conclusion

The molecular dynamics of solid $(CH_3)_3NBH_3$ have been reinvestigated by deuterium NMR spectroscopy. Activation energies and correlation times are given in Table 1. It is evident that the activation energy for methyl rotation is approximately twice that for trimethylamine and borane group rotations. This is in disagreement with previous proton wideline NMR work which assigns $-N(CH_3)_3$ rotation as the higher energy process. Comparison of rotational rates used in spectral simulations and of correlation times obtained from T_1 measurements indicate that $(CH_3)_3NBH_3$ is undergoing a correlated whole molecule rotation about the N–B bond in the solid state.

Table 1.

	Lineshape analysis	T_1 Analysis	
	E_a (kJ/mol)	E_a (kJ/mol)	τ_∞ (s)
$-CH_3$ rotation	27 ± 3	33 ± 3	1.6×10^{-15}
$-N(CH_3)_3$ rotation	19 ± 2	15 ± 1.5	8.9×10^{-14}
$-BH_3$ rotation	12.5 ± 2	14 ± 1.5	6.5×10^{-14}

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