A Deuterium NMR Study of some Ammonium Tetraphenylborates

Marco L. H. Gruwel and Roderick E. Wasylishen
Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada B3H 4J3

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Deuterium nmr has been used to study the rotational dynamics of the ammonium ion in ammonium tetraphenylborate and of the cation in a series of methylammonium tetraphenylborates. The results of variable temperature $^2$H relaxation measurements ($T_1$ and $T_2$) on the parent compound, ND$_4$B(C$_6$H$_5$)$_4$, lead to a low activation energy for reorientation of the ND$_4^+$ ion, 50 ± 0.5 kJ mol$^{-1}$, indicative of weak cation-anion interactions. Related studies of the tetramethyl-$d_4$ ammonium salt indicate rapid jumps of the whole cation ($t \ll 10^{-3}$s) over the complete temperature range investigated, 137 to 385 K, with an activation energy of 14.1 ± 0.5 kJ mol$^{-1}$. Deuterium nmr lineshape studies of the methylammonium salt indicate rapid reorientation of the CD$_3$ and ND$_3$ groups about their C$_3$ axes; however, the motion of the C – N axis is restricted to large amplitude librations. Similar studies of the dimethylammonium salt indicate methyl group jumps at 245 K; at temperatures above 320 K the cation also undergoes two-site jumps about the C$_2$ axis. In the case of the trimethylammonium salt, the nmr lineshapes indicate methyl group jumps superimposed on C$_3$ rotations of the complete cation about the N–H bond axis over the temperature interval 185–348 K. In all the tetraphenylborate salts studied, the $^3$H nmr lineshapes indicate substantial librational motion of the cation at room temperature.

Key words: $^2$H nmr, rotation, ammonium derivatives, tetraphenylborates.

1. Introduction

In aqueous solution, ammonium chloride, or any methyl substituted ammonium halide, will react with sodium tetraphenylborate to yield water insoluble salts of the type: NH$_4$-n(CH$_3$)$_3$ B(C$_6$H$_5$)$_4$ (n = 0 to 4). These salts are particularly interesting because of the peculiar size and shape of the large delocalized tetraphenylborate anion [1–3]. Infrared and x-ray diffraction studies of the parent compound, ND$_4$B(C$_6$H$_5$)$_4$, provide evidence for hydrogen bonding between the N–H bonds and the n-system of the anion phenyl rings [3]. In a more recent infrared study of ammonium tetraphenylborate, Roberts and Strauss [4] claim an extremely low barrier for rotations of the ammonium ion, approximately 20 cm$^{-1}$ (≈ 0.24 kJ mol$^{-1}$). The report of this low barrier has prompted us to study the $^2$H nmr relaxation rates of the deuterated derivative, ND$_4$B(C$_6$H$_5$)$_4$, as a function of temperature. The nmr activation energy for reorientation of the ammonium ion obtained from our relaxation data is compared with the values reported for other ammonium salts [5–13].

In addition, we have used $^3$H nmr to characterize the motion of the cation in methylammonium, dimethylammonium, trimethylammonium and tetramethylammonium tetraphenylborate. The latter compound is of particular interest since its structure is available from single crystal x-ray diffraction data [2] (see Figure 1). The anisotropic temperature coefficients indicate large amplitude motion of the methyl carbon atoms. The results of the present study allow us to comment on the nature of the motion responsible for the large thermal parameters.

II. Theory

For deuterium nuclei the interaction of the nuclear quadrupole moment with fluctuating electric field gradients (EFG’s) is so efficient that relaxation of these spins is completely dominated by the quadrupolar mechanism [14]. The quadrupolar Hamiltonian can be expressed as a sum of products of 2nd rank spin and bath tensor components as given by

$$H_q = \sum_{m=-2}^{2} (-1)^m F_{-m} A_{m}.$$

After rearrangement of common terms, the bath tensor components can be expressed in Wigner rotation

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Fig. 1. Structure for tetramethylammonium tetraphenylborate (from data in [2]).

matrix elements \([15, 16]\]

\[
F_m = D_{m,0}^{(2)}(\Omega) - \eta(<\beta>)^{-1} [D_{m,1}^{(2)}(\Omega) + D_{m,-1}^{(2)}(\Omega)].
\]  

(2)

In the discussion which follows we will assume the electric field gradient to be axially symmetric, i.e., \(\eta = 0\). This is an excellent assumption for deuterium nuclei in the C–H and N–H bonds studied here [17, 18].

The relaxation rate of Zeeman order, \(R_{1Z}\), and quadrupolar order, \(R_{1Q}\), is given by [15]

\[
R_{1Z} = \frac{3}{4} \pi^2 \langle \chi^2 \rangle [J_1(\omega_0) + 4 J_2(2\omega_0)], \\
R_{1Q} = \frac{3}{4} \pi^2 \langle \chi^2 \rangle [3 J_1(\omega_0)],
\]  

(3)

where the quadrupole coupling constant (QCC), \(\chi = eQeq/h\), represents the product of the largest component of the EFG tensor, eq, and the nuclear quadrupole moment \(eQ\). The spectral density \(J_m(\omega)\) is the cosine transform of the bath tensor components correlation function in the laboratory frame [16]:

\[
J_m(\omega) = 2 \frac{\chi}{\omega} \int_0^\infty dt \cos \omega t \langle D_m^{(2)}(\Omega(0)) D_m^{(2)}(\Omega(t)) \rangle_{\text{lab}}.
\]  

(4)

In order to calculate the spectral densities one has to transform the EFG tensor from the molecular frame, in which the principal components are known, into the laboratory frame in which one performs the experiments. First we will discuss these transformations for the tetramethyl-d_{12} ammonium ion and secondly for the ammonium-d_{14} ion.

i) The tetramethylammonium ion. Three successive transformations have to be made for this ion (Figure 2). The first transforms interaction elements from the crystal fixed axis frame to the laboratory frame. This transformation introduces the powder angles \((\theta, \phi)\) [16, 19, 20],

\[
\langle D_m^{(2)}(\Omega(0)) D_m^{(2)}(\Omega(t)) \rangle_{\text{lab}} = \sum_{a, a'} d_m^{(2)}(\theta) d_m^{(2)}(\theta) C_{a, a'}(t) e^{+i(a-a')\psi}.
\]  

(5)

The function \(C_{a, a'}(t)\) is determined by the modulation of the crystal angles \((\Theta, \Phi)\) due to the reorientation of the tetramethylammonium ion in this frame. This modulation can be written as an expansion of Wigner
rotation matrix elements:

\[
C_{a,a'}(t) = \sum_{b,b' = -2}^{2} \langle D_{0,b}^{(2)}(\Omega(0)) D_{0,b'}^{(2)}(\Omega(t)) \rangle C_{3,a} \cdot \langle D_{a,b}^{(2)}(\Omega(0)) D_{a',b'}^{(2)}(\Omega(t)) \rangle_{T_d}. \tag{6}
\]

Here we have assumed the two reorientation processes, methyl \( C_3 \) flips and the tetrahedron (\( T_d \)) motion, to be independent of each other. The ensemble averaging over the tetrahedron motion (= whole ion motion) was approximated by an isotropic reorientation model, fast \( C_2 \) and \( C_3 \) motions compared with the \( QCC \) (vide infra).

Note that a \( C_3 \) jump corresponds to the simultaneous jump of three methyl groups about a particular C–N axis. Also, note that two successive \( C_3 \) jumps about different N–C axes may be equivalent to a \( C_2 \) flip. The assumption of isotropic motion greatly simplifies the calculation of the Zeeman relaxation rate [20]. The effective correlation time for this motion, \( \tau_{C_3} \), can be interpreted in terms of \( C_3 \) and \( C_2 \) reorientational correlation times [19]. For the whole ion reorientation we thus write

\[
\langle D_{a,b}^{(2)}(\Omega(0)) D_{a',b'}^{(2)}(\Omega(t)) \rangle = (1/5) \delta_{a,a'} \delta_{b,b'} e^{-t/\tau_{C_3}}, \tag{7}
\]

where \( \delta_{i,j} \) is the Kronecker delta function. The averaging due to methyl \( C_3 \) flips of the \( C_2-H \) bond was treated in terms of a \( C_3 \) model as described by Torchia and Szabo [20]. This results in the following correlation function:

\[
C_{a,a'}(t) = \sum_{b,b' = -2}^{2} \left| a_{b,b'}^{(2)}(\beta) \right|^2 \left[ \delta_{b,b'} + (1 - \delta_{b,b'}) e^{-t/\tau_{C_3}} \right] \cdot (1/5) \delta_{a,a'} \cdot e^{-t/\tau_{C_3}}. \tag{8}
\]

The assumption of isotropic motion for the whole ion reorientation results in the selection of only diagonal elements of the methyl \( C_3 \) flip reorientation matrix. The non-diagonal terms of this matrix give rise to nonexponential relaxation [20]. These terms were overlooked by Wallach [21] but included in calculations by Edholm and Blomberg [22]. Finally we obtain for the spectral density (m independent):

\[
J(\omega) = (2/5) \left\{ \frac{(1/9) \frac{\tau_{C_3}}{1 + (\omega \tau_{C_3})^2} + (8/9) \frac{\tau_1}{1 + (\omega \tau_1)^2}} \right\}. \tag{9a}
\]

and the \( C^{-2}H \) bond, \( \beta \), is 109.4° \( \tag{9b} \)

\[
ii) Ammonium ion. The rotational motion of the ammonium ion in ammonium tetraphenylborate can be described by the isotropic whole ion reorientation term (7) in the previous section. The resulting spectral density is given by

\[
J(\omega) = (2/5) \frac{\tau_{T_d}}{1 + (\omega \tau_{T_d})^2} \tag{10}
\]

and is identical to that obtained in reference [19] for fast \( C_2 \) and \( C_3 \) flips.

III. Experimental

The \( ^2H \) nmr experiments on tetramethylammonium tetraphenylborate and ammonium tetraphenylborate were performed at 55.42 MHz on a Nicolet 360 NB spectrometer. For tetramethylammonium tetraphenylborate a Nicolet highband probe with typical \( \pi/2 \) pulses of 40–50 \( \mu \)s was used. Ammonium tetraphenylborate was studied with a \( ^2H \) nmr probe of Probe Systems Inc. having typical \( \pi/2 \) pulses of 6–7 \( \mu \)s. Methylammonium, dimethylammonium and trimethylammonium tetraphenylborate were studied at 30.72 MHz on a Bruker MSL 200 using \( \pi/2 \) pulse lengths of 4.5 \( \mu \)s. The temperature in each probe was regulated to 1 K with cold \( N_2 \) gas and a heater built into the probes.
All $R_{1z}$ values were obtained from peak heights obtained at 12 or more different $\tau$ values in the $\pi-\tau-\pi/2$ pulse sequence with phase cycling [23]. To observe $^2$H nmr spectra of methylammonium, dimethylammonium and trimethylammonium tetraphenylborate, a solid echo technique was used [24] with a pulse separation of 40 $\mu$s. The Zeeman relaxation rates, $R_{1z}$, in the latter tetraphenylborate salts were determined by means of an inversion recovery experiment which included a solid echo before signal detection. Quadrupolar order relaxation rates, $R_{1Q}$'s, were measured with the Jeener-Broekaert pulse sequence [25]. After the application of the second pulse in the Jeener-Broekaert three pulse sequence [25, 26],

$$(\pi/2)_{y} - \tau_{1} - (\pi/4)|_{x} - \tau_{2} - (\pi/4)|_{x} - (ACQ)|_{x},$$

one can study the decay of the created quadrupolar order. It can be shown that the magnetization in the $x$-channel of the receiver after the 3 pulse sequence is [27]:

$$\langle I_{x}(t) \rangle = \frac{d}{dt} G(t')|_{t'=\tau_{1}} \frac{d}{dt} G(t')|_{t=\tau_{2}},$$

where $G(t)$ represents the free induction decay after a $\pi/2$ pulse. The maximum transfer of Zeeman into quadrupolar order occurs at a time $\tau_{1}$, where the FID after a $\pi/2$ pulse shows an inflection point. The second delay in the pulse sequence, $\tau_{2}$, is a variable relaxation delay. All $R_{1Q}$ values were calculated from peak heights obtained at 10 or more different $\tau_{2}$ values in the Jeener-Broekaert pulse sequence. The errors in the $R_{1z}$ and $R_{1Q}$ rate measurements are estimated to be less than 5 and 10%, respectively.

The tetraphenylborate compounds were prepared by reaction of sodium tetraphenylborate and the appropriate deuterated amine hydrochloride in aqueous solution. Sodium tetraphenylborate (99+ % pure) and dimethyl-d$_6$ amine-HCl were purchased from Aldrich Chemical Company Inc. Methyl-d$_3$ amine-HCl, tetramethyl-d$_{12}$ amine-HCl and D$_2$O were obtained from MSD Isotopes.

**IV. Results and Discussion**

*i) Tetramethyl-d$_{12}$ Ammonium Tetraphenylborate*

Recently Ratcliffe and Ripmeester [17] used $^2$H nmr to investigate the reorientation processes involving the tetramethylammonium cation in a series of solid salts. The main conclusion of this study was that on heating the samples from low temperature, the onset of methyl $C_{3}$ rotations frequently occurs after the onset of whole ion reorientation. They found that the activation energy for methyl group rotation is generally larger than 17 kJ mol$^{-1}$ in tetramethylammonium salts and that lower activation energies indicate the presence of other reorientation processes. Our $^2$H $T_{1z}$ results for tetramethylammonium tetraphenylborate are summarized in Figure 3. In the temperature region of 137–385 K we obtained an apparent activation energy of 14.1 $\pm$ 0.5 kJ mol$^{-1}$. Because this value of $E_{a}$ is somewhat smaller than the barrier that one would expect for methyl group rotation, we assume it corresponds to a barrier for overall reorientation of the cation. The $^2$H nmr lineshape was isotropic over the complete temperature range investigated, 137–385 K, and exhibited a linewidth of only 2 kHz at the lowest temperature. The implication is that even

![Graph of Deuterium Zeeman relaxation times as a function of reciprocal temperature.](image)
at 137 K, $\tau_{r_a} \ll \chi^{-1} (6 \times 10^{-6} \text{ s})$; note that only rapid tetrahedral jumps about any two of the four equivalent $C_3$ axes of the whole ion are necessary to average the quadrupolar splitting to zero (alternatively jumps about the three equivalent $C_2$ axes or numerous combinations of $C_2$ and $C_3$ jumps will result in an isotropic lineshape).

It is of interest to briefly discuss the $T_{1, \text{min}}$, 3.6 ± 0.2 ms, observed in Figure 3. If one assumes that the motion of the (CD$_3$)$_4$N ion is best described by slow methyl group jumps superimposed on rapid tetrahedral jumps of the whole ion, i.e., $\tau_{C_3} \gg \tau_{r_a}$ the Zeeman relaxation rate can be expressed as

$$R_{1z} = \frac{(3/10) \pi^2 \langle x^2 \rangle}{\left\{ \frac{\tau_{r_a}}{1 + (\omega_0 \tau_{r_a})^2} + 4 \frac{\tau_{r_a}}{1 + 4(\omega_0 \tau_{r_a})^2} \right\}}. \quad (11)$$

The Lorentzian sum at the right hand side of (11) has a maximum at $\omega_0 \tau = 0.6158$. From this we calculate a $^2$H QCC of 151 ± 5 kHz. This value is lower than the values obtained from line shapes at 69–77 K by Ratcliffe and Ripmeester [17], which are typically 168 kHz, for various tetramethylammonium salts. Assuming $\tau_{C_3} = \tau_{r_a}$, substitution of $T_{1, \text{min}}$ and $J(\omega)$ (9) into (3) results in a slightly larger value of $\chi$, 152.7 kHz. If one makes the unreasonable assumption that methyl group rotations are much faster than whole ion rotations, i.e., $\tau_{C_3} \leq 10^{-2} \tau_{r_a}$, then $\chi \approx 160$ kHz. The low value that one obtains for $\chi$ from the $T_{1, \text{min}}$ probably results from the fact that librational motions are not considered in deriving the relaxation expressions. This type of motion can cause additional averaging of the $^2$H QCC and adds to the spectral density [28]. The relatively weak electrostatic interactions between the large tetramethylammonium and tetraphenylborate ions are expected to result in a shallow reorientation potential in which rapid librational motions are possible. This hypothesis is supported by the large thermal ellipsoids observed in the x-ray study of (CH$_3$)$_4$N B(C$_6$H$_5$)$_4$ (see Fig. 2 in [2]).

**ii) Ammonium-d$_4$ Tetraphenylborate**

The crystal structure of this compound shows that the ammonium ions can rotate in a cage with site symmetry $D_{2d}$ and have only small distortions from $T_d$ symmetry [3]. The IR study by Westerhaus et al. [3] indicated a relatively large amount of rotational freedom for the ammonium ion. This is strengthened by our $^2$H relaxation results, presented in Figure 4. These observations allow us to use an isotropic reorientation model, due to fast $C_3$ and $C_2$ flips, for the interpretation of the relaxation rates. The data in Fig. 4 are clearly in the extreme narrowing limit; $\omega_0 \tau_{r_a} \ll 1$. Thus the Zeeman and quadrupolar relaxation rates are

$$R_{1z} = (3/2) \pi^2 \langle x^2 \rangle \tau_{r_a}, \quad (12a)$$
$$R_{1Q} = (9/10) \pi^2 \langle x^2 \rangle \tau_{r_a}. \quad (12b)$$

For this model the theory predicts a temperature independent ratio of $R_{1z}/R_{1Q} = 5/3$. This is, within experi-
Fig. 5. Quadrupolar echo spectra of specifically deuterated methylammonium tetraphenylborate at 298 K.

Table 1. Activation energies for reorientation of ammonium ions in salts with monovalent anions from $^2$H nmr relaxation data.

<table>
<thead>
<tr>
<th>Ammonium Salt</th>
<th>$E_a$ (kJ mol$^{-1}$)</th>
<th>Phase or Temp. Range</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ND$_3$Cl</td>
<td>19.7</td>
<td>CsCl</td>
<td>[7]</td>
</tr>
<tr>
<td>ND$_3$Br</td>
<td>15.1</td>
<td>CsCl</td>
<td>[8]</td>
</tr>
<tr>
<td>ND$_4$I</td>
<td>3.2, 3.5</td>
<td>cubic</td>
<td>[9, 10]</td>
</tr>
<tr>
<td></td>
<td>10.9, 12.5</td>
<td>tetragonal</td>
<td>[9, 10]</td>
</tr>
<tr>
<td>ND$_4$NCS</td>
<td>17.1</td>
<td>monoclinic</td>
<td>[11]</td>
</tr>
<tr>
<td>ND$_4$NO$_3$</td>
<td>10.7</td>
<td>tetragonal</td>
<td>[12]</td>
</tr>
<tr>
<td>ND$_4$B(C$_6$H$_5$)$_4$</td>
<td>5.0</td>
<td>tetragonal</td>
<td>this study</td>
</tr>
<tr>
<td>ND$_4$ClO$_4$</td>
<td>4.0</td>
<td>orthorhombic</td>
<td>[13]</td>
</tr>
</tbody>
</table>

Table 1. Activation energies for reorientation of ammonium ions in salts with monovalent anions from $^2$H nmr relaxation data.

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mental error, what we observe. We conclude that over the temperature range of 148–298 K, the spectral density of the motion can indeed be described by one effective correlation time $\tau_{\text{eff}}$. The activation energy for this process is $5.0 \pm 0.5$ kJ mol$^{-1}$. The activation energy for ammonium ion reorientation in several other salts where the anion has unit charge is given in Table 1. The low value of $E_a$ for ND$_4$B(C$_6$H$_5$)$_4$ is consistent with the observations of Westerhaus et al. [3], who interpreted their results in terms of weak ammonium ion-phenyl ring interactions, but it is more than one order of magnitude larger than the rotational barrier reported by Roberts and Strauss [4].

### iii) Methylammonium Tetraphenylborate

Both the ND$_3$CH$_3$ and NH$_3$CD$_3$ derivatives were studied at 298 K. The $^2$H nmr powder spectra of both compounds (Fig. 5) indicate non-isotropic averaging of the $^2$H EFG. For a deuterium nucleus in a stationary X–D bond the frequency separation between the two allowed nmr transitions is given by

$$\Delta v = (3/4) \sqrt{\langle \chi^2 \rangle} (3 \cos^2 \theta - 1)$$

where $\theta$ is the angle between the largest principal component of the EFG tensor (along the X–D bond) and the applied static magnetic field $B_0$. In a powder sample, averaging over the powder angles results in a characteristic Pake doublet with a peak-to-peak splitting of $(3/4) \sqrt{\langle \chi^2 \rangle}$. Any motion of the X–D bond about a rotation axis with threefold or higher symmetry will modulate the frequency separation given by (13). If the angle between the X–D bond and the rotation axis is $\beta$, the quadrupolar splitting is reduced by a factor $P_2(\cos \beta)$, where $P_2$ is the second order Legendre polynomial [29], i.e., $(3 \cos^2 \beta - 1)/2$. The overall lineshape of the powder spectrum is not influenced by motion provided the time scale of the motion is much smaller than $\chi^{-1}$, however the breadth of the spectrum is reduced when such motion is present. For rapid $C_3$ jumps or diffusion of three equivalent deuterium nuclei in an XD$_3$ group about a stationary $C_3$ axis, (13) predicts a Pake doublet with splitting $(3/4) \sqrt{\langle \chi^2 \rangle}$, assuming tetrahedral geometry. Note that the asymmetry parameter for the motionally averaged lineshape is zero even if the static lineshape has $\eta \approx 0.1$ for each of the equivalent deuterium nuclei [30, 31]. For the CD$_3$NH$_3^+$ ion we assume $\chi = 168$ kHz, $\eta = 0.06$ (the values obtained in several tetramethylammonium salts [17]); therefore one would expect a splitting of 42 kHz. This anticipated splitting is close to the value of 41.6 kHz measured in CD$_3$NH$_3$ClO$_4$ [32] at 100 K. The observed splitting in CD$_3$NH$_3$B(C$_6$H$_5$)$_4$ of 29.1 kHz at 298 K and 34.2 kHz at 158 K implies substantial librational motion of the methyl group in addition to jumps or rotations about a $C_3$ axis. The $^2$H nmr lineshape of the CD$_3$NH$_3$ moiety (see Fig. 5) is clearly asymmetric. We
attribute this asymmetry to large angle librations of the CD\(_3\) group [33–35]. Spectral asymmetry in \(^2\)H nmr lineshapes of rotating – XD\(_3\) groups can also arise from non-equivalence in the static \(\chi\) values for each of the \(^2\)H nuclei [34–36]. Although such asymmetry has been observed for CD\(_3\) and ND\(_3\) groups in the presence of highly polar groups it is not expected to be important in the tetraphenylborate salts.

The \(^2\)H nuclear quadrupolar coupling constant for the ND\(_3\) group in CH\(_3\)ND\(_3\)B(C\(_6\)H\(_5\))\(_4\) is unavailable. Because the ND\(_3\) group can participate in hydrogen bonding, the value of \(\chi\) is expected to be quite dependent on the nature of the anion–cation interactions. In methylammonium perchlorate, where anion–cation interactions are relatively weak, Jurga and Spiess observed a \(^2\)H quadrupolar splitting of 42 kHz at approximately 100 K, implying \(\chi(\text{ND}_3) \approx 168\) kHz [32]. Assuming a similar value for \(\chi(\text{ND}_3)\) in the tetraphenylborate salt, the data in Table 2 lead one to conclude that the librational motions of the ND\(_3\) group are somewhat more restricted than those of the CD\(_3\) group. This conclusion is also supported by the lack of asymmetry observed in the \(^2\)H spectrum of CH\(_3\)ND\(_3\)B(C\(_6\)H\(_5\))\(_4\) (Figure 5).

In order to determine the nature of the CD\(_3\) and ND\(_3\) rotations in the methylammonium tetraphenylborates we have measured Zeeman relaxation rates at 158 K and 295 K (Table 2). Since \(R_{1x}(\theta = 0°) > R_{1x}(\theta = 90°)\) and \(\omega_0 \tau \ll 1\), the data indicate a dominance of C\(_3\) jumps as opposed to diffusion about a C\(_3\) axis [20, 30]. The measurement of \(R_{1x}(\theta = 90°)\) is complicated because both the \(\theta = 35.3°\) and \(\theta = 90°\) orientations contribute to the 90° discontinuity in the Pake doublet. In the case of diffusion, the rate of spin-lattice relaxation of the powder pattern is independent of orientation [20].

Finally it is important to recognize the time-scale for C\(_3\) jumps of the methylammonium cation. The \(T_{1z}\) values are 4.40 s and 6.58 s, respectively, for the ND\(_3\) and CD\(_3\) groups at 298 K, implying \(\tau\) values in the ps time scale. Also, if \(\chi(\text{ND}_3) \approx \chi(\text{CD}_3)\) then \(\tau_{\text{CD}_3} < \tau_{\text{ND}_3}\); that is the methyl groups have a slightly shorter correlation time than the ND\(_3\) groups which are probably involved in weak hydrogen bonding with the aromatic rings of the anions. Regardless of the assumptions regarding the magnitude of \(\chi\), it is clear that the frequency of C\(_3\) jumps for the ND\(_3\) and CD\(_3\) groups are similar and on the ps time-scale. Also, the activation energies for ND\(_3\) and CD\(_3\) groups are equal within experimental error, 4.1 ± 0.5 kJ mol\(^{-1}\) and 4.2 ± 0.5 kJ mol\(^{-1}\), respectively. These low activation energies measured for the methylammonium cation in methylammonium tetraphenylborate are comparable to those reported for C\(_3\) reorientation in methylammonium perchlorate, 3.6 kJ mol\(^{-1}\) (ND\(_3\) group) and 4.3 kJ mol\(^{-1}\) (CD\(_3\) group) [32]. Small \(E_a\) values for NH\(_3\) and CH\(_3\) rotations were also derived from \(^1\)H nmr [37]. Typically much larger \(E_a\) values have been reported for NH\(_3\) and CH\(_3\) rotations in simple methylammonium salts, see e.g., [38–40].

iv) Dimethylammonium Tetraphenylborate

Deuterium nmr spectra of dimethylammonium-d\(_2\) tetraphenylborate, (CH\(_3\))\(_2\)ND\(_2\)B(C\(_6\)H\(_5\))\(_4\), at 145 K and 325 K are shown in Figure 6. The low temperature spectrum represents that of a static N–\(^2\)H bond and could be simulated with \(\chi = 170 ± 5\) kHz. The extra intensity observed in the centre of the spectrum may result from partial saturation because of the short recycle time used in acquiring the spectrum. The spectrum obtained at 325 K indicates rapid two site exchange between sites separated by an angle of 2\(\beta = 103° ± 1°\) (vide infra). That is, the dimethylammonium cation undergoes jumps about a C\(_2\) axis which bisects the H–N–H bond angle.

Deuterium nmr spectra of the methyl deuterium labelled dimethylammonium tetraphenylborate, (CD\(_3\))\(_2\)NH\(_2\)B(C\(_6\)H\(_5\))\(_4\) are shown in Figure 7. At 245 K the quadrupolar splitting is 37° ± 0.5 kHz, consistent with rapid methyl C\(_3\) jumps. The high temperature spectrum at 320 K indicates the presence of
Fig. 6. Deuterium line shapes of dimethylammonium-d$_2$ cations in (CH$_3$)$_2$ND$_2$B(C$_6$H$_5$)$_4$ at 145 K (A) and 325 K (B). Both spectra were simulated with a QCC of 170 kHz, and $\eta = 0$. Spectrum B was simulated assuming fast C$_2$ jumps with a jump angle, $2\beta$, of 103°.

rapid C$_2$ jumps in addition to the methyl group C$_3$ jumps.

From the $T = 320$ K spectrum of the dimethyl-d$_6$ ammonium cations, the C–N–C bond angle can be estimated. To interpret this spectrum, the C$_3$ flip averaged largest principal component of the $^2$H EFG tensor will be assumed to coincide with the z-axis of the coordinate system shown in Figure 8. As EFG tensor components transform as 2nd rank spherical harmonics, it is most convenient to define the y-axis of the jump averaged frame (= $y'$) perpendicular to the C–N–C plane. The jump angle $2\beta$ thus coincides with the C–N–C bond angle. It can be shown that the relation between the flip averaged and “static” components of the EFG tensor are given by [34, 41, 42] (see Fig. 8):

$$V'_{xx} = V_{zz} \sin^2 \beta + V_{xx} \cos^2 \beta,$$

$$V'_{yy} = V_{yy},$$

$$V'_{zz} = V_{zz} \cos^2 \beta + V_{xx} \sin^2 \beta.$$  \hspace{1cm} (14)

The simulation in Fig. 7 was performed with $2\beta = 118.4^\circ \pm 0.5^\circ$. Details of the simulation are given in the legend of Figure 7. All spectra were simulated without a finite pulse correction. Similar values, 116.8° and 119.0°, were obtained for the C–N–C bond angles in the dimethylammonium tin and tellurium hexachloride salts, respectively from $^2$H nmr [43]. The C–N–C bond angle in [(CH$_3$)$_2$NH$_2$]$_2$SnCl$_4$ from $^2$H nmr [43] is in excellent agreement with the value determined from x-ray diffraction, 116.9° ± 0.5° [44].

The $^2$H nmr lineshapes of (CD$_3$)$_2$NH$_2$B(C$_6$H$_5$)$_4$ between 250 K and 300 K (see Figs. 7c and d) are unusual in that they appear to result from the superposition of two different lineshapes: one from cations in which the methyl groups perform rapid C$_3$ jumps (i.e., the 245 K spectrum) and the other from cations where both the methyl groups rotate and the cation itself rapidly jumps about a C$_2$ axis (i.e., the 320 K spectrum). The implication is that there is a temperature dependent distribution of sites where the cation is rigid except for methyl C$_3$ flips and where the cation performs rapid C$_2$ flips in addition to methyl C$_3$ flips. The spectra in this temperature range could not be simulated assuming C$_2$ flips at rates comparable to $\chi^{-1}$ [30, 41]. This behaviour of the dimethylammonium cation contrasts with that recently observed in the tin and tellurium hexachloride salts, where Ikeda...
Fig. 7. Deuterium quadrupolar echo spectra of dimethyl-d$_6$ ammonium tetraphenylborate at 320 K (A), 245 K (B), 275 K (C) and 270 K (D). Spectrum A was simulated with a QCC of 45.8 kHz, a jump angle $2\beta = 118.4^\circ$ and a fast exchange between the sites. Spectrum B was simulated with a QCC of 50.0 kHz. In (A) the principal components $V_j$ in the jump averaged frame are indicated. Both simulations were performed with $\eta = 0$.

et al. [41] clearly observed spectra due to (CD$_3$)$_2$NH$_2$ cations performing $C_2$ flips at rates comparable to $\chi^{-1}$ (the intermediate exchange regime).

The $^2$H Zeeman spin-lattice relaxation times of the dimethyl-d$_6$ ammonium ions between 298 and 355 K are shown in Figure 9. The relaxation times were measured on the $V_{xx}$ discontinuity (see Figure 7). No abrupt change in $T_1$ was observed in this temperature range, suggesting that a phase transition is unlikely. Between 215 and 245 K the $^2$H Zeeman spin-lattice relaxation times showed an activation energy of 9.4 ± 2.0 kJ mol$^{-1}$. This value compares well with the energy barrier for methyl group $C_3$ jumps of 13 kJ mol$^{-1}$ observed in dimethylammonium nitrate [45].

v) Trimethylammonium Tetraphenylborate

Both the trimethyl-d$_6$ ammonium (CD$_3$)$_3$NH, and the trimethylammonium-d$_1$, (CH$_3$)$_3$ND, cations were studied by $^2$H nmr. The deuterium resonance of the (CH$_3$)$_3$ND ion showed a doublet splitting of 112 kHz at 294 K. This value is close to 124 kHz expected for a static N–$^2$H bond. The difference in these values indicates small angle wobbling of the N–$^2$H bond [30]. This is consistent with x-ray crystallographic
Fig. 8. Representation of the two site exchange process using two different coordinate frames. The \( J \)-superscripted axes refer to the jump frame and the second frame is used as a reference for the methyl \( C_3 \) flip averaged frame.

Fig. 9. Deuterium Zeeman spin-lattice relaxation times \( (T_{1Z}) \) as a function of reciprocal temperature for the dimethyl-\( D_6 \) ammonium cation in \((CD_3)_2NH_2B(C_6H_5)_4\).

Fig. 10. Deuterium line shapes of trimethyl-\( D_6 \) ammonium tetraphenylborate at 296 K (A) and 185 K (B). The simulations of both spectra used fast \( C_3 \) and \( C_3 \) flips resulting in a motionally averaged QCC of 17.3 kHz and 19.5 kHz for A and B respectively, with \( \eta = 0 \). In addition, a two site exchange motion was included with flip angles of 12 ± 1° and 13 ± 1° for A and B, respectively.
results which show rather large thermal ellipsoids on the carbon atoms compared with values normally encountered [46]. The vibrationally averaged QCC amounts to 150 ± 5 kHz [16]. This value is close to that obtained for the C−2H bond in the tetramethyl-
d_{12} ammonium ion in part i.

The $^2$H line shape of the trimethyl-d$_4$ ammonium ion is shown in Fig. 10 at 296 and 185 K. At both temperatures the EFG is motionally averaged due to a superposition of fast methyl C$_3$ and cation C$_3$ motions. The spectra could, however, only be simulated assuming small-angle two-site exchange in addition to the C$_3$ and C$_3$ motions. This motion can account for the observed spectral asymmetry of $\eta = 0.07 \pm 0.01$ at both temperatures. The presence of this additional motion was also observed in x-ray data as mentioned above. Details of the spectral simulations are given in the legend of Figure 10. Using the values of the $V_{y}$ EFG components (see Fig. 7), values of the QCC of the C−2H bond can be obtained since $V_{y}$ is not affected by the two site exchange. Assuming fast C$_3$ and C$_3$ flips, a QCC of 156 ± 5 and 175 ± 6 kHz is obtained from the 296 and 185 K $^2$H spectra, respectively. The QCC obtained from the 185 K $^2$H spectrum is in good agreement with values reported for C−2H bonds in other molecules [16, 17]. The assumption of fast C$_3$ and C$_3$ flips is justified since Zeeman spin-lattice relaxation experiments indicate that $\omega_0 \tau < 1$. Also, no change in $^2$H lineshape at 185 K was observed upon changing the quadrupolar echo delay from 40 μs to 140 μs. Between 296 and 348 K the relaxation data indicate that the overall molecular reorientation occurs with an activation energy of 20.1 ± 2.0 kJ mol$^{-1}$. This value agrees well with activation barriers obtained for the C$_3$ motion of trimethylammonium ions in [(CH$_3$)$_3$ND]$_2$MX$_6$ (M = Pt, Sn, Te and X = Cl, Br) [47].

However, the activation energy for reorientation of the ammonium ion determined in this study, 5.0 kJ mol$^{-1}$, is substantially greater than the rotational barrier reported in a recent infrared study [4].

The tetramethylammonium ion also undergoes rapid overall reorientation in the cavity formed by the phenyl rings of the tetraphenylborate anion. The $^3$H $T_{1Z, \text{min}}$ determined in the latter compound is slightly longer than anticipated. It is suggested that this discrepancy arises because the librational motions of the cation are neglected in the relaxation model.

For the less symmetrical methyl-substituted ammonium tetraphenylborates the $^2$H nmr data lead to the following conclusions:

1. Between 158 K and 295 K the CD$_3$ and ND$_3$ groups of the monomethylammonium salt undergo rapid C$_3$ jumps about the C–N axis; however, motion of the symmetry axis is restricted to large amplitude librations.

2. Between 215 K and 245 K the methyl groups of the dimethylammonium salt undergo rapid C$_3$ jumps about their respective C–N axes. Above 320 K the complete cation also executes rapid C$_2$ jumps about its C$_2$ axis. Further studies using other physical techniques will be required to establish the detailed behaviour of the dimethylammonium salt between 250 K and 300 K.

3. In the trimethylammonium salt, the complete cation jumps about the N–H axis over the entire temperature range investigated (185 K–348 K). In addition, the methyl group jumps about their C$_3$ axes and the N–H axis undergoes large amplitude librations.

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