**11B Solid-State NMR Interaction Tensors of Linear Two-Coordinate Boron: The Dimesitylborinium Cation**

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Supporting Information

**ABSTRACT:** Borinium cations (R₂B⁺) are of particular fundamental and applied interest in part due to their pronounced Lewis acidity which enables unique chemical transformations. Solid-state NMR spectroscopy of magic-angle spinning and stationary powdered samples of the dicoordinate boron cation in the recently reported dimesitylborinium tetrakis(pentafluorophenyl)borate compound (Shoji et al. Nature Chem. 2014, 6, 498) is applied to characterize the ¹¹B electric field gradient (EFG) and chemical shift (CS) tensors. The experimental data are consistent with linear C—B⁺—C geometry. The ¹¹B quadrupolar coupling constant, 5.44 ± 0.08 MHz, and the span of the CS tensor, 130 ± 1 ppm, are both particularly large relative to literature data for a variety of boron functional groups, and represent the first such data for the linear C—B⁺—C borinium moiety. The NMR data are similar to those for the neutral tricoordinate analogue, trimesitylborane, but contrast with those of the Cp*₂B⁺ cation. Quantum chemical calculations are applied to provide additional insights into the relationship between the NMR observables and the molecular and electronic structure of the dimesitylborinium cation.

**INTRODUCTION**

The boron sites within neutral molecules, with three substituents and a partially full octet, can still be relatively reactive. If one substituent is removed, then the borinium ion (two-coordinate boron cation) adopts a positive charge, and the reactivity increases significantly. The high reactivity of the boron cation means it can be difficult to produce a stable sample. This instability has made the synthesis of boron cations a challenge for chemists for over 50 years.¹⁻³ A variety of different types of boron cations have been studied, including three- and four-coordinate boron cations, and gas-phase boron cations.⁴ Chemists have succeeded in synthesizing and studying borinium ions where the directly bonded atoms are nitrogen, oxygen, or a transition metal; sometimes, one of the directly bonded atoms has been a carbon, which is part of a bulky group.⁵⁻⁸ However, it was not until recently that borinium ions were synthesized and studied, wherein both of the directly bonded atoms are carbon.⁹ It is this type of borinium ion that is our focus, specifically dimesitylborinium (Mes₂B⁺, Figure 1).

Dimesitylborinium is different from the other borinium ions that have previously been synthesized. Unlike the other borinium ions, dimesitylborinium is relatively stable, yet still extremely reactive.⁵,¹⁰ It is stabilized by π donation rather than lone pair donation, which allows it to keep its high reactivity, making it a strong Lewis acid. Because of its high reactivity, it is extremely air- and moisture-sensitive. Dimesitylborinium tetrakis(pentafluorophenyl)borate (1) features a perfectly linear C—B⁺—C angle of 180° in the solid state.

Boron-¹¹NMR spectroscopy has a long history, and there is a wealth of data available for various functional groups, particularly in solution.¹¹⁻¹⁵ Solid-state nuclear magnetic resonance (SSNMR) can provide information on the structure of a molecule, along with detailed information about bonding environments. Boron has two isotopes that can be observed by NMR, ¹⁰B (I = 3, N.A. = 19.9%, Z = 10.744%) and ¹¹B (I = 3/2, N.A. = 80.1%, Z = 32.084%). The nuclear quadrupole moment, Q, is moderate for both nuclei (Q(¹⁰B) = 84.59 mb; Q(¹¹B) = 40.59 mb).¹⁶ The preferred nucleus for NMR is ¹¹B because of its high natural abundance, manageable quadrupole moment, and availability of its central transition (mₛ = +1/2 ↔ -1/2). One problem with observing either boron isotope is that the stator in many commercial probes contains boron, which may show as a signal in the NMR spectrum. Echo pulse sequences are used to minimize this unwanted signal.

SSNMR spectra of ¹¹B are largely governed by the nuclear magnetic shielding (σ) and the quadrupolar interaction between the electric field gradient (EFG) and Q. From these two interactions, two second-rank tensors can be measured. Diagonalization of the symmetric part of a tensor gives the orientation of its principal axis system (PAS) in the molecular

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and electronic structure and the observed NMR parameters. Since this type of borinium ion is fairly unexplored, yet fairly easily produced in the laboratory, work in this area will lay the groundwork for further understanding of the electronic structure and reactivity of related borinium cations. In this work, the complete $^{11}$B EFG and CS tensors are measured experimentally and interpreted. These tensors are also calculated using cluster models in Gaussian 09, using periodic boundary conditions and the gauge-including projector-augmented wave (GIPAW) formalism in CASTEP, and interpreted using natural localized molecular orbital (NLMO) analyses with Amsterdam Density Functional (ADF) software.

**Experimental Section**

**Sample Preparation.** Dimesitylborinium tetrakis(pentafluorophenyl)borate (1) was prepared as described in ref 9. All subsequent handling of the sample was done in a dry argon-filled glovebox. The sample was ground into a fine powder and packed in a 4 mm outer diameter ZrO$_2$ rotor for SSNMR experiments.

**Solid-state $^{11}$B NMR.** Data were acquired at the University of Ottawa using a Bruker AVANCE III spectrometer at a magnetic field strength of 9.4 T ($\nu_0^{(11)}B = 128.38$ MHz) and at the National Ultrahigh-field NMR Facility for Solids in Ottawa using a Bruker AVANCE II spectrometer at a magnetic field strength of 21.1 T ($\nu_0^{(11)}B = 288.80$ MHz). Chemical shift referencing and set up were done with powdered sodium borohydride, which has a chemical shift of $-42.06$ ppm relative to boron’s primary chemical shift standard, F$_3$B•O(C$_2$H$_5$)$_2$. All data are acquired using Bruker’s TopSpin software.

At 9.4 T, $^{11}$B data were acquired using a 4 mm HXY triple resonance magic-angle-spinning (MAS) probe with a Hahn echo pulse sequence and high-powered proton decoupling ($\pi/2 - \tau - \pi - \text{acquire}$). The echo suppresses the background signal, though it does not remove it entirely. A recycle delay of 5 s was used with a 30 µs delay between the two pulses. 15 808 scans were collected.

At 21.1 T, $^{11}$B spectra of stationary and MAS samples were acquired using a 4 mm HBN triple resonance MAS probe with a Hahn echo pulse sequence and proton decoupling ($\pi/2 - \tau - \pi - \text{acquire}$). Again, the echo reasonably suppresses the background signal, though it can still be seen. The spinning speeds used for subsequent MAS experiments were 7, 8, 9, and 10 kHz. A CT-selective $\pi/2$ pulse length of 2 µs was used. Recycle delays of 5 to 10 s were used. 512 scans were recorded for the MAS spectra and 2048 scans were recorded for the static spectrum.

Spectral fitting was carried out using both WSolids1$^{21}$ and the Solids Line Shape Analysis Guide (SOLA) built into TopSpin 3.0. WSolids1 was used for the spectra of stationary samples, while SOLA was used for the MAS spectra.

**Quantum Chemical Computations.** Calculations of the EFG and magnetic shielding tensor parameters were performed using Gaussian 09$^{20}$ and CASTEP (v. 4.4)$^{11,12}$ Initial models for Gaussian 09 calculations were generated using standard bond lengths and angles in Gaussview 3.0. Unless otherwise indicated, models were optimized in Gaussian 09 using the same functional that is used for the NMR calculation. The B3LYP or RHF methods were used for all Gaussian 09 calculations, normally with the 6-311++G(d,p) basis set unless otherwise indicated. Models for GIPAW calculations were generated in Materials Studio (v. 4.4.0.0) using the crystal structure of Shoji and coworkers.$^{7}$ "On-the-fly" pseudopotentials were used with a 1 x 1 x 3 Monkhorst–Pack grid using two k-points. The basis set cutoff energy was set to 500 eV. The generalized gradient approximation (GGA) with the PBE functional was used for all CASTEP calculations. Further GIPAW calculations with higher energy cut-offs or more k-points were impractical with our resources due to the size of the unit cell. Relevant EFG and magnetic shielding tensor information was parsed from the output files using EFGShield (v. 4.2)$^{23}$

Natural localized molecular orbital (NLMO) calculations were accomplished using the ADF molecular modeling suite (v. 2012.01).

Figure 1. (a) A simple representation of the dimesitylborinium cation. (b) Model of dimesitylborinium tetrakis(pentafluorophenyl)borate generated from the X-ray crystal structure coordinates.$^7$ Carbon atoms are shown in light gray, boron in taupe, and fluorine in green. Hydrogen atoms are omitted for clarity.
The model comprised one dimesitylborinium cation with the atomic coordinates from the crystal structure of Shoji and co-workers. The GGA revPBE method was used, with the TZP basis set on all atoms.

**RESULTS AND DISCUSSION**

The $^{11}$B solid-state MAS NMR spectra of 1 acquired at 21.1 T are shown in Figure 2, with spinning speeds of 7, 8, 9, and 10 kHz. The $^{11}$B solid-state NMR spectra of the central transition of a stationary sample of 1 at magnetic field strengths of 9.4 and 21.1 T are shown in Figure 3. The spectra are somewhat complicated because of the interplay between quadrupolar and CS tensors, and because the spinning speed is not sufficient to remove all of the spinning sidebands. In addition, the baseline shows some unwanted residual broad signal due to the boron background in the probe (marked by an asterisk in Figure 3). All spectra were iteratively simulated to find a unique set of EFG and CS tensor parameters which fit all data simultaneously. These parameters are reported in Table 1. In addition to the dominant signal from the dimesitylborinium cation, signals from the relatively symmetric tetrakis(pentafluorophenyl)borate anion and a trace amount of sodium borohydride at $-42$ ppm are also taken into account in the simulations. BX$_4^-$ anions typically give rise to sharp peaks in $^{11}$B SSNMR spectra due to their relatively high symmetry and...
or due to rapid reorientation. They are for the most part of the same magnitude as the experimental data, with the notable exception of the value for compound 1, which is slightly lower.

The C(t) of the dimesitylborinium cation, 5.44 ± 0.08 MHz, approaches the largest such measured value, to our knowledge, 5.58 MHz, for the anion. The value is a result of the strong coupling between the boron site and the counteranion. The largest component of the EFG tensor, \( Q_{\text{iso}} = 31.2 \) ppm, is oriented along the boron axis.

The CS tensor in I (0.90 ± 0.10) is axially symmetric within experimental error, a small deviation from perfect axial symmetry in the crystal structure as one considers the location of the counteranion, the boron chemical shift tensor reports much more locally on the nature of the boron functional group. The computational model, however, suggests that while the quadrupolar coupling constant may be somewhat influenced by the nature and the location of the counteranion, the boron chemical shift tensor reports much more locally on the nature of the boron functional group. Note, for example, the excellent correspondence between the calculated CS tensor spans for the B3LYP/6-311+G(d,p) calculation (127 ppm), the GIPAW DFT calculation (129 ppm), and the experimental value (130(1) ppm).

A natural localized molecular orbital (NLMO) calculation shows that the two boron–carbon bonding orbitals make the largest contributions to the electric field gradient tensor and thus to the quadrupolar coupling constant (Figure 4). The largest component of the EFG tensor, \( V_{33} \), is aligned along the C—B\(^+\)—C axis. Similarly, the largest component of the magnetic shielding tensor, \( \sigma_{33} \) (and smallest component of the chemical shift tensor, \( \sigma_{33} \)) is oriented along the C—B\(^-\)—C axis (Figure 4). The two other components, \( \sigma_{11} \) and \( \sigma_{22} \), are affected by paramagnetic contributions which may be rationalized with the aid of the molecular orbital diagram presented in ref 9. The HOMO–2 and HOMO–3 orbitals feature strong contributions from \( \pi \)-type bonds between the mesityl groups and boron. Virtual 90° rotation of these orbitals about each of two orthogonal axes which lie perpendicular to the C—B\(^+\)—C axis results in favorable overlap with one of the two orthogonal vacant 2p orbitals of boron (LUMO and LUMO+1). This virtual mixing of orbitals relates to the application of an angular momentum operator causes para-

### Table 2. Calculated \(^{11}\)B Quadrupolar and Magnetic Shielding Tensor Parameters for Compound 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>RHF/6-311+G(^a)</th>
<th>RHF/6-311G++(d,p)(^a)</th>
<th>B3LYP/6-311+G(^a)</th>
<th>B3LYP/6-311G++(d,p)(^a)</th>
<th>GIPAW(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C(t) ) (^{11})B/MHz</td>
<td>6.11</td>
<td>6.50</td>
<td>6.06</td>
<td>5.91</td>
<td>6.55</td>
</tr>
<tr>
<td>( \eta_{\text{iso}} )</td>
<td>0.02</td>
<td>0.03</td>
<td>0.01</td>
<td>0.00</td>
<td>0.02</td>
</tr>
<tr>
<td>( \sigma_{\text{iso}} ) ppm</td>
<td>31.2</td>
<td>27.0</td>
<td>31.8</td>
<td>12.4</td>
<td>0.1</td>
</tr>
<tr>
<td>( \Omega ) ppm</td>
<td>154</td>
<td>155</td>
<td>149</td>
<td>127</td>
<td>129</td>
</tr>
<tr>
<td>( \kappa )</td>
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<td>0.97</td>
<td>1.00</td>
<td>1.00</td>
<td>0.94</td>
</tr>
<tr>
<td>( \beta/\text{deg} )</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

\(^a\)Calculations carried out using Gaussian 09 on a single dimesitylborinium cation. See Experimental section for details. \(^b\)Calculations carried out on the whole crystal structure with periodic boundary conditions using CASTEP. See Experimental section for details.
magnetic deshielding along each of the two orthogonal axes which lie perpendicular to the C—B′—C axis, resulting in the large values observed experimentally for δ11 and δ22, and thus the large CS tensor span. This relationship between electronic structure and the CS tensor components could be particularly valuable in characterizing novel borinium cations in the future.

It is interesting to further compare the EFG and CS tensor data obtained for 1 to the analogous neutral tricoordinate compound, trimesitylborane, as well as to [Cp*2B+] [AlCl4−]. These two compounds are selected for comparison with 1 in part because they all feature boron atoms directly bonded to carbon ligands. The latter compound features a cationic boron interacting in a η1 fashion with one of the Cp* rings and interacting in an η2 fashion with the second Cp* ring. Despite the quite different nature of the bonding to boron, the near-linear geometry at boron makes for an interesting comparison to the data obtained for 1. As seen in Table 1, there are similarities and differences in the 11B EFG and CS tensors across the three compounds. First, the isotropic shift increases from −41.3 ppm for Cp*2B′ to 77.4 ppm for trimesitylborane to 91.2 ppm for 1. These average values can be properly understood by considering the values of the three principal components of the CS tensors, which are depicted graphically in Figure 5, as well as the CS tensor orientations in the molecular frame of reference. All three compounds show axially symmetric CS tensors (κ ≈ 1). Inspection of the tensor components shows a strong similarity between 1 and trimesitylborane, and rather large differences between 1 and Cp*2B′, for each principal component. Conversely, the orientation of the CS tensor for 1 is analogous to that seen for Cp*2B′, i.e., δ33 lies along the C—B′—C direction, whereas in trimesitylborane this most shielded component lies perpendicular to the three boron–carbon bonds. In this sense, the CS tensor for 1 is unique and diagnostic of the linear C—B′—C borinium functional group, but both the tensor magnitude and orientation must be considered. Such information and differentiation is not necessarily as readily available from an inspection only of the isotropic chemical shift. For example, δiso for neutral tricoordinate Cp*2BMe,28 at 81.9 ppm, is not far from the 91.2 ppm observed for 1 (Table 1). Consideration of CS tensor components and isotropic chemical shifts known for other boron functional groups, such as boronic acids and boronate esters, also show a clear differentiation with respect to the borinium ion (Figure 5).

The boron CS tensor spans shown in Table 1 include, to our knowledge, the largest such values measured in solids, i.e., 121 ppm for trimesitylborane, 130 ppm for 1, and 146 ppm for Cp*2BMe. It is perhaps somewhat surprising that the linear geometry at boron in 1 is not accompanied by a larger Ω(11B). For example, it is known from gas-phase microwave spectroscopic experiments on linear molecules such as FBO,

Figure 4. Orientations of the unique components of the boron electric field gradient (V33) and magnetic shielding (σ11) tensors for the dimesitylborinium cation (they are collinear along the direction of the C—B—C bonds). Both tensors are axially symmetric, and the remaining principal components (V11, V22, and σ11, σ22) lie in the plane perpendicular to the C—B′—C bond. The natural localized molecular orbital shown is one of two symmetry-equivalent B—C bonding orbitals which determine the magnitude and direction of the quadrupolar coupling tensor.

Figure 5. (a) Representation of the magnitude of the 11B quadrupolar coupling constant for a range of boron functional groups. The red parts of the bars represent the typical range of values which have been observed for a given functional group. (b) Representation of the principal components of the boron chemical shift tensor (δ11 in green, δ12 in red, and δ33 in blue) for various boron functional groups including boronic acids, boronate esters, trimesitylborane, [Cp*2B+] [AlCl4−], Cp*2BMe, and 1. Error bars are not shown but typically range from 1 to 10 ppm. Data are from refs. 29–36.
ClBO, FBS, and BF, that boron CS tensor spans can be up to 200 to 220 ppm.\textsuperscript{31,32}

The boron quadrupolar coupling data are also informative. Again, considering the first three compounds in Table 1, it is seen that all have axially symmetry EFG tensors at boron (\(\eta_Q \approx 0\)). We again expect to be able to differentiate between the functional groups in these three compounds by inspecting the magnitude and orientation of the tensor components. The \(C_Q(11B)\) values indeed differ clearly between the compounds, with \(Cp^*_2B^+\) at 1.14 MHz, trimesitylborane at 4.75 MHz, and \(1\) at 5.44 MHz. The orientations of the EFG tensors are analogous to those described above for the CS tensors: in the case of \(Cp^*_2B^+\) and \(1\), the largest and unique component \(V_{33}\) lies along the B—C bond, while for trimesitylborane \(V_{33}\) lies perpendicular to the plane containing the boron—carbon bonds. These orientations are determined by the molecular symmetry and the traceless nature of the EFG tensor. Nevertheless, as was seen with the CS tensors, the EFG tensor and the corresponding quadrupolar parameters provide a unique diagnostic of the borinium functional group.

The results of calculations shown in Figure 6 demonstrate how sensitive the boron EFG and magnetic shielding tensors are to the C—B—C angle in a model diphenylborinium cation (see SI). Over the range from 180° to 160°, the calculated quadrupolar coupling constant increases slightly from 6.04 to 6.10 MHz and the asymmetry parameter increases from zero to only 0.013. The isotropic shielding constant decreases by about 3 ppm over the same range, while the span increases by about 4 ppm. These results suggest that the NMR parameters should be moderately sensitive to deviations from perfect linearity at boron. A more pronounced change in the NMR parameters, however, is obtained by varying the nature of the aryl or alkyl groups bonded to boron (see SI). A series of calculations for \(R_2B^+\) cations where \(R = \text{H}, \text{methyl}, \text{phenyl}, \text{and mesityl}\) shows that quadrupolar coupling constants of up to 8.71 MHz are predicted for \(R = \text{H};\) similarly, the span when \(R\) is an alkyl group (e.g., \(\Omega = 339 \text{ ppm}\) when \(R = \text{Me}\)) is.

![Figure 6](image_url)

**Figure 6.** Calculated (B3LYP/6-311++G(d,p)) dependence of the principal components of the \(^{11}\text{B}\) EFG and magnetic shielding tensors on the C—B—C angle (\(\theta\)) in the diphenylborinium cation. The CBCC dihedral angle was fixed at 90°. Fitted trend lines are given as follows: \(V_{33} = (-1.53 \times 10^{-5})(\theta^2) + (5.50 \times 10^{-3})(\theta) + 1.43 \times 10^{-1}, R^2 = 1.00; V_{22} = (-3.43 \times 10^{-6})(\theta^2) + (1.22 \times 10^{-3})(\theta) - 4.28 \times 10^{-1}, R^2 = 1.00; V_{11} = (-5.22 \times 10^{-3})(\theta^2) + (1.82 \times 10^{0})(\theta) - 6.18 \times 10^{1}, R^2 = 0.991; \sigma_{33} = (5.22 \times 10^{-3})(\theta^2) + (1.82 \times 10^{0})(\theta) - 6.18 \times 10^{1}, R^2 = 0.991; \sigma_{22} = (-6.07 \times 10^{-3})(\theta^2) + (2.21 \times 10^{0})(\theta) - 2.28 \times 10^{2}, R^2 = 0.999; \sigma_{11} = (-1.01 \times 10^{-2})(\theta^2) + (3.67 \times 10^{0})(\theta) - 3.62 \times 10^{2}, R^2 = 0.999.\)
calculated to be substantially larger than when it is an aryl group, presumably due to reduced π-donation in the former.

**CONCLUSIONS**

The present work has provided precise experimental $^{11}$B quadrupolar and chemical shift tensor magnitudes and orientations for a linear two-coordinate dimesitylborinium cation by fitting six spectral data sets recorded at two different applied magnetic field strengths. The $^{11}$B quadrupolar coupling constant of 5.44 MHz is one of the largest known for any boron compound. NLOM analysis shows that the large electric field gradient at boron arises largely due to the two boron–carbon bonds. The boron chemical shift tensor span of 130 ppm is also large when compared to literature data for all boron functional groups. The NMR data observed are similar to those for the large when compared to literature data for all boron functional groups. The NMR data observed are similar to those for the neutral tricoordinate analogue, trimesityborane, but contrast strongly with those of the $^{11}B$-C$_{6}$B$_{5}$H$_{5}$ cation. Quantum chemical calculations have provided insight into the relationship between the observed NMR parameters and the local molecular and electronic structure of the borinium cation. Mixing of the low-lying vacant $2p$ orbitals centered on boron with occupied orbitals of B–C bonding character contributes to the large CS tensor span. Further calculations show the sensitivity of the NMR parameters to the nature of the aryl or alkyl groups bonded to boron in the borinium ion, as well as to the degree of linearity at boron. As the chemistry of boron continues to expand in terms of fundamental understanding and diverse applications, this study demonstrates the value of the characterization of the complete boron EFG and CS tensors via solid-state NMR spectroscopy. Such data are particularly valuable, both for fundamental understanding and in a predictive sense, when comparing a series of related boron compounds, when contrasting different functional groups, and when examining compounds for which crystallographic data are unavailable.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.5b02161.

Results of additional calculations of NMR parameters (PDF)

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**Notes**

The authors declare no competing financial interest.

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