

## Experimental Assessment of the Strengths of B–B Triple Bonds

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**S** Supporting Information

**ABSTRACT:** Diborynes, molecules containing homoatomic boron–boron triple bonds, have been investigated by Raman spectroscopy in order to determine the stretching frequencies of their central B≡B units as an experimental measure of homoatomic bond strengths. The observed frequencies between 1600 and 1750 cm<sup>-1</sup> were assigned on the basis of DFT modeling and the characteristic pattern produced by the isotopic distribution of boron. This frequency completes the series of known stretches of homoatomic triple bonds, fitting into the trend established by the long-known stretching frequencies of C≡C and N≡N triple bonds in alkynes and dinitrogen, respectively. A quantitative analysis was carried out using the concept of relaxed force constants. The results support the classification of the diboryne as a true triple bond and speak to the similarities of molecules constructed from first-row elements of the p block. Also reported are the relaxed force constants of a recently reported diborabutatriene, which again fit into the trend established by the vibrational spectroscopy of organic cumulenes. As part of these studies, a new diboryne with decreased steric bulk was synthesized, and a computational study of the rotation of the stabilizing ligands indicated alkyne-like electronic isolation of the central B<sub>2</sub> unit.

We recently reported the synthesis and characterization of B<sub>2</sub>IDip<sub>2</sub> (**1**) (Figure 1), the first room-temperature-stable compound containing a B–B triple bond (diboryne).<sup>1</sup> A bond

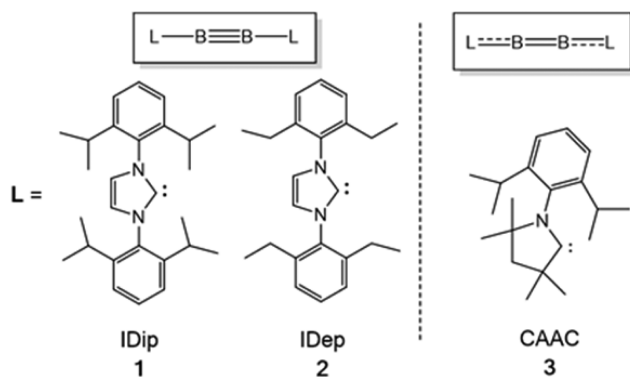


Figure 1. Structures of the studied B<sub>2</sub>L<sub>2</sub> compounds.

order of 3 was assigned to the interaction between the B atoms on account of the very short B–B bond length (1.449(3) Å), the linearity across the C–B–B–C central unit (B–B–C angles of 173.0(2)° and 173.3(2)°), and theoretical descriptions of the compound's electronic structure indicating bonding comprising one σ bond and two degenerate π bonds.<sup>2</sup>

This theoretical description mimics the well-known electronic construction of C≡C triple bonds as well as the triple bond in dinitrogen. It stands in contrast to the known examples of alkyne analogues of the heavier members of the p block, which assume trans-bent geometries.<sup>3</sup> We wished to determine whether diborynes fit into trends long-established in the literature for C≡C and N≡N triple bonds and by doing so complete trendlines described in introductory textbooks and taught to chemistry undergraduates. Comparison of the vibrational spectroscopy of the B≡B bond to the known spectroscopies of R<sub>2</sub>C<sub>2</sub> and N<sub>2</sub> was an intriguing option; however, as **1** is linear, with NMR spectroscopy indicating D<sub>2d</sub> symmetry in solution, the most interesting vibrational mode (ν<sub>B≡B</sub>) of the B<sub>2</sub> unit is IR-inactive. We therefore turned to Raman spectroscopy.

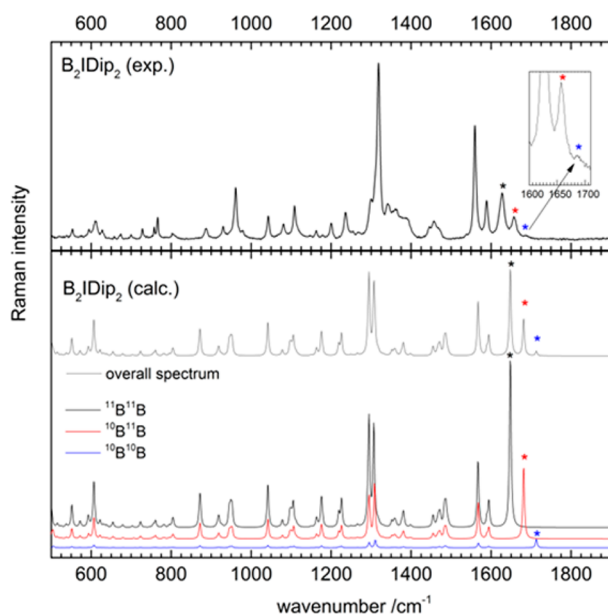
Raman spectroscopy has frequently been employed for the experimental description of novel homoatomic bonding between main-group elements.<sup>4</sup> The existence of both <sup>11</sup>B (~80% natural abundance) and <sup>10</sup>B (~20% natural abundance) provides a useful approach for determining which observed frequencies correspond to vibrational modes involving the central B<sub>2</sub> unit. Statistically, ~64% of any diboryne sample will be composed of the isotopologue containing two <sup>11</sup>B atoms, ~32% will contain one <sup>11</sup>B atom and one <sup>10</sup>B atom, and ~4% will contain two <sup>10</sup>B atoms. In a simplified description assuming an isolated B<sub>2</sub> unit, the mass dependence of the B≡B Raman stretching frequency can be described by the well-known expression for diatomic molecules<sup>5</sup> that relates the force constant of the bond (*k*) and the reduced mass (*μ*) of the oscillator to the stretching frequency for each isotopologue (eq 1). Scaling these frequencies by isotopic abundance yields a pattern of three peaks with an intensity ratio of 16:8:1, providing a useful tool in assigning relevant stretches.

$$\tilde{\nu} = (2\pi c)^{-1} \sqrt{k/\mu}, \quad \mu = m_A m_B / (m_A + m_B) \quad (1)$$

Figure 2 presents the Raman spectrum of **1** along with a compilation of the density functional theory (DFT)-computed spectra of its three constitutive isotopologues. A visual depiction

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**Figure 2.** Comparison of the experimental and B3LYP/6-311G(d)-predicted Raman spectra of **1**.

of the most important vibrational modes relating to the triple bond is given in Figure S1 in the Supporting Information (SI). DFT analysis of **1** predicted the B≡B stretch (Figure S1a) to appear at  $1648\text{ cm}^{-1}$  for the major  $^{11}\text{B}/^{11}\text{B}$  isotopologue and at  $1682$  and  $1713\text{ cm}^{-1}$  for the  $^{11}\text{B}/^{10}\text{B}$  and  $^{10}\text{B}/^{10}\text{B}$  isotopologues, respectively.<sup>6</sup> The observed frequencies at  $1628$ ,  $1657$ , and  $1685\text{ cm}^{-1}$  match these predictions, with intensities corresponding to the abundances of each species in solution. The most intense feature of the experimental spectrum ( $1319\text{ cm}^{-1}$ ) corresponds to a superposition of two peaks calculated to arise at  $1307$  and  $1295\text{ cm}^{-1}$ , deriving from modes in which the symmetric stretching of the C–B≡B–C group is mixed with deformation modes of the NHC ring (Figure S1b). The strong features observed at  $1560$  and  $1589\text{ cm}^{-1}$  arise entirely from the carbene ligand, as determined by comparison to the spectra of unbound carbene (Figure S2). The antisymmetric C–B≡B–C stretch (Figure S1c) is visible only in the IR spectrum (Figure S3), where it appears at  $1390\text{ cm}^{-1}$ . The most important Raman-active modes of **1** are assigned and summarized in Table S1 in the SI.

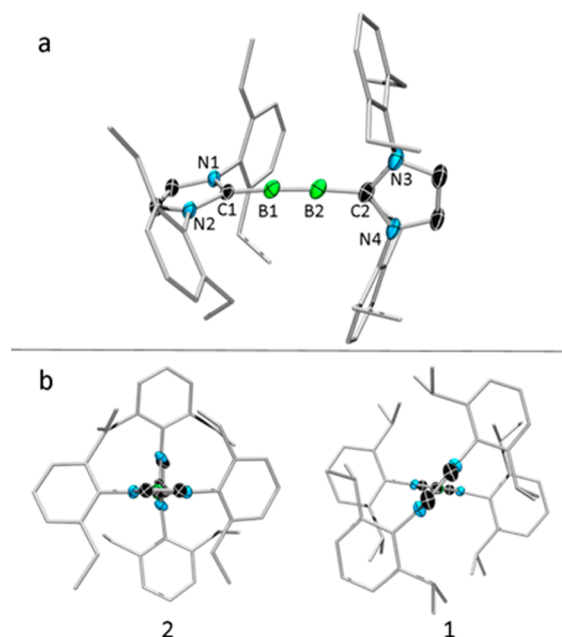
The Raman-active stretching frequency of the triple bond in dinitrogen<sup>5,7</sup> is observed at  $\sim 2300\text{ cm}^{-1}$ . At slightly lower wavenumbers falls the normal range for the stretching frequencies of the C≡C bond in alkynes, generally from  $\sim 2100$  to  $2260\text{ cm}^{-1}$ .<sup>5</sup> The observed B≡B stretching frequencies between  $\sim 1600$  and  $1700\text{ cm}^{-1}$  fit nicely into this trend and stand in contrast to the substantially lower Raman-active stretching frequencies observed for heavier trans-bent alkyne analogues, such as the predicted stretches of *trans*-dimethyldisilyne<sup>8</sup> at  $472$  and  $487\text{ cm}^{-1}$  and the measured stretch of *trans*-bent digermyne at  $397\text{ cm}^{-1}$ .<sup>4d</sup> These frequencies are also in good agreement with theoretical predictions for the Raman-active B≡B stretches of  $\text{CO}\rightarrow\text{B}\equiv\text{B}\leftarrow\text{CO}$  ( $1658\text{ cm}^{-1}$ ) and  $\text{N}_2\rightarrow\text{B}\equiv\text{B}\leftarrow\text{N}_2$  ( $1704\text{ cm}^{-1}$ ) and slightly greater than that of dianionic  $[\text{OB}\rightarrow\text{B}\equiv\text{B}\leftarrow\text{BO}]^{2-}$ , which was predicted to appear at  $1454\text{ cm}^{-1}$ .<sup>9</sup> A rough estimate of the B≡B force constant ( $k$ ) of  $\sim 850\text{ N/m}$  was derived from eq 1 with the assumption that the mode is dominated by  $B_2$  stretching. This value again fits with the decrease in the force constant observed in going from  $\text{N}_2$  ( $\sim 2250\text{ N/m}$ ) to  $\text{C}_2\text{H}_2$  ( $\sim 1600\text{ N/m}$ ).<sup>10</sup>

Although the agreement between the calculated and experimental Raman spectra is convincing and permits a straightforward assignment of the B≡B stretches of the three isotopologues, the isotopic shifts computed using eq 1 are slightly larger than those observed in the collected spectra, showing the limit of this simplified two-atom model. Indeed, the pitfalls of using the force constant derived from eq 1 as a descriptor of bond strength<sup>11</sup> have been discussed extensively.<sup>12</sup> As an alternative, we employed relaxed force constants ( $f_R$ ) derived from the so-called compliance matrix.<sup>12</sup> Relaxed force constants are invariant to the choice of coordinate system and thus provide information on isolated local modes. They can be regarded as the force needed to distort the molecule along a specific coordinate, while all of the other forces are relaxed. As a consequence, they can be related to a specific bond. This approach has been successfully applied to quantify hydrogen-bond strengths in Watson–Crick base pairs<sup>13</sup> and the bond strengths of double and triple bonds of C and Si.<sup>14</sup> We computed the relaxed force constants of compounds **1–3** using the program Compliance 3.0.2.<sup>12,15</sup> For compound **1** we obtained  $f_R = 617\text{ N/m}$ , which is similar to the  $f_R = 676\text{ N/m}$  computed for the B≡B bond in  $\text{CO}\rightarrow\text{B}\equiv\text{B}\leftarrow\text{CO}$ ,<sup>16</sup> which is also thought to show triple-bond character. Comparison of the  $f_R$  values of the B≡B triple bonds to those of  $\text{N}_2$  ( $2500\text{ N/m}$ ) and acetylene ( $1754\text{ N/m}$ ) again shows a decrease in triple-bond strength in going from nitrogen via carbon to boron. For comparison,  $f_R = 489\text{ N/m}$  can be calculated for the B–C single bond in **1**. The  $f_R$  values derived from the B≡B and B–C stretches of these compounds are listed in Table S2.

The exceptionally large steric bulk of the IDip ligand was found to be necessary in order to stabilize **1** against degradation at room temperature; however, this bulk inhibits further reactivity. With hopes of gradually scaling back the bulk of the carbene ligand while preserving the stability, the new diboryne **2** was synthesized in a manner analogous to **1**. In **2**, the isopropyl groups on the phenyl rings of the NHC in **1** have been replaced by ethyl moieties. Like **1**, **2** is bright-green both as a solid and in solution, and it exhibits a broad  $^{11}\text{B}$  NMR resonance at  $41\text{ ppm}$  mirroring the observed resonance in **1** ( $39\text{ ppm}$ ). The decreased steric shielding in **2** was thermochemically evident, as decomposition was observed upon heating to  $100\text{ }^\circ\text{C}$  in vacuum, whereas **1** is stable to  $234\text{ }^\circ\text{C}$ .<sup>1</sup> Figure 3a shows the crystallographically determined structure of **2**. As expected, the B≡B length is short, measuring only  $1.446(3)\text{ \AA}$ , very similar to that in **1** ( $1.449(3)\text{ \AA}$ ).<sup>1</sup> The two B–C bonds from the carbene to  $B_2$  measure  $1.484(3)$  and  $1.488(3)\text{ \AA}$ , again similar to the corresponding bond lengths in **1** ( $1.487(3)$  and  $1.495(3)\text{ \AA}$ ). The central C–B–B–C unit is nearly linear, with B–B–C angles measuring  $175.4(2)^\circ$  and  $172.0(2)^\circ$ . The DFT-optimized geometry of **2** (Figure S4) shows excellent agreement with the solid-state structure in Figure 3a.

The most notable difference between the two species is in the angles made by the planes of the central five-membered rings of their respective carbenes, as displayed in the end-on views of **1** and **2** in Figure 3b. The angle between the planes of the two NHCs in **2** is  $\sim 85^\circ$ , whereas it is substantially more acute in **1**, measuring  $\sim 56^\circ$ . These values are reproduced well by DFT methods, where optimization at the B3LYP/6-311G(d) level predicted a  $90^\circ$  angle in **2** and a  $56^\circ$  angle in **1**.

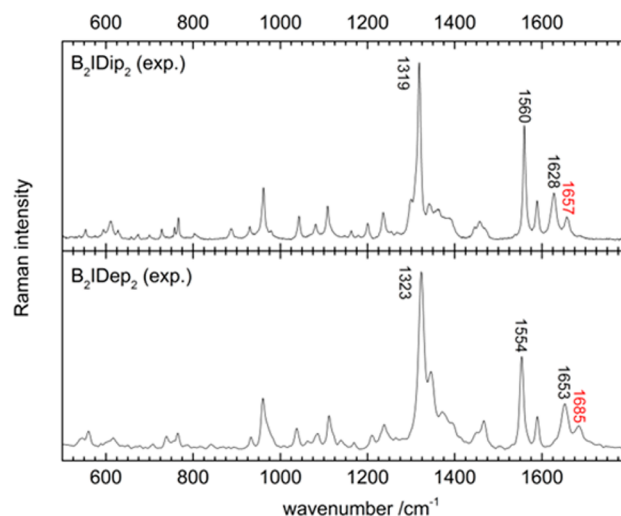
In view of this relatively large difference between the interplanar angles, it is perhaps surprising that no crystallographically significant differences between the structures of the central C–B–B–C units of **1** and **2** are evident. In order to



**Figure 3.** (a) X-ray structure of **2**. Thermal ellipsoids represent 50% probability. H atoms and ellipsoids on the N substituents of the NHC ligands have been omitted for clarity. Selected bond lengths (Å) and angles (deg): B1–B2, 1.446(3); B1–C1, 1.484(3); B2–C2, 1.488(3); C1–N1, 1.388(2); C1–N2, 1.389(2); C2–N3, 1.376(3); C2–N4, 1.387(2); B1–B2–C2, 175.4(2); B2–B1–C1, 172.0(2); N1–C1–N2, 103.6(2); N3–C2–N4, 103.8(2). (b) Comparison of the interplane angles formed by the central rings of the NHC ligands in **2** and **1**.

examine the role of the interplanar angle on the overall energy of the compounds and the structure of the central B<sub>2</sub> unit, DFT calculations (B3LYP/6-31G(d)) were performed in which the orientation of the central five-membered rings of the NHC ligands were fixed at various angles while the rest of the molecule was optimized. The lengths of the B–B and C–B bonds as well as the electronic energies of the compounds were monitored as the interplanar angles in **1** and **2** were varied from 50° to 90° (Table S3). Across this range of angles, the B–C and B–B bonds in **2** were found to be largely invariant, remaining within 0.003 Å of the B3LYP/6-31G(d)-optimized values (B–B, 1.467 Å; C–B, 1.475 Å). The maximum energy difference from the optimized geometry was +1.6 kcal/mol, calculated for the structure with an interplanar angle of 50°. Similarly, very small variations in the B–B bond are observed in **1**, whose length shows only a small increase from the fully optimized value of 1.472 Å to 1.480 Å at an imposed interplanar angle of 90°. The variation in the C–B bond length is even less significant, showing a difference of less than 0.007 Å. Taken together, these calculations indicate the electronic isolation of the  $\pi$  orbitals of the central B<sub>2</sub> unit from the stabilizing carbenes, which function as pure two-electron donors, in agreement with previous orbital analysis.<sup>1</sup> The observed difference between the interplanar angles in **1** and **2** is likely a result of the respective optimal geometries for packing of the bulky steric architectures of the different NHCs.

The B≡B stretching modes (Figure S1a) of the three isotopologues of **2** were observed at 1653, 1685, and 1711 cm<sup>-1</sup>, in agreement with DFT predictions of 1681, 1715, and 1747 cm<sup>-1</sup>, respectively. The spectra in Figure 4 are very similar, with the most notable difference being a slight blue shift (25 cm<sup>-1</sup>) measured for the B≡B stretching frequencies observed in **2**. This shift is likely the result of the slightly shorter average B≡B



**Figure 4.** Comparison of the experimental Raman spectra of (top) **1** and (bottom) **2**. A comparison of the spectrum of **2** with its DFT-predicted spectrum and the spectrum of its ligand is provided in Figure S5.

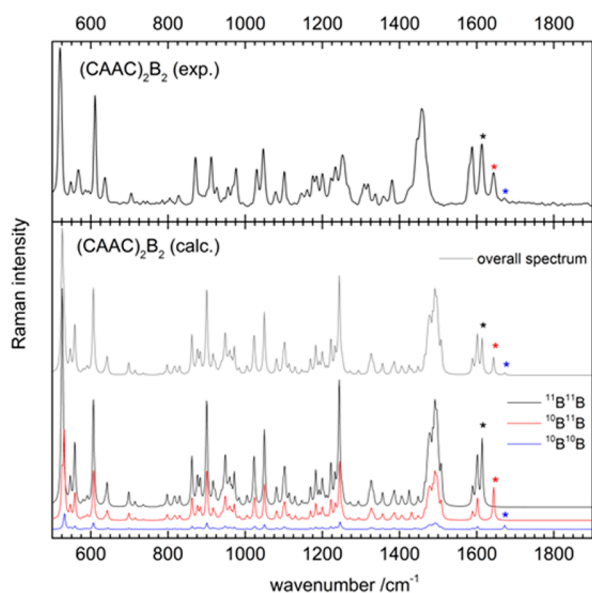
bond length in **2** (calculated to be ~1.467 Å across the range of interplanar angles studied; Table S3) than in **1** (~1.474 Å), stemming from the comparatively larger IDip ligand in **1**. For **2**,  $f_R$  values of 629 and 526 N/m were calculated for the B≡B and B–C stretches, respectively. From these values, both bonds seem to be slightly stronger in **2** than in **1**.

Very recently, we reported the synthesis and characterization of **3**, a B<sub>2</sub>L<sub>2</sub> compound in which 1-(2,6-diisopropylphenyl)-3,3,5,5-tetramethylpyrrolidin-2-ylidene (CAAC)<sup>17</sup> is employed as the stabilizing carbene ligand.<sup>18</sup> As opposed to **1**, which is best described as having a B≡B triple bond flanked by single bonds from the ligands to the B<sub>2</sub> unit, the enhanced  $\pi$  acidity of the CAAC ligand results in the spread of electron density across the entire central C–B–B–C core. Structurally, this is manifested in a relatively longer bond between the boron atoms and shorter ligand–boron bonds. The overall result is a structure that may be described as a diboracumulene, an inorganic/organic structural mimic of the butatriene dication, as depicted in Figure 1.

Figure 5 shows a comparison of the Raman spectrum of **3** with the DFT-calculated spectra of its three constitutive isotopologues. The calculations predicted a Raman-active frequency dominated by B=B stretches at 1614, 1644, and 1673 cm<sup>-1</sup> for the <sup>11</sup>B/<sup>11</sup>B, <sup>10</sup>B/<sup>11</sup>B, and <sup>10</sup>B/<sup>10</sup>B isotopologues of **3**, respectively, which fit with peaks at 1614, 1643, and 1671 cm<sup>-1</sup> in the experimental spectrum. These peaks exhibit a red shift with respect to the B≡B stretch in **1** (1628 cm<sup>-1</sup>), as might be expected for a compound with a longer bond between the boron atoms and less triple-bond character; however, the magnitude of this shift is surprisingly small. The blue shift in the spectrum of **2** with respect to **1** is larger, despite the structural similarities of the two compounds. The reason for the slight red shift becomes clearer when **3** is viewed as a cumulene. The symmetric stretch of the central C<sub>2</sub> unit in butatriene has been measured at 2079 cm<sup>-1</sup>, well above the conventional range for C=C double bonds and in the low-wavenumber range for alkynyl triple bonds.<sup>5,19</sup> In view of this, the relatively small red shift seen in **3** is reasonable and supports the previous assignment of **3** as an inorganic/organic hybrid cumulene.

Again, relaxed force constants can be used to support these qualitative arguments. For compound **3** we calculated  $f_R = 535$  N/m for the bond between the two boron atoms, which is





**Figure 5.** Comparison of the experimental and B3LYP/6-311G(d)-predicted Raman spectra of **3**.

significantly lower than those obtained for **1** and **2** but higher than the value of 412 N/m calculated for a previously reported compound containing a B=B double bond ( $B_2IDip_2Br_2$ , Table S2; the spectrum is shown in Figure S7).<sup>1</sup> We note that  $f_R$  for the B–C bond in **3** is 557 N/m, compared with 489 N/m in **1** and 526 N/m in **2**, indicating increased B–C bond strength. The nearly equal  $f_R$  values for the B=B and B=C stretches in **3** support its assignment as a cumulene-type compound. For comparison, butatriene  $f_R$  values are also given in Table S2.

In the IR spectrum of **3** (Figure S6), the agreement between computation and experiment is again excellent. The B=C stretch appears at 1426  $cm^{-1}$ , which is blue-shifted relative to **1** (the values and assignments of the IR peaks are given in Table S4) in agreement with the proposed increase in B–C bond strength in going from triple-bonded **1** to cumulene **3**.

In summary, the measured B–B stretching frequencies in **1–3** fit into the trends established for multiple bonds consisting of carbon and nitrogen. The study of diboron compounds containing multiple bonds has indicated similarities among the elements of the first row of the p block and differences with similar bonds between heavier atoms.<sup>3</sup> The vibrational and computational data presented here firmly reinforce this notion, filling in the final data point in the trendline connecting the well-known values for  $\nu_{E\equiv E}$  across the first row of the main group and describing an electronic localization of the  $\pi$  bonds in diborynes akin to that found in alkynes.

## ■ ASSOCIATED CONTENT

### Supporting Information

Procedures and additional data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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