Raman Spectroscopic and Quantum Chemical Investigation of the Pyridine-Borane Complex and the Effects of Dative Bonding on the Normal Modes of Pyridine

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ABSTRACT: The pyridine-borane (PyBH₃) complex was analyzed by Raman vibrational spectroscopy and density functional theory to elucidate its structural and vibrational properties and to compare these with those for neat pyridine (Py). The borane–nitrogen (BN) bond length, the BN dative bond stretching frequency, and the effects of dative-bonded complex formation on Py are presented. Rather than having a single isolated stretching motion, the complex exhibits multiple BN dative bond stretches that are coupled to Py’s vibrations. These modes exhibit large shifts that are higher in energy relative to neat Py, similar to previous observations of Py/water mixtures. However, significantly higher charge transfer was observed in the dative-bonded complex when compared to the hydrogen-bonded complex with water. A linear relationship between charge transfer and shifts to higher frequencies of pyridine’s vibrational modes agrees well with earlier observations. The present work is of interest to those seeking a stronger relationship between charge-transfer events and concomitant changes in molecular properties.

INTRODUCTION

A covalent bond typically involves a sharing of electrons between atoms, i.e., both atoms donate a single electron to be shared. A coordinate covalent or dative bond, however, forms from one atom donating a pair of electrons to a Lewis acid. Boron’s three valence electrons allow for the formation of three covalent bonds, with an empty p orbital remaining. This empty p orbital serves as a Lewis acid site and readily dative bonds to nitrogenous Lewis bases. Dative bonds have been investigated both experimentally and computationally for the characterization of their vibrational frequencies, bond energies, and bond lengths. Vibrational frequencies vary because of substituent atoms, but the borane–nitrogen (BN) dative bond has a typical bond length of approximately 1.6 Å and an interaction energy of −43.91 kcal mol⁻¹ at the estimated CCSD(T) complete basis set level.¹

The vibrational frequencies of the BN dative bond stretching motion and dative-bonded complexes as a whole are of interest because of their potential to offer evidence of the significant charge transfer in dative bond formation. Shifts in vibrational energy have been studied extensively as a probe of intermolecular interactions. In 2013, we offered evidence of a strong correlation among charge transfer, vibrational mode shifts to higher energy, and changes in bond length in charge-donating, nitrogen-containing heterocycles. This work showed a linear relationship between the total electronic charge donated in a molecular complex and a shift to higher frequency in vibrational modes, particularly the ring breathing mode. Here, we extend our investigations of the effects of electron transfer in nitrogen-containing heterocycles to include the effects of dative bonding in the pyridine-borane complex. By characterizing the vibrations in this complex through Raman spectroscopy and comparing the spectrum to hydrogen-bonded complexes showing known charge-transfer events with pyridine, a greater understanding of charge transfer in the dative bond, the correlation between charge transfer and changes in molecular properties, and the pyridine-borane complex can be obtained.

Since the development of its facile synthesis in 1954, the pyridine-borane complex (PyBH₃) has been ubiquitous in molecular synthesis in roles such as a reducing agent, a key component in reductive amination, and a precursor to hydroborating alkenes at room temperature. To the best of our knowledge, neither the Raman vibrational spectrum nor the BN dative bond stretch of PyBH₃ has been characterized. Borane–Lewis acid dative bonds have been studied extensively, as mentioned above, but pyridine (Py) has received little study as a Lewis base in dative bonds. Matthäus et al. in 2001 studied boron trichloride-pyridine...
fragments and complexes through their pioneering vibrational fragment mode analysis technique. By describing vibrational modes in a complex as percentages of their fragment mode, they showed mode mixing between Py and BCl3 and large perturbations of the vibrational modes relative to their fragments. In 2003, Tao et al. studied Py bound to Si(100) through vibrational spectroscopy and density functional theory (DFT) calculations to show that Py molecules interact with Si(100) through Si:N dative bonding. Tao et al. in 2008 published a similar work studying pyrrolidine dative bonds to Si(111)-7 × 7. Their work showed shifts to higher energy for pyrrolidine’s ring breathing mode upon charge transfer and dative bond formation. The work by these groups lays a foundation for the study of the PyBH3 dative-bonded complex in the present work.

Here, in an effort to investigate the vibrations of the PyBH3 complex both in isolation and in comparison to Py and provide a greater correlation between charge transfer and vibrational mode shifts, we present a comprehensive Raman spectroscopic and DFT study. Raman spectra of Py and PyBH3 are acquired experimentally and compared to explore the effects of the addition of BH3 to Py’s vibrational modes. These experimental results are also compared to Raman spectra of Py/water mixtures of various mole fractions, similar to the work of Schlucker et al., to compare the results of our work to a known charge-transfer event in Py. DFT calculations were performed to compare the structures of Py and PyBH3, their simulated Raman spectra, and charge-transfer events through the natural electron configuration (NEC) within natural bond orbital (NBO) analyses. These calculations will show changes in bond length and aid in the characterization of PyBH3’s Raman vibrational spectrum.

**METHODS**

Py (99.8%) and PyBH3 (8 M BH3Py) were commercially acquired from Sigma-Aldrich and used without further purification. All experimental data was acquired at ambient temperature using a Horiba LabRAM HR Evolution Raman Spectroscopy system (Horiba Scientific, Kyoto, Japan) equipped with a 600 grooves/mm grating and a charge-coupled device (CCD) detector. A 532 nm Nd:YAG laser (Oxxius, Lannion, France) was used to excite the solutions of Py, PyBH3, and Py/water held in 1 cm cuvettes.

Calculations were carried out using the Gaussian 16 software suite. Geometry optimizations (using the Opt = Very Tight option) and Raman activities were carried out using the Minnesota 06 functional M06-2X with a correlation-consistent basis set augmented with diffuse functions (aug-cc-pVTZ). This method and basis set will be denoted as M06-2X/aVTZ for the remainder of this work. To calculate the harmonic vibrational frequencies, a pruned numerical integration grid composed of 99 radial shells and 590 angular points per shell was employed, and these frequencies were scaled by an empirically determined scaling factor of 0.970 to partially account for anharmonicity and intermolecular interactions in condensed phases. Spectra were simulated by summing Lorentzian profiles constructed from the calculated harmonic frequencies and normalized Raman optical activities.

**RESULTS AND DISCUSSION**

**Theoretical Predictions.** Geometry optimizations and Raman vibrational frequency calculations of both Py and PyBH3 were performed to compare and accurately characterize the vibrations of interest in the experimental data. Optimized structures of the PyBH3 complex and Py are shown in Figure 1 with their associated bond lengths expressed in angstroms (Å) in Table 1. Cartesian coordinates for these molecules are available in the Supporting Information. The bond lengths here are reported to three decimal places to allow comparison; the precision is not intended to reflect the accuracy of the computed geometrical parameters. Upon formation of the PyBH3 complex, NC1 and CSN bonds elongate by 0.006 Å (0.45%), the C2C3 and C3C4 bonds elongate by 0.001 Å (0.07%), and the C1C2 and C4C5 bonds shorten by 0.007 Å (0.50%). Steric hindrance could be present in the complex between the three boro-hydrogens and the neighboring pyridyl-hydrogens. This is relieved by the elongation of the NC1 and CSN bonds and the shortening of all CH bonds. The CIH8 and CSH11 bonds closest to the BH3 group undergo shortening greater in magnitude (0.004 Å, 0.37%) than those further removed (C2H9, C3H7, C4H10, 0.001 Å, 0.09%). We attribute the shortening of the C1C2 and C4C5 bonds to relieved ring strain in the stretched pyridine ring. The BN dative bond length is recorded as 1.615 Å and is in agreement with past works. The BH14, BH13, and BH15 bonds are slightly longer than what has been recorded experimentally for BH3 (1.190 Å) and more closely agree with BH bond lengths for the boron dihydride anion (BH2−) or the boron hydride cation (BH+), both with BH bond lengths of 1.205 Å. The antiplanar BH bond, BH13, is slightly longer than its neighboring BH bonds, alluding to a more delocalized, weaker bond here.

![Figure 1. Optimized structures of PyBH3 and Py at the M06-2X/aVTZ level of theory.](https://doi.org/10.1021/acsomega.2c00636)
Table 1. Bond Lengths ($R$, Å) Associated with Py and PyBH$_3$ Structures Optimized at the M06-2X/aVTZ Level of Theory

| molecule     | R(N C1) | R(C1 H8) | R(C1 C2) | R(C2 C3) | R(C2 H9) | R(C3 H7) | R(C3 C4) | R(C4 C5) | R(C5 H10) | R(C5 H11) | R(NB H14) | R(B H113) | R(B H15) |
|--------------|---------|----------|----------|----------|----------|----------|----------|----------|-----------|-----------|-----------|-----------|----------|
| pyridine     | 1.330   | 1.084    | 1.388    | 1.081    | 1.385    | 1.082    | 1.385    | 1.084    | 1.330     | X         | X         | X         | X        |
| pyridine-borane | 1.336   | 1.080    | 1.381    | 1.080    | 1.386    | 1.081    | 1.386    | 1.080    | 1.336     | 1.615     | 1.206     | 1.209     | 1.206    |
| δ%          | 0.45    | 0.37     | 0.50     | 0.09     | 0.07     | 0.09     | 0.07     | 0.09     | 0.50      | 0.37      | 0.45      |           |          |

"See Figure 1 for atom numbers. Data given to three decimal places to facilitate comparison.

Table 2. Charge Transfer (me$^-$) Associated with the Py Atoms after the Formation of the Dative Bond in PyBH$_3$

| atom$^a$ | $\Delta q$ (me$^-$) |
|----------|---------------------|
| C        | −50                 |
| C        | 0                   |
| C        | 3                   |
| C        | 0                   |
| C        | 5                   |
| N        | −50                 |
| H        | −10                 |
| H        | −40                 |
| H        | −10                 |
| H        | −10                 |
| H        | −40                 |
| B        | 12                  |
| H        | −60                 |
| H        | −60                 |
| H        | −60                 |

"See Figure 1 for atom numbers.

Simulated Raman spectra of both Py (bottom, black) and PyBH$_3$ (top, green) at the M06-2X/aVTZ level of theory are shown in Figure 2, with tabulated spectral shifts recorded in Table 3. Full simulated spectra are available in the Supporting Information. Predicted spectral shifts are demonstrated with red arrows. Mode assignments for Py are based upon work by Wilmshurst and Bernstein$^{42}$ and were employed to assign the modes in PyBH$_3$. In the simulated spectrum of PyBH$_3$, the BN dative-bond stretch appears at two separate energies, both coupled to a pyridine vibration. The first appears at 695 cm$^{-1}$ and is coupled to pyridine’s $\nu_{6a}$ vibrational mode. This mode is predicted to occur in neat pyridine at 594 cm$^{-1}$ and involves a symmetric stretching and contracting of the NC1–C5N and C2C3–C3C4 bonds. The +101 cm$^{-1}$ shift seen upon formation of the PyBH$_3$ complex is correlated with these changes in bond lengths and charge transfer, perturbing the vibrational frequency. The second BN dative-bond stretch is predicted to occur at 1083 cm$^{-1}$, coupled to pyridine’s $\nu_{18a}$ vibrational mode. Neat Py’s $\nu_{18a}$ vibrational mode is predicted to occur at 1070 cm$^{-1}$. This vibration features a shift to higher energy relative to neat Py, correlated with the stretching motions by the elongated NC1–C5N and C2C3–C3C4 bonds.

In Py’s simulated Raman spectrum, the $\nu_{18a}$ vibrational mode is relatively weak compared to the Raman activities of the adjacent vibrations. In the PyBH$_3$ simulated spectrum, $\nu_{18a}$ has undergone a large increase in Raman activity relative to its adjacent modes, indicating an increase in proportion to this vibration.

The $\nu_{6b}$ vibration is predicted to be relatively unperturbed, shifting from 648 cm$^{-1}$ in Py to 645 cm$^{-1}$ in PyBH$_3$. This small shift to lower frequency is attributed to an overall lack of bond...
stretching and compression in this vibrational mode. A similar phenomenon is seen with the \( \nu_{12} \) mode, predicted to occur at 1028 cm\(^{-1}\) in both Py and PyBH\(_3\). The \( \nu_{12} \) vibrational mode is sometimes denoted as a triangle mode and is similar in motion to a ring breathing mode. This mode features a symmetric radial contraction and expansion of C1, C3, and C5. Neither vibrational mode mentioned involves any vibration of the nitrogen atom or the BN dative bond, which correlates with their small predicted shift. There is a small peak observed at 703 cm\(^{-1}\) in the simulated spectrum of isolated pyridine. This mode is an out-of-plane symmetric C–H wagging motion and is present at 690 cm\(^{-1}\) in the PyBH\(_3\) spectrum but is unresolved because of the breadth of the \( \nu_{6a} \) peak.

As mentioned above, the ring breathing mode (\( \nu_1 \)) has long been a probe of interactions in the azabenzenes. This mode, not unlike the triangle mode, involves a symmetrical radial contraction and expansion of N, C2, and C4. Py’s \( \nu_1 \) mode is predicted to occur at 990 cm\(^{-1}\) and undergo a large shift higher in frequency to 1049 cm\(^{-1}\) in PyBH\(_3\). Similar to the vibrations discussed above, it involves a vibration of the nitrogen atom/BN dative bond and is significantly shifted to higher frequency. Theory also predicts a slight shift higher in frequency of the CH stretching modes (approximately 3100 cm\(^{-1}\)) in PyBH\(_3\) relative to neat Py. This change in vibrational frequency is correlated with a shortening and stiffening of the CH bonds upon complex formation.

A 2013 study\(^{19}\) performed by our group examined shifts in vibrational frequency as a function of total electronic charge transferred by a nitrogen-containing heterocycle in complex with several Lewis acid solvents. These earlier results showed a linear relationship between charge transfer and spectral shifts, which was strongest with the \( \nu_1 \) ring breathing mode and had an \( R^2 \) value of 0.952 for >100 unique microsolvated structures. Interestingly, taking the total computed charge transfer into account (Table 2, 180 me\(^{-}\)), the computationally predicted shift in \( \nu_1 \) in nitrogen-containing heterocycles using our previously reported results is about 60 cm\(^{-1}\), in excellent agreement with the computed prediction in Table 3. This result simultaneously strengthens the evidence for the charge-transfer event in the PyBH\(_3\) dative-bond formation and the correlation between charge transfer and shifts to higher vibrational frequency in nitrogen heterocyclic complexes.

**Experimental Results. Mode Assignments.** Characterization of the simulated Raman spectrum of PyBH\(_3\) allows for the assignment of vibrational modes in the experimental spectrum. The simulated Raman spectrum of PyBH\(_3\) at the M06-2X/aVTZ level of theory is compared to experimental data for the same complex (bottom, blue).

Table 4. Predicted (M06-2X/aVTZ) and Experimental Locations of the Vibrational Modes of Interest in PyBH\(_3\)^a

| mode     | theory (cm\(^{-1}\)) | experiment (cm\(^{-1}\)) |
|----------|----------------------|--------------------------|
| \( \nu_1 \) | 1049                 | 1032                     |
| \( \nu_{6a} \) | 695                  | 714                      |
| \( \nu_{6b} \) | 645                  | 651                      |
| \( \nu_{12} \) | 1028                 | 1024                     |
| \( \nu_{18a} \) | 1083                 | 1093                     |

^aThe computed energies have been scaled by 0.97.

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![Figure 3](https://doi.org/10.1021/acsomega.2c00636)

**Figure 3.** Simulated Raman spectra of PyBH\(_3\) (top, green) at the M06-2X/aVTZ level of theory compared to experimental data for the same complex (bottom, blue).

![Figure 4](https://doi.org/10.1021/acsomega.2c00636)

**Figure 4.** Experimental Raman spectra of Py (bottom, black) and PyBH\(_3\) (top, blue). Red arrows denote large shifts in the Raman spectra.

approximately 610 cm\(^{-1}\) in the experimental data that does not appear in the simulated data. Because this feature is present in neat pyridine (Figure 4), we believe that this mode may be a result of some dissociated Py in PyBH\(_3\). The BH stretching region (approximately 2400 cm\(^{-1}\)) is less resolved, with a larger fwhm for each peak. Although this could stem from rovibrational populations within the sample, a more likely explanation is contributions from boron’s two isotopes. The breadth of this region can be replicated in simulated Raman spectra, not unlike what is demonstrated in Figure S3.
Comparison to Neat Pyridine. The assignment of vibrational modes in PyBH$_3$’s Raman spectrum allows for comparison to neat Py’s Raman spectrum in order to track shifts in Py’s peaks as a function of complex formation. Experimental Raman spectra for Py (bottom, black) and PyBH$_3$ (top, blue) are compared in Figure 4. Full experimental spectra are available in the Supporting Information. The results for selected modes of interest are recorded in Table 4. In agreement with theory, both $\nu_1$ and $\nu_{6b}$ shift higher in energy upon complex formation, shifting higher in energy than $\nu_{12}$ and $\nu_{18a}$ respectively. Vibrations $\nu_{6b}$ and $\nu_{12}$ undergo small wavenumber shifts to lower energy, and $\nu_{18a}$ undergoes a shift to higher energy and an increase in intensity relative to $\nu_1$ and $\nu_{12}$, also in agreement with theory. The CH stretching region shifts slightly higher in energy, as predicted.

Comparison to Pyridine/Water Clusters. Past studies$^{12,19}$ have connected charge transfer in nitrogen-containing heterocycles to shifts to higher energy in vibrational modes, particularly $\nu_1$. When forming the dative bond, both of the pyridyl-nitrogen’s lone pairs are donated to the boron atom’s empty orbital. This charge transfer is large in magnitude and should result in a shift to a higher energy of $\nu_1$ that is larger in magnitude than that resulting from a smaller charge transfer. This effect is demonstrated by comparing the results obtained here to spectral shifts observed in Py–water hydrogen-bonded networks, similar to work performed by Schlucker et al.$^{18}$ The experimental shifts of the above studied modes and the CH stretching region due to hydrogen bonding with increasing water molecules through N···H–O hydrogen bonding, resulting in a shift in $\nu_1$ by $+10$ cm$^{-1}$. When this shift is compared to the experimental PyBH$_3$-induced shift of $+41$ cm$^{-1}$, it can be predicted that a much larger amount of charge is transferred during dative-bond formation, in agreement with the results shown in Table 1. The $\nu_{6b}$ vibrational mode serves as another probe of charge transfer in the hydrogen-bonded species, shifting by $+12$ cm$^{-1}$; $\nu_{18a}$ is also minutely affected by the introduction of water, compared to a large change in energy and activity in the PyBH$_3$ complex. The coupling of BN stretching motions to $\nu_{11}$, $\nu_{6b}$, and $\nu_{18a}$ in the PyBH$_3$ complex is further linked to the large shifts in the Raman spectrum of Py. In the Py-water complexes, $\nu_{12}$ and $\nu_{6b}$ are relatively unaffected, indicating a comparable degree of perturbation of energy to the PyBH$_3$ complex. The CH stretching region as a whole also consistently shifts higher in energy upon charge transfer, with the highest shift occurring for the PyBH$_3$ complex. The results here offer strong evidence of the significant amount of charge transferred during PyBH$_3$ complex formation relative to that for hydrogen-bonded complexes. They also strengthen the conclusions stated previously correlating blue shifts with the charge transfer of vibrational modes.$^{19}$

### Table 5. Spectral Shifts Induced in Py by Hydrogen Bonding and PyBH$_3$ Complex Formation

| $\nu$   | Py    | PyBH$_3$ | $\Delta\nu$ | $\nu$   | Py/water | $\Delta\nu$ |
|---------|-------|----------|-------------|---------|----------|-------------|
| $\nu_1$ | 991   | 1032     | 41          | $\nu_1$ | 1001     | 10          |
| $\nu_{6a}$ | 603   | 714     | 111         | $\nu_{6a}$ | 615     | 12          |
| $\nu_{6b}$ | 652   | 651     | $-$1        | $\nu_{6b}$ | 652     | 0           |
| $\nu_{12}$ | 1031  | 1024    | $-$7        | $\nu_{12}$ | 1034    | 3           |
| $\nu_{18a}$ | 1068  | 1093    | 25          | $\nu_{18a}$ | 1069    | 1           |

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Full Raman spectra of all figures and Cartesian coordinates of optimized molecular structures (PDF)

Figure 5. Experimental Raman spectra of decreasing mole fractions of Py/water compared to the PyBH$_3$ complex.
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Notes
The authors declare no competing financial interest.

ABBREVIATIONS
aVTZ, aug-cc-pVTZ; BN, borane–nitrogen; DFT, density functional theory; NBO, natural bond orbital; NEC, natural electron configuration; Py, pyridine; PyBH₃, pyridine-borane complex; aVTZ, aug-cc-pVTZ;

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