Equilibrium Structure and Torsional Barrier of BH_3NH_3

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Born–Oppenheimer equilibrium structures, r_e^{BO}, of the electronic ground state of the borazane (BH_3NH_3) molecule of C_{3v} point-group symmetry are computed ab initio using the CCSD(T) method with basis sets up to quintuple-ζ quality. Inclusion of the counterpoise correction and extrapolation of the structural parameters to the complete basis set limit yield a best estimate of r_e^{BO} of BH_3NH_3. The anharmonic force field of BH_3NH_3, computed at the CCSD(T) level of theory with a basis set of triple-ζ quality, allows the determination of semi-experimental equilibrium rotational constants, which in turn result in a semi-experimental equilibrium structure, r_e^{SE}. The r_e^{BO} and r_e^{SE} structures are in excellent agreement, indicating the validity of the methods used for their determination. The empirical mass-dependent structure, $r_m^{(1)}$, of BH_3NH_3 is also determined. Although it is inferior in quality to the previous two structures, it is much more accurate than the standard empirical r_0 and r_s structures reported earlier for BH_3NH_3. The semi-experimental r_e^{SE} as well as the empirical $r_m^{(1)}$ structures determined are based on experimental ground-state rotational constants available from the literature for nine isotopologues of borazane. The effective barrier to the internal rotation of BH_3NH_3, a molecule isoelectronic with CH_3CH_3, has been computed ab initio, employing the focal-point analysis (FPA) approach, to be 699 ± 11 cm^{-1}. This compares favorably with an empirical redetermination of the effective barrier based on the above r_e^{SE} structure, $V_3 = 718(17)$ cm^{-1}.

1. Introduction

BH_3NH_3 (borane monoammoniate or borazane) is isoelectronic with CH_3CH_3 (ethane) and is the simplest donor–acceptor complex formed by electron donation from a Lewis base (NH_3) to a Lewis acid (BH_3). BH_3NH_3 is a typical example of dihydrogen bonds in the condensed phase.[1] Ammonia–borane complexes are promising materials for hydrogen storage.[2] BH_3NH_3 forms small molecular crystals which decompose at low temperature (>77 °C) giving molecular hydrogen. BH_3NH_3 is thus an oxygen-free hydrogen storage compound exhibiting a high hydrogen storage capacity (20% H) which may be used in fuel cells.

BH_3NH_3 has been the subject of many theoretical studies; those prior to 1999 have been summarized in refs 3 and 4. It was found that the correct description of the electronic structure of BH_3NH_3 is not simple. In particular, the DFT(B3LYP) density functional, that is, Kohn–Sham density functional theory[5] using Becke's three-parameter hybrid exchange[6] and the Lee–Yang–Parr correlation functional,[7] seems to perform poorly in predicting the structure and the BN bond dissociation energy.[8] The optimized structure of BH_3NH_3 was recently determined at the second-order Møller–Plesset perturbation theory (MP2) level,[9] while protonation effects were investigated[10] at the CCSD(T) level, coupled-cluster (CC) method with single and double excitations (CCSD)[11] augmented by a perturbational estimate of the effects of connected triple excitations.[12] To the best of our knowledge, there is no high-accuracy determination of the structure and the torsional barrier of BH_3NH_3.

Experimental information on the structure of BH_3NH_3 is available for the solid state from X-ray[13–15] and neutron[16] diffraction. Gas-phase empirical structures, an effective r_0 and a substitution r_s one, were determined by microwave (MW) spectroscopy.[17] It was found that the BN bond length is considerably shorter in the solid state than in the gas phase, 1.564 Å[15] versus 1.672 Å[17] (r_s value for the latter), a characteristic occurrence in similar donor–acceptor complexes. In the same study, the barrier to internal rotation was determined from the splittings measured in the asymmetrically substituted species, BH_3ND_2H and BHD_2NH_3. The low-resolution infrared spectrum of BH_3NH_3 was also measured in liquid NH_3,[18] in argon matrix,[19] and in the crystalline state.[20] In agreement with the structural change, the BN stretching frequency increases by 200 cm^{-1} when going from the gas phase to the solid state.[21] Note that an even more pronounced (0.4 Å) contraction of the BN bond occurs for $CH_3CN{\cdot}BF_3$.[22]

Elongated bonds are often difficult to describe ab initio with high precision. For instance, for hydrogen-bonded and van der Waals complexes, the basis set convergence is slow and the basis set superposition error (BSSE) can be substantial.[23,24] Further examples are provided by complexes of NO or NO_2 (N_2O_2, N_2O_3, ...) that are characterized by a weak and long bond between the monomers, and a further hindrance is that the dimers have substantial multireference character.[25,26] For these reasons, these complexes are difficult to describe correctly by single-reference electronic structure techniques. More generally, the NX bond in XNO or XNO_2 (X = F, Cl, HO, ...) is weak and long and even the CCSD(T) method results in bond lengths

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which are significantly too short.[27] From this point of view, BH_3NH_3 is a particularly interesting complex, not least because it is easily amenable to high level electronic structure calculations (it only contains 18 electrons and its structure can be described by only 5 independent structural parameters). Furthermore, the rotational constants of nine different isotopologues have been determined, permitting calculation of a semi-experimental equilibrium structure (r_e^{SE}). The r_e^{SE} structure becomes useful (a) to confirm the accuracy of the best ab initio Born−Oppenheimer equilibrium structure (r_e^{BO}) and (b) to check whether internal rotation, a particularly large amplitude motion, affects the utility of the calculated anharmonic force field and of the derived structure. Another point of interest of the structure of this molecule is that the empirical (r_s or r_m) BN bond length is expected to be accurate because both the B and the N atoms are rather far from the center of mass and the molecule is light.[28] In summary, BH_3NH_3 is a particularly interesting molecule that provides a nice test case to check the internal consistency of ab initio Born−Oppenheimer, of semi-experimental and of empirical structures of a molecule with a long and weak bond.

2. Computational Details

Most correlated-level ab initio computations of this study have been carried out at two levels of electronic structure theory, MP2 and CCSD(T). Dunning's correlation-consistent polarized *n*-tuple ζ basis sets cc-pV*n*Z with $n \in \{T, Q, 5\}$[29] were employed extensively. Throughout this paper, these basis sets are abbreviated as V*n*Z. A mixed basis set composed of VQZ on all non-hydrogen atoms and VTZ on H atoms is denoted as V[T,Q]Z. Such a basis set is not supposed to significantly reduce the accuracy of the computation compared with the use of the full set on all atoms while reducing the computation time significantly. Versions of V*n*Z sets augmented with diffuse functions (aug-cc-pV*n*Z,[30] AV*n*Z in short) were also employed. In order to take into account core correlation effects, the correlation-consistent polarized weighted core-valence *n*-tuple ζ (cc-pwCV*n*Z)[31] basis sets were employed. During the optimization, the basis set superposition error (BSSE) was taken into account by inclusion of the so-called counterpoise correction (CP).[32]

The CCSD(T) computations were performed with the ACESII[33] and MOLPRO[34] electronic structure program packages, while most MP2 computations utilized the GAUSSIAN03 program.[35] The frozen-core (FC) approximation, that is, keeping the 1s orbitals of the B and N atoms doubly occupied during correlated-level calculations, was used extensively. Some calculations have also been carried out by correlating all electrons (hereafter denoted as AE).

In order to avoid the nonzero force dilemma,[36,37] the all-electron VTZ CCSD(T) normal coordinate quadratic and cubic force constants of BH_3NH_3 have been determined at the fully optimized reference structure corresponding to the same level of theory. The quadratic force field has been obtained using analytic second derivatives of the energy,[38] while the cubic (and semi-diagonal quartic) force fields have been determined in a normal-coordinate representation via numerical differentiation of quadratic force constants analytically evaluated at several distorted structures.[39]

3. Ab initio Born−Oppenheimer Equilibrium Structure, r_e^{BO}

Results of the geometry optimizations of this study performed at the MP2 and CCSD(T) levels with and without CP correction are reported in Table 1. The coupled-cluster T_1 diagnostic value[40] for BH_3NH_3 is 0.008 at the all-electron wCVQZ CCSD(T) level, much lower than the usual cutoff value of 0.020, indicating dominant single-reference character. This suggests that nondynamical electron correlation is small and that the CCSD(T) energy and structural and frequency results should be reliable.

TABLE 1: Born−Oppenheimer Equilibrium Structures of BH_3NH_3, with Distances in Angstroms and Angles in Degrees, Computed at Standard Levels of Electronic Structure Theory

method[a]	basis[b]	BN	BH	HBN	NH	HNB
CCSD(T)	VTZ	1.6550	1.2101	104.858	1.0148	111.037
	VTZ(AE)	1.6443	1.2031	105.277	1.0126	110.932
	wCVQZ(AE)	1.6458	1.2070	104.947	1.0128	110.938
	wCVQZ	1.6513	1.2094	104.838	1.0139	110.984
	VQZ	1.6506	1.2094	104.872	1.0136	111.007
	VQZ+CP	1.6532	1.2093	104.818	1.0132	111.177
MP2	VTZ	1.6499	1.2059	104.867	1.0132	111.025
	wCVQZ(AE)	1.6397	1.2021	104.986	1.0108	110.950
	wCVQZ	1.6452	1.2047	104.880	1.0119	110.991
	VQZ	1.6457	1.2050	104.872	1.0119	111.002
	AVQZ	1.6470	1.2054	104.837	1.0123	110.979
	VQZ+CP	1.6493	1.2049	104.802	1.0115	111.192
	V5Z	1.6451	1.2046	104.858	1.0117	110.974
	V5Z+CP	1.6471	1.2045	104.828	1.0115	111.012
r_e^{BO}[c]		1.6455	1.2065	104.954	1.0121	110.951

[a] Unless otherwise noted, the frozen-core approximation has been used throughout. [b] AE = all electrons correlated, CP = counterpoise correction. [c] r_e^{BO} = [VQZ CCSD(T) + CP] + [wCVQZ(AE) CCSD(T) − wCVQZ CCSD(T)] + [(V5Z + CP) − (VQZ + CP)] MP2 represents the best estimate of the Born−Oppenheimer equilibrium structure of BH_3NH_3 obtained in this study.

Improvement of the basis set from VTZ to VQZ leads to a significant (0.0044 Å) shortening of the BN bond, the other parameters are much less affected. To check whether the structural parameters are converged when using the VQZ basis, the structure was also calculated at the frozen core V5Z MP2 level. It is well-established that the effects of basis set enlargement can be estimated at the MP2 level, provided these effects are small, that is, the reference basis set is large enough.[41] For instance, improvement of the basis set from VTZ to VQZ leads to a shortening of the BN bond by 0.0042 and 0.0044 Å at the MP2 and CCSD(T) levels, respectively (Table 1). Upon going from VQZ to V5Z, all parameters remain practically unaffected, the largest change is a further decrease of the BN bond length by 0.0006 Å. The effect of the inclusion of diffuse functions in the basis set was also investigated. At the frozen-core AVQZ MP2 level, the effect is quite small; the largest change is an increase of the BN bond length by 0.0013 Å. As the effect of diffuse functions rapidly decreases when the size of the basis set increases, it may be safely neglected at the V5Z level. The contribution of the counterpoise correction leads to a lengthening of the BN bond. This effect is far from being negligible, and it depends on the method of calculation: at the VQZ CCSD(T) level, it amounts to 0.0026 Å, while at the VQZ and V5Z MP2 level, it amounts to 0.0036 and 0.0014 Å, respectively.

Finally, the contribution of core correlation was calculated with the wCVQZ basis set using again the CCSD(T) and MP2 techniques. The first important conclusion is that the two methods give almost identical results. Correlation of all electrons leads to the expected shortening[42] of the BH and NH bonds by 0.0026 and 0.0011 Å, respectively. Shortening of the BN bond is considerably larger, 0.0055 Å. Assuming additivity of the corrections, the best estimate of the equilibrium structure of BH_3NH_3 is obtained by correcting the VQZ CCSD(T) + CP structure for the effects of core correlation calculated at the wCVQZ CCSD(T) level and of basis set enlargement (VQZ → V5Z) calculated at the MP2 + CP level. The last assumption is the weakest one, because, as pointed out above, the effect of the counterpoise correction is quite different at the CCSD(T) and MP2 levels. As a check, we calculated the counterpoise correction for the complex $H_2O\cdots HF$ and found similar results. The uncertainty resulting from the use of the counterpoise correction is small, very likely smaller than 0.002 Å.

For the sake of completeness, the structure optimized at the all-electron VTZ CCSD(T) level, employed as the reference structure for the computation of the anharmonic force field of BH_3NH_3, is also reported in Table 1. It is worth noting that the structure calculated at this level is close to the best estimate of the Born−Oppenheimer equilibrium structure. This is especially true for the BN bond length, whose value, 1.6443 Å, is to be compared to $r_e^{BO} = 1.6455$ Å, the best estimate of this study for this structural parameter.

4. Semi-Experimental Equilibrium Structure, r_e^{SE}

First, it was checked whether the electronic correction to the rotational constants is negligible. The corrected values of the rotational constants are given by the relation[43]

$$B_{\mathrm{corr}}^{\xi} = \frac{B_{\mathrm{exp}}^{\xi}}{1 + (m/M_{\mathrm{p}})g_{\xi\xi}} \tag{1}$$

where $g_{\xi\xi}$ is expressed in units of the nuclear magneton, m and M_p are the electron and proton masses, respectively, and $g_{\xi\xi} = a, b, c$, referring to the principal axes of the molecule. As there are no experimental values available for the $g_{\xi\xi}$ constants, they have been calculated with the help of GAUSSIAN03 at the AVTZ B3LYP level of theory. The results are $g_{aa} = 0.15$ and $g_{bb} = -0.03$, confirming that this correction is indeed negligible (0.3 MHz on B) even at the level of precision seeked in this study.

The semi-experimental equilibrium rotational constants needed to determine the semi-experimental equilibrium structure are thus obtained by correcting the experimental ground-state rotational constants with vibration−rotation interaction constants (α), computed ab initio, via the expression

$$B_{\mathrm{e}}^{\xi} = B_0^{\xi} + \sum_i \alpha_i^{\xi} \frac{d_i}{2} \tag{2}$$

where d_i is a degeneracy factor (1 for nondegenerate vibrations and 2 for doubly degenerate vibrations) and the sum is running over all normal modes.

The full cubic force field in normal coordinates was first obtained for the parent isotopologue ($^{11}BH_3{}^{14}NH_3$) and was then transformed to the normal-coordinate representations of all the other isotopologues for which experimental ground-state rotational constants are available. The experimental ground-state rotational constants (B_0) and the deduced semi-experimental equilibrium rotational constants (B_e^{SE}) of nine isotopologues of borazane are given in Table 2.

The semi-experimental equilibrium structure, given in Table 3, was calculated from a weighted least-squares fit of the related equilibrium moments of inertia. The system of normal equations is well-conditioned, with condition number $\kappa = 49$, and the standard deviation of the derived structural parameters is extremely small, indicating that the r_e^{SE} structure should be accurate. It is indeed in almost perfect agreement with the best ab initio r_e^{BO} structure. The only significant difference, 0.002 Å, is found for the NH bond length. This large discrepancy can be attributed to the fact that the r_e^{SE} NH bond length is most sensitive to the value of $A_e(BH_3ND_2H)$ and the experimental A_0 is considerably less accurate than B_0, the $A_0 - A_e$ correction is much larger and thus less accurate than the smaller $B_0 - B_e$ correction, and that there is some evidence that, for isotopologues which have a symmetry different from the parent, they have less accurate vibration−rotation interaction constants. Overall, the 0.002 Å difference, although about seven times larger than the standard deviation of the r_e^{SE} parameter, is still small and is a better indicator of the accuracy of the r_e^{SE} NH bond length than the standard deviation.

TABLE 2: Ground State (0), Semi-Experimental Equilibrium (SE), and Born−Oppenheimer (BO) Equilibrium (E) Rotational Constants, All in Megahertz, For Nine Isotopologues of the BH_3NH_3 Molecule

	B_0	B_e^{SE}	B_e^{BO}
BH_3NH_3	17517.18	17899.44	17891.18
$^{10}BH_3NH_3$	18054.42	18451.89	18444.10
BH_3ND_3	15076.806	15358.17	15348.12
$^{10}BH_3ND_3$	15562.833	15856.25	15846.48
BD_3NH_3	14420.726	14704.33	14699.01
$BH_3{}^{15}NH_3$	17198.11	17571.66	17563.57
$^{10}BH_3{}^{15}NH_3$	17742.376	18131.26	18123.72
BH_3ND_2H[a]	16019.435	16333.41	16324.49
BHD_2NH_3 [b]	15634.217	15951.23	15945.23

[a] $A_0 = 58736$; $A_e - A_0 = 454$; $A_e(SE) = 59435$; $A_e = 59190$ and $C_0 = 15537.8$; $C_e - C_0 = 291.8$; $C_e(SE) = 15840.6$; $C_e = 15829.6$. [b] $A_0 = 53058$; $A_e - A_0 = 560$; $A_e(SE) = 53705$; $A_e = 53618$ and $C_0 = 14936.5$; $C_e - C_0 = 295.2$; $C_e(SE) = 15237.9$; $C_e = 15231.7$.

The pleasing agreement between the r_e^{BO} and the r_e^{SE} structures leads to the conclusion that both structures are reliable. Particularly noteworthy is the fact that the internal rotation motion has no significant harmful effect on the utility of the cubic force field used to determine semi-experimental equilibrium rotational constants for the isotopologues of borazane.

5. Empirical Structures

The effective (r_0) and the substitution (r_s) structures of BH_3NH_3 have been determined by Thorne et al.[17] As the Cartesian coordinates of both B and N are large, greater than 0.7 Å, in the principal axis system and because the molecule is light, it is tempting to believe that the r_s(BN) value is accurate. However, r_s(BN) is found to be much larger than the corresponding r_e^{BO} and r_e^{SE} values (Table 3).

The mass-dependent (r_m) structure technique developed by Watson et al.[44] should shed light on the origin of this problem and help to remedy it. This technique approximately takes into account the variation of the rovibrational correction upon isotopic substitution and allows the determination of structures close to the assumed equilibrium structure. In this approach, the relation between the ground state and the equilibrium moments of inertia is written as

$$I_{\xi}^{0} = I_{\xi}^{\mathrm{e}} + \varepsilon_{\xi}, \quad \xi = a, b, c \tag{3}$$

where ε_{ξ} is a vibrational correction. Watson et al. have shown that it is possible to express ε_{ξ} approximately as a function of the moments of inertia,

$$\varepsilon_{\xi} = c_{\xi}\sqrt{I_{\xi}^{\mathrm{e}}} \tag{4}$$

This gives the $r_m^{(1)}$ structure. In the present case, a simple way to check the validity of eq 4 is to plot ε_b as a function of I_b^e (see Figure 1). A nice, almost linear relationship is found, except for the species with a deuterated ammonia. This is expected; as

TABLE 3: Structures of BH_3NH_3, with Distances r in Angstroms and Angles ∠ in Degrees

type	characterization	r(BN)	r(BH)	r(NH)	∠(HBN)	∠(HNB)
r_e^{BO}	ab initio	1.6455	1.2065	1.0121	104.954	110.951
r_e^{SE}	semi-experimental	1.6453(1)	1.2058(3)	1.0101(3)	105.00(2)	110.97(2)
r_0	empirical	1.6722(5)	1.210(3)	1.014(4)	104.53(15)	109.85(23)
r_s	empirical	1.6576(16)	1.216(2)	1.014(2)	104.69(11)	110.28(14)
$r_m^{(1)}$	empirical[a]	1.6492(3)	1.2098(2)	1.0083(3)	104.73(1)	110.29(2)
$r_m^{(2)}$	empirical[b]	1.6509(6)	1.2106(3)	1.0084(2)	104.63(3)	110.16(4)

[a] Values reported correspond to $c_a = 0.0119(9)$ and $c_b = c_c = 0.11115(15)$. [b] Values reported correspond to $c_a = 0.005(8)$; $c_b = c_c = 0.086(8)$; $d_a = 0$ (fixed); and $d_b = d_c = 0.097(30)$.

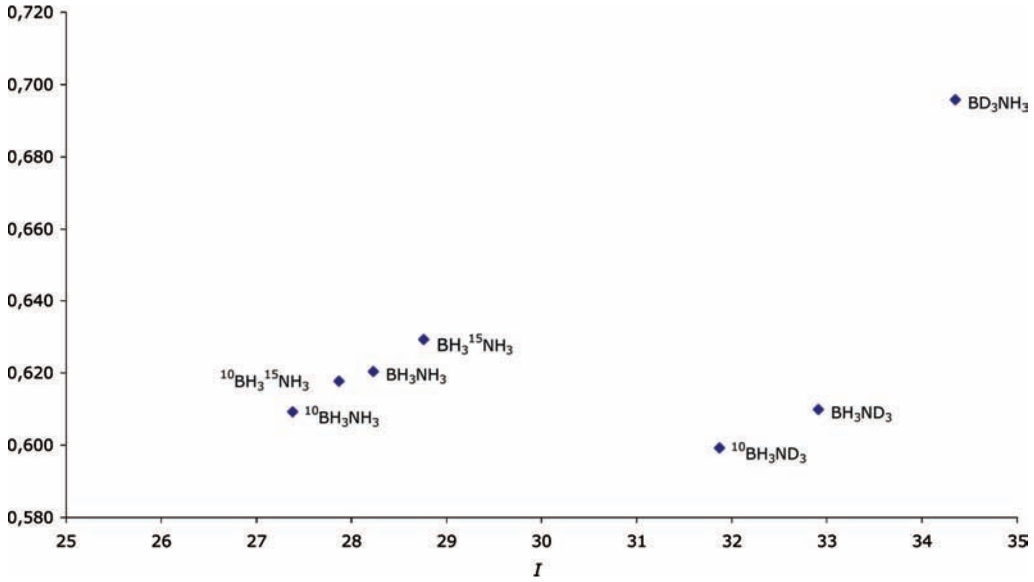

Figure 1. Plot of ε_b as a function of I_b^e (in uÅ^2).

for XH bond lengths, there is an apparent shortening upon deuteration. For this reason, the r_m methods are not appropriate to determine the correct length of a X−H bond. Finally, the correlation coefficient is the largest for $\sqrt{I_b^e}$, as expected. A fit including the three c_ξ parameters indicates that c_b and c_c are almost identical and are fully correlated. For this reason, the fit was repeated with the constraint $c_b = c_c$. This choice does not affect the values of the structural parameters and reduces the standard deviation of the fit. The results are given in Table 3. As usual, the standard deviations of the parameters are extremely small and are not a good indicator of the accuracy of the related parameters. The $r_m^{(1)}$ (NH) bond length is too small, and the $r_m^{(1)}$ (BH) bond length is too large, while the bond angles are in fair agreement with the related r_e^{BO} and r_e^{SE} parameters. Finally, the $r_m^{(1)}$ (BN) bond length is considerably less than the corresponding r_s value, though it is still too large. This probably reflects the approximate nature of the $r_m^{(1)}$ structure.

Compared with values found for rigid molecules,[44] the parameter c_b obtained from the $r_m^{(1)}$ fit is extremely large. This explains why the r_s method, whose basic assumption is that ε_ξ remains constant upon isotopic substitution, fails to give a reliable result in this particular case.

It is tempting to try to refine the empirical structure of borazane by using the $r_m^{(2)}$ method.[44] This method involves a second correction added to eq 4,

$$\varepsilon_\xi = c_\xi\sqrt{I_\xi^e} + d_\xi\left[\frac{\prod_i m_i}{M}\right]^{1/(2N-2)} \tag{5}$$

where N is the number of atoms in the molecule, m_i is the mass of atom i, M is the total mass of the molecule, and c_ξ and d_ξ are altogether six empirical parameters to be determined together with the structural parameters during the least-squares fit. The ensuing $r_m^{(2)}$ structure is in good agreement with the $r_m^{(1)}$ structure (Table 3). However, the system of equations is ill-conditioned, with condition number $\kappa = 1652$, and there are several harmful correlations. Furthermore, c_a and d_a cannot be determined. For this reason, we conclude that the $r_m^{(1)}$ structure is the most reliable empirical structure that can be obtained from the data available.

6. Barrier to Internal Rotation

The barrier to internal rotation of BH_3NH_3 has been determined by Thorne et al.[17] from the related microwave (MW) spectrum. On the basis of the empirical values of 716(3) and 702(1) cm^{-1} for the internal rotation barriers of the isotopically substituted asymmetric-top species BH_3ND_2H and BD_2HNH_3, respectively, they estimated the internal rotation barrier of the symmetric-top BH_3NH_3 molecule to be 724(17) cm^{-1}. This determination was based on a number of assumptions, not always used in similar analysis, as follows: (a) the torsional potential was approximated by only one term, (b) the structure of the molecule was assumed to be approximated well by an effective structure which was proven to be relatively inaccurate in this study, (c) the effective structure determined the moment of inertia of the internal rotor about its figure axis as well as the angle between the figure axis of the rotor and the principal axis a, and (d) the authors used a somewhat ambiguous estimate for the effect of isotopic substitution on the barrier height. Consequently, even the relatively large uncertainty reported by Thorne et al.[17] for the barrier may not reflect well the inaccuracy of the above empirical estimate of the barrier height.

TABLE 4: All-Electron Focal-Point Analysis of the Rotational Barrier of BH_3NH_3[a]

basis set	RHF	δ [MP2]	δ [CCSD]	δ [CCSD(T)]
aug-cc-pCVDZ (108)	681.3	+8.2	−22.3	−4.6
aug-cc-pCVTZ (256)	682.8	+27.6	−23.0	−2.3
aug-cc-pCVQZ (494)	684.7	+30.9	−20.9	−1.9
aug-cc-pCV5Z (842)	684.1	+31.6		
CBS	683.9	+32.3	−19.3	−1.6

[a] Energy values are given in units of wavenumbers. CBS = complete basis set limit. The number of contracted Gaussian functions is given in parentheses after each basis set. The undelying two reference structures have been optimized at the all-electron cc-pVTZ CCSD(T) level. The CBS RHF and MP2 barriers have been obtained by extrapolation from the aug-cc-pCV[Q,5]Z RHF and MP2 results, respectively (see text); the correlation contributions above MP2 have been determined from the aug-cc-pCV[T,Q]Z results (see text).

Since in the previous sections an accurate equilibrium structure of BH_3NH_3 has been derived, the rotational barrier determination of Thorne et al.[17] based on their MW data can be reassessed. For this purpose, the internal axis method (IAM)[45] was used in this study since it is known to have better convergence properties than the principal axis method (PAM)[45] used by Thorne et al.[17] The new IAM results are found to be in fair agreement with those of the previous PAM analysis: $V_3 =$ 717(3) and 711.2(6) cm^{-1} for BH_3ND_2H and BD_2HNH_3, respectively. Harmonic zero-point energy (ZPE) corrections, computed at the all-electron VTZ MP2 level, suggest that the corresponding pure barriers of BH_3ND_2H and BD_2HNH_3 are 714 and 714.5 cm^{-1}, respectively. The weighted average of these two values is taken as $V_3 = 714(17)$ cm^{-1}, where the old uncertainty was reattached to the improved V_3 estimate. This value is taken as the best empirical estimate of the pure barrier to internal rotation in BH_3NH_3.

Since all previous ab initio determinations[46–49] of the barrier to internal rotation of BH_3NH_3 are of much lower quality than that of the present study, no further discussion of these results is warranted.

The focal-point analysis (FPA) approach[50,51] has been used in this study to determine an accurate first-principles estimate of the barrier to internal rotation of BH_3NH_3. The FPA approach has been used in a number of studies to determine accurate internal rotation barriers, for example, in the cases of ethane[50] and acetaldehyde,[52] suggesting that the method is well-suited for this purpose. The all-electron nonrelativistic FPA results concerning the barrier of BH_3NH_3 are summarized in Table 4.

As usual, the nonrelativistic electronic structure computations determine accurately the RHF barrier. The complete basis set (CBS) RHF limit, obtained after a two-point extrapolation,[53,54] is 683.9 ± 1 cm^{-1}. The overall correlation contribution to the CBS RHF barrier is unusually small, only around +10 cm^{-1} with an error estimate of about ±4 cm^{-1}. Since explicit computations have been performed only up to the CCSD(T) level, one must assess the remaining FCI−CCSD(T) correction, where FCI stands for the full configuration interaction limit.[55] Since double excitations, based on energy differences CCSD−RHF, correct the rotational barrier of BH_3NH_3 on the order of 15 cm^{-1} and the triple excitation contribution, based on energy differences CCSD(T)−CCSD, of only about 2 cm^{-1}, it is expected that the contributions beyond CCSD(T) will not exceed 1 cm^{-1}. It is hardly worth performing the related expensive computations; it is enough to increase the uncertainty estimate by 1 cm^{-1} to account for higher-order contributions. Consequently, the nonrelativistic all-electron internal rotation barrier of BH_3NH_3 is estimated to be 695 ± 5 cm^{-1}.

TABLE 5: Equilibrium BH Bond Lengths (in Angstroms) in a Few Molecules

molecule	r_e	ref
BH_3NH_3	1.1872	this work[a]
BH_2F	1.1891(3)	60
BH_2Cl	1.1834(3)	60
BH_2OH H_s[b]	1.1940	61
BH_2OH H_a[c]	1.1884	61
BHFOH	1.1895	61
$BH(OH)_2$	1.1895	61
BH_2NH_2	1.1908	this work[a]

[a] All-electron wCVQZ CCSD(T) value. [b] H syn to OH. [c] H anti to OH.

Relativistic contributions to the rotational barrier are expected to be small.[50–52] The relativistic contribution to the internal rotation barrier of BH_3NH_3 has been computed to be 0.04 cm^{-1} at the all-electron aug-cc-pCVTZ CCSD(T) level, using the one-electron mass-velocity and Darwin formalism.[56,57] Thus, it can safely be neglected.

Somewhat larger and somewhat more uncertain is the zero-point energy contribution to the effective barrier. The quadratic force field, determined at the all-electron VTZ MP2 level at the fully optimized structure, yields a zero-point energy of 15 662 cm^{-1}. The quadratic force field result for the ZPE estimate at the top of the barrier is 15 528 cm^{-1}, after exclusion of the unique, A_2-symmetry internal rotation mode. In order to compare the two ZPEs, one must delete the contribution of the A_2 mode from the equilibrium ZPE value; the corrected ZPE estimate is 15 524 cm^{-1}. One could add to this value the same anharmonic correction as obtained at the bottom of the internal rotation curve, but this would not change the ZPE effect on the barrier height. Therefore, the ZPE correction to the rotational barrier of BH_3NH_3 is a mere +4 cm^{-1}. Of course, the uncertainty of this value should be considerable; a conservative estimate is ±10 cm^{-1}.

In summary, the best ab initio estimate of the effective barrier to internal rotation of BH_3NH_3 is 699 ± 11 cm^{-1}. While the computed result is slightly lower, it is in reasonable agreement with an empirical estimate, 718(17) cm^{-1}, redetermined in this study on the basis of the measurements of Thorne et al.[17]

7. Conclusions

An important result of this work is the good agreement found between the high-quality extrapolated Born−Oppenheimer and the semi-experimental equilibrium structures of BH_3NH_3. This indicates that the approximate handling of the BSSE does not affect the accuracy of the ab initio structure, provided that large basis sets are employed during the electronic structure computations. Furthermore, the internal rotation, a particularly large amplitude motion, has no deteriorating effect on the accuracy of the semi-experimental structure. The empirical r_0 and r_s structures determined previously for BH_3NH_3 are, however, considerably less accurate, and even the empirical $r_m^{(1)}$ structure deduced in this study is of lesser quality.

As to the structural parameters of BH_3NH_3, the BN bond length at $r_e^{SE} = 1.6453(1)$ Å is much larger than that in BH_2NH_2, where $r_e(BN) = 1.388$ Å (an all-electron wCVQZ CCSD(T) value). It is, furthermore, longer than the sum of the van der Waals radii of the atoms, 1.55 Å. It is comparable to the value found for $(CH_3)_3N{\cdot}BF_3$, for which $r_s(BN) = 1.636(4)$ Å.[58] Compared with other molecules (Table 5), the BH bond at $r_e^{BO} = 1.2065$ Å is also long. The originally planar BH_3 molecule, upon polarization by the permanent dipole moment of ammonia and forming a BN bond of dative character, becomes pyramidal with a $\angle$(HBN) angle of 105.0°. The structure of NH_3 changes little. The NH bond length is not significantly different from the value found in NH_3, 1.011 Å; the $\angle$(HNB) angle is slightly smaller than the angle of 106.8° between the NH bond and the symmetry axis of ammonia.[59]

The barrier to internal rotation for borazane has been obtained by high-level ab initio calculations, using the focal-point analysis (FPA) approach. The ab initio effective barrier, 699 ± 11 cm^{-1}, is in good agreement with the corresponding empirical value redetermined in this study, 718(17) cm^{-1}.

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