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Study of the N–H···H–B Dihydrogen Bond Including the Crystal Structure of BH₃NH₃ by Neutron Diffraction

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Abstract: Boraneamines tend to have close N–H^{δ+}···^{δ-}H–B contacts as a result of the intermolecular interaction of the NH proton with the BH bond by a novel type of hydrogen bond (the dihydrogen bond). A CSD structural search provides characteristic metric data for the interaction: the H···H distance is in the range 1.7–2.2 Å, and the N–H···H group tends to be linear while B–H···H tends to be bent. The reported X-ray structure of BH₃NH₃ seemed to provide a singular exception in having bent N–H···H and linear B–H···H. Our neutron diffraction structure of BH₃NH₃ now shows that the B and N atoms must be reversed from the assignment previously published. With the correct assignment we find the expected bent B–H···H and linear N–H···H arrangement in the closest intermolecular N–H···H–B interaction ($d_{\text{HH}} = 2.02 \text{ \AA}$).

Introduction

Classical hydrogen bonds,¹ A–H···B, involve a weak acid hydrogen bond donor, A–H, and the basic lone pair of a hydrogen bond acceptor, B. Recently, π -bonds, especially of alkynes and arenes, have been shown to act as much weaker hydrogen bond acceptors in A–H··· π interactions.² Extrapolating this trend suggests that σ -bonds would not be significant hydrogen bond acceptors. It was therefore surprising^{3,4} that a

number of metal–hydrogen bonds, M–H, are able to act as acceptors to give M–H···H–N hydrogen bonds with strengths^{3b} comparable to those of classical lone pair hydrogen bonds. The $d(\text{H}\cdots\text{H})$ distances for such systems are typically^{3,4} 1.7–2.2 Å, significantly less than the sum of the van der Waals radii for two hydrogen atoms, 2.4 Å. The hydrogen bond can form with a pendant group on a ligand, such as in the 2-aminopyridine complex (**1**)³ or intermolecularly as in [ReH₅(PPh₃)₃]·indole.⁵

Early examples of this new type of hydrogen bond, generally termed a dihydrogen bond, were discovered for transition metal hydrides, where the M–H bond acts as hydrogen bond acceptor (weak base). In these transition metal cases, however, we could not be sure that the acceptor was indeed the M–H σ -bond because these metals also possess nonbonding d_{π} -electrons

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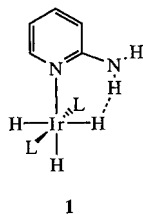
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which could in principle act as alternate H-bond acceptors. Both Brammer and co-workers^{6a} and Albinati, Pregosin and co-workers^{6b} characterized undoubted cases of A–H···M hydrogen bonding. Evidence for true N–H···σ hydrogen bonding came from the finding that d⁰ metal hydrides, not having nonbonding d_π-electrons, also give N–H···H–M dihydrogen bonds of comparable strength.⁷ To probe this point more effectively, we moved to a system that contains no nonbonding valence electrons of any sort. We now report our work on boraneamines, which provides evidence for N–H···H–B dihydrogen bonds being true N–H···σ hydrogen bonds.

A boronated cytosine has recently been shown to have an intramolecular N–H···H–B distance of 2.05 Å,⁸ a value that is well within the range of interest. Intramolecular cases such as this are a little less satisfactory than intermolecular examples, in that conformational effects might possibly affect the distances and conformations adopted. We also published a communication^{9a} on Cambridge Structural Database (CSD) evidence for N–H···H–B dihydrogen bonding.

BH₃NH₃ seemed to us to be a key case. Although ethane and BH₃NH₃ are isoelectronic, there are very large differences in their physical properties, i.e., the melting points are for C₂H₆ –181 °C and for BH₃NH₃ +104 °C. Part of this difference must be related to the polarity of BH₃NH₃ (5.2 D). However, CH₃F (mp –140 °C), also polar (1.8 D), has a proportionally much lower melting point elevation relative to ethane, so we felt that other factors might also play a role. Our prior work on the attractive interaction between the hydridic hydrogens of a number of transition metal complexes and the protonic hydrogens of adjacent OH or NH groups led us to consider that BH₃NH₃ might have close attractive N–H···H–B contacts.

The X-ray data on BH₃NH₃ gave a N–H···H–B conformation that diametrically contradicted our expectations based on

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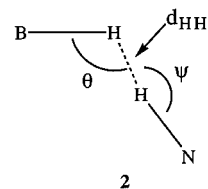
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a CSD search^{9a,10} and on other prior studies.¹ The structure of BH₃NH₃ has a long and checkered history in the literature.¹¹ Initial room-temperature X-ray work by Lipscomb^{11a} and by Hughes^{11b} indicated a body-centered tetragonal structure, but a subsequent paper by Sorokin and co-workers^{11c} suggested a face-centered orthorhombic unit cell instead. Hoon and Reynhardt^{11d} used powder X-ray data for BH₃NH₃ both to confirm the body-centered tetragonal structure at room temperature and also to show that the compound undergoes a phase transition to a low-temperature primitive orthorhombic form at ca. 220 K. Subsequently, what seemed to be the definitive single-crystal X-ray study was carried out at 200 K, also in the primitive orthorhombic space group.^{11e,f,12}

The present neutron diffraction structure of BH₃NH₃ at 200 K has now resolved the problem by correcting the previously published assignment of the boron and nitrogen atoms. The present assignment may help resolve anomalies in the prior results.

Results and Discussion

CSD Search. Twenty-six N–H···H–B intermolecular dihydrogen bonds have been identified with $d_{\text{HH}} < 2.2$ Å in 18 X-ray crystal structures.^{9a} The metric data shown in **2**, obtained from the CSD organic structure database, were studied. The d_{HH} values found in M–H···H–N dihydrogen bonds are usually in the range 1.7–2.0 Å, and so the range found in the structures studied here (1.7–2.2 Å) is compatible with the presence of an H-bond. As a control, no N–H···H–Si distances of <2.2 Å were found in the CSD. As is customary,¹ we normalized the N–H (1.03 Å) and B–H (1.21 Å) distances because of the systematic error associated with hydrogen positions in X-ray structures. By studying a broad range of crystal structures in this way, we aim to establish a general pattern that does not rely on the accuracy of any one particular structure.



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In some cases, the short contacts were noted in the original papers describing the structures and ascribed to various effects, most commonly charge-transfer interactions.^{9j,k} In (H₂N)₂PBH₃,⁹ⁿ where all the hydrogens were located, the author noted that the BH bonds associated with the close contact are not aligned along the B···N vectors with the implication that these are not conventional hydrogen bonds. Apart from the nonlinearity another factor that militated against prior recognition of the interaction is that many of the contacts are intermolecular; authors may not have checked the packing for these molecules, and even if they did, the hydrogens were often not very precisely located, so the contact may have escaped notice or been considered an artifact.

(10) We thank a reviewer for providing much of the text of this paragraph.

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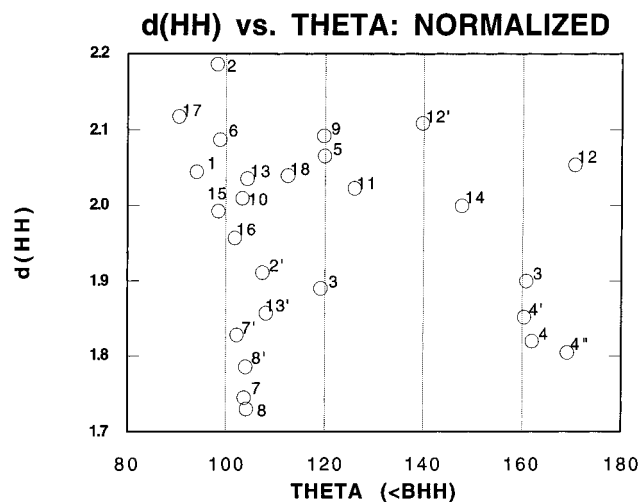
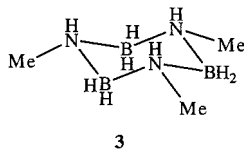


Figure 1. H...H distance, d_{HH} , versus the B-H...H angle, θ , found in the CSD search. The numbers refer to the following compounds, which are listed by their CSD filenames: 1, AZIBOR;^{9b} 2, CESHIR10;^{9c} 3, DITSUU;^{9d} 4, DUJYOW;^{9e} 5, EMOBOR;^{9f} 6, FUDHIV01;^{9g} 7, FUDHOB;^{9h} 8, FUDHOB02;⁹ⁱ 9, FUZSEY;^{9j} 10, GACWUC;^{9k} 11, GALGIJ;^{9l} 12, GALGOP;^{9m} 13, GEWWEK;⁹ⁿ 14, JUJKUU;^{9o} 15, KACRAH;^{9p} 16, KADMEH;^{9q} 17, SORGEL;^{9r} 18, VIJLEF.^{9s} Primes refer to second and third H bonds within a single structure.

The angular data (Figures 1 and 2) show that, while N-H...H (ψ) tends to be more linear than bent, with the majority of data points in the range 150–170°, B-H...H (θ) tends to be more bent than linear, with the majority of data points in the range 95–115°. We examined the structure^{10d} labeled 4 in Figure 1 (shown here as 3) and believe that, as a somewhat rigid molecule with groups projecting in the equatorial plane, it could have limited choices in packing. The scatter in the angular and d_{HH} data suggest that the potential surface for interaction between NH and BH bonds is rather flat and allows significant deviations from the preferred angles and distances. This is entirely appropriate for a weak intermolecular interaction and is also seen in classical hydrogen bonding.¹ Nevertheless a distinct preference for a linear N-H...H (ψ) and a bent B-H...H (θ) arrangement is seen. While a linear ψ seems appropriate for a hydrogen bond, the bent θ was not anticipated and might seem to militate against the proposed description of the interaction; theoretical studies^{9a} help elucidate this preference on purely electrostatic terms, however.



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The CSD data also give us an idea of the types of NH and BH groups that most readily engage in dihydrogen bonding. In most cases, the N-H bonds in the compounds studied were either substituted ammonium ions or substituted pyridinium ions, with a positively charged nitrogen, or aminoboranes, in which the nitrogen can be considered to bear a partial positive charge by virtue of the $R_3B^- - N^+R_3$ resonance form. In either case, the pK_a of the NH in question is likely to be low (e.g., NH_4^+ , 9.2; pyridinium, 5.2) and therefore favor¹ the formation of relatively strong dihydrogen bonds. Similarly, the BH bonds were either exo-BH bonds of boron cluster cage anions, aminoboranes or aluminoboranes, in all of which boron is expected to bear at least a partial negative charge, leading to a

BH group having hydridic character and therefore being relatively basic. The CSD work reported in this section provides a preliminary case for the existence of dihydrogen bonds in boraneamines and establishes their structural characteristics (Table 1).

However, at this point, we made a most unwelcome discovery. Lacking a carbon atom, the structural data¹¹ on BH_3NH_3 did not form part of our initial CSD organic database search results. When we located the published data on this compound, we found one close N-H...H-B contact, as expected, but the B-H...H and N-H...H angles were linear and bent, respectively, the *exact opposite* of what we had been led to expect by all our prior work.³ Since the N-H...H-B bridge in BH_3NH_3 might be considered as the archetype of a dihydrogen bond, we felt we needed to understand this system better. We have now undertaken a neutron diffraction study which has completely clarified the structural situation and a theoretical study^{9a} that helps us understand the bonding.

Neutron Diffraction Structure of BH_3NH_3 . The simplest compound expected to show N-H...H-B dihydrogen bonds is BH_3NH_3 (4), which accordingly seemed especially favorable for structural study. Suitable colorless crystals of the compound were grown from ether solution, and neutron intensity data were collected for a hemisphere of reciprocal space on two separate crystals. These measurements showed that the crystals can be successfully treated^{12a} as orthorhombic. The results of the orthorhombic refinement presented in this paper (Tables 2 and 3 and Figure 3) allow the chemically significant results to be obtained in an unambiguous way.

A succession of structural studies¹¹ has been carried out on BH_3NH_3 , but uncertainties remained regarding the description of the structure. The present neutron work has allowed a number of significant points to be established. First, the assignment of the boron and the nitrogen atoms in our structure is *reversed* relative to the ones previously published.^{11a-f,12b} An unambiguous assignment is possible in neutron diffraction thanks to the very different neutron scattering lengths of B (0.53×10^{-12} cm) versus N (0.94×10^{-12} cm) and bond lengths of B-H (1.17 Å) versus N-H (1.03 Å). We have confirmed the assignment by refining these scattering lengths for our data set, obtaining B = $0.65(7) \times 10^{-12}$ cm and N = $0.83(8) \times 10^{-12}$ cm, in agreement with the present assignment (Figure 4).

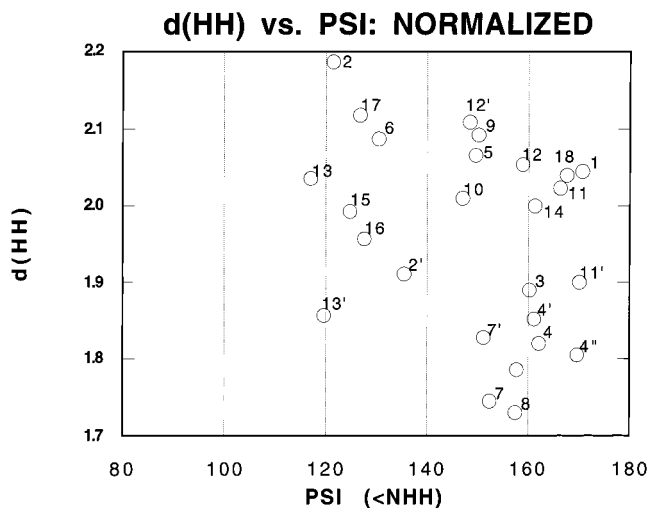
Perhaps the clearest demonstration of the reversed B/N assignment is that refinement with the prior published assignment makes $d(B-H)$ shorter than $d(N-H)$, an absurd outcome (B-H1, 1.08(3) Å; B-H2, 0.96(3) Å; N-H3, 1.12(5) Å; N-H4, 1.14(2) Å). Only refinement with the present assignment gives $d(B-H)$ longer than $d(N-H)$, as expected (B-H3, 1.15(3) Å; B-H4, 1.18(3) Å; N-H1, 1.07(4) Å; N-H2, 0.96(3) Å). In addition, the weighted R values for the prior published assignment, $R_w(F^2) = 0.183$ and $R_w(F) = 0.078$, are significantly larger than those for the new one, $R_w(F^2) = 0.163$ and $R_w(F) = 0.065$. Furthermore, the U_{ij} values for B and N show a greatly improved fit with the present assignment (Table 4). On the prior published assignment, the values for N are large relative to those

(12) (a) Our measurements show that the crystals can be successfully treated as orthorhombic, and the results definitively characterize the chemically important hydrogen-bonding interactions. The small size of the crystal meant that there were insufficient intense reflections ($F^2 > 3\sigma$) to allow us to definitively exclude the alternative of monoclinic symmetry (space group $P2_1$ or P_n). In view of the checkered history of structural work on this compound, we strongly prefer to continue our work on larger crystals rather than try to distinguish the precise symmetry on the basis of the present data, that we regard as inadequate for this purpose. (b) Dr. Boese informs us (1/24/99) that he tried both B/N assignments at the time but inadvertently published the coordinates for the wrong assignment in ref 11f.

Table 1. Characteristics of N–H···H–B Dihydrogen Bonds Found in the CSD Search, in Quantum Chemical Studies by Us^{9a} and Others,¹⁴ and in the Present Neutron Diffraction Study

property	range (extreme range) in CSD search	average in CSD search	C ₂ dimer (theory) ^b	C _{2h} dimer (theory) ^c	BH ₃ NH ₃ (n-diff) ^b
d _{HH} (Å)	1.7–2.2	1.96	1.82	1.99	2.02(3)
θ(∠BHH) (deg)	95–115 (90–171) ^a	120	98.8	88.6	106(1)
ψ(∠BHH) (deg)	150–170 (117–171)	149	158.7	144.8	156(3)
bond strength (kcal/mol)			6.1	7.5	

^a The range shown applies to the majority of structures with the extreme range indicated in parentheses. ^b Theory and diffraction data cannot be directly compared because the former relates to the gas-phase BH₃NH₃ dimer and the latter to the shortest contact in the BH₃NH₃ crystal. Theoretical results are from ref 9a. ^c Theoretical results are from the work of Cramer and Gladfelter.¹⁴

**Figure 2.** H···H distance d_{HH} versus the N–H···H angle, ψ , found in the CSD search. The numbering is the same as in Figure 1.

for B by factors of 3 or more, typical of the behavior seen in cases of atom misassignment.

The erroneous prior published assignment is probably a result of the failure to locate the hydrogens in the early powder X-ray studies on the material.^{11a,b} In such a case, the assignment of B and N amounts to the necessarily arbitrary assignment of the direction of the polar axis in the tetragonal structure (space group, *I4mm*) adopted by BH₃NH₃ above the phase transition at 220 K. In the later work carried out below the phase transition temperature,^{11e} the hydrogen atoms were located. The B/N assignment, of no particular significance for prior work, becomes of critical importance here, where intermolecular interactions become the center of interest. The shortest intermolecular H···H contact obtained in the X-ray work (2.07 Å^{11e}) was close to that we now find (2.02(3) Å), but the resulting N–H···H–B contact had linear B–H···H and bent N–H···H groups, exactly reversed from the usual situation.³ This problem is of course now solved thanks to the present assignment of B and N which leads to the expected¹ arrangement of bent B–H···H and linear N–H···H groups.

The previously published B/N assignment may have caused the displacement parameters for B and N to have very abnormal values, large for B and small for N. This was rationalized, however, as a result of the boron having large cationic charge and nitrogen having large anionic charge as a result of B→N dative bonding.^{11f} The electron density map, calculated from the X-ray data, gave unreasonable charge distributions, however. We conclude that all of these problems may perhaps have arisen because of the reversed assignment.

The BH₃NH₃ molecule has a staggered geometry with a BN distance of 1.58(2) Å, in line with previous determinations in the solid state, notably the value of 1.565(7) Å by Boese and coworkers.^{11f} Interestingly, the gas-phase BN distance obtained

by electron diffraction,^{11g} $r_e = 1.672$ Å, $r_s = 1.657$ Å, is apparently somewhat longer. Charge transfer may be enhanced in the more polar medium of the solid versus the gas phase. Alternatively, the distance in the solid may be foreshortened due to librational effects.

As was noted above, the shortest H···H contact found in the present study, H(2)···H(3) 2.02(3) Å, is close to that found previously, but the N–H···H–B conformation is now normal (Figure 3), having a near-linear N–H···H (156(3)°) and bent B–H···H (106(1)°) arrangement, instead of the reverse as in the X-ray structure.

The packing prohibits all the H···H contacts from having the same preferred conformation of Table 1. Two other longer contacts are also seen in the structure, H(1)···H(4), 2.21(4) Å and H(2)···H(4), 2.23(4) Å. These are close to the sum of the van der Waals radii for two hydrogens, 2.4 Å, and are 0.2 Å longer than the shortest contact, so they are probably considerably less attractive than H(2)···H(3). In these cases we find one very abnormal and one somewhat abnormal N–H···H–B conformation: N–H(1)···H(4), 130(1)°; H(1)···H(4)–B, 156(3)° and N–H(2)···H(4), 137(2)°; H(2)···H(4)–B, 94(2)°, respectively.

As Boese^{11f} points out, the packing of ethane,¹³ which adopts the *P2₁/n* space group, is entirely different from that for the isoelectronic molecule, BH₃NH₃. We see that the BH₃NH₃ packing allows three H···H contacts of <2.4 Å, one of which is very short.

Unpublished work by J. E. Jackson and co-workers^{11h} on the neutron diffraction structure of NaBD₄·2D₂O shows D···D contacts of 1.79–1.94 Å, clearly falling into the range expected for dihydrogen bonds.

Theoretical Studies. An ab initio theoretical study on the BH₃NH₃ dimer, showing intermolecular N–H···H–B interactions such as those in the present crystal structure, was carried out with the PCI-80/B3LYP method and was fully reported in the communication,^{9a} so it will not be discussed in detail here.

Relation to the Classical Hydrogen Bond. At the simplest level, the dihydrogen bond can be considered as a proton–hydride interaction. The predominance of strongly bent B–H···H groups in the CSD study suggests that this model is something of a simplification. In fact it may be better thought of as an interaction between the NH proton and the BH bond as a whole. This would explain the side-on conformation because the NH proton in this way can approach not only the BH hydride but also the BH bond itself. In this picture the hydrogen bond acceptor (weak base) in the dihydrogen bond is the B–H σ -bond as also suggested by Cramer and Gladfelter.¹⁴

The hydrogen bond concept has previously been extended from the classical A–H···lp (lp = lone pair) situation to A–H··· π (π = pi bond) systems, and so we now see that it

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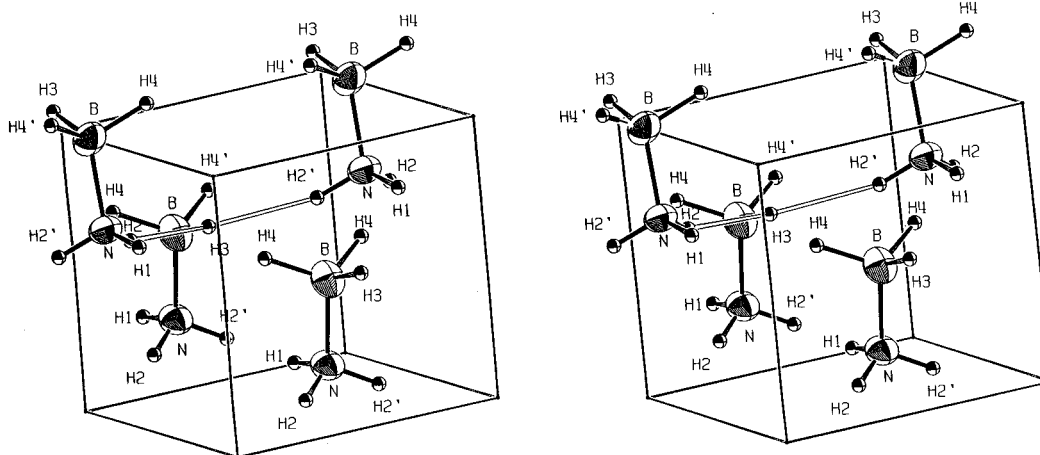


Figure 3. Stereoview of the neutron diffraction structure of BH_3NH_3 with the shortest $\text{H}\cdots\text{H}$ contacts [$\text{H2}-\text{H3}$, $2.02(3)$ Å] indicated.

Table 2. Crystal Structure Data for $[\text{BH}_3\text{NH}_3]$

formula	$\text{H}_3\text{N}\cdot\text{BH}_3$
M_r (amu)	30.8760
space group	$Pmn2_1$ (no. 31)
Z	2
a , Å	5.395(2)
b , Å	4.887(2)
c , Å	4.986(2)
α , β , γ (deg)	90
volume (Å ³)	131.5(16)
how determined	least-squares fit for 32 reflns, $39 < 2\theta < 54$
density calcd (g cm ⁻³)	0.7799
absorption coeff (cm ⁻¹)	10.369
forms	$+(110) \pm(1-10) \pm(001)$
crystal shape	box
crystal color	colorless
crystal dimension (mm)	$0.66 \times 0.46 \times 1.5$
crystal volume (mm ³)	0.46
neutron wavelength (Å)	1.0462(1)
monochromator	Be (002)
scattering lengths ($\times 10^{-12}$ cm) ¹⁹	
N	0.936
B	0.530
H	-0.37406
temp, K	200 ± 0.05
hkl	$-7 \leq h \leq 7; -6 \leq k \leq 6; -6 \leq l \leq 0$
monitor reflns	$(00-4)$ (-420)
no. of reflns collected	548
$(2\theta)_{\text{max}}$ (deg)	90
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.68
no. of reflns averaged	205
R_w int	0.064
no. of ind reflns	207
$I > 3\sigma$	80
variables	sc xyz u_{ij}
no. of variables	42
extinction	not significant
no. of reflns used	197
ratio of reflns/variables	4.7
$R(F_0^2)$	0.257
$R_w(F_0^2)$	0.163
$R_w(F_0 > 3\sigma)$	0.065
S	1.31

can also apply to the $\text{A}-\text{H}\cdots\sigma$ ($\sigma = \text{sigma}$ bond) case. So far only $\text{X}-\text{H}$ bonds where X is an electropositive atom such as B or a transition metal have been suitable as σ component, no doubt because such $\text{X}-\text{H}$ bonds tend to be basic.

The sharp falloff¹ in hydrogen bond strength from $\text{N}-\text{H}\cdots\text{lp}$ (6–8 kcal/mol) to $\text{N}-\text{H}\cdots\pi$ (1–2 kcal/mol) might make it seem that $\text{N}-\text{H}\cdots\sigma$ bonds would have a negligible strength, but our theoretical work^{9a} and prior measurements in

Table 3. Positions, Displacement Parameters (Å²), Selected Distances (Å), and Angles (deg) in $[\text{BH}_3\text{NH}_3]$

Positions						
atom	x	y	z			
N	0	0.235(2)	0.314(4)			
H(1)	0	0.453(7)	0.341(15)			
H(2)	0.140(4)	0.148(5)	0.397(6)			
B	0	0.185(3)	0			
H(3)	0	-0.043(6)	-0.060(6)			
H(4)	0.185(5)	0.264(6)	-0.100(5)			
Displacement Parameters						
atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N	0.037(5)	0.036(5)	0.026(4)	0	0	-0.007(5)
H(1)	0.112(22)	0.058(18)	0.129(44)	0	0	-0.027(30)
H(2)	0.089(15)	0.177(31)	0.017(6)	0.082(22)	0.005(10)	0.004(11)
B	0.038(8)	0.032(9)	0.040(8)	0	0	-0.012(7)
H(3)	0.047(13)	0.094(19)	0.014(11)	0	0	-0.012(13)
H(4)	0.115(15)	0.117(15)	0.025(8)	-0.073(15)	0.023(9)	-0.012(12)
Intramolecular Distances						
N-B	1.58(2)	B-H3	1.15(3)			
N-H1	1.07(4)	B-H4	1.18(3)			
N-H2	0.96(3)					
Intramolecular Angles						
B-N-H1	106(4)	N-B-H3	114(2)			
B-N-H2	111(2)	N-B-H4	112(1)			
B-N-H2'	111(2)	N-B-H4''	112(1)			
H1-N-H2	113(3)	H3-B-H4	102(2)			
H1-N-H2''	113(3)	H3-B-H4''	102(2)			
H2-N-H2''	104(3)	H4-B-H4''	116(3)			
Intermolecular H...H Distances						
H1...H4	2.21(4)	$1/2 - x, 1 - y, 1/2 + z$				
H2...H3	2.02(3)	$1/2 - x, -y, 1/2 + z$				
H2...H4	2.23(4)	$1/2 - x, -y, 1/2 + z$				
Intermolecular Angles						
N-H1...H4	130(1)	H1...H4-B	156(3)			
N-H2...H3	156(3)	H2...H3-B	106(1)			
N-H2...H4	137(2)	H2...H4-B	94(2)			

$\text{N}-\text{H}\cdots\text{H}-\text{M}$ systems³ suggest a bond strength of 4–6 kcal/mol, much larger than we expected and comparable in strength to that in a classical hydrogen bond. Several factors probably favor the formation of a strong interaction in this case. The two H atoms involved each have small radii so the $\text{H}\cdots\text{H}$ distance can be small. Many of the classical H-bond acceptors such as the nitrogen atom in NH_3 are expected to be sterically bulkier than the H-bond acceptor hydrogen atom in a $\text{B}-\text{H}$ bond. In addition the $\text{B}-\text{H}$ bond may be relatively polarizable, and the approach of the $\text{N}-\text{H}$ group may enhance the negative charge on the $\text{B}-\text{H}$ hydride. Proton NMR measurements on

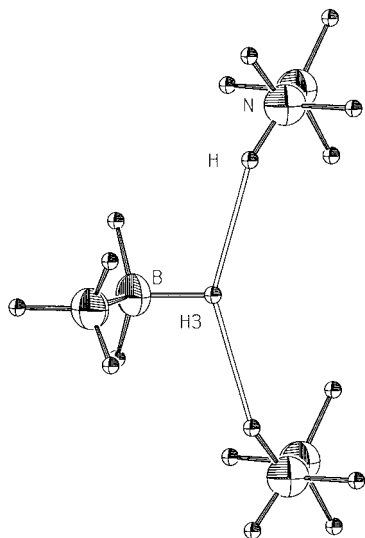


Figure 4. View of the conformation of the closest N–H···H–B contact from the neutron diffraction structure of BH₃NH₃. Distances (Å) and angles (deg): N–H₂, 0.96(3); N–H₂–H₃, 156(3); H₂–H₃, 2.02(3); H₂–H₃–B, 106(1); H₃–B, 1.15(3).

Table 4. Displacement Parameters (Å²) for B and N from the Neutron Diffraction Refinement with the Prior Published and the Present, New Assignments of B and N, Showing the Improved Fit with the Present Assignment

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
	Prior Published Assignment					
N	0.058(5)	0.116(5)	0.064(4)	0	0	–0.011(4)
B	0.018(3)	0.005(2)	0.010(2)	0	0	–0.009(2)
	Present Assignment					
N	0.037(5)	0.036(5)	0.026(4)	0	0	–0.007(5)
B	0.038(8)	0.032(9)	0.040(8)	0	0	–0.012(7)

M–H···H'–N interactions have shown the existence of significant H···H' coupling constants (2–8 Hz.) which implies that there is a small covalent contribution to the H···H bonding.

Reactivity consequences should also be considered. BHHA (AH = acid) bonding may facilitate protonation of boron hydrides because the proton σ -bond attraction may permit easier access to the transition state.

Details of the Work

CSD Search. The search for intermolecular N–H···H–B contacts was carried out by setting $d_{\text{HH}} \leq 2.2$ Å as a cutoff value. The coordinates were retrieved and the reported H atom positions normalized to $d_{\text{NH}} = 1.03$ Å, the conventional neutron diffraction value, by elongating the NH vector. Similarly, d_{BH} was normalized to 1.21 Å, in agreement with literature¹⁵ neutron crystallographic data and our theoretical study.^{9a} The normalized d_{HH} , θ , and ψ values were then calculated and plotted in Figures 1 and 2.

Any error in the H positions is made less problematic because the H atoms can normally be independently located by reference to the heavy atom positions. This is the case, for example, with the H positions for BH in a closo boron cage, or NH in R₃NH⁺

and in pyridinium salts. In the cases studied here, the key H atoms were indeed located in reasonable positions by this criterion. This factor led us to choose to study N–H, rather than O–H hydrogen bonds, where free rotation of the R–OH group makes the proton position independent of the heavy atom positions and so leads to potential problems.

Neutron Diffraction Structure. A saturated solution of BH₃NH₃ in Et₂O was slowly evaporated to produce colorless crystals of the compound suitable for neutron diffraction studies. Neutron diffraction data were obtained on the four-circle diffractometer at beam port H6M of the High Flux Beam Reactor at Brookhaven National Laboratory on two different crystals. The neutron beam, monochromated by beryllium (002) planes in reflection geometry, had a wavelength of 1.0462(1) Å as calibrated against KBr, $a_0 = 6.6000$ Å at 298 K. A single crystal was mounted on an aluminum pin, using halocarbon grease (Dow-Corning), sealed in an aluminum container under a helium atmosphere, and placed in a DISPLEX Model CS-202 closed-cycle refrigerator (APD Cryogenics, Inc.). The crystal was cooled to 200 ± 0.5 K, where the temperature was maintained throughout the measurements and monitored with a Pt resistance thermometer. Data were collected at 200 K, since according to Bühl et al.,^{11e} the quality of the crystal deteriorated dramatically upon further cooling. Both crystals gave similar results, but data from the second crystal are reported here. From $\sin^2 \theta$ values of 32 reflections ($39^\circ < 2\theta < 54^\circ$), the unit cell constants were determined to be $a = 5.395(2)$ Å, $b = 4.887(2)$ Å, $c = 4.986(2)$ Å, $V = 131.5(16)$ Å³. Reflections were scanned for a hemisphere of reciprocal space, $\pm h, \pm k, -l$, for $6.0^\circ < 2\theta < 90^\circ$, using $\omega - 2\theta$ step scans. In the data collection, counts were accumulated at each step for a preset monitor count of the incident beam and the step size was varied to give approximately 65 steps per scan. Intensities of two reflections (00–4 and –420) were monitored every 100 reflections as a check on experimental stability, which proved to be excellent throughout. Altogether, 548 reflections were scanned. An azimuthal scan of reflection (01–3) near $\chi = 90^\circ$ showed some intensity variation. Integrated intensities I_0 and variances $\sigma^2(I_0)$ were derived from the scan profiles as described previously.^{16a} Lorentz factors were applied, as well as an analytical absorption correction.^{16b} Transmission factors were in the range 0.473–0.632 ($\mu = 10.369$ cm^{–1}). Averaging over 205 symmetry-related reflections gave an internal agreement factor of 0.064. This resulted in 207 independent observations, of which 80 had F_o^2 values greater than $3\sigma(F_o^2)$. See Table 2 for details. The B and N positions reported in the X-ray work^{11e} were used as a starting structure. Hydrogen atoms were located in a difference Fourier map. It then turned out that B and N had to be switched from the published X-ray assignment. This resulted in considerably better anisotropic displacement parameters. The structure model was refined based on 197 independent F_o^2 values, using UPALS.¹⁷ The scale factor was varied, together with positional and anisotropic displacement parameters for the six atoms comprising the asymmetric unit, in space group $Pmn2_1$. An extinction correction was not included (type I, isotropic, Lorentzian mosaic¹⁸), since the extinction coefficient was not significant. Using this model, convergence was achieved with $\Delta\rho/\sigma\rho < 0.1$,

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and final agreement factors are as follows: $R(F_o^2) = 0.257$, $wR(F_o^2) = 0.163$, $S = 1.31$ with weights, $w^{-1} = \sigma^2$, $\sigma^2 = \sigma_{\text{count}}^2 + (0.02F_o^2)^2$. Atomic positional and anisotropic displacement parameters are given in Table 3. The final difference Fourier had no residual positive or negative peaks with scattering density exceeding 4% of that at the largest nitrogen atom peak. The goodness of fit, S , is close to 1, as expected; the somewhat high R values are due to the small crystal size, resulting in the majority of reflections having $F^2 < 3\sigma$.

Conclusion

Boraneamines tend to have close H...H contacts as a result of the intermolecular interaction of the NH proton with the BH bond. A CSD structural search provides characteristic metric data for the interaction: the H...H distance is in the range 1.7–2.2 Å, and the N–H...H group tends to be linear while B–H...H tends to be bent. The reported structure of BH_3NH_3 seemed to be a singular exception in having bent N–H...H and linear B–H...H. Our neutron diffraction structure of BH_3NH_3

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shows that despite the simplicity of the molecule B and N were misassigned in the published X-ray structure. With the correct assignment we get the expected bent B–H...H and linear N–H...H in the close ($d_{\text{HH}} = 2.03$ Å) intermolecular N–H...H–B interaction.

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Supporting Information Available: Experimental details, listings of atomic coordinates and displacement parameters, and a listing of bond distances and angles, all with their esd's. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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