Unconventional Hydrogen Bonds: Intermolecular B−H···H−N Interactions

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Received August 16, 1995

Typical hydrogen bond acceptors[1] possess an O or N lone pair, but more recently, the σ-electron pair of a transition metal hydride has been shown[2,3] to give intramolecular N−H···H−M and O−H···H−M hydrogen bonds of an unconventional type, for which we suggest[4] the term dihydrogen bonds. These interactions have bond strengths of 4−6 kcal/mol and H···H distances (d_{HH}) of ca. 1.7−1.9 Å and seem to play a role in proton transfer, fluxional processes, and other reactions.[2,3]

The striking melting point difference between H_3CCH_3 (mp −181 °C) and the isoelectronic H_3BNH_3 (**1**, mp + 104 °C dec) suggested that intermolecular dihydrogen bonds might be present in amine boranes. Of course, H_3BNH_3 is polar, but the polar and essentially non-H-bonding molecule CH_3F, also isoelectronic with ethane, has a melting point of −141 °C, only slightly elevated from that of ethane.

We have now examined the Cambridge Structure Database (CSD)[5] to look for examples among boron nitrogen compounds. Twenty-six N−H···H−B intermolecular dihydrogen bonds have been found with d_{HH} < 2.2 Å[6] in 18 X-ray crystal structures.[7] The following metric data, obtained from the CSD, were studied.

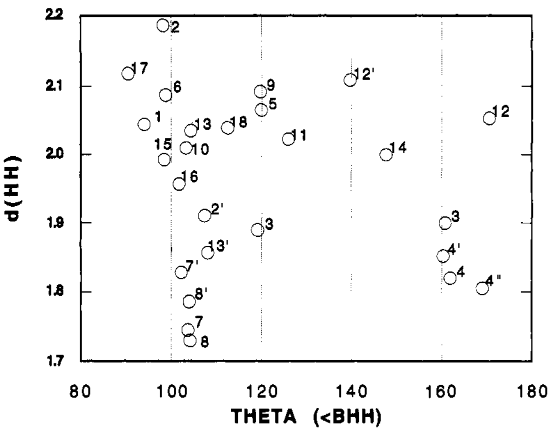
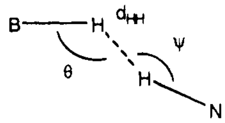


Figure 1. The H···H distance d_{HH} versus the B−H···H angle θ for the compounds studied, normalized. The numbers refer to the following compounds, which are listed by their CSD filenames [R values (%) in parentheses]: 1, AZIBOR (8.7);[7a] 2, CESHIR 10 (4.7);[7b] 3, DITSUU (3.4);[7c] 4, DUJYOW (4.8);[7d] 5, EMOBOR (4.7);[7e] 6, FUDHIV01 (4.7);[7f] 7, FUDHOB (4.1);[7g] 8, FUDHOB02 (4.5);[7h] 9, FUZSEY (6.3);[7i] 10, GACWUC (11.6);[7j] 11, GALGIJ (15.3);[7k] 12, GALGOP (4.2);[7l] 13, GEWWEK (5.0);[7m] 14, JUJKUU (4.3);[7n] 15, KACRAH (4.6);[7o] 16, KADMEH (5.1);[7p] 17, SORGEL (5.5);[7q] 18, VIJLEF (7.7).[7r] Primes refer to second and third H-bonds within a single structure.



In the prior M−H···H−N dihydrogen bonds, d_{HH} was usually in the range 1.7−2.0 Å, and so the range found in the structures studied here (d_{HH} range, 1.7−2.2 Å; average, 1.96 Å, $\sigma = 0.13$ Å) is compatible with the presence of an H-bond. As is usual in structural studies of hydrogen bonding,[1] both N−H (1.03 Å) and B−H (1.21 Å) distances were normalized to minimize the systematic error associated with hydrogen positions in X-ray structures. The N−H value chosen is the standard[1] one in H-bonding studies, and the BH distance chosen was the one found in the theoretical study to be discussed below. By studying a broad range of crystal structures in this way, we hoped to establish a general pattern for behavior for these new interactions.[8]

The N−H···HB angles vary (ψ, average, 149°, σ = 17°; range, 117−171°), but tend to be larger than the NH···H−B angles (θ, average, 120°, σ = 26°; range, 90−171°), shown in Figure 1. In the prior work on M−H···H−N dihydrogen bonds, the NH···H−M angle θ has always been strongly bent. For example, in $ReH_5(PPh_3)_2$·(indole),[9] the NH···H−Re angle θ is 118° (neutron diffraction). In the B−H···H−N cases studied here, we find that θ is usually strongly bent: although the range found for the NH···H−B angle θ is 90−180°, the majority of examples fall in the range θ = 95−120°.[10]

In most cases, the N−H bonds in the compounds studied were either substituted ammonium ions or substituted pyridinium ions,

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[1] Jeffrey, G. A.; Saenger, W. *Hydrogen Bonding in Biological Structures*; Springer: Berlin, 1994.

[2] Lee, J. C.; Peris, E.; Rheingold, A. L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 11014. Peris, E.; Lee, J. C.; Rambo, J. R.; Eisenstein, O.; Crabtree, R. H. *J. Am. Chem. Soc.* **1995**, *117*, 3845.

[3] Park, S.; Ramachandran, R.; Lough, A. J.; Morris, R. H. *J. Chem. Soc. Chem. Commun.* **1994**, 2201.

[4] A referee points out that these unconventional hydrogen bonds require a new name, for which we suggest the term "dihydrogen bond".

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[6] (a) The d_{HH} cutoff of 2.2 Å is adopted here because it is less than the sum of the van der Waals radii (2.4 Å) and is therefore expected to correspond to a significant attractive interaction. (b) An intramolecular B−H···H−N interaction with d_{HH} = 2.05 Å has very recently been found[6c] in a boron-substituted cytosine, but geometries can be strongly constrained in any intramolecular case, hence our interest in looking for intermolecular cases, which should allow a better understanding of the geometrical preferences of the system. (c) Zottola, M. A.; Petersen, L. G.; Singh, P.; Shaw, B. R. *ACS Symp. Ser.* **1994**, *569*, 277.

[7] (a) Ringertz, H. *Acta Chem. Scand.* **1969**, *23*, 137. (b) Vinas, C.; Butler, W. M.; Teixidor, F.; Rudolph, R. W. *Inorg. Chem.* **1986**, *25*, 4369. (c) Shahriari-Zavareh, H.; Stoddart, J. F.; Williams, M. K.; Allwood, B. L.; Williams, D. J. *J. Inclusion Phenom.* **1985**, *3*, 355. (d) Narula, C. K.; Janik, J. Fr.; Duesler, E. N.; Paine, R. T.; Schaeffer, R. *Inorg. Chem.* **1986**, *25* 3346. (e) Base, K.; Brown, M.; Fontaine, X. L. R.; Greenwwod, N. N.; Kennedy, J. D.; Stibr, B.; Thornton-Pett, M. *J. Chem. Soc., Chem. Commun.* **1988**, 1240. (f) Meyer, F.; Paetzold, P.; Englert, U. *Chem. Ber.* **1992**, *125*, 2025. (g) Kester, J. G.; Huffman, J. C.; Todd, L. J. *Inorg. Chem.* **1988**, *27*, 4528. (h) Siriwardane, U.; Chu, S. S. C.; Hosmane, N. S.; Zhang, G.; Zhu, W.; Zhu, H. *Acta Crystallogr. C* **1989**, *45*, 294. (i) Lewin, R.; Simpson, P. J.; Lipscomb, W. N. *J. Chem. Phys.* **1963**, *19*, 1532. (j) Chantler, C. T.; Maslen, E. N. *Acta Crystallogr. B* **1989**, *45*, 290. (k) Fuller, D. J.; Kepert, D. L.; Skelton, B. W.; White, A. H. *Aust. J. Chem.* **1987**, *40*, 2097. (l) Chantler, C. T.; Masien, E. N. *Acta Crystallogr. B* **1989**, *45*, 290. (m) Hargrave. K. D.; McPhail, A. T.; Spielgovel, B. F.; Wisian-Neilson, P. *J. Chem. Soc., Dalton Trans.* **1977**, 2150. (n) Nordman, C. E. *Acta Crystallogr.* **1960**, *13*, 535. (o) Lobkovskii, E. B.; Dorosinskii, A.; Semenenko, K. N. *Zh. Strukt. Khim.* **1974**, *15*, 70. (p) Andrianov, V. I.; Atovmyan, L. O.; Golovina, N. I.; Klitskaya, G. A. *Zh. Strukt. Khim.* **1967**, *8*, 303. (q) Ng, L.-L.; Ng, B. K.; Shelley, K.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1991**, *10*, 4278. (r) Müller, J.; Paetzold, P.; Boese, R. *Heteroat. Chem.* **1990** ,*1*, 461.

[8] Any ambiguity in the hydrogen positions is made less significant because the H atoms can normally be independently located by reference to the heavy atom positions, assuming these have been correctly located. This is the case, for example, with the H positions for BH in a closo boron cage, or NH in R_3NH^+ 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 H-bonds, where free rotation of the R−OH group makes the proton position independent of the heavy atom positions and so leads to ambiguity. Very few neutron diffraction structures of boron compounds have been carried out, perhaps because of the very high neutron absorption cross section of boron.

[9] Wessel, J.; Lee, J. C.; Peris, E.; Yap, Fortin, J. B.; Ricci, J. S.; Sini, G.; Albinati, A.; Kotzle, T. F.; Eisenstein, O.; Yap, G. P. A.; Rheingold, A. L.; Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.*, in press.

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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; $C_5H_5NH^+$, 5.2) and therefore to favor[1] the formation of relatively strong hydrogen bonds. Similarly, the BH bonds were 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 potentially basic.

In only three of these previous structural studies[7a,j,k] was the presence of the close H···H distance noticed, and in each case it was ascribed to a charge transfer (CT) interaction, rather than to H-bonding.

To improve our understanding of this system, we carried out an ab initio theoretical study on the dimer, $[H_3BNH_3]_2$ (**2**), by the PCI-80/B3LYP method.[11-13] The global minimum proved to be the structure shown in Figure 2, containing two B−H···H−N dihydrogen bonds of structure very similar to the bent ones found in the crystallographic study, with $d_{HH} = 1.82$ Å, $\psi = 158.7°$, and $\theta = 98.8°$. The heat of association of **2** is 12.1 kcal/mol, 6.1 kcal/mol per H-bond if we assign half of the total energy to each H-bond. This is well within the range of H-bond energies found in conventional N−H···base examples (3−8 kcal/mol) and shows that the BH bond is a surprisingly effective base.

The strong bending of the E−H···HN angle is a notable feature of H-bonds involving E−H σ-bonds as H-bond acceptors. This is rationalized by the theoretical study, which assigns the atom charges shown in Figure 3. The boron is very negative and is at the negative end of the B−H dipole, so that a collinear N−H···H−B arrangement would lead to an unfavorable (− +)(+ −) arrangement of the two dipoles. It is therefore understandable that the H−B dipole should rotate so as to become more favorably aligned, resulting in a side-on structure. In line with the suggestion that the N−H group is interacting in part with the boron atom, the N−H···B angle is only slightly bent (average, 157°, $\sigma = 15°$; range 121−177°). We have not yet been able to obtain crystals of **1** suitable for a structural study.

Intermolecular E−H···H−N (E = element) dihydrogen bonding, previously seen for Re,[9] is now found for a main group element, boron. The unusual nonlinear structure is rationalized on the basis of the charge distribution calculated for a representative system, $[BH_3NH_3]_2$. The results also suggest that the CSD may be a useful source of information on the structural details of intermolecular interactions in general.

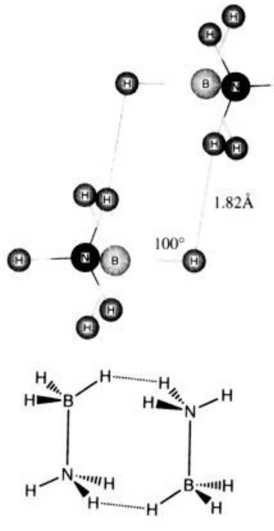

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Figure 2. The structure of $[H_3BNH_3]_2$ (**2**) from PCI-80/B3LYP studies and a structural diagram for **2**.

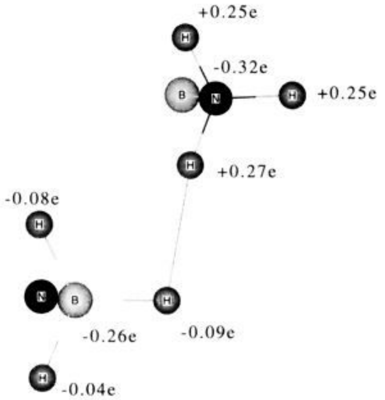

Figure 3. The Mulliken charge distribution in $[H_3BNH_3]_2$ (**2**) from PCI-80/B3LYP studies.

Acknowledgment. We thank the NSF for funding, Prof. Ken Caulton, and a referee for very helpful discussions.

JA952819W

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(10) Detailed inspection of the structures showed that the cases where θ was particularly large (**3**, **4**, and **12**) were the ones in which the conformation of the molecule makes it difficult to attain a packing arrangement with θ and $\psi \ll 180°$.

(11) (a) Details of the theoretical study. The geometries and energies were obtained using density functional theory with the B3LYP functional.[8b] The energies for these optimized structures were then obtained using the PCI-80 method.[8c] Standard double ζ plus polarization basis sets were then used for both geometries and energies. The calculations were performed using the GAUSSIAN 92/DFT[8d] and STOCKHOLM[8e] set of programs. (b) Becke, A. D. *Phys. Rev.* **1988**, *A38*, 3098; *J. Chem. Phys.* **1993**, *98*, 1372, 5648. (c) Siegbahn, P. E. M.; Blomberg, M. R. A.; Svennson, M. *Chem. Phys. Lett.* **1994**, *223*, 35. Siegbahn, P. E. M.; Svennson, M.; Boussard, P. J. E. *J. Chem. Phys.* **1995**, *102*, 5377. (d) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzales, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *GAUSSIAN 92/DFT*, Revision G.1; Gaussian Inc.: Pittsburgh, PA, 1993. (e) STOCKHOLM is a general purpose set of quantum mechanical programs written by Siegbahn, P. E. M.; Blomberg, M. R. A.; Petterson, L. G. M.; Roos, B. O., and Almlöf, J.

(12) (a) The PCI-80 parametrized method has recently been discussed[12b,c] and shown[12c] to give greatly improved results compared to unparametrized methods. In a test involving the atomization energies of 32 neutral first-row molecules, PCI-80 gives an average absolute deviation of only 2.4 kcal/mol, compared to 22 kcal/mol for MP2[12d] and 29 kcal/mol for QCISD. (b) Siegbahn, P. E. M.; Svennson, M.; Crabtree, R. H. *J. Am. Chem. Soc.* **1995**, *117*, 6758. (c) Siegbahn, P. E. M.; Blomberg, M. R. A.; Svennson, M. *Chem. Phys. Lett.* **1994**, *223*, 35. Siegbahn, P. E. M.; Svennson, M.; Boussard, P. J. E. *J. Chem. Phys.* **1995**, *102*, 5377. (d) Johnson, B. G.; Gill, P. M. W.; Pople, J. A. *J. Chem. Phys.* **1992**, *97*, 7846.

(13) Five different structures were tried for **2**: **A**, quasilinear, with a staggered NH_3···BH_3 contact; **B**, quasilinear, with an eclipsed NH_3···BH_3 contact; **C**, parallel (C_s), with NH···H_2B contacts at both ends; **D**, parallel (C_s), with an NH···HB contact at one end and NH_2···H_2B contacts at the other; **E**, parallel (C_2), structure **2**. The energies decreased on going from **A** to **E**. A Hessian computed for **D** had one imaginary frequency and is thus not a true minimum. We cannot exclude the possibility that a lower minimum than **E** exists, but we were not able to find it. An MP2 geometry optimization for **2** gave results insignificantly different in energy and structure from the B3LYP geometry.