Dihydrogen Bonds in Solid BH_3NH_3**

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The "dihydrogen bond" $D-H^{\delta+}\cdots^{\delta-}H-E$—where D is a typical electrostatic atom such as nitrogen or oxygen, and E is a transition metal or boron—was first described by Crabtree and co-workers.[1] Both inter- and intramolecular versions of this bond have been cited, and with typical energies in the range of 12–28 kJ mol^{-1},[2] they are comparable in strength to conventional hydrogen bonds. In particular, the $N-H^{\delta+}\cdots^{\delta-}H-B$ intermolecular contact in solid-state BH_3NH_3 has received special attention.[1–4] The absence of nonbonding valence electrons on boron negates a possible $H^{\delta+}\cdots^{\delta-}E$ interaction that could arise if E were a d-block element. Thus, for BH_3NH_3 the H$\cdots$H contact must result from a sigma-type interaction.

To date, all computational studies investigating properties of this unusual intermolecular bond refer to isolated dimer (i.e., gas-phase) models, which do not resemble the crystal structure all that closely (Figure 1 a, b). The global minimum calculated by Crabtree and co-workers contains two H$\cdots$H contacts (PCI-80/B3LYP, Figure 1 c), which are each assigned an average bond strength of 25.5 kJ mol^{-1} (no basis set superposition error (BSSE) or zero-point energy (ZPE) corrections applied).[2] This value has been described as being "surprisingly large" by the authors, and places the $N-H\cdots H-B$ contact at the upper end of the energy range quoted for dihydrogen bonds. Li et al. cite a different structure comprising four dihydrogen bonds (Figure 1 d), with an average bond strength of 11.6 kJ mol^{-1} (after BSSE and ZPE correction; 6-31++ G*/MP2), that is, at the lower end of the dihydrogen bond energy spectrum.[3] Popelier characterized the intermolecular interaction on the basis of the calculated electron density for a third dimer containing three dihydrogen bonds (Figure 1 e), with an average bond energy of 18.3 kJ mol^{-1} (although bond

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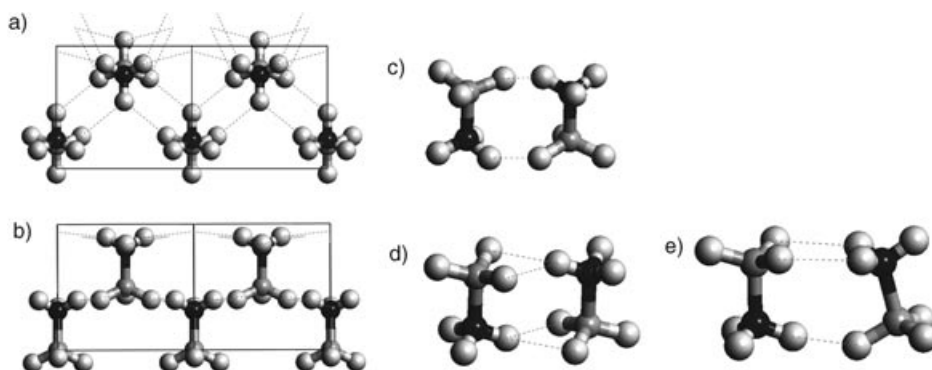
Figure 1. Crystal structure of BH_3NH_3 showing the dihydrogen intermolecular bonding network as viewed along the *c* (a) and *b* axes (b). Dimer models used by Crabtree and co-workers. (c), Li et al. (d), and Popelier (e) to investigate properties of the H···H contacts.

Table 1: Selected parameters for BH_3NH_3.

Parameters	Experimental			Calculated			
	solid[a]	gas[b]	solid			supercell	
				not relaxed	relaxed	dimer	monomer, relaxed
lattice							
a [Å]	5.395(2)	–	5.366	10.0	10.0	12.0	12.0
b [Å]	4.887(2)	–	4.914	10.0	10.0	12.0	12.0
c [Å]	4.986(2)	–	5.100	10.0	10.0	12.0	12.0
α, β, γ [°]	90	–	90	90	90	90.0	90.0
Z	2	–	2	1	1	2	1
volume [Å^3]	131.5(16)	–	134.5	1000.0	1000.0	1728	1728
space/point group	$Pmn2_1$	–	$Pmn2_1$	$P1$	$P1$	C_{2h}	C_{3v}
geometry							
rB–N [Å]	1.58(2)	1.6576(16)	1.580	1.580	1.624	1.606	1.624
rH···H(1) [Å]	2.02(3)	–	1.909	1.909	–	1.940	–
rH···H(2) [Å]	2.23(4)	–	2.174	2.174	–	–	–
rH···H(3) [Å]	2.21(4)	–	2.271	2.271	–	–	–
total energy [eV]	–	–	−896.43917	−447.39887	−447.43142	−895.50251	−447.41750
lattice energy [kJ mol^{-1}][c]	–	–	–	79.2	–	–	–
sublimation energy [kJ mol^{-1}][d]	–	–	–	–	76.0	–	–
H-bond strength [kJ mol^{-1}]	–	–	–	–	12.7[e]	–	16.1[f]

[a] Neutron diffraction study.[7] [b] Microwave spectroscopy study.[8] [c] $\Delta H_{lattice}$ (0 K) $= E_{unit cell}/Z - E_{supercell (not relaxed)}$. [d] ΔH_{sub} (0 K) $= E_{unit cell}/Z - E_{supercell (relaxed)}$. [e] H-bond strength $= \Delta H_{sub}/($intermolecular bond order $= 6$). [f] H-bond strength $= [(E_{dimer}/2 - E_{monomer (relaxed)})/($intermolecular bond order $= 2)]$

ellipticities indicate that not all bonds are of equal strength; 6-31G*/MP2, no BSSE or ZPE correction applied).[4]

Given that the dimer models do not mimic the crystal structure all that closely, it is now timely to revisit the dihydrogen bond found in solid BH_3NH_3 using a periodic quantum mechanical modeling approach, where the full crystallographic unit cell is used as the model for calculation. An optimized structure (unit cell and atomic positions) has been obtained with plane-wave density functional theory (PW-DFT) and the energy per molecule in the crystal lattice calculated. Deleting all but one molecule from the crystal lattice, and stretching the unit cell parameters (i.e., creating a pseudo-isolated molecule) effectively takes us to the gas phase. As the same basis set and level of theory are used in both calculations, comparison of the energies obtained gives the interaction energy, from which the average hydrogen bond strength can be obtained. (A full discussion of the computational methods is available in the Supporting Information.) We have recently demonstrated the success of this method for the test systems ammonia and urea.[5]

The results obtained from the PW-DFT calculations are given in Table 1. Although the simulation slightly overestimates the volume of the unit cell ($+2\%$), this is commonly observed with generalized gradient approximation (GGA) DFT functionals and translates to an increase in lattice parameters of no more than 0.1 Å. Similarly, all bond distances are reproduced to within approximately 0.1 Å. In the supercell calculation (i.e. pseudo-isolated molecule) the

B−N bond lengthens by 0.044 Å, which is consistent with experimental values (Δ0.078 Å in going from the solid state to the gas phase).

Comparing the energy per molecule from the crystal lattice with that from the supercell calculation (with one molecule still in the crystal geometry, that is, no atom relaxation at this stage) enables the lattice energy[6] at 0 K for the crystal to be determined (79.2 kJ mol^{-1}). Taking atomic relaxation for the isolated molecule into account gives a value of 76.0 kJ mol^{-1} for the sublimation energy[6] at 0 K.[†] As each BH_3NH_3 molecule in the crystal lattice is connected by twelve intermolecular dihydrogen bonds to its neighbours (that is, an intermolecular bond order of six, see Figure 1 a) we estimate the average value for the dihydrogen bond present in the crystal structure to be 12.7 kJ mol^{-1}.[††]

To demonstrate that the PW-DFT supercell method can reliably calculate binding energies for this system, we have also performed calculations for the dimer structure obtained by Li et al. (see Figure 1 d and Table 1) for direct comparison with the results obtained from ab initio molecular orbital calculations.[3] Comparing the energies of the dimer and monomer structures located in the center of a 12 × 12 × 12 Å supercell, we calculate the total binding energy (per molecule) to be 32.2 kJ mol^{-1}, thus giving a dihydrogen bond strength for this complex of 16.1 kJ mol^{-1}. This is largely consistent with Li's value of 13.4 kJ mol^{-1} (after BSSE correction, ZPE correction not applied for consistency with our calculations). We note that our optimized structure exhibits a slightly shorter H···H interaction (1.94 versus 2.04 Å obtained by Li et al.), and this may explain why our simulations return a slightly stronger bond.

In conclusion, we have performed PW-DFT calculations to investigate the strength of the dihydrogen bond in the solid-state structure of BH_3NH_3. The initial parameters used in our periodic calculations are taken directly from the experimental crystallographic coordinates and unit cell, thus bypassing the need to construct a dimer model to mimic features of the solid-state geometry. Our simulations predict an average value of 12.7 kJ mol^{-1} (no ZPE correction) for the interaction in solid BH_3NH_3, thus reassigning it towards the lower end of the dihydrogen bond strength spectrum.

[†] This value does not include a ZPE correction, which would require the full set of vibrational modes to be averaged over all of k-space. This calculation is currently beyond our computational resources. Unfortunately there is no experimental sublimation energy available in the literature for comparison.

[††] As the PW basis set is by its very nature delocalized, no correction for BSSE is necessary.
The current generation of DFT functionals cannot account for nonlocal dispersion interactions. However, such contacts are likely to be of minimal importance for the first row element compound BH_3NH_3.

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