Supplementary Information

Synthesis, structural analysis, and thermal decomposition studies of $[(NH_3)_2BH_2]B_3H_8$

Zhenguo Huang,[#,†] Hima K. Lingam,[‡] Xuenian Chen,[†,‡] Spencer Porter,[#] Aijun Du,[$] Patrick M. Woodard,[‡] Sheldon G. Shore[‡,*] and Ji-Cheng Zhao[†,*]

Structure Solution

The powder pattern of $[(NH_3)_2BH_2]B_3H_8$ was indexed in Topas Pro (Bruker AXS; Karlsruhe, Germany). Possible solutions were modeled and geometry optimized through density functional theory (DFT) calculations where the lowest energy lattices were prioritized as structure solution candidates. DFT calculations using CASTEP (Accerlys, Inc; San Diego, California, USA) employ a norm-conserving non-local pseudopotential generated by the Kerker scheme with an energy cut-off of 420 eV. An energy charge per atom convergence criterion of 0.00002 eV, a root-mean-square displacement of 0.001 Å, and a root-mean-square residual force on movable atoms of 0.05 eV/Å were utilized. Electron exchange interactions and correlations were developed by Wu and Cohen via a generalized gradient approximation.[i] The structure was then geometry optimized using the Broyden-Fletcher-Goldfarb-Shanno scheme, which enabled bond geometries and the atomic coordinates.
Rigid bodies ($B_3H_8^-$ and $(NH_3)_2BH_2^+$) were constructed in Topas based on X-ray diffraction data. Simulated annealing allowed for rotational, translational, and torsional degrees of freedom which determined subunit orientation within the unit cell. This geometry and orientation underwent Rietveld refinement which yielded the best fit in $P2_12_12_1$. Thermal parameters for hydrogens were constrained to a reasonable value and like atoms within a subunit were refined together.

Table S1. Experimental and crystallographic details of $[(NH_3)_2BH_2]B_3H_8$.

Formula	$[(NH_3)_2BH_2]B_3H_8$
MW	87.38
Space group	$P2_12_12_1$
Data collection temperature	Ambient
Radiation type	Cu Kα_1
Z	4
a (Å)	8.2202(3)
b (Å)	9.2554(4)
c (Å)	9.3847(4)
Volume (Å^3)	714.00(5)
R factors and goodness-of-fit	R_p = 0.064, R_{wp} = 0.085, R_{exp} = 0.075, R_B = 0.040, χ^2 = 0.015
Sample color	White
Density (g/cm^3)	0.81295(6)
Refinement method	Rietveld

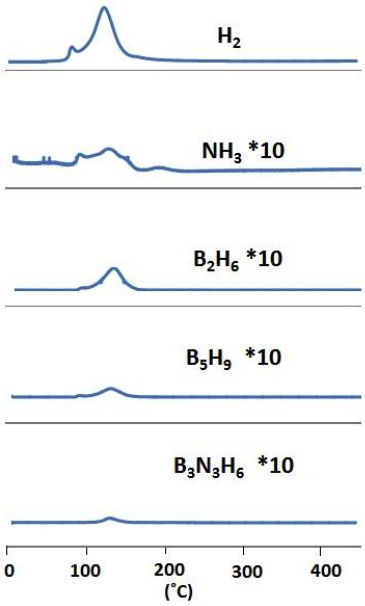
Table S2. Fractional atomic coordinates from XRD data.

Atom	x	y	z	B_{eq}
N1	0.27745	0.20699	0.58435	2.1(2)
N2	0.22872	0.44837	0.71618	2.1(2)
B1	0.23296	0.37192	0.56619	1.1(5)
H1	0.39241	0.19297	0.62912	3
H2	0.28375	0.16221	0.48239	3
H3	0.19711	0.14281	0.64309	3
H4	0.2173	0.55902	0.69845	3
H5	0.33585	0.43503	0.77472	3
H6	0.12943	0.41838	0.77858	3
H7	0.33969	0.42713	0.49532	3
H8	0.09952	0.38305	0.51177	3
B2	0.63808	0.34203	0.8141	1.3(3)
B3	0.76636	0.32249	0.96499	1.3(3)
B4	0.85355	0.35149	0.79424	1.3(3)
H9	0.57793	0.45737	0.78147	3
H10	0.58189	0.23645	0.75415	3
H11	0.77884	0.20277	0.01658	3
H12	0.77358	0.41908	0.05138	3
H13	0.90364	0.25138	0.72215	3
H14	0.8987	0.47014	0.75435	3
H15	0.93174	0.33589	0.91001	3
H16	0.59169	0.32095	0.94152	3

Table S3. Selected bond distances in Å.

Bond	Distance
B–N	1.58
B–B	1.78
B–H	1.21 (terminal),1.27 and 1.45 (bridging)
N–H	1.04-1.05

Mass spectra of gaseous decomposition products



---

i. Z. Wu and R. E. Cohen, *Phys. Rev. B*, 2006, **73**, 235116.