Thomas K. Nielsen July 5, 2011
Supporting Information

Methods to Stabilize and Destabilize Ammonium Borohydride

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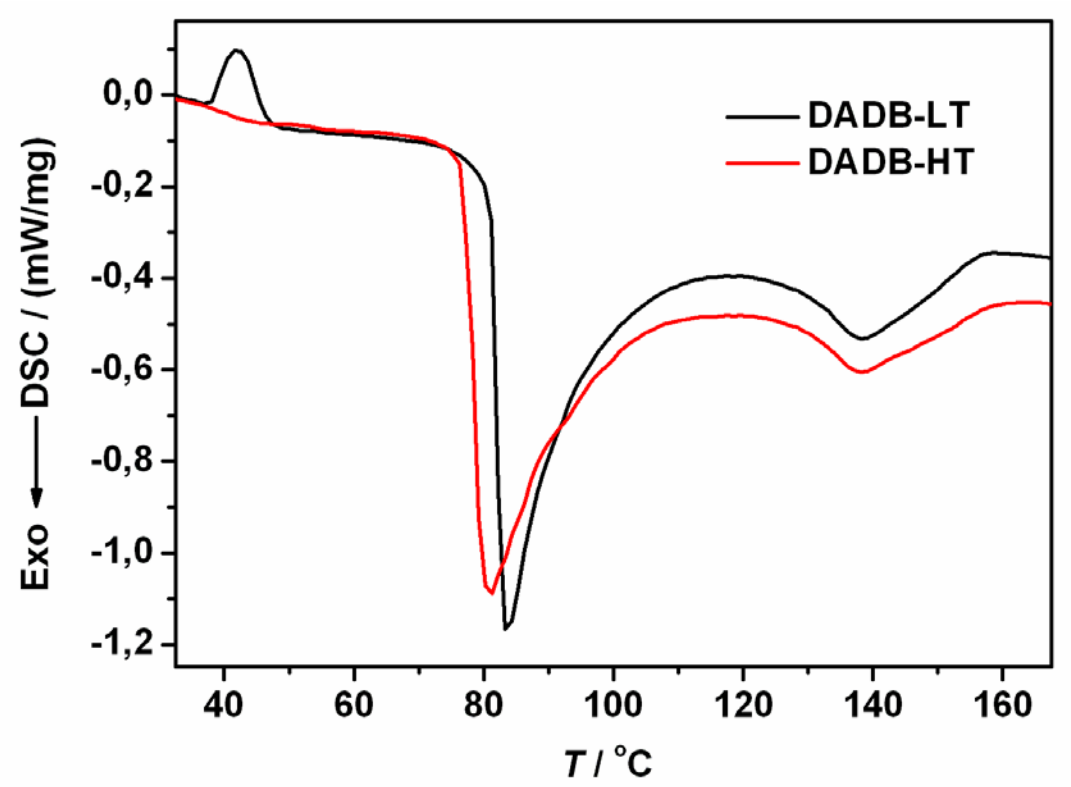

Figure S1. Differential scanning calorimetry (DSC) of sample DADB-HT and DADB-LT. Samples were heated from -30 °C to 190 °C (heating rate 1 °C/min).

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Details of crystal structure refinement

Two identical and symmetric $NH_3BH_2NH_3$ fragments were refined in the unit cell. The N-H and B-H distances were fixed at 0.85 and 1.01 Å respectively from the corresponding values in the high temperature structure (refined from neutron data). The N-B-N angle refined to 107.6(9)°; all other angles were set to the tetrahedral angle of 109.47° where possible. The positions of these fragments were defined by the boron atoms and refined to x = 0.1389(6), y = 0.4310(18), z = 0.7683(14) and x = 0.3995(5), y = 0.4888(12), z = 0.784(2) respectively. The rotational orientation of each fragment was refined independently.

The BH_4 fragments were treated as regular tetrahedra with B-H distances of 1.16 Å, again from the high temperature structure. The positions and orientations of both were also refined independently, leading to boron positions of x = 0.0105(10), y = 0.7694(18), z = 0.508(2) and x = 0.7750(9), y = 0.2627(17), z = 0.0050(18). The orientations and therefore H positions should be regarded as approximate at best given the weak scattering power of hydrogen.

The resulting coordinates of all atoms are given in the following table. All atoms belong to Wyckoff site 8*c* and have occupancy of 1.

Table S1 Crystallographic coordinates from refinement against synchrotron data.

Atom	*x*/*a*	*y*/*b*	*z*/*c*
B1	0.1389	0.4310	0.7683
HB11	0.123	0.365	0.696
HB12	0.112	0.512	0.774
B2	0.3995	0.4888	0.784
HB21	0.379	0.538	0.704
HB22	0.384	0.524	0.876
B3	0.0105	0.7694	0.508
HB31	0.039	0.860	0.471
HB32	0.039	0.692	0.568
HB33	-0.010	0.717	0.411
HB34	-0.026	0.809	0.581
B4	0.7750	0.2627	0.0050
HB41	0.781	0.163	0.068
HB42	0.816	0.330	0.019
HB43	0.734	0.321	0.046
HB44	0.769	0.238	-0.113
N1	0.1417	0.3593	0.9150
HN11	0.165	0.290	0.910
HN12	0.155	0.416	0.977
HN13	0.107	0.332	0.939
N2	0.2020	0.4785	0.7266
HN21	0.201	0.518	0.645
HN22	0.215	0.535	0.789
HN23	0.225	0.408	0.723
N3	0.3867	0.3325	0.7721
HN31	0.400	0.302	0.693
HN32	0.404	0.290	0.841
HN33	0.349	0.319	0.776
N4	0.4676	0.5114	0.7759
HN41	0.475	0.598	0.782
HN42	0.484	0.469	0.845
HN43	0.481	0.480	0.697

[a] Space group *Pbca*, a = 22.7835(12), b = 9.8448(6) c = 9.5444(4) Å. B_{iso} for all atoms = 4.8(3) Å^2. R_{wp} = 2.13%, R_B = 1.49%

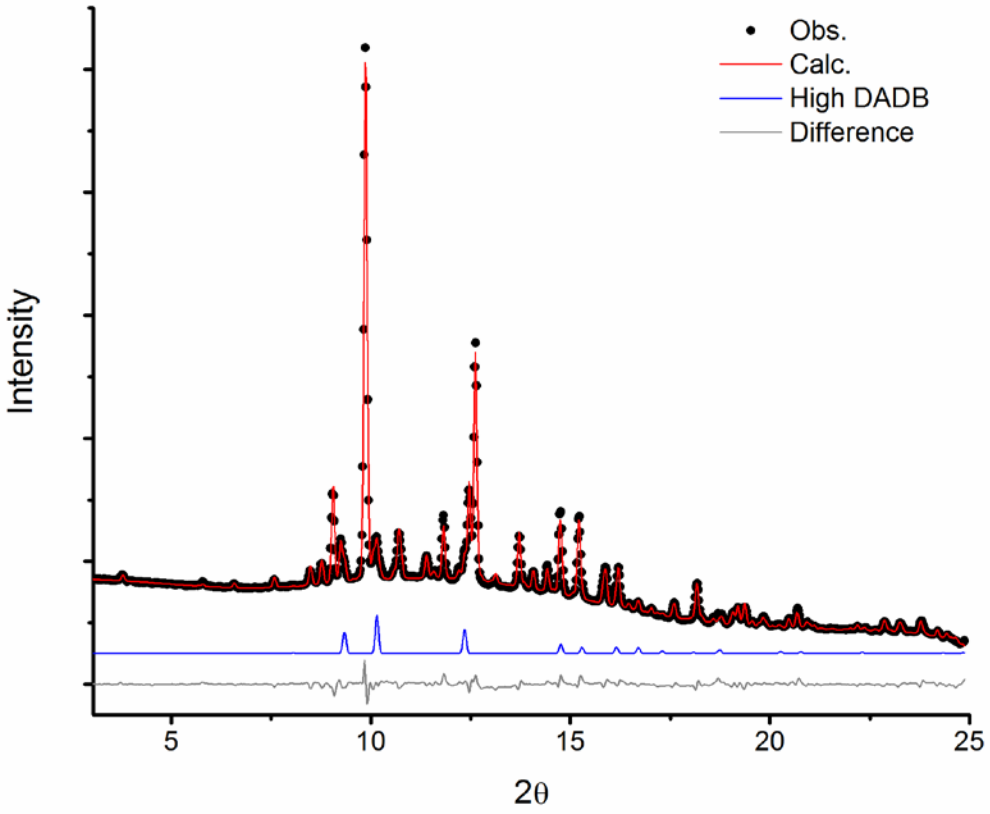

Figure S2. Observed and calculated synchrotron diffraction patterns for low temperature DADB (λ = 0.75338 Å). The calculated pattern from the high temperature phase is shown in blue, corresponding to 6.4 wt% of the sample; all other peaks belong to the low temperature phase. The broad background arises from the glass capillary used to contain the sample.

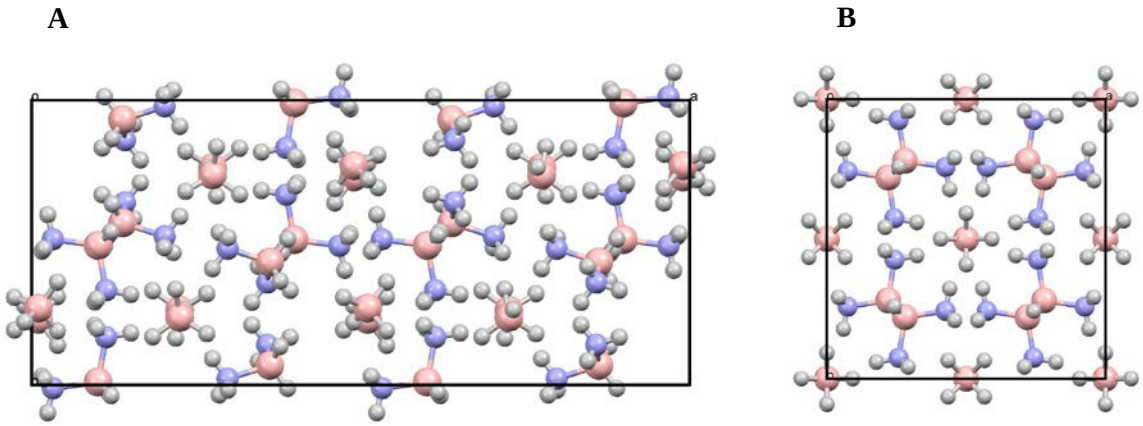

Figure S3. (001) projections of low temperature (A) and high temperature (B) DADB structures.