crystals

Supplementary Materials: Non-Covalent Interactions in Hydrogen Storage Materials $LiN(CH_3)_2BH_3$ and $KN(CH_3)_2BH_3$

Filip Sagan, Radosław Filas and Mariusz P. Mitoraj

Table S1. Overall bonding energies ΔE_{total} (in kcal/mol) describing the interaction between two dimeric fragments in $LiN(CH_3)_2BH_3$ (the fragmentation as shown in Figure 2A) from Gaussian program.

Gaussian	BLYP-D3	MP2/6-311 + G **	PBE-D3/6-311 + G **	MO6-2X/6-311 + G **	WB97xd/6-311 + G **
ΔE_{total}	−29.57	−29.19	−29.00	−27.72	−31.20

Table S2. ETS energy decomposition results describing the interaction between two dimeric fragments in $LiN(CH_3)_2BH_3$ (the fragmentation as shown in Figure 2A) from ADF program.

ADF	BLYP-D3/TZP	PBE-D3/TZP	BP86-D3/TZP
ΔE_{total}	−29.67	−29.44	−29.95
ΔE_{orb}	−18.17	−17.79	−18.31
ΔE_{elstat}	−35.56	−34.16	−35.48
ΔE_{Pauli}	29.48	27.78	30.21
ΔE_{disp}	−11.38	−11.03	−11.75
ΔE_{dist}	6.06	6.00	5.10

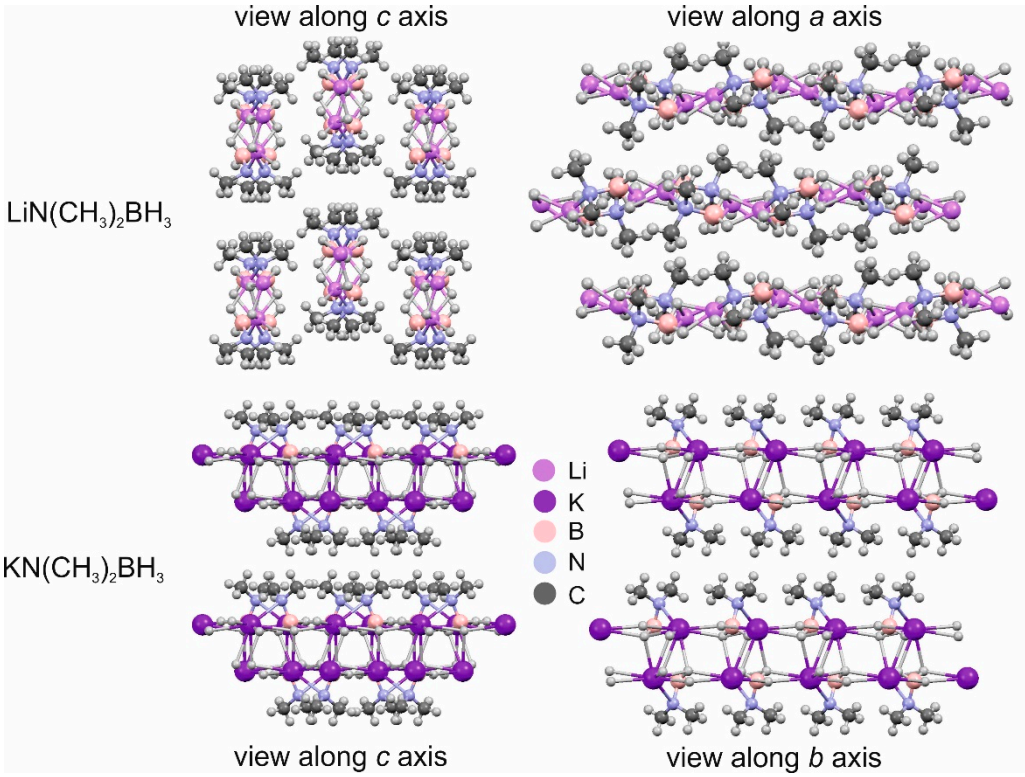


Figure S1. Alternative views of $LiN(CH_3)_2BH_3$ and $KN(CH_3)_2BH_3$ crystals.

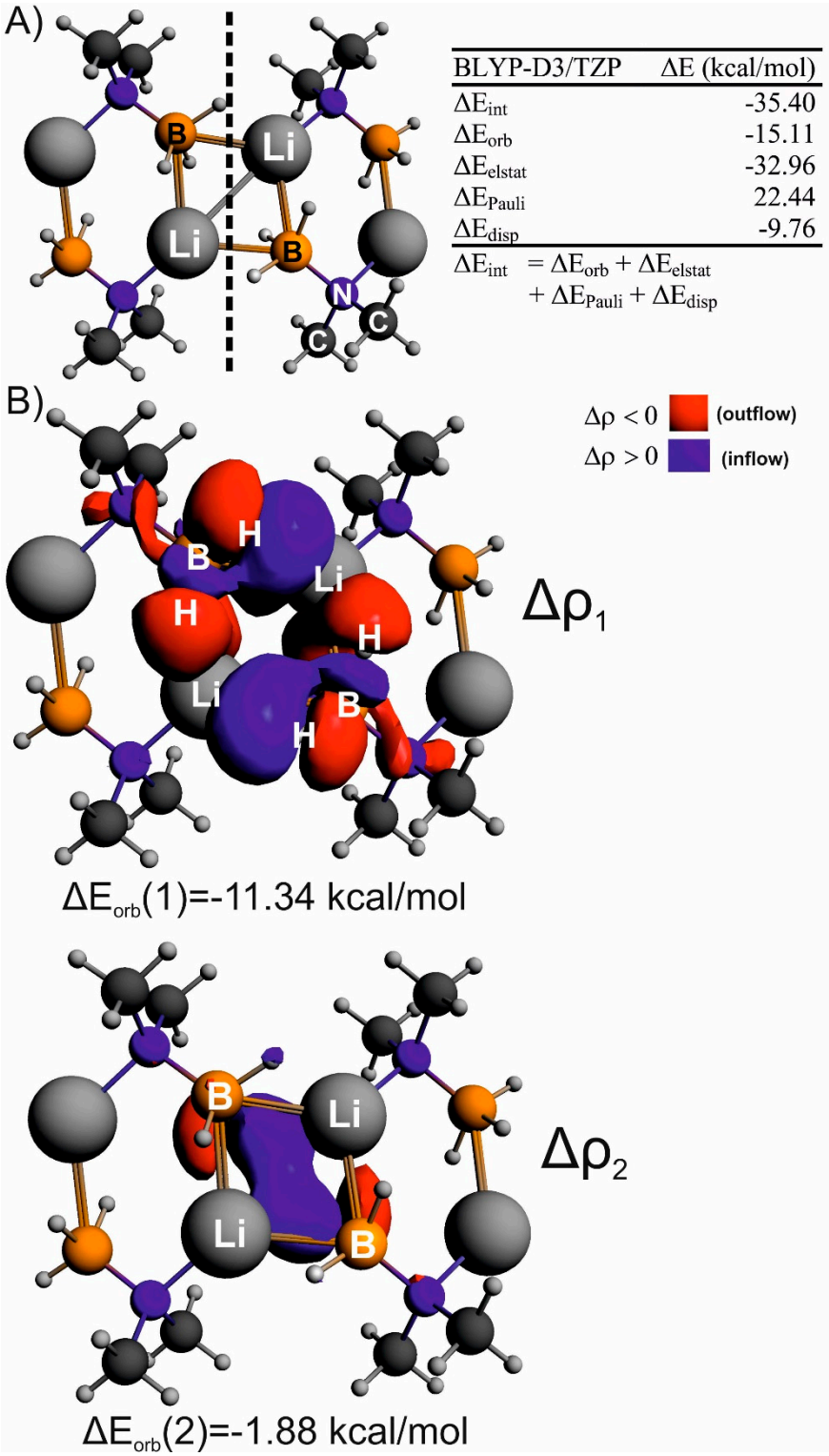
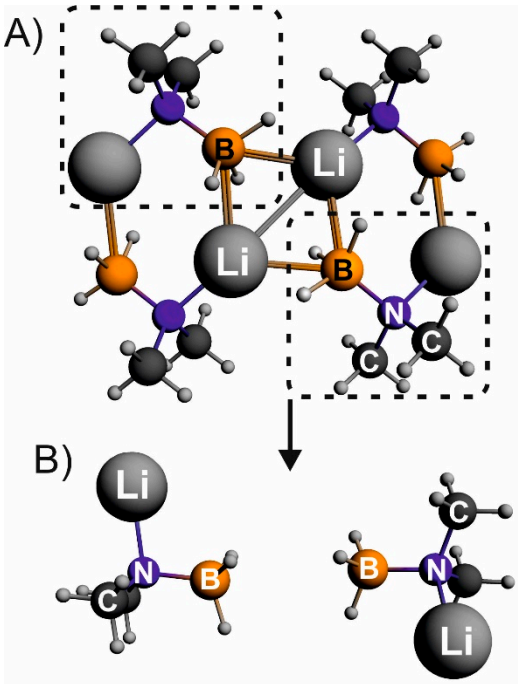


Figure S2. The tetrameric cluster model of $LiN(CH_3)_2BH_3$ directly taken from the crystal structure along with energy decomposition results describing the interaction between two dimeric fragments in $LiN(CH_3)_2BH_3$ (part **A**). Fragmentation pattern used in ETS-NOCV analysis is indicated by black dotted line. Part (**B**) displays the most relevant deformation density contributions describing Li···H–B interactions. Red color of deformation densities shows charge depletion, whereas blue an electron accumulation due to Li···H–B interaction.



BLYP-D3/TZP	ΔE (kcal/mol)
ΔE_{int}	6.18
ΔE_{orb}	-1.90
ΔE_{elstat}	7.08
ΔE_{Pauli}	3.09
ΔE_{disp}	-2.10

$$\Delta E_{int} = \Delta E_{orb} + \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{disp}$$

Figure S3. Dimer of $LiN(CH_3)_2BH_3$ from the crystal structure containing BH···B interactions together with results of ETS-NOCV analysis (in part (**B**)). Dimer was cut from the crystal structure as it is marked with black dotted lines (part (**A**)).

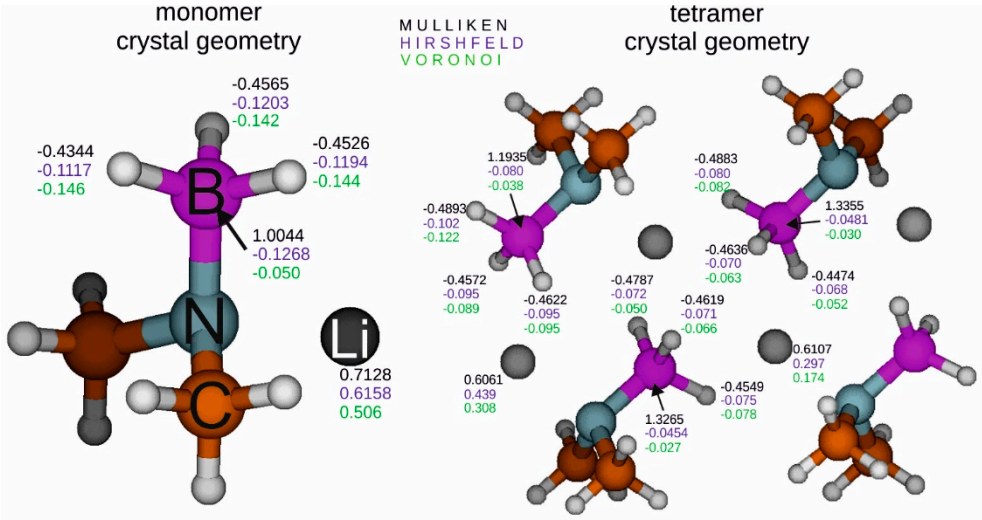


Figure S4. Atomic charges for the monomer and crystal tetramer of $LiNMe_2BH_3$ obtained from the Mulliken (black), Voronoi (green) and Hirshfeld (blue) approaches.

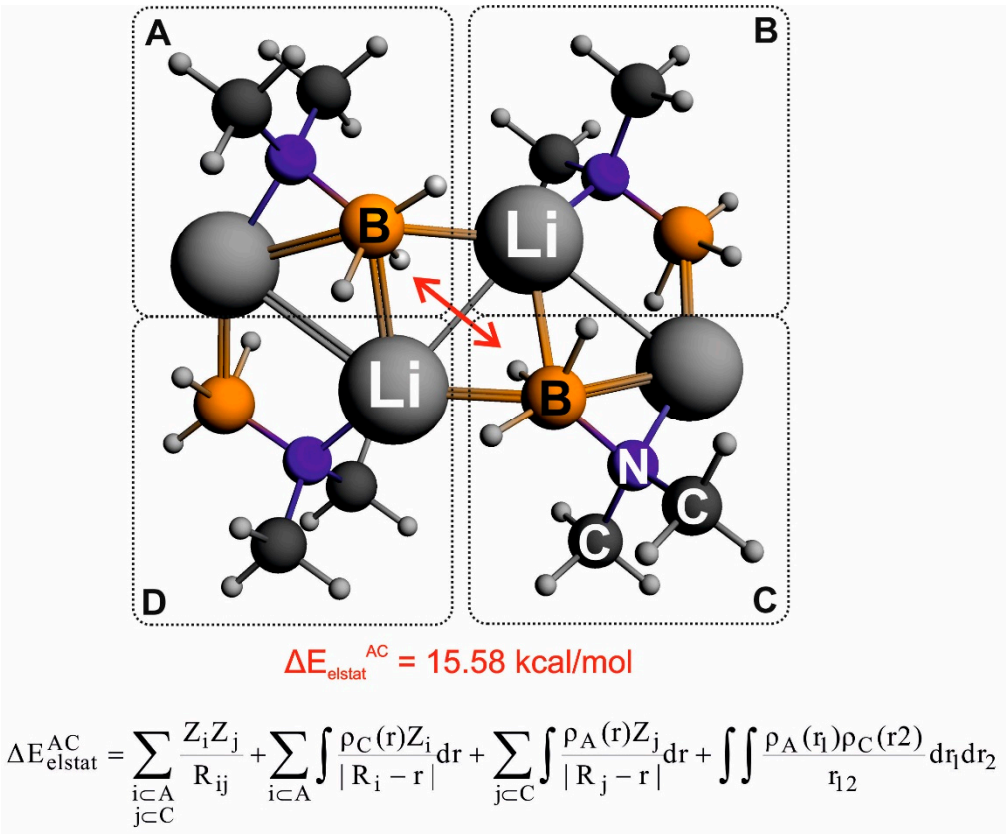


Figure S5. The electrostatic interaction between the monomers of $LiNMe_2BH_3$ connected through BH_3 units (**A**,**C**) calculated in the presense of the remaining two monomers (**B**,**D**).

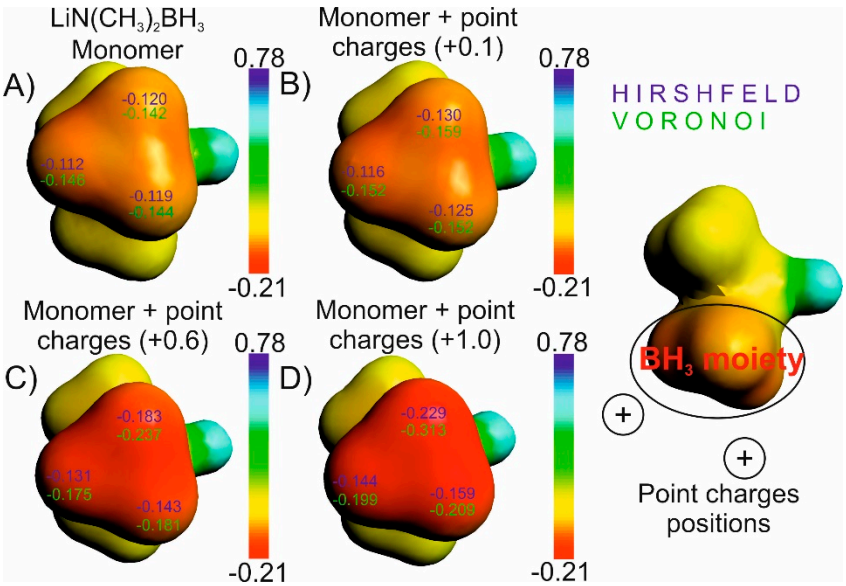


Figure S6. The contours of molecular electrostatic potential for the $LiNMe_2BH_3$ monomer in the presense of point charges (placed in the Li positions) with different values: +0.1a.u, +0.6a.u. and 1.0 a.u. In addition Hirshfeld and Voronoi atomic charges are depicted.