

# Superoctahedral two-dimensional metallic boron with peculiar magnetic properties

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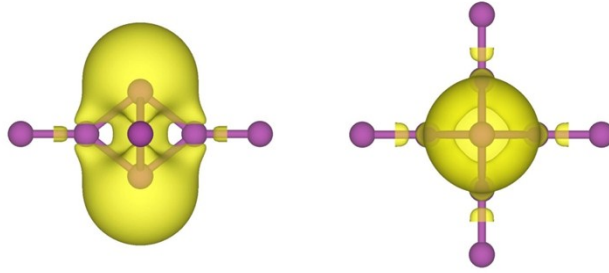
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KEYWORDS: ferromagnetic boron, two-dimensional ferromagnetism, SSAdNDP analysis

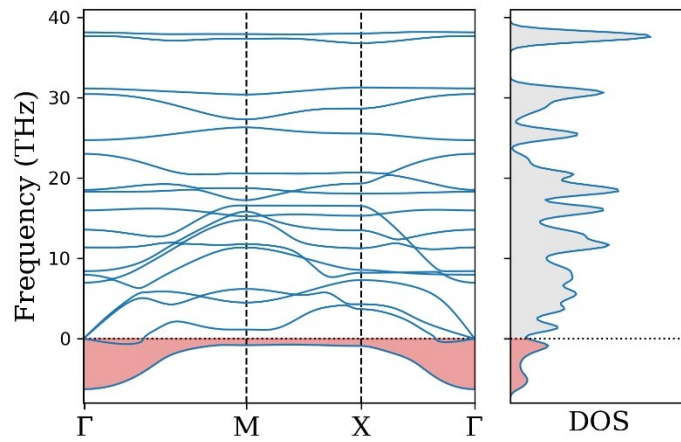
## Supporting Information

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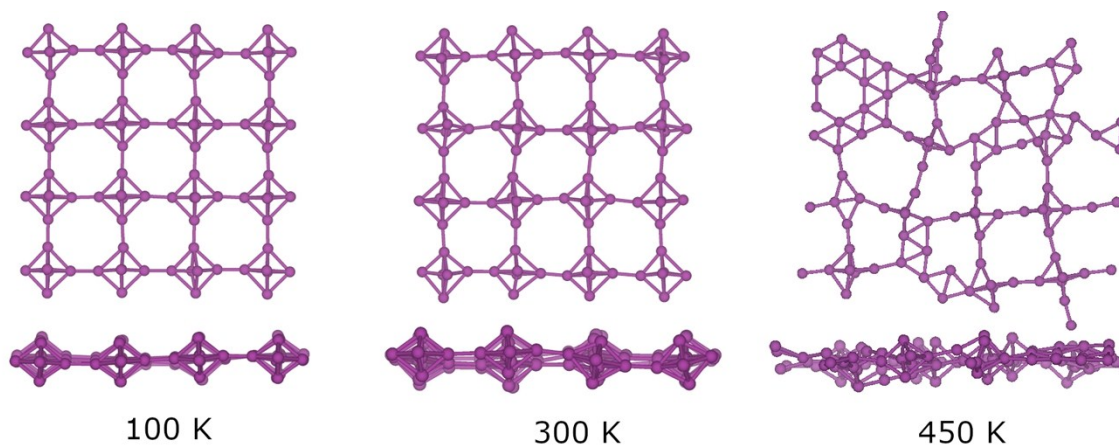
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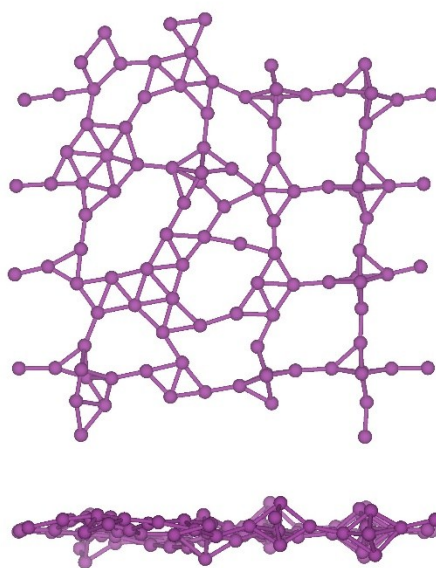
**Figure S1.** Spin charge density distribution with isosurface  $0.002 \text{ e}/\text{\AA}^{-3}$  for the ferromagnetic 2D-B<sub>6</sub>.



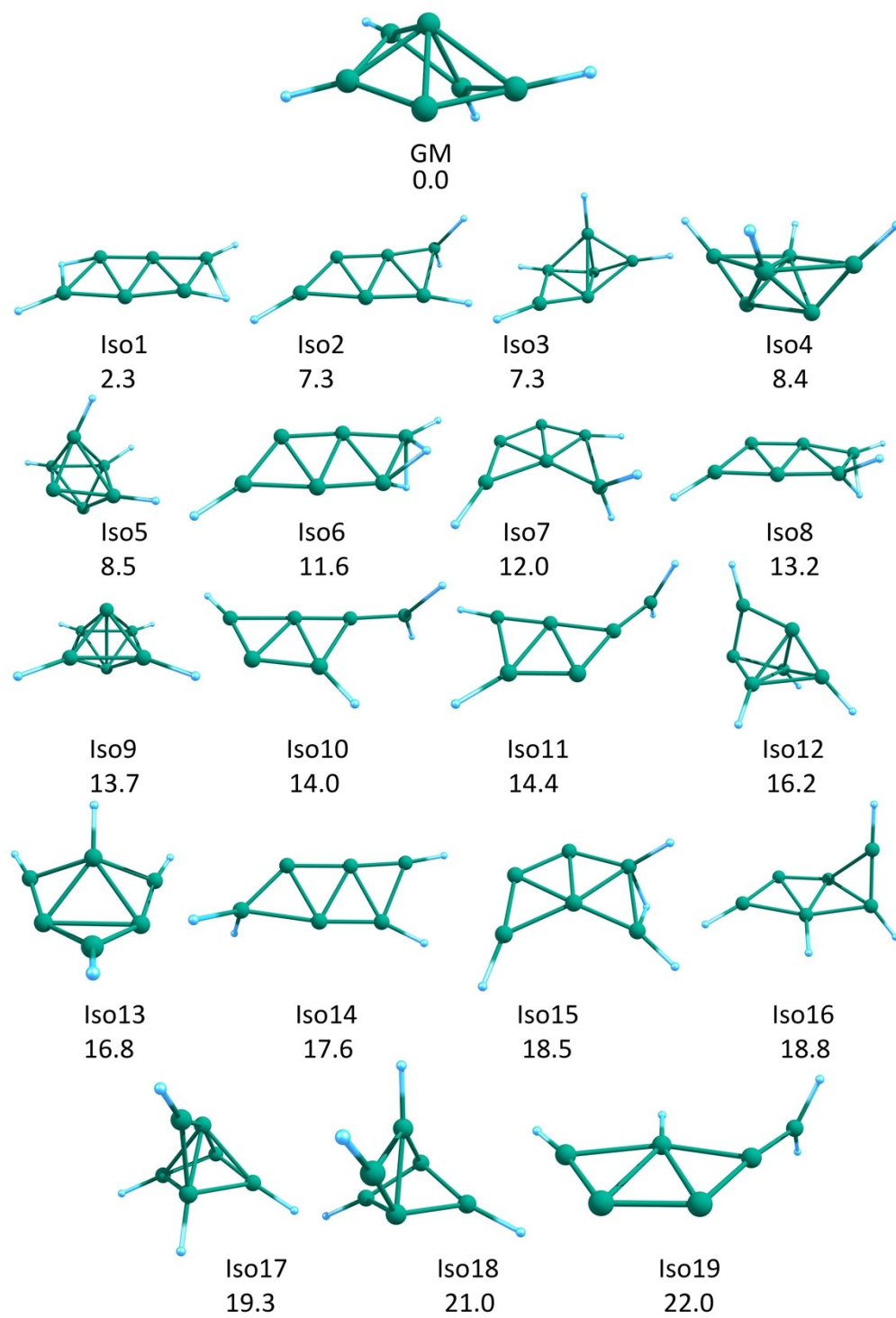
**Figure S2.** Calculated phonon dispersion curves along  $\Gamma$ -M-X- $\Gamma$  path and phonon density of states for the nonmagnetic 2D-B<sub>6</sub>.



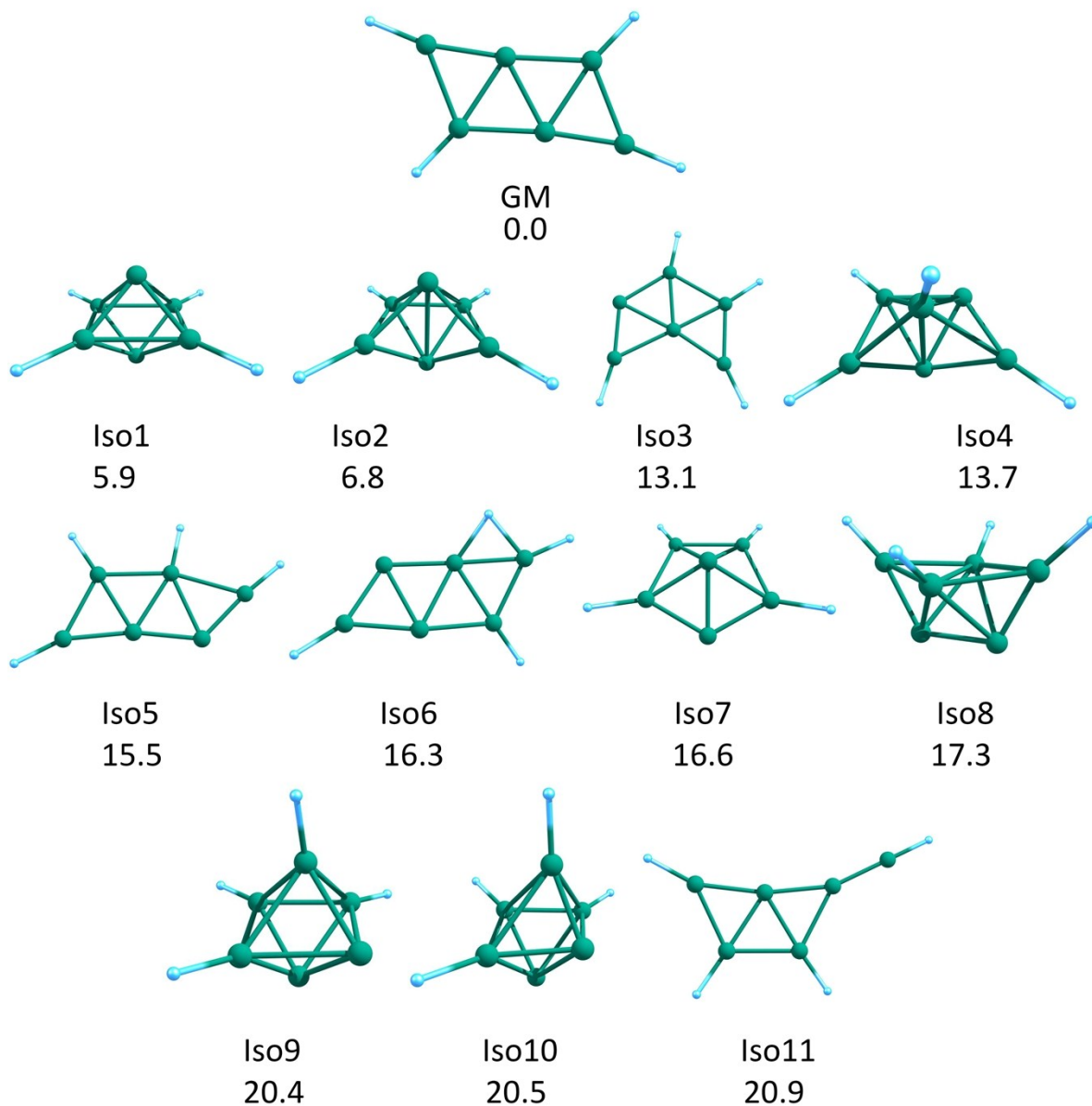
**Figure S3.** Top and side views of final frames of each MD simulation test at different temperatures.



**Figure S4.** Top and side views of final frame of MD simulation test after 3.5 ps at 600 K.



**Figure S5.** Structures and relative energies of the lowest  $B_4H_6$  singlet isomers.

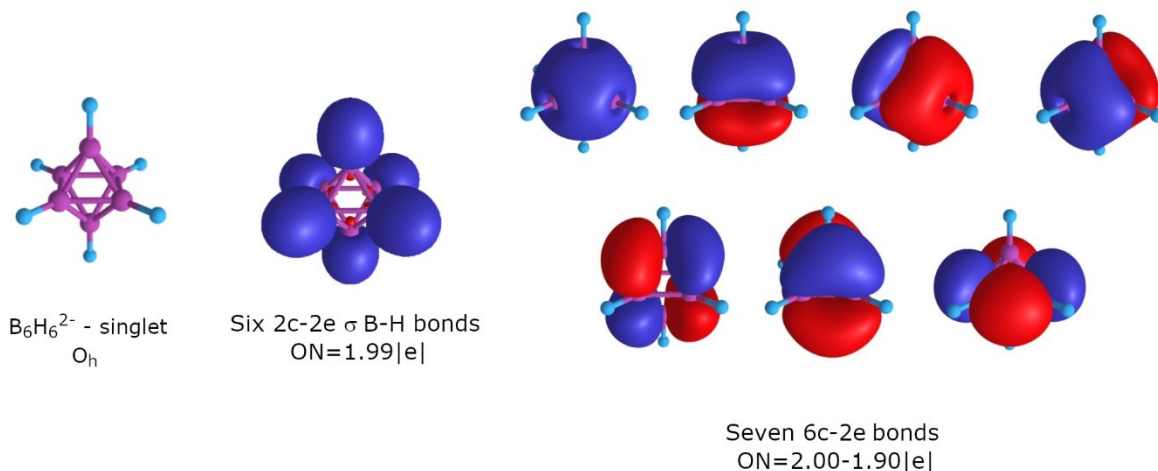


**Figure S6.** Structures and relative energies of the lowest  $B_4H_6$  triplet isomers.

### Chemical bonding analysis of $B_6H_6^{2-}$ , $B_6H_4^{2-}$ and $B_6H_4$ species.

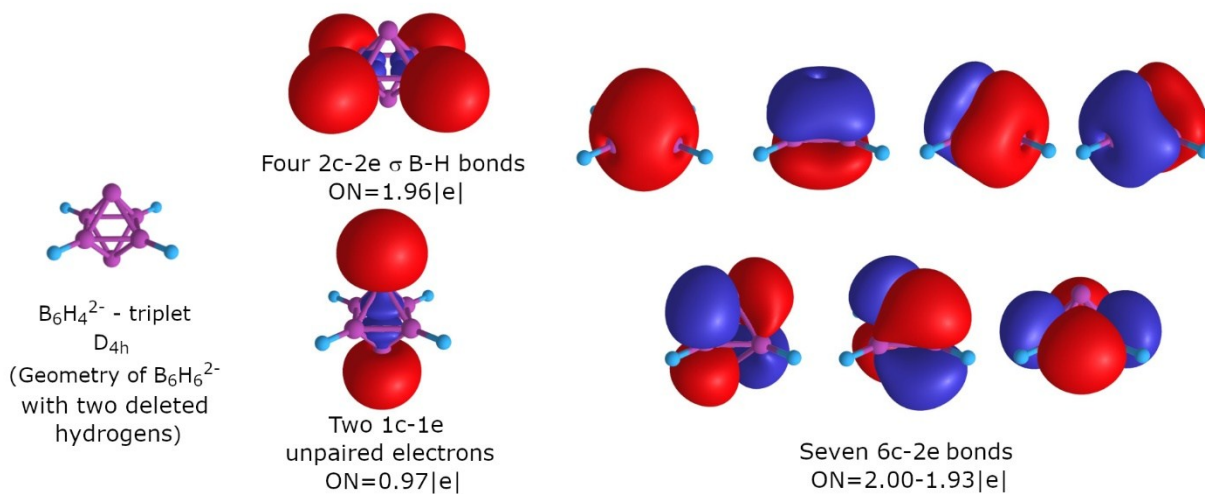
To reveal the bonding pattern evolution from  $B_6H_6^{2-}$  molecule to  $B_6H_4$  molecule, we should start our analysis from the former species. The structure was optimized at PBE0/aug-cc-

pvtz level. The AdNDP results are shown in Figure S7. The bonding pattern consists of six 2c-2e B-H  $\sigma$ -bonds with  $\text{ON}=1.99|e|$  and seven 6c-2e bonds with  $\text{ON}=2.00-1.90|e|$ .



**Figure S7.** Overall bonding pattern for  $\text{B}_6\text{H}_6^{2-}$  molecule.

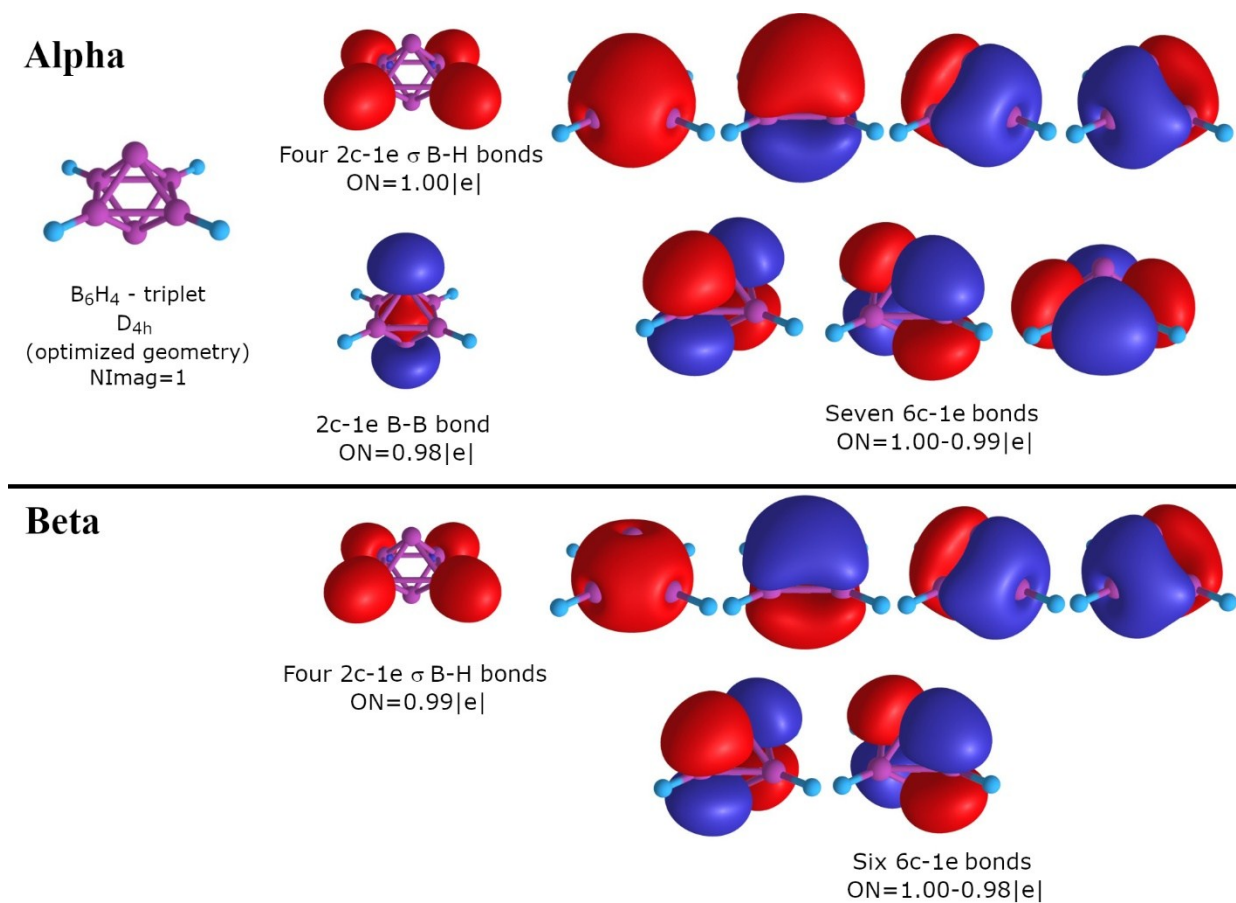
To observe the further change in bonding pattern, we detached two hydrogens from the top and from the bottom of the  $\text{B}_6\text{H}_6^{2-}$  octahedron (obtaining  $\text{B}_6\text{H}_4^{2-}$  molecule). Without the optimization of the geometry we calculated bonding pattern for this molecule in the triplet state. The results are shown in Figure S8.



**Figure S8.** Overall bonding pattern for  $\text{B}_6\text{H}_4^{2-}$  molecule in the triplet state.

Predictably, the four 2c-2e B-H  $\sigma$ -bonds and seven 6c-2e bonds preserve the same as in the case of  $B_6H_6^{2-}$ . The remaining two alpha electrons are localized in two 1c-1e unpaired electrons on boron atoms.

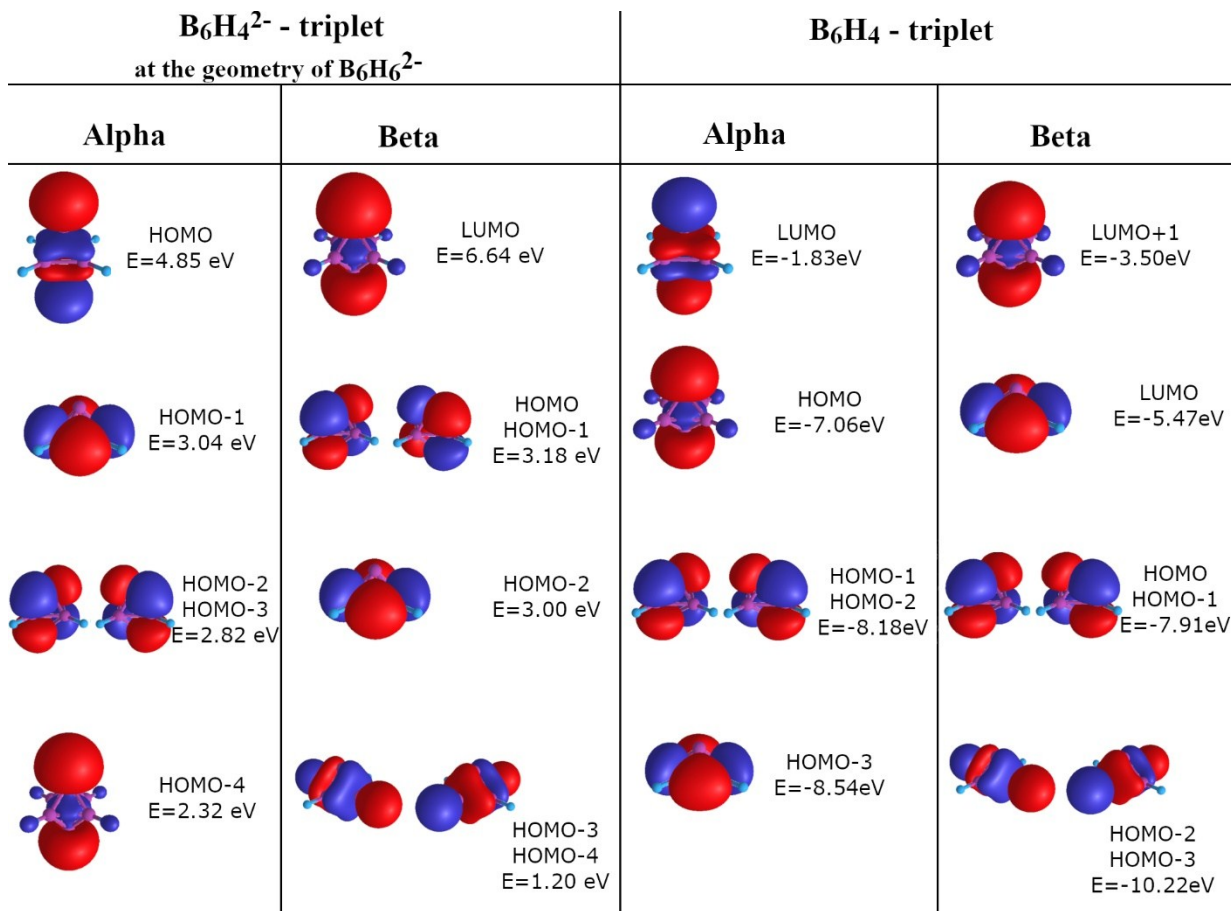
The things become more interesting if we detach two electrons from the  $B_6H_4^{2-}$  structure. The following bonding pattern was obtained for the optimized geometry, that forced it to be  $D_{4h}$  to preserve symmetry of the 2D-B6 plane. The results are shown in Figure S9. Surprisingly, we found that we can not localize 1c-1e unpaired alpha electrons anymore. Instead of those unpaired electrons the new 2c-1e B-B bond appears. Moreover, one electron from beta 6c-2e bond is gone.



**Figure S9.** Overall bonding pattern for  $B_6H_4$  molecule in the triplet state. Alpha and beta electron bonds are presented separately.



To make sure that the presented pattern is consistent with MOs, we performed the analysis of MOs for  $B_6H_4^{2-}$  and  $B_6H_4$  molecules (Fig. S10). Analyzing this picture, we can notice that linear combination of HOMO and HOMO-4 for  $B_6H_4^{2-}$  alpha electrons will give us two 1c-1e unpaired electrons on boron atoms. There are no such analogical orbitals for beta electrons, which is consistent with the AdNDP picture for  $B_6H_4^{2-}$ . We also can notice that by detaching one alpha electron it should go away from the alpha HOMO orbital, so in  $B_6H_4$  we cannot built any linear combination to obtain unpaired 1c-1e bonds. Thus, two 1c-1e bonds transform to one 2c-1e. The picture of MOs for beta electrons is consistent with AdNDP analysis too.



**Figure S10.** HOMOs and LUMOs with orbital energies for  $B_6H_4^{2-}$  and  $B_6H_4$  structures.