Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

SUPPLEMENTARY INFORMATION

Pentagonal five-center four-electron π bond in ternary $B_3N_2H_5$ cluster: an extension of the concept of three-center four-electron ω bond†

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Figure S1. Alternative optimized low-lying structures of $B_3N_2H_5$ neutral cluster at the B3LYP/aug-cc-pVTZ level. Relative energies are indicated in kcal mol^{-1} at B3LYP with zero-point energy (ZPE) corrections, as well as at the single-point CCSD(T) level (in the parentheses) for top 4 isomers. The B, N, and H atoms are in pink, blue, and gray, respectively.

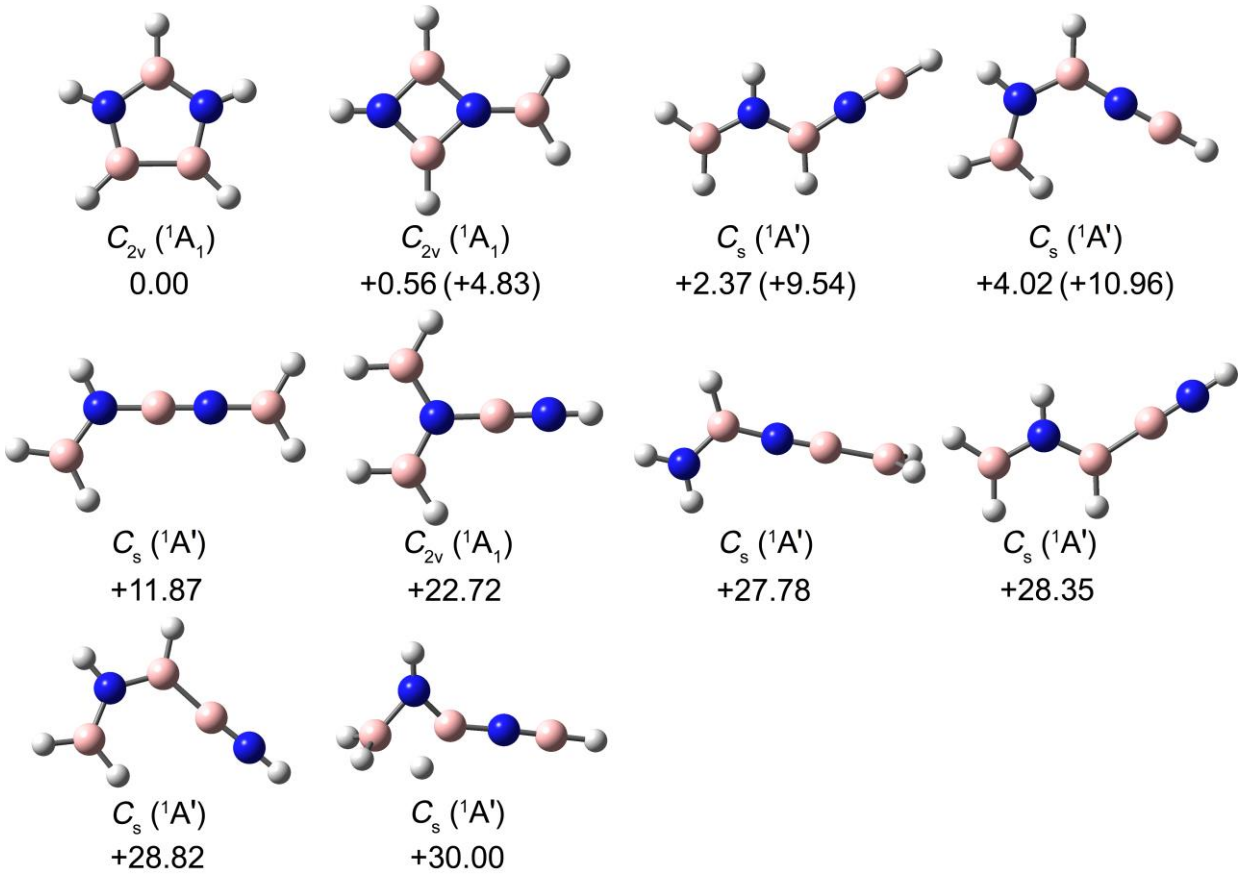


Figure S2. Alternative optimized low-lying structures of $B_3N_2H_5^-$ monoanion cluster at the B3LYP/aug-cc-pVTZ level. Relative energies are indicated in kcal mol^{-1} at B3LYP with zero-point energy (ZPE) corrections, as well as at the single-point CCSD(T) level (in the parentheses) for top 4 isomers. The B, N, and H atoms are in pink, blue, and gray, respectively.

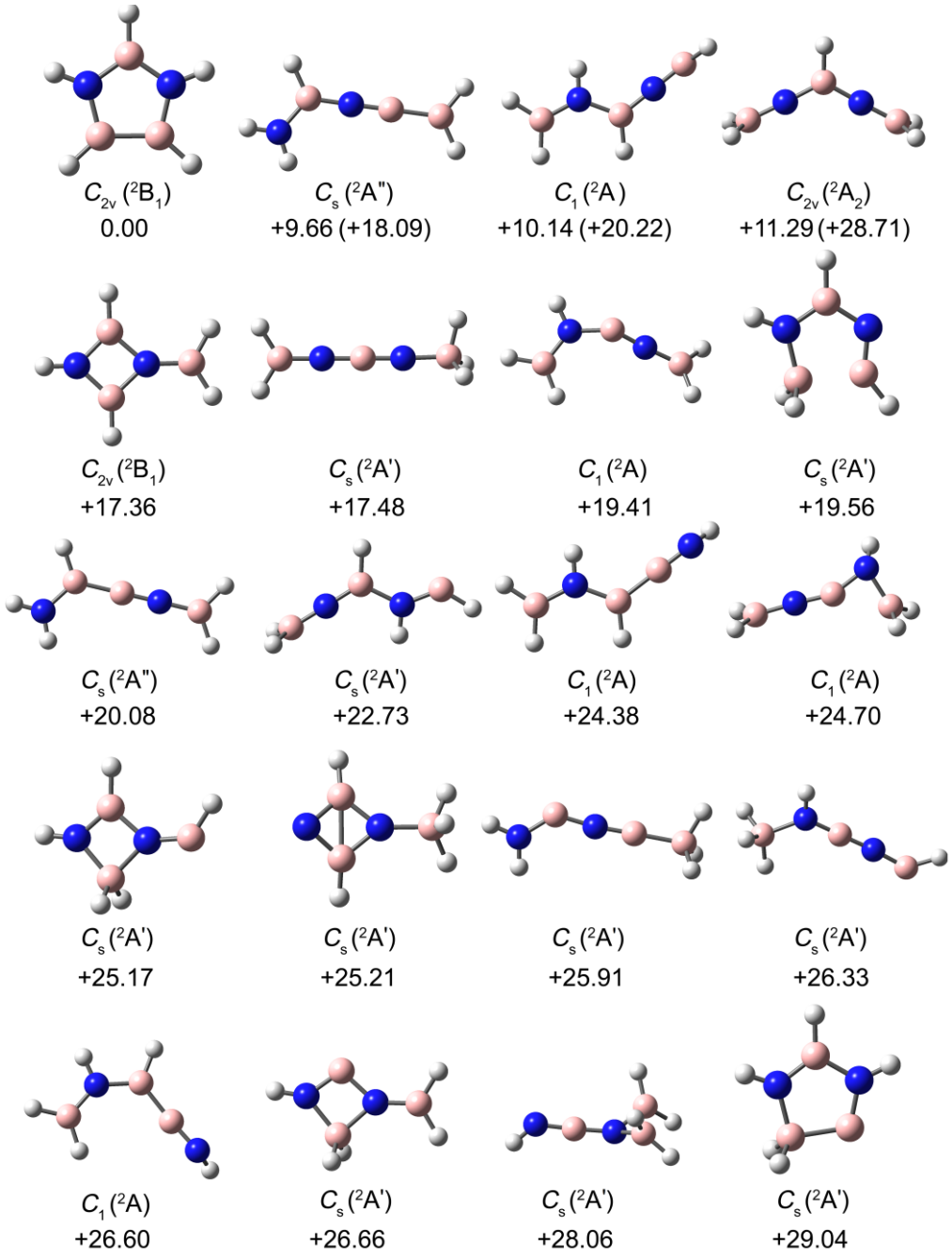


Figure S3. Alternative optimized low-lying structures of $B_3N_2H_5^{2-}$ dianion cluster at the B3LYP/aug-cc-pVTZ level. Relative energies are indicated in kcal mol^{-1} at B3LYP with zero-point energy (ZPE) corrections, as well as at the single-point CCSD(T) level (in the parentheses) for top 4 isomers. The B, N, and H atoms are in pink, blue, and gray, respectively.

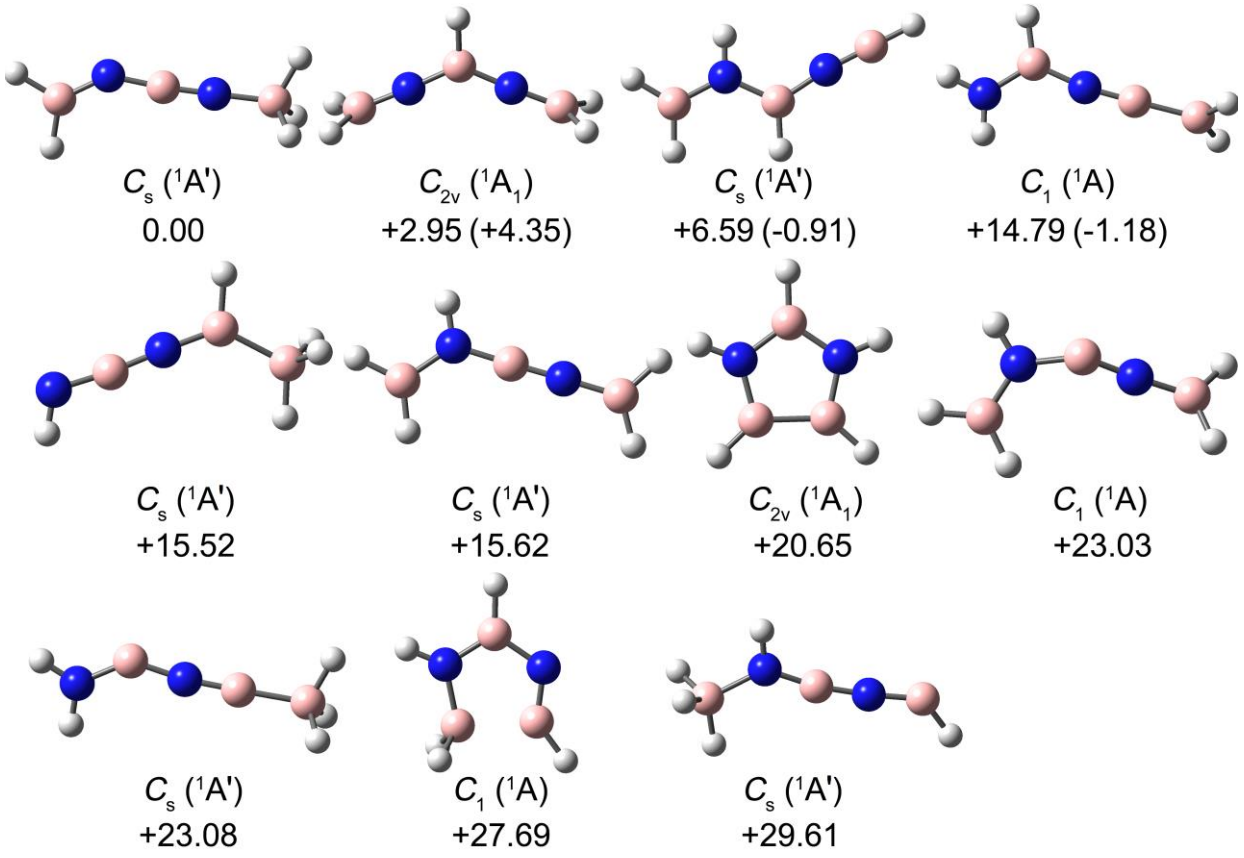


Figure S4. Structure and bonding of the chain-like isomer of $B_3N_2H_5^{2-}$. The B–N distances (from left to right) are 1.36, 1.38, 1.27, and 1.50 Å, respectively. Two extra charges are located primarily on the two N centers (26% versus 43%). (a) Optimized C_s ($^1A'$) structure at the B3LYP/aug-cc-pVTZ level. (b) Lewis presentation.

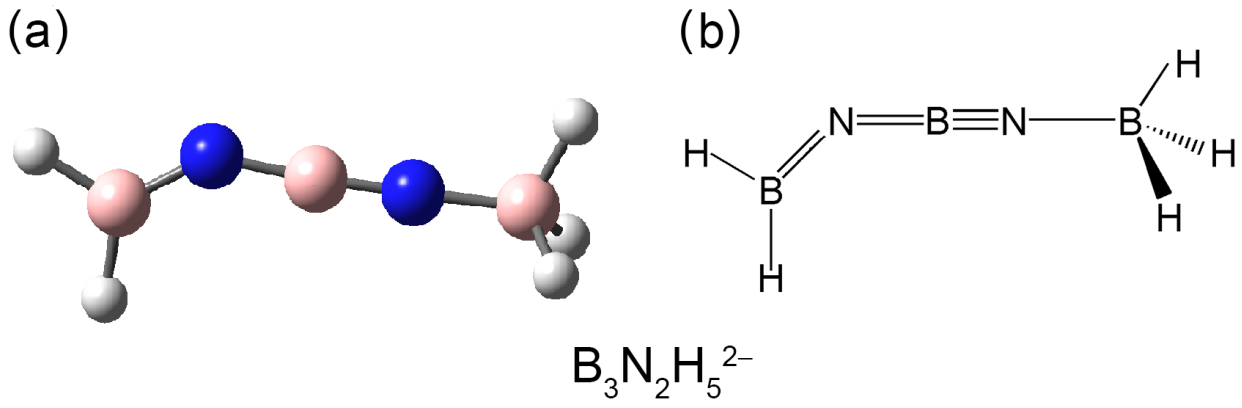


Figure S5. Bonding pattern of the chain-like open structure C_s ($^1A'$) of $B_3N_2H_5^{2-}$ dianion cluster, based on the adaptive natural density partitioning (AdNDP) analysis. Occupation numbers (ONs) are shown.

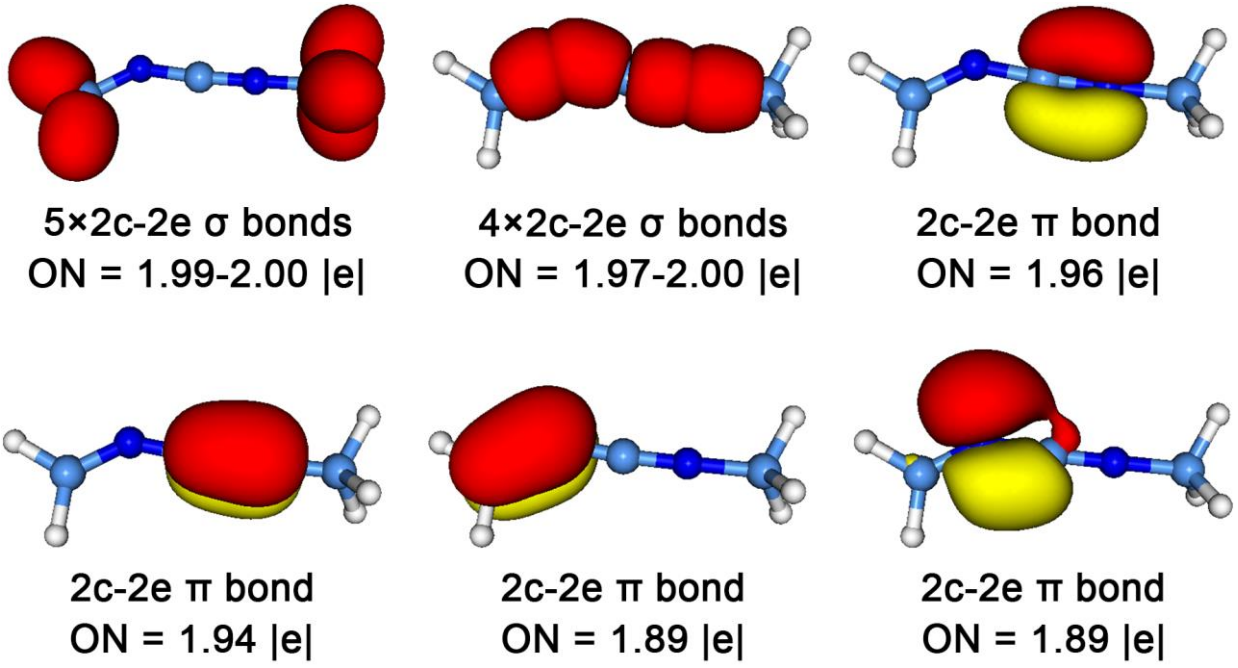
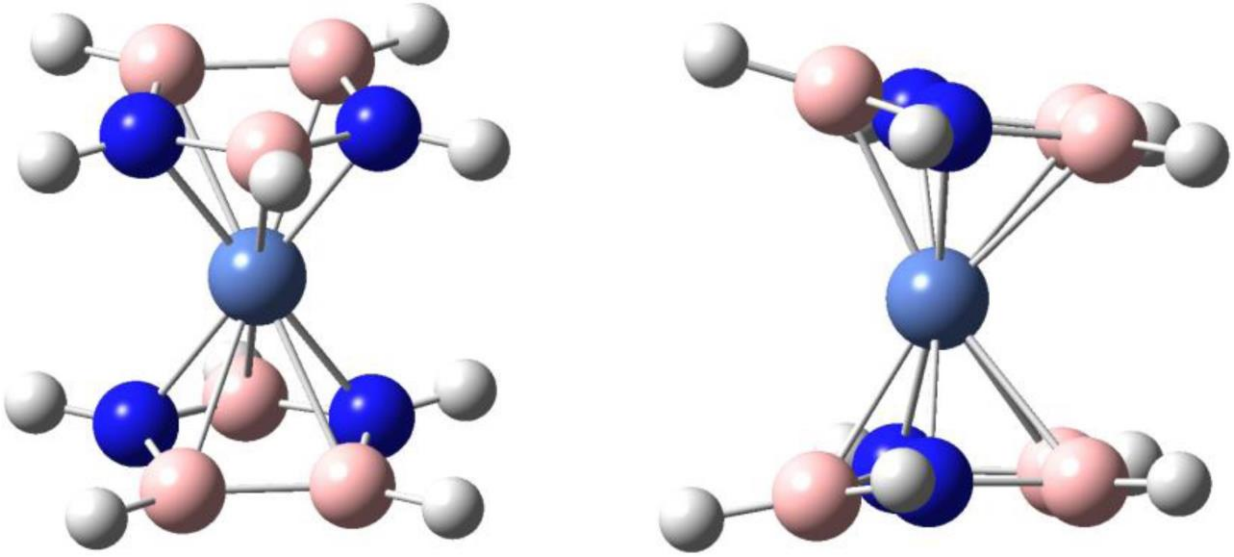


Figure S6. Optimized sandwich complexes of C_{2h} [$(B_3N_2H_5)_2Ni$] (^1A_g) and C_{2v} [$(B_3N_2H_5)_2Ni$] ($^1A_1$) at the B3LYP level. Calculated lowest vibrational frequencies (ν_{min}) are also given. The C_{2h} structure is more stable (by 6.07 kcal mol^{-1}) than the C_{2v} one. The B atom is in pink, N in blue, and H in gray.



C_{2h} [$(B_3N_2H_5)_2Ni$] (^1A_g)
114.27 cm^{-1}

C_{2v} [$(B_3N_2H_5)_2Ni$] ($^1A_1$)
100.92 cm^{-1}