Searching for doubly $\sigma$- and $\pi$-aromaticity in borazine derivatives

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Figure S1.- Structures, symmetry point group and relative energy of the 23 lowest energy singlet state structures (within the range of 0-135 kcal·mol⁻¹ with respect to the putative global minimum structure) of the B₃N₃H₆⁺ system at the PBE0-D3/def2-TZVP level. Relative energies are listed in kcal·mol⁻¹, with zero-point energy (ZPE) corrections. *AUTOMATON did not identify the structure.
Figure S2. Structures, symmetry point group and relative energy of the 19 lowest energy singlet state structures within the range of 0-69 kcal·mol$^{-1}$ with respect to the putative global minimum structure of the B$_3$N$_3$(TeH)$_6^{2+}$ system at the PBE0-D3/def2-TZVP level. Relative energies are listed in kcal·mol$^{-1}$, with zero-point energy (ZPE) corrections.
Figure S3. Structures, symmetry point group and relative energy of the 10 lowest energy singlet state structures (within the range of 0-30 kcal·mol$^{-1}$ with respect to the putative global minimum structure) of the B$_3$N$_3$I$_6^{2+}$ system at the PBE0-D3/def2-TZVP level. Relative energies are listed in kcal·mol$^{-1}$, with zero-point energy (ZPE) corrections.
**Figure S4.** Structures, symmetry point group and relative energy of the 4 lowest energy triplet state structures within the range of 0-30 kcal·mol$^{-1}$ with respect to the putative global minimum structure of the B$_3$N$_3$I$_6^{2+}$ system at the PBE0-D3/def2-TZVP level. Relative energies are listed in kcal·mol$^{-1}$, with zero-point energy (ZPE) corrections.
Figure S5. AdNDP bonding pattern of $B_3N_3(\text{TeH})_6^{2+}$

- $6 \times 1c\text{-}2e$ Te-LPs
  - ON = 1.98 – 1.99 |e|

- $6 \times 2c\text{-}2e$ Te-H σ-bonds
  - ON = 1.97 – 2.00 |e|

- $6 \times 2c\text{-}2e$ B-N σ-bonds
  - ON = 1.98 |e|

- $6 \times 2c\text{-}2e$ B(N)-Te σ-bonds
  - ON = 1.97 – 1.98 |e|

- $3 \times 6c\text{-}2e$ π-bonds
  - ON = 1.98 – 1.99 |e|

- $5 \times 6c\text{-}2e$ σ-bonds
  - ON = 1.92 – 1.97 |e|
Figure S6. Vector maps of dissected Magnetically induced current density (MICD) at 1 $a_0$ above the molecular plane of $B_3N_3(\text{TeH})_6^{2+}$

(a) $B_3N_3(\text{TeH})_6^{2+}$ outer-$\sigma$ current density map

8.5 nA.T$^{-1}$

(b) $B_3N_3(\text{TeH})_6^{2+}$ inner-$\pi$ current density map

3.6 nA.T$^{-1}$
Table S1. Extra cyclic resonance energies (kcal/mol) and RCSs values (nA/T) of five member rings C₄XH₄.

| Compound | ECRE | RCS (X1-C2) | RCS (C3-C4) |
|----------|------|-------------|-------------|
| AlH      | -3.5 | -3.0        | -2.8        |
| CH⁻      | 19.1 | 13.1        | 13.1        |
| CH₂      | 3.4  | 5.6         | 5.7         |
| NH       | 17.9 | 11.6        | 12.0        |
| O        | 12.8 | 10.2        | 10.5        |
| PH       | 17.9 | 12.5        | 12.8        |
| S        | 12.7 | 11.9        | 12.1        |
| SiH⁺     | -15.5| -10.4       | -10.1       |
| SiH⁻     | 17.2 | 12.5        | 12.4        |
| SiH₂     | -0.8 | 1.7         | 1.8         |

Scheme S1. Resonance energy definitions of five membered rings and their acyclic counterparts according to ref. 60.

E⁰_R(1)
Table S2.- Cartesian coordinates at the PBE0/def2-TZVP level of the global minimum of B₃N₃H₃⁺, B₃N₃(TeH)₆²⁺ and B₃N₃I₆²⁺. Coordinates for the doubly aromatic local minimum (B₃N₃H₃⁺, and B₃N₃(TeH)₆²⁺) and lowest triplet of B₃N₃I₆²⁺ are also included. Relative energies are listed in kcal·mol⁻¹.

|                  | B₃N₃H₃⁺ (0.00) singlet state | B₃N₃H₃⁺ (49.30) singlet state | B₃N₃I₆²⁺ (0.00) singlet state | B₃N₃I₆²⁺ (2.00) triplet state | B₃N₃(TeH)₆²⁺ (0.00) singlet state | B₃N₃(TeH)₆²⁺ (68.69) singlet state |
|------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|---------------------------------|-----------------------------------|
|                  | H 4.595360000 -0.000687000 -0.000422000 | B -0.962163000 0.000000000 0.000000000 | B -1.126786000 -0.713673000 0.000000000 | B -1.126786000 -0.713673000 0.000000000 | Te -3.312911000 -1.496944000 -0.095722000 | Te -3.312911000 -1.496944000 -0.095722000 |
|                  | H -3.647992000 -0.849144000 0.000226000 | B 0.481083000 0.833258000 0.000000000 | B -1.245264000 0.715413000 0.000000000 | B -1.245264000 0.715413000 0.000000000 | Te 3.154792000 1.425438000 0.999906000 | Te 3.154792000 1.425438000 0.999906000 |
|                  | B 3.424898000 -0.000474000 -0.000187000 | B 0.481083000 -0.833258000 0.000000000 | N 2.158522000 -0.000007000 0.000600000 | N -0.804731000 -1.393893900 0.000000000 | N 2.158522000 -0.000007000 0.000600000 | N -0.804731000 -1.393893900 0.000000000 |
|                  | H -3.648940000 0.847917000 0.000221000 | N 0.000000000 3.076241000 0.000000000 | N 0.000000000 3.076241000 0.000000000 | N 0.000000000 3.076241000 0.000000000 | I 2.990960000 -1.977917000 0.000000000 | I 2.990960000 -1.977917000 0.000000000 |
|                  | N 3.100004000 -0.000443000 0.000154000 | N 0.000000000 3.076241000 0.000000000 | N 0.000000000 3.076241000 0.000000000 | N 0.000000000 3.076241000 0.000000000 | 1.161433000 -0.804731000 0.000000000 | 1.161433000 -0.804731000 0.000000000 |
|                  | B 0.835464000 0.000471000 -0.000077000 | B 2.091598000 0.000000000 0.000000000 | B 1.269102000 -0.714011000 0.000000000 | B 1.269102000 -0.714011000 0.000000000 | 1.375691000 0.000000000 0.000000000 | 1.375691000 0.000000000 0.000000000 |
|                  | B -1.755249000 0.000371000 -0.000151000 | N 2.986723000 1.425438000 0.099906000 | N 2.986723000 1.425438000 0.099906000 | N 2.986723000 1.425438000 0.099906000 | 2.903897000 -1.019116000 0.000000000 | 2.903897000 -1.019116000 0.000000000 |
|                  | N -0.461945000 0.000498000 -0.000461000 | B 3.647992000 1.425438000 0.099906000 | B 3.647992000 1.425438000 0.099906000 | B 3.647992000 1.425438000 0.099906000 | 0.019841000 -1.019116000 0.000000000 | 0.019841000 -1.019116000 0.000000000 |
|                  |                                |                               |                               |                               |                                |                                  |

- (TeH) is also included. Relative energies are listed in kcal·mol⁻¹.