Electronic Supplementary Material (ESI) for RSC Advances.

Searching for doubly σ- and π-aromaticity in borazine derivatives

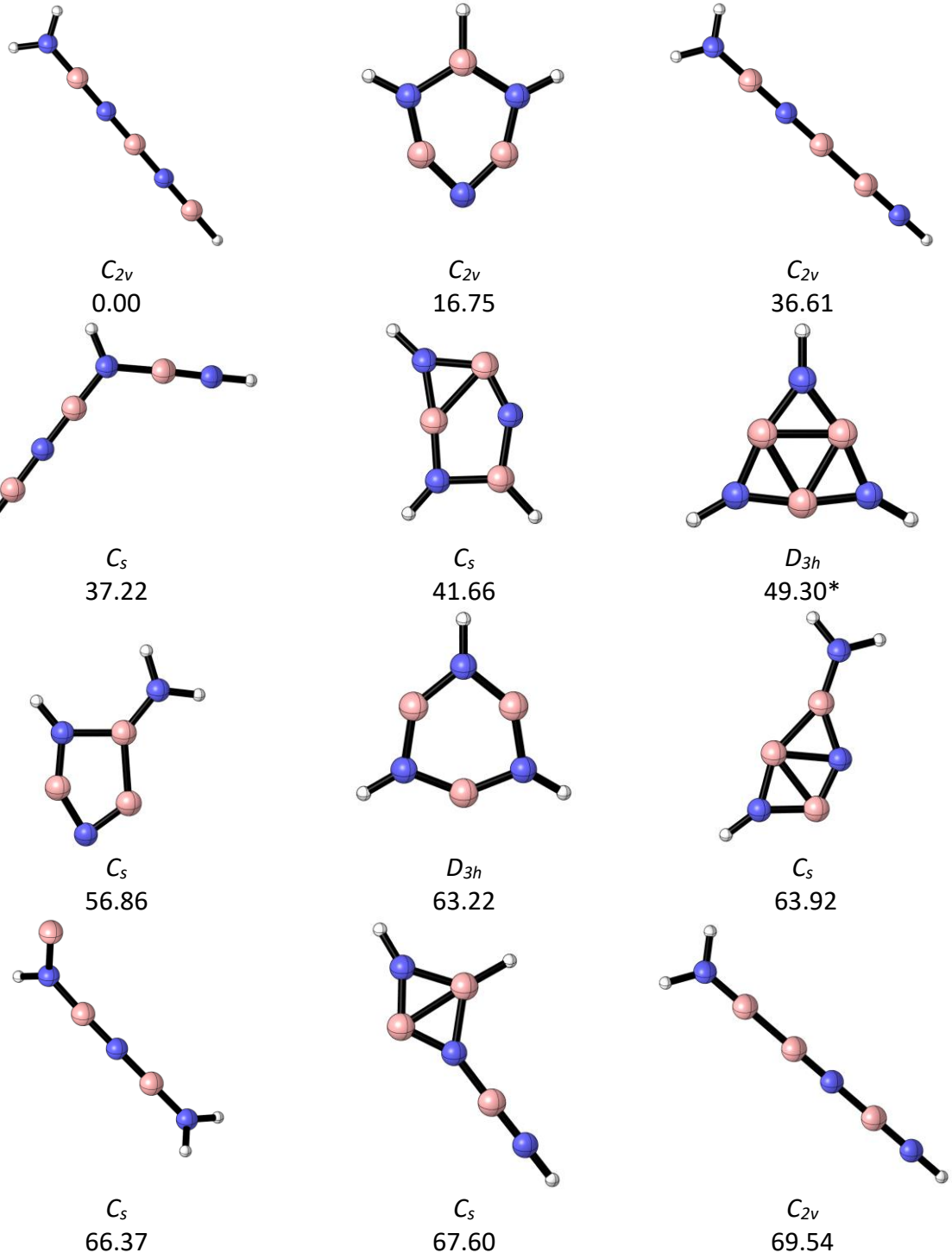
Ricardo Pino-Rios[a], Alejandro Vásquez-Espinal[b], Osvaldo Yañez[b,c] and William Tiznado*[b]*

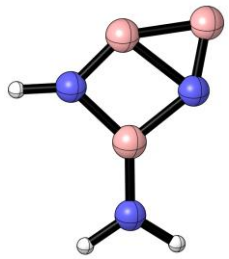
[a]Laboratorio de Química Teórica, Facultad de Química y Biología, Universidad de Santiago de Chile (USACH), Av. Libertador Bernardo O'Higgins 3363, Santiago, Estación Central, Región Metropolitana, Chile

[b]Computational and Theoretical Chemistry Group, Departamento de Ciencias Químicas, Facultad de Ciencias Exactas, Universidad Andres Bello, República 498, Santiago, Chile.

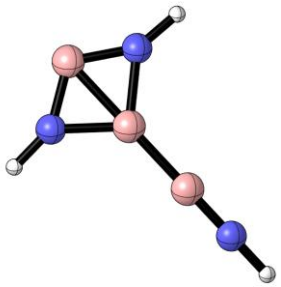
[c]Center for Bioinformatics and Integrative Biology (CBIB), Facultad de Ciencias de la Vida, Universidad Andres Bello, Av. Republica 330, Santiago 8370146, Chile

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 $B_3N_3H_3^+$ 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.

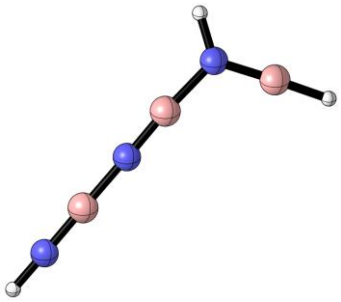




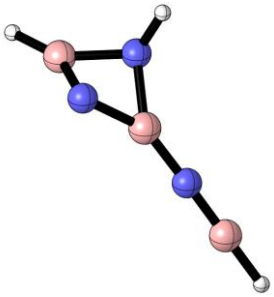
C_s
71.27



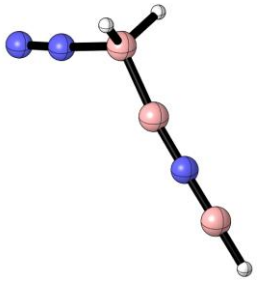
C_{2v}
74.08



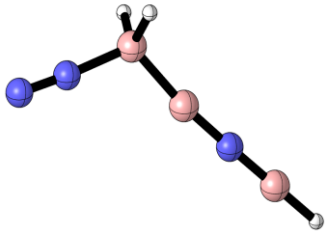
C_s
74.60



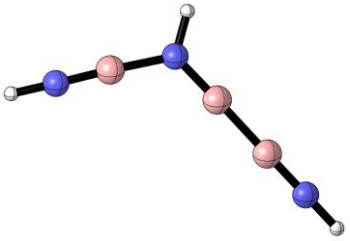
C_1
75.69



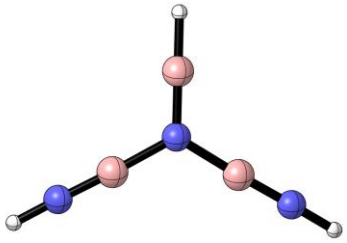
C_s
77.74



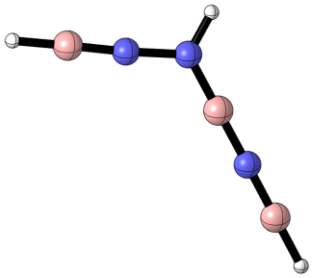
C_s
77.74



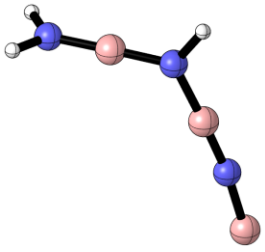
C_s
81.73



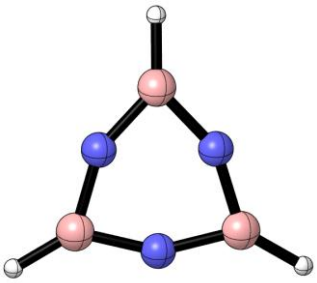
C_{2v}
85.83



C_s
86.64

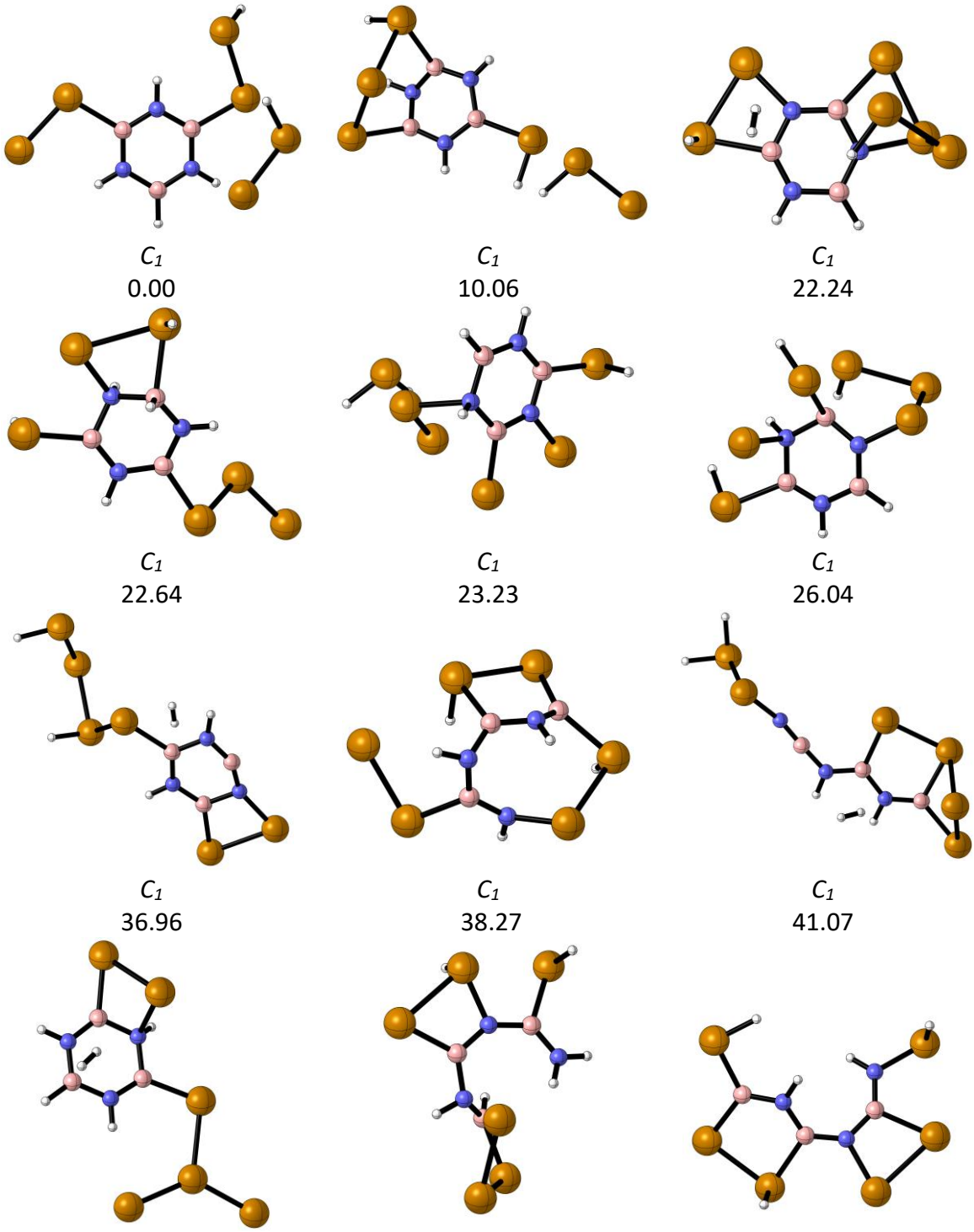


C_s
90.64

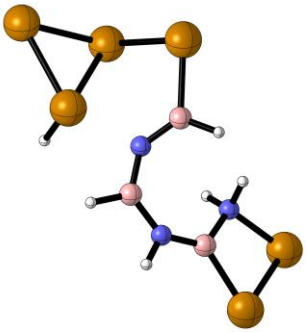


D_{3h}
134.35

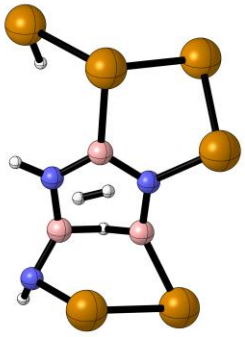
Figure S2. Structures, symmetry point group and relative energy of the 19 lowest energy singlet state structures within the range of 0-69 kcal·mol^{-1} with respect to the putative global minimum structure of the $B_3N_3(TeH)_6^{2+}$ system at the PBE0-D3/def2-TZVP level. Relative energies are listed in kcal·mol^{-1}, with zero-point energy (ZPE) corrections.



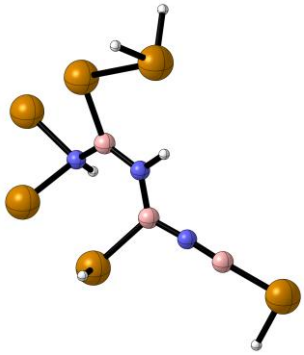
C_1
44.83



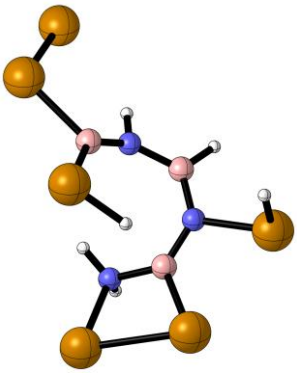
C_1
45.43



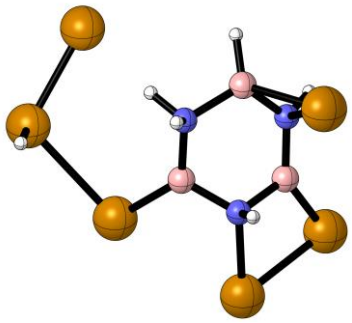
C_1
49.99



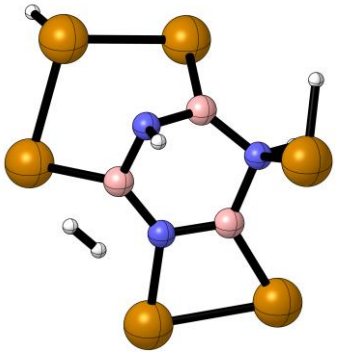
C_1
50.83



C_1
56.53



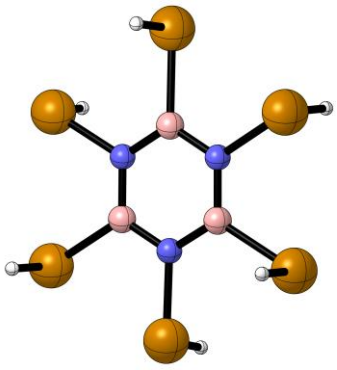
C_1
63.33



C_1
63.87

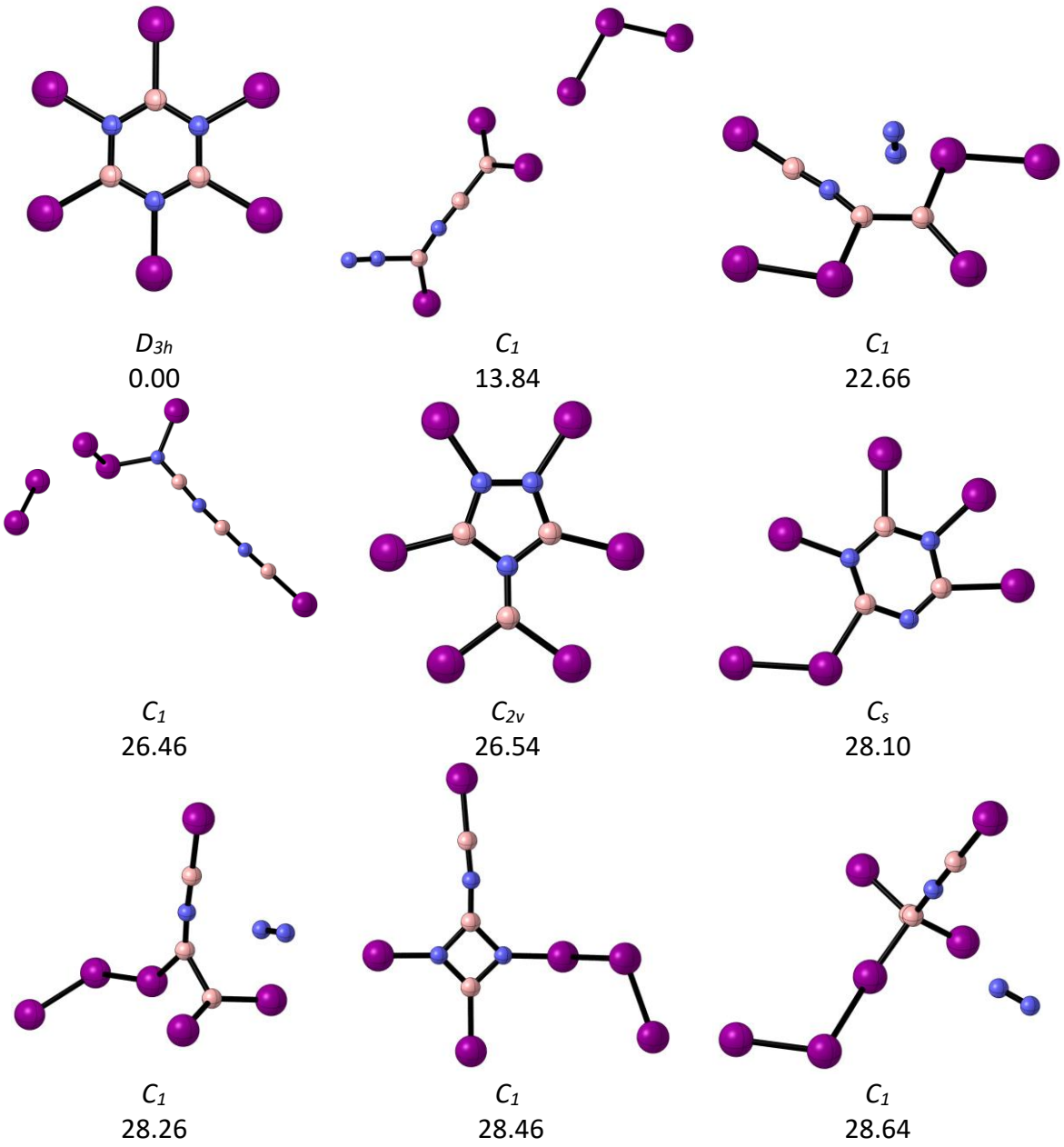
C_1
65.84

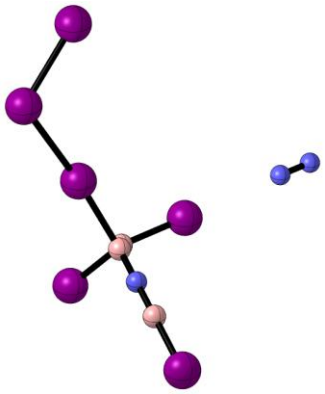
C_1
68.14



C_{3v}
68.69

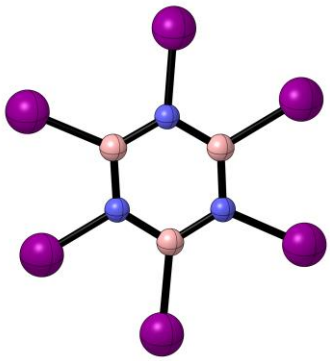
Figure S3. Structures, symmetry point group and relative energy of the 10 lowest energy singlet state structures (within the range of 0-30 kcal·mol^{-1} with respect to the putative global minimum structure) of the $B_3N_3I_6^{2+}$ system at the PBE0-D3/def2-TZVP level. Relative energies are listed in kcal·mol^{-1}, with zero-point energy (ZPE) corrections.



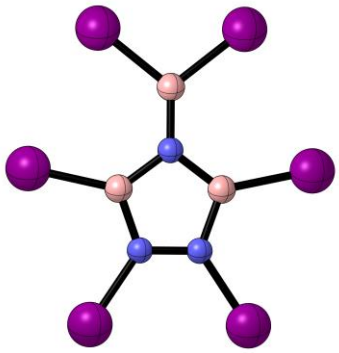


C_1
28.72

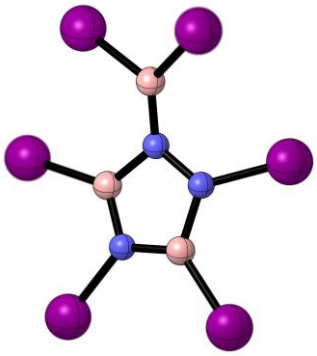
Figure S4. Structures, symmetry point group and relative energy of the 4 lowest energy triplet state structures within the range of 0-30 kcal·mol^{-1} with respect to the putative global minimum structure of the $B_3N_3I_6^{2+}$ system at the PBE0-D3/def2-TZVP level. Relative energies are listed in kcal·mol^{-1}, with zero-point energy (ZPE) corrections.



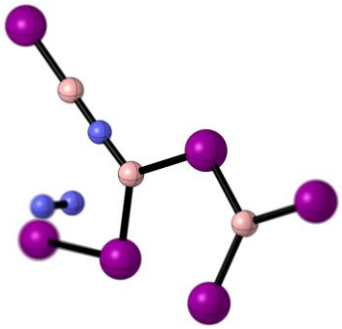
C_{2v}
2.00



C_{2v}
13.96

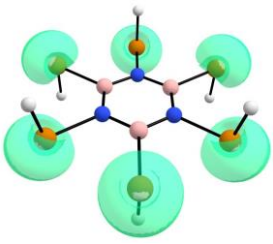


C_1
25.84

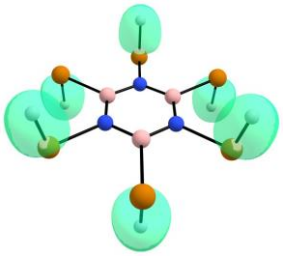


C_1
27.57

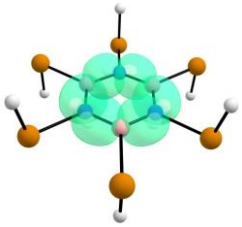
Figure S5. AdNDP bonding pattern of $B_3N_3(TeH)_6^{2+}$



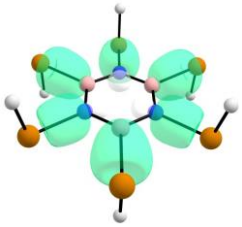
6 x 1c-2e Te-LPs
ON = 1.98 – 1.99 |e|



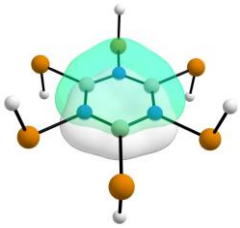
6 x 2c-2e Te-H σ-bonds
ON = 1.97 – 2.00 |e|

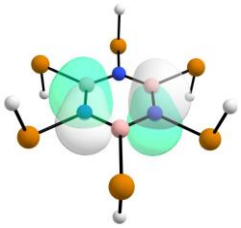


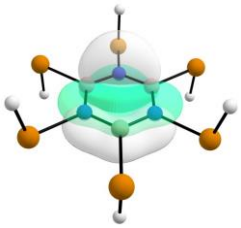
6 x 2c-2e B-N σ-bonds
ON = 1.98 |e|



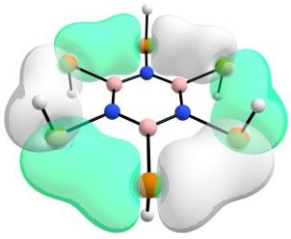
6 x 2c-2e B(N)-Te σ-bonds
ON = 1.97 – 1.98 |e|

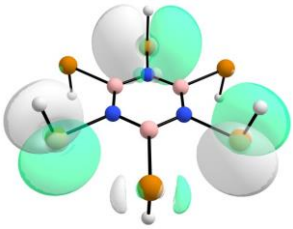


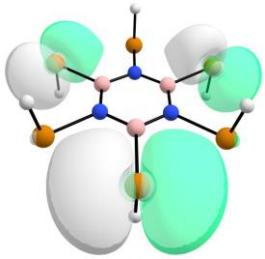


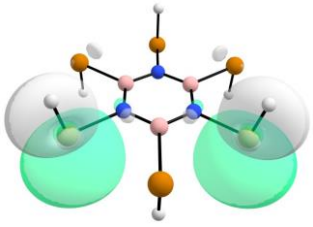


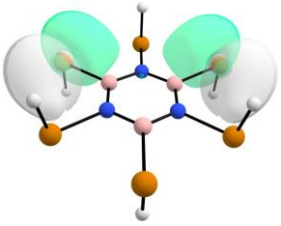
3 x 6c-2e π-bonds
ON = 1.98 – 1.99 |e|





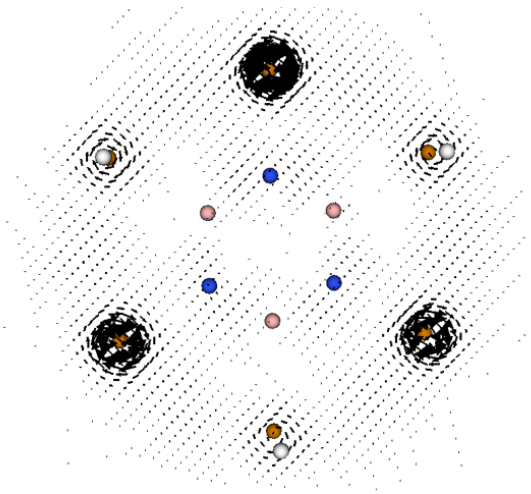




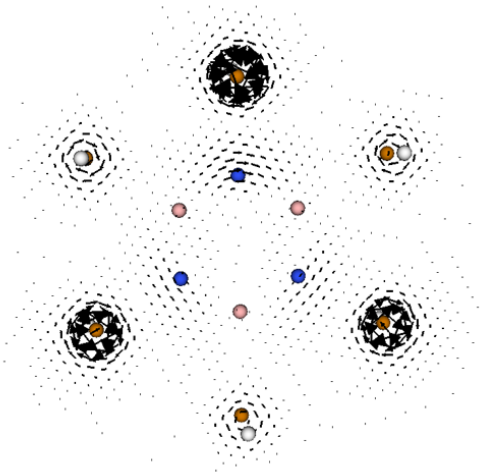


5 x 6c-2e σ-bonds
ON = 1.92 – 1.97 |e|

Figure S6. Vector maps of dissected Magnetically induced current density (MICD) at 1 a_0 above the molecular plane of $B_3N_3(TeH)_6^{2+}$



8.5 nA.T^{-1}
(a) $B_3N_3(TeH)_6^{2+}$ *outer*-σ current density map



3.6 nA.T^{-1}
(b) $B_3N_3(TeH)_6^{2+}$ *inner*-π current density map

Table S1. Extra cyclic resonance energies (kcal/mol) and RCSs values (nA/T) of five member rings C_4XH_4.

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.

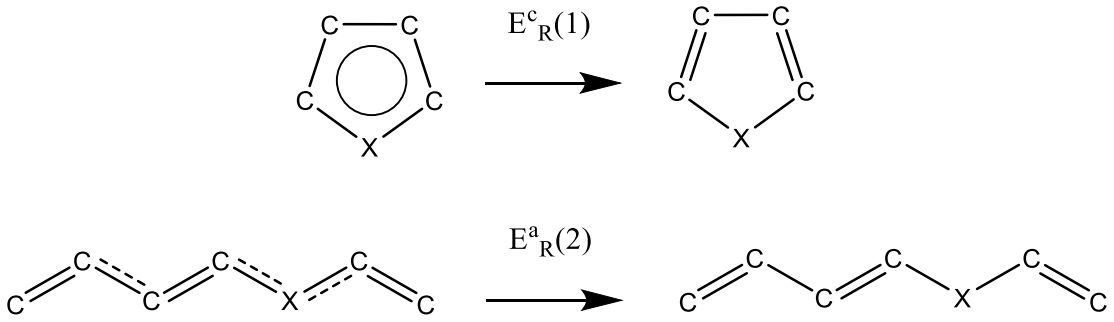


Table S2.- Cartesian coordinates at the PBE0/def2-TZVP level of the global minimum of $B_3N_3H_3^+$, $B_3N_3(TeH)_6^{2+}$ and $B_3N_3I_6^{2+}$. Coordinates for the doubly aromatic local minimum ($B_3N_3H_3^+$, and $B_3N_3(TeH)_6^{2+}$) and lowest triplet of $B_3N_3I_6^{2+}$ are also included. Relative energies are listed in kcal·mol^{-1}

$B_3N_3H_3^+$ (0.00) singlet state

H	4.595360000	-0.000687000	-0.000422000
H	-3.647992000	-0.849414000	0.000226000
B	3.424898000	-0.000474000	-0.000187000
H	-3.648940000	0.847917000	0.000221000
N	2.158522000	-0.000007000	0.000600000
N	-3.100004000	-0.000443000	0.000154000
B	0.835464000	0.000471000	-0.000077000
B	-1.755249000	0.000371000	-0.000151000
N	-0.461945000	0.000498000	-0.000461000

$B_3N_3H_3^+$ (49.30) singlet state

B	-0.962163000	0.000000000	0.000000000
B	0.481083000	0.833258000	0.000000000
B	0.481083000	-0.833258000	0.000000000
N	1.609467000	0.000000000	0.000000000
N	-0.804731000	-1.393839000	0.000000000
N	-0.804731000	1.393839000	0.000000000
H	2.620718000	0.000000000	0.000000000
H	-1.310358000	-2.269606000	0.000000000
H	-1.310358000	2.269606000	0.000000000

$B_3N_3I_6^{2+}$ (0.00) singlet state

B	0.000000000	1.240158000	-0.715878000
N	0.000000000	0.000000000	-1.410032000
N	0.000000000	1.221216000	0.705216000
I	0.000000000	0.000000000	-3.428257000
I	0.000000000	2.969327000	1.713977000
B	0.000000000	-1.240158000	-0.715878000
B	0.000000000	0.000000000	1.432255000
I	0.000000000	-3.076241000	-1.776100000
I	0.000000000	0.000000000	3.552405000
N	0.000000000	-1.221216000	0.705216000
I	0.000000000	-2.969327000	1.713977000
I	0.000000000	3.076241000	-1.776100000

$B_3N_3I_6^{2+}$ (2.00) triplet state

B	-1.268786000	-0.713673000	0.000000000
N	-1.245264000	0.715413000	0.000000000
N	0.000000000	-1.375691000	0.000000000
I	-2.903897000	1.897765000	0.000000000
I	-0.000390000	-3.400331000	0.000000000
B	0.000471000	1.398886000	0.000000000
B	1.269102000	-0.714011000	0.000000000
I	-0.000411000	3.555701000	0.000000000
I	2.990960000	-1.977917000	0.000000000
N	1.245814000	0.715071000	0.000000000
I	2.904743000	1.897326000	0.000000000
I	-2.991152000	-1.977064000	0.000000000

$B_3N_3(TeH)_6^{2+}$ (0.00) singlet state

Te	-2.154013000	1.321219000	1.246680000
Te	-2.524572000	-2.986723000	-0.558777000
B	-0.286182000	0.126959000	1.081656000
Te	-3.897534000	-0.848936000	-0.295364000
Te	-1.651750000	3.086823000	-0.751338000
Te	5.686961000	-0.960169000	-0.017187000
N	0.885949000	0.665334000	0.467056000
Te	3.941375000	0.841162000	-0.424837000
N	-0.247110000	-1.168439000	1.633530000
N	2.106253000	-1.388574000	1.021147000
B	0.943725000	-1.974034000	1.624313000
B	2.076855000	-0.103129000	0.470426000
H	-1.054949000	-1.566568000	2.088908000
H	-2.032237000	4.348933000	0.255220000
H	2.959923000	-1.930518000	1.019116000
H	-3.391510000	0.028493000	-1.632314000
H	0.845403000	1.601647000	0.086149000
H	0.961474000	-3.064786000	2.091598000

$B_3N_3(TeH)_6^{2+}$ (68.69) singlet state

Te	-3.312911000	-1.496944000	-0.095722000
Te	3.154792000	1.425438000	0.099906000
Te	2.952827000	-2.120471000	-0.095679000
Te	0.360141000	3.617467000	-0.095733000
Te	-0.342824000	-3.444924000	0.099900000
Te	-2.812002000	2.019437000	0.099950000
N	1.295667000	0.585492000	-0.018992000
N	-0.140874000	-1.414868000	-0.019125000
N	-1.154956000	0.829386000	-0.018984000
B	1.161433000	-0.834121000	-0.019980000
B	-1.303189000	-0.588820000	-0.019966000
B	0.141563000	1.422947000	-0.019841000
H	-3.372772000	-1.525234000	1.563181000
H	3.350875000	1.513803000	-1.549135000
H	3.006858000	-2.158593000	1.563228000
H	0.366477000	3.683533000	1.563165000
H	-0.364144000	-3.659018000	-1.549125000
H	-2.986442000	2.145211000	-1.549072000