Supporting Information

Unravelling phenomenon of internal rotation in B_{13}^+ through chemical bonding analysis

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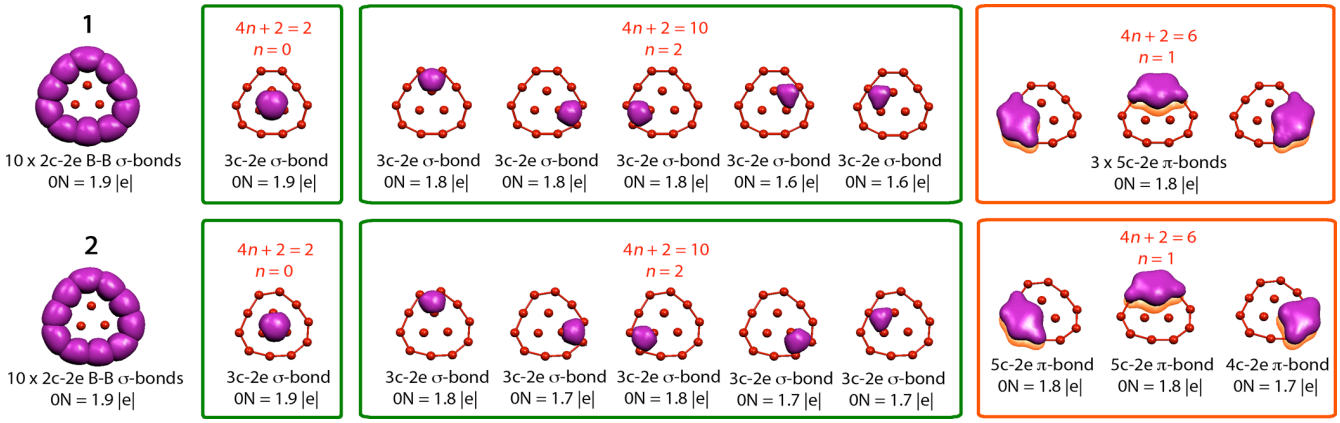

Figure 1-SI. Chemical bonding pattern revealed for 1 and 2 using Adaptive Natural Density Partitioning method. The delocalized σ-bonds are enclosed in green rectangles, while the delocalized π-bonds are enclosed in

The AdNDP analysis revealed ten 2c-2e B-B σ-bonds on the periphery of **1** with occupation number (ON) of 1.9 |e| (See Figure 2). There is also one 3c-2e σ-bond with ON of 1.9 |e|, which is delocalized over the central boron triangle. The AdNDP search also recovered five 3c-2e σ-bonds with ON ranging from 1.6 |e| to 1.8 |e|, which are responsible for the bonding between the central triangular unit and the peripheral B_{10} ring. So, there are two concentric σ-systems, which both satisfy the 4n+2 Hückel rule separately. Therefore, the global minimum is doubly concentric σ-aromatic. Concurrently, there are six π-electrons satisfying the Hückel rule, which form three delocalized 5c-2e π-bonds. Thus, B_{13}^+ is also π-aromatic. Similar results are found for the transition state **2**, which are presented side by side with those for **1** in Figure 1-SI. So, both the global minimum **1** and the transition state **2** are doubly σ- and π-aromatic.

The positions of the boron atoms in **1** (Figure 1-SI) correspond to the $\mathbf{1_4}$ global minimum presented in Figure 2-SI, whereas positions of the boron atoms in **2** (Figure 1-SI) correspond to the $\mathbf{2_{3\text{-}4}}$ transition state.

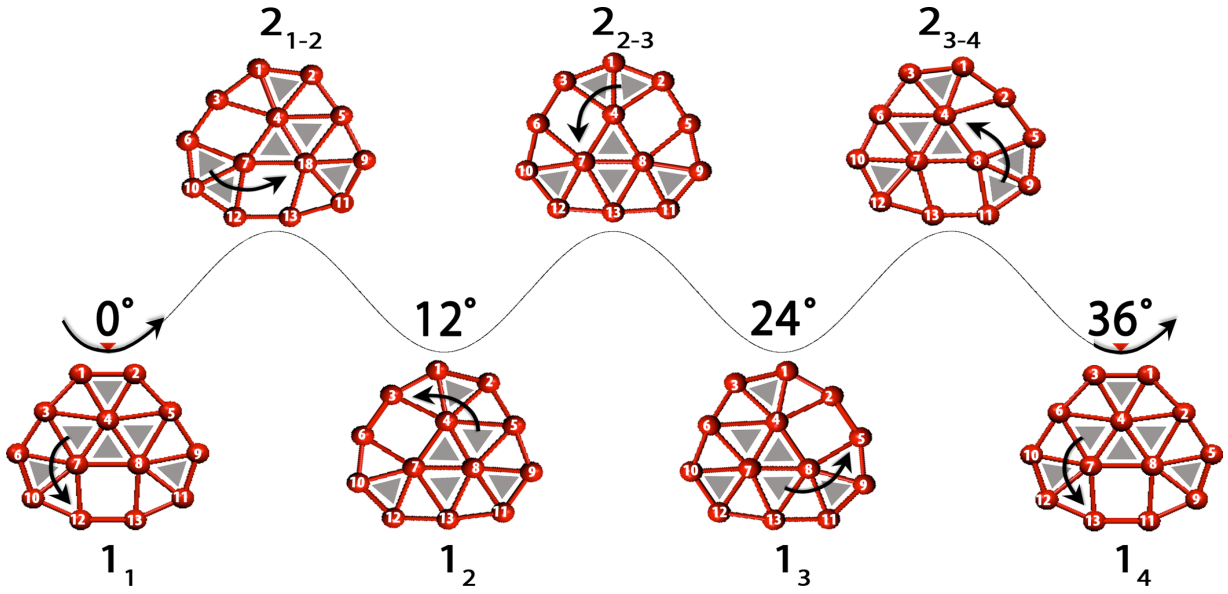

Figure 2-SI. The schematic representation of the 3c-2e σ-bonds migration during the internal rotation of B_{13}^+.

Let's envision the fluxionality of B_{13}^+ as a clockwise rotation of the outer B_{10} ring with respect to inner B_3 triangle, whose atoms positions are held fixed (Figure 2-SI). The internal rotation can be then presented as the following process: ⇔ $\mathbf{1}_1$ ⇔ $\mathbf{2}_{1\text{-}2}$ ⇔ $\mathbf{1}_2$ ⇔ $\mathbf{2}_{2\text{-}3}$ ⇔ $\mathbf{1}_3$ ⇔ ... ⇔ $\mathbf{1}_{29}$ ⇔ $\mathbf{2}_{29\text{-}30}$ ⇔ $\mathbf{1}_{30}$ ⇔ $\mathbf{2}_{30\text{-}1}$ ⇔ $\mathbf{1}_1$⇔, where $\mathbf{1}_i$ represent the global minima (i = 1-30), which differ in relative arrangement of the outer ring with respect to the fixed inner ring. Each $\mathbf{2}_{i\text{-}j}$ species stands for the transition state connecting global minima $\mathbf{1}_i$ and $\mathbf{1}_j$ (i, j = 1-30). In global minimum $\mathbf{1}_1$ the B7-B8 edge of the inner B_3 triangle is coordinated to the B12-B13 peripheral bond, whereas the B7-B8 edge of the inner triangle is coordinated to the B13-B11 peripheral bond in $\mathbf{1}_4$. On the way from $\mathbf{1}_1$ to $\mathbf{1}_4$ the outer B_{10} ring is slowly and gradually rotating clockwise by one peripheral bond through the transitional species ⇔ $\mathbf{2}_{1\text{-}2}$ ⇔ $\mathbf{1}_2$ ⇔ $\mathbf{2}_{2\text{-}3}$ ⇔ $\mathbf{1}_3$ ⇔ $\mathbf{2}_{3\text{-}4}$ ⇔ with respect to the inner triangle, whose atoms positions are held fixed. If we consider the outer ten-atomic ring as a concentric circle, then the rotation by one peripheral bond of the ten-atomic ring is the same as rotation by 360°/10 = 36 degrees. In other words, the outer B_{10} ring makes a 36°-turn going from $\mathbf{1}_1$ to $\mathbf{1}_4$. To make a full 360°-turn of the outer B_{10} ring with respect to the fixed B_3 triangle, one needs 30 different global minima ($\mathbf{1}_i$, i = 1-30) and 30 different transition states ($\mathbf{2}_{i\text{-}j}$, i, j = 1-30). The atoms of the global minima and the transition states throughout the rotation were numerated on the basis of careful exploration of potential energy surface around the transition state.