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## CA<sub>11</sub><sup>−</sup>: a molecular rotor with a quasi-planar tetracoordinate carbon†

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**In this work, we analyzed the bonding and fluxional character of the global minimum of CA<sub>11</sub><sup>−</sup>. Its structure is formed by two stacked layers, one of them resembles the well-known planar tetracoordinate carbon CA<sub>4</sub> on top of a hexagonal Al@Al<sub>6</sub> wheel. Our results show that the CA<sub>4</sub> fragment rotates freely around the central axis. The exceptional stability and fluxionality of CA<sub>11</sub><sup>−</sup> derive from its particular electron distribution.**

In principle, boron and aluminum are similar. Both belong to the same group in the periodic table with comparable electronegativity values. The major distinction is their size; the covalent radius of boron is about 30% smaller, which along with its electron deficiency, plays a crucial role in its structural diversity. In fact, the architectural zoo is so vast that boron clusters stand out for their unusual chemical bonding, aromaticity, and fluxionality.<sup>1–4</sup> In 2010, the first case of fluxionality in boron clusters was published, B<sub>19</sub><sup>−</sup>.<sup>5,6</sup> In this system, an inner B<sub>6</sub> fragment rotates freely within the peripheral B<sub>13</sub> ring, mimicking a rotary internal-combustion engine, hence the name of the molecular Wankel rotor. Shortly after, similar dynamic behavior in other boron clusters was discovered.<sup>7–12</sup> The most renowned case is B<sub>13</sub><sup>+</sup> because its fluxionality was experimentally corroborated by cryogenic ion vibrational spectroscopy,<sup>13</sup> and it has been used to study how to control the internal rotation by circularly polarized laser radiation.<sup>14</sup>

The fluxionality is not exclusive to bare boron clusters.<sup>15–17</sup> We recently introduced B<sub>3</sub>Al<sub>4</sub><sup>+</sup>.<sup>18</sup> This system is formed by a

triangular B<sub>3</sub> unit rotating on top of an Al<sub>4</sub> square, simulating the motion of a three-dimensional Reuleaux triangle. This has motivated us to reconsider designing molecular rotors based on aluminum clusters. This is a complex task. In essence, fluxionality in boron clusters is primarily driven by the multi-center nature of their chemical bonds, *i.e.*, doping or replacing boron with other atoms might shut down such dynamic behavior. For example, substituting a single boron with a carbon atom in B<sub>19</sub><sup>−</sup> and B<sub>11</sub><sup>−</sup> stops the rotation due to the formation of a localized σ-bond.<sup>19,20</sup> This may suggest that clusters with carbon elude this type of fluxional behavior.

Recently, Zheng *et al.* studied a series of clusters CA<sub>*n*</sub><sup>−</sup> (*n* = 6–15).<sup>21</sup> According to their photoelectron spectroscopy study, in conjunction with a global minimum computational search, CA<sub>11</sub><sup>−</sup> is formed by a CA<sub>4</sub> unit on top of a hexagonal Al@Al<sub>6</sub> quasi-planar fragment. In other words, it is another two-layer system resembling the B<sub>3</sub>Al<sub>4</sub><sup>+</sup> Reuleaux triangle.<sup>22–25</sup> Noticeably, one of the layers in CA<sub>11</sub><sup>−</sup> resembles the well-known CA<sub>4</sub><sup>2−</sup>, which is one of the most studied planar tetracoordinate carbons (ptCs) with aluminum.<sup>26–28</sup> Can CA<sub>11</sub><sup>−</sup>, a system with a ptC already experimentally detected in the gas phase, be fluxional? In this study, we analyze the bonding nature and fluxional character of CA<sub>11</sub><sup>−</sup>. Our results show that the CA<sub>4</sub> unit rotates freely around the central axis, implying that CA<sub>11</sub><sup>−</sup> is the first aluminum-based ptC molecular rotor.

To identify the energetic landscape of CA<sub>11</sub><sup>−</sup>, the exploration of its potential energy surface (PES) for singlet and triplet states was carried out through coalescence kick and genetic algorithms.<sup>29,30</sup> An initial screening was done at the PBE0/3-21G level.<sup>31</sup> The twenty lowest-lying energy isomers were re-minimized at the PBE0/def2-QZVP level.<sup>32</sup> The vibrational frequencies were computed at the same level to characterize the nature of the stationary points. Relative energies for the four lowest-energy isomers were refined using single-point CCSD(T)/def2-QZVP computations,<sup>33</sup> including the ZPE corrections at the PBE0/def2-QZVP level. Thus, the energy discussion is based on the CCSD(T)/def2-QZVP//PBE0/def2-QZVP results. All these computations were conducted with Gaussian 16.<sup>34</sup> Wiberg Bond Index (WBI) and Natural Population Analysis

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† Electronic supplementary information (ESI) available: Supplementary Table S1, Fig. S1–S3, and one BOMD movie. See DOI: <https://doi.org/10.1039/d3cc00855j>



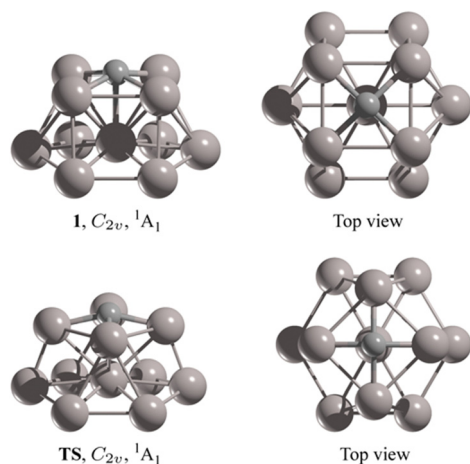


Fig. 1 Side and top views of the global minimum and transition state of the  $\text{CAL}_{11}^-$  global minimum.

(NPA) were estimated following the NBO6 scheme.<sup>35</sup> The adaptive natural density partitioning (AdNDP)<sup>36</sup> analysis was done using the Multiwfn program.<sup>37</sup> For a better understanding of electron delocalization, the magnetically induced current density ( $\mathbf{j}^{\text{ind}}$ ) and the induced magnetic field ( $\mathbf{B}^{\text{ind}}$ ) were estimated using the GIMIC<sup>38</sup> and Aromagnetic<sup>39</sup> programs, respectively. The orbital contribution to  $\mathbf{B}^{\text{ind}}$  was determined through NCS analysis.<sup>40</sup> To assess the contribution of core electrons to the magnetic response, the removing valence electron method was utilized.<sup>41</sup> The dynamical behavior of  $\text{CAL}_{11}^-$  was confirmed by Born-Oppenheimer Molecular Dynamics (BOMD)<sup>42</sup> simulations at temperatures of 300 and 500 K at the PBE0/6-31G(d) level. Each simulation ran for 30 ps with a step size of 2.2 fs from the equilibrium global minimum structure with random velocities assigned to the atoms according to a Maxwell-Boltzmann distribution for both temperatures and then normalized so that the net moment for the whole system is zero.

Fig. 1 shows the top and side views of the global minimum of  $\text{CAL}_{11}^-$ , **1**. The relative energy between **1** and the nearest local minimum is 5.8 kcal mol<sup>-1</sup>. Fig. S1 (ESI†) includes the remaining low-lying isomers. The structure of **1** adopts  $C_{2v}$  symmetry with two stacked layers (with a C-Al interlayer spacing of 2.31 Å), a planar  $\text{CAL}_4$  quasi-square (carbon is just 0.41 Å above the  $\text{Al}_4$  plane) on top of a hexagonal  $\text{Al}_7$  wheel. The C-Al bond lengths in the  $\text{CAL}_4$  framework are 1.99 Å, just 0.03 Å longer than in  $D_{4h}$   $\text{CAL}_4^{2-}$  and halfway between the lengths in  $C_{2v}$   $\text{CAL}_4^-$  (1.95 and 2.00 Å, respectively). The Al-Al distances, including those between layers, range between 2.66 and 2.83 Å, similar to those in  $\text{CAL}_4^{2-}$  (2.87 Å) and  $\text{CAL}_4^-$  (2.69–2.93 Å).

According to NBO analysis (Fig. S2, ESI†), the negative charge ( $-0.5 |e|$ ) is spread evenly across the two fragments. Remarkably, the ptC has a natural charge of  $-2.4 |e|$ , which is identical to other ptC clusters such as  $\text{CAL}_4^{2-}$ . With respect to the Wiberg bond indices, the corresponding values in the  $\text{CAL}_4$  unit are 0.44 for C-Al and 0.26–0.32 for Al-Al (Fig. S2, ESI†). In contrast, the  $\text{WBI}_{\text{Al-Al}}$  at the  $\text{Al}_7$  periphery range from 0.64 to 0.72, and 0.40 for the radial Al-Al bonds. This indicates a stronger electron localization in the perimeter of the  $\text{Al}_7$  ring,

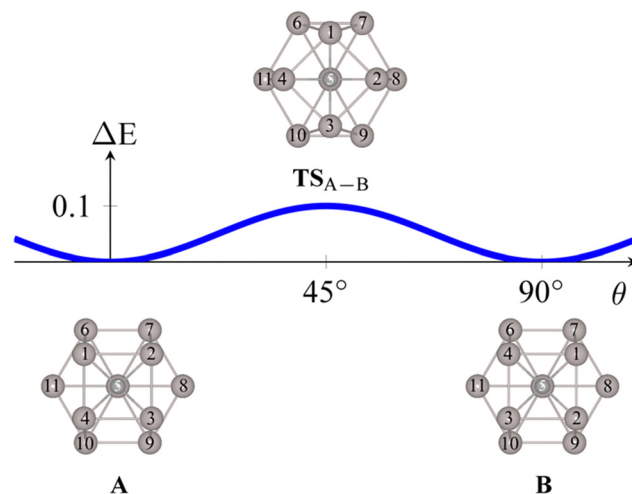


Fig. 2 Rotational mechanism of  $\text{CAL}_{11}^-$ .

*i.e.*, a higher covalent character in the outer Al-Al bonds. Moreover, the values between layers are significant. Specifically, the  $\text{WBI}_{\text{C-Al}}$  between layers is 0.42, while the  $\text{WBI}_{\text{Al-Al}}$  is 0.40–0.62, implying a considerable interaction between the two moieties.

So far, we have described the structure of  $\text{CAL}_{11}^-$  including some details to understand how the fragments are bound; nothing different from what Zheng *et al.* reported. The oddity emerges by inspecting the frequency analysis. There is a soft mode of just 23 cm<sup>-1</sup> associated with the rotation of the  $\text{CAL}_4$  moiety around the central axis of the  $\text{Al}_7$  wheel (Fig. S3, ESI†). This implies that the system may be fluxional. In fact, there is a transition state (TS) with an imaginary frequency ( $\nu_{\text{min}} = 18i \text{ cm}^{-1}$ ) corresponding to a 45° rotation of the  $\text{CAL}_4$  fragment (Fig. 2). Such TS also has  $C_{2v}$  symmetry and is just 0.1 kcal mol<sup>-1</sup> above **1**! The structural parameters, WBIs, and atomic charges of TS are quite similar to those of **1** (Fig. S2, ESI†).

BOMD simulations were performed at the PBE0/6-31G(d) level to corroborate the dynamic fluxionality of the global minimum of  $\text{CAL}_{11}^-$ . The simulations, at 300 and 500 K, confirm the rotation around the central axis of the  $\text{CAL}_4$  framework. The rotation resembles a molecular rotor from the top view. A short movie with a simulation of over 30 ps at 500 K is included as an example in the ESI† Both layers in  $\text{CAL}_{11}^-$  maintained their structural integrity, *i.e.*, no fragment dissociation or significant distortion was perceptible.

The charge distribution and bond orders indicate that the two pieces interact significantly. So, why does  $\text{CAL}_{11}^-$  exhibit such unusual dynamic behavior? AdNDP (Fig. 3) reveals three delocalized 5c-2e  $\sigma$ -bonds within the  $\text{CAL}_4$  fragment, and a delocalized 6c-2e  $\pi$ -bond involving the carbon and the central Al atom of the  $\text{Al}_7$  wheel. In addition, there are six localized 2c-2e Al-Al  $\sigma$ -bonds at the perimeter of the  $\text{Al}_7$  ring and three radial  $\sigma$ -bonds entirely delocalized. Besides the delocalized 6c-2e  $\pi$ -bond, the interaction between layers is recovered by the AdNDP through four 2c-2e Al-Al and two 3c-2e  $\sigma$ -bonds. This is relevant for fluxionality since only the interlayer bonds change during the rotation process. Specifically, four 2c-2e Al-Al  $\sigma$ -bonds in **1** evolved into four delocalized 3c-2e  $\sigma$ -bonds in TS, while the two interlayer 3c-2e  $\sigma$ -bonds in **1** become 2c-2e bonds in TS. This process happens every 45° (Fig. 2).



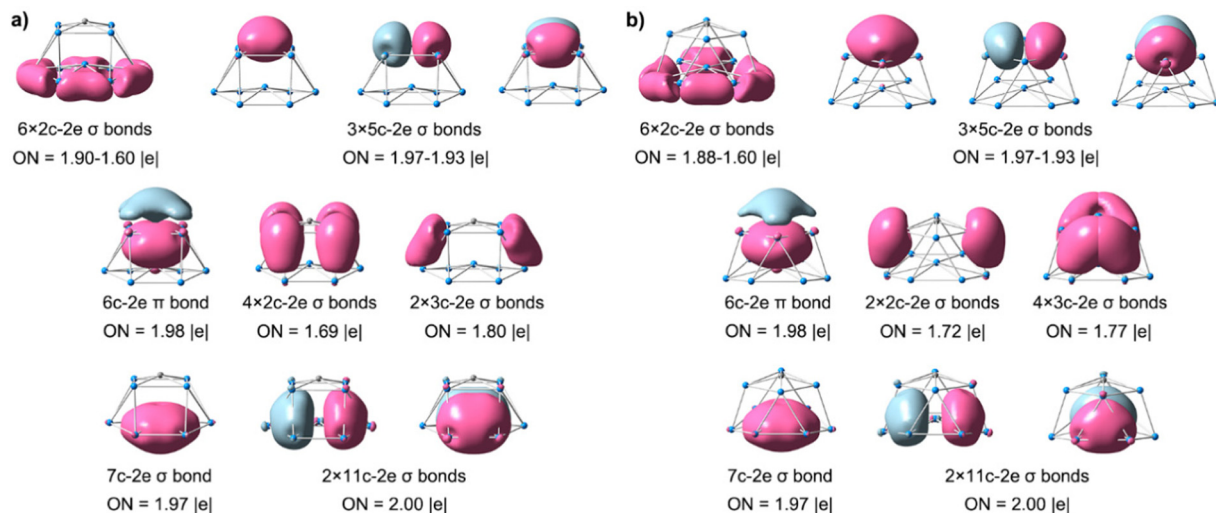


Fig. 3 The adaptive natural density partitioning (AdNDP) analysis for **1** (left) and **TS** (right). The occupation numbers (ONs) are shown.

In summary, the main components remain unchanged as the connectivity between them changes from localized to delocalized and *vice versa*.

Electron delocalization of  $\text{CAL}_{11}^-$  is examined by its magnetic response to an external magnetic field parallel to the rotation axis (Fig. 4). An entirely diatropic ring current flows clockwise in and between layers. Concomitantly, this current

creates a  $\mathbf{B}^{\text{ind}}$ , whose main component, the z-component ( $B_z^{\text{ind}}$ ), reveals that the cluster is strongly shielded due to the σ-electrons ( $B_z^{\text{ind}}$  values even lower than −50 ppm). The π-electrons also contribute to the shielding, but weakly. Analysis of the ring current shows that the strongest  $\mathbf{J}^{\text{ind}}$  flux is near the  $\text{Al}_7$  wheel. The  $\mathbf{J}^{\text{ind}}$  integration results in a global ring current strength of  $91.3 \text{ nA T}^{-1}$ . However, the magnetic response is contaminated by the core electrons, especially near the nuclei. Because the integration plane crosses two nuclei, it is best to disregard their contribution. As a result, subtracting the intensity of the core electrons ( $28.19 \text{ nA T}^{-1}$ ) from the total yields  $63 \text{ nA T}^{-1}$ . This suggests that the system is highly delocalized, with a ring current five times stronger than that of benzene ( $12 \text{ nA T}^{-1}$ ).

In summary, the structure of  $\text{CAL}_{11}^-$  consists of two stacked layers; one is a  $\text{CAL}_4$  framework containing a quasi-planar tetracoordinate carbon on a hexagonal  $\text{Al}_7$  wheel. Our computations revealed that, although there is strong contact between the two layers, there are almost no barriers to the rotation of one over the other. BOMD simulations show that the dynamic behavior occurs without severe distortions. Along the rotation, both fragments remain unchanged as the connectivity between them changes from localized to delocalized and *vice versa*. So,  $\text{CAL}_{11}^-$  is the first aluminum-based ptC molecular rotor with outstanding stability and fluxionality.

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## Conflicts of interest

There are no conflicts to declare.

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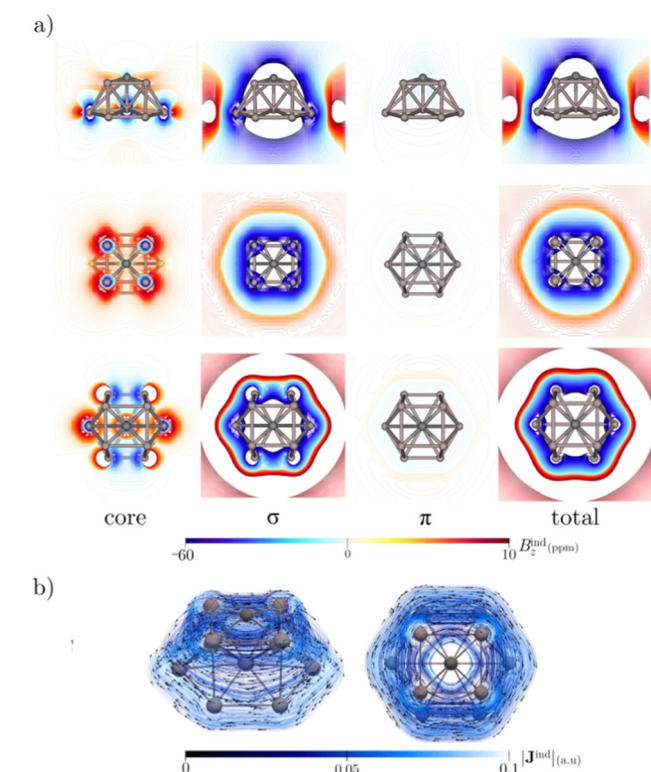


Fig. 4 (a)  $B_z^{\text{ind}}$  isolines plotted in the plane of the  $\text{Al}_7$  (bottom), of the  $\text{CAL}_4$  framework (middle), and in a transverse plane (top) to  $\text{CAL}_{11}^-$ . (b)  $\mathbf{J}^{\text{ind}}$  maps plotted near  $\text{CAL}_{11}^-$ . The arrows indicate the direction of the current density. The  $|\mathbf{J}^{\text{ind}}|$  scale is in atomic units ( $1 \text{ a.u.} = 100.63 \text{ nA T}^{-1} \text{ Å}^{-2}$ ).





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