Molecular structures of M$_2$N$_2$$^\text{2−}$ (M and N = B, Al, and Ga) clusters using the gradient embedded genetic algorithm†

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Al$_4$$^\text{2−}$ was the first discovered σ + π aromatic all-metal cluster. In the present work we analyze the molecular structure, relative stability, and aromaticity of lowest-lying isomers of related M$_2$N$_2$$^\text{2−}$ (M and N = B, Al, and Ga) clusters, with special emphasis devoted to the cis (D$_{2h}$) and trans (D$_{2h}$) isomers of the M$_2$N$_2$$^\text{2−}$ clusters. For such purpose, we start by performing the search of the global minimum for each cluster through the Gradient Embedded Genetic Algorithm (GEGA). Energy decomposition analyses and the calculated magnetic- and electronic-based aromaticity criteria of the lowest-lying isomers help to understand the nature of the bonding and the origin of the stability of the global minima. Such methodology should allow guiding future molecular design strategies.

Introduction

In 2001, Li et al.$^1$ obtained by laser vaporization Al$_4$$^\text{2−}$, the first all-metal cluster to be considered aromatic from the ab initio calculations that show two electrons residing in a π molecular orbital (MO) and satisfying the Hückel rule$^2$ for aromatic compounds. Also, they found that the pyramidal structures of the Al$_4$$^\text{2−}$ face-capped by an M$^+$ cation (M = Li, Na, and Cu) are the global minima based on the good agreement between the theoretical and experimental vertical detachment energies. In their work, Li et al.$^1$ concluded that the π-orbital “holds the key for understanding the structure and bonding of Al$_4$$^\text{2−}$ species.” That work broke with the idea that only organic species can be aromatic and extended the concept of aromaticity to all-metal systems starting the quest for species belonging to this new class of aromatic compounds.$^3$

The main difference with the aromatic organic compounds is the multifold (anti)aromatic character of these inorganic systems.$^{3\text{v},4}$ Moreover, in this all-aluminum cluster σ-electrons are highly delocalized. This conclusion is drawn from the analysis of the valence MOs of Al$_4$$^\text{2−}$ that can be separated into four sets: the σ$_r$ set consisting of four filled MOs obtained by combination of the 3s Al atomic orbitals (AOs), the π set with one filled MO formed by in-phase combination of 3p out-of-plane AOs, and the σ$_t$ (radial) and σ$_r$ (tangential) sets containing two electrons each and generated from combinations of 3p in-plane AOs.$^5$

It is usually considered that the aromaticity in Al$_4$$^\text{2−}$ comes from these π, σ$_r$, and σ$_t$ orbitals, the σ$_r$ orbital having a larger contribution to σ-aromaticity than the σ$_t$ orbital.$^{5\text{b},6}$ Several studies were performed in a way to probe this π- and σ-aromatic behavior, such as nucleus-independent chemical shift (NICS)$^7$ and canonical MO-NICS calculations,$^8$ induced magnetic field analysis,$^9$ plots of aromatic ring current shieldings (ARCS),$^{10}$ gauge-including magnetically induced currents (GIMIC),$^{11}$ ring current maps,$^{12}$ bond magnetizabilities,$^{13}$ resonance energy (RE) calculations,$^{4\text{a},14}$ valence bond (VB) estimations,$^{15}$ chemical reactivity descriptors,$^{16}$ analysis of the electron localization function (ELF),$^{17}$ and multicenter delocalization indices.$^{5\text{v},18}$

This double (or triple if the σ function is divided into its radial and tangential components) aromaticity in the Al$_4$$^\text{2−}$ is also present in the valence isoelectronic B$_4$$^\text{2−}$ and Ga$_4$$^\text{2−}$ species, where the electron delocalization of the π- and σ-electrons is similar to that of the tetraaluminum cluster dianion.$^{5\text{b},14,18,19}$

The all-metal and semimetal Al$_2$B$_2$$^\text{2−}$, Ga$_2$Al$_2$$^\text{2−}$, and Ga$_2$B$_2$$^\text{2−}$ are also valence isoelectronic to Al$_4$$^\text{2−}$, so they are expected to be aromatic compounds too. In a previous work, the aromatic behavior in Ga$_2$Al$_2$$^\text{2−}$ was confirmed by some of the present authors.$^{18c}$ For the M$_2$N$_2$$^\text{2−}$ (M and N = B, Al, and Ga with M ≠ N) compounds there are two possible cyclic planar structures corresponding to the cis (C$_2v$) and trans (D$_{2h}$) configurations. The relative stability of these isomers depends on the nature of the M and N atoms. Thus, for related systems it has been found that the Al$_2$Ge$_2$$^\text{2−}$, Si$_2$Ge$_2$$^\text{2−}$, $^{20b}$ S$_2$N$_2$$^\text{21}$ clusters, and diazacyclobutadiene$^{22}$ are more stable in the trans configuration. On the other hand, for Ga$_2$Ge$_2$$^\text{20}$, Al$_2$Si$_2$$^\text{10,20}$, Ga$_2$Si$_2$$^\text{20}$...
The preparation energy, $\Delta E_{\text{prep}}$, corresponds to the energy required to deform the separated fragments from their equilibrium geometries into the molecule. The interaction energy, $\Delta E_{\text{int}}$, corresponds to the actual energy released when the deformed fragments are combined to generate the final molecule. This energy can be divided into three physical meaningful terms: the Pauli repulsion, $\Delta E_{\text{Pauli}}$; the classical electrostatic interaction, $\Delta E_{\text{elstat}}$; and the orbital interaction energy, $\Delta E_{\text{oi}}$ (see eqn (2)). The orbital interaction energy term can be decomposed into the contributions from each irreducible representation $\Gamma$ of the interacting system, in particular, in planar systems the $\sigma/\pi$ separation is possible.

$$\Delta E_{\text{int}} = \Delta E_{\text{Pauli}} + \Delta E_{\text{elstat}} + \Delta E_{\text{oi}}$$

For aromaticity analysis, $B^{\text{ad}}$ calculations were realized in the cyclic systems at the PW91/IGLO-III level, employing the deMon program for the MOs and the deMon-NMR package for the shielding tensors. The induced magnetic field was computed using the expression

$$B^{\text{ad}}(r) = -\sigma_2(r) B^{\text{ext}},$$

where $\sigma_2$ is the shielding tensor and $B^{\text{ext}}$ represents the external magnetic field applied perpendicular to the molecular plane. Assuming $B^{\text{ext}} = 1$ T, the units of $B^{\text{ad}}$ are 1 $\mu$T or 1 ppm of the shielding tensor. The induced magnetic field was computed along the highest symmetry axis, which is parallel to the $z$-axis of the Cartesian coordinates system. The $B^{\text{ad}}$ can be separated into its orbital contributions for deeper study of the $\pi$ and $\sigma$ electron behavior. The $\sigma$- and $\pi$-contribution to the induced magnetic field has been separated using the IGLO method, where localized molecular orbitals (LMOs) have been created using the procedure proposed by Pipek and Mezey. For comparison purposes, it must be mentioned that $B^{\text{ad}}$ is equivalent to NICs$_{zz}$.37

For the aromaticity analysis we have also applied the multicenter index (MCI). MCI is a particular extension of the $I_{\text{ring}}$ index.

$$I_{\text{ring}}(A) = \sum_{i_1,i_2,...,i_N} n_{i_1} \cdots n_{i_N} S_{i_1i_2}(A_1)S_{i_2i_3}(A_2)\cdots S_{i_Ni_1}(A_N)$$

where $n_i$ is the occupancy of MO $i$ and $A = \{A_1, A_2, ..., A_N\}$ is a string containing the set of $N$ atoms forming the ring structure. Summing up all $I_{\text{ring}}$ values resulting from the permutations of indices $A_1, A_2, ..., A_N$, the mentioned MCI index is defined as:

$$MCI(A) = \frac{1}{2N} \sum_{P(A)} I_{\text{ring}}(A)$$

where $P(A)$ stands for a permutation operator which interchanges the atomic labels $A_1, A_2, ..., A_N$ to generate the $N!$ permutations of the elements in the string $A$. MCI and $I_{\text{ring}}$ give an idea of the electron sharing between all atoms in the ring. The more positive the MCI values, the more the aromatic the rings. For planar species with only $\sigma$- and $\pi$-occupied orbitals, the MCIs can be exactly split into the $\sigma$- and $\pi$-contributions:

$$MCI(A) = MCI_{\sigma}(A) + MCI_{\pi}(A)$$

MCI values were computed at the B3LYP/6-311++G* level with the help of the ESI-3D program.
cyclic system is more stable than the equivalent linear one. The next lowest-energy isomer has a difference of 69.8 kcal mol\(^{-1}\) with respect to the global minima at the MP2/6-311G* level, but presents three imaginary frequencies and, for that reason, the single-point energy calculation at the CCSD(T)/6-311G* level was not carried out in this case. The lowest-lying triplet isomer \((D_{2h} \text{ symmetry})\) is higher in energy by 63.7 kcal mol\(^{-1}\). The scanning for \(\text{Al}_4\) found the \(D_{4h}\) structure as the most stable isomer, while the \(C_{2v}\) molecule was the next lowest-lying isomer. The difference in energy between these two isomers is 18.3 kcal mol\(^{-1}\) and the \(D_{2h}\) triplet for \(\text{Al}_4\) is just 11.1 kcal mol\(^{-1}\) higher in energy. The linear isomer is found to be 33.6 kcal mol\(^{-1}\) higher in energy (CCSD(T)/6-311G*/MP2/6-311G* results), not far from the 26.7 kcal mol\(^{-1}\) found by Chattaraj et al. at the B3LYP/6-311+G* level.\(^{16}\) The T1 test\(^{29}\) for the linear \(\text{B}_4\) and \(\text{Al}_4\) species yielded values of 0.031 and 0.055, respectively. This shows that, at least for the linear \(\text{Al}_4\) compound, the multireference character in these species is relatively important. Nevertheless, neither for \(\text{B}_4\) nor for \(\text{Al}_4\) do we expect the linear isomer to become the most stable isomer when using a method that could deal with the multireference character of these species. In between the \(C_{2v}\) and \(D_{2v}\) structures lie the \(C_{3v}\) \(\text{Al}_4\) isomer. In the case of gallium, the lowest-lying structure is also the \(D_{4h}\) species. The linear structure is not a minimum in this case and the closest isomer is a molecule with \(C_{2v}\) symmetry which is 21.7 kcal mol\(^{-1}\) over the global minimum. As stated for the \(\text{Al}_4\) cluster, in \(\text{Ga}_4\) a structure with \(C_{3v}\) symmetry is 26.6 kcal mol\(^{-1}\) more energetic than the \(D_{4h}\) structure (Fig. 1).

2. \(\text{M}_2\text{N}_2\)\(^2-\) systems

These molecules were built mixing two different elements of Group 13 (M and N = B, Al, and Ga with M ≠ N). The same search was performed to locate the global minimum. Thus, GEGA at B3LYP/3-21G was employed to explore the PES of the different systems, the minima found were reoptimized with MP2/6-311G*, and the energy refinements were done at the CCSD(T)/6-311G* level. Interestingly, the \(C_{2v}\) structures with boron atoms, \(\text{Al}_2\text{B}_2\)\(^2-\) and \(\text{Ga}_2\text{B}_2\)\(^2-\), that present a short B–B bond are more stable than the \(D_{2h}\) alternate systems. These geometries are less symmetric than alternate systems but they are energetically favored. In fact, the next lowest-lying isomers for \(\text{Al}_2\text{B}_2\)\(^2-\) and \(\text{Ga}_2\text{B}_2\)\(^2-\) are not the planar \(D_{2h}\) structures, but the linear \(C_{nv}\) with a short B–B bond of about 1.57 Å (see Fig. 2). The T1 test for these linear structures gives 0.027 for both \(\text{Al}_2\text{B}_2\)\(^2-\) and \(\text{Ga}_2\text{B}_2\)\(^2-\). Therefore, the linear \(\text{Al}_2\text{B}_2\)\(^2-\) and \(\text{Ga}_2\text{B}_2\)\(^2-\) species do not have a strong multireference character and we consider that the relative energies presented in this work are reliable. For the \(\text{Ga}_2\text{Al}_2\)\(^2-\) the cyclic structures are the most stable isomers, the \(D_{2h}\) geometry being more stable than the \(C_{2v}\). In this case the most symmetric molecule is the most stable but the relative energy difference is quite small, only 2 kcal mol\(^{-1}\). This result suggests that the two isomers

![Fig. 1](image-url)
can coexist. High-energy isomers are not further considered. The Al–Ga bond lengths in both systems are basically the same, around 2.58 Å. For Al2B2−2, Ga2B2−2, and Al2Ga2−3 we have analyzed the energy difference between the C2v and D2h structures when a counterion such as Li+ is taken into account to see how a stabilizing environment affects the relative energy of these isomers. For LiAl2B2− and LiGa2B2− the C2v isomer is the most stable by 31.6 and 36.4 kcal mol−1, respectively, at the CCSD(T)/6-311G*/MP2/6-311G* level of theory. These values are not far from the 27.1 and 30.1 kcal mol−1 of energy difference found for isolated Al2B2−2 and Ga2B2−2 (see Fig. 2). For LiAl2Ga2−, the D2h structure is found to be 1.5 kcal mol−1 more stable than the C2v isomer (to be compared with the 2.0 kcal mol−1 obtained in Al2Ga2−2). Therefore, relative energies for the isolated M2N2−2 species do not differ significantly from those obtained for the same species in the presence of a counterion.

The valence MOs for all cyclic and quasi-cyclic molecules are depicted in Fig. 3. All the molecules have quite similar orbital distribution; this is due to their valence isoelectronic character. The rings have 14 valence electrons distributed in 7 valence molecular orbitals, six of them σ (the four lowest-lying constitute the σs set and two highest-lying are the tangential σt and the radial σr) and one π. The presence of this π MO provides the π-aromatic behavior according to Hückel’s rule. Most likely the π-aromaticity does not vary when going from D2h to C2v structures because the π MO does not change significantly in the cyclic molecules. The σ-aromaticity of these compounds is originated by the two independent types of σ MOs, the radial σr and the tangential σt, which separately obey the 4n + 2 Hückel rule for aromatic compounds. In the D2h structures these σ-orbitals are spread over all the atoms, but in the Al2B2−2 and Ga2B2−2 the HOMO − 1 σt orbital does not cover the complete molecule, showing a σ orbital “free” region between the aluminum and gallium atoms, respectively. Of course, depending on the isosurface values used to depict the orbital one can see it visually disconnected or not. But more importantly, the picture shows a non-homogeneous distribution in the C2v compounds, especially in the case of the σt orbital (the one that contributes the most to the σ-aromaticity in Al42−2), which implies a lower electronic delocalization that may reduce the σ-aromatic character. This is quite interesting because the isomers of Al2B2−2 and Ga2B2−2 with D2h symmetry, with a higher delocalization of the σ electrons, are less stable than these C2v structures. Although this result is somewhat unexpected, it has to be said that in many cases, among different isomers, the most aromatic compound is not always the most stable.

Fig. 2 Optimized structures of M2N2−2 (where M and N = B, Al, Ga with M ≠ N). Pink, blue and yellow spheres represent boron, aluminum and gallium atoms, respectively. The relative energies for the isomers were computed at the CCSD(T)/6-311G* level of theory for the MP2/6-311G* optimized structures. The M2N2−2 potential energy surfaces were explored with GEGA at the B3LYP/3-21G level. The bond distances are in Å.
This happens, for instance, in cyclopentafused pyrene congeners,\textsuperscript{44} in heterobicyclic isomers,\textsuperscript{45} in fullerenes isomers,\textsuperscript{46} or for the ortho-, meta-, and para-benzene species.\textsuperscript{47}

To confirm the possible non-cyclic nature of the structures with $C_{2v}$ symmetry, QTAIM calculations at the B3LYP/6-311G* level were employed to find the bond critical points (BCP) and the ring critical points (RCP) in the cyclic structures (Fig. 4). For the $D_{2h}$ isomers of the $\text{Al}_2\text{B}_2\text{Z}^{-}$, $\text{Ga}_2\text{Al}_2\text{Z}^{-}$, and $\text{Ga}_2\text{B}_2\text{Z}^{-}$ and the $C_{2v}$ isomer of $\text{Ga}_2\text{Al}_2\text{Z}^{-}$, four BCP and one RCP were found in each molecule. This analysis confirms the closed structure and the existence of a ring. In counter sense, for the $C_{2v}$ isomers of $\text{Al}_2\text{B}_2\text{Z}^{-}$ and $\text{Ga}_2\text{B}_2\text{Z}^{-}$, the
The results of the EDA obtained at the BP86/TZ2P level of theory are shown in Table 1. The deformation energy in all cases is lower than 0.3 kcal mol\(^{-1}\), and therefore it plays a negligible role. The calculations for the \(M_4z^2\) systems predict that bonding energy is higher in \(B_4z^2\) than in \(Al_4z^2\) and \(Ga_4z^2\). Dissociation of two B–B bonds in \(B_4z^2\) to get two \(B_2z^2\) fragments requires 50.1 kcal mol\(^{-1}\), i.e., while for the same dissociation process in \(Al_4z^2\) one needs only 2.7 kcal mol\(^{-1}\), and for \(Ga_4z^2\) it is even an exothermic process that releases 6.7 kcal mol\(^{-1}\). Clearly the B–B bond in \(B_4z^2\) is much stronger than the Al–Al or Ga–Ga bonds in the analogous clusters. A similar result is obtained when comparing the experimental48 and BP86/TZ2P\(^{49}\) dissociation energies of neutral \(B_2\) and \(Al_2\) in their triplet ground states. The origin of the largest stability of the \(D_{4h}\) \(B_4z^2\) species comes from the higher favorable orbital energy and electrostatic interactions in \(B_4z^2\) as compared to the other two \(D_{4h}\) clusters. The trend of orbital overlaps in \(B_2\) shows that the overlap increases until very short B–B distances.\(^{49}\) The final B–B bond length (almost 1 Å smaller as compared to \(Al_4z^2\) and \(Ga_4z^2\)) is the result of the interplay between attractive, \(\Delta E_{elstat}\) and \(\Delta E_{elstat}\) terms, and repulsive Pauli interactions at short distances.\(^{49}\) The high Pauli repulsion present in \(B_4z^2\) is still much lower than the absolute value of the sum of the two stabilizing \(\Delta E_{elstat}\) terms. Since the Pauli repulsion in this species comes only from the \(\sigma\) electrons, the total \(\sigma\) interaction (excluding electrostatic interaction), \(\Delta E_{elstat} + \Delta E_{Pauli}\), is repulsive by 119.7 kcal mol\(^{-1}\). In the three \(M_4z^2\) clusters, the \(\sigma\) contribution to \(\Delta E_{elstat}\) is about five times bigger than the \(\pi\), indicating that the formation of the \(\sigma\)-framework is more stabilizing than the \(\pi\) one as the orbital interaction term is concerned. The \(\pi\)-component, which measures the contribution of \(\pi\)-bond formation including delocalization to the bonding energy, is in \(B_4z^2\) more than two times more stabilizing than that of \(Al_4z^2\) or \(Ga_4z^2\). The fact that the bonding energy in \(Ga_4z^2\) is positive means that the system is energetically stabilized by dissociation into two \(Ga_2z^2\) fragments. Therefore, \(Ga_4z^2\) is a metastable species with a barrier for the dissociation into identical fragments, in a similar way as the \(N_2z^2\) compound.\(^{50}\)

For the \(M_2N_2z^2\) systems, comparison of the EDA for the \(D_{2h}\) and the \(C_{2v}\) isomers is interesting to get insight into the relative energy differences observed. Moreover, one can understand the role of the B–B bond present in some \(M_2N_2z^2\) isomers. The EDA has been carried out using MN\(^{-1}\) fragments in their quartet open-shell valence configuration. In this EDA, we analyze the simultaneous formation of two \(\sigma\)-bonds and a \(\pi\)-bond. One can construct MN\(^{-1}\) fragments from the \(D_{2h}\) and the \(C_{2v}\) isomers (see Scheme 2) and these fragments will be slightly different. We have analyzed the bonding situation in \(D_{2h}\) isomers obtained from \(D_{2h}\) fragments \((D_{2h}/D_{2h})\) and \(C_{2v}\) isomers generated by means of fragments obtained from the \(C_{2v}\) isomer \((C_{2v}/C_{2v})\). Moreover, we have also analyzed the result of generating \(C_{2v}\) isomers using \(D_{2h}\) fragments \((C_{2v}/D_{2h})\), which is an intermediate “nonrealistic” situation.\(^{22}\) This latter case corresponds to breaking the \(D_{2h}\) molecule into

<table>
<thead>
<tr>
<th>(Al_2B_2z^2)</th>
<th>(Ga_2Alz^2)</th>
<th>(Ga_2B_2z^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C_{2v})</td>
<td>(D_{2h})</td>
<td>(C_{2v})</td>
</tr>
</tbody>
</table>

Fig. 4 Critical points calculated with QTAIM in the different isomers of the \(M_2N_2z^2\) clusters (where M and N = B, Al, and Ga with M ≠ N). Pink, blue and yellow spheres represent boron, aluminum and gallium atoms, respectively.
two MN⁻¹ fragments and turning one of the fragments upside-down before the molecule is built with the M–M and N–N distances of the optimized C_{2v} molecule to give an intermediate species of C_{2v} symmetry. The results of the C_{2v}//D_{2h} scheme are almost identical to those of the D_{2h}//D_{2h} scheme and for this reason they have not been included in Table 1.

Results in Table 1 show that Al₂B₂²⁻ and Ga₂B₂²⁻ yield similar trends. Basically, the C_{2v} structure is the global minimum due to larger attractive orbital interactions despite the higher Pauli repulsion as compared to the D_{2h} counterpart. Both the ΔE_{smin} and ΔE_{smax} terms are more stabilizing for the C_{2v} symmetry. However, the main difference comes from the σ-component of the ΔE_{smin} term and it is likely the result of the strong B–B bond formed in the C_{2v} symmetry, and not due to higher σ-aromaticity (vide infra). The Al₂B₂²⁻ and Ga₂B₂²⁻ molecules energetically prefer to keep a short B–B bond and a long M–M (M = Al, Ga) one and this leads to a partial breaking of the M–M bond. In fact, this is likely the reason why in these species the linear isomer is more stable than Al₂B₂²⁻. The ΔE_{smax} stabilization remains almost constant for the two forms.

### 3. Aromaticity

The aromaticity of these clusters pointed out in the previous section will be assessed further by an in-depth analysis of the induced magnetic field (B^{ind}) and the multicenter delocalization indices (MCI). Calculations were performed in the cyclic molecules in order to gain further insight into their electron delocalization. Fig. 5 and 6 show the profiles of the B^{ind}, equivalent to NICS_{zz}. The induced magnetic field has been separated into its MO contributions to understand the role of the π- and σ-electronic delocalization in the aromaticity of the different cyclic isomers. The induced magnetic field is generated from the electronic delocalization in ring currents parallel to the molecular plane. For that reason only the cyclic structures were analyzed by this methodology. All the structures reported here are valence isoelectronic with Al₂B₂²⁻, which has 14 valence electrons, two of them delocalized in a π-orbital. A profile of the π contribution of the B^{ind} (B^{ind}_{πz}) is plotted in Fig. 5. As expected from the MO analysis, all systems present a similar response of their respective π-electrons. Only the B^{ind} shows a more diatropic character from the ring center up to 1.5 Å over the ring and this is likely due to the well-known ring-size dependence of NICS values, especially at close distances to the center of the ring. The other molecules have the same tendency along the principal symmetry axis. The value of the B^{ind}_{πz} in the center of the structures (where r = 0 Å, equivalent to NICS(0)_{πz}) is around −8 ppm for
all systems, except for \( \text{B}_4 \). All \( \text{M}_2 \text{N}_2 \) (\( \text{M} = \text{B}, \text{Al}, \text{and} \text{Ga} \)) isomers present a similar trend as expected due to the presence of the \( \pi \)-MO similar to that present in \( \text{Al}_2 \).

In the \( \text{Al}_2 \), the HOMO = 1 and HOMO - 2 \( \sigma \)-orbitals are responsible for the \( \sigma \)-aromatic behavior. They are formed by the interaction between the in-plane \( p \) AOs of the aluminum atoms. In the \( \text{Al}_2 \text{B}_2 \) and \( \text{Ga}_2 \text{B}_2 \), the MOs depicted in Fig. 3 show that the radial MO present in these molecules does not cover all the atoms, and this affects the \( \sigma \)-aromaticity. In the profile of the \( B_{\text{out}}^{\text{ind}} \) depicted in Fig. 6 all the systems have the same tendency as \( \text{Al}_2 \text{B}_2 \), except \( \text{B}_4 \) (again it is likely a ring-size effect), and the global minima of \( \text{Al}_2 \text{B}_2 \) and \( \text{Ga}_2 \text{B}_2 \) with \( C_2v \) symmetry. In the all-boron cluster, \( \text{B}_4 \), the profile shows that this structure presents the most intense diatropic response. The value in the ring center of \( \text{B}_4 \) shows a difference of more than 20 ppm as compared to the other cyclic clusters. For the global minima of \( \text{Al}_2 \text{B}_2 \) and \( \text{Ga}_2 \text{B}_2 \), both of \( C_2v \) symmetry, the diatropic character decreases around 10 ppm along the \( z \)-axis if it is compared with their respective \( D_{2h} \) isomers. This is a consequence of the non-symmetrical structure and the less effective overlap of the \( p \) orbitals of gallium and aluminum atoms that led to the formation of the \( \sigma \)-MO. The tangential molecular orbitals, on the other hand, present an important diatropic behavior in all cases.

To complete the study of aromaticity, the MCI and its orbital contributions were computed. All the MCI, MCI\(_z\) and MCI\(_{xz}\) values are presented in Table 2. For the \( \text{M}_2 \text{N}_2 \) structures, the most aromatic system is the gallium cluster, followed by the aluminum and the boron structures, exactly the opposite tendency found using the induced magnetic field, where the values of the \( B_{\text{ind}}^{\text{ind}}(0) \) denote that the \( \text{B}_4 \) structure is the most diatropic cluster among the \( \text{M}_2 \text{N}_2 \) systems. The fact that NICS(0) or NICS(0)\(_{zz}\) yield opposite trends to MCI is not unusual.\(^{18e}\) It is not an easy task to decide which of the two descriptors is the most reliable. Preliminary results seem to indicate the superior behavior of MCI to describe the aromaticity of all-metal clusters.\(^{18e}\) The MCI\(_x\) for these \( D_{2h} \) \( \text{M}_4 \) structures has the same value (0.1875 e) due to the number of \( \pi \)-electrons and the symmetry of the systems.\(^5\) Consequently, the MCI\(_{xz}\) component determines the global MCI for the \( D_{2h} \) \( \text{M}_4 \) molecules (\( \text{M} = \text{B}, \text{Al}, \text{and} \text{Ga} \)). For the boron and aluminum clusters the main contribution is that of \( \pi \). For the all-gallium molecule the \( \sigma \) contribution is larger, indicating a more intense \( \sigma \) aromaticity, in agreement with the orbital contributions to the \( B_{\text{ind}}^{\text{ind}} \) calculations for the \( \text{Ga}_4 \). According to MCI, in general, Ga containing compounds have larger \( \sigma \)-aromaticity than Al containing clusters and these, in turn, are more \( \sigma \)-aromatic than species having B in their structure. For the \( \text{M}_2 \text{N}_2 \) structures, the MCI shows that the two cyclical \( \text{Ga}_2 \text{Al}_2 \), both \( C_2v \) and \( D_{2h} \) isomers, are more aromatic than \( \text{Ga}_2 \text{B}_2 \) and \( \text{Al}_2 \text{B}_2 \), in this order. Basically, the two isomers of the \( \text{Ga}_2 \text{Al}_2 \) present almost the same electron delocalization and aromaticity and, therefore, the reason for the larger stability of the \( D_{2h} \) species cannot be attributed to higher aromaticity. The MCI\(_{xz}\) is the same in both isomers and the values are very close to the \( \pi \) contribution of the \( \text{M}_2 \text{N}_2 \) systems and both MCI\(_{xz}\) values are larger than the \( \sigma \) contribution, as opposed to the results of the \( B_{\text{ind}}^{\text{ind}} \), where the \( \sigma \) electrons present the prevalent

### Table 2

<table>
<thead>
<tr>
<th>( \text{B}_2 ) ( \text{N}_2 ) (( \text{M} = \text{B}, \text{Al}, \text{and} \text{Ga} ))</th>
<th>MCI</th>
<th>MCI(_z)</th>
<th>MCI(_{xz})</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Al}_2 \text{B}<em>2 ) ( \text{C}</em>{2v} )</td>
<td>0.290</td>
<td>0.188</td>
<td>0.102</td>
</tr>
<tr>
<td>( \text{Al}_2 \text{B}<em>2 ) ( \text{D}</em>{2h} )</td>
<td>0.356</td>
<td>0.188</td>
<td>0.168</td>
</tr>
<tr>
<td>( \text{Ga}_2 \text{B}<em>2 ) ( \text{C}</em>{2v} )</td>
<td>0.388</td>
<td>0.188</td>
<td>0.200</td>
</tr>
<tr>
<td>( \text{Ga}_2 \text{B}<em>2 ) ( \text{D}</em>{2h} )</td>
<td>0.202</td>
<td>0.129</td>
<td>0.073</td>
</tr>
<tr>
<td>( \text{Al}_2 \text{B}<em>2 ) ( \text{C}</em>{2v} )</td>
<td>0.240</td>
<td>0.155</td>
<td>0.085</td>
</tr>
<tr>
<td>( \text{Al}_2 \text{B}<em>2 ) ( \text{D}</em>{2h} )</td>
<td>0.202</td>
<td>0.129</td>
<td>0.073</td>
</tr>
<tr>
<td>( \text{Al}_2 \text{B}<em>2 ) ( \text{C}</em>{2v} )</td>
<td>0.240</td>
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<td>( \text{Al}_2 \text{B}<em>2 ) ( \text{D}</em>{2h} )</td>
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<td>( \text{Al}_2 \text{B}<em>2 ) ( \text{C}</em>{2v} )</td>
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<td>( \text{Al}_2 \text{B}<em>2 ) ( \text{D}</em>{2h} )</td>
<td>0.202</td>
<td>0.129</td>
<td>0.073</td>
</tr>
</tbody>
</table>

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\( \text{B}_2 \) shows the prevalent \( \sigma \)-aromatic behavior.
Conclusions

In the present work a search of the global minima of group 13 $\text{M}_2\text{N}_2\text{Z}^2$ (M and N = B, Al, and Ga) clusters employing an automated scanning of the potential energy surfaces of different systems was done. With this methodology all local and the respective global minima were found. The lowest-lying in energy isomers were reoptimized at a higher level of theory to obtain better energetics with the objective to establish the correct global minima and more accurate energy differences. To get a better insight into the bonding situation in these clusters, EDA calculations were also performed. The information of the energy decomposition analysis indicates that all the cyclic (or quasi-cyclic) clusters have strong covalent bonds. It was found that the B-B bond has an important stabilization role because the isomers that present this bond are more stable than the alternated systems, despite being less aromatic than higher symmetric systems. With the induced magnetic field and the MCI results, the double aromatic behavior of all these species was confirmed. Moreover, the important role of the electron delocalization in the molecular design has been put forward, except in $\text{Al}_2\text{B}_2\text{Z}^2$ and $\text{Ga}_2\text{B}_2\text{Z}^2$, where the less aromatic ring is the global minimum in the respective PES. Interestingly, NICS results indicate that the $\pi$-aromaticity is much more important than the $\sigma$-one in the systems analyzed, whereas the MCI descriptor gives similar weights to the $\sigma$- and $\pi$-aromaticities.

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