Molecular structures of $M_2N_2^{2-}$ ($M$ and $N = B$, Al, and Ga) clusters using the gradient embedded genetic algorithm†

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Al$_4^{2-}$ was the first discovered $\sigma + \pi$ aromatic all-metal cluster. In the present work we analyze the molecular structure, relative stability, and aromaticity of lowest-lying isomers of related $M_2N_2^{2-}$ ($M$ and $N = B$, Al, and Ga) clusters, with special emphasis devoted to the cis ($C_{2v}$) and trans ($D_{2h}$) isomers of the $M_2N_2^{2-}$ 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$_4^{2-}$, the first all-metal cluster to be considered aromatic from the ab initio calculations that show two electrons residing in a $\pi$ molecular orbital (MO) and satisfying the Hückel rule$^2$ for aromatic compounds. Also, they found that the pyramidal structures of the Al$_4^{2-}$ 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.$^3$ concluded that the $\pi$-orbital “holds the key for understanding the structure and bonding of MAI$_4^{2-}$ 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.$^{3a-c}$ Moreover, in this all-aluminum cluster $\pi$-electrons are highly delocalized. This conclusion is drawn from the analysis of the valence MOs of Al$_4^{2-}$ that can be separated into four sets: the $\sigma_s$ set consisting of four filled MOs obtained by combination of the 3s Al atomic orbitals (AOs), the $\pi$ set with one filled MO formed by in-phase combination of 3p out-of-plane AOs, and the $\sigma_r$ (radial) and $\sigma_t$ (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$_4^{2-}$ comes from these $\pi$, $\sigma_s$, and $\sigma_t$ orbitals, the $\sigma_r$ orbital having a larger contribution to $\sigma$-aromaticity than the $\sigma_t$ orbital.$^{5b,6}$

Several studies were performed in a way to probe this $\pi$- and $\sigma$-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,$^{4e,14}$ valence bond (VB) estimations,$^{15}$ chemical reactivity descriptors,$^{16}$ analysis of the electron localization function (ELF),$^{17}$ and multicenter delocalization indices.$^{5,18}$

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

The all-metal and semimetal Al$_2B_2^{2-}$, Ga$_2Al_2^{2-}$, and Ga$_2B_2^{2-}$ are also valence isoelectronic to Al$_4^{2-}$, so they are expected to be aromatic compounds too. In a previous work, the aromatic behavior in Ga$_2Al_2^{2-}$ was confirmed by some of the present authors.$^{18c}$ For the $M_2N_2^{2-}$ ($M$ and $N = B$, Al, and Ga with $M \neq N$) 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$_2Ge_2^{20}$ Si$_2Ge_2^{20}$, $^{20}$ $S_2N_2^{21}$ clusters, and diazacyclobutadiene$^{22}$ are more stable in the trans configuration. On the other hand, for Ga$_2Ge_2^{20}$ Al$_2Si_2^{10,20}$ Ga$_2Si_2^{20}$
The preparation energy, as implemented in the ADF2010 package at the BP86/TZ2P level. The overall bond energy, of a molecule from two fragments is divided into two major meaningful terms: the Pauli repulsion, the classical electrostatic interaction, \( V_{\text{elstat}} \) and the orbital interaction energy, \( \Delta E_{\text{int}} \) (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.

\[
\Delta E_{\text{int}} = \Delta E_{\text{Pauli}} + V_{\text{elstat}} + \Delta E_{\text{oi}} \quad (2)
\]

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

\[
B^{\text{ind}}(r) = -\sigma_{\text{ad}}(r) B^{\text{ext}}, \quad (3)
\]

where \( \sigma_{\text{ad}} \) 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 \( B^{\text{ind}} \) 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 \( B^{\text{ind}} \) can be separated into its orbital contributions for deeper study of the \( \pi \) and \( \sigma \) electrons 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 \( B^{\text{ind}} \) is equivalent to NICS at.

The potential energy surfaces (PESs) of the different clusters were explored at the B3LYP/3-21G level, employing the Gradient Embedded Genetic Algorithm (GEGA) developed by Alexandrova and coworkers. This program makes an intense search of different isomers for the specific number and type of atoms. For every structure, four searches were performed for singlets and two for triplets. The isomers having a relative energy lower than 15 kcal mol\(^{-1}\) as compared to the global minimum at the B3LYP/3-21G level were re-optimized and characterized at the B3LYP/3-21G level. The isomers found to be higher in energy than the global minima by less than 35 kcal mol\(^{-1}\) and the cyclic structures (even those rings whose relative energy is higher than 35 kcal mol\(^{-1}\)) were recomputed at the MP2/6-311G* level, and single-point energy calculations were carried out in the molecules higher in energy for the few lowest-energy isomers at CCSD(T)/6-311G** for more accurate energy values employing the MP2/6-311G* structures. Despite \( D_n \) Al\(^{4-}\) being unstable with respect to Al\(^{4+}\) + free e\(^-\), we consider following the arguments by Boldyrev and Zubarev that calculations for isolated Al\(^{4-}\) and related species using the CCSD(T)/6-311G*/MP2/6-311G* methodology is an adequate model for Al\(^{4-}\) in a stabilizing environment such as LiAl\(^{4+}\) or similar. The same applies to the rest of the systems studied in this work.

To gain more insight into the nature of the bonding in these clusters, an energy decomposition analysis (EDA) was performed as implemented in the ADF2010 package at the BP86/TZ2P level. The overall bond energy, \( \Delta E \), corresponding to the formation of a molecule from two fragments is divided into two major components (see eqn (1))

\[
\Delta E = \Delta E_{\text{prep}} + \Delta E_{\text{int}} \quad (1)
\]

The preparation energy, \( \Delta E_{\text{prep}} \), corresponds to the energy required to deform the separated fragments from their equilibrium structures to the geometries they acquire 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, the classical electrostatic interaction, \( V_{\text{elstat}} \) 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.
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 (\(D_{2h}\) symmetry) is higher in energy by 63.7 kcal mol\(^{-1}\) than 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 (\(D_{2h}\) symmetry) is higher in energy by 63.7 kcal mol\(^{-1}\) than 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.

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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 \(\neq\) 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 \(C_{N}\) 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  Optimized structures of \(\text{M}_4^{2-}\) (where M = B, Al, and Ga). 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 \(\text{M}_4^{2-}\) potential energy surfaces were explored with GEGA at B3LYP/3-21G. The bond distances are in Å.
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 Al$_2$B$_2$$^2$–, Ga$_2$B$_2$$^2$–, and Al$_2$Ga$_2$$^2$– we have analyzed the energy difference between the $C_{2v}$ and $D_{2h}$ structures when a counterion such as Li$^+$ is taken into account to see how a stabilizing environment affects the relative energy of these isomers. For LiAl$_2$B$_2$$^2$– and LiGa$_2$B$_2$$^2$– the $C_{2v}$ isomer is the most stable by 31.6 and 36.4 kcal mol$^{-1}$, respectively, at the CCSD(T)/6-311G*//MP2/6-311G* level of theory. These values are not far from the 27.1 and 30.1 kcal mol$^{-1}$ of energy difference found for isolated Al$_2$B$_2$$^2$– and Ga$_2$B$_2$$^2$– (see Fig. 2). For LiAl$_2$Ga$_2$$^2$–, the $D_{2h}$ structure is found to be 1.5 kcal mol$^{-1}$ more stable than the $C_{2v}$ isomer (to be compared with the 2.0 kcal mol$^{-1}$ obtained in Al$_2$Ga$_2$$^2$–). Therefore, relative energies for the isolated M$_2$N$_2$$^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 $\sigma$ (the four lowest-lying constitute the $\sigma_s$ set and two highest-lying are the tangential $\sigma_t$ and the radial $\sigma_r$) and one $\pi$. The presence of this $\pi$ MO provides the $\pi$-aromatic behavior according to Hückel’s rule. Most likely the $\pi$-aromaticity does not vary when going from $D_{2h}$ to $C_{2v}$ structures because the $\pi$ MO does not change significantly in the cyclic molecules. The $\sigma$-aromaticity of these compounds is originated by the two independent types of $\sigma$ MOs, the radial $\sigma_r$ and the tangential $\sigma_t$, which separately obey the $4n + 2$ Hückel rule for aromatic compounds. In the $D_{4h}$ structures these $\sigma$-orbitals are spread over all the atoms, but in the Al$_2$B$_2$$^2$– and Ga$_2$B$_2$$^2$– the HOMO – 1 $\sigma_t$ orbital does not cover the complete molecule, showing a $\sigma_t$ 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 $C_{2v}$ compounds, especially in the case of the $\sigma_r$ orbital (the one that contributes the most to the $\sigma$-aromaticity in Al$_4$$^2$–), which implies a lower electronic delocalization that may reduce the $\sigma$-aromatic character. This is quite interesting because the isomers of Al$_2$B$_2$$^2$– and Ga$_2$B$_2$$^2$– with $D_{2h}$ symmetry, with a higher delocalization of the $\sigma$ electrons, are less stable than these $C_{2v}$ 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 M$_2$N$_2$$^2$– (where M and N = B, Al, Ga with M $\neq$ N). Pink, blue and yellow spheres represent boron, aluminum and gallium atoms, respectively.](View Online)
This happens, for instance, in cyclopentafused pyrene congeners, in heterobicyclic isomers, in fullerenes isomers, or for the ortho-, meta-, and para-benzene species.

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 $Al_2B_2^{2-}$, $Ga_2Al_2^{2-}$, and $Ga_2B_2^{2-}$ and the $C_2v$ isomer of $Ga_2Al_2^{2-}$, 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 $Al_2B_2^{2-}$ and $Ga_2B_2^{2-}$, the
Fig. 4  Critical points calculated with QTAIM in the different isomers of the $\text{M}_2\text{N}_2^{2-}$ clusters (where $\text{M}$ and $\text{N}$ = B, Al, and Ga with $\text{M} \neq \text{N}$). Pink, blue and yellow spheres represent boron, aluminum and gallium atoms, respectively.

analysis reveals only three BCP, thus indicating that they are not closed cycles in QTAIM view. Due to the lack of the Al-\cdots-Al and Ga-\cdots-Ga BCP for the cis $\text{Al}_2\text{B}_2^{2-}$ and $\text{Ga}_2\text{B}_2^{2-}$ species, we have performed broken symmetry unrestricted calculations to confirm that the singlet closed-shell (and not the singlet open-shell) is the ground state for these species.

Our results show that for $\text{Al}_2\text{B}_2^{2-}$ and $\text{Ga}_2\text{B}_2^{2-}$ the cis ($D_{2h}$) is the most stable cyclic isomer, whereas the trans ($D_{2h}$) configuration is preferred for $\text{Ga}_2\text{Al}_2^{2-}$. As said in the introduction there is not a general behavior for these isomers and their relative stability depends on the nature of the $\text{M}$ and $\text{N}$ atoms. To gain insight into the origin of the relative stability of the cis and trans $\text{M}_2\text{N}_2^{2-}$ ($\text{M}$ and $\text{N}$ = B, Al, and Ga with $\text{M} \neq \text{N}$) configurations and the nature of the $\sigma$- and $\pi$-bonding in these systems, energy decomposition analysis (EDA) calculations were carried out. To this end, we have considered the partition into two fragments as depicted in Scheme 1. The $\text{M}_4^{2-}$ systems were analyzed too. The $\text{M}_2^{2-}$ or $\text{MN}^{\cdots}$ fragments considered were in their quartet open-shell valence configuration (three spin up in the bonding orbitals $\sigma_{p\sigma}$, $\pi_{p\pi}$, and $\pi_{p\pi}$, one of the diatomic fragments and three spin down in the same orbitals of the other) in order to correctly build the $\sigma$, $\pi$, and $\sigma_{p\sigma}$ MOs of $\text{M}_2^{2-}$ and $\text{M}_2\text{N}_2^{2-}$.

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 $\text{M}_4^{2-}$ systems predict that bonding energy is higher in $\text{B}_4^{2-}$ than in $\text{Al}_2^{2-}$ and $\text{Ga}_4^{2-}$. Dissociation of two B-B bonds in $\text{B}_2^{2-}$ to get two $\text{B}_2^{\cdots}$ fragments requires 50.1 kcal mol\(^{-1}\), i.e., while for the same dissociation process in $\text{Al}_2^{2-}$ one needs only 2.7 kcal mol\(^{-1}\), and for $\text{Ga}_4^{2-}$ it is even an exothermic process that releases 6.7 kcal mol\(^{-1}\). Clearly the B-B bond in $\text{B}_2^{2-}$ is much stronger than the Al-Al or Ga-Ga bonds in the analogous clusters.

A similar result is obtained when comparing the experimental and BP86/TZ2P dissociation energies of neutral $\text{B}_2$ and $\text{Al}_2$ in their triplet ground states. The origin of the largest stability of the $D_{2h}$ $\text{B}_2^{2-}$ species comes from the higher favorable orbital energy and electrostatic interactions in $\text{B}_2^{2-}$ as compared to the other two $D_{2h}$ clusters. The trend of orbital overlaps in $\text{B}_2$ shows that the overlap increases until very short B-B distances. The final B-B bond length (almost 1 Å smaller as compared to $\text{Al}_2^{2-}$ and $\text{Ga}_2^{2-}$) is the result of the interplay between attractive, $\Delta E_{\text{elstat}}$ and $\Delta E_{\text{electron}}$ terms, and repulsive Pauli interactions at short distances. The high Pauli repulsion present in $\text{B}_2^{2-}$ is still much lower than the absolute value of the sum of the two stabilizing $\Delta E_{\text{elstat}}$ and $\Delta E_{\text{electron}}$ terms. Since the Pauli repulsion in this species comes only from the $\sigma$ electrons, the total $\sigma$ interaction (excluding electrostatic interaction), $\Delta E_{\text{elstat}} + \Delta E_{\text{Pauli}}$, is repulsive by 119.7 kcal mol\(^{-1}\). In the three $\text{M}_4^{2-}$ clusters, the $\sigma$ contribution to $\Delta E_{\text{elstat}}$ 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 $\text{B}_4^{2-}$ more than two times more stabilizing than that of $\text{Al}_4^{2-}$ or $\text{Ga}_4^{2-}$. The fact that the bonding energy in $\text{Ga}_4^{2-}$ is positive means that the system is energetically stabilized by dissociation into two $\text{Ga}_2^{\cdots}$ fragments. Therefore, $\text{Ga}_2^{\cdots}$ is a metastable species with a barrier for the dissociation into identical fragments, in a similar way as the $\text{N}_2^{2+}$ compound.

For the $\text{M}_2\text{N}_2^{2-}$ 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 $\text{M}_2\text{N}_2^{2-}$ isomers. The EDA has been carried out using $\text{MN}^{\cdots}$ 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 $\text{MN}^{\cdots}$ 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. This latter case corresponds to breaking the $D_{2h}$ molecule into...
two MN\textsuperscript{1}—\cdots 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\textsubscript{2v} molecule to give an intermediate species of C\textsubscript{2v} symmetry.\textsuperscript{22} The results of the C\textsubscript{2v}/D\textsubscript{2h} scheme are almost identical to those of the D\textsubscript{2h}/D\textsubscript{2h} scheme and for this reason they have not been included in Table 1.

Results in Table 1 show that Al\textsubscript{2}B\textsubscript{2}\textsuperscript{2}– and Ga\textsubscript{2}B\textsubscript{2}\textsuperscript{2}– yield similar trends. Basically, the C\textsubscript{2v} structure is the global minimum due to larger attractive orbital interactions despite the higher Pauli repulsion as compared to the D\textsubscript{2h} counterpart. Both the ΔE\textsubscript{int} and ΔE\textsubscript{exc} terms are more stabilizing for the C\textsubscript{2v} symmetry. However, the main difference comes from the σ-component of the ΔE\textsubscript{int} term and it is likely the result of the strong B–B bond formed in the C\textsubscript{2v} symmetry, and not due to higher σ-aromaticity (vide infra). The Al\textsubscript{2}B\textsubscript{2}– and Ga\textsubscript{2}B\textsubscript{2}– 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 the upside-down before the molecule is built with the M–M and this leads to a partial breaking of the M–M bond. In fact, this is likely the reason

For Ga\textsubscript{2}Al\textsubscript{2}\textsuperscript{2}–, the global minimum is quite close to the next isomer, so a coexistence of the two structures is likely to occur. As found in Ga\textsubscript{4}\textsuperscript{2}–, Ga\textsubscript{2}Al\textsubscript{2}\textsuperscript{2}– is a metastable species with a marginally exothermic dissociation into two GaAl\textsuperscript{1}– fragments. The EDA calculations show the same tendency: the two isomers show almost the same values and the difference in their respective ΔE\textsubscript{int} is less than 1 kcal mol\textsuperscript{−1}. The slightly larger stability of the D\textsubscript{2h} clusters comes from smaller Pauli repulsion, which are mainly attributed to the existence of the Ga–Ga direct bond in the C\textsubscript{2v} cluster (Ga has more electrons than Al). The ΔE\textsubscript{int} 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\textsubscript{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\textsubscript{ind} and NICS\textsubscript{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 Al\textsubscript{4}\textsuperscript{2}–, which has 14 valence electrons, two of them delocalized in a π-orbital. A profile of the π contribution of the B\textsubscript{ind} (B\textsubscript{ind}\textsuperscript{π}) 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\textsubscript{ind}– cluster 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.\textsuperscript{7,51} The other molecules have the same tendency along the principal symmetry axis. The value of the B\textsubscript{ind}\textsuperscript{π} in the center of the structures (where \( r = 0 \) Å, equivalent to NICS(0)\textsubscript{π}) is around −8 ppm for

| Table 1 | BP86/TZ2P energy decomposition analysis for the cyclic molecules. Energies are in kcal mol\textsuperscript{−1}. |
|------------------|------------------|------------------|------------------|------------------|------------------|
| B\textsubscript{4}\textsuperscript{2}– | Al\textsubscript{2}B\textsubscript{2}\textsuperscript{2}– | Ga\textsubscript{4}\textsuperscript{2}– | Al\textsubscript{3}B\textsubscript{2}\textsuperscript{2}– | Ga\textsubscript{2}Al\textsubscript{2}\textsuperscript{2}– | Ga\textsubscript{2}B\textsubscript{2}\textsuperscript{2}– |
| ΔE\textsubscript{Pauli} | ΔE\textsubscript{stat} | ΔE\textsubscript{int} | ΔE\textsubscript{exc} | ΔE\textsubscript{def} | ΔE\textsubscript{tot} | ΔE |
| ΔE\textsubscript{int} | ΔE\textsubscript{def} | ΔE\textsubscript{tot} | ΔE |
| ΔE\textsubscript{int} | ΔE\textsubscript{def} | ΔE\textsubscript{tot} | ΔE |

\( a \) r(B–B) = 1.684 Å; \( b \) r(Ga–Al) = 2.579 Å; \( c \) r(Al–Al) = 2.596 Å; \( d \) r(Al–B) = 2.064 Å; \( e \) r(B–B) = 1.599 Å; \( f \) r(Al–Al) = 2.617 Å; \( g \) r(Ga–Ga) = 2.625 Å; \( h \) r(Ga–Ga) = 2.560 Å; \( i \) r(Ga–B) = 2.124 Å; \( j \) r(B–B) = 1.561 Å; \( k \) r(Ga–Ga) = 3.260 Å; \( l \) r(Ga–B) = 2.197 Å.

Scheme 2

![Scheme 2](image-url)
all systems, except for B\textsubscript{4}\textsuperscript{2−}. All M\textsubscript{2}N\textsubscript{2}\textsuperscript{2−} (M and N = B, Al, and Ga with M ≠ N) isomers present a similar trend as expected due to the presence of the π-MO similar to that present in Al\textsubscript{2}\textsuperscript{2−}.

In the Al\textsubscript{2}\textsuperscript{2−}, the HOMO = 1 and HOMO – 2 σ-orbitals are responsible for the σ-aromatic behavior. They are formed by the interaction between the in-plane p AOs of the aluminum atoms. In the Al\textsubscript{2}B\textsubscript{2}\textsuperscript{2−} and Ga\textsubscript{2}B\textsubscript{2}\textsuperscript{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 σ-aromaticity. In the profile of the B\textsuperscript{ind\textsubscript{2}}\textsuperscript{2} depicted in Fig. 6 all the systems have the same tendency as Al\textsubscript{2}\textsuperscript{2−}, except B\textsubscript{4}\textsuperscript{2−} (again it is likely a ring-size effect), and the global minima of Al\textsubscript{2}B\textsubscript{2}\textsuperscript{2−} and Ga\textsubscript{2}B\textsubscript{2}\textsuperscript{2−} with C\textsubscript{2v} symmetry. In the all-boron cluster, B\textsubscript{4}\textsuperscript{2−}, the profile shows that this structure presents the most intense diatropic response. The value in the ring center of B\textsubscript{4}\textsuperscript{2−} shows a difference of more than 20 ppm as compared to the other cyclic clusters. For the global minima of Al\textsubscript{2}B\textsubscript{2}\textsuperscript{2−} and Ga\textsubscript{2}B\textsubscript{2}\textsuperscript{2−}, both of C\textsubscript{2v} symmetry, the diatropic character decreases around 10 ppm along the z-axis if it is compared with their respective D\textsubscript{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 σ, 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\textsubscript{z} and MCI\textsubscript{zz} values are presented in Table 2. For the M\textsubscript{2}N\textsubscript{2}\textsuperscript{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\textsuperscript{ind\textsubscript{2}}(0) denote that the B\textsubscript{4}\textsuperscript{2−} structure is the most diatropic cluster among the M\textsubscript{2}N\textsubscript{2}\textsuperscript{2−} systems. The fact that NICS(0) or NICS(0)zz yield opposite trends to MCI is unfortunately not unusual.\textsuperscript{18c} 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.\textsuperscript{18c} The MCI\textsubscript{z} for these D\textsubscript{2h} M\textsubscript{4}\textsuperscript{2−} structures has the same value (0.1875 e) due to the number of π-electrons and the symmetry of the systems.\textsuperscript{6} Consequently, the MCI\textsubscript{zz} component determines the global MCI for the D\textsubscript{2h} M\textsubscript{4}\textsuperscript{2−} molecules (M = B, Al, and Ga). For the boron and aluminum clusters the main contribution is that of π. For the all-gallium molecule the σ contribution is larger, indicating a more intense σ aromaticity, in agreement with the orbital contributions to the B\textsuperscript{ind\textsubscript{2}} calculations for the Ga\textsubscript{4}\textsuperscript{2−}. According to MCI, in general, Ga containing compounds have larger σ-aromaticity than Al containing clusters and these, in turn, are more σ-aromatic than species having B in their structure. For the M\textsubscript{2}N\textsubscript{2}\textsuperscript{2−} structures, the MCI shows that the two cyclical Ga\textsubscript{2}Al\textsubscript{2}\textsuperscript{2−}, both C\textsubscript{2v} and D\textsubscript{2h} isomers, are more aromatic than Ga\textsubscript{2}B\textsubscript{2}\textsuperscript{2−} and Al\textsubscript{2}B\textsubscript{2}\textsuperscript{2−}, in this order. Basically, the two isomers of the Ga\textsubscript{2}Al\textsubscript{2}\textsuperscript{2−} present almost the same electron delocalization and aromaticity and, therefore, the reason for the larger stability of the D\textsubscript{2h} species cannot be attributed to higher aromaticity. The MCI\textsubscript{z} is the same in both isomers and the values are very close to the σ contribution of the M\textsubscript{2}N\textsubscript{2}\textsuperscript{2−} systems and both MCI\textsubscript{zz} values are larger than the σ contribution, as opposed to the results of the B\textsuperscript{ind\textsubscript{2}}, where the σ electrons present the prevalent

\begin{table}[h]
\centering
\begin{tabular}{cccccccccc}
\hline
&M1\textsubscript{2} & Al\textsubscript{2}\textsuperscript{2−} & Al\textsubscript{2}B\textsubscript{2}\textsuperscript{2−} & Al\textsubscript{2}Ga\textsubscript{2}\textsuperscript{2−} & Al\textsubscript{2}B\textsubscript{2}\textsuperscript{2−} (C\textsubscript{2v}) & Al\textsubscript{2}Ga\textsubscript{2}\textsuperscript{2−} (C\textsubscript{2v}) & Al\textsubscript{2}B\textsubscript{2}\textsuperscript{2−} (D\textsubscript{2h}) & Al\textsubscript{2}Ga\textsubscript{2}\textsuperscript{2−} (D\textsubscript{2h}) & Ga\textsubscript{2}Al\textsubscript{2}\textsuperscript{2−} (D\textsubscript{2h}) & Ga\textsubscript{2}B\textsubscript{2}\textsuperscript{2−} (D\textsubscript{2h}) \\
\hline
MCI & 0.290 & 0.356 & 0.388 & 0.202 & 0.240 & 0.367 & 0.359 & 0.273 & 0.321 \\
MCI\textsubscript{z} & 0.188 & 0.188 & 0.188 & 0.129 & 0.155 & 0.187 & 0.185 & 0.149 & 0.187 \\
MCI\textsubscript{zz} & 0.102 & 0.168 & 0.200 & 0.073 & 0.085 & 0.180 & 0.174 & 0.124 & 0.134 \\
\hline
\end{tabular}
\caption{The B3LYP/6-311+G* MCI, MCI\textsubscript{z} and MCI\textsubscript{zz} values (in a.u.) of the M\textsubscript{2}N\textsubscript{2}\textsuperscript{2−} clusters (where M and N = B, Al, and Ga).}
\end{table}
electronic delocalization. Interestingly, MCI results show that the more stable \( C_2 \) isomer of \( \text{Ga}_2 \text{B}_2^2^- \) and \( \text{Al}_2 \text{B}_2^2^- \) is less \( \sigma \) and \( \pi \)-aromatic than the \( D_{2h} \) form. While the reduction in \( \sigma \)-aromaticity when going from \( D_{2h} \) to \( C_2 \) is in agreement with \( B_{\text{ind}}^2 \) trends given in Fig. 6, the reduction in the \( \pi \)-aromaticity is less evident from the profiles of \( B_{\text{ind}}^2 \). Finally, we have checked that MCI values and NICS profiles keep almost constant when including diffuse functions in the basis set (see Table S2 and Fig. S1, ES†).

Conclusions

In the present work a search of the global minima of group 13 \( M_2 \text{N}_2^2^- \) (\( M = \text{B}, \text{Al}, \text{and Ga} \)) 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 \( \text{B}–\text{B} \) 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 \( \text{Al}_2 \text{B}_2^2^- \) and \( \text{Ga}_2 \text{B}_2^2^- \), 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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