All-metal aromatic clusters $M_4^{2-}$ ($M = B$, Al, and Ga). Are $\pi$-electrons distortive or not?\footnote{Electronic supplementary information (ESI) available: Additional EDA results and Cartesian coordinates of all stationary points. See DOI: 10.1039/c1cp22759a}

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The $\pi$-electrons in benzene, the quintessential aromatic molecule, were previously shown to be distortive, \textit{i.e.}, they prefer localized double bonds alternating with single bonds. It is the $\sigma$-electrons that force the double bonds to delocalize, leading to a regular, $D_{6h}$ geometry. Herein, we computationally investigate the double-bond localizing or delocalizing propensities of $\sigma$- and $\pi$-electrons in the archetypal all-metal aromatic cluster $\text{Al}_4^{2-}$ and its second- and fourth-period analogs $\text{B}_4^{2-}$ and $\text{Ga}_4^{2-}$, using Kohn–Sham molecular orbital (MO) theory at BP86/TZ2P in combination with quantitative bond energy decomposition analyses (EDA). We compare the three all-metal aromatic clusters with the structurally related organic species $\text{C}_4\text{H}_4^{1+}$, $\text{C}_6\text{H}_6$ and $\text{C}_4\text{H}_4^{2+}$. Our analyses reveal that the $\pi$-electrons in the group-13 $\text{M}_4^{2-}$ molecules have a weak preference for localizing the double bonds. Instead, the $\sigma$-electrons enforce the regular $D_{6h}$ equilibrium geometry with delocalized double bonds.

1. Introduction

All-metal and semimetal aromatic clusters are among the most exciting molecules synthesized since the beginning of the present century.\textsuperscript{1} These compounds can have not only the conventional $\pi$-(anti)aromaticity of classical organic compounds, but also $\sigma^2$- and even $\sigma^3$- and $\pi$-(anti)aromaticity,\textsuperscript{2} thus giving rise to the so-called multifold aromaticity.\textsuperscript{3} The first all-metal compound, $\text{Al}_4^{2-}$, face-capped by an $\text{M}^+$ cation ($M = \text{Li}$, Na, Cu), was synthesized by Boldyrev, Wang, and coworkers in 2001 using a laser vaporization technique.\textsuperscript{4} While computed NICS values indicated an aromatic character of this compound, molecular orbital (MO) analyses pointed out that $\text{Al}_4^{2-}$ has double ($\sigma + \pi$)-aromatic character.\textsuperscript{5} These conclusions were later on confirmed through multiple aromatic criteria, such as further NICS\textsuperscript{6} and canonical MO-NICS calculations,\textsuperscript{7} induced magnetic field analysis,\textsuperscript{8} plots of aromatic ring current shieldings (ARCS),\textsuperscript{9} gauge-including magnetically induced currents (GIMIC),\textsuperscript{10} ring current maps,\textsuperscript{11} resonance energy (RE) calculations,\textsuperscript{12} valence bond (VB) estimations,\textsuperscript{13} chemical reactivity descriptors,\textsuperscript{14} analysis of the electron localization function (ELF),\textsuperscript{15} and multicenter delocalization indices.\textsuperscript{16} Nowadays, many newly observed inorganic clusters with aromatic characteristics have been described.\textsuperscript{17} Clearly, the concept of aromaticity is no longer confined to “carbon chemistry” but can be applied to the entire periodic table.

The $\pi$-electrons in benzene are distortive in the sense that they favor the $D_{6h}$ symmetric structure of benzene over the $D_{3h}$ one. This was proposed first by Berry\textsuperscript{17} in an attempt to account for the observed increased frequency of the $\text{b}_{2u}$ Kekulé vibrational mode from 1309 to 1570 cm$^{-1}$ when going from the ground $\text{A}_{1g}$ to the first $\text{B}_{2u}$ excited state.\textsuperscript{18} This $\text{B}_{2u}$ vibrational mode has bond length alternation (BLA) character and connects the symmetric $D_{6h}$ benzene with a Kekulé-like structure of $D_{3h}$ symmetry. The upshift of the frequency of this vibrational mode in the excited state, which was unexpected in the context of the $\pi^* \rightarrow \pi$ nature of this electronic transition, was explained considering that the promotion of a $\pi$-electron to an antibonding orbital reduces the $\pi$-distortivity power and, consequently, increases the frequency of this Kekuléan vibrational mode as observed experimentally. This line of reasoning was reinforced later on by the work of Haas and Zilberg,\textsuperscript{19} and, in fact, the theory about the distortive character of $\pi$-electrons in aromatic systems has gained support over the years, especially thanks to the work of Hiberty, Shai, and co-workers\textsuperscript{20} among others.\textsuperscript{21} One of us has devised an MO model of aromaticity based on accurate Kohn–Sham density functional theory (DFT) analyses of the bonding that explains, in terms of orbital-overlap arguments, why benzene has a regular structure with delocalized double bonds whereas the geometry of 1,3-cyclobutadiene is distorted with localized double bonds.\textsuperscript{22} According to these studies the tendency of
π-electrons in classical organic aromatic molecules is always to localize the double bonds, against the delocalizing force of the σ-electrons. This propensity is higher for the antiaromatic species thus explaining the π-localization in C₆H₆ or delocalization in C₆H₄.¹² As a result of all these investigations, it seems now clear that, while many of the properties attributed to aromaticity derive from the π-electrons, the σ-electrons are the ones responsible for the symmetric framework of monocyclic aromatic compounds.

As said before, a paradigmatic case of metalloaromaticity in all-metal clusters is Al₄⁻ and related species. Al₄⁻ contains a pair of delocalized π-electrons (orbital 1a₂g) and two pairs of σ-electrons (orbitals 1b₂g and 2a₁g) that contribute to the overall aromaticity of this species (vide infra).¹³,¹⁰,¹¹ The two π-electrons obey the 4n + 2 Hückel rule for monocyclic π-systems.¹⁵ Although, this is not the case for the σ-electrons, the two pairs of delocalized σ-electrons belong to MOs that follow orthogonal radial (orbital 2a₁g) and tangential (orbital 1b₂g) directions, which makes them independent,¹⁴ thus separately following the 4n + 2 rule. According to its electronic structure, Al₄⁻ can be considered as a “3-fold” aromatic system.

In the present study, we wish to evaluate the above situation in a more quantitative manner. Are the π-electrons of the Al₄⁻ cluster distortive, i.e., do they work against the regular “aromatic” structure with delocalized, equivalent bonds? Or is this propensity a characteristic of only classical aromatic organic molecules? In addition, the role of the four σ-electrons in this Al₄⁻ cluster is not entirely clear. Therefore, we have carried out a detailed investigation of the role of σ- and π-electrons in the formation of the D₄h delocalized structure of the Al₄⁻ cluster using MO theory and the “interpenetrating-fragnments model” already employed to analyze classical organic and inorganic benzene analogues.²² For comparison, the B₄⁺ and Ga₄⁻ clusters together with the structurally similar organic C₆H₄, C₆H₄⁺, and C₆H₄⁻ molecules are also included in our analyses.

2. Theoretical methods

All Density Functional Theory (DFT) calculations were performed with the Amsterdam Density Functional (ADF) program.²⁴ The MOs were expanded in a large uncontracted set of Slater type orbitals (STOs) of triple-ζ quality for all atoms and two sets of polarization functions (TZ2P basis set) were included: 2p and 3d on H; 3d and 4f on B, C, and Al; 4d and 4f on Ga.²⁵ The 1s core electrons of boron and carbon, the 1s2s2p core–shells of aluminium, and the 1s2s2p3s3p for gallium were treated by the frozen core approximation as it was shown to have a negligible effect on the obtained geometries and energetics.²⁶ An auxiliary set of s, p, d, f, and g STOs was used to fit the molecular density and to represent the Coulomb and exchange potentials accurately for each SCF cycle.

Energies and gradients were computed using the local density approximation (Slater exchange and VWN correlation) with non-local corrections for exchange (Becke88) and correlation (Perdew86) included self-consistently (i.e., the BP86 functional). All open-shell systems were treated with the spin-unrestricted formalism. All the geometry optimizations were performed with the QUILD³⁰ (QUantum-regions Interconnected by Local Descriptions) program, which functions as a wrapper around the ADF program. The QUILD program constructs all input files for ADF, runs ADF, and collects all data; ADF is used only for the generation of the energy and gradients. Furthermore, the QUILD program uses improved geometry optimization techniques, such as adapted delocalized coordinates.³⁰

We report here results for an unstable dianion such as Al₄⁻. Lambrecht et al.³¹ proved that Al₄⁻ is unstable as compared to Al₄⁻ + free e⁻ and, consequently, its computed properties change significantly when increasing the number of diffuse functions in the basis set. Indeed, after inclusion of certain number of diffuse functions, the Al₄⁻ evolves to Al₄⁻ + free e⁻. In this sense, Lambrecht and coworkers warned about the validity of calculations carried out for such unstable diadions. In a subsequent comment (see also the rebuttal in ref. 33) on the work by Lambrecht et al.,³¹ Zubarev and Boldyrev argued against this point of view and considered that the bound state of the individual Al₄⁻ is an adequate model of Al₄⁻ in a stabilizing environment such as in Li₅Al₄⁻ or Li₂Al₄. They also considered that calculations for isolated Al₄⁻ species using a 6-311+G(d) basis provide an accurate model for the Al₄⁻ unit embedded in a stabilizing environment. Following the Zubarev and Boldyrev arguments,³² we will discuss the properties of the bound state of Al₄⁻ by employing a doubly polarized triple-ζ basis set.

To get a deeper insight into the distortive or symmetrizing propensity of the σ- and π-electrons, an energy decomposition analysis (EDA) has been carried out considering two fragments and how the different components of the energy change when going from θ = 90° (delocalized structure) to 100° (localized structure) as depicted in Fig. 1 for M₄⁻. In this analysis, the total binding energy ΔE associated with formation of the M₄⁻ molecule with different θ angles (see Scheme 1) from two identical triradicals, M₂(zzzz) + M₂(βββ), with the electronic configuration shown, later on, in Fig. 3,

\[
\Delta E: M₂(zzzz) + M₂(βββ) \rightarrow M₄⁻ (1)
\]

was made up of two major components (eqn (2)):

\[
\Delta E = \Delta E_{\text{peep}} + \Delta E_{\text{int}} (2)
\]

In this formula, the preparation energy ΔE_{peep} is the amount of energy required to deform two individual (isolated) triradicals from their equilibrium structure to the geometry that they acquire in the overall molecule. The interaction energy ΔE_{int} corresponds to the actual energy change when these geometrically deformed triradicals are combined to form the M₄⁻ molecule. It is analyzed in the framework of the Kohn–Sham MO model using a quantitative decomposition of the bond energy into electrostatic interaction, Pauli repulsion (or exchange repulsion or overlap repulsion), and orbital interactions (eqn (3)):³⁴,³⁵

\[
\Delta E_{\text{int}} = \Delta V_{\text{elstat}} + \Delta E_{\text{pauli}} + \Delta E_{\text{oi}} (3)
\]

The term ΔV_{elstat} corresponds to the classical electrostatic interaction between the unperturbed charge distributions.
The orbital interaction energy can be decomposed into the contributions from each irreducible representation $I$ of the interacting system (eqn (4)) using the extended transition state (ETS) scheme developed by Ziegler and Rauk$^{34a,36}$ (note that this approach differs in this respect from the Morokuma scheme,$^{34a,b}$ which instead attempts a decomposition of the orbital interactions into polarization and charge transfer).

$$\Delta E_{oi} = \Sigma_I \Delta E_I$$  \hspace{1cm} (4)

In systems with a clear $\sigma/\pi$ separation, this symmetry partitioning proves to be most informative.

Finally, because in our construction of $B_4^{2-}$, the $\pi$-electrons do not contribute to the Pauli repulsion, we can write for $B_4^{2-}$:

$$\Delta E_{int} = \Delta V_{\text{estat}} + \text{“total } \sigma \text{“} + \text{“total } \pi \text{“}$$  \hspace{1cm} (5)

in which “total $\sigma$“ = $\Delta E_{\text{Pauli}} + \Delta E_\sigma$ and “total $\pi$“ = $\Delta E_\pi$. For $Al_4^{2-}$, eqn (5) is not exact since there is a small contribution to the Pauli repulsion of the $\pi$-electrons in the doubly occupied $Al$ ($2p_z)^2$ core orbitals of the initial fragments. However, since the overlap between these ($2p_z)^2$ orbitals is small, we expect this contribution to be minor and the error produced assuming the validity of eqn (5) should not be significant. The situation for $Ga_4^{2-}$ is analogous but now involves $Ga$ ($2p_z)^2$ as well as ($3p_z)^2$ $\pi$-electrons.

### 3. Results and discussion

In the present section, we first discuss the results concerning the role of the $\sigma$- and $\pi$-electrons in the formation of the $D_{2h}$ delocalized structure of the $B_4^{2-}$ cluster. Afterwards, $B_4^{2-}$ will be compared with the all-metal clusters $Al_4^{2-}$ as well as $Ga_4^{2-}$ and, finally, with the isostructural (but not isoelectronic) $C_4H_4$ and $C_4H_4^{+}$.

First, we focus on $B_4^{2-}$, which has a $D_{2h}$ symmetric equilibrium geometry, with four equivalent $B-B$ bonds of 1.657 Å (see Scheme 1). To understand why $B_4^{2-}$ opposes to localization, we have examined the energy and bonding of this species along a distortion mode proceeding from a regular delocalized structure with all $B-B$ bonds equivalent towards a geometry with alternating single and double bonds (Fig. 1). A key step in our approach is that this localization of double bonds can be achieved by rotating two equivalent and geometrically frozen fragments relative to each other. For $B_4^{2-}$, we go from a $D_{2h}$ symmetric equilibrium geometry ($R_{B-B} = 1.657 \text{ Å}$) to a $D_{2n}$ symmetric structure with alternating $B-B$ bonds of 1.795 and 1.506 Å by changing the angle between the two $B_2^{2-}$ fragments ($\theta$) from $\theta = 90^\circ$ ($D_{2h}$) to $\theta = 100^\circ$ ($D_{2n}$), with steps of $1^\circ$. Note that along this distortion of $B_4^{2-}$ we preserve the singlet electron configuration of the equilibrium structure, as we wish to understand the behavior of the latter. This non-stationary singlet $D_{2h}$ structure with $\theta = 100^\circ$ is 17.4 kcal mol$^{-1}$ above the singlet $D_{2h}$ equilibrium structure (optimization of $B_4^{2-}$ as a triplet biradical yields a $D_{2h}$ equilibrium structure which is 21.1 kcal mol$^{-1}$ above the singlet $D_{2h}$ species).

The change in energy $\Delta E$ that goes with distorting $B_4^{2-}$ from its $D_{2h}$ to $D_{2n}$ structure is equal to the change in
interaction energy $\Delta E_{\text{int}}$ between the two geometrically frozen $B_2^-$ fragments in their quartet open-shell valence configuration: three spins up ($\alpha$) and three spins down ($\beta$), respectively (see Fig. 3). The preparation energy $\Delta E_{\text{prep}}$ vanishes in this analysis because it is constant for fragments that are geometrically frozen (the geometry they have in the $D_{4h}$ $M_4^{2-}$ optimized structure). Each pair of fragments has mutually opposite spins to allow for the formation of two delocalized $\sigma$-electron pair bonds plus one delocalized $\pi$-electron-pair bond.

Fig. 2, top left, shows the interaction-energy decomposition as a function of the bond localization distortion $\theta$ angle for $B_4^{2-}$. The absolute values of each decomposition term in the $D_{4h}$ equilibrium geometry ($\theta = 90^\circ$) of $B_4^{2-}$ and all other model systems can be found in Table S1 of the ESI. The interaction energy $\Delta E_{\text{int}}$ of $B_4^{2-}$ becomes less stabilizing ("energy goes up") along the deformation mode from $D_{4h}$ to $D_{2h}$ structure. Thus, $\Delta E_{\text{int}}$ is against localization, as expected. As can be seen in Fig. 2, this behavior originates from the $\sigma$ electrons ("total $\sigma$" curve). The $\pi$ electrons favor localization towards the $D_{2h}$ structure, but only very slightly so. The electrostatic attraction ($\Delta V_{\text{elstat}}$) also favors localization of the bonds, even a bit more pronouncedly than the $\pi$ orbital interactions. However, all together, the $\sigma$ electrons dominate which leads to the $D_{4h}$ equilibrium geometry with delocalized double bonds.

The above trends are reminiscent of those found earlier in benzene. The $\sigma$ bonds achieve an optimum stabilization around a given, finite bond distance (for C–C bonds as they occur in benzene, this distance is ca. 1.5 Å) because of a favorable balance between electron-pair bonding and closed shell–closed shell repulsive interactions. Also, the $\sigma$ bond overlap integral achieves its optimum value around that finite bond distance. Deviations from this distance, due to contraction or elongation lead to loss of bonding overlap (and also increased Pauli repulsion) in each bond and thus to a destabilization of the $\sigma$ electrons.

Fig. 2  Bond-energy decomposition ($\Delta E$ in kcal mol$^{-1}$) of $M_4^{2-}$ and $C_4H_4^q$ ($M = B, Al, Ga; q = +2, 0, -2$) constructed from two equivalent rigid fragments, along the localization distortion ($\theta$ in $^\circ$) from delocalized to localized structure as defined in Fig. 1, computed at BP86/TZ2P.
As an example, we take the 1b_{2g} orbital which in our fragment partitioning results from the bonding combination of the tangential \sigma_T fragment molecular orbitals (FMOs) on the two interpenetrating B_2 \sigma^\infty fragments shown in Fig. 3. The latter illustration schematically depicts the frontier-orbital interactions emerging from our quantitative Kohn–Sham MO analysis of the bonding mechanism. In elongating bonds, \langle \sigma_T^+ | \sigma_T^+ \rangle overlap is reduced simply due to the movement of fragment-orbital lobes away from each other. In contracting bonds, \langle \sigma_T^+ | \sigma_T^- \rangle overlap is reduced because the fragment-orbital lobes pointing toward each other begin to penetrate across nodal surfaces of their partner orbital of the other fragment, leading to cancellation of overlap (destructive interference). The fact that localization of the B–B bonds leads to loss of bond overlap \langle \sigma_T^+ | \sigma_T^- \rangle is indicated in Fig. 3 with four green minus signs around the 1b_{2g} orbital. The quantitative evolution along the B_4 \sigma^2– localization distortion of the \sigma_T overlap \langle \sigma_T^+ | \sigma_T^- \rangle (i.e. a decrease) as well as the tangential \sigma bond orbital energy \epsilon[1b_{2g}] is shown in Fig. 4.

Interestingly, the \sigma electrons in B_4 \sigma^2– come in two categories with different behavior. In the first place, there are the \sigma-bonding electrons in “tangential” \sigma orbitals discussed above (see 1b_{2g} orbital in Fig. 3). They have the same bond overlap behavior and favor delocalization of double bonds, i.e., a regular, \textit{D}_{4h}-symmetric structure. In the second place, there are also \sigma-bonding electrons in “radial” \sigma orbitals. They are contained in the 2a_{1g} MO of B_4 \sigma^2– which arises from the bonding combination of the tangential \sigma_R fragment molecular orbitals.

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**Fig. 3** Schematic MO interaction diagram of M_4^{2–} constructed from two M_2 \sigma^\infty fragments in their quadruplet valence configuration, emerging from quantitative Kohn–Sham MO analyses at BP86/TZ2P (see also the text).
orbitals (FMOs) on each of the two interpenetrating \( B_2 \) \( \cdots \) fragments (see Fig. 3). The corresponding \( \langle \sigma_R | \sigma_R \rangle \) overlap has a similar pattern and qualitatively a similar dependence on bond localization as that of the \( \pi \) electrons in the \( 1a_{2u} \) orbital, i.e., \( \langle \pi | \pi \rangle \): it increases and thus favors double-bond localization (see Fig. 4). Note that the slope of \( \langle \sigma_R | \sigma_R \rangle \) towards bond localization is even steeper than that of \( \langle \pi | \pi \rangle \). Nevertheless, the tangential \( \sigma \) electrons dominate leading to the overall preference of the \( \sigma \)-electron system of \( B_2 \) \( \cdots \) to preserve a regular structure with delocalized double bonds. The different behavior of the tangential \( \langle 1b_{2g} = \sigma_T + \pi_T \rangle \) tends to delocalize double bonds) and radial \( \langle 2a_{1g} = \sigma_R + \pi_R \rangle \) \( \sigma \) electrons was also observed through their contributions to nucleus-independent chemical shifts (NICS) and electronic multicenter indices (MCI). Thus, the decomposition of the NICS into their canonical molecular orbital (CMO) components\(^{37} \) indicates that the tangential \( 1b_{2g} \) orbital has a paratropic contribution to NICS (NICS(1b\( _{2g} \)) = +10.8 ppm), while the radial \( 2a_{1g} \) orbital sustains a diatropic current (NICS(2a\( _{1g} \)) = −3.9 ppm)\(^{160} \). In line with this result, electronic multicenter index (MCI) calculations indicate that the contribution to the \( \sigma \)-aromaticity in \( A_l \) \( \cdots \) species of the two electrons in the radial \( \sigma \)-orbital is much more important than that from the two electrons in the tangential \( \sigma \)-orbital\(^{160} \).

Next, we compare \( B_2 \) \( \cdots \) with the other all-metal aromatic clusters \( A_l \) \( \cdots \) and \( G_a \) \( \cdots \) and, afterwards, with the organic species \( C_4H_2 \) \( \cdots \), \( C_6H_4 \) \( \cdots \), and \( C_8H_4 \) \( \cdots \). The series of three group-13 aromatic clusters, \( B_2 \) \( \cdots \), \( A_l \) \( \cdots \), and \( G_a \) \( \cdots \), are valence-electronic and isolobal. Our Kohn–Sham MO analyses reveal that these \( M_2 \) \( \cdots \) clusters have very similar MO electronic structures, characterized by the same generic orbital interaction diagram shown in Fig. 3. In line with this, the energy-decomposition analysis for \( A_l \) \( \cdots \) and \( G_a \) \( \cdots \) are very similar to that of \( B_2 \) \( \cdots \) discussed above in detail: in all cases, it is the \( \sigma \)-electron interactions that prefer a regular structure with delocalized double bonds and which dominate the \( \pi \) electrons that show a weak bias towards bond localization. A more detailed examination of Fig. 2 shows that the \( \Delta E \) and \( \Delta V \) curves achieve larger destabilizing and stabilizing, respectively, values along \( B_2 \) \( \cdots \), \( A_l \) \( \cdots \), and \( G_a \) \( \cdots \). This is the direct consequence of having an increasing number of closed-shells in combination with an increasing nuclear charge along this series. The bias of \( \pi \) electrons to localize becomes less pronounced along \( B_2 \) \( \cdots \), \( A_l \) \( \cdots \), and \( G_a \) \( \cdots \) because the \( n_\pi \)-derived fragment orbitals of the interpenetrating and interacting \( M_2 \) \( \cdots \) fragments become more and more diffuse and begin to contain core wiggles if we go from \( M = B \) to \( A_l \) to \( G_a \) (see Fig. 3). The net result is a slight reduction along this \( M_2 \) \( \cdots \) series in the tendency of the system to resist bond localization.

Finally, we compare the bonding in the all-metal aromatic clusters \( B_2 \) \( \cdots \), \( A_l \) \( \cdots \), and \( G_a \) \( \cdots \) with that in the structurally related organic systems \( C_4H_2 \) \( \cdots \), \( C_6H_4 \) \( \cdots \), and \( C_8H_4 \) \( \cdots \) in their singlet ground state. The differences and similarities can be best understood on the basis of the frontier orbital electronic structure. For clarity in the above discussion of \( M_2 \) \( \cdots \), Fig. 3 has been incomplete as far as the occupied \( \pi \) MOs of some of the organic species are concerned, in particular, the \( \pi^* \) fragment MOs on each of the interpenetrating fragments. In Fig. 5, we have added these \( \pi^* \) fragment MOs but have omitted most of the \( \sigma \) orbitals to keep this figure again as clear as possible. Note, however, that the in-plane partner orbitals of the \( \pi \) and \( \pi^* \) fragment MOs (which enter into the \( \sigma \) system) are still present in the illustration to facilitate recognition of the connection with Fig. 3.

The aromatic dication \( C_4H_2 \) \( \cdots \) is isolobal with respect to our all-metal aromatic clusters. In particular, it has the same number of \( \pi \) electrons, i.e., two, in a \( \pi \) MO that is completely analogous to the \( M_2 \) \( \cdots \) \( 1a_{2u} \), i.e., a bonding \( \pi + \pi \) combination of fragment MOs (situation 1 in Fig. 5). Likewise, the two interpenetrating \( C_2H_2 \) \( \cdots \) fragments from which we construct \( C_4H_2 \) \( \cdots \) are also isolobal to the two \( M_2 \) \( \cdots \) fragments which \( M_2 \) \( \cdots \) is composed of in our quantitative bonding analyses. In line with this, the EDA diagram of \( C_4H_2 \) \( \cdots \) in Fig. 2 qualitatively shows the same picture as the diagrams for \( B_2 \) \( \cdots \), \( A_l \) \( \cdots \), and \( G_a \) \( \cdots \): the \( \sigma \)-orbital interactions strongly oppose double-bond localization and override the effect of the weakly localizing \( \pi \) orbital interactions as well as the electrostatic interactions. A difference between \( C_4H_2 \) \( \cdots \) and \( M_2 \) \( \cdots \) is the stronger effects in the individual energy terms in the former, a result of the extra valence electrons in the \( C \)–\( H \) bonds, among others. Adding two electrons to \( C_4H_2 \) \( \cdots \) brings us to the neutral 1,3-cyclobutadiene \( C_4H_2 \) \( \cdots \) with four \( \pi \) electrons (situation 1 + 2 in Fig. 5) which we have also analyzed in a previous paper\(^{22a} \). This antiaromatic species has strongly localizing \( \pi \) orbital interactions because, in the singlet ground state, the two additional electrons go into the \( \pi^* - \pi^* \) MO which strongly favors localization of the double bonds. This is reflected in the EDA diagram in Fig. 2 by the strong bias of the \( \pi \) orbital interactions to localize the double bonds which dominates the overall trend, leading to the \( D_2 \) symmetric equilibrium geometry. Adding another two \( \pi \) electrons brings us from the antiaromatic \( C_4H_4 \) to the

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**Fig. 4** Analysis of bonding in \( B_4 \) \( ^{2-} \) between two \( B_2 \) \( \cdots \) fragments along the localization distortion \( \theta \) (in °). (a) Change in selected overlap integrals \( \Delta S \) between \( B_2 \) \( \cdots \) fragment orbitals relative to \( D_{an} \) (90°). (b) Change in corresponding \( B_2 \) \( ^{2-} \) bond orbital energies \( \Delta \varepsilon \) relative to \( D_{an} \) (90°).
aromatic dianion $C_4H_4^{-}/C_0$ which has six $p$ electrons (situation 1 + 2 + 3 in Fig. 5). The additional pair of $p$ electrons goes into the $p^* + p^*$ orbital which, in a $D_{4h}$ symmetric arrangement, is degenerate with the $p^* - p^*$ MO. This orbital is destabilized if we follow the localization mode that stabilizes its $p^* - p^*$ partner orbital (see Fig. 5). Thus, as can be seen in Fig. 2, the $\pi$ electrons of $C_4H_4^{-}$ lose their strongly localizing tendency and the $s$ electrons keep the molecule in a regular, $D_{4h}$ symmetric geometry with delocalized double bonds.

4. Conclusions

The $\pi$-electrons in the $D_{4h}$-symmetric all-metal aromatic $M_4^{-2}$ rings ($M = B$, Al, and Ga) have a rather weak propensity to localize double bonds and adopt a $D_{2h}$ structure. This behavior is very similar to that of the $\pi$ electrons in benzene but differs fundamentally from the situation in cyclobutadiene in which the $\pi$-electrons have a strong bias to localize the double bonds. The propensity of $\pi$ electrons to localize the double bonds originates from the well-known fact that $\pi$ overlap is optimal at zero bond distance. The reason that this propensity is weak in our $M_4^{-2}$ rings can be easily understood on the basis of the overlap pattern which is initially subject to much cancellation between loss and gain in bonding overlap as we leave the regular $D_{4h}$ structure towards the bond-localized $D_{2h}$ geometry.

Thus, the clear preference of the $s$-electrons in $M_4^{-2}$ to adopt a regular, $D_{4h}$ symmetric geometry prevails and is
responsible for the eventual regular, aromatic structure with delocalized double bonds. This behavior again closely resembles that of σ-electrons in benzene and also those in the cyclobutadiene dication. The reason is that all single bonds between a given type of atoms are associated with an optimum σ-bond overlap at the same finite bond distance.

Interestingly, the σ-bonding electrons in the all-metal \( \text{M}_2 \) rings come in two categories with different behavior: (i) those in “tangential” σ-orbitals which favor delocalization \((D_{4h})\); and (ii) those in “radial” σ orbitals which in fact favor localization, similar to \((\text{and for the same reason as})\ the \( \pi \) electrons.

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