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Polyhedral Borane Analogues of the Benzynes and Beyond: Bonding in Variously Charged $B_{12}H_{10}$ Isomers

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Ⓢ *Supporting Information*

ABSTRACT: The effect of removing two protons, hydrogen atoms, or hydrides from the stable icosahedral $B_{12}H_{12}^{2-}$ is investigated theoretically. The resulting $B_{12}H_{10}^{q}$ (q = 4−, 2−, 0) isomers show interesting and understandable bond distance and stability variations, as well as special deformations associated with the apex-ring configuration typical of the underlying polyhedron. The dianions are analogous to *o*-, *m*-, and *p*-benzyne and have the special feature of distinct singlet and triplet states not far removed from each other in energy.

1. INTRODUCTION

Removal of two hydrogen atoms from the paradigmatic aromatic system of benzene leads to three biradicals, with fascinating geometric and electronic features.[1] Could something analogous take place in dehydrogenated polyhedral boranes, profitably considered to be 3D aromatic systems? And could the anionic nature of the parent aromatic lead to even more diverse electronic behavior?

Further motivation for thinking about didehydropolyhedral boranes comes from experimental characterization of $B_{10}H_9^-$ as early as 1966,[2] the quite recently reported neutral $CB_{11}Me_{11}$ boronium[3] or carbonium[4] ylides as intermediates, and the characterization[5] and exciting properties[6] of 1,2-dehydro-*o*-carborane $C_2B_{10}H_{10}$ (an analogue of *o*-benzyne). Also YB_{66} and other related borides of the type MB_{66} are known to have icosahedral B_{12} units where exo-substituents show partial occupancy. This implies the stable existence of a *m*-didehydropolyhedral isomer, possibly to compensate the electron deficiency in the network.[7] The first molecular example of an icosahedral gallium cluster, $Ga_{12}R_{10}^{2-}$, also has two gallium atoms without exohedral substituents,[8] defying Wade's rule.[9] Heteropolyhedral boranes such as $Sn_2B_{10}H_{10}$ and $Ge_2B_{10}H_{10}$ are also known in this series.[10]

Computational studies reported on the isomers of some of the carboranes[3c,11] and their analogues[12] show curious stability patterns, indicating boron atoms are ready to lose either hydrogen atoms or hydride ions. To encompass the entire range of charge and spin possibilities, we explore in this work the effect of removing either two protons, or two H atoms, or two H^- anions from the ortho, meta, and para positions of $B_{12}H_{12}^{2-}$, i.e., the series of molecules $B_{12}H_{10}^{q}$, with q = 4−, 2−, or 0.

2. RESULTS AND DISCUSSION

2.1. Two Frontier Orbitals.

To make sense of the entire series, we found it useful to begin with a picture of the orbitals involved that is not dependent on the charge. The charging of the molecule will then move these orbitals in quite predictable ways, up with greater negative charge. The extended Hückel method[13] (eH) provides that simple framework. Figure 1 shows the frontier molecular orbitals (FMOs) of the three isomers of $B_{12}H_{10}^{q}$.

In the ideal $B_{12}H_{12}^{2-}$, both the HOMO (g_u) and LUMO (g_g) are comprised purely of "tangential" B 2p orbitals.[14] In the various didehydro species, removal of two hydrogens, a "radial" perturbation, hardly affects these MOs (at the eH level; of course they will move with charging), but two new MOs pop up in between them. This is what one would expect—two B-based and reasonably localized orbitals; these are the two frontier orbitals marked in red and blue in Figure 1. Note the large gap in which these frontier orbitals fall. For the para isomer, the antisymmetric combination of the sp^x hybrids lies below the symmetric form, while for the other two forms it is the symmetric combination that lies lower (a similar pattern occurs for the benzynes.) Both red and blue MOs are unfilled for a neutral $B_{12}H_{10}$; half-filled in the dianion, and completely filled in the tetraanion.

While the existence of the two frontier orbitals was anticipated, their energy ordering (is the symmetric combination of hybrids at lower or higher energy?) needs to be explained. The variations in the spacing between these FMOs in the different isomers can be understood by a "retro-

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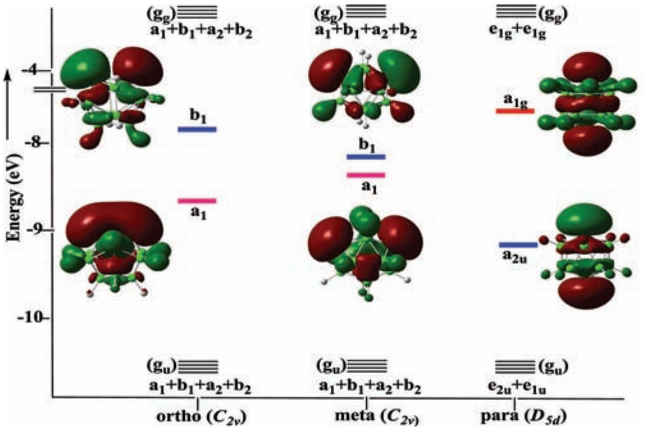


Figure 1. Frontier energy window (from eH calculations) showing the MOs arising from the removal of two hydrogens from $B_{12}H_{12}^{2-}$ to form ortho, meta, and para isomers along with the unperturbed HOMO (g_u) and LUMO (g_g) of $B_{12}H_{12}^{2-}$.

Table 1. Relative Energies of $B_{12}H_{10}$ Isomers with Varying Charges from CCSD(T)/cc-pVDZ//CCSD/cc-pVDZ Calculations[a]

no.	system	S	relative energy (kcal/mol)
1	o-$B_{12}H_{10}^{4-}$	0	15.2
2	m-$B_{12}H_{10}^{4-}$	0	3.7
3	p-$B_{12}H_{10}^{4-}$	0	0.0
4	o-$B_{12}H_{10}^{2-}$ [b]	0	0.0
		1	10.0
5	m-$B_{12}H_{10}^{2-}$ [b]	0	7.4
		1	8.7
6	p-$B_{12}H_{10}^{2-}$ [b]	0	3.9
		1	10.1
7	o-$B_{12}H_{10}$	0	12.1
8	m-$B_{12}H_{10}$	0	0.0
9	p-$B_{12}H_{10}$	0	2.4

[a]The results from other methods are given in the SI. [b]Energies obtained using broken symmetry unrestricted calculations.

interaction” analysis that begins with two hybrids on B left by the “departing” H atoms, and then interacts these hybrids with each other and with the underlying framework orbitals of icosahedral $B_{12}H_{12}^{2-}$. The Supporting Information (SI) to this paper contains a detailed analysis of the parentage of the frontier orbitals—into them enter as much unfilled orbitals of the icosahedron as filled ones. So for instance, in the para form the a_{1g} and a_{2u} arise exclusively from h_g (HOMO−1 and LUMO+2) and t_{1u} (HOMO−2, LUMO+1, etc.) MOs of the $B_{12}H_{12}^{2-}$, respectively. The level ordering of the a_{1g} and a_{2u} frontier orbitals in the para isomer, with the antisymmetric combination lying at lower energy, can thus be traced to greater contributions of unfilled icosahedral orbitals to a_{2u} (stabilizing it), while filled and unfilled orbitals mix about equally into a_{1g}. Through-space interactions[15]—significant overlap of the two boron-based hybrids—set the level ordering in the ortho form. In the meta form one finds a small gap, consistent with little through-space interaction and balanced mixing with filled and unfilled framework orbitals.

Qualitative as the above arguments are, they provide a starting point to think about what better calculations show. We proceeded to optimize the structures of the isomers of $B_{12}H_{10}^{q}$ (q = 4−, 2−, 0) at the B3LYP/6-31G(d) and MP2/6-31G(d) levels of theory.[16] Vibrational calculations at both these levels show that the closed-shell singlets for all charges are local minima. The geometries were further optimized at the CCSD level with an improved cc-pVDZ basis set (this level works well for the benzynes[17]). The relative energies shown in Table 1 were computed with CCSD(T) calculations (of demonstrated accuracy for benzyne isomers[18]) using the CCSD geometries of Table 2. B3LYP and MP2 results are given in the SI. These calculations also show the same orbital ordering as in Figure 1 in all the cases.

2.2. Classical Tetraanions.

Let us begin with the simplest systems, the tetraanions. These should be reasonably classical species, their stability likely governed by lone pair−lone pair repulsions. Indeed, this is obtained (see Table 1), with relative isomer energies of para < meta < ortho. Table 2 shows the optimized geometries; most of the distances, especially those involving the deprotonated B atoms, are elongated (relative to 1.79 Å in $B_{12}H_{12}^{2-}$) in all the isomers. The extreme of elongation is the unique deprotonated−deprotonated B separation of 2.035 Å in the ortho isomer. The tetraanions should be excellent bases.[10d]

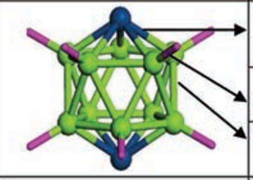
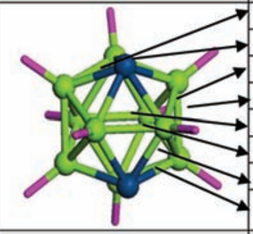
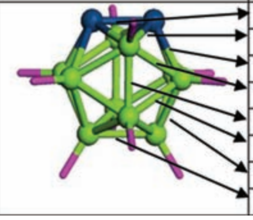
2.3. The Dianions: Singlets and Triplets.

For $B_{12}H_{10}^{2-}$, whatever the isomer, triplet states are energetically close to singlets (see Table 1). Since the frontier levels, blue and red in Figure 1, are close to each other in energy (especially for the meta isomer), the stability of the wave functions was checked for all the isomers. In fact, all the singlet $B_{12}H_{10}^{2-}$ isomers showed instability with respect to spin-symmetry breaking at both levels of theory studied, indicative of their inherent biradical character, much as one finds for the benzynes. Reoptimization of the singlet biradicals with broken symmetry UB3LYP[19] and UMP2 calculations led to energy minima with moderate bond alteration. Multiconfigurational SCF calculations with the two split-off MOs using 3-21G* basis show the contribution from the first excited-state configuration increasing in the order ortho (20%) < para (32%) < meta (39%) isomer.

As one finds in benzynes (and in the still more closely related $C_2B_{10}H_{10}$ isomers[11c]), all three $B_{12}H_{10}^{2-}$ isomers have singlet ground states. The singlet−triplet gap is found to be very small, 1.3 kcal/mol, for meta. This is expected from the small orbital gap in the eH calculations shown above in Figure 1. The ortho form shows a larger singlet−triplet difference, presumably due to B_{naked}−B_{naked} multiple bonding. And its singlet state is the most stable of the three isomers. The ground state triplets of the three isomers are not that different from each other in energy, a finding quite consistent with the simple level ordering pattern of Figure 1. As far as the distances go, in all the dianionic isomers, the B−B distances show moderate variation in the B_{12} skeleton. All B−B bonds (except the B_{naked}−B_{naked} bond in the ortho form) are in the range of 1.78−1.82 Å, compared to the $B_{12}H_{12}^{2-}$ B−B distance of 1.79 Å. The striking short B_{naked}−B_{naked} distance of 1.674 Å in the ortho isomer is an expected consequence of the extra direct B−B bonding. This distance is 0.12 Å shorter than in $B_{12}H_{12}^{2-}$ and approaches a B═B double bond distance[19] of 1.56 Å. Note how the same distance elongates in the triplet state of the molecule, coming back to the B−B distance in $B_{12}H_{12}^{2-}$.

In the dianionic $B_{12}H_{10}$ isomers, both the singlet and triplet states do not deviate substantially from the $B_{12}H_{12}^{2-}$ geometry, except for the ortho singlet, which behaves like o-benzyne in showing a reduced B_{naked}−B_{naked} distance. As these molecules

Table 2. B−B Distances (in Å) of the Optimized Minimum Energy Geometries of *o*-, *m*-, and *p*-$B_{12}H_{10}$ Isomers with 4−, 2− (Singlet and Triplet), and Neutral Charges at the CCSD/cc-pVDZ Level[a]

Isomer	Molecule	$B_{12}H_{10}^{4-}$ (Singlet)	$B_{12}H_{10}^{2-}$ (Triplet)	$B_{12}H_{10}^{2-}$ (Singlet)	$B_{12}H_{10}$ (Singlet)	Description
Para (D_{5d})		**1.887**	1.794	1.790	**1.729**	B_{ring}-B_{cap}
		1.777	1.814	1.808	**1.874**	B_{ring}-B_{ring} (intra)
		1.845	1.810	1.820	1.806	B_{ring}-B_{ring} (inter)
Meta (C_{2v})		1.785	1.809	1.810	1.850	B_{ring}-B_{ring} (intra)
		1.887	1.794	1.790	**1.726**	B_{ring}-B_{cap}
		1.799	1.811	1.818	1.855	B_{ring}-B_{ring} (intra)
		1.846	1.814	1.809	1.816	B_{ring}-B_{ring} (inter)
		1.793	1.807	1.813	1.827	---
		1.767	1.812	1.821	**1.923**	B_{ring}-B_{ring} (intra)
		1.916	1.798	1.795	**1.730**	B_{ring}-B_{cap}
		1.878	1.794	1.798	**1.734**	B_{ring}-B_{cap}
Ortho (C_{2v})		**2.035**	1.807	**1.674**	**1.710**	B_{naked}-B_{naked}
		1.870	1.801	1.784	1.754	B_{ring}-B_{cap}
		1.896	1.795	1.800	**1.713**	B_{ring}-B_{cap}
		1.804	1.816	1.805	**1.875**	B_{ring}-B_{ring}
		1.850	1.808	1.798	1.817	---
		1.820	1.808	1.823	1.825	---
		1.834	1.808	1.809	1.805	---
		1.812	1.805	1.802	1.807	---

[a] The singlet biradicals were optimized using spin-unrestricted calculations with external mixing of HOMO and LUMO. The borons without hydrogen are shown in blue. Elongated and compressed B−B distances with reference to B−B distance of $B_{12}H_{12}^{2-}$ (1.79 Å) are shown in red and blue, respectively, if they vary by more than 0.02 Å, and are in bold if the variation exceeds 0.05 Å.

are essentially open shell systems, bonding in both singlets and triplets requires multideterminantal treatment and, as such, may not be amenable to a simple FMO analysis. Still, the triplet states, in which both the FMOs are equally (partially) occupied show much smaller deviation from icosahedral symmetry than the open shell singlets, in which the contributions from the two low lying configurations differ substantially.

m-Benzyne features an unusual deformation—a bringing together of the two carbons. Getting this right has been a theoretical challenge; our reading of the latest calculations is that there is a pretty flat potential energy surface between a benzene diradical structure and one with a nearly fully formed CC bond.[20] We looked for a similar deformation in the singlet *m*-$B_{12}H_{10}^{2-}$ and did not find it; the "B−B bond-formed" structures are very high in energy (see SI). Also diamond-square-diamond-type rearrangement between the three isomers has very high activation energies.

2.4. Neutral $B_{12}H_{10}$.

The neutral $B_{12}H_{10}$ systems obtained from $B_{12}H_{12}^{2-}$ by the removal of two hydride ions are also stable singlets. Interestingly, the meta form is found to be more stable, followed by para, while ortho is consistently high in energy at all the level of theories employed (see SI). The neutral isomers show a greater variation than the dianions in the distances in the B_{12} skeleton (1.71−1.92 Å), but are still well within the range of B−B distances observed in polyhedral boranes (1.65−1.98 Å).[21]

Since the frontier orbitals (now empty) appear close in energy to the filled framework orbitals (see Figure 1), we examined triplets based on excitations from the icosahedral g_u, but these did not converge. The HOMO−1 (h_g) and HOMO−2 (t_{1u}) MOs of the $B_{12}H_{12}^{2-}$ are always bonding between boron and hydrogen atoms, so their mixing with the empty p orbital of the naked boron atom increases the gap between the HOMO and split off MOs of the neutral isomers. The complete absence of biradical character in the neutral form suggests that the closed shell singlet configurations might be stable Lewis acids, available for interaction with incoming bases. Some interesting adducts are expected.[22]

In the neutral systems we also studied a potential deformation that arises from the electron-deficient nature of the system. Neutral $B_{12}H_{10}$ has two low-lying empty orbitals, seats of electrophilic activity. Could there possibly be an interaction between these orbitals and the relatively electron-rich neighboring B−H bonds? The outcome would be B−H—B bridges. We studied this possibility in a model with one H^- removed from $B_{12}H_{12}^{2-}$, $B_{12}H_{11}^{-}$. No bridging was observed. We also looked at *o*-$B_{12}H_{10}$ which gives a possibility of face-bridging. The resulting C_{3v}-symmetric structure gave two imaginary frequencies (doubly degenerate 837 cm^{-1}) that correspond to movement of the bridging hydrogen toward one of the boron atoms, restoring the original C_{2v} symmetry.

2.5. The Effect of Overall Charge.

Can we trace some of the effects to specific frontier orbitals occupied? Consider, for instance, the para isomer. The a_{2u} and a_{1g} orbitals occupied as one adds electrons are both B_{cap}−B_{ring} bonding, B_{ring}−B_{ring} (intra)bonding. And they differ in the bonding between borons in the five-membered rings—the a_{2u} is antibonding, and the a_{1g} is bonding. The distance trends calculated do not follow these orbital patterns—the singlet and triplet states of the dianion are not very different from each other, and the B_{cap}−B_{ring} distance just elongates with electron filling. Similar trends are observed for other isomers as well (see Table 2). The B_{cap}−B_{ring} and the

B_{ring}–B_{ring} (inter)bonds always expand. While it appears that the overall elongation of bonds is set by simple electrostatics, the B_{ring}–B_{ring} (intra)bond shrinks in all cases. We attempt to explain these geometrical changes in the next section, classifying the borons involved into rings and caps; caps being always the bare boron atoms. Such simplifications have always helped us analyze complex borane structures.[23]

2.6. Caps and Rings. There is an important change in the geometry of the clusters as electrons are added to them, a change that becomes apparent only when one looks at the geometries in detail (see SI). In all isomers, the naked boron atom moves significantly away from the pentagonal ring it is capping for the 4− charge, but comes closer to that ring for the neutral polyhedra. In $B_{12}H_{12}^{2-}$, the distance between the capping boron and the centroid of its pentagonal ring is 0.94 Å. For $B_{12}H_{10}^{4-}$, this distance expands by ~0.2 Å in all the isomers, but for neutral $B_{12}H_{10}$ systems, it is reduced, again for all isomers, by even more. In the para isomer, the effect gives the polyhedron an ellipsoidal shape, prolate or oblate.

The distortion can be measured in another way by means of pyramidalization at the capping B. The pyramidalization angle is computed as deviation of the sum of all the B–B–B angles around the cap from 360°. This method is slightly different from that used for fullerenes,[24] which is based on the p-orbital projection vector, as use of the latter would result in more than one value for the low-symmetry ortho and meta forms. For $B_{12}H_{12}^{2-}$ the pyramidalization angle is 60° by icosahedral symmetry. The computed values (see SI) clearly show that 4− charge on $B_{12}H_{10}$ increases pyramidalization, while neutrality reduces it substantially (20–30° deviation).

How can one explain this deformation? When hydrogens are removed from $B_{12}H_{12}^{2-}$ as protons, the resulting lone pairs of electrons at the B_{cap} atom "demand" more space. That is achieved by expanding the distance between the cap and ring. An accompanying effect is a repulsive interaction with the nearby B–H bonds; this results in the movement of the B–H bonds toward the plane of the pentagonal ring. This effect is seen as well in our optimized structures—the angle subtended by the B–H bonds from B5 ring is 27° in $B_{12}H_{12}^{2-}$, as enforced by icosahedral symmetry; it reduces by ~5° for various isomers of $B_{12}H_{10}^{4-}$. The elongation in the distance between the cap and ring entails a compression of the B–B bonds of the pentagonal ring for better overlap. As a result, the pentagonal ring shrinks, so as to enhance the overlap between cap $2p_x$, $2p_y$ orbitals with the doubly degenerate π-MOs of the ring.[23] As hydrogens are moved toward the ring plane, the B_{ring}–B_{ring} (inter)bond also has to expand for better overlap.

In the case of neutral $B_{12}H_{10}$ isomers, the compression of B_{cap} toward the pentagonal ring appears counterintuitive, as the electrons are removed from MOs that are substantially bonding between the ring and cap. Understanding this peculiarity requires a detailed nature of interaction between the cap and the ring; this is provided in the SI. Overall, the bond lengths follow a reverse trend compared to the tetraanion analogues. The B_{cap}–B_{ring} bond shortens expanding the B_{ring}–B_{ring} (intra)bond. As the hydrogens move away from the plane of the ring, the B_{ring}–B_{ring} (inter)bond shrinks, compared to $B_{12}H_{12}^{2-}$.

What is happening in $B_{12}H_{10}$ skeleton when one move from a 4− charge to 2− to neutral is similar to what one finds on progressing from CH_3^- to $CH_3^\bullet$ to CH_3^+. CH_3^+ is planar, or "depyramidalized all the way", the difference between the CH_3 and $B_{cap}(B_5H_5)$ systems is that the apical B atom cannot go into the plane, as ring B–B bonding must be maintained. It is interesting to note that in the case of p-$C_2B_{10}H_{10}$ (isoelectronic with $B_{12}H_{10}$ dianion), where carbon forms a cap, Wang and Schleyer[25] calculated that C_{cap} falls into the center of the ring forming a molecular wheel. The odd electrons on the C_{cap}s are involved in the axial C–C bonding. This structure is reported to be less favorable compared to the polyhedral forms (both singlet and triplet), but is preferred in the case of a C capping a six-membered ring as in $C_{14}H_{12}$.

Perhaps a better model, one that features electron deficiency as well as ring-cap bonding, is the square pyramidal $C_5H_5^+$ system (Figure 2), the organic analogue of B_5H_9. Table 3 shows the results of a calculation optimizing the geometry of this molecule at B3LYP/6-31G* level of theory, and of removing H^+, $H^\bullet$, and H^- from it. We follow the same definition of pyramidalization angle as for $B_{12}H_{10}$ isomers. Note the motion of the apex or cap atom, exactly as in our didehydroicosahedral boranes. The bond length variation also follows the same trend. The C_{cap}–C_{ring} expands and C_{ring}–C_{ring} compresses for the neutral system with respect to its parent C_5H_5 molecule and vice versa for 2+ charged species.

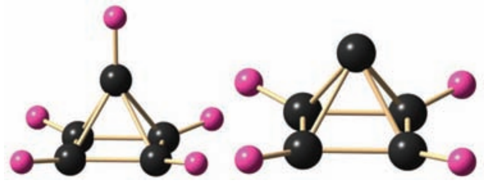


Figure 2. Structure of the parent $C_5H_5^+$ and the dehydro-$C_5H_4^n$ molecule.

Table 3. Geometrical Parameters of Optimized C_5H_5 and $C_5H_4^n$ Molecules

structure	charge n	pyramidalization angle (deg)	$C5_{centroid}$–C_{cap} (Å)	C_{cap}–C_{ring} (Å)	C_{ring}–C_{ring} (Å)
C_5H_5	1+	137.6	1.18	1.57	1.47
C_5H_4	0	152.9	1.31	1.66	1.45
	1+	134.3	1.16	1.56	1.48
	2+	112.2	1.03	1.50	1.55

3. CONCLUDING COMMENTS

We have presented a framework for understanding the molecules that result by removing two protons, two H atoms, or two hydrides from the three-dimensionally aromatic icosahedral $B_{12}H_{12}^{2-}$. The electronic structure of the ortho, meta, and para isomers of each system can be analyzed starting from a simple picture of two frontier orbitals between filled and unfilled icosahedral cluster orbitals. As for the analogous o-, m-, and p-benzyne, the ordering of the levels can be related to a balance of through-space and symmetry-conditioned through-bond interactions.

The stabilities of the tetraanions follow what one would expect for two lone pairs on a ring. The dianions, $B_{12}H_{10}^{2-}$ are analogues to the benzynes, and feature an interesting interplay of singlets and triplets. The neutral molecules should be good Lewis acids. Overall the polyhedron expands with increasing negative charge, not a surprise. But there are very specific elongations and contractions of the B–B distances in the polyhedron, up and down by as much as 10% of the $B_{12}H_{12}^{2-}$ value. With reference to $B_{12}H_{12}^{2-}$, removal of hydrogen as an anion results in increased pyramidalization of the associated B_{cap} followed by the movement of hydrogens (B_{ring}−H) away from the cap. This leads to the elongation of B_{cap}−B_{ring} bond and compression of B_{ring}−B_{ring} (intra)bond. The isomers of neutral $B_{12}H_{10}$ exhibit an exact reversal, i.e., a decrease in the pyramidalization of the associated B_{cap} followed by the movement of hydrogens toward the cap, compression of B_{cap}−B_{ring} bond, and elongation of B_{ring}−B_{ring} (intra)bond. Accordingly the B_{ring}−B_{ring} (inter)bond also expands and shrinks for tetraanions and neutral molecules, respectively. No such pronounced skeletal deformations are observed in $B_{12}H_{10}^{2-}$, due to its open shell character. In general the analogy to the benzynes holds up well, with very interesting differences that promise a diverse chemistry for this series.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Extended discussion on bonding and details of isomerization pathways along with optimized Cartesian coordinates and respective total energies of all the discussed molecules. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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