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Hot Paper

The Possible Aromatic Conjugation via the Different Edges of (Car)Borane Clusters: Can the Relationship Between 3D and 2D Aromatic Systems Be Reconciled?

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The possible aromatic conjugation between 3D and 2D aromatic units is in the focus since the synthesis of benzocarborane. It has been showed that in the 3D aromatic icosahedral 1,2-dicarba-*closo*-dodecaborane systems fused with 2D aromatic rings a global 3D/2D aromaticity does not exist. Despite this fact during the last years several studies proposed interactions between 2D and 3D moieties. Herein, while tuning the size and the effective charge of the (car)borane systems, we demonstrate that global aromatic character can be excluded in any investigated cases, and the detectable conjugative properties can be explained the effect of the well-known negative hyperconjugation.

Introduction

The concept of aromaticity has greatly evolved since the first description of Kekulé on the structure of benzene.[1] Nowadays it is well-known that, the concept of aromaticity is not a privilege of 2D organic platforms, 3D units like boranes can also possess high aromatic character.[1–3] The similar nature of these compounds was realized and discussed,[4–7] and the question arose whether 3D- and 2D-aromatic systems could form conjugated aromatic systems,[8–11] with similar behaviour to their planar polycyclic counterparts. The first synthesized example was benzocarborane (**I**, Figure 1),[12] which - as the analogue of the aromatic naphthalene - should also possess a high 2D aromatic character. However, a study on the reactivity of this system revealed exactly the opposite, as no aromatic properties were observed on the *exo* benzene ring, therefore concluding the lack of significant aromatic conjugation between the 3D and the 2D parts of the system.[13] After deboronation of **I**, the corresponding *nido*-carborane derivative keeps the same non 2D-aromatic character based on Diels-Alder reactivity.[14] Very recently, Teixidor and Solà also verified the nonaromatic character of benzocarborane derivatives, and this statement was extended to systems fused through the boron vertices.[15] On the other hand, significant π-aromatic character was reported for five-membered heterocycles (**III**–**IV**, Figure 1).[8–10]

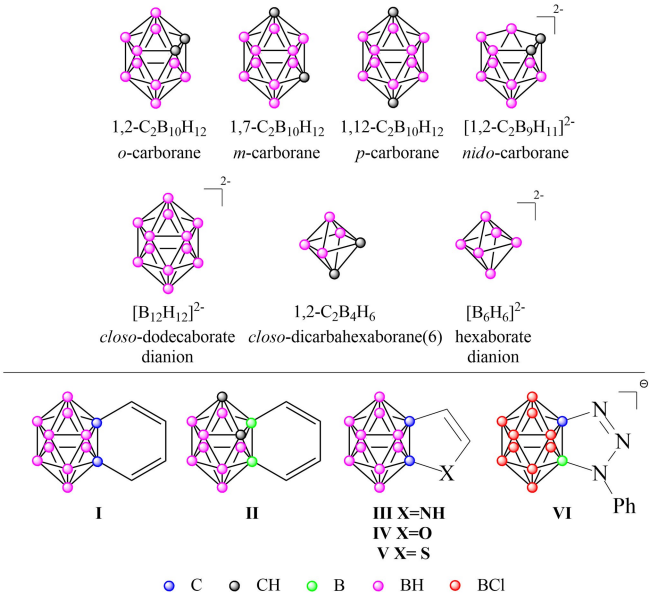

Figure 1. Top: Selected, representative examples of (car)borane clusters Bottom: Selected representative examples where, where the possibility of 2D –3D aromatic conjugation was discussed.

A possible explanation for the aromatic conjugation is a hyperconjugative interaction,[10] where electron donation occurs from the π-system of the substituent to the σ* orbitals of the carborane cluster. It was previously demonstrated that this interaction might cause significant C–C bond elongation which was demonstrated both theoretically[16] and experimentally.[17] However, it remains unclear why this effect does not occur in the case of benzocarborane.[12] As a solution to these somewhat ambiguous observations, we used different aromatic descriptors for various systems fused via the C–C bond of the *ortho*-carborane.[18] We concluded that simply leaning on the Nucleus Independent Chemical Shift (NICS) values can lead to a false description, as the magnetic shielding of the carborane cluster

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has a serious impact on the diatropic magnetic shielding in a huge radius around the cluster, therefore greatly affecting the magnetic shielding of the *exo* ring. In parallel with us, Teixidor and Solà arrived to the same conclusion in the case of benzocarborane derivatives, establishing that 3D and 2D aromatic units indeed behave like oil and water.[15] Nevertheless, the debate regarding the potential conjugation between 2D and 3D moieties is still ongoing. Interestingly, a very recent study was able to show a highly extended conjugation after single-oxidation of dimesitylboryl-substituted *p*-carborane derivative.[19] Certain (but not aromatic) conjugation was observed in case of *nido*-carborane fused bicyclic systems,[20] however, the increased downfield in the NMR sign of the middle ring proton was proved to be induced by the carborane moiety, establishing the earlier statement.[10,18] Similar conclusion was inferred in case of carboxonium derivatives of *closo*-dodecaborate anions,[21] which suggests that the denial behaviour against π-conjugation is not exclusively unique to carbon-carbon bonds, but it can also happen on boron-boron bonds as well.[15] Therefore, we perform a thorough investigation on the effect of different sizes and charges in the (car)borane cluster, while fusing the *exo* ring to other edges (bonds) of the framework, trying to understand the possible reasons behind this phenomenon.[15,18–20] We systematically investigated the possible aromatic conjugation of different (car)borane clusters (Figure 1) with various ring systems related to benzene, pyrrole, thiophene, or furan, focusing on the differences compared to their carbon fused counterparts.

Computational Details

Methodology and the concept of aromaticity is discussed in the SI.[22–30] Calculations based on density functional theory were carried out with Gaussian 16 quantum chemistry package.[31] Geometry optimizations in succession with frequency calculations were performed at the B3LYP/6-311+G** level of theory, which were widely used for related systems[4–6] and delivers reasonable accuracy, which was validated by us earlier by localized coupled-cluster (CC) method at the LNO-CCSD(T)/6-311+G** level of theory.[18] Utilizing B3LYP may lead to an overestimation of the extent of aromaticity[5] therefore other DFT functionals were tested as well, giving similar results (Table S1). For NICS calculations, B3LYP/cc-pVTZ single point calculations were performed.

Results and Discussion

As we have demonstrated recently, the magnetic shielding of the carborane cluster has a great impact on the accurate description of the *ortho*-carborane fused cycles via its cluster carbon atoms (defined as C_c atoms in this study).[18] As the size and the effective charge of the cluster can definitely affect various properties,[32] including the magnetic current around the system, we have selected seven borane and carborane clusters, namely $[B_6H_6]^{2-}$, $[B_{12}H_{12}]^{2-}$, 1,2-$C_2B_4H_6$, 1,2-$C_2B_{10}H_{12}$, 6 1,7-$C_2B_{10}H_{12}$, 1,12-$C_2B_{10}H_{12}$ and *nido*-[7,8-$C_2B_9H_{11}]^{2-}$. Firstly, we performed a scan by calculating the magnetic shielding of ghost atoms (point in the space without any subatomic particles) along the perpendicular bisector line of all chemically different bonds of the investigated systems (Figure 2 and

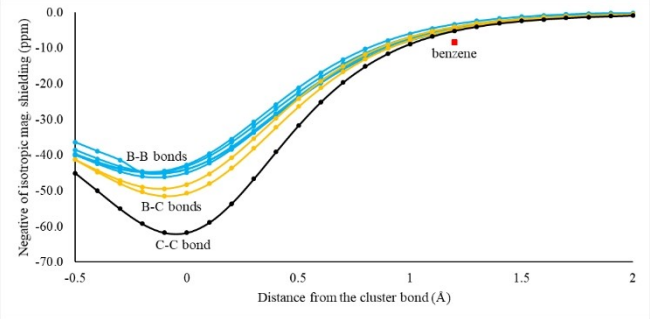

Figure 2. The calculated negative magnetic shielding of ghost atoms along the perpendicular bisector line of the various bonds of *o*-carborane cluster. The NICS(0) value of benzene is also shown as a comparison of the effect, with the distance between the center and the C–C bond of benzene (1.2 Å). Similar data for other clusters can be found in Figures S1–S5 in the SI.

Figure S1–S5 show respective information about the other studied compounds). Interestingly, the magnetic shielding is the highest along the perpendicular bisector line of the C_c–C_c bond, which is followed by B–C bonds, while B–B bonds have the lowest values, showing small deviation within the group. Similar trends can be seen in case of 1,2-$C_2B_4H_6$ and *nido*-[7,8-$C_2B_9H_{11}]^{2-}$ (Figure S3 and S4 in the SI). As the results demonstrate, the NICS values at 1.0 Å (estimated center of a connected five-membered ring) and at 1.2 Å (estimated center of a connected six-membered ring) distances from the middle point of the actual bond are close to −5.0 ppm which would definitely impact the magnetic properties of the connected rings. Interestingly, the smaller $[B_6H_6]^{2-}$ cluster exhibits somewhat stronger magnetic shielding farther from the cluster compared to the other investigated systems, as much as −8.0 ppm was observed at 1.2 Å possibly due to the negative charge of the system. As the NICS(0) value of benzene is −8.3 ppm at this level of theory, it is clearly shown that the magnetic effect of the fused cluster definitely cannot be neglected. Therefore, it can be established that similarly to the *o*-carborane fused heterocycles (fused via its carbon atoms), the NICS values should be used with caution for the description of the aromatic properties of these compounds. Therefore, we expand the characterization of aromaticity to include a set of indicators that are based on different approaches.[33]

As a next step, the geometric parameters of the fused systems are investigated. The bond length equalization is well-known in aromatic compounds, and it is a good indicator of the aromatic character. There are multiple geometric aromaticity indices which can define the aromatic properties of 2D systems (e.g. Bird index[34]). However, carboranes usually contain cluster bonds longer than a single C–C bond (covering a wide range between 1.5–2.1 Å, while the bond length is 1.54 Å in an ethane molecule), since these values are determined via interpolation

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between normal chain single and double bonds, they cannot be used for these compounds. Therefore, we simply try to draw conclusion from the calculated bond lengths of the investigated systems. Figure 3 shows the systems fused with

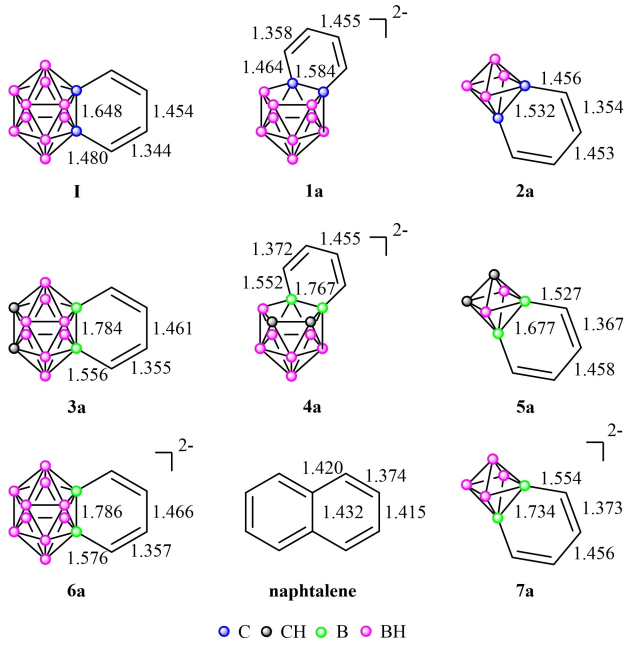

Figure 3. Selected bond lengths [in Å] of **I**, and **1a–7a.**

–CH=CH–CH=CH–, while the values of the other related systems can be found in Figure S6–S10 in the SI. A major difference arises from the different nature of the bonds (e.g. fused to the C_c–C_c or B–B bonds) and consequently the bond lengths between the connecting cluster atoms. While the length of C_c–C_c bond is around 1.62–1.65 Å in case of the *o*-carborane unit (Figure S6 in the SI), it is 1.50–1.53 Å in case of 1,2-$C_2B_4H_6$, (Figure S7 in the SI) and 1.54–1.58 Å in case of *nido*-[7,8-$C_2B_9H_{11}]^{2-}$ (Figure S10 in the SI). While comparing the bond length of **I** with **1a**, the C_c–C bond length decreases in case of **1a** (1.480 Å in **I** and 1.464 Å in **1a**) and the *exo* C=C bond becomes longer (1.344 Å in **I** and 1.358 Å in **1a**). On the other hand, very similar bond lengths were obtained in case of **2a**, where the cluster C_c–C_c bonds are similar to **1a**. In view of these data, the slight change in the bond lengths comparing **I** and **1a** can be attributed mainly to the different C_c–C_c bond lengths, which was simply compensated by the other bonds of the fused ring. It was supported by the very similar bond length of the *exo* C–C bond farthest from the carborane, which seems to be independent of the substitution side, however in case of any aromatic stabilization this bond should be altered (as it can be seen in case of naphthalene). In the same way, the systems fused via the boron vertices exhibit similar structural motives (**3a**–**7a**). Even if the difference is significant between C_c–C_c and the B–B bond lengths (0.13–0.18 Å), the alteration within the *exo* ring are greatly damped. Similar conclusion can be reached for systems fused with a –CH=CH–NH– unit (Figures S6–S10 in the SI). In these cases, pyramidal character of the nitrogen atom indicates low degree of aromatic properties as well (more details in the SI).

In the following step, the thermodynamic stability of these systems was investigated with different isodesmic reactions. Equations **I** and **II** (Figure 4) can be applied for systems fused

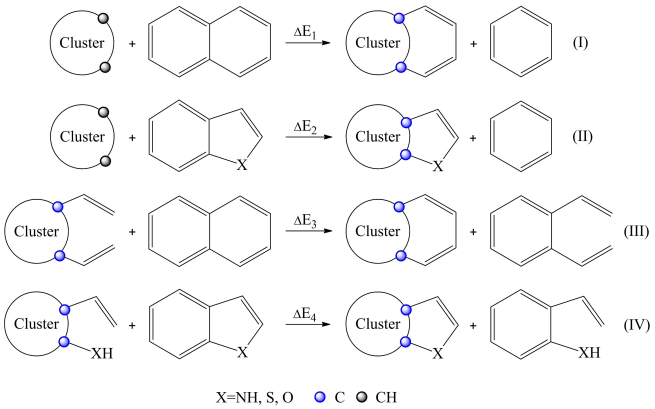

Figure 4. Isodesmic reactions to evaluate aromatic conjugation between 2D and 3D systems connected via carbon atoms of the (car)borane clusters.

via the C_c–C_c bond; the highly positive ΔE values (22.7–30.2 kcal/mol, Table 1) indicate the lack of aromatic conjugation

Table 1. Reaction energies of the isodesmic reactions depicted at Figure 4.

Cluster	ΔE_1	ΔE_3	ΔE_2 X=NH	ΔE_4 X=NH	ΔE_2 X=S	ΔE_4 X=S	ΔE_2 X=O	ΔE_4 X=O
1,2-$C_2B_{10}H_{12}$	26.5	23.4	24.3	15.5	21.5	13.9	24.6	12.7
nido-[7,8-$C_2B_9H_{11}]^{2-}$	10.6	19.7	16.8	14.5	1.8	13.8	9.9	12.5
1,2-$C_2B_4H_6$	22.7	21.8	29.0	24.8	22.3	23.0	30.2	22.5

in case of *closo* clusters, therefore no aromatic stabilization can be considered. Interestingly, in the case of the dianionic *nido* derivatives, where the ring connected to the open face of the cluster the corresponding reaction energies decreased significantly (1.8–16.8 kcal/mol). It is important to note that other isodesmic reactions lead to a similar conclusion (Equations **S-1**, **S-II**, **S-III** and **S-IV**, see Figure S11 and Table S2 in the SI). Accordingly, these results may indicate certain aromatic conjugation. However, one cannot abstract from the fact that the possible hyperconjugation of the double bond or the lone pairs of the hetero atoms with the cluster are clearly not balanced in Equations **I** and **II** In order to take this effect into account, Equations **III** and **IV** were investigated (Figure 4), which can be considered as hyperhomodesmotic reactions. In these cases, *nido*-[7,8-$C_2B_9H_{11}]^{2-}$ systems gave very similar reaction energies, indicating the identical non-aromatic character to their *closo* counterparts. Similarly, the benzo derivative of 1,2-$C_2B_4H_6$ exhibit similar reaction energies to its 1,2-$C_2B_{10}H_{12}$ counterpart, while higher values were computed in case of the five-membered heterocycles. This discrepancy can be explained by

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different ring strains in the investigated systems, which is more significant in case of smaller ring size. While the C1–C2–H angle in case of 1,2-$C_2B_{10}H_{12}$ is 116.1°, the same angle is 127.7° in case of 1,2-$C_2B_4H_6$ (Figure S12 in the SI). In order to judge this destabilization effect in case of 1,2-$C_2B_{10}H_{12}$, 1,2-$C_2B_4H_6$ and *nido*-[7,8-$C_2B_9H_{11}]^{2-}$, restricted optimizations were performed where the C–C–H bond angles were set to different selected bond angles between 100° and 120° (Table S3 in the SI). Adjusting the C1–C2–H bond angle to 120°, which is relevant to benzo fused systems, incurs a destabilization energy of only 1.6 kcal/mol in case of *o*-carborane. In contrast, modifying the bond angle to 100° or 105°, which corresponds to the bond angles observed in five-membered heterocycles, results in significantly higher destabilization energies of 21.5 and 14.4 kcal/mol, respectively. The results of this simple models are fully consistent with the increased isodesmic reaction energies (ΔE_2 and ΔE_4), therefore supporting our theory about the destabilizing effect of the ring strain. Apart from the bond angles, the different lengths of the cluster bonds can also alter the geometry of the rings (as it was discussed above), and consequently the stability of the investigated compounds. While the systems fused through the carbon atoms are simpler to investigate, in case of B–B fused systems, the direct comparison with the aromatic counterpart is more complicated since the fused ring is connected via B–C bonds. In order to cancel out the effect of the different bridging atoms Equations **V** and **VI** (see Figure 5 and Table 2) can be applied, in which the

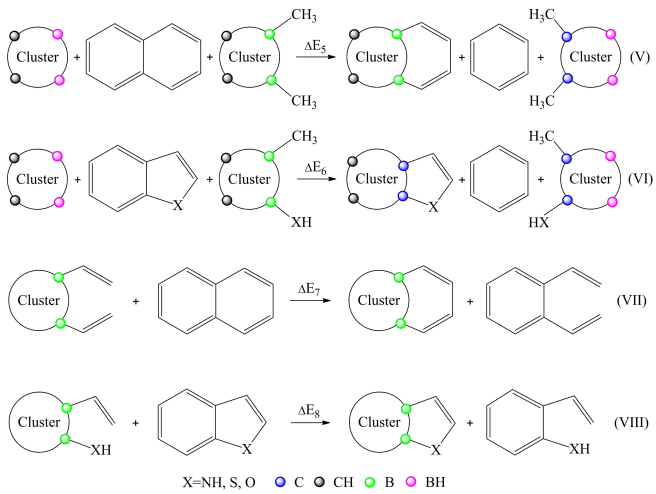

Figure 5. Isodesmic reactions to evaluate aromatic conjugation between 2D and 3D systems connected via boron atoms of the (car)borane clusters.

different bonds (B–C *vs* C–C) was corrected by the energy difference of two carboranes substituted by two methyl groups at carbon/boron atoms.

Similarly to the C-fused system, Equations **VII** and **VIII** (Figure 5) can be applied to cancel out the effect of the possible hyperconjugation between the connected π-system and the cluster. Generally, the values in case of the smaller $[B_6H_6]^{2-}$ and 1,2-$C_2B_4H_6$ systems show significant difference compared to the icosahedral compounds (see Table 2). In a similar manner to the

Table 2. Reaction energies (in kcal/mol unit) of the isodesmic reactions depicted at Figure 5.

Cluster	ΔE_5	ΔE_7	ΔE_6 X=NH	ΔE_8 X=NH	ΔE_6 X=S	ΔE_8 X=S	ΔE_6 X=O	ΔE_8 X=O
1,2-$C_2B_{10}H_{12}$	27.1	25.6	21.2	15.0	23.1	17.1	24.3	15.4
$[B_{12}H_{12}]^{2-}$	–	24.9	–	19.5	–	20.5	–	14.4
***nido*-[7,8-$C_2B_9H_{11}]^{2-}$**	13.1	27.0	21.3	25.4	8.4	24.2	15.0	20.7
1,2-$C_2B_4H_6$	33.2	31.5	42.3	38.2	35.5	35.8	47.5	39.7
$[B_6H_6]^{2-}$	–	31.9	–	32.2	–	31.1	–	26.9

C_c-fused counterparts, this effect can also be attributed to the ring strain, although this effect should be more effective as the original B–B–H angles are bigger compared to the C–C–H angles (135.0° for $[B_6H_6]^{2-}$ and 142.2° for 1,2-$C_2B_4H_6$, see Figure S12). Consequently, greater distortion occurs, leading to increased destabilization. Finally, it is important to note that the effect of the different connection sides (systems fused via different B vertices) was investigated in case of *o*-carborane fused systems, and it can be established that the stability of these systems do not depend on the connection side (Table S4 in the SI). Apart from various isodesmic reactions, isomer stabilization energies were computed (Equations **S-V** and **S-VI** in Figure S13 and Table S5 in the SI). As it can be expected, the computed values are rather small, which indicate no aromatic conjugation. In case of the heterocycles, the obtained values remain close to values, which describing the conjugation between a sole double bond and the lone pair of the heteroatom (α,β-unsaturated compounds). The aforementioned hypothetical reactions highlight that although these compounds do not display aromatic conjugation between 2D and 3D systems, other factors significantly contribute to their overall stability. Notable among these factors are the negative hyperconjugation and ring strain, both of which should be considered when evaluating the potential for aromatic conjugation in these systems.

Apart from the energetic and geometric parameters, indices based on the electron delocalization character of the investigated system should also be considered (more details in the SI). Therefore, we applied Electron Density of Delocalized Bonds[28] (using $EDDB_P$, counting only cyclically delocalized π electrons in the ring), MCI (which is a measure of electron delocalization between multiple atomic centers on the basis of natural orbitals)[29] and AV1245 (average of the 4-center multicenter indices along the ring)[30] on the 6-membered *exo* ring of **I** and **1a–7a**, and compared these values to a 6-membered ring of naphthalene (Table 3). All investigated systems show much lower values compared to naphthalene, indicating highly decreased aromatic properties. Moreover, values of **1a**, **2a** and **4a**, **5a** compared to **3a** and **6a**, respectively, suggest that octahedral clusters can result slightly higher delocalization in the *exo* benzene ring compared to the icosahedral structures, which correlates well with the higher level of bond equalization observed during the geometric study. This phenomenon can be mainly attributed to the shorter cluster bond length, which causes less distortion of the *exo* ring.

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Table 3. Electron delocalization-based aromaticity descriptor values ($EDDB_p$, AV1245, MCI) of the investigated cluster systems.

Investigated system	$EDDB_p$	AV1245	MCI
naphthalene	2.586	8.905	0.050
I	0.378	0.994	0.004
1a	0.214	0.847	0.008
2a	0.579	1.977	0.008
3a	0.233	2.002	0.005
4a	0.388	2.346	0.016
5a	0.447	2.867	0.013
6a	0.227	1.932	0.004
7a	0.404	2.456	0.011

Conclusions

In conclusion it was showed that, the magnetic field induced by the 3D clusters has a strong impact in a huge radius around the center of all investigated (car)borane systems, therefore the simple evaluation based on the NICS indices can lead to the false detection of 2D aromatic properties. We state that the application of the magnetic properties as an estimation of aromaticity should be performed with precaution. The investigation of the geometric properties showed the absence of bond equalization in the *exo* rings, also suggesting the lack of aromaticity. Considering energetic criteria of the aromaticity, isodesmic and isomer stabilization reaction energies indicate no 2D aromatic character of the fused rings. On top of that, we highlight that isodesmic reactions should be properly selected to cancel out other interactions such as negative hyperconjugation, which can alter the global properties of the investigated systems and can be falsely detected as an aromatic stabilization effect. In summary, the aromatic conjugation is not possible in case of (car)borane fused ring systems. Although other interactions of 2D moieties with the 3D clusters, such as negative hyperconjugation are more likely to influence the properties of these systems. These results provide additional insight into the unique properties of the carborane-based systems, potentially resolving the ongoing debate about 2D/3D conjugation in these compounds. Based on these theoretical concepts, we plan to synthetize some of these molecules to explore their reactivity and investigate the possible photophysical properties.

Supporting Information Summary

Supporting Information (including XYZ coordinates and total energies of the computed systems) is available from the Wiley Online Library

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Aromaticity · Borane clusters · Aromatic conjugation · DFT calculations

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