A Theoretical Study of the Aromaticity in Neutral and Anionic Borole Compounds

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Abstract: In this contribution, we have evaluated the (anti)aromatic character of thirty-four different borole compounds in their neutral and reduced states based on two aromaticity indices, namely nucleus-independent chemical shift (NICS) and multicenter indices (MCI), calculated at the PBE0/6-31+G(d,p) level of theory. Both indices corroborate the notion that neutral borole compounds are antiaromatic and become increasingly aromatic upon addition of electrons. Effects of the ring substituents on the degree of (anti)aromaticity are discussed together with differences in the two theoretical methods, which are on the one hand based on magnetic (NICS) and on the other hand based on electronic criteria (MCI).

Introduction

Antiaromatic compounds that do not obey Hückel's rule of 4n+2 π-electrons have fascinated chemists for decades, over time becoming an important class of molecules with intriguing physical and chemical properties.[1,2] To this class of compounds belong the five-membered boroles, compounds that are isoelectronic to the cyclopentadienyl cation $C_5H_5^+$ and comprise four π electrons. The unfavorable π-conjugation in these systems exerts a destabilizing effect and thus contributes to their high reactivity, which is the reason why stable borole derivatives can only be achieved by annulation[3] or employing bulky substituents around the reactive BC_4 core. Since the first report of a stable borole by the group of Eisch in 1969, a pentaphenyl-substituted borole (**1**),[4] several other aryl[5-7] and heteroaryl ring substituents[8] have been found to be effective in the stabilization of borole compounds, thereby enabling detailed investigations of their chemical and physical properties.[9] Nevertheless, isolable boroles are typically highly reactive species and follow various pathways to reduce their antiaromaticity, namely by activation of H−H and Si−H bonds,[10-12] [4+2] cycloaddition reactions,[13,14]

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adduct formation with Lewis bases[15,16] or one- and two-electron reductions to form the corresponding radical anions and dianions, respectively.[17,18] Besides their rich reactivity profile, boroles display chromophoric properties, i.e. they absorb light strongly in the UV-vis region of the spectrum, and are highly Lewis acidic due to the presence of a vacant p-orbital on boron.[9] Notably, these features can readily be altered by modifying the exocyclic substituents. As illustrated in Figure 1, changes in the boron substituent in a 2,3,4,5-tetraphenylborole framework result in characteristic shifts in the UV-vis absorptions, thereby giving rise to a large gamut of colors.
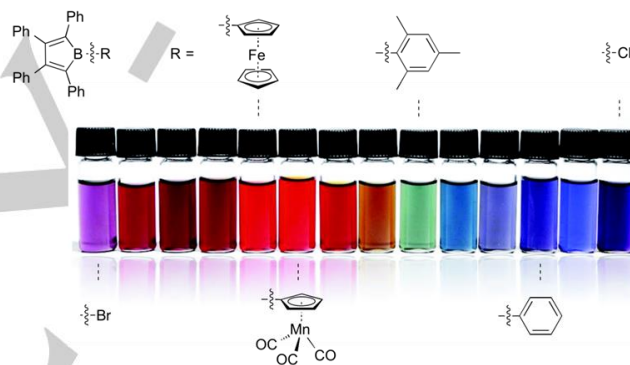

Figure 1. Absorption behavior of 2,3,4,5-tetraphenylboroles as a function of the nature of the boron substituent (R).

The intriguing electronic and optical properties of boroles, combined with their facile control through variation of the exocyclic substituents, make them also interesting for a broad range of applications in materials science such as sensors or optoelectronics.[19,9b] Given that these properties are closely linked to the extent of antiaromaticity in boroles, an understanding of the contributing factors to this elusive property is particularly important. We have thus set out to systematically study the substituent effects on the cyclic delocalization in borole compounds by density functional theory, i.e. the calculation of nucleus-independent chemical shifts (NICS) and multicenter (MCI) indices, general theoretical methods to quantify (anti)aromaticity. In this contribution, we report our results for a series of mono-, bis- and tris(borole)s in their neutral and reduced states and discuss differences between the two aromaticity criteria.

Computational Details

All calculations were performed with the Gaussian03 computational package.[20] Geometries were optimized with the PBE0 hybrid functional,[21,22] which combines the pure nonlocal functional PBE[23,24] with 25% of exact HF exchange, and the 6-31+G(d,p) basis set. Harmonic frequency calculations were carried out to verify that the optimized structures are true minima on the potential energy surface (Hessian eigenvalues are all positive numbers). Moreover, we have tested the performance of our computational method [PBE0/6-31+G(d,p)] by performing calculations on the ferrocene-containing compounds with the OLYP functional[25] and the def2-SVPD basis set;[26] when comparing with experimental data, PBE0 gave better results than OLYP, but the difference in the basis sets was quite small (see Supporting Information for further details).

The nucleus-independent chemical shifts (NICS) have become the most popular aromaticity index since they are an easy option in computations and give direct information on the effects of an applied magnetic field on the ring current that is intrinsically related to the delocalized π electrons.[27,28] As a result, the various boroles can be classified according to this index as aromatic (diamagnetic) or antiaromatic (paramagnetic). Simply put, a system is more aromatic when the NICS value is more negative and more antiaromatic when that value is more positive. We have computed the NICS values at the PBE0/6-31+G(d,p) level of theory through the gauge-including atomic orbital (GIAO)[29,30] method implemented in Gaussian03. The magnetic shielding tensor was calculated as a single-point run for the ghost atoms located as a series of points from the geometric center of each ring (from the optimized geometry) – the so-called NICS(0) index – up to five angstroms above and below the ring plane with steps of 0.2 Å. By plotting NICS values as a function of the corresponding distance from the ring (expressed as NICS(r)), we have generated NICS profiles (also known as NICS scans) that have been shown to be very useful in assessing the (anti)aromaticity in organic, inorganic, and organometallic species.[31-33]

On the other hand, electronic delocalization descriptors have gained an important role in the characterization of aromaticity. Among these tools, the multicenter indices are the most versatile and popular. Unlike other descriptors such as FLU[34] or PDI,[35] they can be applied to all sorts of molecules (including inorganic species) and do not rely on reference values. Some of us have recently shown that multicenter descriptors perform the best in controversial molecular species like all-metal clusters.[36] The I_{ring} was the first of these descriptors and measures the electron delocalization along the molecular ring.[37] MCI was suggested as an improvement to I_{ring} that also includes the delocalization across the ring.[37] Recently, we have introduced a normalization for these indices that avoids the ring-size dependency of these quantities resulting in the I_{NG} and I_{NB} indices that are the normalized versions of I_{ring} and MCI, respectively.[38] The atomic partition used is Becke-rho, which performs close to Bader's quantum theory of atoms in molecules (QTAIM) but it is computationally less demanding.[39-41] Calculation of atomic overlap matrices (AOM) needed for the computation of I_{NG} and

I_{NB} indices have been performed with the APOST-3D program.[42] I_{NG} and I_{NB} were obtained with the ESI-3D package.[43]

Results and Discussion

This section has been organized as follows. Firstly, neutral monoborole systems will be discussed, followed by a treatment of their corresponding anionic derivatives and lastly, we present a comparison of aromaticity between neutral and anionic mono-, bis- and tris(borole)s.

Monoboroles

In this category, we have chosen the archetypical pentaphenylborole (**1**) by Eisch[4] as our reference system. As has been previously reported in the literature and as expected from the Hückel 4n+2 rule,[44] this compound is antiaromatic based on the magnetic aromaticity index (NICS(0) = 12.90).[8] Our calculated value of NICS(0) = 12.92 is in excellent agreement with the reported value. With the aim to determine the influence of the boron substituents on the degree of (anti)aromaticity, we have set out to calculate corresponding NICS values for borole systems containing the same tetraphenyl-substituted backbone but varying *B*-substituents (Figure 2). The incorporation of electronegative halogen substituents (**2**, **3**) at boron, despite their electron-withdrawing inductive effect, has hardly any effect on the observed antiaromaticity (see Table 1). The change in antiaromaticity relative to **1** is also small for boroles with ferrocenyl (**4**)[5] or cymantrenyl (σ-η^5-$C_5H_4Mn(CO)_3$) substituents at the boron atom (**5**),[45] although Raman spectroscopic data indicates a significant decrease in the antiaromatic character due to electron donation of a filled metal d orbital to the vacant 2p orbital on boron. This is further reflected in the bending of the borolyl unit toward the metal center in the molecular structures.[46-48] While the gas-phase optimized geometry matches the experimentally observed structure well (the dip angle α*, defined between the cyclopentadienyl ring plane and the borolyl unit, is 29.4° (exp.)[5] vs. 19.2° (calc.)), neither the two-center C−B and C−C delocalization indices nor the aromaticity indices are affected by the ferrocenyl substituent, thus indicating no increase in electron density at the boron atom. In contrast, borole **6** with an electron donating amino substituent was found to possess a decreased antiaromatic character based on the NICS value (NICS(0) = 10.58), in line with the experimental data.[49] However, according to the multicenter indices the antiaromatic character of **6** remains unaffected (I_{NG}) or is even slightly increased (I_{NB}) compared to pentaphenylborole (see Table 1). This can be explained by a twisted arrangement of the NR$_2$ (R = SiMe$_3$) group with respect to the borole plane (ca. 60°) which reduces the overlap of the lone pair on nitrogen with the empty p-orbital on boron, an effect that is better reflected by the multicenter indices.
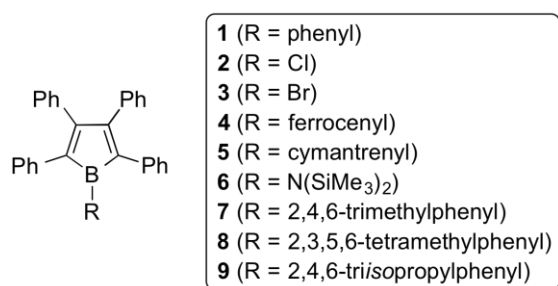
1 (R = phenyl)
2 (R = Cl)
3 (R = Br)
4 (R = ferrocenyl)
5 (R = cymantrenyl)
6 (R = N(SiMe$_3$)$_2$)
7 (R = 2,4,6-trimethylphenyl)
8 (R = 2,3,5,6-tetramethylphenyl)
9 (R = 2,4,6-tri*iso*propylphenyl)

Figure 2. Neutral monoborole systems studied in this work.

A comparison between boroles with different aryl substituents (**1**: R = phenyl;[7] **7**: R = 2,4,6-trimethylphenyl;[17] **8**: R = 2,3,5,6-tetramethylphenyl;[50] **9**: R = 2,4,6-tri*iso*propylphenyl)[50] reveals distinct changes in the NICS(0) values. Based on the NICS profiles for boroles **1**, **7**, **8** and **9** (Figure 3), it is possible to establish an antiaromaticity scale: **8** (14.37) ≈ **9** (14.28) > **7** (13.52) > **1** (12.92), which is also in line with both multicenter indices (I_{NG} and I_{NB}). Pentaarylboroles **7**, **8** and **9** show negative I_{NB} values, which are indicative of a strongly antiaromatic character. The data also suggests that the antiaromaticity of the boroles correlates with the steric demand of the *B*-aryl substituent: the higher the steric bulk of the R substituent, the higher the antiaromaticity. This can be understood by an increasingly weaker π-overlap of the aryl group with the borole unit due to the steric crowding around the exocyclic B−C bond. It is worth mentioning, however, that on the basis of a resonance Raman investigation this π-interaction of the aryl moiety with the borole unit is rather weak.[46] More conclusive evidence for π-conjugation of an exocyclic substituent with the borole ring was found in 1-heteroaromatic-substituted tetraphenylboroles, in which the electron-rich heterocycles (furan, thiophene or pyrrole) are essentially coplanar with the borole ring plane. This interaction is further manifested in characteristic hypsochromic shifts in their UV-vis absorption maxima compared to borole **1**, which correspond to a reduced antiaromaticity, as well as in the calculated NICS values for the contrasting ring systems.[51] Moreover, all the 1-aryl-substituted borole compounds display a common feature in their NICS profile, namely a maximum NICS value in the center of the ring and a monotonic decrease to zero when moving away from the ring center, a behavior typical of fully antiaromatic systems.
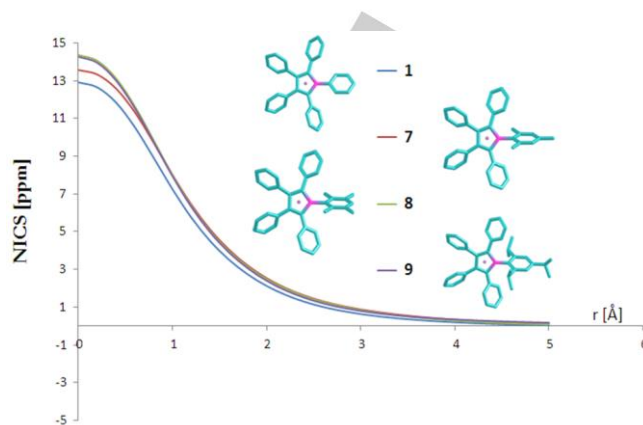

Figure 3. NICS profiles for the series of monoborole compounds **1**, **7**, **8**, and **9**. The dots indicate the center of each borole ring.

In addition, we have investigated corresponding NICS values for the negatively charged derivatives. As previously reported by the groups of Herberich, [52] Yamaguchi[18] and Braunschweig, [15,17,53-55] the synthesis and isolation of various dianionic and a monoanionic species has been successfully achieved (Figure 4). The addition of one electron noticeably decreases the antiaromatic character of boroles, as judged by both the NICS and multicenter indices. The two different indices also agree that addition of a second electron transforms boroles into aromatic species, a notion which is supported by experimentally observed structural and spectroscopic changes.[9b] The subtle difference between the two aromaticity criteria is based on the fact that NICS values predict larger differences upon addition of electrons than multicenter indices do. Interestingly, the NICS profiles of this series (Figure 5) show that, while neutral **1** and monoanionic compound [**1**]$^-$ behave the same way, the dianion [**1**]$^{2-}$ exhibits a shallow minimum at *ca.* 1 Å above/below the central ring. Moreover, according to Baird's rule,[56] the triplet state of **1** becomes more aromatic with a minimum at 1.0 Å above the borole plane (NICS(1) = −3.29, see Fig. 2), in agreement with the large I_{NB} value of 30.1. The same holds true for boroles **7** and **5**, whereas for the dianions of boroles **2** and **3**, the minimum NICS value is located at the borole ring center with the usual monotonic decrease of the curve. The NICS(1) minima found for the peraryl-substituted dianions can be understood by an interaction between the π-systems of the respective *B*-aryl substituent and the borole unit, an effect which is lacking in case of the halogen-substituted derivatives **2** and **3**.

The difference in the degree of (anti)aromaticity between anionic aryl- and halogen-substituted borole systems is subtle and varies between the different indices. According to the NICS values the chloro-substituted borole [**2**]$^-$ is less antiaromatic than its phenyl- ([**1**]$^-$), bromo- ([**3**]$^-$), and 2,4,6-trimethylphenyl-substituted ([**7**]$^-$) counterparts, while I_{NG} reports the opposite, although these differences are only minor in both cases. The dianions of haloboroles **2** and **3** show an increase in aromaticity

compared to the parent borole **1** ([**1**]$^{2-}$: NICS(0) = −2.74, I_{NB} = 31.6; [**2**]$^{2-}$: NICS(0) = −4.04, I_{NB} = 31.6; [**3**]$^{2-}$: NICS(0) = −4.26, I_{NB} = 32.1). On the other hand, I_{NG} suggests that the aromaticity in these series does not markedly change.

The series of negatively charged borolylferrocenes ([**4**]$^-$ and [**4**]$^{2-}$)[53] follows the same trend. Addition of one or two electrons to the electron-deficient π-system in **4** interrupts the existing metal-to-boron through-space interaction and causes the borole ring to lie in the same plane as the adjacent Cp ring (*i.e.* the dip angle α* becomes smaller, *ca.* 2.0°). While the NICS profile of the radical anion [**4**]$^-$ is analogous to the ones of the other anions ([**1**]$^-$, [**2**]$^-$ and [**3**]$^-$), the dianion [**4**]$^{2-}$ shows two minima around ca. ±1 Å, which are slightly more pronounced than the one in [**1**]$^{2-}$ (see Figures 5 and 6). The different NICS values for the two minima in [**4**]$^{2-}$ are an indication of the influence of the magnetic field from the iron atom. As a consequence, there is an apparent difference in the NICS profile when following a path above and below the borole ring plane (i.e. *syn* and *anti* to the ferrocenyl unit). The direction affected by the magnetic field of the ferrocenyl unit shows a slightly smaller NICS value.
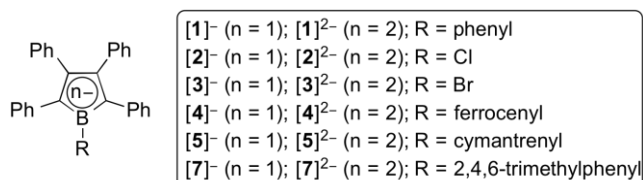

Ph, Ph, Ph, Ph around ring with (n−) and B, R	[**1**]$^-$ (n = 1); [**1**]$^{2-}$ (n = 2); R = phenyl [**2**]$^-$ (n = 1); [**2**]$^{2-}$ (n = 2); R = Cl [**3**]$^-$ (n = 1); [**3**]$^{2-}$ (n = 2); R = Br [**4**]$^-$ (n = 1); [**4**]$^{2-}$ (n = 2); R = ferrocenyl [**5**]$^-$ (n = 1); [**5**]$^{2-}$ (n = 2); R = cymantrenyl [**7**]$^-$ (n = 1); [**7**]$^{2-}$ (n = 2); R = 2,4,6-trimethylphenyl

Figure 4. Mono- and dianionic borole systems studied in this work.
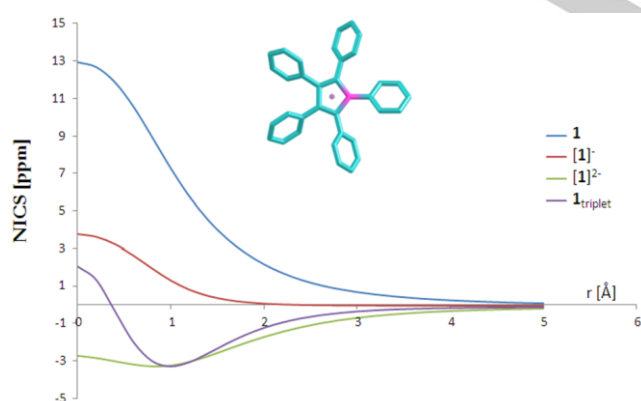

Figure 5. NICS profiles for the neutral pentaphenylborole **1** (singlet and triplet states) and its mono- and dianion.
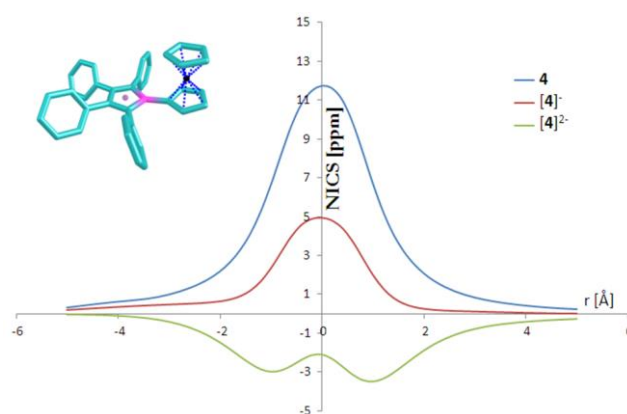

Figure 6. NICS profiles for **4** and its mono- and dianion. The left side of the graph corresponds to the calculations done above the borole plane (*syn* to the ferrocenyl unit), whereas the right side shows the results below the ring plane (*anti* to the ferrocenyl unit).

Bis- and tris(borole)s

The Braunschweig group has recently reported the successful synthesis of systems containing two and three borolyl units.[51,55,57-59] Figure 7 displays all derivatives used for this study. By comparing the 1,3- and 1,4-disubstituted bis(borolyl)benzenes **10** and **11**,[57] respectively, compound **11** was found to be 4.3 kcal/mol more stable than **10**. The reason for the decreased thermodynamic stability of **10** is likely due to the destabilizing π-conjugation of the two π-accepting borolyl units through the phenylene bridge. In terms of antiaromaticity in the borole rings, however, there is no noticeable difference between the two isomers. A comparison of the NICS profiles of monoborole **1**, bis(borole)s **10** and **11**, and tris(borole) **12** is shown in Figure 8.
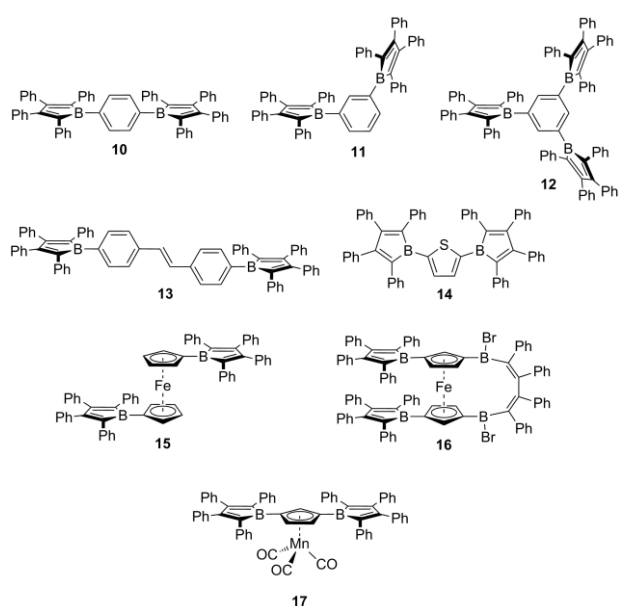
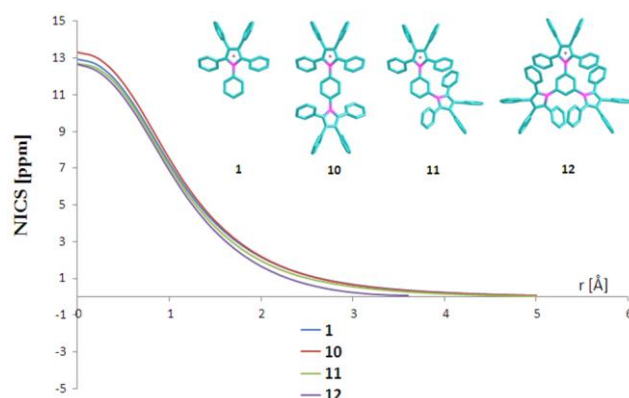**Figure 7.** Neutral bis- and tris(borole) systems studied in this work.

Figure 8. Comparison of NICS profiles for mono-, bis- and tris(borole) compounds. The dot in the center of the borole ring indicates the starting point for the calculations. Note that in case of tris(borole) **12** the calculation was stopped at a certain point due to fluctuations with phenyl groups of the other boroles.
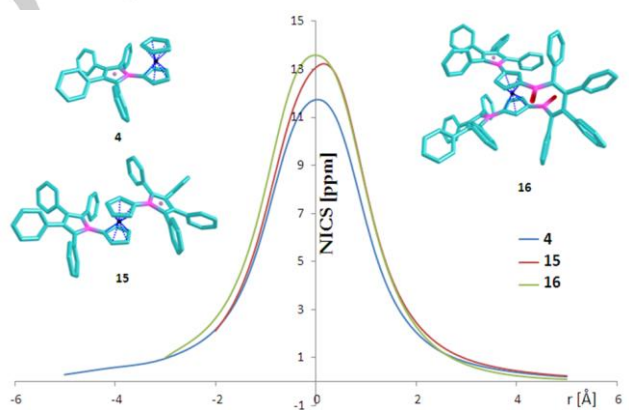

Figure 9. NICS profiles for the borolyl-substituted ferrocene derivatives. The dots indicate the center of each borole ring where the calculations were done. The left side of the graph corresponds to the series of ghost atoms placed along the iron side (*syn*), whereas the right side shows the results in the opposite direction (*anti*). Note that in the left side some lines are cut off due to fluctuations when approaching the vicinity of other atoms.

The longer *trans*-stilbenyl spacer in bis(borole) **13** does not significantly change the degree of antiaromaticity with respect to the bis(borole)s **11** or **10**.[59] However, replacing the phenylene linker with an electron-rich heterocycle, such as a thiophene in compound **14**,[51] has a more pronounced effect on the antiaromaticity. Bis(borole) **14** contains two borolyl moieties which are less antiaromatic than the parent borole **1** or other bis- and tris(borole)s (except for **11**) based on I_{NB}, whereas the I_{NG} and NICS values show no qualitative differences. The sulfur atom in the molecule allows for higher cross delocalizations in the borole ring, thus enhancing the value of I_{NB} in this compound. A conjugation between the aromatic heterocycle and the vacant p-orbital on boron seems to be effective in these compounds leading to the observed coplanar arrangement of the contrasting ring systems.[51]

Other significant differences are found by comparison of transition-metal-containing mono- and bis(borole)s. For the borolyl-functionalized ferrocenes,[58] the differences in the NICS profiles are shown in Figure 9. The bis(borole) systems **15** (NICS(0) = 13.07, I_{NB} = 17.6) and **16** (NICS(0) = 13.58, I_{NB} = 16.7) exhibit an increased antiaromaticity in comparison to their corresponding monoborole **4** (NICS(0) = 11.75, I_{NB} = 18.7). This result is in agreement with a mitigation of the stabilizing through-space boron-iron interaction, as seen by a decreased bending of the borolyl unit towards the iron atom in the molecular structures (**4** (α^* = 19.2°) > **15** (α^* = 14.7°) > **16** (α^* = 8.1°)).

The (anti)aromatic character of anionic derivatives of bis- and tris(borole)s seems to follow the same trend as for the above-discussed mono(borole)s (Figure 10). In other words, the anionic [**5**]²⁻, [**14**]²⁻, and [**15**]²⁻ (calculated as open-shell, triplet state molecules), which have one extra electron in each borolyl unit, are less antiaromatic than their neutral counterparts. In fact, it was found that [**14**]²⁻ is better described as a closed-shell singlet species with a bipolaron structure, in which the unpaired electrons on the borolyl units are paired across the thiophene bridge.[60] Again, when [**14**]²⁻ and [**15**]²⁻ are further reduced by two electrons resulting in tetraanionic borole derivatives, the aromatic character of each borole is further increased, as was

previously found for dianionic monoborole species (*vide supra*).[9b,61] The same happens for the hexaanionic [**12**]^6− species. Figure 11 shows the NICS profiles for the series of cymantrene-containing mono- and bis(borole) systems.[55] As the borole units in 1,3-bis(borolyl)cymantrene **17** are not equivalent in the geometry-optimized structure, each BC_4Ph_4 group was treated separately. As one might expect from their different arrangement with respect to the metal fragment, the two borolyl substituents in **17** exhibit a slightly different degree of antiaromaticity. For the neutral species, the nearly coplanar borole group with respect to the Cp ring (NICS(0) = 12.37, I_{NB} = 18.4) shows an almost identical antiaromaticity compared to that of **5** (NICS(0) = 12.36, I_{NB} = 18.7), whereas the more twisted borolyl group in **17** (NICS(0) = 13.67, I_{NB} = 16.8) features a higher antiaromaticity.
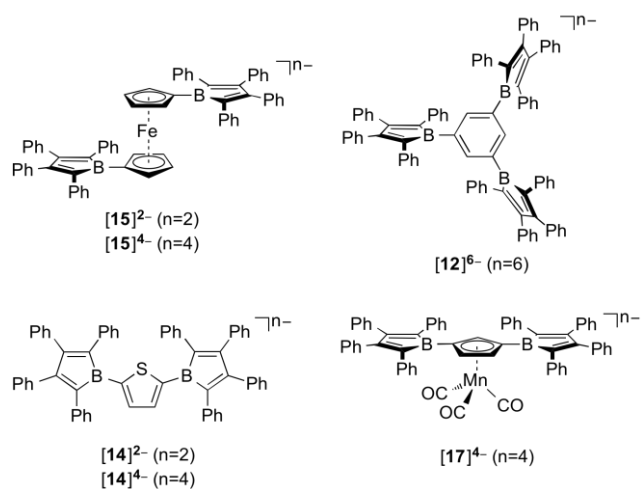

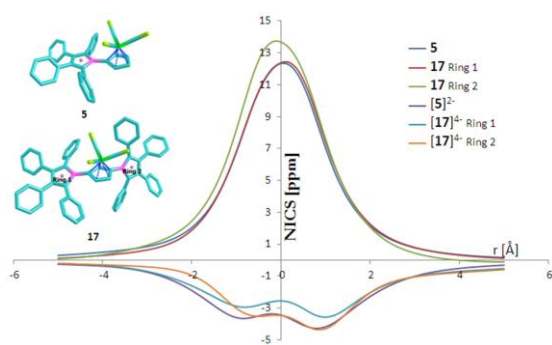**Figure 10.** Anionic bis- and tris(borole) systems studied in this work.

Figure 11. NICS profiles for the cymantrenyl-containing mono- and bis(borole)s **5** and **17**, respectively. Dots in the center of each borole ring show where the calculations were done. The left side of the graph corresponds to the series of points in *syn* position with respect to $Mn(CO)_3$, whereas the right side shows the results in the opposite direction.

Table 1. Maximum or minimum values of NICS[a] along the *z*-axis direction perpendicular to the center of the borole ring and multicenter indices (multiplied by 10^3) of the studied systems calculated at the PBE0/6-31+G(d,p) level.

Molecule	R[b]	NICS	I_{NG}	I_{NB}
1	0.0	12.92	27.4	17.7
[**1**]−	0.0	3.74	29.7	29.8
[**1**]^2− [c]	(0.8)	(−3.30)	32.7	31.6
2	0.0	12.99	28.1	20.3
[**2**]−	0.0	2.81	29.4	29.9
[**2**]^2−	(0.0)	(−4.04)	32.5	31.6
3	0.0	13.52	28.3	21.1
[**3**]−	0.0	3.04	29.7	30.3
[**3**]^2−	(0.0)	(−4.26)	32.9	32.1
4	0.0	11.75	27.3	18.7
[**4**]−	0.0	4.94	29.7	29.8
[**4**]^2− [c]	(1.0)	(−3.51)	32.8	31.7
5	0.0	12.36	27.6	18.7
[**5**]^2− [c]	(0.8)	(−4.27)	33.2	32.1
6	0.0	10.58	27.0	14.8
7	0.0	13.57	27.3	12.2
[**7**]−	0.0	4.06	29.8	29.9
[**7**]^2− [c]	(0.8)	(−2.58)	32.6	31.5
8	0.0	14.37	27.0	14.9
9	0.0	14.28	27.0	15.1
10	0.0	13.33	27.5	17.8
11	0.0	12.71	27.5	17.7
12	0.0	12.65	27.5	17.1
[**12**]^6− [c]	(1.4)	(−1.55)	31.8	30.1
13	0.0	12.74	27.6	18.7
14	0.0	13.27	27.7	19.4
[**14**]^2−	0.0	3.99	29.3	29.3
[**14**]^4− [c]	(1.0)	(−2.37)	32.2	30.8
15 [c]	0.2	13.21	27.3	17.6
[**15**]^2−	0.0	4.10	31.7	29.6
[**15**]^4− [c]	(1.0)	(−2.90)	32.2	30.8
16	0.0	13.58	27.3	16.7
17[c]	0.0, 0.2[d]	12.37, 13.67[d]	27.6, 27.6	18.4, 16.8
[**17**]^4− [c]	(1.0, 0.8)[d]	(−3.56, −4.38)[d]	32.4, 32.5	31.1, 31.1

[a] Minimum values are shown in parenthesis. [b] Distance (in Å) from the geometric center for the NICS maximum or minimum. [c] NICS(0) values in these compounds are as follows: [**1**]^2− = −2.74; [**4**]^2− = −2.10; [**5**]^2− = −3.44; [**7**]^2− = −2.03; [**12**]^6− = 0.07; [**14**]^4− = −1.54; **15** = 13.07; [**15**]^4− = −1.29; **17** = 12.37, 13.66; [**17**]^4− = −2.53, −3.49. [d] Values are different for the individual borole rings.

Figure 12 summarizes the main results obtained in this work. NICS and multicenter indices agree on classifying the set of compounds into three different groups. The first group contains the most aromatic species, which are the compounds with two additional electrons per borole unit, the second one includes molecules with one additional electron per borole ring, i.e. borole radical anions, and the third group contains neutral borole compounds. While the NICS(0) values make a clear distinction between these three groups, the multicenter indices draw a slightly less sharp line between the groups. Thus, in some cases, using multicenter indices as criteria for (anti)aromaticity, it can become difficult to assign the borole structures to a specific group. Nevertheless, there are very few exceptions to these general trends, which are associated with the different charge states of the boroles. The most remarkable difference between the two multicenter indices is evident for the neutral borole systems, for which two separate groups of points are obtained, suggesting that I_{NB} better captures the increase in aromaticity upon reduction of the compounds than I_{NG} does. However, as seen in Figure 12, the overall picture for the aromaticity in these compounds is qualitatively the same.
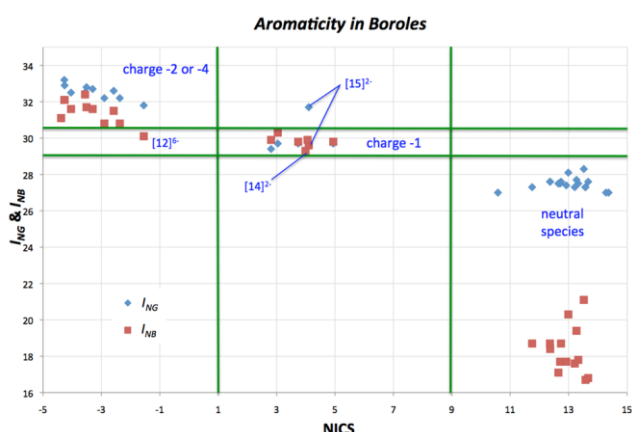

Figure 12. Multicenter indices (I_{NG} and I_{NB}) against NICS values for the series of boroles studied. The illustration is subdivided into boxes that separate the three different aromatic characters of the studied species.

Conclusions

In this manuscript we surveyed the aromaticity of thirty-four borole compounds in their various reduction states through assessment of the NICS and MCI aromaticity indices, with the goal of getting an understanding of how the electron delocalization in the ring is affected by the substituents. As one might expect, the neutral borole structures with four π-electrons are antiaromatic and become increasingly more aromatic by addition of one and two electrons, according to Hückel's rule. While the uptake of one electron to the borole leads to a

nonaromatic system, addition of a second electron fully aromatizes the ring and reliefs the system from its inherent electron deficiency. This finding is also supported by the magnetic response seen in the NICS profiles as the maximum moves from the center of the borole ring (in neutral, antiaromatic species) to a local minimum at a certain distance up/above the ring (in dianionic, aromatic species). In addition, the theoretical results show that the exocyclic substituent at the boron atom has a considerable influence on the degree of antiaromaticity in the borole ring. Substituents with π-donating abilities, such as an amino or thiophene group, seem to mitigate the destabilizing electron delocalization in the ring, whereas π-accepting groups result in an enhanced antiaromatic destabilization. These findings are in good agreement with corresponding experimental studies aimed to assess the antiaromaticity in boroles by structural and spectroscopic analysis.

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The (anti)aromatic character of a wide variety of borole compounds in their neutral and reduced states was assessed based on nucleus-independent chemical shift (NICS) and multicenter aromaticity indices (MCI), with a specific focus on effects of the ring substituents.
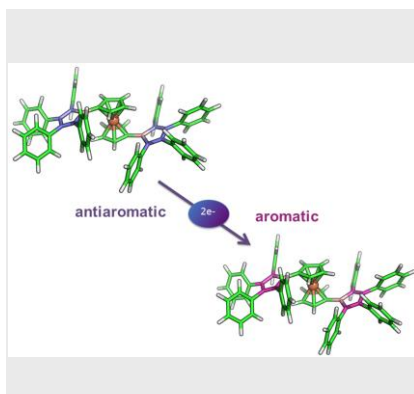
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