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The influence of heteroatoms on the aromatic character and the current pathways of B₂N₂-dibenzo[a,e]pentalenes[†]

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Four polycyclic molecules have been investigated at the DFT B3LYP/def2-TZVP level of theory using calculated magnetically induced current densities as an indicator of their (anti)aromaticity. Complicated current pathways were found in the dibenzo[a,e]pentalene and its three heterocyclic analogues each containing two boron and two nitrogen atoms. The antiaromatic character of the pentalene moiety is weaker in the hydrocarbon molecule and in 5,11-dihydrobenzo[d]benzo[4,5][1,2,3]azadiborolo[3,2-b][1,2,3]azadiborole as compared to the pentalene molecule. The antiaromatic character of the pentalene moiety is completely absent in the other two heterocyclic structures. In 6,12-dihydrobenzo[d]benzo[4,5][1,2,3]diazaborolo[2,1-a][1,2,3]diazaborole all four molecular rings are aromatic according to the ring-current criterion, and in 6,12-dihydrobenzo[d]benzo[3,4][1,2,5]azadiborolo[1,2-a][1,3,2]diazaborole, the diazaborole ring is aromatic, while the azadiborole ring is antiaromatic. In all four molecules the six-member rings are aromatic sustaining a weaker ring current than benzene does.

Introduction

Aromaticity is a property of unsaturated cyclic molecules that is typically associated with electron delocalization, equalization of chemical bonds, planarity, increased stability, and low chemical reactivity. Conversely, antiaromatic molecules tend to exhibit low stability, and high chemical reactivity, lowered symmetry.^{1–11} Also, bond-length alternation is less pronounced in antiaromatic molecules as compared to non-aromatic ones as seen in Figure 18 of Ref. 11. The degree of (anti)aromaticity correlates with the chemical and electronic properties of molecules. The most simple criterion for predicting the aromatic character of a structure is Hückel's π -electron rule.^{12,13} It states that molecules with $(4n + 2)$ π electrons are aromatic, and molecules with $4n$ π electrons are antiaromatic. Even though its history dates back to the mid-19th century, our understanding of aromaticity is still behind a shroud of many unresolved problems.¹ Aromaticity is a particularly elu-

sive property in large polycyclic molecules.^{14–19}

An experimental technique to study molecular aromaticity is nuclear magnetic resonance (NMR) spectroscopy.^{20,21} External magnetic fields induce current densities in molecules, which in turn induce weak secondary magnetic fields. Magnetically induced currents can flow around atomic nuclei and chemical bonds, as well as around molecular rings or the whole molecule. Magnetically induced current densities flowing in the classical direction predicted by the right-hand rule are called diatropic, whereas currents circulating in the opposite direction are termed paratropic.²² Diatropic currents induce a secondary magnetic field, which is in the opposite direction to the applied one, therefore the protons outside the ring-current flow of aromatic molecules are deshielded as compared to protons in similar molecules without any ring current. Analysis of the chemical shifts for ¹H NMR signals is an indirect means of studying ring-current effects and the degree of aromaticity.⁹

In the present study, we investigate the magnetically induced current densities of dibenzo[a,e]pentalene (1), and three of its heterocyclic analogues each containing two boron and two nitrogen atoms. Dibenzo[a,e]pentalene was originally synthesized in 1912 by Brand.²³ Almost a century later new synthesis routes with very high yield were reported.^{24,25} Even though the molecule with 16 π electrons should be antiaromatic according to the Hückel rule, it is experimentally fairly stable.²⁶ If a carbon-carbon moiety of the pentalene is replaced with its

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[†] Electronic Supplementary Information (ESI) available: The ESI contains the optimized Cartesian coordinates of the studied molecules and calculated isotropic nuclear magnetic shielding constants. Profile plots of the current density passing through the planes in Figure 1 are also shown. See DOI: 10.1039/b000000x/

isoelectronic boron-nitrogen bond, the heterocyclic molecule is expected to have electronic properties that differ from those of the corresponding hydrocarbon.^{18,27,28} Two heterocyclic BN analogues 6,12-dihydrobenzo[d]benzo[4,5][1,2,3]diazaborolo[2,1-a][1,2,3]diazaborole (2) and 6,12-dihydrobenzo[d]benzo[3,4][1,2,5]azadiborolo[1,2-a][1,3,2]diazaborole (3) were recently synthesized and thoroughly analysed experimentally by Wang *et al.*²⁸ One of the highlighted observations reported by Wang *et al.* is the relatively strong fluorescence of molecule (2) at 403 nm with quantum yield of 18%.²⁸ For completeness, we also include 5,11-dihydrobenzo[d]benzo[4,5][1,2,3]azadiborolo[3,2-b][1,2,3]azadiborole (4) in our study, which to our knowledge has not been synthesized so far.

The current densities of the pentalene molecule have been studied by several research groups in the past decade,^{17,29–31} because it can serve as a building block for more complicated molecules even though it is very unstable.³² Annulation of benzene rings to the pentalene core can yield stable molecules with antiaromatic character that potentially possess molecular properties of practical importance. The aromaticity of such structures has been investigated both experimentally and computationally^{17,18,28,33–35} because polycyclic organic molecules may be useful alternatives to inorganic semiconductors in light-emitting diodes, field-effect transistors and solar cells.^{36,37} Organic materials have the advantage of being flexible and light. Their molecular structures can be modified in order to fine-tune the electronic properties of the material for the desired application.^{38,39}

The article is structured in the following manner. The computational details are explained in Section 2, followed by a discussion of the calculated current densities and current pathways in Section 3. The calculated ¹H NMR chemical shifts are compared with experimental data in Section 4. Conclusions are drawn in Section 5.

Computational methods

The molecular structures of the investigated molecules were fully optimized at the density functional theory (DFT) level using Becke's three-parameter exchange functional^{40,41} in combination with the Lee-Yang-Parr correlation functional⁴² (B3LYP) and the Karlsruhe def2-TZVP basis set.^{43–45} The structural optimization as well as calculations of nuclear magnetic shieldings were performed with TURBOMOLE.^{46,47} The NMR chemical shifts were obtained from the nuclear magnetic shieldings by using tetramethylsilane (TMS) as reference. The isotropic shielding constant for TMS is 31.93 ppm at the employed computational level. The Cartesian coordinates of the optimized molecular structures and the calculated nuclear magnetic shielding constants are reported as Electronic Supplementary Information (ESI).†

The magnetically induced current densities analysis has been performed at the same level of theory using the gauge including magnetically induced current (GIMIC) program.⁴⁸ Actually, we investigate current density susceptibilities at zero magnetic field, which show how the current density changes with the strength of the applied external magnetic field. The word susceptibility will be omitted in the discussion of the results. GIMIC is an open-

source program, which uses the one-electron density matrix, the magnetically perturbed one-electron matrices, and basis set data as input information.^{48–51} Thus, the GIMIC calculation must be preceded by an NMR shielding calculation using an electronic structure code which employs Gaussian basis sets. The GIMIC code is freely available online.⁵² Interfaces to some of the popular quantum chemistry programs and a number of useful scripts are provided on the website. The GIMIC program can perform numerical integration on a two dimensional grid across the current density passing a selected bond rendering quantitative analysis of the current strengths feasible.^{17,53–56} Current densities can also be evaluated on a three-dimensional grid covering the whole molecule. The current density field can then be inspected visually, providing information about the current flow. Current densities and the current profiles are visualized with Gnuplot⁵⁷, GIMP⁵⁸, VMD⁵⁹ and Paraview.⁶⁰ The streamline graphics have been done with the line integral convolution (LIC) plug-in for Paraview.

The current pathways have been identified by integrating different contributions to the current density that pass planes perpendicularly to the molecular plane at chosen locations. The integration planes usually begin at the centre of a molecular ring and pass either through an atom from the ring or through the midpoint of a chemical bond. The end of the integration plane is often chosen to be very far outside the molecule where the electron density vanishes. In this work, the integration planes extend 10 bohr horizontally and vertically from the molecule. Further insights can be obtained by integrating independently a series of narrow, *e.g.* 0.02 bohr wide, slices of the two-dimensional integration plane. The current strengths from each slice are the differential contribution to the total current strength passing the plane. The diatropic and paratropic contributions to the integrated current strength are identified and plotted separately to obtain the profile of the current density passing the plane. (*current profile*) Analysis of the current density profile can be used for identifying *local currents* that flow around a single molecular ring, around a chemical bond, or around an atom. The strength of the *global ring current*, which loops around the entire molecule, can be used for assessing the extent of the (anti)aromatic character of the molecule. Integration of the current density also reveals whether the molecule sustains *semi-local* currents *i.e.*, currents that follow the perimeter of more than one ring but do not go around the entire molecule.^{17,51,61} The current density profiles consist of multiple peaks and domains originating from the magnetically induced currents. Plotting the current profile on the three-dimensional representation of the current densities makes it possible to identify the currents that contribute to the domains. It also shows details about the direction of the current density flow at the integration plane. The local tropicity of the current flow depends on the choice of origin. For annelated rings, a paratropic ring current in one molecular ring appears as a diatropic domain with respect to the central vortex of the adjacent ring.

Current densities and current pathways

Strategy for the current density analysis

An overview of the integration planes employed in the studies of the current density pathways of the four molecules is shown in Figure 1. A summary of the net current strengths passing the planes, as well as the diatropic and paratropic components are listed in Table 1, while the various ring currents in the investigated compounds are presented in Table 2 .

Fig. 1 Top view of the integration planes (marked in red) in the four molecules.

The integration of the diatropic and the paratropic contributions separately do not always add up to the reported net current strengths because the integration is done in an interval between two points of zero current. The paratropic and the diatropic currents usually do not vanish at the same point in space, therefore the net current is integrated at a slightly different interval as compared to its constituting contributions. All profiles of the current density passing the planes in Figure 1, as well as the integrated domains (in nA/T), are given in the ESI.†

Table 1 The magnetically induced currents (in nA/T) in the three molecules integrated along selected planes labelled in Fig. 1

Plane	Net	Diatropic	Paratropic
Molecule (1)			
a	5.43	13.08	-7.74
b	6.10	12.40	-6.34
c	-7.23	6.48	-13.78
d	3.59	9.25	-5.66
e	-7.31	7.96	-15.27
f	-7.18	5.52	-12.75
g	7.27	10.24	-2.97
h	-12.85	4.78	-17.74
i	-0.01	11.11	-11.12
j	-2.87	0.50	-3.37
Molecule (2)			
a	10.03	16.47	-6.44
b	10.16	15.45	-5.28
c	2.58	9.41	-6.82
d	12.31	17.35	-4.65
e	2.60	8.99	-6.24
f	2.54	8.78	-6.27
g	14.09	15.48	-1.39
h	-7.68	5.42	-13.20
i	0.00	10.04	-10.05
j	0.43	4.58	-4.15
k	-4.14	4.79	-8.93
Molecule (3)			
a	8.81	15.44	-6.62
b	8.85	14.40	-5.52
c	-3.94	5.48	-9.39
d	6.29	13.07	-6.78
e	-3.94	7.63	-11.57
f	-3.94	5.79	-9.73
g	10.86	11.95	-1.09
h	-12.87	5.51	-18.48
i	-6.56	4.98	-11.52
j	7.88	12.21	-4.31
k	-8.16	1.71	-9.86
l	0.71	4.20	-3.49
m	2.33	13.60	-11.27
n	-6.27	1.78	-8.05
o	1.86	5.32	-3.46
p	5.35	8.96	-3.59
q	13.29	16.09	-2.68
r	10.38	16.87	-6.48
s	10.49	15.82	-5.31
t	2.69	10.51	-7.74
Molecule (4)			
a	8.57	22.82	-14.26
b	7.13	13.24	-6.12
c	-5.41	6.43	-11.95
d	1.63	12.77	-11.14
e	-4.77	19.79	-24.69
f	-5.31	5.90	-11.21
g	8.43	20.51	-12.08
h	-11.99	5.01	-16.99
i	0.00	7.33	-7.26

Table 2 Overview of the local, semi-local and global currents (in nA/T) for molecules (1), (2), and (3).

Molecule (1)	
rings A and D	-3.37
rings B and C	-8.87
local current in rings A and D	4.65
crescent-shaped current in rings A and D	1.23
semi-local current in rings B and C	-1.29
global current	4.91
Molecule (2)	
rings A and D	-2.88
rings B and C	-3.00
crescent-shaped current	-0.67
local current in rings A and D	3.8 ± 0.9
ribbon-shaped current	-3.4 ± 0.9
global current looping inside rings B and C	3.6 ± 0.9
exterior global current	5.58
Molecule (3)	
ring A	-3.72
ring B	-5.8 ± 0.5
ring C	-1.82
ring D	-2.40
crescent current in ring D	1.16
local currents in ring A	10.19
local current in ring B	-0.5 ± 0.5
local current in ring D	5.4 ± 0.5
semi-local current in rings C and D	5.0 ± 0.5
global current	2.41
Molecule (4)	
rings A and D	-4.02
rings B and C	-6.11
local current in rings A and D	9.77
local current around the N atoms	4.58
semi-local current in rings B and C	-2.45
global current	2.62

In Figure 2, the current density profile for plane **d** in molecule (1) is plotted and overlaid on the 3D representation of the current density. Three separate domains are obtained for the diatropic component and one complicated domain in the paratropic contribution. The integration plane bisects the carbon-carbon bond, therefore the bond current contributes to the first domain between 0 and 1.3 bohr from the midpoint of the C7 – C8 bond. From the top view of the molecule one sees that the integration plane also crosses the semi-local current in the pentalene moiety. Hence, the integrated value for the current strength passing this plane cannot be directly used to separately estimate the strengths of the bond current and the semi-local current. The second sharp peak in the current profile between 1.3 and 1.7 bohr from the midpoint of the C7 – C8 bond is the atomic current. The third diatropic domain between 1.9 and 6 bohr from the bond centre begins where the currents surrounding the C8 carbon atom end and the global ring current starts. The integration plane does not cross any other currents, allowing us to assign the integrated value of 4.91 nA/T to the global ring current surrounding the entire molecule. The complicated current profiles do not prevent the assignment of the individual current flows, since one can integrate along different planes in order to identify the global, local and semi-local currents as sums of different contributions by simple arithmetics.

Fig. 2 Current profile for the integration in the plane **d** along the bond between atoms C7 and C8 in molecule (1). (a) The current density profile in (b) is overlaid on the 3D representation. The vertical line at a distance of 0 bohr corresponds to the centre of the bond. Picture (c) shows the current density in the molecular plane and in the integration plane.

Molecule (1)

The initial visual inspection reveals the presence of the localized atomic, bond, and ring currents in the molecular plane as shown in Figure 3. The global molecular current is also highlighted in the picture. The current density distributions change when plotting the current density in planes at different distances from the molecular plane, therefore some current pathways can only be found at certain distances. The current density 0.6 bohr from the molecular plane is visualized in Figure 4. The domains of the atomic currents are missing and the domains of the bond currents are less prominent. A new local diatropic current is found along the exterior of the six-member rings and a semi-local paratropic current appears to be flowing around the perimeter of the pentalene moiety. Farther away from the molecule, 1.5 bohr from its plane, a crescent-shaped diatropic current can be identified in the

six-member rings. In the absence of the small atomic domains the loops of the magnetically induced currents extend beyond the borders of the molecular rings. Vortices tend to cluster and eventually coalesce when moving away from the molecule. At a distance of 1.5 bohr, a semi-local current is circling around the pentalene moiety as shown in Figure 5.

Fig. 3 LIC representation of the current density in the molecular plane of molecule (1). The yellow curve corresponds to the global diatropic ring current. Local ring currents are highlighted in blue and representative examples for bond currents are shown in magenta. No indications of semi-local currents can be seen in the figure.

Fig. 4 LIC representation of the current density in molecule (1) 0.6 bohr from the molecular plane. The local current in the six-member rings is drawn in blue and the semi-local current in the pentalene moiety is highlighted in magenta.

Fig. 5 LIC representation of the current density in molecule (1) 1.5 bohr from the molecular plane. The loop in white shows the pathway of the crescent-shaped current. The semi-local current is drawn in blue and the current loops outside the pentalene moiety are highlighted in yellow.

Molecule (2)

Molecule (2) differs from molecule (1) by having four heteroatoms in the pentalene moiety. Two [1,2,3]-diazaborole rings are annelated at the N – N bond forming the B – N – N – B string of atoms. Molecule (2) belongs to the C_{2h} point group like dibenzo[a,e]pentalene (1). However, the heteroatoms change the pathways of the current flow as well as the strength of the currents as compared to molecule (1). The current density in the molecular plane shown in Figure 6 reveals an additional global current that makes a loop inside the five-member rings. A local current along the external perimeter of the six-member rings can be seen by plotting the current density in a plane 0.5 bohr away from the molecular plane (Figure 7). A ring current circulates around the nitrogen atoms and avoids the borons as seen in Figures 6 and 7. A ribbon-shaped current flows around all bonds that the nitrogen atoms have with the adjacent atoms as shown in Figure 7. The crescent-shaped current is weak flowing 1.5 bohr away from the molecular plane (Figure 8).

Fig. 6 LIC representation of the current density in the molecular plane of molecule (2). The current pathway in cyan represents the global diatropic ring current. Another global diatropic ring current specific to this molecule is drawn in yellow.

Fig. 7 LIC representation of the current density in molecule (2) 0.5 bohr from the molecular plane. The local currents in the six-member ring are presented in blue. A ribbon-shaped current surrounding the nitrogen atoms is shown in yellow.

Fig. 8 LIC representation of the current density in molecule (2) 1.5 bohr from the molecular plane. A crescent-shaped current can be found in the six-member rings.

Molecule (3)

Molecule (3) is an isomer of molecule (2), where a boron and a nitrogen atom are interchanged. The molecule formally consists of annelated [1,2,5]-azadiborole and [1,3,2]-diazaborole rings in such a way that they share a B–N bond, forming the B–N–B–N string of atoms (Figure 1). Molecule (3) belongs to the C_s point group, because it does not have any C_2 axis perpendicular to the molecular plane as the two other molecules do. The current densities in all its rings are therefore different. It is possible to identify a local ring current in the molecular plane along the exterior of ring A as shown in Figure 9. The ring currents seem to avoid the boron atoms as in molecule (2), while the nitrogen atoms are surrounded by semi-local ring currents involving rings C and D. The local ring current in ring B can be seen 0.6 bohr above the molecular plane (Figure 10). A weak crescent-shaped ring current in ring D is seen 1.5 bohr away from the molecular plane (Figure 11).

Fig. 9 LIC representation of the current density in molecule (3) in the molecule plane. The local current in ring A is drawn in green. The semi-local current involving ring D is given in yellow. The local currents around the nitrogen atoms are presented in magenta. The atomic currents, bond currents and the global ring current are not marked.

Fig. 10 LIC representation of the current density in molecule (3) 0.6 bohr from the molecular plane. The local current around the six-member ring is drawn in blue and the local current involving the five-member ring is drawn in yellow.

Fig. 11 LIC representation of the current density in molecule (3) 1.5 bohr from the molecular plane. Two semi-local currents involving the six-member ring are drawn in white and blue. The crescent-shaped current is presented in yellow.

Molecule (4)

Molecule (4) is an isomer of molecule (2), where both boron

atoms are exchanged with the nitrogen atoms. The common bond between the two [1,2,3]-azadiborole rings consists of the two boron atoms. The current density of molecule (4) resembles of that of molecule (1) in the sense that they sustain paratropic semi-local currents in the five-member rings. Local currents around the nitrogen atoms, similarly to the ones found in molecule (3) can be distinguished in the molecular plane, as well as 0.5 bohr from the molecular plane (Figures 12 and 13). As the current flow changes with the distance from the molecular plane, similar local current pathways are found as in molecule (1) (compare Figures 5 and 13). The semi-local current becomes prominent 1.0 bohr away from the molecular plane and beyond.

Discussion of the current densities

The magnetically induced current densities in dibenzopentalene calculated using the GIMIC method are qualitatively the same as those obtained by Fowler *et al.*³³ in their study using the ipsocentric CTOCD-DZ (continuous transformation of origin for current density, diamagnetic-zero) method.^{62,63} For dibenzopentalene, they reported a global ring-current strength of 70-100% of the benzene value, whereas we obtain a global ring-current strength of 4.91 nA/T for dibenzopentalene, which is about 2.5 times weaker than the benzene value of 11.8 nA/T.¹⁰ However, adding the global current and the local current in the six-member rings yields a current strength of 9.56 nA/T, which is 81% of the net ring-current strength of benzene. The GIMIC calculations yielded a net current strength of 6.10 nA/T that passes through plane **b** in molecule (1). The diatropic and paratropic contributions are 12.40 nA/T and -6.34 nA/T, respectively. The net current strength is half the net current strength for benzene. The diatropic and paratropic contributions are 16.7 nA/T and -4.9 nA/T, respectively.¹⁰ These values are also comparable to the corresponding ring-current strengths of 12.99 nA/T, 17.67 nA/T, and -4.68 nA/T for the six-member ring of naphthalene.¹⁷

Fig. 12 LIC representation of the current density in the molecular plane of molecule (4). The local currents around the nitrogen atoms are drawn in magenta.

Fig. 13 LIC representation of the current density in molecule (4) 1 bohr from the molecular plane. Two semi-local currents involving the five-member rings is drawn in blue. The local current in the six-member rings is presented in red. The currents around the nitrogen atoms are marked in cyan.

The net ring current passing plane **d** in molecule (1) is 3.59 nA/T with diatropic and paratropic contributions of 9.25 nA/T and -5.66 nA/T, respectively. These values can be compared to the current strengths of -7.47 nA/T (net), 7.65 nA/T (diatropic) and -15.12 nA/T (paratropic) passing the same plane in pentalene. The electronic properties of the pentalene moiety in (1) seem to be very different from those of pentalene. The integration of the current passing plane **c** in molecule (1) resulted in a net current of -7.23 nA/T, whose diatropic and paratropic components are 6.48 nA/T and -13.78 nA/T, respectively. The net ring-current strength is almost three times smaller than the net ring-current strength of pentalene of -19.91 nA/T with the diatropic and paratropic contributions of 4.95 nA/T and -24.86 nA/T. The ring current strengths of the five-member rings in dibenzopentalene of -8.87 nA/T and -9.73 nA/T are slightly smaller than the ring-current strength of the individual rings in pentalene. The semi-local ring-current strength of the pentalene moiety in molecule (1) is only -1.29 nA/T, which is ten times smaller than the paratropic current flowing around the perimeter of the pentalene molecule (-13.70 nA/T). Therefore, even though the five-member rings in dibenzopentalene have some antiaromatic character, it is significantly weaker than in pentalene.

Introducing heteroatoms into the five-member rings significantly changes the current density pathways leading to many local and semi-local ring currents. The pentalene moieties with heteroatoms are found to lose their antiaromatic character in molecules (2) and (3). The six-member rings in molecules (2) and (3) are more aromatic than in dibenzopentalene. The strength of the net ring current passing plane **b** is 10.16 nA/T in molecule (2), whereas the current strength passing the same planes in rings **A** and **D** of molecule (3) are 8.85 nA/T and 10.49 nA/T, respectively. In molecule (4) a net current of 7.13 nA/T passes that plane. The five-member rings in molecule (2) are weakly aromatic sustaining a net current of 2.58 nA/T that passes plane **c**. The strength of the local ring current in ring **B** of molecule (2) is -3.00 nA/T, which is three times weaker than

the ring current in pentalene and dibenzopentalene. There is no indication of a semi-local current along the perimeter of the pentalene moiety in molecule (2). Instead, there is a ribbon-shaped current isolating the nitrogen atoms and the bond current vortices for the N – C and N – B bonds. The currents avoid the boron atoms as seen in Figure 8.

In molecule (3), three of the rings are aromatic. The current strengths are stronger in the rings C and D on the nitrogen side of the molecule. The net ring-current passing plane s in ring D is 10.49 nA/T. Thus, ring D is slightly more aromatic than ring A. Ring B is weakly antiaromatic as a current strength of -3.94 nA/T passes plane c, whereas ring C is very weakly aromatic with a net current strength of 2.69 nA/T passing plane t.

The current density in molecule (4) shares some similarities with dibenzopentalene (1) by having a weak semi-local paratropic current of -2.18 nA/T along the perimeter of the five-member rings. The five-member rings are also antiaromatic with a net current strength of -5.41 nA/T passing plane c, which is though weaker than the corresponding current in molecule (1), and only 25% of the strength of the corresponding current in pentalene. The ring current strength of -6.11 nA/T in the five-member rings in molecule (3) is also relatively weak. The six-member rings are aromatic with a net current of 7.13 nA/T passing plane a. It is as strong as in molecule (1) but weaker than in benzene and in molecules (2) and (3).

Nucleus-independent chemical shifts

The nucleus-independent chemical shifts (NICS) method is a popular approach to estimate the degree of aromaticity.^{7,64,65} Albeit it is very simple to apply, one has to keep in mind that estimating ring current strengths and current pathways for polycyclic molecules using NICS values and magnetic shielding functions is may be unreliable. The results obtained using NICS calculations should therefore be taken with caution as pointed out by various groups.^{17,22,65–75} NICS values reported in the literature are summarised in Table 3.

Table 3 NICS values (in ppm) reported in the literature.^{24,28,33}

Molecule (1)	Ref. 28 NICS(1) _{zz}	Ref. 24 NICS(1)	Ref. 33 NICS(0)
Six-member ring	-13.6	-6.23	-9.8
Five-member ring	+23.7	+5.88	+7.4
Molecule (2)			
Six-member ring	-23.0		
Five-member ring	-0.12		
Molecule (3)			
Ring A	-20.6		
Ring B	+18.7		
Ring C	-2.6		
Ring D	-24.3		
Molecule (4)			
Benzene		-11.31	
Pentalene		+18.42	

For dibenzopentalene (1), Kawase *et al.* reported NICS(1) values of -6.23 ppm at the center of the six member rings,²⁴ which is about one half of the NICS(1) value of -11.31 ppm for benzene, calculated at the same level of theory. The five-member rings are antiaromatic with a NICS(1) value of +5.88 ppm, which is three

times smaller than the NICS value of +18.42 ppm obtained for pentalene. According to the NICS calculations, the six-member ring is less aromatic than benzene and the five-member ring is less antiaromatic than pentalene, which qualitatively agrees with the conclusions drawn from the present GIMIC study. Fowler *et al.* reported the NICS(0) values of -9.8 ppm and 7.4 ppm for the six-member and five-member rings of dibenzopentalene. However, no reference values for benzene and pentalene calculated at the same level of theory were reported.^{26,33}

Wang *et al.* calculated NICS(1)_{zz} values at the B3LYP/6-311+G(2d,p) level for molecules (1 – 3) with mesityl protective groups in the five-member rings.²⁸ They concluded that the six-member ring in molecule (2) is a strongly aromatic and the five-member ring is weakly aromatic. In molecule (3), they found that the six-member rings are aromatic, the azadiborole ring is antiaromatic, and the diazaborole ring is weakly aromatic. It appears that the aromatic character obtained using the NICS method qualitatively agrees with the GIMIC results. NICS calculations do not provide any details about the current pathways, whereas the current density calculations show that the current density flow is much more complex than NICS calculations suggest. More advanced NICS based methods such as NICSXY scans have been developed.⁷³ However, for molecules consisting of annelated aromatic and antiaromatic rings the NICSXY scan yielded incorrect current pathways.¹⁷

Calculation of ¹H NMR chemical shifts

The experimental NMR spectrum for molecule (1) is in a nearly perfect agreement with the calculated chemical shifts, which fall in the typical range of 6 – 8 ppm for aromatic protons.⁷⁶ Experimental NMR spectra are available for the derivatives of molecules (2) and (3) where the hydrogen atoms at the heteroatoms are substituted with mesityl (Mes) groups.²⁸ Chemical shifts were calculated for the substituted and non-substituted structures. In Table 4, we report NMR data for the molecules without mesityl groups. The NMR data for the derivatives are available in the ESI†. We assigned the experimental spectra of (2) and (3) using the experimental spin-spin coupling constants.²⁸

Table 4 ^1H NMR shifts (in ppm) calculated at the B3LYP/def2-TZVP level of theory. Tetramethylsilane (TMS) is used as reference. The experimental values for (1), (2), (3), and benzene are taken from Refs. 76, 28, 28, and 77, respectively.

Atom	Calculated	Experimental
Molecule (1)		
H1	6.94	6.85 – 6.90 (m, 6H)
H2	6.93	6.85 – 6.90 (m, 6H)
H3	7.06	7.0 – 7.8 (m, 2H)
H4	6.87	6.85 – 6.90 (m, 6H)
H10	6.40	6.40 (s, 2H)
Molecule (2)		
H1	7.37	7.09 – 7.02 (m, 2H)
H2	7.72	7.31 – 7.21 (m, 2H)
H3	7.80	6.81 (d, $J = 8.1$ Hz, 2H)
H4	8.07	7.55 (d, $J = 7.2$ Hz, 2H)
H10	6.09	–
Molecule (3)		
H1	7.52	7.27 – 7.16 (m, 2H),
H2	7.51	7.27 – 7.16 (m, 2H),
H3	7.60	7.12 – 7.03 (m, 3H),
H4	7.83	7.34 (d, $J = 7.2$ Hz, 1H)
H5	5.84	–
H6	7.05	6.43 (d, $J = 7.6$ Hz, 1H),
H7	7.21	6.79 (td, $J = 7.5, 1.5$ Hz, 1H),
H8	7.20	6.86 (td, $J = 7.5, 1.5$ Hz, 1H),
H9	7.56	6.71 (d, $J = 7.6$ Hz, 1H),
H10	6.37	–
Molecule (4)		
H1	6.68	–
H2	7.30	–
H3	6.87	–
H4	7.34	–
H-N	5.54	–
Benzene		
H	7.64	7.339
Pentalene		
H_α	4.97	–
H_β	4.85	–

Fig. 14 Labels of the hydrogen atoms reported in Table 4.

The calculated ^1H NMR shifts for molecule (1) have a mean deviation of 0.04 ppm from the experiment, for molecule (2) and molecule (3) they deviate by 0.57 ± 0.25 ppm and 0.48 ± 0.20 ppm, respectively. The discrepancies can be attributed to solvent and vibrational effects, as well as to additional interactions between the main heterocyclic rings and the protective mesityl groups. When the calculation is performed on the mesityl-substituted structures, the deviation for molecule (2) drops to 0.26 ± 0.34 ppm and to 0.26 ± 0.29 ppm for molecule (3). No experimental data is available for molecule (4) since, to our knowledge, it has not been synthesized so far. In the computed spectrum, the protons in the five-member heterocyclic rings are upshifted to 5.8 – 6.4 ppm.

The NMR chemical shifts for the hydrogen atoms in the six-member rings are affected by the global and local currents at these rings. In the heterocyclic molecules, the currents in the six-member rings are 12–13 nA/T, whereas in molecule (1) they are 9.5 nA/T. The corresponding chemical shifts are 7.5 ± 0.2 ppm and 6.93 ppm, respectively, reflecting the ring-current contribution to the ^1H NMR chemical shifts at the six-membered rings. The protons at the five-member rings are affected by a more complicated current flow.

Summary and conclusions

The present work reveals that molecular (anti)aromaticity can be hard to predict by simple chemical intuition. Particularly for molecules with fused rings it is necessary to analyse the quantum mechanical origin of the aromatic properties. One common criterion for aromaticity is the strength and pathways of the magnetically induced current densities flowing around molecular ring(s). The analyses of the current densities yield an accurate description of the current flow in the molecules when they are exposed to an external magnetic field, whereas the commonly used NICS calculations do not provide any information about the current strengths and the current-density pathways.

The molecules studied in this work possess 16 π electrons implying that they according to the Hückel rule are expected to be antiaromatic. The GIMIC calculations show that the six-member rings in the four molecules sustain aromatic currents, while the pentalene moiety is antiaromatic only in dibenzopentalene (1) and the heterocyclic molecule (4). Substitution of two C – C bonds in the pentalene fragment with two B – N bonds gives rise to new complex current pathways.

In 6,12-dihydrobenzo[d]benzo[4,5][1,2,3]diazaborolo[2,1-a][1,2,3]diazaborole (2), the current flow in the five-member rings is dominated by diatropic currents, implying that they are weakly aromatic, whereas in 6,12-dihydrobenzo[d]benzo[3,4][1,2,5]azadiborolo[1,2-a][1,3,2]diazaborole (3), the diazaborole ring is weakly aromatic as it is dominated by diatropic currents, whereas the azadiborole ring sustains a local paratropic ring current making it weakly antiaromatic. The weaker antiaromaticity of the five-member rings in dibenzopentalene-type molecules leads to a stronger aromaticity of the six-member rings. The ^1H NMR chemical shifts calculated at the B3LYP/def2-TZVP level of theory are in a very good agreement with available experimental data.

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