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Modulating Paratropicity in Heteroarene-Fused Expanded Pentalenes

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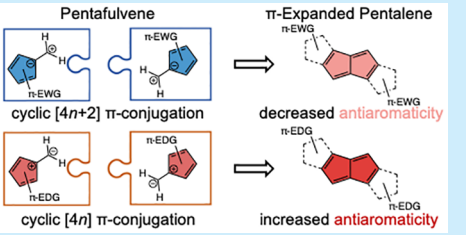
ABSTRACT: Pentalenes are formally eight-π-electron antiaromatic, but π-expanded pentalenes can display varying levels of paratropicity depending on the choice of annelated (hetero)arenes and the geometry of π-expansion (i.e., linear vs bent topologies) around the [4n] core. Here, we explain the effects of annelation on the paratropicity of π-expanded pentalenes by relating the electronic structure of pentalenes to a pair of conjoined pentafulvenes.



The independent reports of Kawase, Kubo, and co-workers[1] and Tilley et al.[2] of simple synthetic protocols for preparing symmetrical dibenzopentalenes kindled strong interest in the preparation of expanded pentalene derivatives and studies of their optoelectronic properties in the past decade.[3−12] The potential for high charge mobilities was linked to a narrow highest occupied molecular orbital−lowest unoccupied molecular orbital energy gap and strong paratropicity of the pentalene core. Even though some structure−property relationships have been observed, for example, that a high bond order between the [4n] core and annelated arene indicates increased paratropicity of the antiaromatic core,[13] how annelation impacts the paratropicity of π-expanded pentalenes remains a mystery.

π-Expanded pentalenes can exhibit varying degrees of antiaromatic character, depending on the numbers, types, and arrangements of fused rings connected to the [4n] core. For example, dibenzopentalene is only weakly antiaromatic,[14] but *syn*-dithienopentalenes[14,15] and *anti*-dithienopentalenes[17] restore the antiaromaticity of the pentalene core, while di(3,4)-thienopentalene[16] is weakly antiaromatic (Figure 1a). Compared to that of pentalene, 1,4-diazapentalene exhibits reduced antiaromaticity as adding two N atoms increases bond length alternation, but clamping the two ends of 1,4-diazapentalenes by thiophene rings restores antiaromaticity, as annelation gives rise to a more bond delocalized [4n] core.[15] Many other π-expanded pentalenes, e.g., arenopentalenes, bispentalenes, and nanohoops containing dibenzopentalene units, have been prepared, and their paratropicities investigated.[17,18] Here, we elucidate the impact of annelation of heteroaromatic rings on the antiaromaticity of π-expanded pentalenes by relating the electronic structure of pentalene to a conjoined pair of pentafulvenes.

Pentafulvenes have been called "aromatic chameleons" because the five-membered ring can be either aromatic or antiaromatic, depending on the polarization of the exocyclic

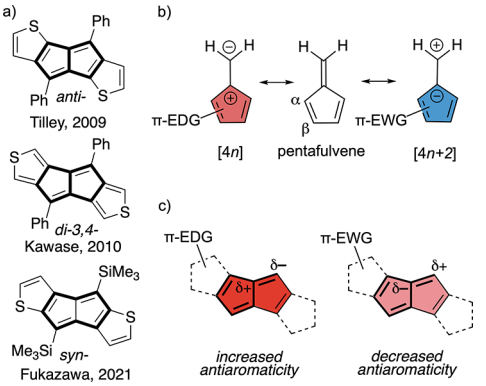


Figure 1. (a) Examples of dithiophene-fused pentalenes. Relationship between (b) substituted pentafulvenes and (c) heteroarene-fused pentalenes. For the sake of clarity, only one of the pentafulvene moieties (bold) in each pentalene is outlined.

C═C bond (Figure 1b).[19,20] π-Electron-donating groups (π-EDGs) at the α or β positions polarize the exocyclic π-bond away from the ring and can increase the [4n] character (Figure 1b, left). Conversely, π-electron-withdrawing groups (π-EWGs) at the α or β positions polarize the exocyclic π-bond toward the ring and can increase [4n+2] character (Figure 1b, right). This relationship is supported by past theoretical studies. For example, Hess and Schaad found, on the basis of extended Hückel calculations, that the resonance energies of pentafulvenes increase with π-donating substituents.[21] Kilså

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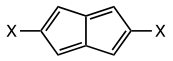
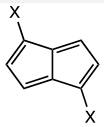
Table 1. Computed NICS(1)$_{zz}$ Values for Disubstituted *syn*- and *anti*-Pentalenes (X = OH, SH, CH_3, or BH_2) (all C_{2h} minima) at the B97-2/6-311+G(d,p)//M11/6-311+G(d,p) Level of Theory

Compound	X	NICS(1)$_{zz}$
syn-		
	OH	+47.6 ppm
	SH	+42.6 ppm
	CH_3	+44.2 ppm
	BH_2	+38.2 ppm
anti-		
	OH	+61.2 ppm
	SH	+51.1 ppm
	CH_3	+47.7 ppm
	BH_2	+41.6 ppm

and Ottosson reported that substituents can alter the vertical electron affinities and ionization energies of the tria-, penta-, and heptafulvenes and explained their findings on the basis of changes in the aromatic and antiaromatic character of the cross-conjugated rings.[22] We recognize that heteroarene-fused pentalenes are subject to the same sorts of effects present in the substituted pentafulvenes.

As shown in Figure 1c, the [4*n*] core can be seen as a conjoined pair of pentafulvenes (see one of the two pentafulvene fragments outlined in thick bold lines). Like the pentafulvenes, π-EDGs can polarize the "exocyclic" double bond(s) and increase cyclopentadienyl cation character in the five-membered ring(s), thereby increasing antiaromaticity. π-EWGs can polarize the "exocyclic" double bond(s) in the opposite direction and increase cyclopentadienyl anion character in the five-membered ring(s), thereby decreasing antiaromaticity. In this work, we investigate whether this relationship predicts the effects of heteroarene annelation in a series of π-expanded pentalenes.

We first investigated a set of symmetrically disubstituted pentalenes, with π-EDGs (X = OH or SH) or a π-EWG (X = BH_2) placed at the *syn* (2,5-) and *anti* (3,6-) positions. X = CH_3 derivatives were included as a reference. X = NH_2 derivatives led to a bond-flipped structure and were excluded from this analysis. Following Figure 1c, pentalenes with disubstituted π-EDGs display enhanced antiaromatic character, while those with π-EWGs display reduced antiaromatic character. Computed nucleus-independent chemical shift,[23−25] NICS(1)$_{zz}$, values for the *syn* derivatives decrease in the following order: 47.6 ppm > 42.6 ppm > 44.2 ppm > 38.2 ppm for X = OH, SH, CH_3, and BH_2, respectively (Table 1). Those for the *anti* derivatives decrease in the following order: 61.2 ppm > 51.1 ppm > 47.7 ppm > 41.6 ppm for X = OH, SH, CH_3, and BH_2, respectively. NICS(1)$_{zz}$ data for substituted pentafulvenes are included in the Supporting Information and show the same trends. All geometries were optimized at the M11/6-311+G(d,p) level of theory. NICS(1)$_{zz}$ values were computed at the B97−2/6-311+G(d,p) level of theory.

Next, we investigated a series of linearly expanded pentalenes by varying the π-EDG/π-EWG nature of the heteroatom embedded in the annelated heteroarene. Our test set includes pentalene annelated to heteroarenes (PDH), to benzo-fused heteroarenes (PDB), and to naphtho-fused heteroarenes (PDN) (Figure 2). Even though a heteroarene can be aromatic (e.g., pyrrole, furan, and thiophene) or antiaromatic (e.g., borole) and thus is not the same as a NH_2, OH, SH, or BH_2 substituent, the π-donating/accepting ability of the heteroatom is intact and thus can polarize the π-system of the pentalene core in the same way.

NICS-XY scans,[26] using the NICS(1)$_{zz}$ metric, show that the π-EDGs (X = NH, O, or S) preserve or increase the antiaromaticity of the [4*n*] core. Thus, in Figure 3a−c, all of the colored curves either overlap or lie above the black curve (pentalene). In contrast, having a π-EWG (X = BH) decreases the antiaromaticity of the pentalene core (Figure 3d), and all of the colored curves lie below the black curve. The NICS-XY scans also reveal that extending the annelation of the heteroarenes increases the antiaromaticity of the [4*n*] core. Thus, for the same X groups, the *syn*/*anti*-PDN derivatives exhibit the highest paratropicity (purple), followed by the *syn*/*anti*-PDB derivatives (pink) and finally the *syn*/*anti*-PDH derivatives (orange). We do not observe a large difference between the *syn* and *anti* isomers.

NICS2BC[27] plots provide further insight (for details on NICS2BC, see the Supporting Information and ref 27). NICS2BC plots translate NICS values to bond currents and show a weighted superposition of localized currents. Plots generated from NICS(1)$_{zz}$ values for the *syn*/*anti*-PDH, PDB, and PDN derivatives with X = NH and X = BH are shown in the first three columns of Figure 4 (plots for the X = O and S sets are included in the Supporting Information). Clockwise/

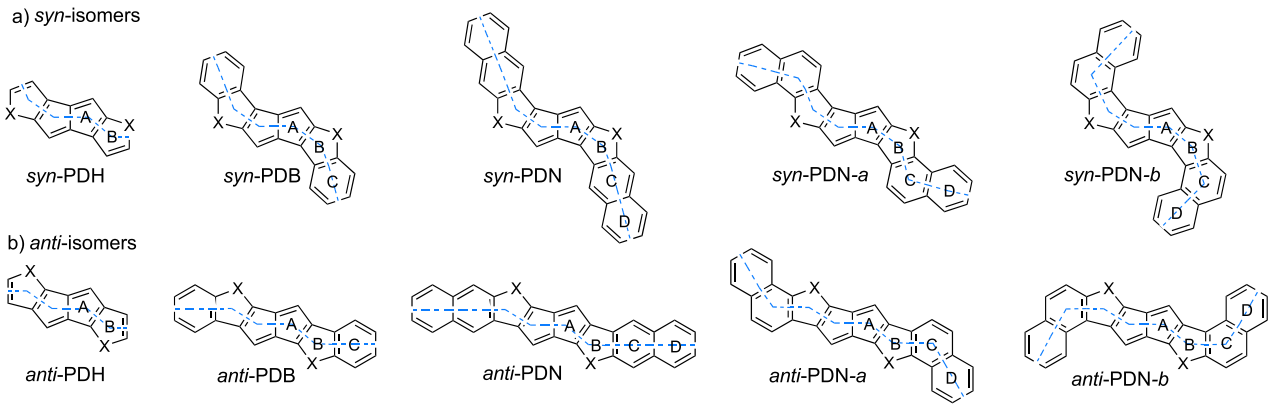


Figure 2. Studied (a) *syn*- and (b) *anti*-heteroarene-fused (PDH), benzo-heteroarene-fused (PDB), and naphtho-heteroarene-fused (PDN) pentalenes (X = NH, O, S, or BH). NICS-XY-scan paths are indicated by blue dashed lines. Borole derivatives were considered with a flipped bonding pattern (i.e., rings A and B share a formal single bond).

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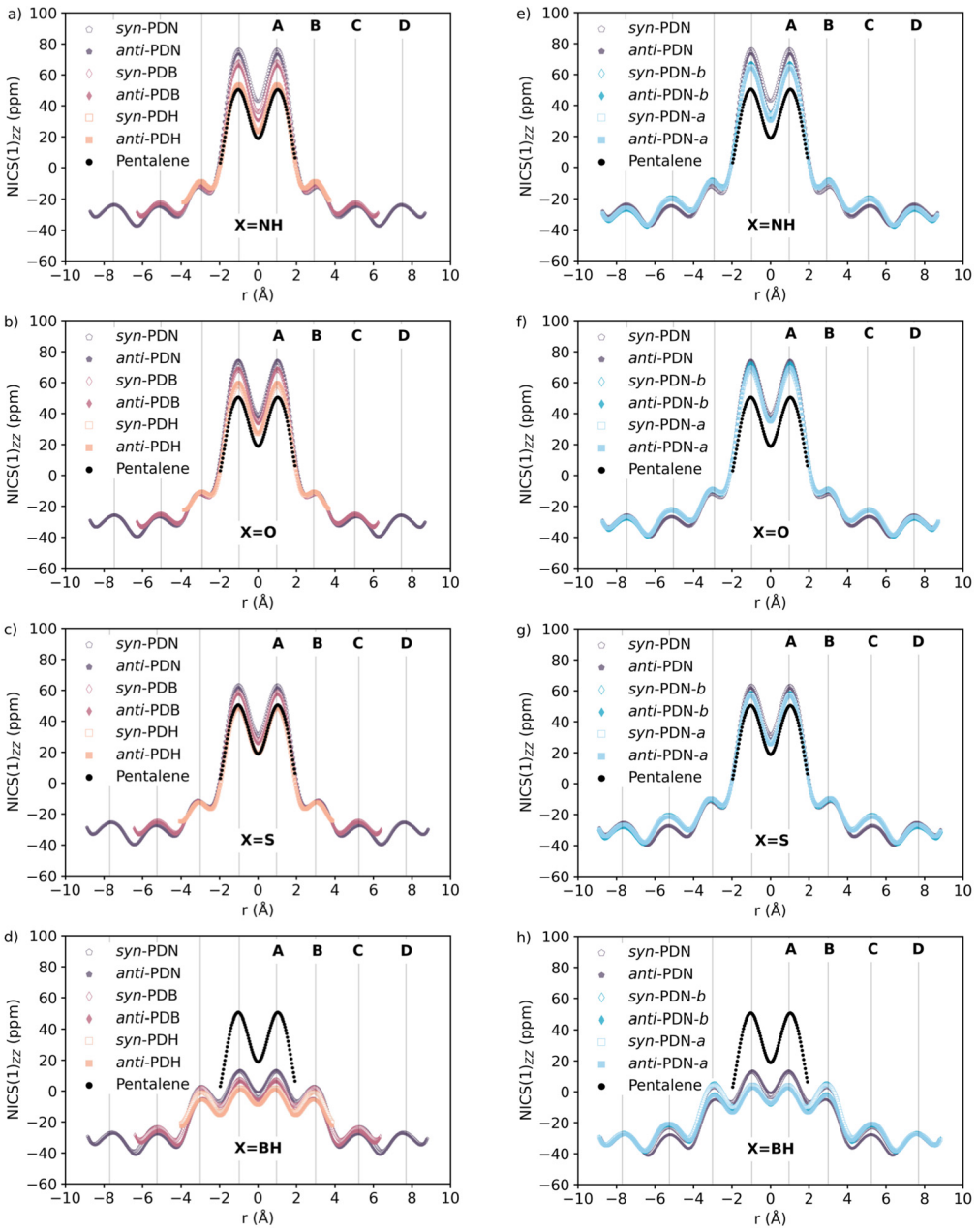

Figure 3. NICS-XY scans for pentalene (black) and *syn*- and *anti*-PDH, PDB, and PDN, where X = (a) NH, (b) O, (c) S, or (d) BH, as well as *syn* and *anti* linear (PDN) and bent (PDN-*a* and PDN-*b*) naphthoheteroarene-fused pentalenes, where X = (e) NH, (f) O, (g) S, or (h) BH. NICS values were computed at the B97-2/6-311+G(d,p) level of theory. A–D mark the positions of the centroids of each ring.

anticlockwise circulations indicate a diatropic/paratropic current, and a thicker arrow indicates a stronger ring current.

NICS2BC plots for the X = NH set all show a strong paratropic current encircling the [4*n*] pentalene core (Figure 4a,b). Two diatropic currents encompass the two individual annelated sections of the molecule in their entirety. We draw attention to the fusion between the pyrrole and the benzene/naphthalene moieties. The bond current here indicates that the apparent semiglobal diatropic current is most likely a superposition of a local current within the pyrrole and a local current in the benzene/naphthalene fragment. As explained in the Supporting Information, the direction of the current along this bond indicates that the current around the benzenoid component is somewhat stronger than that in the pyrrole fragment in all cases.

Notably, the bond currents around the pentalene core strengthen with an increasing degree of linear annelation: *syn*/*anti*-PDH < *syn*/*anti*-PDB < *syn*/*anti*-PDN. According to the proposed pentafulvene model, this trend suggests that the π-EDG character of the heteroarene increases with linear annelation. It appears that extending the conjugation in a linear fashion shifts the cyclic delocalization toward the benzenoid component, and the NH group becomes more amine-like (i.e., more π-electron-donating). Direct comparisons of computed π-electron densities at the N atoms of pyrrole (1.44), indole (1.53), and 1*H*-benzo[*f*]indole (1.56) confirm that benzannelation makes the N atom more amine-like. In agreement, computed NICS(1)$_{zz}$ values show decreasing diatropicity for the five-membered rings of pyrrole (−31.4 ppm), indole (−29.0 ppm), and 1*H*-benzo[*f*]indole

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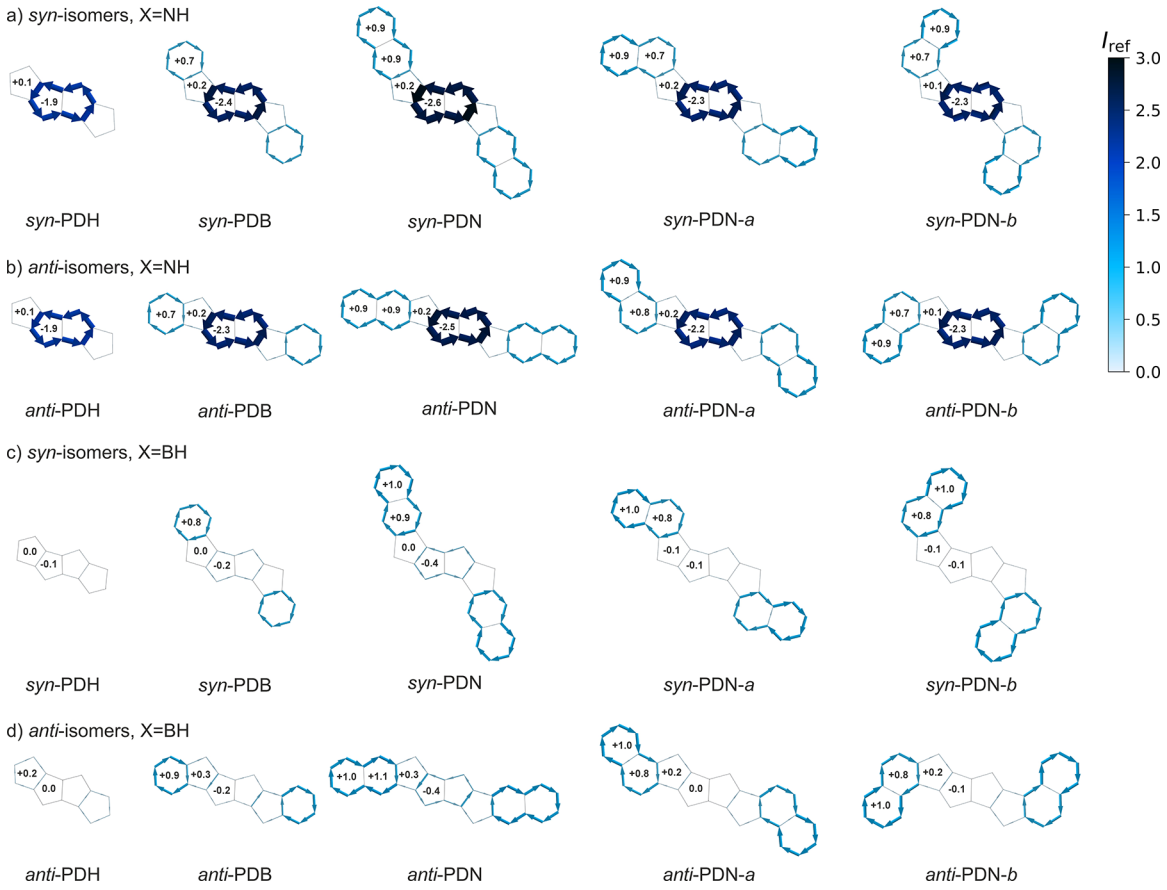

Figure 4. Computed NICS2BC plots for the PDH, PDB, PDN, and PDN-*a* and -*b* derivatives, where (a and b) X = NH and (c and d) X = BH. Weighted ring current values are included to the center of each ring. I_{ref} is the bond current strength with respect to benzene.

(−26.2 ppm) (see also data for the X = O and S sets in the Supporting Information). In a related study, Haley et al. reported a highly antiaromatic naphthothiophene-fused *s*-indacene isomer and reasoned that strong paratropicity arises as "the thiophene [unit] acts as a thioether spacer."[28]

NICS2BC plots for the X = BH set show a steep decrease in the antiaromaticity of the pentalene core (Figure 4c,d), as predicted by the pentafulvene model. The [4*n*] pentalene core appears to be essentially nonaromatic, and it is clamped by two diatropic ring currents encircling the annelated components. Despite the overall weakness of the antiaromaticity, there is a gradual increase in the paratropicity of the pentalene core (*syn*/*anti*-PDH < *syn*/*anti*-PDB < *syn*/*anti*-PDN). Computed π-electron density values for the B atom in borole (0.04), benzoborole (0.06), and naphthoborole (0.08) increase as the heteroaromatic component is extended, indicating weaker π-EWG behavior.

Accordingly, computed $NICS(1)_{zz}$ values for the borole ring decrease in the following order: borole (34.5 ppm) > benzoborole (30.3 ppm) > naphthoborole (23.6 ppm). These results suggest that the BH groups become more borane-like (i.e., less π-electron-withdrawing) with extended linear annelation. We note that the borole-fused pentalene derivatives adopt a bond-flipped structure (i.e., in which the pentalene core is fused to the borole ring via a formal single and not double bond). This, too, is consistent with the observation of Haley et al.,[13] who found that a lower bond order for the fused (hetero)arene bond predicts the decreased antiaromaticity of the [4*n*] core. Discussions based on evaluations of bond length alternations around the pentalene core are supportive and are included in the Supporting Information.

Finally, we examined naphtho-heteroarene-fused pentalenes with linear (PDN) versus bent (PDN-*a* and PDN-*b*) arrangements of the naphthalene moiety. Pairs of π-EDGs (X = NH, O, or S) and π-EWGs (X = BH) were placed symmetrically at the *syn* and *anti* positions of the [4*n*] core (Figure 2). For all heteroarene-fused derivatives, NICS-XY scans show that the linear derivatives (purple) are more antiaromatic than the bent derivatives (blue and light blue) (Figure 3e−h).

Differences between the linear and bent derivatives for the X = NH, O, and S sets may be explained by considering rings B−D in the linear *syn*/*anti*-PDN as analogues of "anthracene" units and those in the bent *syn*/*anti*-PDN-*a* and -*b* analogues as "phenanthrene" units. It has been suggested that annelation to less diatropic components can increase the antiaromaticity of π-expanded pentalene cores.[14] For example, pentalene annelated to the less aromatic central ring of a phenanthrene unit is strongly paratropic.[29] In anthracene, the side rings have weaker current density compared to that of the central ring, whereas in phenanthrene, the two side rings have the greatest current density.[30,31] Consistent with this analogy, ring B for the linear derivative of X = NH [$NICS(1)_{zz}$ = −26.2 ppm] is less diatropic, and thus, the pentalene core shows stronger paratropicity. While ring B for the bent derivatives of X = NH, bent-*a* (−28.8 ppm) and bent-*b* (−29.0 ppm), is more diatropic, the pentalene core displays weaker paratropicity.

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Higher computed π-densities for the N atoms of the linear derivative (1.66) compared to the two bent forms, bent-*a* (1.62) and bent-*b* (1.62), also indicate the stronger π-EDG behavior of the heteroatom. Computed data for the X = O and S sets are included in the Supporting Information and show the same trends.

Stronger paratropicity of the linear versus bent derivatives of the X = BH set is consistent with a less π-accepting BH group of the linear isomer, as indicated by computed π-densities at the B atom: linear (0.08), bent-*a* (0.06), and bent-*b* (0.06). Accordingly, ring B of the linear isomer (23.6 ppm) is less antiaromatic than those of bent-*a* (39.9 ppm) and bent-*b* (39.2 ppm), suggesting that for linear isomers, the BH groups are more borane-like. See discussions on bond length alternations in the Supporting Information.

By relating pentalenes to a pair of conjoined pentafulvenes, we provide a framework for explaining the effects of heteroarene annelation on the antiaromaticity of π-expanded pentalenes. Highly paratropic π-expanded pentalenes may be achieved by annelation to heteroarenes containing π-donating heteroatoms and then by linear expansion of these π-systems.

■ ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.4c00188.

Details and references for computational methods, NICS2BC plots, computed NICS(1)$_{zz}$ values, bond length alternation (BLA) values, computed π-densities, and optimized Cartesian coordinates for all compounds (PDF)

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Notes

The authors declare no competing financial interest.

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