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Prediction of Spin Density, Baird-Antiaromaticity, and Singlet-Triplet Energy Gap in Triplet-State Polybenzenoid Systems from Simple Structural Motifs

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Abstract

Triplet-state aromaticity has been recently proposed as a strategy for designing functional organic electronic compounds, many of which are polycyclic aromatic systems. However, in many cases, the aromatic nature of the triplet state cannot be easily predicted. Moreover, it is often unclear how specific structural manipulations affect the electronic properties of the excited state compounds. Herein, we study the relationship between the structure of polybenzenoid hydrocarbons (PBHs) and their spin density distribution and aromatic character in the first triplet excited state. Though a direct link is not immediately visible, classifying the PBHs according to their annulation sequence reveals regularities. Based on these, we define a set of guidelines to qualitatively predict the location of spin and paratropicity and the singlet-triplet energy gap in larger PBHs, using only their smaller tri- and tetracyclic components and subsequently test the validity of the guidelines on larger systems.

Introduction

Aromaticity is one of the most commonly used concept in chemistry. Despite being not well-defined, it plays a major role in the rationalization of chemical properties (e.g., thermodynamic stability of compounds,^[1–3] chemical shifts,^[4,5] and bond-lengths^[6,7] in conjugated systems) and chemical reactivity (e.g., selection rules in pericyclic reactions).^[8–10] Historically, these discussions have focused on molecules in the ground state, however, over the past decade or so, aromaticity in the excited state has received increasing attention.^[11–14]

The notion of excited-state aromaticity can be traced back to Dewar^[15] and Zimmerman's^[16] Aromatic Transition State Theory for rationalization of thermal and photochemical pericyclic reactions. It was generalized by Baird in 1972 to describe the first $\pi\pi^*$ triplet excited state (T_1),^[17] though the term “Baird’s Rule” was coined much later, in 2008, by Soncini and Fowler.^[18] This rule essentially states that the aromatic nature of a compound will “reverse” upon excitation from the singlet ground state to the first $\pi\pi^*$ triplet state. For example, benzene is Hückel-aromatic in the ground state, and Baird-antiaromatic in the $\pi\pi^*$ triplet excited state; conversely, cyclobutadiene is Hückel-antiaromatic in S_0 and Baird-aromatic in $\pi\pi^*$ T_1 . In the time since this rationalization first paved the way to thinking about aromaticity of excited molecules, additional work has been

done to verify and expand our understanding of this behavior, using other types of methods, such as *ab initio*^[19] and density functional theory (DFT) calculations.^[20–23]

Aside from the conceptual questions that accompany the investigation of aromaticity, there is also the practical aspect. Excited-state aromaticity has been discussed in various contexts. For example, several reports demonstrate that aromatic and antiaromatic character drive reactivity in excited states and therefore can be used to describe and predict photochemical reactions.^[24–30] Additionally, new functional materials have been designed using the concept of excited-state aromaticity and antiaromaticity as a strategy to modulate the singlet-triplet (S-T) energy gap,^[20,31,32] which is relevant to organic electronics,^[32–34] photoswitching,^[35,36] photoluminescence,^[37] and singlet-fission^[33,38–40] capable materials. One possible avenue to modulating the S-T gap is through the use of compounds with “adaptive aromaticity”, which are aromatic in both the ground state and the excited state, such as metallocenes^[41,42] or aromatic chameleons.^[43–45]

In general, the field of aromaticity suffers from a lack of clear definitions and benchmarking, which can sometimes lead to over-interpretation and even incorrect assignments of aromatic character.^[46–48] Excited-state aromaticity is not exempt from these challenges, and perhaps is even more susceptible to them at this time, due to the rising popularity of the concept coupled with the relative paucity of data. Indeed, specific examples of difficulties in characterizing and evaluating the extent of Baird-aromaticity have already been reported.^[49] There is still a great deal we do not know about the aromaticity of excited-state systems but we expect that the notion will receive further scrutiny in the coming years, hopefully leading to clearer definitions and classifications. Such efforts will require both additional data and careful analysis, studying diverse types of molecule classes in a systematic manner. Most studies to date, such as the ones referenced above, have focused either on relatively small molecules, or on molecules that have specific use.

Considering the existing knowledge and the growing interest in excited-state aromaticity, our goal was two-fold: (a) to extend our knowledge and understanding of larger polycyclic molecules and (b) to investigate structure-property relationships in these compounds in the first excited triplet state. The latter could then lead to a simple tool for evaluation of triplet-state systems, which could aid chemists in design of new compounds and in planning synthetic steps.

To achieve these goals, we focused on polybenzenoid hydrocarbon (PBH) molecules containing N rings, where $1 \leq N \leq 6$. To the best of our knowledge, there has not yet been such a comprehensive study of these systems reported in the literature. Thus, we believe that the characterization of these molecules is interesting and provides relevant and useful data to the community. Furthermore, for each N , the family of compounds are isomers, meaning that the only differences are in the annulation patterns between the rings (linear or angular). Comparison between such isomers allows us to look into the connection between these topological differences and changes to aromaticity trends. We recently performed a similar study on these PBHs in the ground state and our results led to the identification of a structure-aromaticity relationship that allowed us to devise an additivity scheme for PBHs^[50] using NICS-XY-Scans^[51] (further information on this technique is given in the Computational Methods section), which we later expanded to heteroaromatic systems, as well.^[52] The additivity method enables rapid prediction of

the aromatic character of large polycyclic systems, and has since also been automated for even faster generation of NICS-XY-Scans.^[53] Now, in an analogous manner, we identify guidelines that enable quick and straightforward prediction of the aromatic character of PBHs in T₁. These guidelines enable tailoring of the PBHs to afford specific electronic features.

The Results and Discussion section is structured as follows: the first three subsections detail correlations observed from the data obtained; the fourth subsection presents a set of guidelines for prediction of the antiaromaticity and spin density distribution in PBHs using the smaller subunits contained in the PBH; the fifth subsection puts our guidelines to the test by applying them to larger systems; the sixth section extends the guidelines to prediction of energy trends for the excited-state molecules and their S-T gaps.

Computational Methods

There are many methods of quantifying aromaticity, which are based on the various manifestations of aromatic character in energy,^[2,54] geometry,^[55,56] magnetic,^[5] and electronic properties.^[57] Within each of these criteria there are many available techniques, each with its advantages and disadvantages. In continuation of our work on S₀ PBHs,^[50] and in keeping with our overarching goal of developing easy-to-use and accessible techniques, we used Nucleus Independent Chemical Shifts (NICS)^[58,59] as our method of choice. NICS uses a probe atom to report the induced magnetic field in the vicinity of an aromatic ring. The conventional placement of the NICS probe is above the center of the ring (the heights of 1 Å or 1.7 Å are commonly used). The reported chemical shift serves as an evaluator of the existing induced ring currents. Negative NICS values indicate a diatropic current is present (usually implying an aromatic system) and positive NICS values indicate a paratropic current is present (usually implying an antiaromatic system). NICS is easily calculated and quite readily interpreted, and for these reasons, it is one of the most commonly used methods for aromaticity assessment. Because we focus here on polycyclic systems, we made use of the NICS-XY-Scan^[51] method, which places a series of probes along a pathway at a constant height above the molecule. In the text, we sometimes refer to these scans as “aromatic profiles”. The resulting plot shows the changes to the induced magnetic field along the entire pathway. In this work, we chose to characterize the aromaticity of the compounds using the NICS(1.7)_{ZZ} metric, which considers only the ZZ component of the chemical shift tensor. It has been shown to be a safe choice (i.e., allowing for identification of local trends in the aromaticity of polycyclic systems and showing satisfactory correlation to other indices of aromaticity) when the more refined metric, NICS(1.7)_{πZZ}, cannot be used.^[51] In this study, we could not use the more refined metric because the two methods of dissection that are common (Natural Chemical Shielding and the σ-Only Model) could not be applied reliably. The former cannot be used for open-shell systems and the latter showed spurious results when we applied it to our systems (in addition, it has not been benchmarked for triplet-state compounds). Therefore, we selected the less sophisticated metric, which is semi-quantitative but more reliable under these circumstances.

All structures were optimized with the B3LYP functional^[60–62] and the 6-311G(d,p) basis set,^[63–68] followed by a frequency analysis to ensure real minima on the potential energy surface and to obtain the zero-point energy (ZPE), using the Gaussian suite of programs, version 09 Revision D.01.^[69] Optimization of some of the molecules led to non-planar geometries in either S₀, T₁, or

both (these are detailed in Table S3 in the Supporting Information, SI). In such cases, a second optimization was undertaken, in which the starting geometry was made planar. The planarity was then retained throughout the optimization process. Both the planar and non-planar versions were characterized with spin-density maps. In all cases, unless specifically stated differently, the trends were similar (see complete data in Section S6 of the SI). Because NICS-XY-Scans are much clearer for planar structures (non-planar geometries sometimes cause discontinuities in the plots), these scans were calculated only for the planar geometries. This allowed us to clearly discern the variations in the aromatic profiles. A recent report mentioned that, for triplet state polycyclic aromatic systems, B3LYP gives qualitatively different geometries (and hence, different bond length alternation) from those obtained with other functionals and with CASSCF.^[70] Therefore, we repeated the calculations with the PBE and PBE0 functionals,^[71–73] both with the def2-TZVP basis set.^[74] In all cases, the results were consistent (see bond-length comparison in Section S2 of the SI).

Computational characterization of compounds such as those studied in this work can be challenging, due to close-lying molecular orbitals leading to multi-reference character, which DFT often describes inadequately. To investigate the robustness of our DFT results, we used ORCA version 4.2.0^[75–77] to perform complete active space self-consistent field (CASSCF) (12e, 12o) optimizations with the def2-SVP basis set on a subset of compounds from Family 6. We used MP2 natural orbitals for the starting wavefunction and selected the active space orbitals around the HOMO-LUMO gap. Although the active space selection was done in a simple manner and the size of the active space is certainly insufficient for quantitative calculations on these systems,^[78] we reasoned that qualitative effects due to static correlation would be visible from these calculations. The geometric parameters and spin-density distributions were again consistent with B3LYP (see complete data in Section S5.3 of the SI).

All NICS calculations were performed using the Gauge Including Atomic Orbital (GIAO)^[79] method with the B3LYP functional and the 6-311+G(d,p) basis set, using the *integral=(grid=ultrafine)* and *cphf=(grid=fine)* keywords. The Aroma^[51,80–82] software was used to generate NICS-XY-Scan input files for Gaussian 09, and later to extract the relevant NICS data from the output files. NICS-XY-Scans were calculated at a height of 1.7 Å above the molecular plane (as was demonstrated in Ref^[51] to be an optimal choice). The trajectories link the centers of each of the rings and the centers of the fused bonds between the rings.

Spin densities were calculated for the B3LYP/6-311G(d,p) optimized geometries using ORCA 4.2.0, with the B3LYP/6-311+G(d,p) combination, as well as with CAM-B3LYP/EPR-II combination, which was very recently shown to be among the most accurate combinations for calculation of spin density in open-shell PBHs.^[83] The results were similar, so we show here only those obtained with the B3LYP/6-311+G(d,p) combination. The spin densities were visualized at an isovalue of 0.02 au with Pymol (version 1.7.4).^[84]

The input file templates for the calculations and the spin density visualization are provided in Section S1 of the SI.

Investigated Molecules

We performed calculations on all *cata*-condensed, unbranched PBHs containing 1–6 rings, with the exception of 6-helicene because it cannot be planarized (**6_24** in our list; shown for completeness of the dataset). Figure 1 depicts the molecules calculated with their assigned notation, separated into their respective families according to the number of rings contained. To analyze the relationship between topology and aromaticity, we focused on Family 6, as it contains a sufficient number of isomers to reveal trends. Data for all molecules are provided in the SI.

Figure 1. All molecules investigated in this work, including their respective notation.

Results and Discussion

Our group previously reported on topology-aromaticity relationships in the class of PBHs compounds in the ground state.^[50] We showed that tricyclic subunits can be identified within larger PBHs, and that the tricyclic annulation pattern determines the trends in aromatic character throughout the larger compound. Herein, we denote angular tricyclic subunits (phenanthrene, **3_1**) as “*A*” and linear tricyclic subunits (anthracene, **3_0**) as “*L*”, and can describe a larger polycyclic system using its annulation sequence. For example, starting from the left-hand side of the molecule, **6_6** is described as *ALLA* (Figure 2).

Figure 2. Demonstration of identification of the tricyclic subunits contained within a larger PAH. Starting from the left, each subset of 3 adjacent rings is reported as *L* or *A* (linear or angular annulation), to form the final sequence of the molecule, *ALLA*.

We use this notation extensively throughout this report, and refer to it interchangeably as “annulation pattern” or “annulation sequence”. In this report, we discuss the results for the planarized molecules from Family 6. The scans for the rest of the studied molecules can be found in the SI.

Correlation between Annulation Patterns and NICS-XY-Scans

Our previous work demonstrated that the NICS-XY-Scan of a PBH can be predicted simply by knowing the sequence of tricyclic annulations and piecing together the respective contributions coming from the mono-, bi-, and tricyclic subunits (mono- and bicyclic contributions are the same, regardless of annulation pattern, therefore, only the tricyclic subunits change the shape of the aromatic profile; see References 50 and 52 for further details). This procedure has been recently automated, allowing very rapid generation of predicted NICS-XY-Scans for PBHs and other polycyclic aromatic systems containing heterocycles.^[53] By extension, it can be understood, and we have indeed shown, that two isomeric PBHs with the same annulation pattern will have a similar aromatic profile in the ground state, even though they are geometrically distinct. This behavior has been termed “equiaromaticity”.^[85] The term was originally coined to refer to the case

whereby the π -currents of two compounds can be mapped to each other in a one-to-one way and was demonstrated on a collection of PBHs with distinct structural features using graph-theory and valence-bond calculations. Our work has shown that the annulation sequence is a simple way of identifying which isomers will be equiaromatic.

With this in mind, we performed a similar analysis of the T_1 PBHs. We identified the sequence notation for each molecule in Family 6 (Table 1) and compared the NICS-XY-Scans of molecules having the same annulation pattern (e.g., **6_3** and **6_6** are both *ALLA* sequences). Note that linear annulations can only have one “direction”, while angular annulations can curve in two possible “directions”. Hence, it can be seen from Table 1 that the number of possible isomers per sequence increases as the number of *A* increases. Note, also, that the molecule/sequence scan be “read” either from left to right or right to left, e.g., *ALLL* = *LLLA*, corresponding to “reading” the molecule from either direction. The direction of the sequences reported in Table 1 was chosen arbitrarily, such that there is the minimal number of unique sequences (e.g., *ALAL* can also be read as *LALA*, so these structures are combined under the former sequence).

Table 1. Annulation Sequences of the isomers of Family 6 displayed in Figure 1.

Sequence	# Isomer
<i>LLLL</i>	0
<i>ALLL</i>	2
<i>LALL</i>	1
<i>ALLA</i>	3, 6
<i>ALAL</i>	4, 7
<i>AALL</i>	5, 8
<i>LAAL</i>	9, 18
<i>ALAA</i>	13, 14, 20, 23
<i>AAAL</i>	11, 15, 17, 21
<i>AAAA</i>	10, 12, 16, 19, 22, 24

Figure 3 shows the comparisons of five sets of isomers from Family 6 with similar annulation sequences, divided into their respective sequences. For each molecule, we present the NICS-XY-Scans of both the S_0 (gray) and T_1 (pink) states. NICS values are usually negative for aromatic species and positive for antiaromatic species. Thus, we observe that the NICS values for all ground state molecules are negative. We also observe that all of the molecules lose aromaticity upon excitation to T_1 , meaning their values become less negative, or even positive. It can be seen that, for four of the annulation sequences, there is great similarity between the isomers that share the same pattern, both in the ground state—which is not surprising, given our previous analysis—and in the excited state. These gratifying (and perhaps surprising) results suggest that there might indeed be a similar topology-aromaticity relationship in the T_1 state as there is in the S_0 state.

Figure 3. NICS-XY-Scans (using the NICS(1.7)_{ZZ} metric) in S_0 (gray) and T_1 (pink) states for the isomers of Family 6, separated according to the annulation sequences.

However, one type of sequence—the all-*A* sequence—behaves differently, breaking the generality of this conclusion. For *AAAA* six hexacyclic isomers exist (**6_10**, **6_12**, **6_16**, **6_19**, **6_22**, and **6_24**). Because **6_24** cannot be planarized, we focus here on the remaining five isomers. While two pairs of isomers, (**6_10** and **6_12**, **6_16** and **6_22**, respectively) show similar aromatic profiles in T_1 , the collection of five isomers does not show the same uniformity as seen in the previous sets. Even more surprisingly, the aromatic profiles of **6_10** and **6_16** are not symmetric on either side of the mid-distance point, even though their S_0 aromatic profiles are.

From the entirety of these data, we conclude that it is likely that there is a relationship between the topology of the PBH and its aromatic profile in the T_1 state. However, this relationship is not the same as the one observed in the S_0 state. In S_0 , this relationship can be defined in terms of tricyclic annulation patterns and is (to a good approximation) quantitatively additive. In T_1 the sequence of

tricyclic annulations alone cannot provide a prediction of the aromatic profile. Specifically, in the all-*A* sequences, it would be impossible to predict the aromatic profile of a PBH simply from its tricyclic annulation sequence. Yet, aside from these “problematic” sequences, we observe a remarkable regularity in the agreement of isomers with similar annulation patterns. In the subsequent sections, we explore the origins of both the regularities and of this apparent discrepancy.

Correlation between Spin Localization and Annulation Pattern

We chose to begin the search for factors that affect aromaticity in T_1 in the spin density maps. One advantage to this analysis is that the spin density description of the system is mapped to its structure, as opposed to being a global property, such as energy. This allows a relatively direct comparison to aromaticity, which we also map to the structure via the NICS-XY-Scan. The electronic structures, and specifically spin densities, of ground-state polyacenes (linearly annulated PBHs, consisting only of anthracene subunits) have been discussed at length in the literature. Though Houk and coworkers initially predicted a triplet ground state for acenes comprising more than eight rings,^[86] Bendikov and coworkers subsequently showed with DFT and CASSCF that, for acenes comprising more than six rings, the ground state is a singlet with diradical character.^[87] Due to the importance of these compounds for singlet fission and the relevance of their magnetic behavior for other uses, this prompted further investigation into their nature.^[88–90] Similarly, polyphenacenes (“zig-zag” annulated PBHs, consisting only of phenanthrene subunits) have been studied for their potential use in organic field-effect transistors, and thus both experimental and computational data can be found for them.^[91–93] In addition, several T_1 PBH systems (including *peri*-condensed systems, such as pyrene and coronene) were investigated by Papadakis et al.^[94] However, we could not find in the literature any comprehensive study of the electronic structure of PBHs that are not of the two aforementioned specific families, either in S_0 or in T_1 . Thus, to the best of our knowledge, this is the first comprehensive collection of data characterizing triplet state spin densities of PBH isomers.

Figure 4 presents the spin-density maps for some of the planarized molecules, separated according to their annulation sequences. Spin-density maps for the remaining isomers and for the fully optimized geometries are provided in Sections S5 of the SI, respectively.

Figure 4. Spin-density plots for the isomers of Family 6, separated by annulation pattern. We highlight in pink the areas where molecules with the same annulation pattern also show similar spin density distribution. Spin density visualized at the 0.02 au isosurface. Molecules have been oriented to highlight the similarities in spin-distribution.

In the previous section we saw that, for the most part, molecules with the same annulation sequence had similar aromatic profiles. Now, in Figure 4, by shading the two rings with the highest spin density in each molecule in pink, we observe similarities in the spin-density maps of isomers with the same annulation pattern, as well. As can be seen, molecules that share the same annulation sequence also accumulate the highest spin density in the same rings within the sequence. For example, in both *ALLA* isomers the spin density is located in the center of the molecule, on the two rings in the middle of the linear tetracyclic component; in both *ALAL* isomers it is mostly located on the second ring from the left, on the middle ring of the outer anthracene subunit; in all of the *ALAA* isomers the majority of the spin is found on the central ring of the anthracene subunit. At the same time, as in the previous section, the molecules that do not exhibit any regularities are those with the *AAAA* sequence (Figure 4, bottom).

We also note reiterate the observation regarding symmetry in some of the compounds. Certain molecules (e.g., the two *AAAA* isomers **6_10** and **6_16**) have a C_2 axis of symmetry in S_0 , but their symmetry is reduced in T_1 . This is seen in the geometries themselves (Cartesian coordinates are provided in the SI), but is much more clearly apparent in their spin-density maps (shown in Figure 4). For example, **6_16** shows a clear distribution of spin on the left-hand phenanthrene subunit and little to no spin on the right-hand phenanthrene subunit. It is clear that any structure-property

relationship we will define must be able to predict this breaking of symmetry. We investigate this more thoroughly in the following subsections.

Correlation between Spin Density and NICS-XY-Scans

In the previous two subsections, we observed that isomers with the same annulation pattern display similar aromatic profiles and similar spin-density distributions, with the exception of the all-*A* sequences. The fact that the same molecules are the “outliers” both in their NICS-XY-Scans and in their spin density distributions suggests that there is a connection between the aromatic profile and the distribution of spin. This conclusion is further strengthened by the observation that the rings with the largest spin density correspond to the areas of the molecule where the NICS values are most positive (or least negative). To better illustrate this, we summed the total spin density per ring (TSDR) and plotted it against the NICS-XY-Scan of the T_1 . Figure 5 presents these comparison plots for a representative molecule from each annulation sequence (isomers with similar annulation sequences have very similar plots, as seen above, and therefore we do not show all of them here; the results for all molecules are provided in Section 7 of the SI).

Figure 5. Plots of TSDR and NICS-XY-Scans for representative members of Family 6 in T_1 . TSDR is shown as bars (pink) corresponding to each ring and the NICS-XY-Scan shown as an overlaid curve (black). The ring numbers and the direction of the scan are according to the left-to-right direction of “reading” the molecule.

It can be seen that the highest bars for each compound (which indicate the rings with the largest magnitude of total spin density) correspond to the largest positive (or least negative) NICS values

(which indicate the strongest paratropicity or weakest diatropicity). To verify this observed trend, we plotted the spin density in each ring against the NICS(1.7)_{zz} value calculated in the center of the ring (Figure 6). The resulting linear correlation ($R^2 = 0.895$ for only Family 6 molecules; $R^2 = 0.943$ with the CAM-B3LYP/EPR-II combination, see Figure S20 in the SI) indeed supports our conclusion: where there is spin density there is paratropicity (Baird-antiaromaticity), and the higher the spin density, the greater the Baird-antiaromaticity. The trend shown here persists when all molecules are considered ($R^2 = 0.863$, excluding **1_0**; see Figure S19 in the SI).

Figure 6. Plot of NICS(1.7)_{zz} against TSDR for all of the rings in the isomers of Family 6. $R^2 = 0.875$.

The three main observations described in the first three subsections can be summarized as:

- Baird-antiaromaticity coincides with the location of spin density and both properties are linked to the geometry.
- The molecules with all-*A* sequences do not display the same regularities.
- Some molecules with C_2 -symmetric geometries and NICS-XY-Scans in S_0 break symmetry in T_1 (this is manifested in their geometries, NICS-XY-Scans, and spin density distributions).

The observation that the greatest paratropic NICS values coincide with the location of the greatest spin density is perhaps not too surprising. Within a given molecule, the rings with the greatest spin density are the ones that most resemble T_1 -benzene, and could therefore also be expected to have the aromatic character most similar to T_1 -benzene, i.e., the strongest Baird-antiaromaticity relative to the other rings in the same molecule. However, this does not yet describe how these two properties are linked to the geometry. In the following section, we define a set of guidelines connecting the annulation pattern of T_1 PBHs to their aromaticity and spin density. These guidelines use simple structural motifs to qualitatively predict where the two properties will appear within any given PBH, including the all-*A* isomers.

Structure-Property Relationships in the PBHs

To formulate a structure-property relationship for all PBHs, we applied our approach of viewing larger PBHs as sequences of tricyclic subunits. Doing so forms a unified basis for dealing with PBHs of various sizes and topologies, because these subunits are shared by all PBHs (containing

3 or more rings). It also simplifies the treatment of complex systems to a small number of more easily-handled molecules. Accordingly, we began with a close inspection of the characteristics of the two tricyclic systems, anthracene (**3_0**) and phenanthrene (**3_1**), the *L* and *A* structural motifs (Figure 7).

Figure 7. Spin-density maps and NICS-XY-Scans of structural motifs a) *L*, b) *A*, c) *Z*, and d) *C*.

As seen in the spin-density plots (Figure 7a and b), in both of these systems the spin is distributed over all three rings and is greater in the central ring than in the side rings. These results are in agreement with the report by Papadakis et al,^[94] which found that the middle rings in both systems were the sites of addition of a SiEt₃ group when the reaction was performed under photochemical conditions, indicating that this is the location of the unpaired electrons, i.e., spin density.

The NICS-XY-Scans (Figure 7a and b) show that, for both systems, the Baird-antiaromaticity is greater in the central ring than in the two side rings (central ring: NICS(1.7)_{zz} ≈ 10, 20 ppm; side rings: NICS(1.7)_{zz} ≈ −5, 10 ppm, for **3_0** and **3_1**, respectively), which was also reported by Papadakis et al. The aromaticity of these two systems corresponds to their relative stability. Whereas phenanthrene is the more thermodynamically stable isomer in *S*₀, anthracene is more stable isomer in *T*₁ (the differences are approximately 5 kcal mol^{−1} in *S*₀ and 16 kcal mol^{−1} in *T*₁, ZPE-corrected energies with B3LYP/6-311G(d,p)). The relative stability of *S*₀-phenanthrene has been attributed to its greater aromaticity.^[95,96] Analogously, it can be observed that the relative stability of *T*₁-anthracene agrees with its overall lower NICS values (Figure 7a and b).

The substantial difference in relative stability between the two T_1 isomers, combined with our annulation sequence-based description of higher PBHs, allows us to form an initial expectation of where spin-density (and, hence, Baird-antiaromaticity) should be found: whenever possible, spin-density will localize on the central ring of a linear tricyclic subunit within a larger PBH. In other words, if there exists within a PBH a chain of three linearly annulated rings (i.e., an anthracene subunit), the majority of spin density will be found on the 1 and 8 carbons of the central ring of that chain (Figure 7a) and, accordingly, the paratropicity is expected to be most pronounced in that ring. This is indeed borne out, as one can see from the spin-density maps and aromatic profiles of compounds such as **6_11**, **6_14**, **6_17**, **6_20**, and **6_21** (Figure 3 and Figure 4). Compounds that have longer linear chains (e.g., 4 or 5 rings) can be thought of as having 2 or 3 overlapping anthracenes. In such cases, the central rings of each anthracene subunit will display a portion of the spin density. Some examples of this are seen in molecules **6_0**, **6_1**, **6_2**, **6_3**, **6_5**, **6_6**, and **6_8** (Figure 4 and Figures S7 and S8 in the SI). In molecules where two separate linear chains are found, the spin tends to be found on the longer of the chains, e.g., **6_1**. Another conclusion that can be drawn from the relative stability of the T_1 tricycles is that the unpaired electrons tend to avoid angular subunits. Thus, if there is more than one linear subunit of the same length, the spin density will be found on the one that does not overlap with an angular subunit, e.g., **6_4**.

To summarize this in terms of annulation sequence, this means that any sequence that contains an L can be predicted to have the unpaired electrons on the L . What happens if there is more than one L ? As mentioned above, if the L subunits are non-identical, the preference is toward the longer chain and/or the chain that does not overlap with an A . If the two L subunits are identical (as in **6_9**), then the spin is found (mostly or exclusively) on only one of the L subunits (see Figure 4). Indeed, this explanation goes directly to our observation (c) above: molecules that are C_2 -symmetric in S_0 break symmetry in T_1 . The distortion allows (or is the result of) the spin localization on only one of the anthracene subunits. In terms of aromaticity this leads to a pronounced effect: while one part of the molecule becomes Baird-antiaromatic, the other part retains (most or all of) its Hückel-aromatic character (indicated by NICS values in those rings being similar in S_0 and T_1). This suggests that the localization of spin resulting in stronger aromatic and antiaromatic character in separate subsections of the system is preferred over delocalization, whereby the entire system would become Baird-antiaromatic to a lesser extent (“spread out”). We note that though **6_18** does not display this breaking of symmetry, additional systems with these structural considerations were tested (see Section S8 of the SI) and reinforce this conclusion. Therefore, in this context, we consider **6_9** to be an exemplar of the expected behavior and **6_18** to be the outlier. Two additional cases of symmetry-retention are observed in Family 5 (**5_2** and **5_8**, see SI).

Continuing in this vein, the next logical question is: what happens when there are no linear subunits in the system? This is exactly the case for all- A molecules, meaning the answer to this question is pertinent to the observations we are attempting to rationalize. Understanding these cases is key to unraveling the reason for these molecules’ different behavior. We began with a visual inspection of the spin-density plots (Figure 4). It showed that, whereas the anthracenic pattern of spin distribution (maximal spin density on centers 1 and 8, Figure 7a) can be quite readily identified (e.g., **6_4**, **6_23**), the phenanthrenic spin-distribution pattern (maximal spin density on centers 1

and 2, Figure 7b) is not observed in the larger PBHs. Moreover, we identified in the plots of the all-*A* isomers (Figure 4) a pattern similar to **4_2**, and in **6_18** a pattern similar to **4_3** (the distribution of spin density in **6_18** is surprising in that it does not accumulate on either of its *L* subunits, however, as we noted above, this molecule is also unique in that it does not break symmetry, despite having two equivalent *L* subunits). Thus, this suggests that the angular subunits that we need to consider are tetracyclic ones, corresponding to the tetracyclic subunits **4_2** and **4_3** (Figure 7c and d).

We term the **4_2** structural motif “*Z*” and the **4_3** structural motif “*C*” (for the letter shapes that they are reminiscent of). In *S*₀, these two compounds have essentially identical NICS-XY-Scans (Figure 7c and d, gray curves), indicating that the difference in their aromatic character is negligible. However, in *T*₁ they are different. This is seen in the location of the unpaired electrons in the spin density maps and in the values of their NICS-XY-Scans (maxima of ~19 and ~23 ppm for **4_2** and **4_3**, respectively, Figure 7c and d, pink curves). Furthermore, of the two isomers, the *Z* motif is the thermodynamically preferred one in *T*₁, by approximately 5.5 kcal/mol (ZPE-corrected energy, B3LYP/6-311G(d,p) for the freely-optimized structures). Thus, while tricyclic subunits were sufficient for the ground-state description of the higher PBHs tricyclic, for the triplet excited-state description we need to consider also the tetracyclic subunits. We note that in *T*₁ both **4_2** and **4_3** optimize to nonplanar geometries (the spin-density maps do not change upon planarization but the energy gap increases to 11.5 kcal/mol; data is provided in the SI), while in *S*₀ **4_2** is planar and **4_3** is nonplanar.

To summarize these observations into guideline phrasing: when both *C* and *Z* motifs exist within a PBH, the probability will be higher for the spin to be on the *Z* subunit (e.g., **5_4**, shown in Figure S10 in the SI). When there is more than one *Z* subunit, the preference is toward the one that has the least overlap with a *C* subunit, e.g., **6_12**. When equivalent *Z* or *C* motifs exist, the molecules break symmetry to place the spin on only one of the subunits (e.g., **6_16** and **6_24**, respectively).

Going back to one of our original queries, we can now use the different patterns obtained in the tetracyclic subunits to explain why the all-*A* sequences showed “anomalous” behavior. As written above, when there is an *L* subunit in the PBH, the nature of the *A* subunits is not important, as the spin will accumulate in the *L* subunit. In cases where there is no *L* subunit, the type of sequential *A* subunits becomes important. In such cases, it is not enough to describe the sequence of tricyclic annulation (i.e., *L* and *A*), we also need to describe the sequence of tetracyclic annulations, which we do with the letters *C* and *Z* (Table 2).

Table 2. Tetracyclic Annulation Sequences of the *AAAA* isomers of Family 6 displayed in Figure 1.

Isomer	Sequence
6_10	<i>ZZZ</i>
6_12	<i>ZZC</i>
6_16	<i>ZCZ</i>
6_19	<i>CZC</i>
6_22	<i>ZCC</i>
6_24 (not analyzed)	<i>CCC</i>

When we combine the guidelines described above with this new nomenclature, it becomes easier to identify the underlying trends in the previously “anomalous” all-*A* compounds. For example, in **6_19** there is only one *Z* subunit, and the spin is indeed found mostly there, with the same distribution pattern as in **4_2**. **6_12** has one *C* and two *Z* subunits, and indeed the larger spin density is in the *Z* subunit that has less overlap with the *C* subunit. **6_10** and **6_16** allow us to observe what happens when there are multiple identical *Z* subunits: Analogously to the compounds containing identical *L* subunits, both **6_10** and **6_16** break their C_2 -symmetry, as can be clearly seen in the asymmetric spin density maps of the compounds (as well as in their NICS-XY-Scans and geometries). Similarly, compound **6_24** (shown in the SI), which contains only *C* subunits and is C_2 -symmetric in the ground state, also breaks symmetry in T_1 (although we note that **5_8**, the shorter helicene, does not).

Testing the Guidelines on Larger PBHs

In the previous section we put forth a set of guidelines that allow qualitative prediction of the location of spin density and paratropicity accumulation based on a simple structural analysis of isomers of Family 6. To test the generality and robustness of our guidelines, we performed calculations on a selection of larger PBHs (containing 7-9 rings), termed **T1-T4**. The results for these systems, including the spin density maps and NICS-XY-Scan, are presented in Figure 8.

Figure 8. Spin density maps, NICS-XY-Scans, and Total Spin Density per Ring (TSDR) in T_1 for a) **T1**, b) **T2**, c) **T3**, d) **T4**. TSDR is shown as bars (pink) corresponding to each ring and the NICS-XY-Scan shown as an overlaid curve (black). The ring numbers and the direction of the scan are according to the left-to-right direction of “reading” the molecule.

In **T1**, we observe that when the *L*, *Z*, and *C* motifs are all present, the spin accumulates in the center of *L* subunit. From **T2**, we see that when no *L* subunit is present, the preference is for the *Z* motif. Thus, these two test cases reinforce the “hierarchy” we outlined above. In **T3** we observe that when two *L* motifs are present the preference is for the longer one (in this case, four linearly annulated cycles versus three). **T4** demonstrates that, when there are two degenerate “best” options, the symmetry of the system reduces and the spin—and hence, paratropicity—will accumulate on only one of the degenerate substructures.

A general conclusion arises from our results, which was outlined above and is reemphasized in the test compounds. It is that, in large enough PBHs, spin delocalization does not encompass the entire molecule. It also echoes similar conclusions found regarding the distribution of spin in conjugated polymers, i.e., solitons.^[97,98] The fact that the spin localizes onto preferred motifs, even when

broader delocalization is in principle possible, indicates an energetic driving force for localization. In conjugated polymers, this has been associated with the cost of bond deformation.^[98–100] In the molecules studied herein, this could be framed in terms of aromatic character. In simple terms, the molecule has two options: (a) localizing the spin and creating a Baird-antiaromatic part and one (or more) Hückel-aromatic part(s); or (b) fully delocalizing the spin and thus “spreading out” the Baird-antiaromaticity over the entire molecule. The observation that localization occurs in all of the larger PBHs indicates that option (a) is the more stabilizing solution. We believe the stabilization afforded by spin localization also underpins the breaking of symmetry upon excitation from S_0 to T_1 that was observed in some molecules.

Extension of the Guidelines to Energy Prediction

The previous sections focused on two specific properties that characterize T_1 PBHs—namely, spin-density and Baird-antiaromaticity—and how their location on the molecule can be qualitatively predicted from the annulation pattern. These guidelines make an implicit assumption: that the preference for accumulation of these properties on one substructure over another occurs because it has an overall stabilizing effect for the molecule. This section investigates that assumption more explicitly, to see if our simple guidelines can be used to predict energetic characteristics of T_1 PBHs, which could considerably enhance their usability as a design tool.

The observation that both spin-density and Baird-antiaromaticity accumulate in the same location within the molecule implies that the main changes to the electronic structure are concentrated on this specific substructure. Therefore, it may play an important role in determining other molecular properties, as well. Further, we observed a clear hierarchy of substructures, in which the aforementioned accumulation occurs preferentially on L subunits over A subunits, and longer linear stretches have preference over shorter ones (i.e., order of preference is $L < LL < LLL < LLLL$). Combined, these observations led us to hypothesize that the relative energy of an isomer is mostly determined by the longest linear stretch contained in the molecule. To probe this, we plotted the S_0 and T_1 energies of Families 3-6 (Figure 10a, the plotted energies are relative to the ground-state fully-linear isomer in the respective family) as a function of the number of L subunits in the longest linear stretch. In S_0 , the fully-linear isomers (i.e., **3_0**, **4_0**, **5_0**, and **6_0**) are the least stable within their respective families (according to SCF energy), but no other clear trends are identified. In contrast, in T_1 , a rather clear trend is seen, wherein the energy decreases as the linear stretch lengthens and the differences become smaller with each additional L subunit. This is in agreement with previous reports on the energies of T_1 polyacenes,^[101,102] though we note that we compare relative energies within isomer families, whereas previous reports compared systems with varying numbers of rings (i.e., different chemical formulas). This supports the hypothesis that the behavior of the molecule is mostly determined by its longest linear stretch.

We also consider the all- A isomers (plotted on the 0 point on the horizontal axis in Figure 10). When the all- A isomers are studied as separate series (Figure 10, inset), we observe that the relative energies of the isomers decrease with the increase in number of Z motifs, in accordance with the preference we identified in all- A isomers. Thus, the relative energies of the PBH isomers agree with the hierarchy and guidelines we discuss above.

Figure 9. Main plot: Relative S_0 (rectangle) and T_1 (triangle) energies of compounds in Families 3-6 (color-coded as in the legend shown beneath the main plot). All energies are of freely-optimized geometries. The plotted energies are relative to the S_0 fully-linear isomer in the respective family. Enlarged region: Relative T_1 energies of all- A isomers in Families 4-6 with their respective notations and tetracyclic annulation patterns.

In addition to the relative energies of the isomers, we also plotted the S-T gap (Figure 10), which is an important factor in many functional molecules, against the number of L subunits in the longest linear stretch. We observed a clear relationship, whereby the longer the linear stretch, the smaller the S-T gap. This is in agreement with other computational and experimental reports of S-T gaps for polyacenes.^[103,104] Gratifyingly, this relationship appears to be quite robust, spanning not only Families 3-6, but also the test molecules, which contain up to 9 rings (shown in purple in Figure 10). In this case, the actual (not relative) energies are plotted and we can observe that molecules with similar linear stretches have S-T gaps within a range of values that spans ≤ 1 eV, even though their total number of rings may vary widely. Because each length of linear stretch corresponds to a quite clear range of energy values, with relatively little overlap, this provides a simple and easy way to predict the S-T gap for a given system within given boundaries. Furthermore, it can be a very useful tool in designing PBH molecules to have desired structural and electronic properties. Here, also, we looked at the all- A compounds (displayed on the 0 point of the horizontal axis). The S-T gaps for these molecules appear to lie within a smaller range of values, which conforms with reports showing that the S-T gaps for the polyphenacenes (zig-zag molecules) do not change with molecule length.^[91-93] However, no clear relationship between the presence of C/Z motifs and the S-T gaps of these molecules was found.

We have added to this plot a selection of experimentally measured S-T gaps for representative isomers^[105,106] (the specific isomers and their respective values are detailed in Table S2 of the SI; it is worth noting that data are not available for most of the compounds we studied in this work). Though these data were collected from various reports and measured under different conditions (e.g., solvents), there is a satisfactory agreement with the calculated values, implying that the observed trends do reflect the true nature of the compounds. In addition, we note that we repeated the analysis with optimized geometries and energies calculated with two different functionals, PBE and PBE0, and the results are consistent (data are presented in Section S3 of the SI).

Figure 10. S-T gaps of Families 3-6 and Test compounds. Circles represent calculated values; stars represent experimental values obtained from the literature.^[105,106] The colors within the circles/stars corresponds to the color-coding of the different families, as shown in the legend.

Conclusions

In this work we investigated a collection of triplet-state PBHs containing 1-6 rings with the aim of understanding the relationship between structure and two electronic properties: spin location and aromaticity. For each system, the aromatic behavior was characterized with NICS-XY-Scans of the S_0 and T_1 states and the spin density in T_1 was mapped. Using our approach of decomposing the higher PBHs into their tri- and tetracyclic components led us to identify regularities that link the structural motifs and the molecular properties of spin density and aromaticity:

- When present, spin will accumulate in the center ring(s) of a linear (L) subunit. Anthracene is the smallest such linear subunit.
- When more than one L subunit is present, the spin will accumulate in the longer linear stretch and/or in the one that has least overlap with angular (A) subunits.
- When no L subunit is present, the tetracyclic subunits (C/Z motifs) of the compound determine the location of the spin. The preference is for the Z motif.
- When there are two identical (i.e., equivalent) motifs that share highest priority (e.g., identical L or Z subunits), symmetry can be broken and the spin will accumulate on one of the motifs. Note: identical motifs that are of lower priority will not affect the symmetry.

To test these guidelines, we studied larger PBHs and observed that they hold true for these compounds, as well. We found that these guidelines are reiterated in the relative energies of the T₁ PBH isomers and, further, identified a relationship between the length of the longest linear stretch and the S-T gap in PBHs of varying sizes. We found specific energetic spans corresponding to certain lengths of linear stretches, independent of the total number of rings in the PBH, such that the S-T gap can be predicted within a certain range simply from the annulation sequence of the molecule.

In summary, we identified a link between the tri- and tetracyclic structural motifs contained in a T₁ PBH and the spin distribution and aromatic character of the compound. The guidelines we propose here allow for qualitative prediction of these electronic properties, as well as relative energy, using a simple back-of-the-envelope analysis directly from the structure of the compound, without need of explicit quantum chemical computations. These guidelines can be used for rapid and intuitive assessment of properties, which can inform decisions on molecular design and synthetic approaches. The benefit of such assessment was demonstrated in a recent report by Wang et al, in which the authors designed a stable triplet ground state polycyclic aromatic system by fine-tuning the spin-density distribution and aromaticity through incorporation of an electron-withdrawing pyrazine moiety.^[107] We envision that the principles outlined in this report can be employed in a similar manner to design novel compounds for, e.g., organic spintronics. Work is currently underway in our group both to provide a conceptual framework for these empirically-defined relationships, and to extend this investigation to heteroatom-containing polycyclic aromatic systems, which are important components such functional compounds.

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Conflict of Interest

There are no conflicts to declare.

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Table of Contents

Characterization of T_1 polybenzenoid hydrocarbons (PBHs) reveals that spin density localizes on specific substructures, according to a hierarchy of motif. A set of general guidelines is defined, allowing prediction of the location of spin density and Baird-antiaromaticity on PBHs of varying topology and, in addition, prediction of relative T_1 energies and singlet-triplet gaps.

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