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On the Spectacular Structural Isomorphism between C_nH_s Monoradical and $C_{n+s}H_{s+3}$ Diradical Benzenoid Hydrocarbons: From Reactive Intermediates to Vacancy (Hole) Defects in Graphite

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The formula/structure informatics of monoradical and diradical benzenoid hydrocarbons that are potential reactive intermediates is studied. Some new enumeration and structural results with analytical expressions are presented. The topological paradigm and one-to-one correspondence between the monoradical and diradical constant-isomer series is demonstrated. Constant-isomer benzenoid monoradicals of the formula C_nH_s have a one-to-one correspondence in isomer number and topology to constant-isomer diradicals of the formula $C_{n+s}H_{s+3}$. Some electronic properties of benzenoid radicals are delineated. Excising out a monoradical or diradical benzenoid carbon molecule from a perfect hexagonal graphite layer leaves a matching monoradical or diradical vacancy hole defect called an antimolecule; this observation can be generalized to include excising out all nondisjoint and obvious benzenoid polyradicals from a perfect (Kekuléan) hexagonal graphite layer. It is shown that the characteristics of graphite vacancies (antimolecules) can be deduced from knowledge about the carbon molecules removed in their formation.

Introduction

Free-radical benzenoid hydrocarbons corresponding to the first- and second-generation members of our monoradical one-isomer series,¹ the D_{3h} phenalenyl/circumphenalenyl ($C_{13}H_9$ / $C_{37}H_{15}$), C_{2v} benzo[*bc*]pyrene/circumbenzo[*bc*]pyrene ($C_{19}H_{11}$ / $C_{47}H_{17}$), and C_{2v} benzo[*bc*]coronene/circumbenzo[*bc*]coronene ($C_{27}H_{13}$ / $C_{59}H_{19}$), have been identified as intermediates in acetylene and benzene flames by time-of-flight mass spectrometry.² Also, free-radical benzenoids and/or their carbocation analogues can possibly form in the outflows of red giant stars and are candidates for diffuse interstellar spectroscopic bands of interest to astronomers and astrophysicists.³ Gomberg's triphenylmethyl monoradical and Schlenk's (*m*-diphenylmethyl)-triphenylmethyl diradical are well-known chemical species.^{4,5} Free-radical benzenoids have potential applications in the synthesis of organic electronic and magnetic materials.⁶ Depending on solid-state packing, magnetic susceptibility measurements suggest that such radicals may not exist as isolated free radicals but can engage in considerable spin–spin interactions between the molecules.⁶ The triangulene diradical has been shown to have a triplet ground state both experimentally and theoretically.⁷ Bimolecular formation of benzenoid radicals by hydrogen transfer occurs in coal liquefaction processes.⁸ Benzenoid free radicals play a role in pitch mesophase formation.⁹ The EPR spectra of phenalenyl ($C_{13}H_9$), benzo[*a*]phenalenyl ($C_{17}H_{11}$, benzo[*de*]anthracenyl), and benzo[*cd*]pyrenyl ($C_{19}H_{11}$) monoradicals has been reported.¹⁰

Comparing relatively more reactive open-shell (i.e., free-radical) to closed-shell molecular species is important from the point-of-view of understanding fundamental bonding principles and reaction mechanisms proceeding via radical intermediates. Also, there are strong relevant parallelisms between these benzenoid radicals and the corresponding carbanions and

carbocations. The synthesis and characterization of benzo[*cd*]perylene ($C_{23}H_{13}$)¹¹ and trinaphtho[*bcd, fgh, jkl*]phenalenyl ($C_{31}H_{15}$, benzo[*cd*]phenaleno[1,2,3,4-*pqra*]perylene) cations have been accomplished. Phenalenyl ($C_{13}H_9$), benzo[*a*]phenalenyl (benzanthrenyl, $C_{17}H_{11}$), and benzo[*cd*]pyrenyl ($C_{19}H_{11}$) anions have been prepared.¹³ The synthesis and reactions of the cation of benzo[*cd*]pyrenyl was reported in 1965.¹⁴ The synthesis and ¹H NMR of the triangulene ($C_{22}H_{12}$) dianion¹⁵ and the dibenzo[*de, jk*]pentacenyl ($C_{28}H_{16}$)¹⁶ and dibenzo[*de, hi*]naphthacenyl ($C_{24}H_{14}$)¹⁷ dications and dianions have been reported. Note that in these examples, the monocations and monanions are analogues of odd carbon monoradicals, and the dianions and dications are analogues of even carbon diradicals. Recently, an interest in monocationic odd carbon benzenoids as being candidates for galactic extended red emission has been reported.¹⁸ In some of this work, Hudgins and co-workers report the B3LYP-computed IR spectra of the first and second generation of members of our monoradical one-isomer series,¹ the D_{3h} phenalenyl ($C_{13}H_9$), C_{2v} benzo[*bc*]pyrene/circumbenzo[*bc*]pyrene ($C_{19}H_{11}$ / $C_{47}H_{17}$), and C_{2v} benzo[*bc*]coronene/circumbenzo[*bc*]coronene ($C_{27}H_{13}$ / $C_{59}H_{19}$).¹⁸

This paper is a continuation of our quest for the development of a unified structure theory of conjugated hydrocarbons. Herein, we present a systematic study of monoradical- and diradical-related benzenoid hydrocarbons (i.e., polycyclic aromatic hydrocarbons composed of only hexagonal rings). Extended monoradicals and triplet diradicals with singly occupied MOs in their energy gap are molecular analogues of semiconductors with defect states. Thus, understanding mono- and diradical benzenoids has implications toward reaction chemistry and molecular electronics.

Results and Discussion

Some Preliminaries and Definitions. Aromatic Kekulé structures have no unpaired π -electrons and correspond to one-

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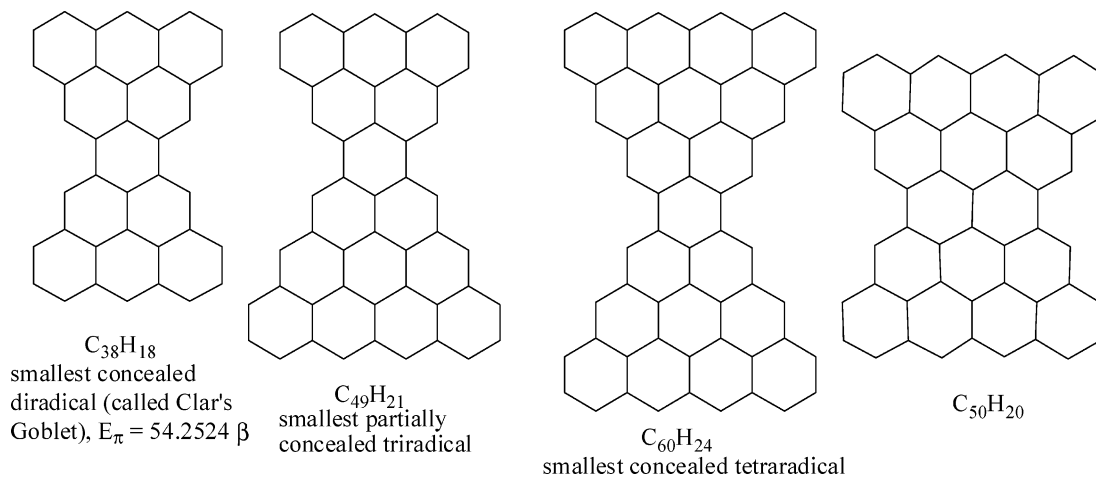


Figure 1. The smallest topologically concealed and partially concealed benzenoid hydrocarbon radicals.

factor subgraphs. The number of different arrangements of $p\pi$ -bonds in a benzenoid (nonradical)-conjugated system corresponds to Kekulé resonance structures and is designated by K . The numbers of different electronic arrangements possible in a benzenoid-radical-conjugated structure having one or more unpaired $p\pi$ -electrons are resonance structures (SC) but are not Kekulé structures (i.e., they have no one-factor subgraphs). In general, benzenoid radicals have far more resonance structures than Kekulé benzenoids of similar size.

There are two major types of benzenoid hydrocarbon radicals, those which obey the Gordon–Davison peak-to-valley test and those which do not.¹⁹ A benzenoid structure can be oriented three different ways, with approximately one-third of its edges in a vertical direction. A benzenoid structure so oriented has peaks (upward-pointing vertices on the upper periphery) denoted by Λ and valleys (downward-pointing vertices on the lower periphery) denoted by V . Whenever $\Lambda \neq V$, then the corresponding benzenoid structure represents a radical species. Odd-carbon benzenoid structures always have $\Lambda \neq V$. For well-behaved benzenoid systems, $\Lambda - V = 1$ for monoradicals, $\Lambda - V = 2$ for diradicals, and so forth. When $\Lambda = V$, the even-carbon benzenoid structure may or may not be an even-degree radical. If it is a radical, it is called a concealed (hidden) non-Kekulé benzenoid ($K = 0$). Many of this type of radicals have a narrow isthmus of fewer vertical edges than peaks or valleys (cf. Figure 1). Also, partially concealed triradicals (Figure 1) and higher odd-degree radicals are possible. For example, a partial concealed triradical would have $\Lambda - V = 1$ which is predicted to be a monoradical by the Gordon–Davison test.

The carbon vertices of any alternate hydrocarbon may be separated into s starred sites and u unstarred sites such that no two members of s are adjacent and no two members of u are adjacent. By convention, the sets are chosen so that $s \geq u$. For a well-behaved, maximally starred radical benzenoid system, it can be shown that the unpaired electrons are only found on the starred sites. Concealed non-Kekulé benzenoids formally have the same number of starred and unstarred carbon vertices ($s = u$), have the same number of peaks and valleys ($\Lambda = V$), and are made by joining together two (obvious) radical benzenoid systems having the same $\Lambda - V$ value through their unstarred peaks either directly or through a nonradical spacer group. Such constructed concealed non-Kekulé benzenoids are essentially disconnected (disjoint) $p\pi$ -electronic systems, and the unstarred sites of one of the components become formally starred, though the unpaired electrons do not travel these sites.^{20,21} Thus, concealed non-Kekulé benzenoids have their unpaired electrons confined to the corresponding components used to

construct them. While even-carbon diradical benzenoids, like triangulene ($C_{22}H_{12}$), are triplet diradicals,⁷ in compliance with Hund's rule, the concealed even-radical benzenoid systems have low-stability singlet electronic ground states that are nearly degenerate with their triplet states.²¹ While, in the valence bond perspective, catafusenes are invariably Kekuléan, heptacene and larger acenes have very small HOMO/LUMO gaps and are very reactive.²² Thus, longer (linear) acenes will probably have close-lying singlet/triplet ground states and might even be regarded as singlet diradicals. Concealed non-Kekulé benzenoids and longer acenes should be candidates for bistable devices in which the lowest singlet and triplet states need to be nearly degenerate.²³ In fact, phenalenyl-based hydrocarbons having two joined phenalenyl units with strong resemblance to concealed non-Kekulé benzenoids have been studied via ESR, ENDOR, and optical spectroscopy and cyclic voltammetry for their singlet biradical character.²⁴

The general periodic table for benzenoid hydrocarbons (polycyclic aromatic hydrocarbons composed of only hexagonal rings, Table PAH6) can be partitioned into even-carbon formulas, as in Table 1 [Table PAH6(even)], and odd carbon formulas, as in Table 2 [Table PAH6(odd)], by sorting out every other row. The formulas of the catacondensed benzenoids ($C_{4r+2}H_{2r+4}$, r = number of hexagonal rings) define the right-hand uppermost horizontal edge of both Table PAH6 and Table PAH6(even). The left-hand staircase edges of all of these tables contain the constant-isomer benzenoid series. In the columns of Table PAH6(even), the number of carbons N_c increases downward from the top according to the even-residue classes of congruent modulo 6. In the $d_s = 0, 1, 2$ column series, for example, the number of carbons follows $N_c = 4(\text{mod } 6)$, $2(\text{mod } 6)$, and $0(\text{mod } 6)$, respectively. Table PAH6(even) has $N_{lc} = \text{even number}$ and has corresponding structures with aromatic $(4n + 2)$ perimeter circuits, and Table PAH6(odd) has $N_{lc} = \text{odd number}$. The latter has odd radical species with antiaromatic $(4n)$ perimeter circuits. N_{lc} is constant for any given row in these tables. Thus, partitioning Table PAH6 into Table PAH6(even) and Table PAH6(odd) sorts benzenoid hydrocarbons into more and less stable sets, respectively. Table PAH6(even) can be further partitioned to give only formulas with the number of carbons divisible by 6 to give Table PAH6(sextet). In Table PAH6(sextet), only the total resonant sextet (TRS) benzenoid isomers are considered, that is, only those benzenoid structures which are completely covered by disjoint Clar sextets.²⁵ Table PAH6(sextet) is a subset of Table PAH6(even), which is a subset of Table PAH6. Every third column of Table PAH6(even) contains formulas where N_c is divisible by 6 [$N_c = 0(\text{mod } 6)$].

TABLE 2: [Table PAH6(odd)]. Formula Periodic Table for Benzenoid Polycyclic Aromatic Hydrocarbons (PAH6)

$(N_C = 3 N_H - 14 - 2 d_S)$

$d_S = -8$	$d_S = -7$	$d_S = -6$	$d_S = -5$	$d_S = -4$	$d_S = -3$	$d_S = -2$	$d_S = -1$	$d_S = 0$	$d_S = 1$	N_{Ic}				
FORBIDDEN REGION								$C_{13}H_9$ (1)	$C_{17}H_{11}$ (1)	... 1				
								$C_{19}H_{11}$ (1)	$C_{23}H_{13}$ (4)	... 3				
$C_{00}H_{00}$								$C_{25}H_{13}$ (3)	$C_{29}H_{15}$ (21)	... 5				
								$C_{27}H_{13}$ (1)	$C_{31}H_{15}$ (15)	$C_{35}H_{17}$ (123)	... 7			
$2 < (N_C/N_H) < 3$								$C_{33}H_{15}$ (8, 1)	$C_{37}H_{17}$ (98, 2)	$C_{41}H_{19}$ (864, 14)	... 9			
								$C_{35}H_{15}$ (2)	$C_{39}H_{17}$ (60, 1)	$C_{43}H_{19}$ (693, 15)	$C_{47}H_{21}$ (6426, 168)	... 11		
$(N_C/N_H) > 3$								$C_{37}H_{15}$ (1)	$C_{41}H_{17}$ (34, 1)	$C_{45}H_{19}$ (517, 16)	$C_{49}H_{21}$ (5438, 174)	... 13		
								$C_{43}H_{17}$ (15, 1)	$C_{47}H_{19}$ (336, 11)	$C_{51}H_{21}$ (4341, 160)	$C_{55}H_{23}$	$C_{59}H_{25}$... 15	
$(N_C/N_H) > 3$								$C_{45}H_{17}$ (4)	$C_{49}H_{19}$ (213, 10)	$C_{53}H_{21}$ (3272, 142)	$C_{57}H_{23}$	$C_{61}H_{25}$	$C_{65}H_{27}$...
								$C_{47}H_{17}$ (1)	$C_{51}H_{19}$ (111, 6)	$C_{55}H_{21}$ (2322, 115)	$C_{59}H_{23}$	$C_{63}H_{25}$	$C_{67}H_{27}$	$C_{71}H_{29}$
$(N_C/N_H) > 3$								$C_{53}H_{19}$ (50, 3)	$C_{57}H_{21}$ (1558, 89)	$C_{61}H_{23}$...			
								$C_{55}H_{19}$ (17, 1)	$C_{59}H_{21}$ (950, 59)	$C_{63}H_{23}$...			
$(N_C/N_H) > 3$								$C_{57}H_{19}$ (4)	$C_{61}H_{21}$	$C_{65}H_{23}$...			
								$C_{59}H_{19}$ (1)	$C_{63}H_{21}$ (270, 20)	$C_{67}H_{23}$...			
$(N_C/N_H) > 3$								$C_{65}H_{21}$ (118, 8)	$C_{69}H_{23}$...				
								$C_{71}H_{23}$...					

$r = d_S + N_{Ic} + 2 = \frac{1}{2}(N_C - N_H + 2)$

one goes along a row toward the right and as one goes down in a column. The left-hand staircase edge starts with a three formula step followed by two and one formula steps. In the first row, the catacondensed benzenoids ($N_{lc} = 0$) are incapable of having valence bond diradicals. In the second row ($N_{lc} = 2$), the first diradical is dibenzo[*de,hi*]naphthacene ($C_{24}H_{14}$). All diradicals in the $N_{lc} = 2$ row of Table 1 must have molecular graphs with disconnected internal degree-3 vertices. In the third row ($N_{lc} = 4$), the first diradical is triangulene ($C_{22}H_{12}$), followed by benzo-*[a]*triangulene ($C_{26}H_{14}$). For the rows headed by the formulas of the members of the three Kekuléan (nonradical) one-isomer series ($C_{24}H_{12}$, $C_{32}H_{14}$, $C_{42}H_{16}$, $C_{54}H_{18}$, ...), the next row formula ($C_{30}H_{14}$, $C_{38}H_{16}$, $C_{48}H_{18}$, $C_{60}H_{20}$, ...) has diradical isomer numbers of increasing magnitude and contains connected diradical excised internal structures. As these formulas increase and the formulas within each corresponding row increase, so do their numbers of isomers. Only for the rows headed by the formulas of the members of the three Kekuléan one-isomer series are there no radical isomers; all other rows are headed by formulas with radical isomers. Circumscribing the triangulene diradical ($C_{22}H_{12}$) gives the circumtriangulene diradical ($C_{52}H_{18}$) further down the staircase edge of Table 1. The rows headed by $C_{30}H_{14}$ and $C_{40}H_{16}$ are diradical members of the first-generation matching four-isomer series (three Kekuléan and one non-Kekuléan isomers), both with C_{2v} symmetry. The formulas of $C_{22}H_{12}$, $C_{30}H_{14}$, and $C_{40}H_{16}$ correspond to the first-generation members of the three one-isomer diradical series.

The structure count (SC = number of resonance structures) for select diradical isomer series in the $N_{\text{ic}} = 4, 8, 12, 16, 20, 24, \dots$ rows of Table 1 starting with formulas of $\text{C}_{22}\text{H}_{12}$, $\text{C}_{30}\text{H}_{14}$, $\text{C}_{38}\text{H}_{16}$, $\text{C}_{46}\text{H}_{18}$, $\text{C}_{54}\text{H}_{20}$, $\text{C}_{62}\text{H}_{22}$, ... has been published in Figure

4 of ref 30. Figure 2 gives the SC for another select diradical series in the $d_s = -1, -2, -3, -4, -5, \dots$ columns with a corresponding analytical expression; note that the first-row series that starts with triangulene (SC = 306) is not explicitly shown in Figure 2, but solving the overall analytical expression for $t = 1$ gives SC = $(1/120)(8n^5 + 260n^4 + 2480n^3 + 10480n^2 + 15692n + 7800)$ for that series. The structural origin of the first coefficient in these series can be obtained by pruning off m -quinodimethane from the lower right-hand corner of every member in a given row series.³¹ This process gives structures having the same K values which, when multiplied by 2, give the corresponding first coefficient of the analytical expression. For example, pruning off m -quinodimethane from the lower right-hand corner of the first structure ($C_{30}H_{14}$) in Figure 2 gives anthanthrene ($C_{22}H_{12}$, dibenzo[*def,mno*]chrysene) with $K = 10$ which, when multiplied by 2, gives 20; in fact, performing this process on every member of this series gives a successor molecular graph with $K = 10$ as a result of bond fixation. The SC and other data for benzo[*a*]triangulene ($C_{26}H_{14}$) can be found in the work of Hosoya and co-workers.³²

The $C_{50}H_{20}$ concealed diradical is shown in Figure 1. Because of the presence of an isthmus, concealed radicals cannot occur for benzenoids having molecular graphs with less than four internal degree-3 vertices;^{20,21,28} note that the asterisks only occur at or after the third formula of each row in Table 1 below the $N_{lc} = 2$ row. Circumscribing Clar’s goblet ($C_{38}H_{18}$) six times gives $C_{470}H_{54}$, which is the first-generation formula of a constant-isomer series. While $C_{470}H_{54}$ has an unknown number of Kekuléan and diradical isomers, it has 1 concealed diradical and 162 tetraradicals, where the latter number was deduced from our topological paradigm.^{33,34}

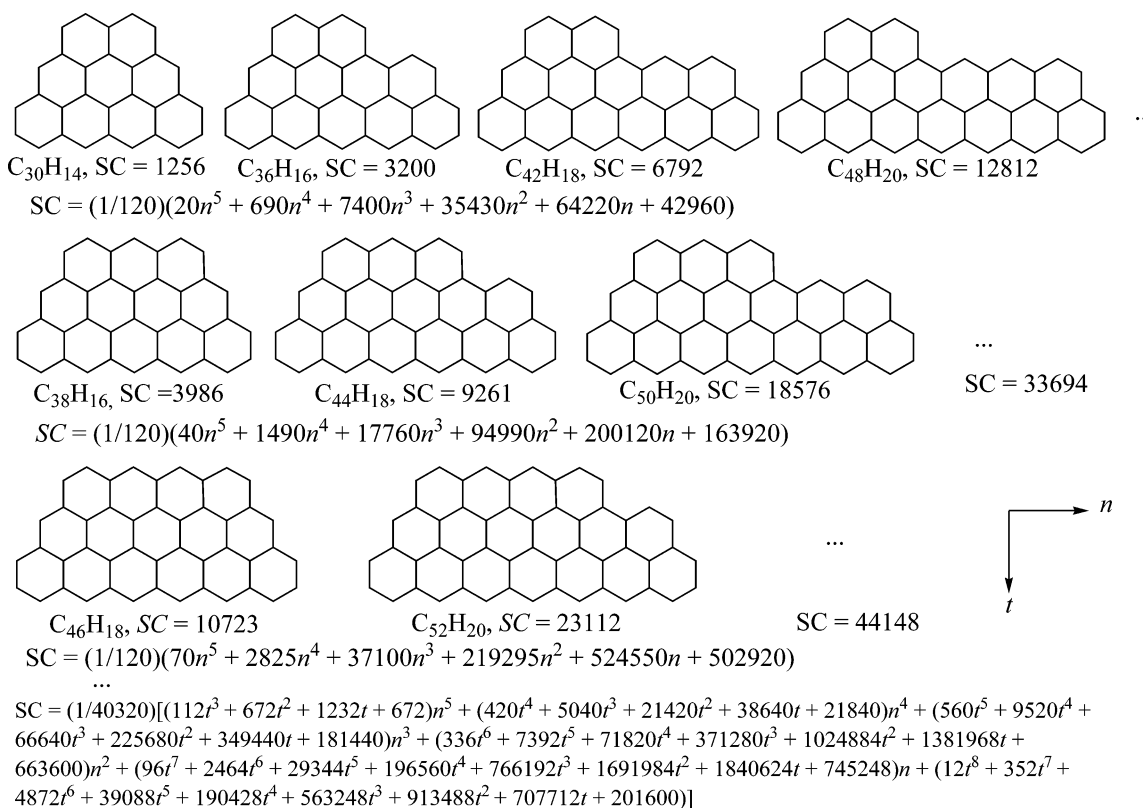


Figure 2. Two-dimensional array of diradical benzenoid series with analytical expressions for counting the number of resonance structures (SC).

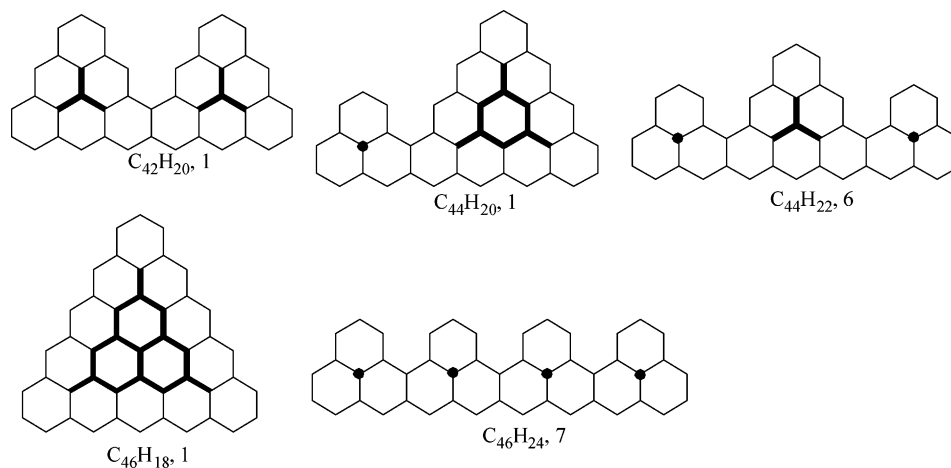


Figure 3. Representative smallest benzenoid tetradicals with their excised internal structures shown in bold. Their number of tetradical isomers are given after the comma.

The $C_{44}H_{20}$ tetradical in row 6 ($N_{ic} = 10$) of Table 1 is shown in Figure 3, and the $C_{48}H_{20}$ tetradical in row 8 ($N_{ic} = 14$) is shown in Figure 4, both of which cannot be circumscribed because they have a cove on their perimeter. Figure 4 also gives the tetradical isomer of $C_{52}H_{20}$ in row 10 ($N_{ic} = 16$), which, because of the presence of a cove, cannot be circumscribed. Figure 5 gives the other isomer of $C_{52}H_{20}$. The bay region of this benzo $C_{50}H_{20}$ predecessor isomer allows one to successively generate the only tetradicals of $C_{54}H_{20}$, $C_{56}H_{20}$, and $C_{58}H_{20}$ by successive attachment of the C_2 aufbau unit.

The $C_{46}H_{18}$ triangle-shaped tetradical shown in Figure 3 belongs to row 9 ($N_{ic} = 16$) of Table 1 and, when circumscribed twice, gives $C_{142}H_{30}$, which is the first-generation member of the one-isomer tetradical series; this is the most condensed tetradical. Since the infinite graphite sheet has a total of four degenerate nonbonding molecular orbitals (NBMO),³⁵ the compact triangular $C_{46}H_{18}$ tetradical might serve as a more

appropriate model for graphite. The singlet–triplet splitting of the $C_{46}H_{18}$ tetradical has been computed by the unrestricted Hartree–Fock Hubbard method.³⁶ This $C_{46}H_{18}$ tetradical was also depicted as structure 5 in Figure 75 in an extensive review by Randić.³⁷ The $C_{60}H_{24}$ concealed tetradical is shown in Figure 1. Among the largest literature depictions of benzenoid diradicals, $C_{76}H_{32}$ and $C_{148}H_{32}$ can be found in the work of Dietz and co-workers,³⁸ where the $C_{76}H_{32}$ diradical contains a Schlenk hydrocarbon substructure; there are 298 286 897 $C_{76}H_{32}$ diradical, tetradical, and so forth benzenoid isomers.²⁶

Odd (Carbon) Degree Radicals. The numbers in parentheses in Table PAH6(odd) (Table 2) gives, in succession, the number of monoradical, triradical, pentaradical, and so forth isomers, if known; if only the total number of radical species is known, then this is indicated by square brackets. The isomer numbers increase as one goes along a row toward the right and as one goes down in a column. The left-hand staircase edge starts with

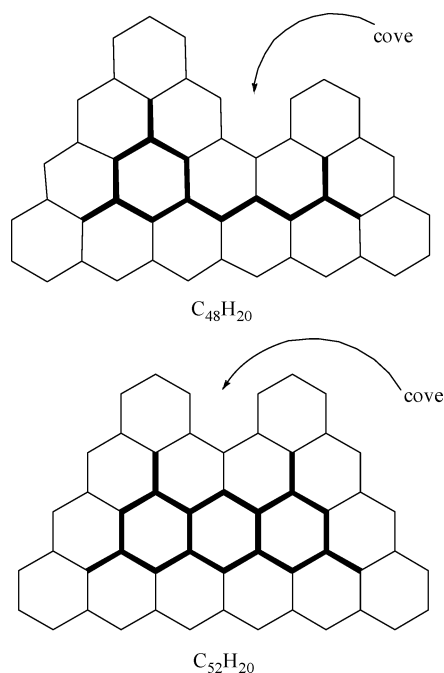


Figure 4. Two tetradradical benzenoids that cannot be circumscribed because of the presence of a cove (two adjacent bay regions) on their perimeter.

a three formula step followed by two and one formula steps. All of the rows in Table 2 headed by formulas having one monoradical isomer are those which correspond to the three one-isomer series (first generation $C_{13}H_9$, $C_{19}H_{11}$, $C_{27}H_{13}$; second generation $C_{37}H_{15}$, $C_{47}H_{17}$, $C_{59}H_{19}$, ...). There are 153 $C_{33}H_{17}$ (in the $N_{ic} = 5$ row) monoradicals and 1 triradical; one pair of the $C_{33}H_{17}$ monoradicals was shown to be isospectral.³⁹ Partially concealed triradicals (cf. Figure 1) and higher odd radicals have not been the object of study. At this point, it is worthy to note that the idea of local confinement of unpaired electrons used to construct concealed or partially concealed non-Kekuléan benzenoids by joining two components through their unstarred positions^{20,21} was utilized by Morikawa and co-workers.⁴⁰ This work depicts examples of $C_{41}H_{17}$, $C_{43}H_{19}$, and $C_{53}H_{23}$ monoradical benzenoids; the number of $C_{41}H_{17}$ and $C_{43}H_{19}$ radical isomers can be found in Table 2, and there are 51 691 $C_{53}H_{23}$ radical isomers. An example depiction of one monoradical $C_{77}H_{31}$ out of 262 398 390 radical benzenoid isomers can be found in the work of Dietz and co-workers.³⁸ The structure count (SC = number of resonance structures) for select monoradical isomer series in the $N_{ic} = 1, 3, 5, 7, \dots$ rows of Table 2 starting with formulas of $C_{13}H_9$, $C_{19}H_{11}$, $C_{25}H_{13}$, $C_{31}H_{15}$, ... has been published in Figure 3 of ref 30. The enumeration, SC, and other data for radical benzenoids having $r = 7$ can be found in the work of Hosoya and co-workers.³²

Triradicals cannot occur for benzenoids with less than three internal degree-3 vertices (i.e., they do not occur for benzenoids having formulas in row 1 [$N_{ic} = 1$] of Table 2). In row 2 of Table 2, the first triradical occurs for the formula of $C_{35}H_{19}$, tribenzo[de,hi,lm]hexacene, which has a molecular graph containing three disconnected internal degree-3 vertices. All formulas bordering the left-hand staircase edge of Table 2 must have connected excised internal structures (cf. with Figures 4–10). The smallest and most condensed triradical is the $C_{33}H_{15}$ triangle-shaped structure in Figure 6, which has its corresponding formula at the head of row 5 ($N_{ic} = 9$) in Table 2 and can be circumscribed to give the first-generation member ($C_{69}H_{21}$) of one of the three one-isomer triradical benzenoid series. This

$C_{33}H_{15}$ triradical was depicted along with other radical benzenoids by Randić in his Figure 75.³⁷ Figure 6 also gives the two triradical isomers for $C_{37}H_{17}$ in row 5. In row 6 of Table 2, the $C_{39}H_{17}$ triradical is shown in Figure 7. Figure 7 also shows how the bay region of this $C_{39}H_{17}$ isomer allows one to successively generate the only triradicals of $C_{41}H_{17}$ and $C_{43}H_{17}$ by successive attachment the C_2 Aufbau unit. The three $C_{53}H_{19}$ triradicals in row 11 ($N_{ic} = 21$) of Table 2 are shown in Figure 8. The C_2 Aufbau attachment to the bay regions either of the lower two $C_{53}H_{19}$ isomers in Figure 8 generates the same $C_{55}H_{19}$ triradical as that shown in Figure 9, which can be circumscribed to give the first-generation member ($C_{99}H_{25}$) of one of the three one-isomer triradical series. The $C_{61}H_{21}$ triradical in row 13 of Table 2 (shown in Figure 10) can be circumscribed four times to give the first-generation member ($C_{325}H_{45}$) of one of three one-isomer triradical series.

Algorithm for Generation of the Constant-Isomer Series.

Using the series in Figure 10, we will now more fully describe the generation of the constant-isomer series per our previously published algorithm and the corresponding topological paradigm.³⁴ We now review the steps of this algorithm: (1) systematically enumerate all excised internal structures of the formula $C_{n-2s-6}H_{s-6}$ ($N_{ic} = n - 2s + 6$) and circumscribe them with a perimeter of $q_p = 2s + 6$ carbon atoms, incrementing them with six hydrogen atoms to give strictly pericondensed benzenoids of the formula C_nH_s ; (2) if $C_{n-4}H_{s-2}$ exists in Table PAH6, obtain all combinatorial benzo derivatives; (3) if $C_{n-2}H_{s-2}$ exists in Table PAH6, obtain all ethenyl and dimethylenyl derivatives; (4) if $C_{n-1}H_{s-1}$ exists in Table PAH6, obtain all methylenyl derivatives; (5) if $C_{n+1}H_{s-1}$ exists in Table PAH6, obtain all combinatorial deletions of solo positions. (6) in doing steps 2–4, be sure that two carbon gaps exist everywhere on the perimeters. (7) sum the results of steps 1–4, and subtract the results of step 5; circumscribe all of these C_nH_s isomers from step 6 to obtain all of the $C_{n+2s+6}H_{s+6}$ benzenoid isomers. (8) iterate until steps 2–5 cannot be further performed. The resulting isomer set of strictly pericondensed benzenoids represents the base (first-generation) members of a constant-isomer series. One can verify that the resulting isomer set represents the first-generation members of the constant-isomer series by using the following equation⁴¹

$$n = s + 2 \lfloor \frac{1}{12}(s^2 - 8s + 19) \rfloor \quad (1)$$

Here, $\lfloor x \rfloor$ is the floor function and corresponds to the largest integer not larger than x . Equation 1 determines the first-generation formula for any given constant-isomer series. To use eq 1, input the number of benzenoid hydrogens for the formula of the resulting isomer set. For example, $s = 11$ gives $n = 11 + 2 \lfloor 4.333 \rfloor = 11 + 2 \times 4 = 19$, which gives $C_{19}H_{11}$ as the first-generation formula for the C_{2v} one-isomer monoradical benzenoid series. As another example, $s = 14$ and 16 give $n = 14 + 2 \lfloor 8.58 \rfloor = 14 + 2 \times 8 = 30$ and $n = 16 + 2 \lfloor 12.25 \rfloor = 16 + 2 \times 12 = 40$, which gives $C_{30}H_{14}$ and $C_{40}H_{16}$, respectively, as the first-generation formulas for the matching pair of four-isomer series, each of which has one diradical isomer member.

Application of our published algorithm³⁴ starting with $C_{61}H_{21}$ leads to the constant-isomer benzenoid series that begins with $C_{325}H_{45}$, as shown in Figure 10. Successive application of this algorithm beginning with the $C_{325}H_{45}$ first-generation isomer set leads to no further increase in the number of isomers because only the circumscribing process becomes operative. The distribution of isomer numbers for $C_{61}H_{21}$, $C_{109}H_{27}$, and $C_{169}H_{33}$ can be found in Table 6 in the work of Brunvoll, Cyvin, and Cyvin,²⁵ which collected data from various sources, including

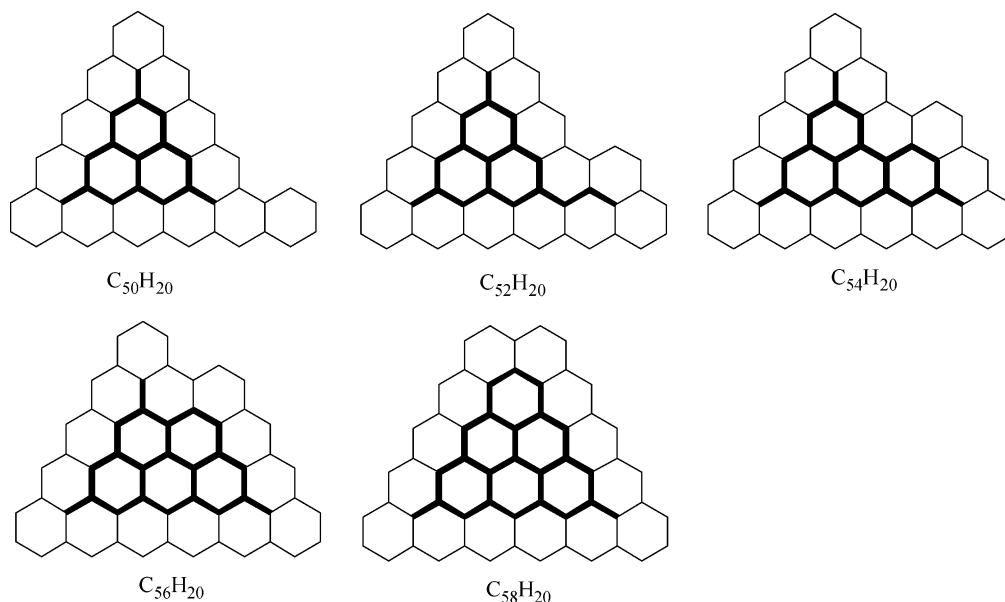


Figure 5. Successive tetradicals generated by attachment of the C_2 aufbau to bay regions.

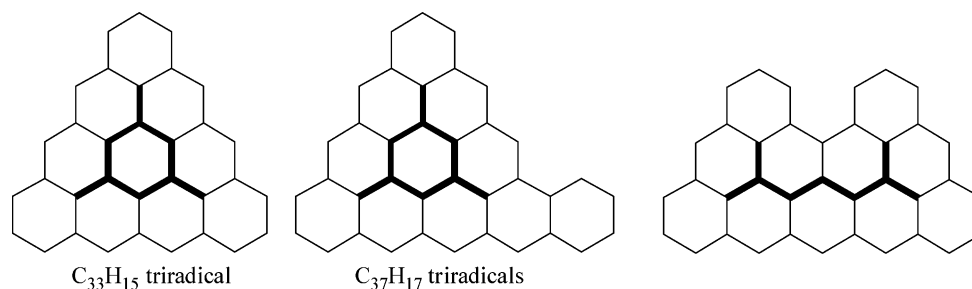


Figure 6. Triradical benzenoids belonging to the $N_{lc} = 9$ row series.

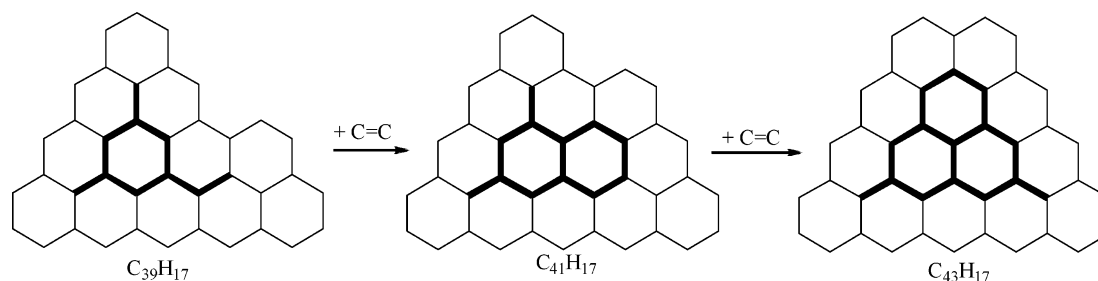


Figure 7. Triradical construction succession from $C_{39}H_{17}$ to $C_{43}H_{17}$ via the C_2 elementary aufbau unit.

our prior work. Using a modified form of our algorithm, Cyvin and Brunvoll deduced that the constant-isomer series begins with $C_{325}H_{45}$ and has 1634 benzenoid isomers.⁴² The determination of this number required that they knew that $C_{241}H_{39}$ had 1624 benzenoid isomers, but this could not be found in any of their papers. Using our topological paradigm, we subsequently showed that $C_{325}H_{45}$ had 162 triradical and 1 tetradical benzenoid isomers, leaving 1471 monoradical isomers.^{1,33,34} Reversing our algorithm from $C_{325}H_{45}$ shows that there are no benzo isomers of $C_{241}H_{39}$ (i.e., there are no extreme left-hand staircase edge $C_{237}H_{37}$ formulas in Table PAH6) but that there are methylenyl isomers of $C_{241}H_{39}$ (i.e., $C_{240}H_{38}$ is an extreme left-hand staircase edge formula in Table PAH6).^{33,34} In fact, $C_{240}H_{38}$ is the sixth-generation member of the naphthalene (or ovalene) one-isomer series. Figure 11 gives 2 of the 10 possible methylenyl isomers of $C_{241}H_{39}$ shown in bold with their corresponding circumscribed $C_{325}H_{45}$ benzenoids. Thus, there are 1461 monoradical, 162 triradical, and 1 pentaradical $C_{241}H_{39}$ benzenoid isomers.

Topological Paradigm. Part of our topological paradigm is that congruency of the isomer numbers exists between the various sets of constant-isomer series of different radical degrees and the one-to-one correspondence in the topology between the members having the same isomer number.^{1,33,34} The following list gives the formula of the first-generation members for the known odd-carbon constant-isomer series and their corresponding monoradical isomer numbers in parentheses:

$C_{13}H_9$ (1), $C_{19}H_{11}$ (1), $C_{27}H_{13}$ (1),
 $C_{35}H_{15}$ (2), $C_{45}H_{17}$ (4), $C_{57}H_{19}$ (4),
 $C_{69}H_{21}$ (12), $C_{83}H_{23}$ (19), $C_{99}H_{25}$ (19),
 $C_{115}H_{27}$ (46), $C_{133}H_{29}$ (70), $C_{153}H_{31}$ (70),
 $C_{173}H_{33}$ (162), $C_{195}H_{35}$ (239), $C_{219}H_{37}$ (239),
 $C_{243}H_{39}$ (504), $C_{269}H_{41}$ (726), $C_{297}H_{43}$ (726),
 $C_{325}H_{45}$ (1471), $C_{355}H_{47}$ (2062), $C_{387}H_{49}$ (2062).

For comparison, the following list gives the formula of the first-generation members for the known even-carbon constant-isomer series and their corresponding diradical isomer numbers in parentheses:

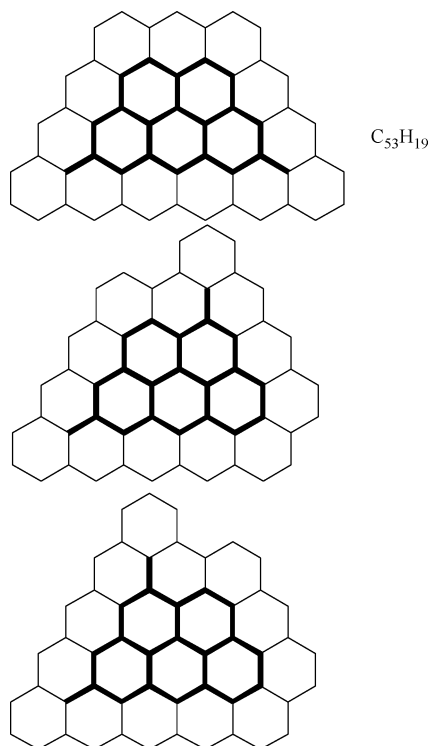


Figure 8. The only three $C_{53}H_{19}$ triradical benzenoids with their excised internal structures shown in bold.

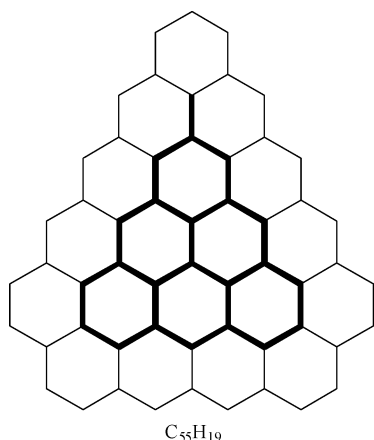


Figure 9. The $C_{55}H_{19}$ triradical, which is constructed by attaching the C_2 aufbau to either of two $C_{53}H_{19}$ triradicals in Figure 8.

$C_{22}H_{12}$ (1), $C_{30}H_{14}$ (1), $C_{40}H_{16}$ (1),
 $C_{50}H_{18}$ (2), $C_{62}H_{20}$ (4), $C_{76}H_{22}$ (4),
 $C_{90}H_{24}$ (12), $C_{106}H_{26}$ (19), $C_{124}H_{28}$ (19),
 $C_{142}H_{30}$ (46), $C_{162}H_{32}$ (70), $C_{184}H_{34}$ (70),
 $C_{206}H_{36}$ (162), $C_{230}H_{38}$ (239), $C_{256}H_{40}$ (239),
 $C_{282}H_{42}$ (504), $C_{310}H_{44}$ (726), $C_{340}H_{46}$ (726),
 $C_{370}H_{48}$ (1471), $C_{402}H_{50}$ (2062), $C_{436}H_{52}$ (2062).

As these lists show, the isomer numbers for the diradical constant-isomer series are exactly the same as the isomer numbers for the monoradical constant-isomer series. Note the repetitive a, b, b isomer number pattern. For those sets having the same constant-isomer numbers, there is a one-to-one matching of the topology (i.e., symmetry and the number of bay regions and selective lineations) between benzenoid members belonging to the sets. These same isomer numbers and one-to-one topological correspondence are also found for the triradical, tetradical, pentaradical, and so forth constant-isomer series. When two constant-isomer series have the same isomer

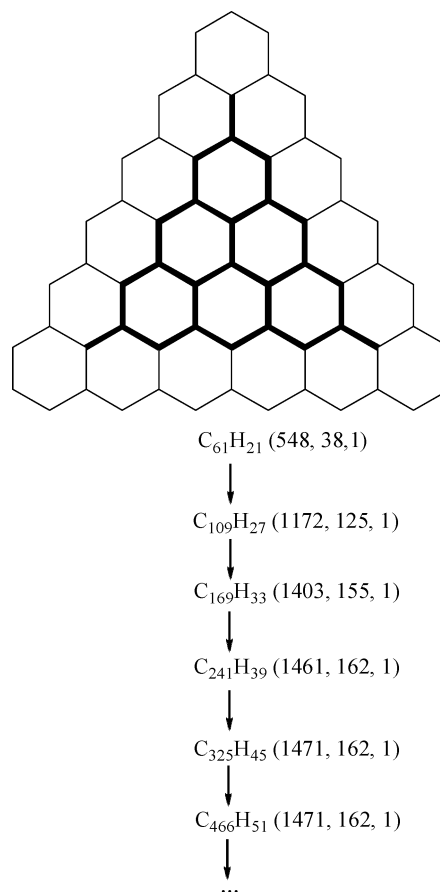


Figure 10. A pentaradical precursor to the first-generation ($C_{325}H_{45}$) D_{3h} constant-isomer series. The number of mono-, tri-, and pentaradical isomers are given in parentheses at each stage of circumscribing ($C_nH_s \rightarrow C_{n+2s+6}H_{s+6}$).

numbers and one-to-one matching in topology, they are said to be isotopological. To illustrate this paradigm more completely, consider the monoradical and diradical benzenoid structures in Figure 12. The four one-isomer series beginning with the formulas of $C_{19}H_{11}$, $C_{27}H_{13}$, $C_{30}H_{14}$, and $C_{40}H_{16}$ all have C_{2v} point group symmetry, no bay regions, and one selective lineation. The monoradical $C_{19}H_{11}$ and $C_{27}H_{13}$ constant-isomer series are correspondents as are the diradical $C_{30}H_{14}$ and $C_{40}H_{16}$ constant-isomer series, and the former pair is an associate to the latter pair. Correspondents and associates are isotopological. The two two-isomer series beginning with $C_{35}H_{15}$ and $C_{50}H_{18}$ each have one member with C_s symmetry and no bay regions or selective lineations and another member with C_s symmetry and one bay region and one selective lineation. The four four-isomer series beginning with the formulas of $C_{45}H_{17}$, $C_{57}H_{19}$, $C_{62}H_{20}$, and $C_{76}H_{22}$ (structures not shown) each have one isomer with C_{2v} symmetry, no bay regions, and one selective lineation, one isomer of C_s symmetry, one bay region, and no selective lineation, and two isomers of C_s symmetry, one bay region, and two selective lineations. Selective lineation is a quick topological method to determine the presence of HMO eigenvalues of ± 1 and is a line drawn from one side of a polyhex benzenoid graph to the other, such that each end is relatively convex.¹

The correspondence between the formulas in Table 1 for diradicals and Table 2 for monoradicals, which associates the equivalence between the constant-isomer series, is given by

$$N_c(\text{diradical}) = N_c(\text{monoradical}) + N_H(\text{monoradical})$$

$$N_H(\text{diradical}) = N_H(\text{monoradical}) + 3$$

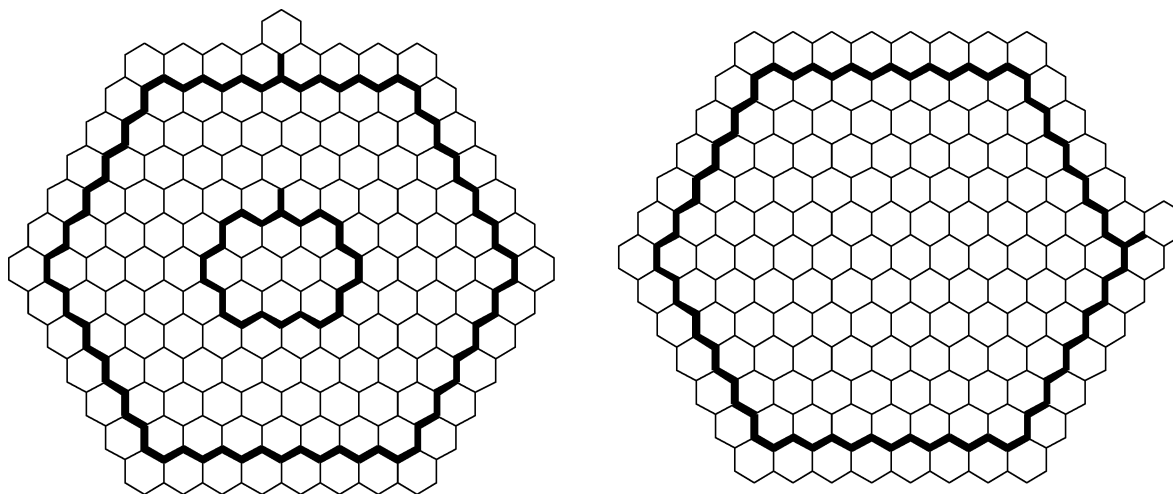


Figure 11. Two of the 10 methylenyl $C_{241}H_{39}$ benzenoid derivatives are shown in bold, which, when circumscribed, give 10 corresponding $C_{325}H_{45}$ benzenoids.

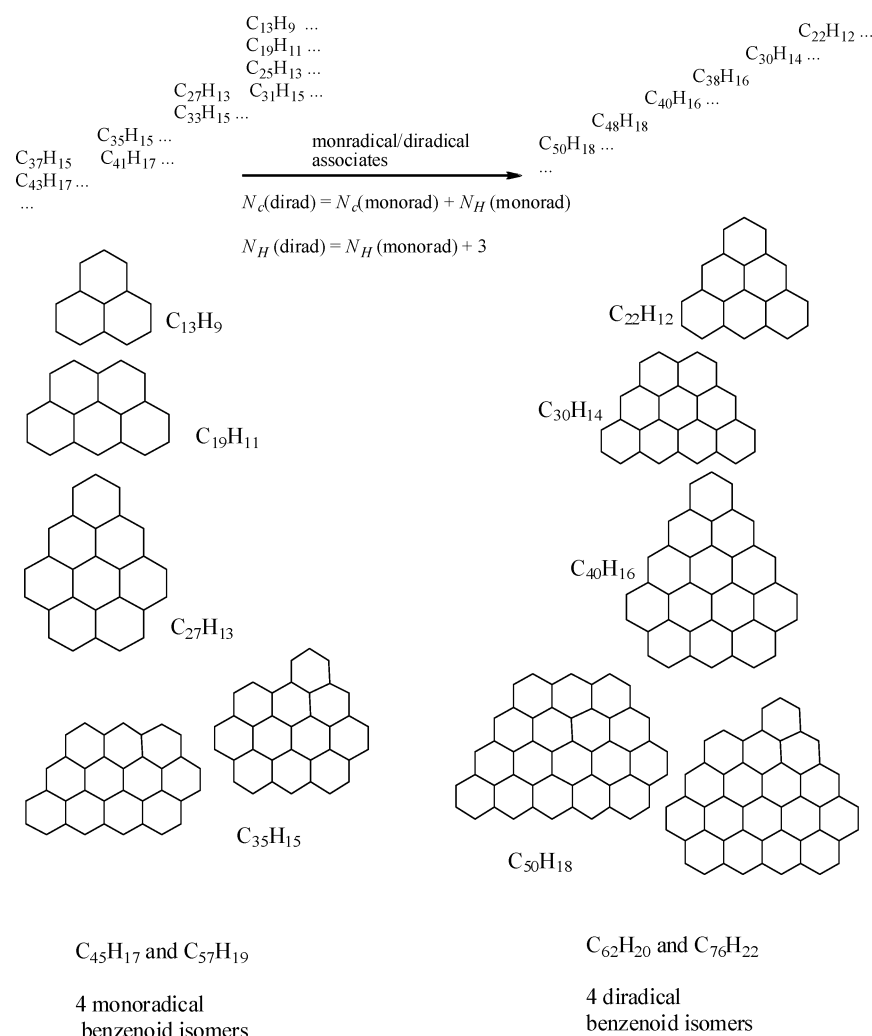


Figure 12. Constant-isomer monoradicals of the formula of C_nH_s have a one-to-one correspondence in isomer number and topology to constant-isomer diradicals of formula $C_{n+3}H_{s+3}$.

It needs to be emphasized that this one-to-one correspondence is strictly for members of the constant-isomer series and that constant-isomer series have formulas only on the left-hand staircase boundary edge of Table PAH6. The equations in this paragraph map all of the formulas between Tables 1 and 2. Thus, we see that they show that $C_{35}H_{15}$ gives $C_{50}H_{18}$; these are located on the staircase boundary edge of Table PAH6 (and Tables 1

and 2) and are formulas of first-generation members of the two-isomer series (Figure 12).

Let us look at formulas $C_{31}H_{15}$ (Table 2) and $C_{46}H_{18}$ (Table 1), which are compliant with the equations in the prior paragraph and are more remote to this staircase boundary edge, that is, they are not first-generation constant-isomer formulas. There are 15 monoradical $C_{31}H_{15}$ (Figure 13) and 20 diradical $C_{46}H_{18}$

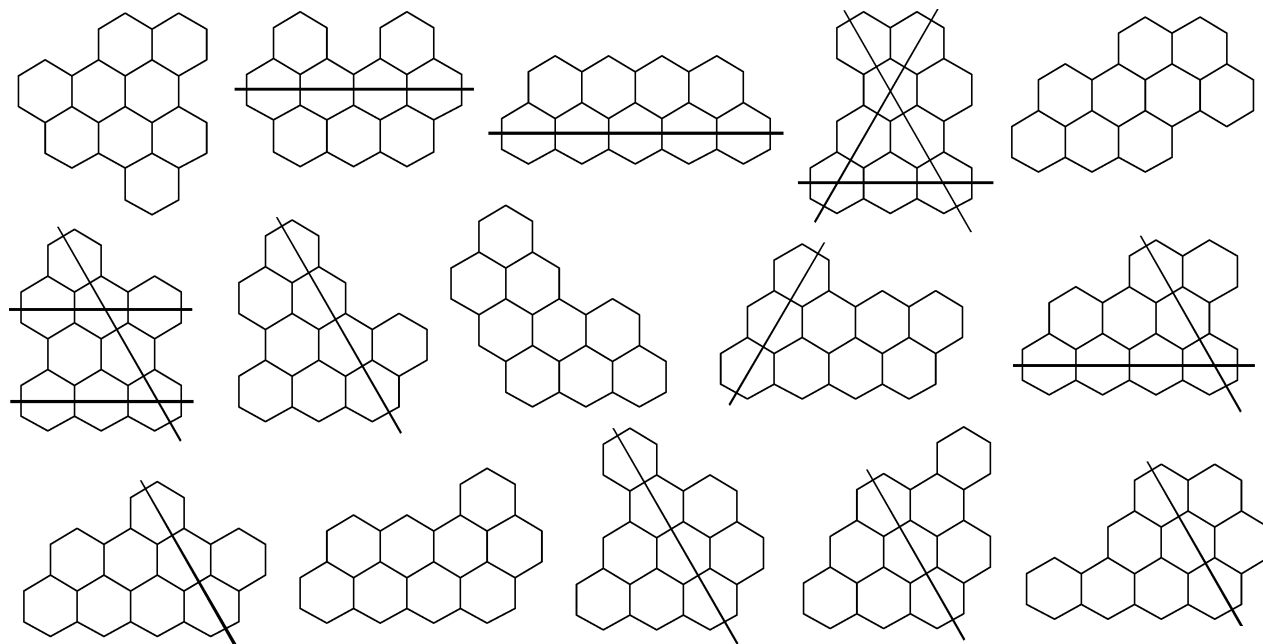


Figure 13. All $C_{31}H_{15}$ monoradical benzenoid hydrocarbons.

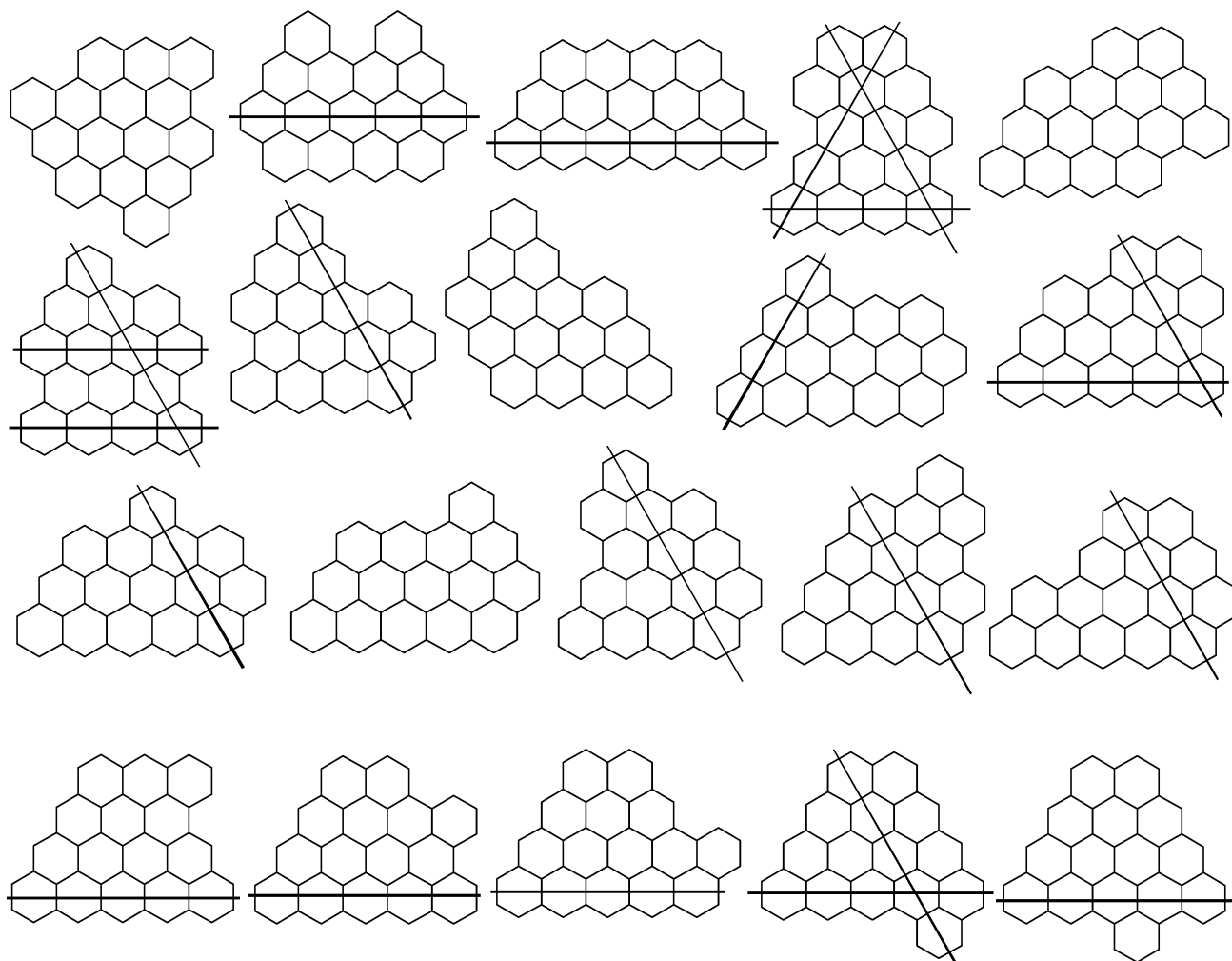


Figure 14. All $C_{46}H_{18}$ diradical benzenoid hydrocarbons.

(Figure 14) benzenoids. The first 15 structures in Figure 14 are isotopological to those in Figure 13; the carbocation of the first C_{3h} $C_{31}H_{15}$ structure in Figure 13 has been synthesized.¹² Employing our algorithm on both of these sets of structures, it is found that after circumscribing twice, we obtain first-

generation formulas for constant-isomer series having 46 $C_{115}H_{27}$ monoradicals and 46 $C_{142}H_{30}$ diradicals, respectively. It can be determined that there are 27 circumscribable methylenyl-substituted $C_{30}H_{14}$ benzenoids with the formula of $C_{31}H_{15}$. Adding these 27 structures to the 14 circumscribable structures

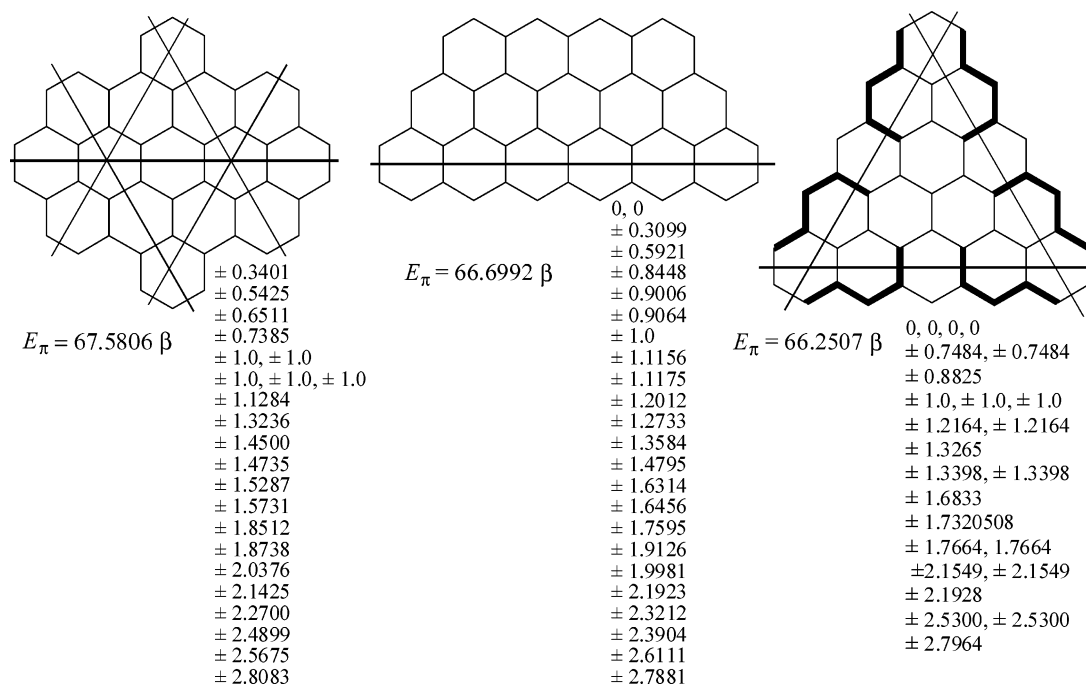


Figure 15. Representative $C_{46}H_{18}$ benzenoid isomers out of 49 Kekuléan, 20 diradical, and 1 tetraradical benzenoid isomers.

in Figure 13 and circumscribing gives 41 $C_{67}H_{21}$ benzenoids; the second structure in Figure 13 has a cove and cannot be circumscribed. There are 5 methylenyl-substituted $C_{66}H_{20}$ circumvalene (dicircumnaphthalene) benzenoids of the formula $C_{67}H_{21}$, which, when added to the 41 prior benzenoid isomers, gives 46 structures that can be circumscribed to give 46 $C_{115}H_{27}$ monoradical benzenoids. Similarly, there are 22 circumscribable diradical methylenyl-substituted $C_{45}H_{17}$ benzenoids of the formula of $C_{46}H_{18}$. Adding these 22 structures to the 19 circumscribable structures in Figure 14 and circumscribing gives 41 $C_{88}H_{24}$ benzenoids; the second structure in Figure 14 has a cove and cannot be circumscribed. There are 5 diradical methylenyl-substituted $C_{87}H_{23}$ (dicircumbenzo[*cd*]pyrenyl) benzenoids of the formula $C_{88}H_{24}$, which, when added to the 41 prior benzenoid isomers, gives 46 structures that can be circumscribed to give 46 $C_{142}H_{30}$ diradical benzenoids. What these examples illustrate is that the equations in the prior paragraph associate the isotopological sets of monoradical and diradical constant-isomer series on the left-hand staircase edge of Table PAH6 and the nonboundary formulas which correspond to antecedent benzenoid structure sets that, when circumscribed and augmented per our algorithm³⁴ a sufficient number of times, give isotopological monoradical/diradical constant-isomer series.

Relative Stability of Kekuléan versus Non-Kekuléan Benzenoids. It is well-known that radical benzenoids are less stable than their nonradical isomers. For example, the $C_{24}H_{14}$ diradical, dibenzo[*de,hi*]naphthacene, has an HMO total π -electronic energy of $E_\pi = 33.4554 \beta$ compared to its Kekuléan isomer, dibenzo[*fg,op*]naphthacene, with $E_\pi = 34.1644 \beta$, and triangulene diradical ($C_{22}H_{12}$) has an HMO total π -electronic energy of $E_\pi = 30.8098 \beta$ compared to its Kekuléan isomers, anthanthrene and benzo[*ghi*]perylene, with $E_\pi = 31.2529$ and 31.4251β , respectively. It is of interest to compare the relative stability of a diradical versus tetraradical isomer. Figure 15 presents one Kekuléan, one diradical, and one tetraradical $C_{46}H_{18}$ benzenoid isomer along with their HMO π -electronic energy levels (molecular graph eigenvalues) and total π -energy (E_π); as expected, the π -energy decreases in that order. This decreasing of E_π upon the increase in the number of NBMOs is in agreement with the results of Gutman and co-workers⁴³ on the

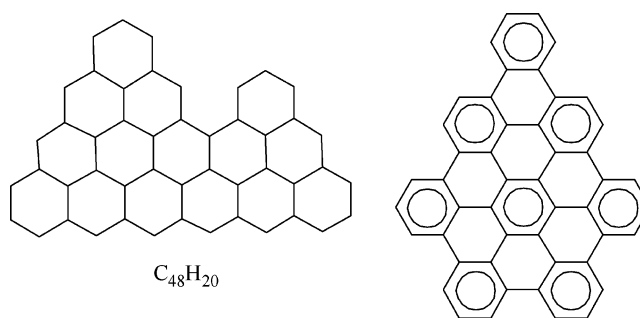


Figure 16. The least and most stable $C_{48}H_{20}$ benzenoid hydrocarbons. The only $C_{48}H_{20}$ tetraradical and the only $C_{48}H_{20}$ TRS benzenoid hydrocarbons.

dependence of E_π on the number of NBMOs. A number of other features for the structures in Figure 15 are relevant. First, the number of selective lineations (lines drawn through the molecular graphs from one convex perimeter sections to another)¹ is equal to the number of eigenvalues ± 1 . Second, the tetraradical molecular graph can be embedded by Hall pentadienyl subgraphs (shown in bold), which means that the eigenvalues of the pentadienyl radical ($\pm 1, \pm\sqrt{3}, 0$) must be among the eigenvalues of the tetraradical.^{44,45} Third, because of the three-fold symmetry of the tetraradical, two-thirds of its eigenvalues must be a doubly degenerate subset.^{44,46} Figure 16 gives the only $C_{48}H_{20}$ tetraradical and TRS benzenoid, where the former is the least stable isomer and the latter is the most stable isomer; the $C_{48}H_{20}$ TRS benzenoid is the leapfrog ($C_nH_s \rightarrow C_{3n-3s+6}H_{2s-6}$) of the $C_{27}H_{13}$ monoradical shown in Figure 12. At the HMO level, the $C_{38}H_{18}$ concealed diradical (Clar's goblet in Figure 1) is less stable ($E_\pi = 54.2524 \beta$) than its obvious diradical isomer, tetrabenzo[*a,ef,kl,p*]coronene ($E_\pi = 54.4476 \beta$). In general, the more NBMOs a benzenoid has, the less stable it is on a per carbon basis.

Resonance-Theoretic Treatment of Conjugated Radicals. The quantitative number and qualitative location of unpaired electrons and their spin densities are dealt with by the resonance-theoretic approach of Klein and co-workers.⁴⁷ This resonance-theoretic approach gives the correct ground-state spin multi-

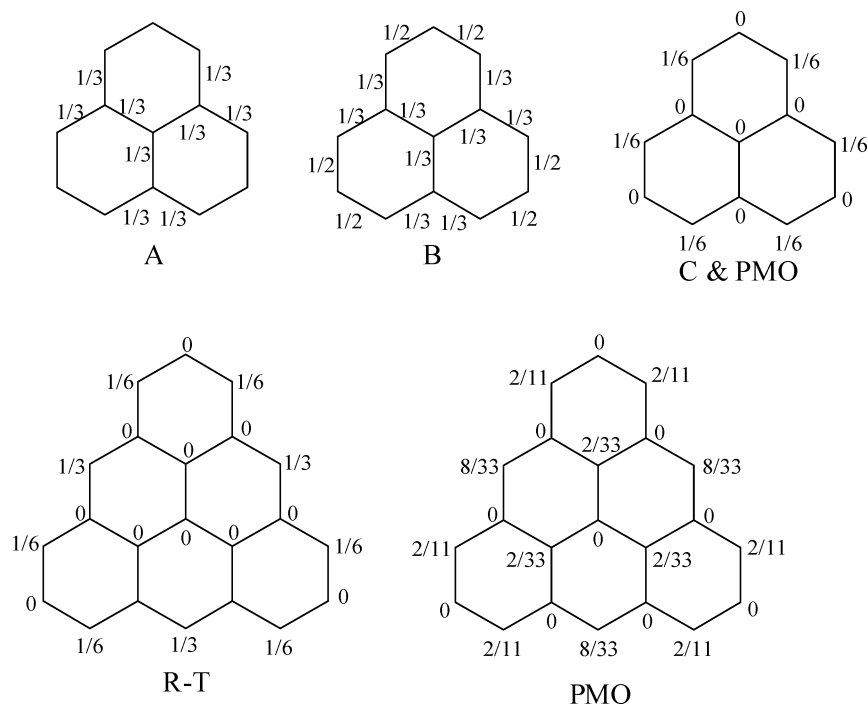


Figure 17. Comparison of resonance-theoretic (R-T) and PMO determinations of spin densities of radical benzenoid hydrocarbons.

plicity (no. unpaired electrons = $s - u$) for alternate hydrocarbon (AH) $p\pi$ -molecular systems. The simple rules for determining the zero-order unpaired π -spin density given by Klein and co-workers are the following: (a) assign zero-order π -bond orders of $1/3$ to each edge issuing from a site of degree-3; (b) assign the remaining π -bond orders to be as large as possible, subject to the constraint that the sum of the π -bond orders into no site exceeds 1. (c) calculate zero-order free valences v_i (site spin density) at each site i as the deficit from 1 of the sum of the π -bond orders p_e incident at that site (i.e., $v_i = 1 - \sum p_e$); (d) the unpaired spin density at an edge is the difference between the net free valence of the starred and unstarred sites nearby on an edge. We will now illustrate the application of these rules to the phenalenyl monoradical. In Figure 17, rule (a) gives A, rule (b) gives B, and rule (c) gives C. Result C is exactly what is obtained using the maximum starring/zero-sum rule procedure of Longuet-Higgins⁴⁸ extensively employed in Dewar's perturbation molecular orbital (PMO) method.⁴⁹ By Herndon's corrected structure count (CSC),⁵⁰ the phenalenyl monoradical has CSC = 18, and by the maximum starring/zero-sum rule method, it has been shown that the unpaired electron is localized at each starred perimeter site 3 times out of 18 corrected resonance structures; the central starred vertex is coincidentally 0. Thus, both methods seem to eliminate the antiaromatic contribution of the $4n$ perimeter of phenalenyl by maintaining the unpaired electron on the perimeter so as to exclude compliance to the antiaromatic $4n = \text{number of } p\pi\text{-electrons}$ rule; this is a type of electron-correlation effect. As another example, consider triangulene also in Figure 17. The resonance-theoretic method gives the spin densities shown on the first molecular graph, and PMO gives the spin densities shown on the second molecular graph. From these two examples, it should be evident that the sum of free valences (spin densities) on the perimeter of the monoradicals is 1 electron, and on the perimeter of the diradicals, it is 2 electrons, as it should be. Also, the resonance-theoretic method places greater spin density on the perimeter of radical benzenoids and is easier to apply and has been shown to become more reliable when applied to the boundary edges of more extended conjugated systems.⁴⁷

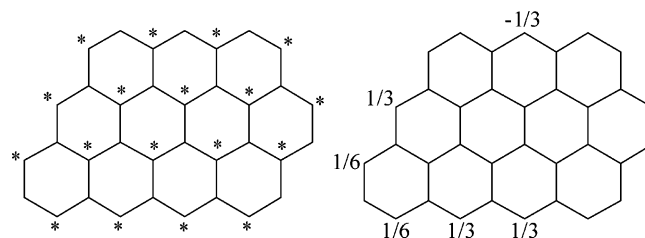


Figure 18. Modified resonance-theoretic determination of the spin density of radical benzenoid hydrocarbons in that starred positions are positive and unstarred positions are negative. Zeros are omitted from the molecular graphs.

We now add a modification to Klein's assignment of free valences. (c') Free valences on starred positions are always positive, and on unstarred positions, they are negative; this also requires that the word "difference" in (d) be changed to "sum". In this way, the sum of zero-order free valences is always 1 electron on benzenoid monoradicals, 2 electrons on benzenoid diradicals, 3 electrons on benzenoid triradicals, and so on, that is, the sum of free valence for radical benzenoids corresponds to the number of electrons in the NBMOs. Application of this modified Klein's method of assigning zero-order free valences to one of the first-generation members of the two-isomer monoradical benzenoids (cf. Figure 12) is given in Figure 18. In general, solo starred positions always have a zero-order free valence of $+1/3$ and are the most chemically reactive positions, the noncentral trio starred positions always have a zero-order free valence of $+1/6$ and are the second most reactive positions, the unstarred solo positions always have a zero-order free valence of $-1/3$ and are the least reactive positions, and the noncentral trio unstarred positions always have a zero-order free valence of $-1/6$ and are the second least reactive positions. As examples, consider benzo[bc]ovalene monoradical in Figure 18. Radical substitution at either of the $+1/3$ positions gives Kekuléan benzenoid successors having $K = 60$ and 45 , respectively, from left to right, radical substitution at either $+1/6$ position gives vinylovalene-related isomers having $K = 50$, and radical substitution at the $-1/3$ position gives a diradical benzenoid successor.

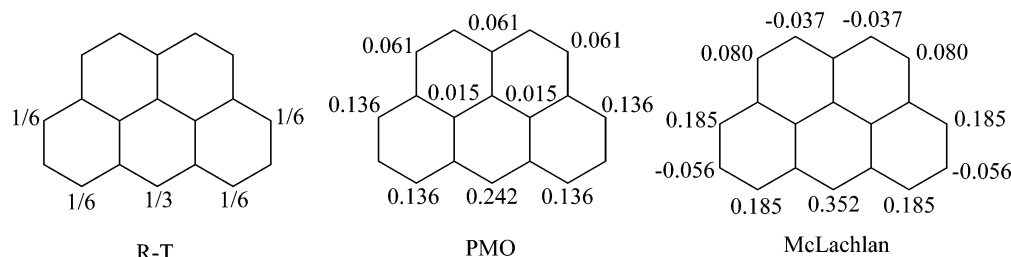


Figure 19. Comparison of spin densities determined by three different methods for the benzo[cd]pyrenyl radical. The zero spin densities are not shown.

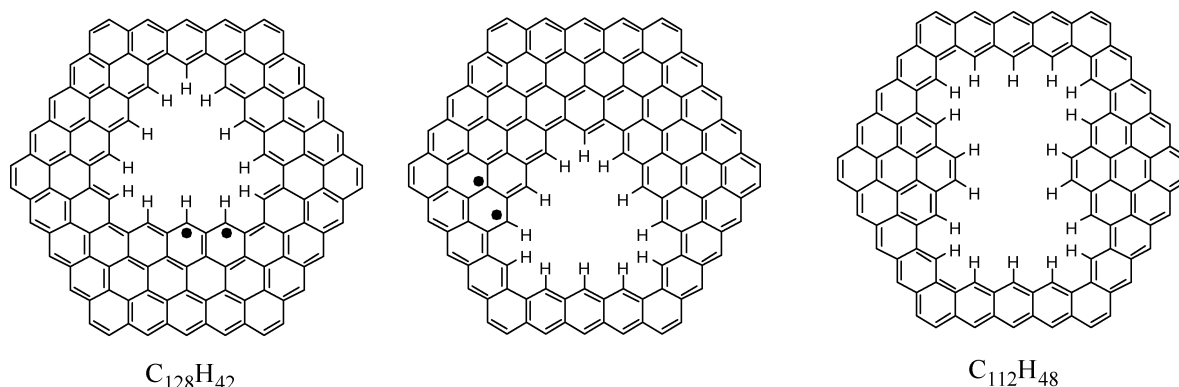


Figure 20. Excising out the carbon skeleton corresponding to triangulene ($C_{22}H_{12}$) from tricircumcoronene ($C_{150}H_{30}$) gives a diradical $C_{128}H_{42}$ diradical circulene, but in comparison, excising out the $C_{38}H_{18}$ concealed diradical leaves the $C_{112}H_{48}$ Kekuléan (nonradical) circulene.

In Figure 19, the first molecular graph of benzo[cd]pyrene ($C_{19}H_{11}$ in cf. Figure 12) gives unpaired electron spin densities determined by the Klein resonance-theoretic method (R-T), the second one gives those determined by the zero-sum PMO, and the third one gives the McLachlan unpaired electron spin densities determined by Lewis and Singer.¹⁰ Clearly, the resonance-theoretic and the McLachlan unpaired electron spin densities values agree more closely; the latter computed spin densities gave a high correlation when plotted against ENDOR proton coupling constants for this and other benzenoid mono-radicals.¹⁰

Electronic Conductivity and Molecular Magnetism in Graphite-Like Systems. Let us consider graphitic monolayers having either triangle-shaped or hourglass-shaped boundaries. The triangle-shaped monolayers considered are those like the polyradical systems shown in Figures 3–10, and the hourglass-shaped are those like the ones shown in Figure 1. The rapid escalation in the number of resonance structures in radicals relative to equally sized Kekuléan benzenoids, as illustrated in Figure 2, no doubt also contributes to the conductivity of graphite systems. Because of the greater variety of triangular-related mono- and polyradical benzenoid systems, it is anticipated that fabrication of conductive graphite-related systems will be relatively easy. Such conductive benzenoids would constitute what is referred to as synthetic metals.⁷

Because in concealed radical benzenoid hydrocarbons the exchange integral, which determines the separation between the singlet and triplet ground state is zero, the “excited singlet” will be (nearly) degenerate with the triplet ground state.²¹ This singlet requires two determinants to describe it; therefore, it cannot be represented by conventional Kekulé structures. If one of these concealed radical benzenoid hydrocarbons can be synthesized or such an hourglass-shaped graphite structure can be fabricated, it should be relatively stable in its singlet state but would acquire a strong magnetic moment in a magnetic field.²¹ Partially concealed radical benzenoids should be both conductive and acquire a strong magnetic moment in an applied field.

Hole Defects in Graphite. Removal of a single carbon atom from a graphite system generates a point defect that is a one-atom hole (called a Schottky defect).³⁸ A type of graphite lattice defect involving larger (multiatom) holes can be modeled by circulenes (coronoids), which we now consider.⁵¹ The extensive work published on coronoids by Cyvin and co-workers can serve the reader with background.⁵² Consider a macromolecular hexagonal graphite structure (i.e., polycircumcoronene with $N_c = 6p^2$ and $N_H = 6p$, $p = 1, 2, 3, 4, \dots$) comprised of only six duo ($\eta_2 = 6$) and the remaining solo ($\eta_1 = 6p - 12$) perimeter sites. Well-defined nanosized polycyclic aromatic hydrocarbons like the larger members to polycircumcoronene are called graphenes by Müllen and co-workers.⁵³ Excising out the carbon skeleton of a monoradical benzenoid (C_nH_s) from any appropriate polycircumcoronene (graphenes of D_{6h} symmetry) and installing s hydrogens to the internal dangling bonds within the remaining hole will give a monocirculene (coronoid) which is also a monoradical. Excising out a benzenoid diradical in a similar manner will generate a diradical monocirculene. Figure 20 shows a diradical monocirculene ($C_{128}H_{42}$) generated by excising out the carbon skeleton of triangulene ($C_{22}H_{12}$) from tricircumcoronene ($C_{150}H_{30}$). With the exception of concealed benzenoid radicals, excising any radical benzenoid from a perfect hexagonal graphite layer will generate a radical vacancy-like hole. In general, excising any nondisjoint diradical, like the trimethylenemethane diradical, from a perfect hexagonal graphite layer will generate a diradical hole. This observation of excising a nondisjoint even-carbon diradical from an even-carbon Kekuléan benzenoid to generate a diradical monocirculene is equivalent to the phenomenon noted by Ivanciuc, Klein, and Bytautas⁴⁷ for vacancy defects in graphite where the net spin density of the vacancy and the deleted set of contiguous carbon atoms are identical.

Vacancy Defects as Antimolecules. The excised carbon molecule from graphite leaves a hole (vacancy) defect called an antimolecule.⁴⁷ A perfect graphite has a local balance of starred s and unstarred u sites, and in the formation of an

antimolecule, the balance or unbalance of starred and unstarred sites in the region of the antimolecule ($u \geq s$) must be the same as that in the carbon molecule removed ($s \geq u$), except for sign. If the excised carbon molecule has an aromatic or antiaromatic circuit on its outer perimeter, then the perimeter of the cavity of the antimolecule formed is also an aromatic or antiaromatic circuit, respectively. This shows that the excised carbon molecule/vacancy hole antimolecule matching relationship allows one to transfer what is known about benzenoid hydrocarbons, which are hydrogen analogues of the excised carbon molecules, to the vacancy antimolecules formed upon excision. Thus, the isomorphism, including the number of isomers, topology, and radical character, that exists between the C_nH_s benzenoid monoradicals and $C_{n+s}H_{s+3}$ diradicals can be transferred directly to the corresponding vacancy hole defects in graphite and graphenes.

Let us examine more generally the concept of the excised carbon molecule/vacancy hole antimolecule and their matching relationship. Because the variation of the nature of the periphery has a distinct impact upon the electronic properties of graphenes,⁵³ let us consider the topology of the vacancy hole antimolecule in graphite systems versus the perimeter topology^{54,55} of the corresponding benzenoid analogue to the excised carbon molecule. The number of peripheral degree-3 vertices, N_{pc} , on the perimeter of a benzenoid (polyhex) molecular graph is $N_{pc} = N_H - 6$, where N_H = number of degree-2 vertices. There can be 0, 1, 2, 3, and 4 successive degree-2 vertices between any two nearest peripheral degree-3 vertices designated as bay, solo, duo, trio, and quarto regions, respectively; $\eta_0, \eta_1, \eta_2, \eta_3$, and η_4 designate the number of bay, solo, duo, trio, and quarto regions on a given benzenoid molecular graph. The perimeter topology of any benzenoid molecular graph is described by $-\eta_0 + \eta_2 + 2\eta_3 + 3\eta_4 = 6$, which is independent of the number of solo regions (η_1). The molecular graph for any first-generation member of the benzenoid constant-isomer series will have $\eta_4 = 0$ (except for naphthalene), and for any second-generation and higher member, $\eta_3 = \eta_4 = 0$. In analogy, the topology for the vacancy hole antimolecule (here, we assume that hydrogens are installed to the dangling bonds inside of the cavity) is described by $N'_{pc} = N'_H + 6$ and $-\eta'_0 + \eta'_2 + 2\eta'_3 + 3\eta'_4 = -6$, where the prime emphasizes that these relationships are for the antimolecule. Note the change in sign before the number 6 in these equations in going from the carbon molecule to corresponding antimolecule. For the antimolecule corresponding to a constant-isomer benzenoid carbon molecule, $-\eta'_0 + \eta'_2 = -6$ becomes applicable. On the basis of Hall's work⁵¹ on graphenes with holes, the relative stability of isomeric antimolecules follows the same order as their excised carbon molecules.

The constant-isomer benzenoids are the most condensed PAHs with the smallest hydrogen-to-carbon ratios. Thus, extracting out the carbon molecule corresponding to these constant-isomer systems to form a vacancy antimolecule in a graphene or graphite would involve the breaking of the fewest carbon-carbon bonds for a specified number of carbons. For this reason, the formation of graphite vacancies having antimolecules corresponding to a benzenoid constant-isomer should be energetically more favorable. For example, there are 12 $C_{22}H_{14}$ catacondensed benzenoids and 3 $C_{22}H_{12}$ benzenoids, and extracting out 1 of the 12 carbon molecules corresponding to the former would involve breaking 14 carbon-carbon graphite bonds, whereas extracting out 1 of the 3 carbon molecules corresponding to the latter would involve breaking 12 carbon-carbon bonds. On this basis, since 1 of the 3 $C_{22}H_{12}$ benzenoids is a triangulene diradical, one should expect that the formation

of the antimolecule diradical of triangulene should be more favorable (by approximately 320 kcal/mol) than the formation of 1 of the 12 antimolecules corresponding to the carbon molecule of the $C_{22}H_{14}$ benzenoids. Figure 20 gives examples of the triangulene antimolecule diradical in a $C_{128}H_{42}$ graphene.

Conclusion

This work presents an organized framework for studying the radical benzenoid hydrocarbons and related graphenes. A one-to-one relationship between the structures having diradical formulas in Table 1 and the structures having monoradical formulas in Table 2 has been further clarified; C_nH_s monoradicals are uniquely associated to $C_{n+s}H_{s+3}$ diradicals.

The study of radical benzenoid hydrocarbons is important from numerous points of view. They and their closed-shell analogues are representative of reactive intermediates in pyrolytic and astronomical processes and have many implications in the understanding and fabrication of electronic materials. Some understanding of how both types of boundary edge effects and vacancy hole defects can dramatically affect the electronic properties of benzenoid hydrocarbons and graphite-like materials has been uncovered. In general, the body of knowledge applicable to benzenoid hydrocarbons can be transferred to the vacancy antimolecule resulting from removal of a carbon molecule analogue of the corresponding benzenoid hydrocarbon. Herein, one will find a comprehensive summary of lead references to the field benzenoid free radicals.

References and Notes

- (1) (a) Dias, J. R. *Theor. Chim. Acta* **1991**, 81, 125–138. (b) Dias, J. R. *Theor. Chim. Acta* **1990**, 80, 143–162. (c) Dias, J. R. *J. Phys. Org. Chem.* **1990**, 3, 765–783. (d) Dias, J. R. *Struct. Chem.* **1992**, 3, 389–398.
- (2) Keller, A.; Kovacs, R.; Homann, K.-H. *Phys. Chem. Chem. Phys.* **2000**, 2, 1667–1675.
- (3) (a) Leach, S. Z. *Phys. Chem.* **1996**, 195, S.15–42. (b) Salaman, F. *J. Mol. Struct.* **2001**, 563–564, 19–26.
- (4) Gomberg, M. J. *Am. Chem. Soc.* **1900**, 22, 757–771.
- (5) Schlenk, W.; Brauns, M. *Chem. Ber.* **1915**, 48, 661–716.
- (6) (a) Rajca, A. *Chem. Rev.* **1994**, 94, 871–893. (b) Mandal, S. K.; Samanta, S.; Itkis, M. E.; Jensen, D. W.; Reed, R. W.; Oakley, R. T.; Tham, F. S.; Donnadieu, B.; Haddon, R. C. *J. Am. Chem. Soc.* **2006**, 128, 1982–1994.
- (7) (a) Allinson, G.; Bushby, R. J.; Paillaud, J.-L.; Oduwale, C.; Sales, K. *J. Am. Chem. Soc.* **1993**, 115, 2062–2064. (b) Bearpark, M. J.; Robb, M. A.; Bernardi, F.; Olivucci, M. *Molecular Chem. Phys. Lett.* **1994**, 217, 513–519. (c) Allinson, G.; Bushby, R. J.; Paillaud, J.-L.; Thornton-Pett, M. *J. Chem. Soc., Perkin Trans. 1* **1995**, 385–390. (d) Allinson, G.; Bushby, R. J.; Jesudasan, M. V.; Paillaud, J.-L.; Taylor, N. J. *Chem. Soc., Perkin Trans. 2* **1997**, 147–156. (e) Fukui, K.; Kubo, T.; Nakazawa, S.; Aoki, T.; Morita, Y.; Yamamoto, K.; Sato, K.; Shimi, D.; Nakasuji, K.; Takui, T. *Synth. Met.* **2001**, 121, 1824–1825.
- (8) Morgenthaler, J.; Ruchardt, C. *Eur. J. Org. Chem.* **1999**, 2219–2230.
- (9) Lewis, I. C.; Kovac, C. A. *Carbon* **1978**, 16, 425–429.
- (10) Lewis, I. C.; Singer, L. S. *Magn. Reson. Chem.* **1985**, 23, 698–704.
- (11) Yamamura, K.; Miyake, H. *J. Org. Chem.* **1986**, 51, 251–253.
- (12) Suenaga, M.; Miyahara, Y.; Shimizu, N.; Inazu, T. *Angew. Chem., Int. Ed.* **1998**, 37, 90–91.
- (13) (a) Streitwieser, A., Jr.; Word, J. M.; Guibe, F.; Wright, J. S. *J. Org. Chem.* **1981**, 46, 2588–2589. (b) van Dijk, J. T. M.; van de Panne, B. J.; Bleeker, A. C.; Lugtenburg, J.; Cornelisse, J. *Tetrahedron* **1996**, 52, 2647–2662.
- (14) Reid, D. H.; Bonthron, W. J. *Chem. Soc.* **1965**, 5920–5926.
- (15) Hara, O.; Tanaka, K.; Yamamoto, K.; Nakazawa, T.; Murata, I. *Tetrahedron Lett.* **1977**, 28, 2435–2436.
- (16) Hara, O.; Yamamoto, K.; Murata, I. *Tetrahedron Lett.* **1977**, 28, 2431–2434.
- (17) Yamamoto, K.; Matsue, Y.; Hara, O.; Murata, I. *Tetrahedron Lett.* **1982**, 23, 877–880.
- (18) (a) Rhee, Y. M.; Lee, T. J.; Gudipati, M. S.; Allamandola, L. J.; Head-Gordon, M. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, 104, 5274–5278. (b) Hudgins, D. M.; Bauschlicher, C. W., Jr.; Allamandola, L. J. *Spectro-*

- chim. Acta* **2001**, 57A, 907–930. (c) Weisman, J. L.; Lee, T. J.; Head-Gordon, M. *Spectrochim. Acta* **2001**, 57A, 931–945.
- (19) Gordon, M.; Davison, W. H. T. *J. Chem. Phys.* **1952**, 20, 428–435.
- (20) Dias, J. R.; Cash, G. C. *J. Chem. Inf. Comput. Sci.* **2001**, 41, 129–133.
- (21) (a) Pogodin, S.; Agrat, I. *J. Org. Chem.* **2003**, 68, 2720–2727. (b) Dias, J. R. *Phys. Chem. Chem. Phys.* **1999**, 1, 5081–5086. (c) Baumgarten, M.; Karabunarliev, S. *Chem. Phys.* **1999**, 244, 35–47. (d) Hall, G. G.; Dias, J. R. *J. Math. Chem.* **1989**, 3, 233–242.
- (22) Mondal, R.; Adhikari, R. M.; Shah, B. K.; Neckers, D. C. *J. Am. Chem. Soc.* **2006**, 128, 9612–9613.
- (23) (a) Guihery, N.; Maynaud, D.; Malrieu, J.-P. *New J. Chem.* **1998**, 281–286. (b) Kubo, T.; Shimizu, A.; Sakamoto, M.; Uruichi, M.; Yakushi, K.; Nakano, M.; Shiomi, D.; Sato, K.; Takui, T.; Morita, Y.; Nakasuji, K. *Angew. Chem., Int. Ed.* **2005**, 44, 6564–6568.
- (24) (a) Gerson, F.; Knöbel, J.; Metzger, A.; Murata, I.; Nakasuji, K. *Helv. Chim. Acta* **1984**, 67, 934–939. (b) Kubo, T.; Shimizu, A.; Uruichi, M.; Yakushi, K.; Nakano, M.; Shiomi, D.; Sato, K.; Takui, T.; Morita, Y.; Nakasuji, K. *Org. Lett.* **2007**, 9, 81–84.
- (25) (a) Clar, E. *The Aromatic Sextet*; Wiley: London, 1972. (b) Balaban, A. T.; Schmalz, T. G. *J. Chem. Inf. Model.* **2006**, 46, 1563–1579. (c) Dias, J. R. *J. Chem. Inf. Model.* **2007**, 47, 20–24. (d) Balaban, A. T.; Schleyer, P. v. R.; Rzepa, H. S. *Chem. Rev.* **2005**, 105, 3436–3447.
- (26) (a) Brinkmann, G.; Caporossi, G.; Hansen, P. *J. Chem. Inf. Comput. Sci.* **2003**, 43, 842–851. (b) Brinkmann, G.; Grothaus, C.; Gutman, I. *J. Math. Chem.* **2007**, 42, 909–924.
- (27) Brunvoll, J.; Cyvin, B. N.; Cyvin, S. J. *Top. Curr. Chem.* **1992**, 162, 181–221.
- (28) Xiaofeng, G.; Fiji, Z.; Brunvoll, J.; Cyvin, B. N.; Cyvin, S. J. *J. Chem. Inf. Comput. Sci.* **1995**, 35, 226–232.
- (29) Dias, J. R. *J. Mol. Struct.: THEOCHEM* **1986**, 137, 9–29.
- (30) Dias, J. R. *J. Chem. Inf. Comput. Sci.* **2000**, 40, 810–815.
- (31) Dias, J. R. *J. Chem. Inf. Comput. Sci.* **2001**, 41, 686–691.
- (32) Hosoya, H.; Uchiyama, A.; Kadota, M.; Chida, K.; Aida, M.; Yamaguchi, T. *Nat. Sci. Rep. Ochanomizu Univ.* **1986**, 37, 133–168.
- (33) (a) Dias, J. R. *Polycyclic Aromat. Compd.* **2002**, 22, 353–357. (b) Dias, J. R. *Chemist* **2002**, 79, 17–24. (c) Dias, J. R. *Aust. J. Chem.* **2004**, 57, 1039–1049. (d) Dias, J. R. The Periodic Table Set as a Unifying Concept in Going from Benzenoid Hydrocarbons to Fullerene Carbons. In *The Periodic Table: Into the 21st Century*; Rouvray, D. H., King, R. B., Eds.; Research Studies Press Ltd.: Baldock, Hertfordshire, England, 2004; pp 371–396.
- (34) (a) Dias, J. R. *J. Chem. Inf. Comput. Sci.* **1990**, 30, 251–256. (b) Dias, J. R. *J. Mol. Struct.: THEOCHEM* **1991**, 230, 155–190.
- (35) Yoshida, M.; Fujita, M.; Fowler, P. W.; Kirby, E. C. *J. Chem. Soc., Faraday Trans.* **1997**, 93, 1037–1043.
- (36) Li, S.; Ma, J.; Jiang, Y. *J. Phys. Chem. A* **1997**, 101, 5587–5592.
- (37) Randić, M. *Chem. Rev.* **2003**, 103, 3449–3605.
- (38) (a) Dietz, F.; Tyutyukov, N.; Madjarova, G.; Müllen, K. *J. Phys. Chem. B* **2000**, 104, 1746–1761. (b) Dietz, F.; Tyutyukov, N. *Chem. Phys. Lett.* **1999**, 246, 255–265. (c) Tyutyukov, N.; Madjarova, G.; Dietz, F.; Müllen, K. *J. Phys. Chem. B* **1998**, 102, 10183–10189.
- (39) Babic, D. *J. Math. Chem.* **1993**, 12, 137–146.
- (40) Morikawa, T.; Narita, S.; Shibuya, T. *Chem. Phys. Lett.* **2003**, 375, 191–195.
- (41) Dias, J. R. *J. Chem. Inf. Model.* **2007**, 47, 707–715.
- (42) Cyvin, S. J.; Brunvoll, J. *Chem. Phys. Lett.* **1991**, 176, 413–416.
- (43) Gutman, I.; Cmiljanović, N.; Milosavljević, S.; Radenković, S. *Monatsh. Chem.* **2004**, 135, 765–772.
- (44) Dias, J. R. *Molecular Orbital Calculations Using Chemical Graph Theory*; Springer-Verlag: Berlin, Germany, 1993.
- (45) Dias, J. R. *Mol. Phys.* **1995**, 85, 1043–1060.
- (46) Dias, J. R. *J. Mol. Struct.: THEOCHEM* **1988**, 165, 125–148.
- (47) (a) Klein, D. J.; March, N. H. *Int. J. Quantum Chem.* **2001**, 85, 327–344. (b) Ivanciuc, O.; Klein, D. J.; Bytautas, L. *Carbon* **2002**, 40, 2063–2083. (c) Ivanciuc, O.; Bytautas, L.; Klein, D. J. *J. Chem. Phys.* **2002**, 116, 4735–4748.
- (48) Longuet-Higgins, H. C. *J. Chem. Phys.* **1950**, 18, 265–274.
- (49) Dewar, M. J. S. *The Molecular Orbital Theory of Organic Chemistry*; McGraw-Hill: New York, 1969.
- (50) (a) Herndon, W. C. *Tetrahedron* **1973**, 29, 3–12. (b) Cash, G. G.; Dias, J. R. *J. Math. Chem.* **2001**, 30, 429–444.
- (51) (a) Hall, G. G. *Theor. Chim. Acta* **1988**, 73, 425–435. (b) Dias, J. R. *J. Chem. Inf. Comput. Sci.* **1990**, 30, 251–256.
- (52) Cyvin, S. J.; Brunvoll, J.; Chen, R. S.; Cyvin, B. N.; Zhang, F. J. *Theory of Coronoid Hydrocarbons II. Lecture Notes in Chemistry*; Springer-Verlag: Berlin, Germany, 1994; Vol. 62.
- (53) Wu, J.; Pisula, W.; Müllen, K. *Chem. Rev.* **2007**, 107, 718–747.
- (54) Dias, J. R. *J. Chem. Inf. Model.* **2005**, 45, 562–571.
- (55) Kastler, M.; Schmidt, J.; Pisula, W.; Sebasriani, D.; Müllen, K. *J. Am. Chem. Soc.* **2006**, 128, 9526–9534.