

Partitioning of π -Electrons in Rings of Polycyclic Conjugated Hydrocarbons. 5. Nonalternant Compounds[†]

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All possible nonalternant hydrocarbons with a total of two, three, or four 5-, 6-, and 7-membered rings have been examined for the partition of their π -electrons by averaging over all Kekulé structures (considered to contribute equally to the electron distribution) the π -electrons in each ring in accordance to the rules introduced earlier: for each double bond shared with another ring one π -electron is taken into account, and for double bonds that are not shared two π -electrons are added. The trends observed for the partitions are discussed, and a comprehensive bibliography is provided as Supporting Information for all such systems, including both experimental and theoretical published data.

INTRODUCTION

In the previous three Parts of this series we have examined how different rings of a benzenoid hydrocarbon (catafused, coronoids, and perifused) may be assigned their corresponding *averaged part of the π -electrons* if in a Kekulé structure any shared π -electron pair is divided equally between the two condensed rings, and any unshared π -electron pair is assigned entirely to one benzenoid ring. The overall partition is obtained by averaging over all Kekulé structures, which are assigned equal weight. The present Part 5 of the series continues by discussing nonbenzenoid nonalternant catacondensed and pericondensed conjugated hydrocarbons, which can be aromatic, antiaromatic, or somehow in between. We shall limit the discussion to nonbenzenoid Kekuléan systems having two, three, or four 5-, 6-, and 7-membered rings that do not introduce significant steric strain in planar conjugated hydrocarbons. Also, neither charged hydrocarbons (cationic or anionic) nor heterocyclic analogues will be included in the present discussion.

As a general rule, Kekuléoid catacondensed systems (and pericondensed hydrocarbons, each of whose pericondensed rings has two internal vertices) must have rings whose sizes sum up to an even number. Pericondensed systems with one internal vertex must have rings whose sizes sum up to an odd number. Whereas benzenoid hydrocarbons may have many Kekulé structures, in the present case all the nonalternant systems that have been examined have between two and six Kekulé structures.

In Table 1 we present the ring sizes of all possible bi-, tri-, and tetracyclic nonbenzenoid hydrocarbons that obey the above restrictions. The formulas of all nonbenzenoid systems discussed in the present paper, and their numbering

Table 1. Nonbenzenoid Aromatics Discussed in the Present Paper

ring size	sum of sizes	catafused nonalternant systems			perifused nonalternant systems		
		internal vertices	compd	isomers	internal vertices	compd	isomers
5,5	10	0	1	1 ^a		none	0
5,7	12	0	2	1 ^{a,b}		none	0
7,7	14	0	3	1 ^a		none	0
5,5,5	15		none	0	1	4	1
5,5,6	16	0	5–7	3 ^a		none	0
5,5,7	17	0	none	0	1	8	1
5,6,6	17		none	0	1	9	1
5,6,7	18	0	10–14	5 ^{a,b}		none	0
5,7,7	19		none	0	1	15	1
6,6,7	19		none	0	1	16	1
6,7,7	20	0	17–20	4 ^a		none	0
5,5,5,5	20	0	21, 22	2 ^a	2	23	1 ^a
7,7,7	21		none	0	1	24	1
5,5,5,6	21		none	0	1	25, 26	2
5,5,5,7	22	0	27–33	7 ^a	2	34, 35	2 ^a
5,5,6,6	22	0	36–48	13	2	49–51	3
5,5,6,7	23		none	0	1	52–62	11
5,6,6,6	23		none	0	1	63–656	4
5,5,7,7	24	0	67–84	18 ^{a,b}	2	85–87	3 ^a
5,6,6,7	24	0	88–112	25 ^b	2	113–116	4
5,6,7,7	25		none	0	1	117–130	14
6,6,6,7	25		none	0	1	131–135	5
5,7,7,7	26	0	136–149	14 ^a	2	150, 151	2 ^a
6,6,7,7	26	0	152–171	20	2	172–174	3
6,7,7,7	27		none	0	1	175–180	6
7,7,7,7	28	0	181–188	9 ^a	2	189	1 ^a

^a All isomers have integer partitions. ^b Aromatic systems.

corresponding to Table 1, are displayed in Figure 1. Partitions were easily calculated either from Pauling bond orders or directly as the average of partitions for all Kekulé structures (assuming that each of them contributes equally to the resonance hybrid), because the numbers of Kekulé structures are so low.

Whereas the previous Parts of this series discussed only aromatic polycyclic benzenoids,^{1–3} in the present paper we include also antiaromatic systems such as pentalene (**1**) and heptalene (**3**), as well as systems with special HOMO–LUMO situations such as **21, 22, 75, 76, 181–187**.^{4–12} There

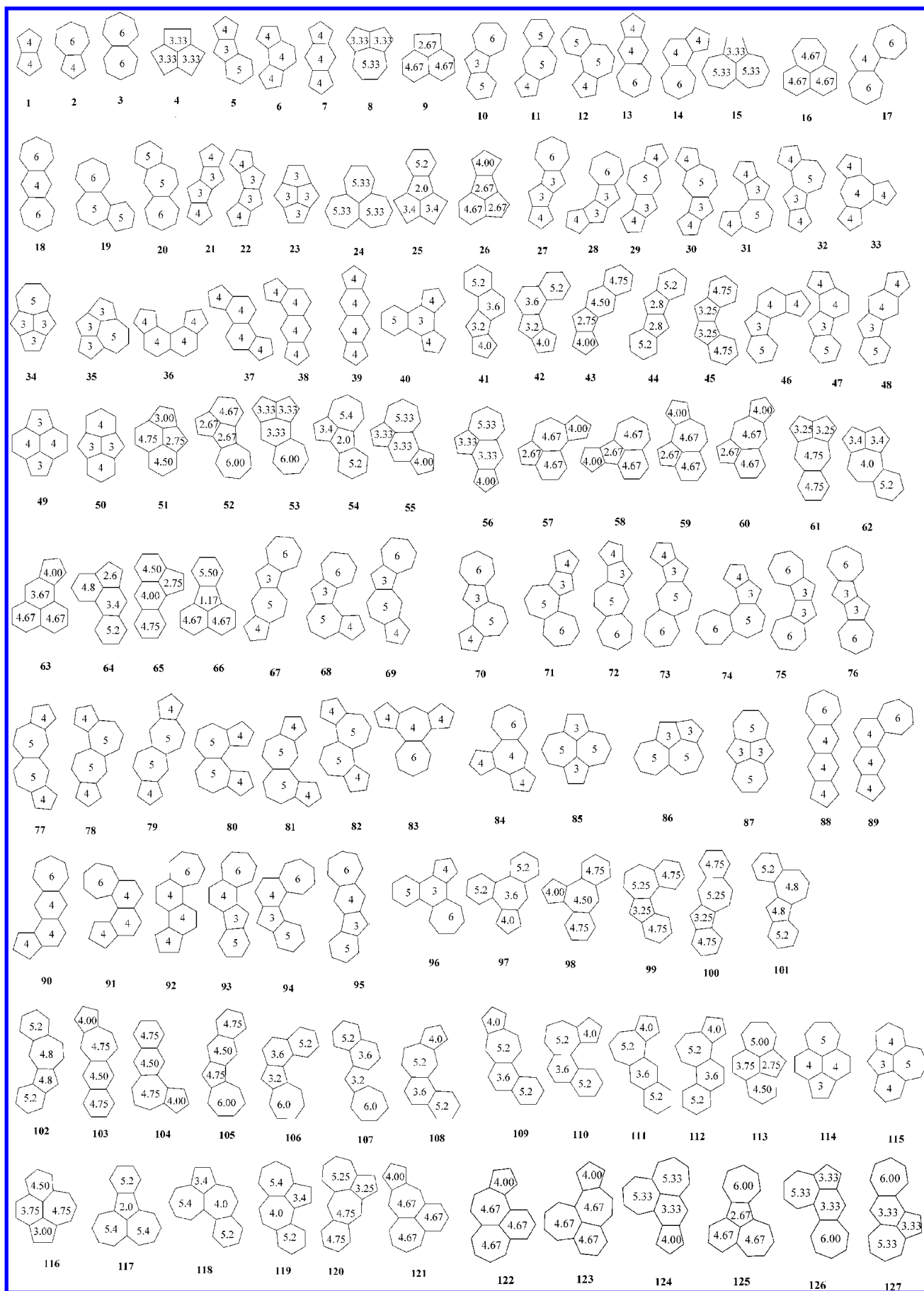
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[†] The previously used title in Part 2 of this series (*Partitioning of π -Electrons in Rings of Polycyclic Benzenoid Hydrocarbons*) has been changed (replacing *Benzenoid* by *Conjugated*).

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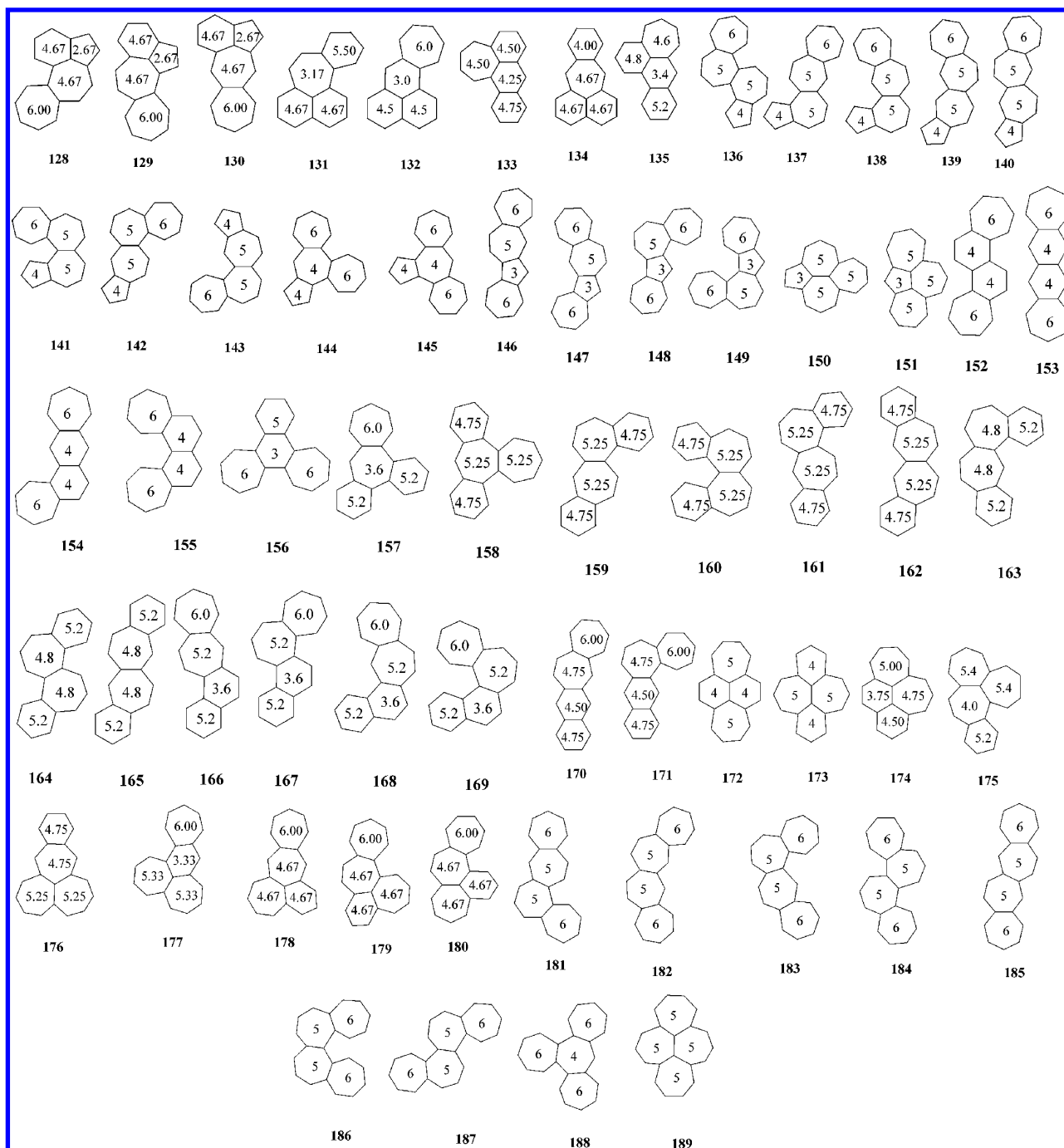


Figure 1. Structures of the 189 nonalternant conjugated hydrocarbons containing two, three, or four 5-, 6-, and/or 7-membered rings. Part of the π -electrons is inscribed in each ring.

exist many monographs on the aromaticity of benzenoid compounds that have been cited in previous Parts of this series. The problems connected with the aromaticity of nonbenzenoid nonalternant hydrocarbons were reviewed in fewer monographs and reviews.^{13–26}

Table 2 provides common and IUPAC names of some of the nonalternant hydrocarbons from Table 1 and Figure 1. In the Supporting Information we provide an extensive bibliography for many of the compounds contained in Figure 1 and some of their substituted derivatives with their names, irrespective of their stability (many early references for antiaromatic unsubstituted compounds were only theoretical calculations). However, by using kinetic stabilization by means of bulky substituents or electronic push–pull substitu-

tion, some of the antiaromatics could be obtained and studied in Hafner's,²⁷ Paquette's,²⁸ Dauben's,²⁹ Vogel's research groups,³⁰ and other research laboratories. Using special techniques even the very unstable unsubstituted pentalene could be trapped.³¹

DISCUSSION

Several interesting observations may be made on considering Figure 1. We shall use the term “part” for the components of the partition. First, it is striking that many systems have only integer parts in the partition of the π -electrons in each ring of the system, namely 101 out of 189 systems, i.e., about 53%. As seen from Table 1, for the nonalternant hydrocarbons examined here with two, three, or four 5-, 6-, and

Table 2. Common and IUPAC Names of Some Nonalternant Aromatics

compd	formula	name
1	C ₈ H ₆	pentalene
2	C ₁₀ H ₈	azulene
3	C ₁₂ H ₁₀	heptalene
4	C ₁₀ H ₆	acepentalene
5	C ₁₂ H ₈	benzopentalene (cyclopent[<i>a</i>]indene)
6	C ₁₂ H ₈	<i>as</i> -indacene (cyclopent[<i>e</i>]indene)
7	C ₁₂ H ₈	<i>s</i> -indacene (cyclopent[<i>f</i>]indene)
8	C ₁₂ H ₈	aceazulene (cyclopent[<i>cd</i>]azulene)
9	C ₁₂ H ₈	acenaphthylene
10	C ₁₄ H ₁₀	benz[<i>a</i>]azulene
11	C ₁₄ H ₁₀	benz[<i>f</i>]azulene
12	C ₁₄ H ₁₀	benz[<i>e</i>]azulene
15	C ₁₄ H ₁₀	aceheptylene (cyclopenta[<i>ef</i>]heptalene)
16	C ₁₄ H ₁₀	pleiadylene (pleiadene, cyclohepta[<i>de</i>]-naphthalene)
19	C ₁₆ H ₁₂	benzo[<i>a</i>]heptalene
20	C ₁₆ H ₁₂	benzo[<i>b</i>]heptalene
21	C ₁₄ H ₁₀	pentaleno[2,1- <i>a</i>]pentalene
22	C ₁₄ H ₁₀	pentaleno[1,2- <i>a</i>]pentalene
23	C ₁₂ H ₆	dicyclopenta[<i>cd,gh</i>]pentalene
40	C ₁₆ H ₁₀	benz[<i>c</i>]- <i>as</i> -indacene
44	C ₁₆ H ₁₀	dibenzo[<i>a,e</i>]pentalene (indeno[2,1- <i>a</i>]indene)
45	C ₁₆ H ₁₀	dibenzo[<i>a,d</i>]pentalene (indeno[1,2- <i>a</i>]indene)
49	C ₁₄ H ₈	pyracylene (cyclopenta[<i>fg</i>]acenaphthylene)
50	C ₁₄ H ₈	cyclopenta[<i>def</i>]fluorene
51	C ₁₄ H ₈	cyclopent[<i>bc</i>]acenaphthylene
64	C ₁₆ H ₁₀	acephenanthrylene
65	C ₁₆ H ₁₀	aceanthrylene
66	C ₁₆ H ₁₀	fluoranthene (benz[<i>a</i>]acenaphthylene)
85	C ₁₆ H ₁₀	azupyrene (dicyclopenta[<i>ef,kl</i>]heptalene)
86	C ₁₆ H ₁₀	<i>as</i> -azupyrene (pentaleno[2,1,6- <i>def</i>]heptalene)
87	C ₁₆ H ₁₀	isopyrene (dicyclohepta[<i>cd,gh</i>]pentalene, azuleno-[2,1,8- <i>ija</i>]azulene)
113	C ₁₆ H ₁₀	cyclohepta[<i>ab</i>]benz[<i>cd</i>]indene (cyclohept[<i>bc</i>]-acenaphthylene)
114	C ₁₆ H ₁₀	acepleiadylene (cyclohept[<i>fg</i>]acenaphthylene)
115	C ₁₆ H ₁₀	cyclohepta[<i>def</i>]fluorene
116	C ₁₆ H ₁₀	naphthazulene (cyclohepta[<i>klm</i>]benz[<i>e</i>]indene)
131	C ₁₈ H ₁₂	benzo[<i>e</i>]pleiadylene (benzo[4,5]cyclohepta-[1,2,3- <i>de</i>]naphthalene)
132	C ₁₈ H ₁₂	cyclohepta[<i>a</i>]phenalene
134	C ₁₈ H ₁₂	benzo[<i>f</i>]pleiadylene
150	C ₁₈ H ₁₂	dicyclohept[<i>cd,ij</i>]azulene
151	C ₁₈ H ₁₂	azuleno[2,3,4- <i>jkl</i>]heptalene
172	C ₁₈ H ₁₂	dipleiadene

7-membered rings there are 123 catacondensed and 67 pericondensed systems. The latter have either one or two internal carbon atoms.

We will discuss first *systems with integer partitions*, namely those indicated in Table 1 by superscript *a* (which have exclusively integer parts) and also some other systems belonging to the same set of isomers but having also isomers with noninteger partitions among this set. Such systems are indicated in Figure 1 by parts without decimal points. Catacondensed systems with integer partition can either have a *string-like structure*, where no ring is condensed with more than two other rings, or a *branched structure* otherwise. This is illustrated by string-like compounds **1–3**, **5–7**, **10–14**, **17–22**, **27–32**, **36–39**, **46–48**, **67–82**, **88–95**, **136–143**, **146–149**, **152–155**, **181–187** and by branched systems: compounds **33**, **40**, **83**, **84**, **96**, **144**, **145**, **156**, **188**.

In catacondensed nonbranched polycyclic rings with the bonds of fusion having Pauling bond orders (PBOs) equal to one (i.e. zero π -bond character), which will be henceforth called “zero” bonds, the two terminal *m*-membered rings (where *m* is a generic number that may vary from one ring

to another) have parts equal to $m - 1$, and the internal ring or rings (if any) have parts equal to $m - 2$. This is easy to interpret, as a terminal ring has $m - 2$ nonshared carbon atoms (each contributing one π -electron) and one shared bond adding one more π -electron; an internal ring in a string of catacondensed ring shares two bonds, hence its part is $m - 2$. For branched catacondensed tetracyclic rings with exclusively integer parts, the three terminal rings have parts equal to $m - 1$ (explained as for terminal rings in string-like systems), whereas the central ring has part $m - 3$ (because the central ring has $m - 6$ nonshared carbon atoms, each contributing one π -electron, and six shared carbon atoms adding three more electrons). It may be observed that exclusively integer parts also appear for catacondensed string-like tetracyclic systems with (i) pairwise odd- and even-membered rings arranged with outer odd-membered rings and inner even-membered rings or (ii) odd-even-odd-even arrangement of *m*-membered rings.

For tetracyclic pericondensed systems with exclusively integer parts having two internal vertices that can give rise to an inner “double” bond (compounds **23**, **34**, **35**, **49**, **50**, **85–87**, **114**, **115**, **150**, **151**, **172**, **173**, **189**), all rings have parts equal to $m - 2$. It can be seen that such tetracyclic systems have (i) only odd-membered rings or (ii) pairwise odd- and even-membered rings with the inner bond shared by rings of the same parity.

Next, we arrive at *systems with noninteger parts (which may have, in addition, integer parts)*. This includes the case of tetracyclic string-like catacondensed systems with pairwise odd- and even-membered rings, namely compounds **44**, **45**, **99–102**, **159–165** that have outer even-membered rings and inner odd-membered rings) and **41–43**, **103–112**, **166–171** (with odd-odd-even-even arrangement of ring sizes).

Let us look at what happens when a benzenoid (six-membered) ring becomes annelated to the marginal ring of a tricyclic system resulting in a string-like catacondensed tetracyclic compound. The resulting π -electron part of the “extra benzenoid ring” depends on the Pauling bond order (PBO) of the bond of fusion in the tricyclic compound. When there are several nonequivalent bonds in the tricyclic compound that may be shared with the “extra benzenoid ring”, different partitions of π -electrons will be obtained for the resulting tetracyclic system. We start by examining string-like catacondensed tetracyclic compounds. The “extra benzenoid ring” has a part equal to 5.2 π -electrons when the bond of fusion has a higher PBO, but only 4.75 π -electrons when the bond of fusion has a lower PBO. Examples for the former case are compounds **41**, **42**, **44**, **101**, **102**, **106–112**, **163–169**, and for the latter case compounds **43**, **45**, **99**, **100**, **103–105**, **159–162**, **170**, **171**. Continuing with branched catacondensed tetracyclic compounds, again we have as examples for the former case compounds **97**, **157**, and for the latter case compounds **98**, **158–160**. Pericondensed tetracyclic systems obtained by annelating tricyclic systems that share a single vertex among all three rings also present the same two values for the part of the “extra benzenoid ring”: 5.2 π -electrons for compounds **54**, **62**, **64**, **117–119**, **135**, **175** and 4.75 π -electrons for compounds **61**, **65**, **120**, **133**, **176**.

The explanation lies in the PBO of the bond of fusion of the tricyclic system. Two fused odd-membered rings have a “zero-bond” for their bond of fusion, and this “zero-bond”

can be ignored when one looks at the π -electron partition, leaving an annulene with periphery of the fused odd-membered rings. Then one can easily obtain the PBOs for catafusenes; for tricyclic systems that share a single vertex, their bonds of fusion can be either at a distance that involves an odd number of edges from the “triple point”, when the PBO is higher, or an even number of edges from the “triple point”, when the PBO is lower.

The same idea may be expressed in a different way. We begin by recalling what was discussed in the first part of this series.¹ On annelating benzene with one extra benzenoid ring to obtain naphthalene, the resulting partition of the 10 π -electrons in the naphthalene rings becomes 5 + 5, meaning that the extra benzenoid ring gets 5 electrons (from its two double bonds and the shared double bond) and the initial benzene ring loses one π -electron because of the shared bond.

When two terminal benzenoid rings are condensed with an intermediate system, they get a larger share of the π -electrons (if, in any Kekulé structure of this intermediate system, both bonds of the intermediate system to which the two terminal benzenoid rings are condensed are double bonds) than when only one is a double bond. This was exemplified for alternant aromatics by comparing phenanthrene (whose two terminal rings have 5.2 π -electrons) with anthracene (the two terminal rings of which have 4.75 π -electrons). One can see that both terminal rings of phenanthrene get 0.2 electrons more than the “normal share” of five π -electrons, and the intermediate ring loses more than the “normal share” of two π -electrons; by contrast the terminal rings of anthracene gain less than the “normal share” of five π -electrons, and the middle ring loses less than the “normal share” of two π -electrons. Exactly the same figures are observed for nonalternant systems by comparing compounds **101–102** with **99–100**, in which the intermediate system is azulene. A similar situation occurs when the intermediate system is pentalene (compare **44** with **45**) or heptalene (compare **163–165** with **159–162**, and **157** with **158**). Also, when only one benzenoid ring is attached to a conjugated hydrocarbon, this annelated benzenoid ring gains more electrons than its “normal share” when it shares a bond with a higher Pauling bond order than when it shares a bond with a lower bond order. This is illustrated by comparing catacondensed systems: **106–112** with **103–105**; **166–169** with **170–171**; **175** with **176**; and pericondensed systems: **133** with **135**; **117–119** with **120**; **62**, **64** with **61**, **65**.

In fullerenes, the Stone-Wales rearrangement is able to automerize pyracylene units;^{32,33} it was found that it can also isomerize azupyrene to pyrene (by a convolute mechanism),³⁴ and this type of isomerization could be generalized theoretically.³⁵ Also, other theoretical connections between alternant and nonalternant hydrocarbons are obtained by connecting carbon atoms of annulenes via zero-atom bridges: cyclo-decapentaene thus gives rise either to alternant hydrocarbons (naphthalene, bicyclo[4.2.0]decapentaene,^{36–38} or even cyclodecatetraene-yne) or to nonalternants, namely azulene and bicyclo[5.1.0]decapentaene. Since azulene has only two Kekulé structures, it has equal PBOs for all its peripheral bonds, and its annelation with one benzenoid ring leads to simple integer partitions, as seen for compounds **10–12**. By annelating bicyclo[4.2.0]decapentaene with one benzenoid ring the initial partition (three π -electrons for the four-membered ring and five π -electrons for the eight-membered

ring) changes according to the PBO of the fusion bond: an excess of 0.2 π -electrons for the terminal rings in the case of linear annelation (higher PBO for the bond of fusion in the initial bicyclic compound) but a deficit of 0.25 π -electrons for the terminal rings in the case of annelation to bonds of fusion with the lower PBO. This parallels exactly what happens on annelating naphthalene, as discussed above.

On going from conjugated hydrocarbons to their hetero-analogues, which can be electron-excessive or electron-deficient, the electronic effects of the heteroatom(s) will affect the partition in predictable ways.³⁹ This idea, as well as the effect of electron-donor or electron-acceptor substituents that mimic the effect of heteroatoms (and vice-versa), will be examined in a future paper.

AROMATICITY. KEKULÉ, FRIES, AND CLAR STRUCTURES. PARTITION OF π -ELECTRONS AND LOCAL AROMATICITIES

For catacondensed polycyclic conjugated hydrocarbons, with a few exceptions that will be discussed below, the Hückel Rule applied to the perimeter holds: systems that have odd numbers of double bonds (or $4n + 2$ π -electrons, where n is a natural integer) on the continuously conjugated periphery are aromatic, and those with even numbers of double bonds (or $4n$ π -electrons) are antiaromatic.⁴⁰ The exceptions appear when strained 3- or 4-membered rings are formed by the zero-atom bridges between the peripheral carbon atoms, as in bicyclo[6.2.0]decapentaene, and *a fortiori* bicyclo[7.1.0]decapentaene. A different type of exception appears when bonding orbitals are vacant, or antibonding orbitals are occupied as noted for the first time by Bochvar, Stankevich, and Tutkevich for compound **21**,⁴¹ and studied later by several research groups.^{4–12}

For benzenoids, the set of all possible Kekulé structures, as well as the Fries and Clar structures graphically convey information about the distribution of π -electrons. (One may recall that a Fries structure of an aromatic benzenoid has the maximum possible rings with three double bonds, e.g. one of the $K = 3$ possible Kekulé structures of naphthalene, one of the $K = 5$ structures for phenanthrene, and so on for all the following fibonacenes, one of the 12,500 Kekulé structures for buckminsterfullerene). However, a more detailed picture is provided, in numerical form, by the partition of π -electrons, which accounts for local aromaticity of rings, as will be shown in detail in the next part of this series, which will present comparisons with other methods for computing local aromaticity.

For catacondensed benzenoids (or for coronoids, whose aromaticity is an established fact) the partition of π -electrons in an individual ring gives an indication on the availability of π -electrons and on their tendency to undergo preferentially either electrophilic substitution or addition. Thus, benzene with 6 π -electrons and naphthalene with 5 π -electrons in each ring undergo substitution, but anthracene and phenanthrene may react either by addition in the middle ring with the lower partition or by substitution. For fibonacenic coronoids (which were discussed in Part 2 of the present series³ and in which each ring has a part equal to four π -electrons) or for isoarithmic catafusenes that have no anthracenic subgraphs (zigzag catafusenes such as chrysene, picene, etc., or helicenes) with parts close to 4 π -electrons

in each ring, substitutions are the preferred pathway. It was shown in Part 3 of the present series that in pericondensed benzenoids there are rings whose part can be close to one π -electron.² In a pericondensed benzenoid system with many rings such as a graphene sheet, the marginal (borderline) rings have 3 π -electrons and the internal rings have 2 π -electrons, but the shape of the borderline (zigzag or armchair) influences the borderline rings.⁴²

Now, coming to nonalternants that have been examined in the present paper, the same rules apply. This is what motivated us to indicate in Table 1 that catacondensed systems are aromatic when they have C cycles and sums S of ring sizes, resulting in odd numbers (D = 5, 7, and 9) of double bonds. A simple relationship connects these three integers: $D = (S - 2C + 2)/2$. Of course, exceptions such as **21**, **22**, **181–187**, which have odd numbers of double bonds but “abnormal HOMO–LUMO situations”, do not have the footnote marking them as aromatic in Table 1.

In Part 4 of the present series it was shown that there may exist two or more polycyclic benzenoids with a given geometric Kekulé structure corresponding to the same algebraic Kekulé structure.⁴³

CONCLUSIONS

We have presented all possible Kekuléan nonalternant hydrocarbons with a total of two, three, or four 5-, 6-, and 7-membered rings with the partition of their π -electrons according to the conventions that (i) all Kekulé structures are assumed to contribute equally and that (ii) the average distribution of π -electrons in each ring over all these Kekulé structures can be calculated for each Kekulé structure by assigning to each ring two π -electrons for a nonshared double bond and one π -electron for a shared double bond. The same result can be computed using Pauling bond orders.

The Kekuléan nonalternants discussed in the present paper are systems with catacondensed rings, or with pericondensed rings having two internal vertices and ring sizes that sum up to an even number, or with pericondensed rings having one internal vertex and ring sizes that sum up to an odd number.

Among the 189 nonalternant systems presented in Figure 1 and Tables 1 and 2, more than half have exclusively integer parts in each ring. Trends in these partitions have revealed similarities with those discussed in previous parts of this series, which had dealt with catacondensed benzenoids,¹ pericondensed benzenoids,² and corona-condensed benzenoids.³ Previously, only for a restricted class of benzenoids had exclusively integer parts been found as a general case for fibonacenic coronoids.³ Differences from alternant compounds arise when noninteger parts are examined, and in this case some generalizations could be observed.

ACKNOWLEDGMENT

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Supporting Information Available: A detailed bibliography for experimental and theoretical papers associated with almost all the nonalternant hydrocarbons examined in the present paper. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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