

Partitioning of π -Electrons in Rings for Clar Structures of Benzenoid Hydrocarbons

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Received May 12, 2005

Resonance structures of polycyclic aromatic hydrocarbons can be associated with numerical formulas by assigning π -electrons of C=C double bonds to individual benzenoid rings. Each C=C double bond in a resonance structure assigns two π -electrons to a ring in a fused-benzenoid system if it is not shared by adjacent rings and one π -electron when it is common to two rings, obtaining thus a “local” characterization of rings in polycyclic conjugated hydrocarbons. In the present contribution we extend this approach to the aromatic π -sextet model of Clar, which offers an alternative description of benzenoid hydrocarbons. In this model local characteristics of individual benzenoid rings are based on partitioning of π -electrons but only for those resonance structures (fewer in number) that contribute to Clar’s formula of benzenoid hydrocarbons.

THE “CIRCLE” NOTATION OF CLAR

The catchy phrase “aromatic sextet” originated with Armit and Robinson,¹ who suggested in 1925 to collect π -electrons in benzenoids, when possible, into groups of six, which are located within single nonadjacent benzenoid rings. An inscribed circle within a ring on which it is located represents an aromatic π -sextet. It was Eric Clar who offered a body of experimental data in his book “*The Aromatic Sextet*”² that supported the π -sextet model. In Figure 1 we show Clar formulas for a selection of smaller benzenoid hydrocarbons. For historically relevant citations concerning the aromatic sextet, see refs 3 and 4.

One can observe three types of Clar formulas exhibited in Figure 1. Some benzenoid hydrocarbons (like triphenylene in Figure 1), called by Clar “fully benzenoid”, have only two types of rings: rings with π -sextets and “empty” rings; for some benzenoids (e.g., phenanthrene) one may have also rings with a single CC double bond; and finally there are benzenoids such as naphthalene or anthracene, in which there are benzenoid rings with two CC double bonds, and for which one can write two or more alternative Clar valence formulas. Following Clar, instead of listing additional Clar structures, one usually writes a single formula and indicates possibilities for multiple location of the aromatic sextet by adding an arrow to indicate the presence of the “migrating” sextets, as illustrated in Figure 2 for the same benzenoid hydrocarbons of Figure 1. Whenever such an arrow is present in a Clar formula, this is a sign that one can write more than one Clar structure. It will be observed that (except as in coronene) the benzenoids with arrows in Figure 2 have two double bonds in the same ring.

Clar structural formulas can be constructed following a simple “geometrical” rule:^{5,6} *Draw the maximal possible number of π -sextet-circles inscribed in nonadjacent rings*

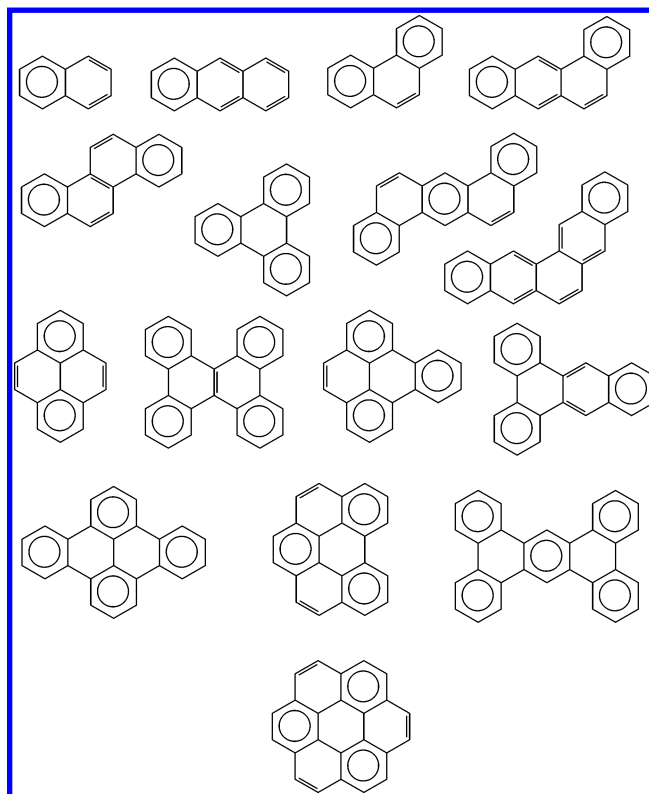


Figure 1. Clar valence structures for a collection of smaller benzenoid hydrocarbons. Several of the molecules have alternative additional Clar structures signifying “migrating” sextets (indicated by arrows in Figure 2).

subject to the requirement that the carbon atoms not involved in these rings should be coupled to form C=C double bonds.

Recently Klavžar, Zigert, and Gutman⁷ have demonstrated that in the case of cata-condensed benzenoid hydrocarbons one can find the number of π -aromatic sextets by constructing the smallest number of straight line segments that cross all benzenoid hexagons. Moreover, as has been pointed out by one of the present authors,^{5,8} if the crossing line segments

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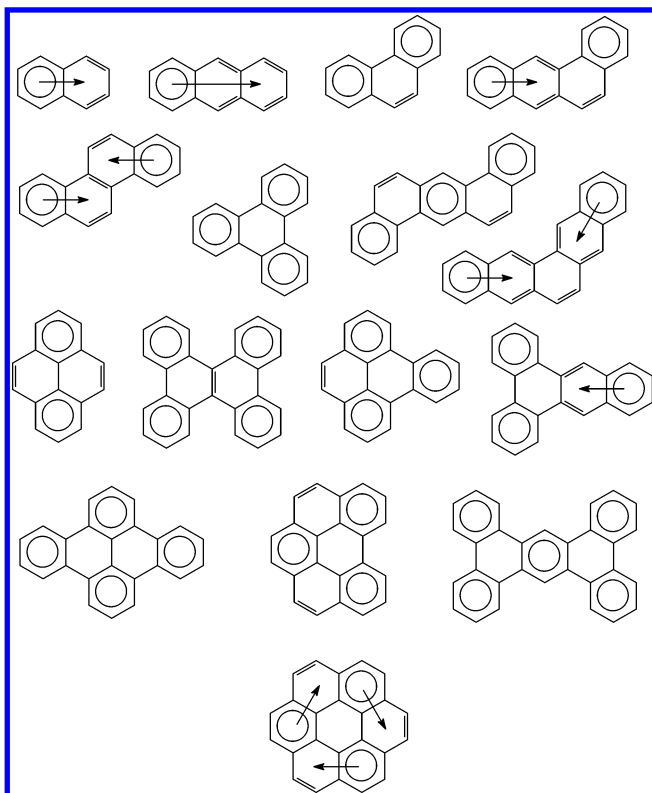


Figure 2. Clar structures with arrows indicating migrating sextets for the same selection of benzenoid hydrocarbons as in Figure 1, for which numerical values will be displayed in Figures 9 and 10. For benzenoids having a single Clar structure, we will prefer not to include arrows in such cases, although Clar did occasionally.

are drawn so as to afford the maximal number of crossings, the “crossing sites” indicate the benzenoid rings that cannot become sites of aromatic sextets. On the other hand, as illustrated in Figure 3 on a 14-ring cata-condensed benzenoid hydrocarbon, parts of segments that are not crossed indicate benzenoid rings that can assume the location of aromatic sextets. Moreover, if parallel lines occur in adjacent hexagons, this indicates the location of benzenoid rings that can be sites of aromatic sextets, but not simultaneously.

QUANTITATIVE RESONANCE FORMULAS OF BENZENOIDS

In view of the very long history behind the resonance formulas, it was only relatively recently that numerical resonance formulas have been introduced.^{9,10} Such numerical formulas offer some insights on the local properties of benzenoid hydrocarbons and conjugated polycyclic systems in general, including fullerenes.^{9–20} We illustrate in Figure 4 the construction of the numerical resonance structures on six symmetry-distinct resonance structures of coronene, which has $K = 20$ valence structures.

As we see from Figure 4, in each ring is inscribed an *integer* which signifies the partitioning of the 24 π -electrons of coronene to its seven rings. The integer represents the count of π -electrons associated with each ring, obtained according to the following rules:

- (1) Each C=C double bond not common to other rings contributes two π -electrons to the ring.
- (2) Each C=C double bond common to two rings contributes one π -electron to each ring.

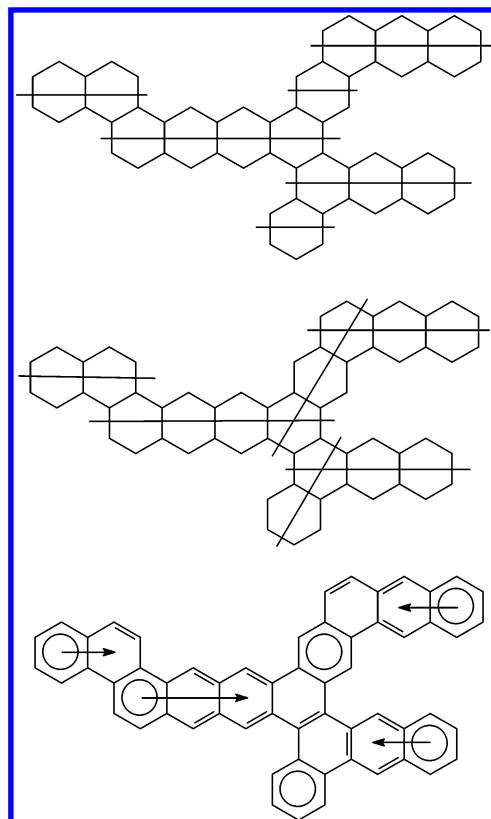


Figure 3. Graphical count of π -sextets in cata-condensed benzenoids illustrated on a 14-ring system with six straight lines crossing all rings. Top: with parallel lines. Middle: with lines having a maximal number of crossings. Bottom: Clar structure.

Hence the numbers inscribed in individual benzenoid rings have a simple structural meaning: *they count π -electrons within a ring*, taking into account that rings having common double bonds *share* π -electrons. As expected, for each resonance structure of coronene the total count of π -electrons in all rings adds to 24 π -electrons.

Numerical (or algebraic) resonance structures have some advantages over the traditional (geometric) resonance structures. Thus, they allow *simple computer manipulations* of resonance structures, and they also allow *less simple algebraic manipulations* of resonance valence structures. Consider the six symmetry nonequivalent resonance structures of coronene illustrated in Figure 4. With each structure we can associate a code, obtained by listing π -electron partitioning contents of individual rings in decreasing order. This, for the first resonance structure (A) we obtain: 4 4 4 4 4 0, because the central ring has no π -electron content (having all CC double bonds exocyclic to the central ring), while all the remaining benzenoid rings are associated with four π -electrons. Codes allow partial ordering of resonance structures based on the rules for construction of partial orders as set up by Muirhead and illustrated in Figure 5. To obtain an ordering of sequences, Muirhead suggested that one first constructs the sequences of partial sums of elements in the sequence and then considers dominance relations.^{21–25} Consider two sequences:

$$A = a_1, a_2, a_3, \dots, a_n$$

$$B = b_1, b_2, b_3, \dots, b_n$$

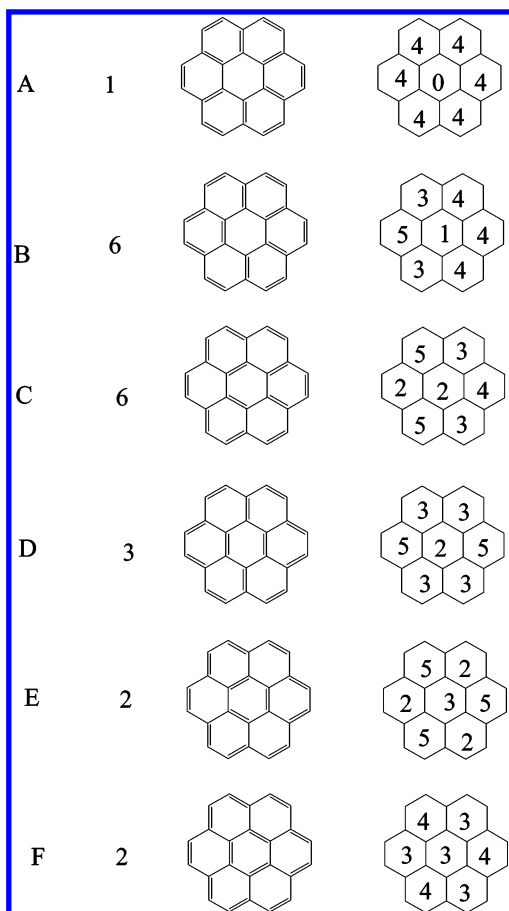


Figure 4. Numerical resonance structures for the six symmetry-distinct Kekulé structures of coronene. The second column lists the number of symmetry-equivalent resonance structures.

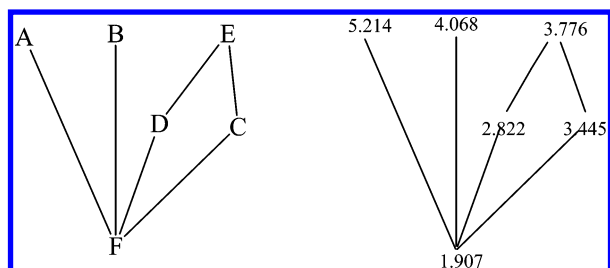


Figure 5. Partial ordering of symmetry-distinct resonance structures of coronene (left-hand column) and their contributions to molecular resonance energy (right-hand column).

If then the following inequalities are satisfied

$$a_1 \geq b_1$$

$$a_1 + a_2 \geq b_1 + b_2$$

$$a_1 + a_2 + a_3 \geq b_1 + b_2 + b_3$$

.....

$$a_1 + a_2 + a_3 + \dots a_n \geq b_1 + b_2 + b_3 + \dots b_n$$

one says that A dominates B, while if at least one of the inequalities is not satisfied, one says that A and B are not comparable (except in the case when in all inequalities \geq is replaced by \leq and in this case B dominates A). The diagram that depicts the dominance relationships is referred to as a

Hasse diagram. Partial orderings appear not to be sufficiently well recognized in many fields of chemistry for various applications. They have, however, found considerable use in various areas of mathematical chemistry,^{25–34} including applications of partial ordering for identifying pharmacophores in QSAR (Quantitative-Structure–Activity Relationship) studies^{35–38} and construction of periodic tables for isomers.^{39–43}

Partial orderings can offer qualitative pictures of trends in relative magnitudes of molecular properties when only partial data are available, which is of considerable importance in various structure–property/activity studies. For example, in the case of Figure 5 we can replace the structure labels A–F in the diagram of partial order at the left with a selected structure/property and discern the trend that dominates this particular property. We have illustrated in Figure 5 (on the right) the contributions of individual resonance structures to the molecular resonance energy (RE) as obtained using the conjugated circuits model.^{47–61} In this model, the molecular RE is obtained by adding contributions from individual resonance structures, which are obtained by counting conjugated circuits of different size. By using the following parameters, $R_1 = 0.869$ eV, $R_2 = 0.246$ eV, and $R_3 = 0.100$ eV for contributions of conjugates circuits of size 6, 10, and 14, respectively, we obtain the numerical values for contributions of resonance structures A–F as shown in Figure 5 at the right. The sequences of π -electron ring contents, their partial sums, and the expressions for the RE are shown in Table 1. It can be seen that both sides of Figure 5 agree with each other.

For most benzenoid hydrocarbons there is a one-to-one correspondence between the “geometrical” (i.e., the traditional) and “algebraic” (i.e., numerical) resonance structures. The exceptions include pyrene, perylene with some of their derivatives,⁹ and coronoid fibonacenes,¹² when a single numerical structure may correspond to two or more geometrical valence structures, but we have to emphasize that even in such cases one can reconstruct *all* geometrical valence structures from the numerical structures.

ALGEBRAIC RESONANCE STRUCTURES

By superposition of the 20 resonance structures of coronene we obtain the overall distribution of π -electrons in coronene. Thus one finds that four resonance structures (E and F in Figure 4) have the central ring of coronene with three assigned π -electrons, nine structures (C and D) have two π -electrons, six structures (B) one π -electron, and in one structure (A, also known as the Fries structure, see below) no π -electron is associated with the central ring. By summing the contributions of all 20 resonance structures we obtain as the average $36/20$ or 1.80 π -electrons associated with the central ring. This leaves 3.70 π -electrons associated with each of the six peripheral rings, giving the overall total of 24 π -electrons of coronene. As we see, in the case of coronene the peripheral benzenoid rings are visibly more “aromatic” than the central ring, which is consistent with the two Clar structures of coronene shown in Figure 6.

In Table 2 we illustrate the results of the analysis of the π -electron ring partitions for smaller fibonacenes, the family of catacondensed benzenoid hydrocarbons in which every rings is, in Gordon and Davison’s terminology,⁶² a “kink”

Table 1. π -Electron Ring Partition Sequence, Partial Sum Sequence, Conjugated Circuits Count, and Contribution of Resonance Structure to Molecular RE

	π -electron ring partition	partial sum sequence	conjugated circuits count	contribution to RE (in eV)
A	4, 4, 4, 4, 4, 0	4, 8, 12, 16, 20, 24, 24	$6R_1 + R_4$	5.214
B	5, 4, 4, 4, 3, 3, 1	5, 9, 13, 17, 20, 23, 24	$4R_1 + 2R_2 + R_1$	4.068
C	5, 5, 4, 3, 3, 2, 2	5, 10, 14, 17, 20, 22, 24	$3R_1 + 3R_2 + R_1$	3.445
D	5, 5, 3, 3, 3, 3, 2	5, 10, 13, 16, 19, 22, 24	$2R_1 + 4R_2 + R_1$	2.822
E	5, 5, 3, 3, 2, 2, 2	5, 10, 15, 18, 20, 22, 24	$4R_1 + 3R_3$	3.776
F	4, 4, 4, 3, 3, 3, 3	4, 8, 12, 15, 18, 21, 24	$R_1 + 3R_2 + 3R_1$	1.907

Table 2. Partitioning of π -Electrons into Individual Rings for Resonance Structures of Fibonacenes^a

fibonacene	R	A	B	C	D	sum
phenanthrene	3	26/5	18/5			14
chrysene	4	41/8	31/8			18
picene	5	67/13	49/13	54/13		22
fulminene	6	108/21	80/21	85/21		26
[7]-zigzag-fibonacene	7	175/34	129/34	139/34	134/34	30
[8]-zigzag-fibonacene	8	283/55	209/55	224/55	219/55	34

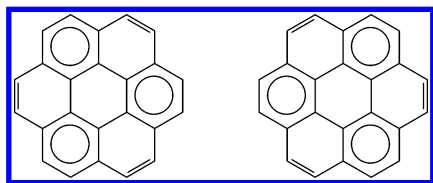
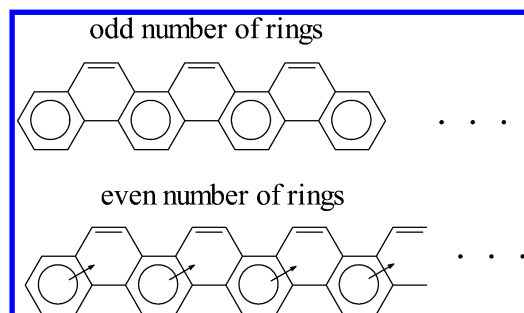
fibonacene	R	A	B	C	D	sum
phenanthrene	3	5.2000	3.6000			14
chrysene	4	5.1250	3.8750			18
picene	5	5.1538	3.7692	4.1538		22
fulminene	6	5.1429	3.8095	4.0476		26
[7]-zigzag-fibonacene	7	5.1471	3.7941	4.0882	3.9411	30
[8]-zigzag-fibonacene	8	5.1455	3.8000	4.0727	3.9818	34

^a R gives the number of fused rings, letters A, B,... denote individual rings starting from the left terminal ring

ring. In other words, fibonacenes are cata-condensed benzenoids devoid of anthracenic subgraphs, e.g helicenes or zigzag catafusenes. Fibonacenes with the same number of rings (R) have the same resonance structure count (which is a Fibonacci number), i.e., are “isoarithmic”,⁶³ or isoresonant.^{64,65} They have different geometric structures, but they share the same algebraic structure.

To obtain a quantitative structural formula for a benzenoid molecule we take the average of its numerical resonance structures, as has been already illustrated on coronene. It is instructive to look more closely into the partitioning of π -electrons of fibonacenes shown in Table 2, whose Clar structures are illustrated in Figure 7.

As we see from Table 2, for individual rings typically we obtain fractional π -electron counts, which however add

**Figure 6.** Clar valence structures for coronene.**Figure 7.** Clar valence structures for fibonacenes.

correctly to the total number of π -electrons of the molecule. Observe that fibonacenes with odd R have a single Clar structure, whereas fibonacenes having an even number of rings have “migrating” π -sextets. This is reflected in the relative magnitudes of the π -electron partitions in Table 2, where fibonacenes with an odd number of rings have more pronounced differences between the π -content of rings that hold π -sextets and rings with fixed C=C double bond(s). As the number of rings increases we see that the differences between the partitioning of π -electrons to individual rings steadily decrease and in the limit of an infinitely long fibonacene one would obtain a uniform partitioning of π -electrons among all rings. For finite fibonacene systems, however, typically terminal rings have more π -electrons than adjacent nonterminal rings. The same is again often the case with the “kink” rings in the interior part of catacondensed benzenoids. On the other hand, the rings that Clar’s formula indicates as the region of “migrating” sextets are found to have a higher π -electron count than the rings having fixed C=C double bond(s).

QUANTITATIVE CLAR FORMULAS FOR BENZENOIDS

Clar structures can be considered as a “distillate” of resonance structures obtained by discarding the resonance structures with a minor contribution to the resonance energy. We consider now the partitioning of π -electrons belonging to various rings of polycyclic benzenoid hydrocarbons, but we restrict the selection of resonance structures only to those contributing to the Clar structure(s). For example, in the case of phenanthrene, if we discard the resonance structure with the smallest degree of freedom,^{3,66,67} that is the valence structure having the two terminal rings with four assigned electrons, and consider only the remaining four out of the five resonance structures, we obtain (instead of the ring partitions 26/5, 18/5 shown in Table 2) slightly different π -electron ring partitions: 22/4 and 12/4, respectively, which when added for all three rings, again add to 14 π -electrons. Thus the Clar structure of phenanthrene has two π -electron-sextet circles and corresponds to the superposition of $2^2 = 4$ resonance structures each of which has two benzenoid rings with three double bonds. It has been pointed out that only resonance structures of the maximal degree of freedom contribute to Clar valence structures.^{66,67} The degree of freedom (*df*) of a resonance structure is defined as the smallest number of C=C double bonds that when selected determines fully the locations of the remaining C=C double bonds.^{68,69}

In a series of recent papers^{10–15} we have analyzed π -electron ring partitions for a number of benzenoid and nonbenzenoid conjugated hydrocarbons. In these previous studies, all resonance structures were considered to have

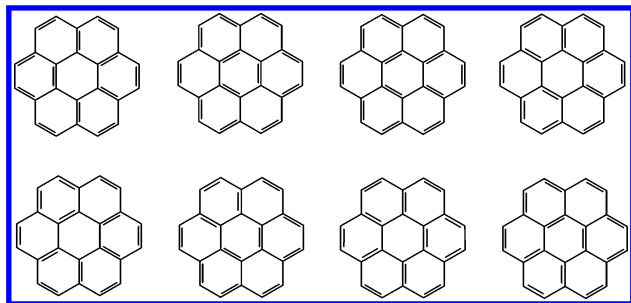


Figure 8. The eight resonance structures of coronene whose superposition produces one of the two Clar structures of coronene.

equal weight. In the present work, the resonance structures which do not have the highest degree of freedom have zero weight. One can conceive intermediate cases where the resonance structures that do not have the highest degree of freedom have reduced weights in the interval (0, 1), on a scale inversely proportional to their degrees of freedom (but also taking size consistency into account),^{70–72} but we will not pursue here this possibility.

A single aromatic π -sextet is obtained by superposition of two resonance structures (e. g., benzene), the presence of two aromatic π -sextets in a Clar structure requires a superposition of four corresponding resonance structures (e.g., pyrene), and three aromatic π -sextets that occur in each Clar structure of coronene involves eight resonance structures (e.g., triphenylene). Of the 20 resonance structures of coronene, 15 have $df = 3$, while the remaining five (D and F in Figure 4) have $df = 2$. In Figure 8 we show $2^3 = 8$ of the 15 structures of coronene with highest degree of freedom, which when superimposed give the Clar structure of coronene shown in Figure 6 at the left. One obtains the other Clar structure of Figure 6 (shown on the right of Figure 6) by combining the first resonance structure of Figure 8 with seven resonance structures which are the mirror images of the remaining valence structures shown in Figure 8. Thus structure A in Figure 4 (the structure with the maximal number of benzenoid rings with three C=C double bonds, also known as Fries structure⁶⁸) is involved in the construction of both Clar structures of Figure 6.

In addition to the outlined construction of Clar structures based on considering a *superposition* of all resonance structures with the highest degree of freedom, there are two other schemes, (2) and (3), which produce somewhat modified forms of Clar structures, and which will be discussed below.

MODIFIED APPROACH: SUPERPOSITION OF CLAR STRUCTURES

(2) In this case for molecules having “migrating” π -sextets one first constructs all possible Clar structures (like the two structures of Figure 6 in the case of coronene). Then for each such nonunique Clar structure one constructs the underlying resonance structures and partitions their π -electrons to their rings. The superposition of all *partitions of π -electrons of all possible Clar structures* then gives the resulting distribution of π -electrons for such a model of Clar structures. The two approaches differ only for molecules with “migrating” π -sextets. Now the same resonance structure may occur in several Clar structures, while before it would have been considered only once. Thus for example, for

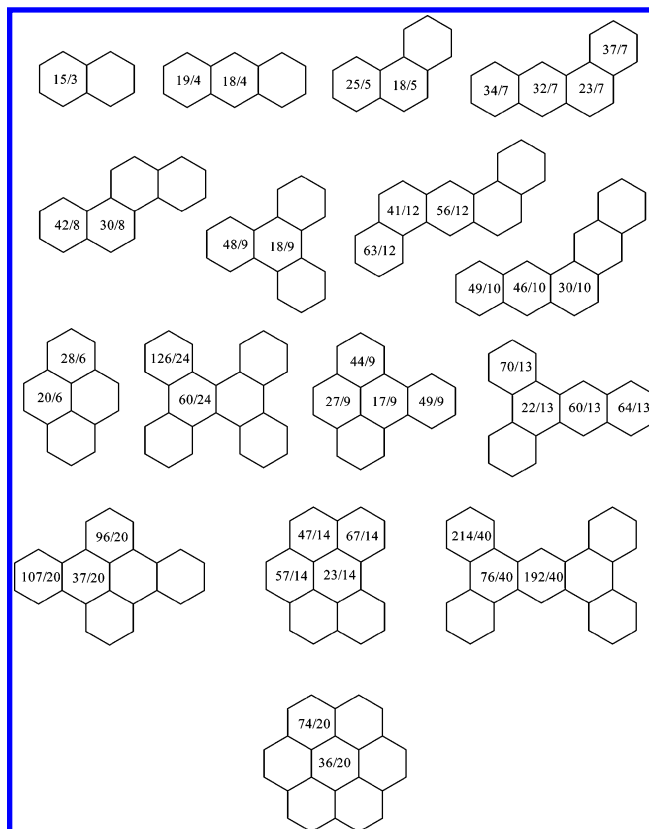


Figure 9. Partitioning of π -electrons into individual rings for benzenoid hydrocarbons of Figures 1 and 2.

constructing the Clar structures of coronene, in one case we superimposed 16 resonance structures, while in the other case we superimposed 15 resonance structures, with the first resonance structure of Figure 6 (A in Figure 4) being used twice. In general, the Clar structure obtained as the average of several Clar structures is not equivalent to the Clar structure using “arrows” to depict migrating π -electrons. This particular point apparently has not been hitherto fully recognized.

In Figures 9 and 10 we show the average π -electron counts for individual rings for the same collection of benzenoids, whose Clar structures were shown in Figures 1 and 2. The inscribed numbers in rings of Figure 9 are obtained when contributions from all resonance structures are considered. When only resonance structures of the maximal degree of freedom are considered in the superposition, we obtained the ring partitions shown in Figure 10. The values displayed in this figure are the same as in Figure 9 only for acenes, which have $df = 1$. As one may expect, in Figure 10, on comparing with values from Figure 9, the terminal rings and rings associated with π -aromatic sextets have increased their “benzenoid-character” relative to the “empty” rings of Clar structures when compared with the same rings based on using all resonance structures. Among the 16 benzenoids from Figure 10, the 6th, 13th, and 15th are fully resonant, and therefore their number of Clar valence structures is 2^S , where S is the number of benzenoid sextets. It will be observed, however, that six additional benzenoids from this figure have 2^S Clar valence structures.

In Table 3 we have collected the partitions of π -electrons based on Clar structures of fibonacenes, to be compared with the corresponding entries of Table 2 in which all resonance

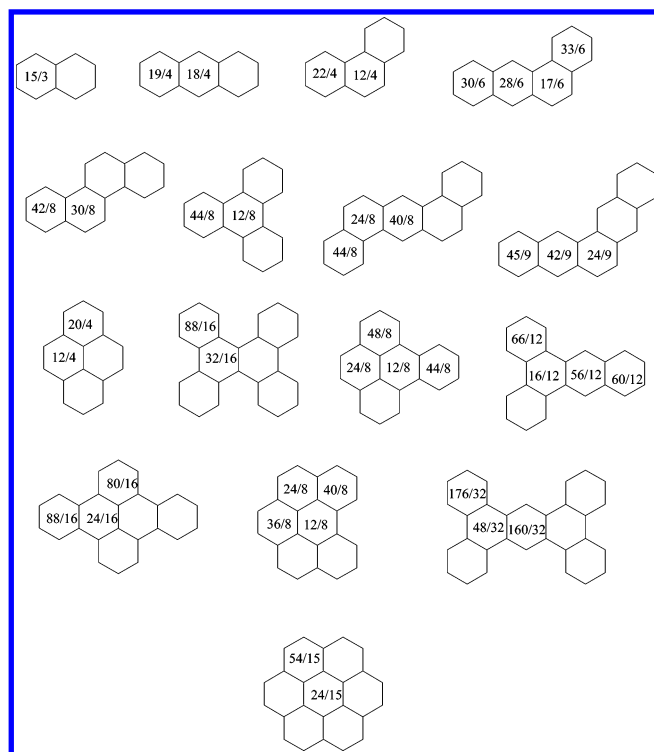


Figure 10. Partitioning of π -electrons into individual rings for the same benzenoid hydrocarbons of Figures 1 and 2 when resonance structures are restricted to those giving the corresponding Clar structures.

Table 3. Partitioning of π -Electrons into Individual Rings for Clar Structures of Fibonacenes^a

	R	A	B	C	D	sum
phenanthrene	3	22/4	12/4			14
chrysene	4	41/8	31/8			18
picene	5	44/8	24/8	40/8		22
fulminene	6	108/21	80/21	85/21		26
[7]-zigzag-fibonacene	7	88/16	48/16	80/16	48/16	30
[8]-zigzag-fibonacene	8	283/55	209/55	224/55	219/55	34

	R	A	B	C	D	sum
phenanthrene	3	5.5000	3.0000			14
chrysene	4	5.1250	3.8750			18
picene	5	5.5000	3.0000	5.0000		22
fulminene	6	5.1429	3.8095	4.0476		26
[7]-zigzag-fibonacene	7	5.5000	3.0000	5.0000	3.0000	30
[8]-zigzag-fibonacene	8	5.1455	3.8000	4.0727	3.9818	34

^a Letters A, B,... denote rings starting from a terminal one.

structures were considered in constructing numerical resonance formulas. First one may observe that the entries for fibonacenes with even numbers R of rings are the same in the two tables, which is the consequence of the fact that for fibonacenes with even numbers of rings all resonance structures have the same degree of freedom. On the other hand, in the case of fibonacenes with odd numbers of rings, as we see from Table 3, the magnitudes of π -electron partitions are constant for the rings in the same relative location from the terminal rings. These new values show a visible enhancement of the aromatic character for rings associated with π -sextets and reduced π -electron content for rings having C=C double bond(s).

(3) Gutman and collaborators¹⁸ envisaged another route to numerical Clar structures that can be combined with either of the two approaches described above. They decided to

associate with each π -sextet six π -electrons rather than considering the underlying resonance structures. Thus they differentiate only four types of benzene rings: π -sextet ring, ring with two C=C double bonds, ring with a single C=C double bond, and “empty” ring. In this approach the “empty” rings are indeed empty of π -electrons. Recent comparisons of these approaches have shown minor differences in the distribution of π -electrons within different rings.⁷³ It has yet to be better established in which cases these schemes give significantly different results. An obvious advantage of the scheme of Gutman et al. is that it is computationally very simple, as it does not require examining large numbers of resonance structures.

UNIQUE CLAR FORMULAS OF BENZENOID HYDROCARBONS

The significance of numerical valence structures resides in (i) a successful transformation of a collection of *geometrical* structural formulas into a *numerical* structural formula, and (ii) in doing this, one obtains a *single* structural formula for a molecule that has numerous resonance structures or more than one Clar structure. Hence, with this approach, the distinction between molecules having one or several Clar structures (i.e., those with migrating π -sextets) vanishes, and we can speak of a *single* Clar structure for *any* benzenoid hydrocarbon. The same is true for benzenoids having numerous resonance structures, which are summarized in Figure 9 or 10 by showing a *single* numerical structural formula for each benzenoid hydrocarbon. It is this quality of *uniqueness* of the quantitative numerical valence structures that appears very attractive. This allows one to propose for any benzenoid a *unique* structural formula, be it based on all resonance structures, a selection of resonance structures, or a single resonance structure. The same approach can be extended to any limited number of resonance structures, such as for instance Fries structures⁷⁴ or anti-Fries structures⁷⁵ of any benzenoid, whether there is a single such structure or several ones. A Fries structure of a benzenoid is defined as the resonance structures having the maximal number of rings with alternating C=C double and C—C single bonds such as those given by Kekulé formulas of benzene, and according to Fries these are the most important resonance structures of any polycyclic benzenoid system. Anti-Fries structures are resonance structures in which the location of a single CC double bond determines the location of very many other CC double bonds.⁷⁵ These are valence structures illustrating “long range” order, as seen on examples of phenanthrene and triphenylene presented in Figure 11.

While in many cases (e.g. fibonacenes) there is just one such Fries structure among many resonance structures, in some instances there are several resonance structures that qualify as Fries structures. In Figure 12 we have illustrated a few such cases.

A short-cut to finding the maximum number and the position of resonant sextets in perifusenes was devised by Ruiz-Morales under the name “Y-rule”.^{76,77} In the hydrogen-depleted graph of the perifusene, “internal” aromatic carbon atoms with a connectivity of 3 (i.e. bounded by three benzenoid rings, such as the two inner carbon atoms of perylene) are designated as C_Y atoms. The Y-rule stipulates that the resonant sextets are located in the hexagons that

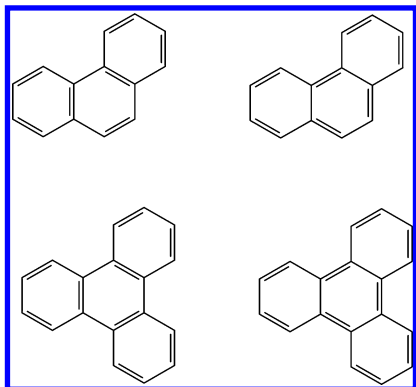


Figure 11. Fries (on the left) and anti-Fries structures (on the right) for phenanthrene and triphenylene.

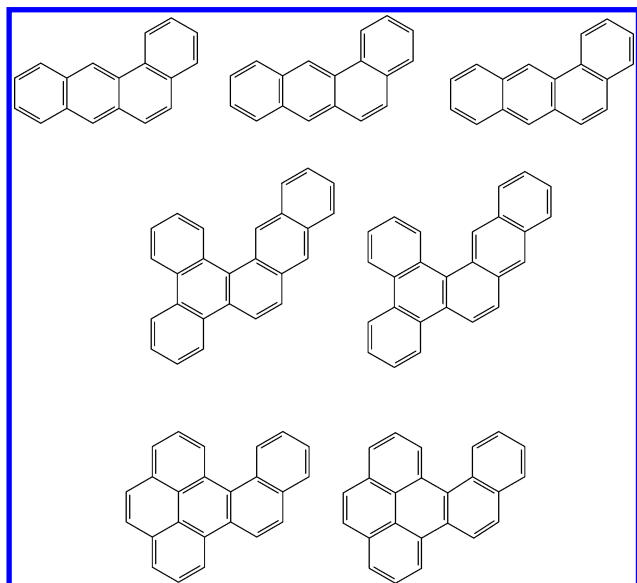


Figure 12. Smaller benzenoid hydrocarbons having more than one Fries structure.

contain the C_Y atoms and that all of the C_Y carbons have to be included. Translated into the dualist (inner dual) graph of the perifusene, this rule is equivalent to having the *maximum number of nonadjacent vertices* coding for resonant sextet rings. In Figure 13 one may see the dualist graphs of the nine fully benzenoid hydrocarbons that were presented in Figure 6 of ref 76 illustrating that for such benzenoids starting with triphenylene all marginal vertices are marked by circles. In the above-mentioned references, a good agreement was found between Schleyer's nucleus-independent chemical shifts (NICS values)⁷⁸ and the π -electronic distribution obtained by the Clar sextet principle and predicted by the Y-rule. On examining the benzenoids from Figure 10, a similar agreement can be observed. One may also mention interesting conclusions on Clar structures published by Zhang et al.^{79–81}

In concluding this report we would like to emphasize the potential of *algebraic* valence structures, which can be constructed for an individual resonance structure, or several of Clar valence structures (when there is more than one Clar structure). Aside from Pauling bond-order designation (with a partitioning of π -electrons among bonds rather than rings), now for the first time one can offer a *single (numerical) structure* for a molecule having *many* resonance structures

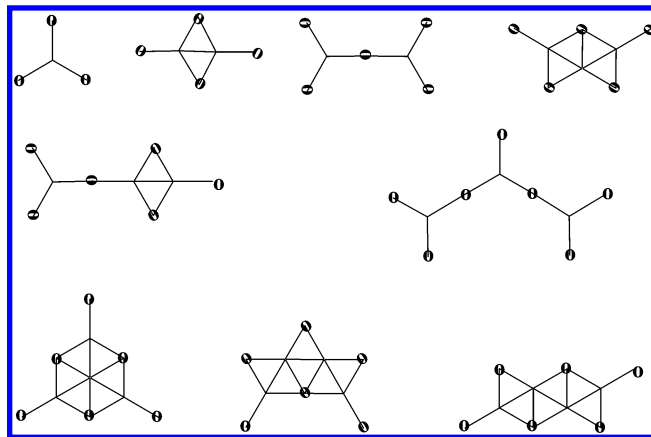


Figure 13. Dualist graphs of nine fully resonant benzenoids from Figure 6 of ref 76. The circles correspond to benzenoid rings with resonant sextets.

(see Figure 9) as well for molecules having *several* Clar valence structures (as shown in Figure 10).

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