

Algebraic Kekulé Formulas for Benzenoid Hydrocarbons[†]

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By assigning two π -electrons of CC double bonds in a Kekulé valence structure to a benzene ring if not shared by adjacent rings and one π -electron if CC double bond is shared by two rings we arrived at numerical valence formulas for benzenoid hydrocarbons. We refer to numerical Kekulé formulas as *algebraic* Kekulé valence formulas to contrast them to the traditional *geometrical* Kekulé valences formulas. The average over all numerical Kekulé valence structures results in a *single* numerical structure when a benzenoid hydrocarbon molecule is considered. By ignoring numerical values the novel quantitative formula transforms into a qualitative one which can replace incorrectly used notation of π -electron sextets to indicate aromatic benzenoids by placing inscribed circles in adjacent rings—which contradicts Clar's characterization of benzenoid hydrocarbons.

INTRODUCTION

Most chemists are quite familiar with Kekulé valence structures, which have been around for almost 140 years, yet few are aware of the riches of information “hidden” in these simple structural formulas that have surfaced in recent years. These include the *conjugated circuits*, the *innate degree of freedom*, and as we will see in this contribution, the possibility to express Kekulé valence structures *algebraically*, rather than geometrically. “Conjugated Circuits,” which are the circuits within an individual Kekulé valence structure in which there is a regular alternation of CC double and CC single bond, were observed for the first time about 25 years ago, which in view of the long history of Kekulé valence structures is relatively recently.^{1–3} The same has been the case with the “innate degree of freedom” of individual Kekulé valence structures, that were “discovered” only about 15 years ago and only very recently were identified as a very important structural element for Clar's model of aromatic sextets.^{4,5} In a recent review article on aromaticity of polycyclic conjugated hydrocarbons⁶ we have referred to conjugated circuits and the degrees of freedom of Kekulé valence structures as “hidden treasures,” in view of their unsuspected relevance for quantitative characterization of aromaticity. The importance of conjugated circuits follows from their use for analytical expressions for molecular resonance energy (RE). The importance of “degree of freedom” relates to recognition that only the Kekulé valence structures of a maximal degree of freedom contribute to Clar structures of benzenoid hydrocarbons.^{7,8} Because Clar structures can be viewed as a superposition of a selection of Kekulé valence structures, in a way we can view Clar structures also as a “hidden treasure” of Kekulé valence structures. The present paper will focus on yet another, the latest, “hidden treasure” of geometrical Kekulé valence structures: their algebraic equivalents. As we will see,

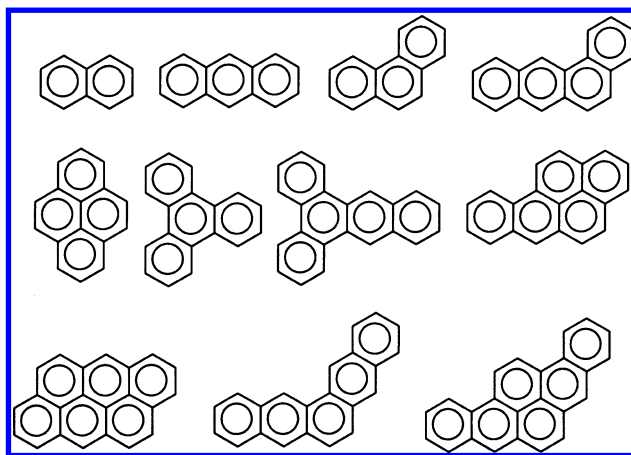


Figure 1. Notations for benzenoid hydrocarbon that is widespread but incorrect despite occasional warnings of its absurdity when the count of π -electrons is considered.

besides the familiar geometrical Kekulé valence structure it is possible to construct algebraic, that is numerical, Kekulé valence structures. Numerical Kekulé valence formulas, besides offering an alternative, nongeometrical representation of Kekulé structures of benzenoid hydrocarbons, lead also to a *single* (numerical) structural formula for benzenoid hydrocarbons. Moreover, as we will demonstrate, one can construct a plausible qualitative representation for polycyclic aromatic hydrocarbons that can replace a qualitative but incorrect use of inscribing circles (that represent aromatic sextets) to adjacent rings of aromatic benzenoids. It is quite common to see benzenoid hydrocarbons depicted with inscribed circles in adjacent benzene rings as illustrated in Figure 1. According to Armit and Robinson⁹ inscribed circles represent π -aromatic sextets. Placing inscribed circles in both rings of naphthalene incorrectly implies that naphthalene has 12 π -electrons instead of ten. From time to time chemists were reminded of *incorrectness* of such a notation^{10,11} but nevertheless many continue to use an incorrect circle notation. Probably in part this happens because of the lack of an equally simple *correct* notation to substitute for the incorrect notation. In this contribution by modifying the

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[†] This article is dedicated to W. G. A. Milne, on the occasion of his retirement after serving 15 years as the Editor-in-Chief of the *Journal of Chemical Information and Computer Science*.

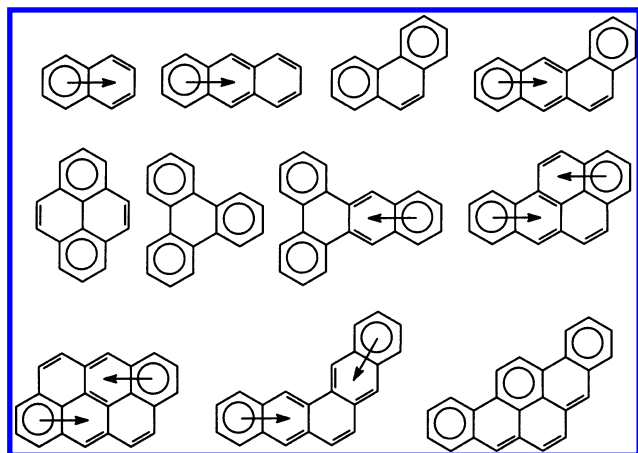


Figure 2. Clar valence structures for a collection of smaller benzenoid hydrocarbons.

numerical Kekulé valence structure we offer an alternative to the incorrect “circle” notation for benzenoid hydrocarbons.

THE “CIRCLE” NOTATION OF CLAR

The notion of an aromatic π -sextet originated with Armit and Robinson⁹ who in 1925 suggested collecting π -electrons in polycyclic benzenoid hydrocarbons into a group of six to be associated with a single benzene ring attributed to a selection of non-adjacent benzene rings. Because an inscribed circle stands for *six* π -electrons and placing two such circles in *adjacent* rings imply that two rings have 12 π -electrons, which of course is not the case. Hence *inscribed circles that represent aromatic sextets cannot be placed in adjacent benzene rings*. It was Eric Clar who further developed the idea of aromatic sextets, and his book “*The Aromatic π -Sextet*”¹² gives experimental evidence to support the π -sextet model and offers an excellent introduction to the aromatic π -sextet theory. In Figure 2 we show how Clar represented the benzenoids in Figure 1 combining the sextet notion with the “classical” CC double bond notation. Although at the first sight Clar’s formula may appear convoluted, at least they immediately offer the correct π -electron count when with each C=C bond we associate two π -electrons and with each inscribed ring six π -electrons. Clar structural formulas can be constructed following the simple “geometrical” rules:

- (1) Never draw inscribed circles in adjacent benzene rings.
- (2) Draw the maximal number of inscribed circles possible subject to the requirement that the carbon atoms not involved should be coupled to form CC double bonds.

The arrows that suggest “migrating” π -electrons occur for benzenoids having more than one Clar formula. By following the above rules construction of Clar structures is straightforward. Importance of Clar structures is in that they offer valuable insights into local characteristics of benzenoid hydrocarbons. It is very encouraging to see that after a long time finally rigorous ab initio quantum chemical calculations appear to support an intuitive picture of Clar of benzenoid hydrocarbons.^{13,14}

ALTERNATIVE NOTATION FOR AROMATIC RINGS

The misuse of circle notation in part may be due to a *lack of a suitable simple alternative* notation that will differentiate

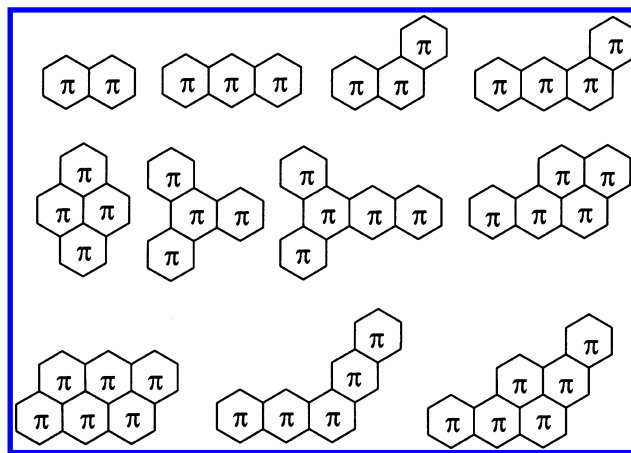


Figure 3. Proposed alternative notation for polycyclic aromatic hydrocarbons to eradicate a deeply seated and widespread erroneous “circle” notation for benzenoid hydrocarbons that retains simplicity and does not compromise correctness.

fused aromatic benzene rings, such as those of naphthalene $C_{10}H_8$, from fused six-carbon saturated rings, such as those of decalin, decahydronaphthalene $C_{10}H_{18}$. Clar’s formulas, though simple enough, imply a particular theoretical model for benzenoid hydrocarbons, just as do collections of Kekulé valence structures, thus both are not necessarily suitable for a notational design. To break the widespread misuse of the circle notation we need a *simple, unique, and viable* alternative. In Figure 3 we illustrate our proposed alternative notation on the very same benzenoids shown in Figure 1. There is this time some basis to be optimistic that novel notation may succeed in replacing the incorrect circle notation. One of the editors of “*Polycyclic Aromatic Compounds*,” (A. T. Balaban), expressed an interest in instructing authors submitting manuscripts to that journal to stop representing aromatic compounds with circles (π -sextets) in adjacent rings.¹⁵

Recall that here we consider a notational device. The use of π appears plausible as a symbol to replace inscribed circles as it immediately suggests that corresponding rings involve π -electrons. Moreover, as we will see later the proposed notation can be viewed as a *qualitative* notation that can be upgraded into a *quantitative* notation which indicates *numerically* the partition π electrons associated with the individual benzene rings of polycyclic aromatic benzenoids. In addition, as will be shown in subsequent sections, the novel numerical representation of the π -content of individual benzene rings also leads to unique (numerical) molecular structures for benzenoid hydrocarbons. To obtain a unique *single* valence structure for a benzenoid hydrocarbon as a whole one simply superimposes numerical Kekulé valence structures of the molecule. Thus for the first time, ever since Kekulé introduced two valence formulas for benzene over 140 years ago, we have a general scheme that allows one to write a single molecular formula for any benzenoid hydrocarbon.

QUANTITATIVE VALENCE FORMULAS OF BENZENOIDS

Figure 3 tells us that rings of fused benzenoids contain π -electrons. We can modify this qualitative information and calculate the exact *portion of* π -electrons that are assigned

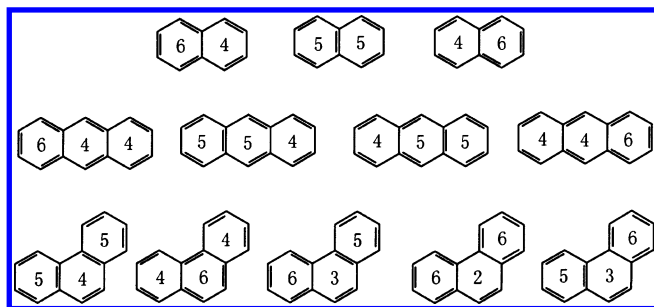


Figure 4. The Kekulé valence structures of naphthalene, anthracene, and phenanthrene with inscribed integers indicating an equal partitioning of the π -electrons between adjacent rings having a common CC double bond.

to individual benzene rings! Consider the Kekulé valence structures of naphthalene, anthracene, and phenanthrene illustrated in Figure 4 where in each ring we have inscribed an *integer*. The inscribed integer represents the count of π -electrons associated with individual rings, and it is obtained according to the following simple rules:

- (1) CC double bonds not common to other rings contribute two π -electrons to the ring.
- (2) A CC double bond common to two rings contributes one π -electron to each ring.
- (3) The portion of π -electrons to be assigned to individual benzene rings is obtained by summing contributions from CC double bonds present in a ring.

Clearly the numbers inscribed in each benzene ring have a simple structural meaning: *they count π -electrons belonging to a ring*, taking into account that rings having common double bonds *share* π -electrons. Thus the first Kekulé formula of naphthalene, which contains three CC double bonds, has six π -electrons and the adjacent ring with two CC double bonds has four π -electrons. The two rings of naphthalene together have $6\pi + 4\pi = 10\pi$ -electrons, as they must, which is the number of π -electrons of naphthalene. In the case of the central Kekulé structure of naphthalene in Figure 4 each ring is associated with five π -electrons because the two rings share a common central CC bond. Again the total number of π -electrons is 10, as it should be. Similarly numerical Kekulé structures of anthracene and phenanthrene illustrate the partition of π -electrons to the individual benzene rings in the Kekulé structures of those molecules. As it is to be expected, π -electrons in individual rings of each Kekulé structure of anthracene and phenanthrene add to 14 π -electrons.

ALGEBRAIC KEKULE VALENCE STRUCTURES

We refer to the numerical valence structures in Figure 4, which give the partition of molecular π -electrons to individual rings associated with individual Kekulé valence structures, as the *algebraic* Kekulé structures in order to distinguish them from the traditional “geometric” Kekulé valence structures. In Figure 5 we illustrate the nine *algebraic* Kekulé structures of benzo[*a*]pyrene. Because we are so used to a *geometrical* representation of Kekulé formulas with CC double and CC single bonds the nine numerical Kekulé structures of benzo[*a*]pyrene in Figure 5 at first sight do not appear as “valence” structures. However, the nine structures in Figure 5 do represent valence structures and are as legitimate as the traditional geometrical valence structures

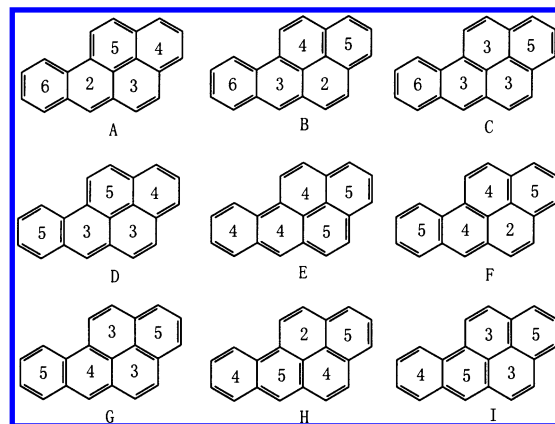


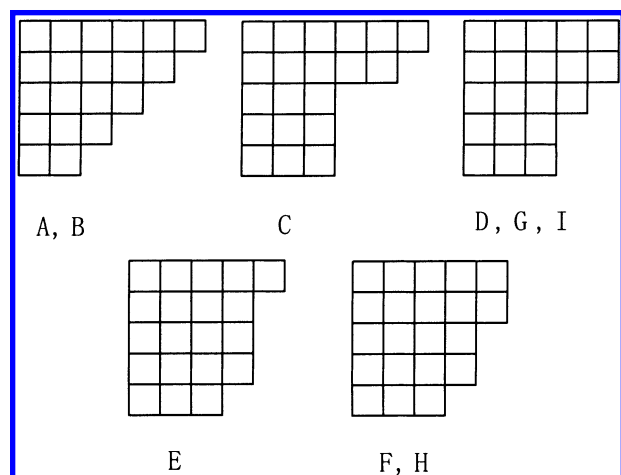
Figure 5. The nine Kekulé valence structures of benzo[*a*]pyrene showing distribution of the 20 π -electrons between the five benzene rings.

with which we all are so familiar. Whenever numerical Kekulé structures are unique, as is the case with naphthalene, anthracene, phenanthrene, and benzo[*a*]pyrene, there is a one-to-one correspondence also between the geometrical and the algebraic valence structures of benzo[*a*]pyrene. In such instances reconstruction of a “geometrical” valence structure from “algebraic” is rather straightforward. Consider, for instance, the first Kekulé structure of benzo[*a*]pyrene in Figure 5. Evidently the three CC double bonds of the terminal ring “6” are all exocyclic to the pyrene core as they are not shared with any other benzene ring. The same is true for the CC double bond in the adjacent ring. The ring with three π -electrons has an exposed CC bond, which has to be double thus leaving a single π -electron to be shared with the rings above, but this cannot be the ring above at the left because then that ring should have five and not four π -electrons! Thus we arrived at an assignment of all CC double bonds for the algebraic Kekulé structure considered. Similar considerations apply to the remaining eight “numerical” Kekulé structures of benzo[*a*]pyrene. Almost nowadays extinct “on the back of the envelope” theoretical chemistry, has been apparently resurrected, this time concerning Kekulé valence structures, rather than the Hückel MO theory.

A one-to-one correspondence between the *geometrical* and the *algebraic* Kekulé valence structures demonstrated on several smaller benzenoids does not guarantee that a one-to-one correspondence necessarily holds for all benzenoid hydrocarbons. In fact it does not. It does not hold for benzene, which has two Kekulé structures both having the same numerical value of 3. Other smaller benzenoids for which a one-to-one correspondence does not hold include pyrene, perylene, and a selection of their derivatives, and kekulene.^{16,17} Gutman et al.¹⁶ proved that in the case of cata-condensed benzenoids (but excluding cyclic systems such as kekulene) the numerical Kekulé valence structures are unique and have a one-to-one correspondence with the traditional (geometric) Kekulé valence structures. However, peri-condensed systems as well as cyclic cata-condensed systems may have single algebraic Kekulé structures corresponding to two or more geometrical Kekulé structures. We should, however, point out that also in the case of a “one-to-many” correspondence between numerical and geometrical Kekulé valence structures there is no loss of information associated with the set of numerical Kekulé structures. This follows because even then one has to reconstruct *all*

Table 1. Partition of 20 π -Electrons of Benzo[*a*]pyrene to Individual Benzene Rings for Each of Its Nine Kekulé Valence Structures and Decomposition of the Individual Kekulé Valence Structures into Conjugated Circuits

Kekulé valence structure	distribution of π -electrons to individual rings	conjugated circuits decomposition
A	6, 5, 4, 3, 2	$2R_1 + R_2 + R_3 + R_4$
B	6, 5, 4, 3, 2	$3R_1 + R_2 + R_4$
C	6, 5, 3, 3, 3	$2R_1 + 2R_2 + R_3$
D	5, 5, 4, 3, 3	$2R_1 + 2R_2 + R_3$
E	5, 4, 4, 4, 3	$R_1 + 2R_2 + 2R_3$
F	5, 5, 4, 4, 2	$4R_1 + R_3$
G	5, 5, 4, 3, 3	$3R_1 + 2R_2$
H	5, 5, 4, 3, 3	$3R_1 + R_2 + R_3$
I	5, 4, 4, 4, 3	$2R_1 + 3R_2$

**Figure 6.** Young diagrams corresponding to the Kekulé valence structures of benzo[*a*]pyrene.

geometrical Kekulé valence structures from the set of *all* algebraic structures. It then happens that a *single* numerical structure may give rise to two or more alternative “geometrical” solutions. In contrast a typical one-to-many correspondence found for topological indices is associated with a loss of information and does not allow, in general, a reconstruction of a molecular graph from a limited set of molecular invariants.

In Table 1 we have summarized information on the nine numerical Kekulé structures of benzo[*a*]pyrene by listing the ring π -electron counts in descending order. In the right-hand column we give the decomposition of the same Kekulé valence structures in conjugated circuits. As we can see different Kekulé structures may have the same distribution of π -electrons but a different count of conjugated circuits [e.g., structures (A, B), (D, E), and (F, G, H)] and the same count of conjugated circuits but a different distribution of ring π -electrons [e.g. structures (C, D)]. This need not be surprising, and it merely points out that the two graph theoretical algorithms refer to two different structural features of the Kekulé valence structures. In particular ring π -electron distributions reflect on the local variations of π -electrons, while the conjugated circuits summarize the global features of π -electrons. It is of some interest to point out that the numerical Kekulé valence structures allow representation of the Kekulé valence structures, as illustrated in Figure 6 for the nine Kekulé structures of benzo[*a*]pyrene, by the Young diagrams.

In Table 2 we listed the π -electron ring partitions for a dozen smaller benzenoid hydrocarbons shown in Figure 7 but only for the Kekulé structure having a different ring π -electron distribution. The number of fused rings gives the length of the code, while the sum of the entries in a code gives the number of π -electrons of the benzenoid considered. Entries in Table 2 for each benzenoid are listed lexicographically; that is, the first is the largest number, followed by the next largest number and so on. We refer to the first numerical Kekulé valence structure in the list of Kekulé structures as the leading Kekulé valence structure, which is the structure depicted in Figure 6. We observe that in general the leading Kekulé valence structure does not coincide with the Fries structure. This is already visible in triphenylene with the leading Kekulé structure (6, 6, 6, 0), while the Fries structure of triphenylene is (5, 5, 5, 3). The leading Kekulé valence structure (because of the underlying lexicographic ordering of structures) is one with the maximal number of a leading “6” in the code and represents one of the Kekulé valence structures contributing to the Clar structure of the benzenoid considered. The nonadjacent Kekulé benzene rings in such a structure point to locations of the aromatic π -sextets.

QUANTITATIVE STRUCTURAL FORMULAS FOR BENZENOIDS

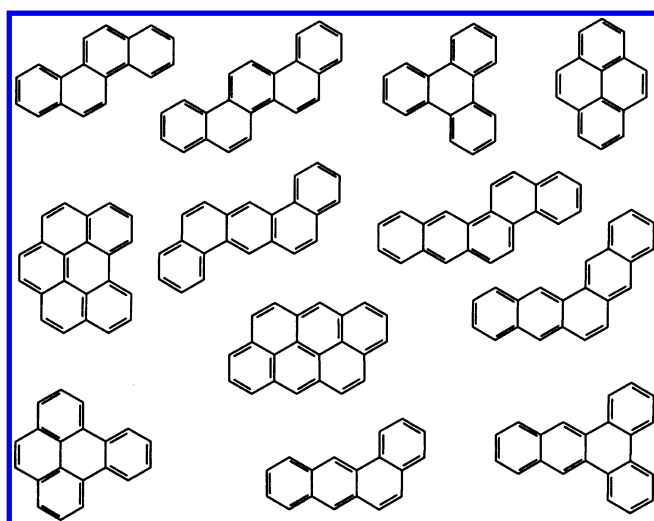
To obtain a quantitative structural formula for a benzenoid molecule we take the average of its numerical Kekulé valence structures. Thus in the case of naphthalene the average of the algebraic Kekulé valence structures (6, 4), (5, 5), and (4, 6) gives for each of the two rings of naphthalene (15/3, 15/3) and thus assigns to each ring of naphthalene five π -electrons. Similarly the algebraic formulas for anthracene results in the following partition of the 14 π -electrons for the three rings: (19/4, 18/4, 19/4). The sum of contributions from the three rings adds to 56/4 or 14, which is the correct number of π -electrons in anthracene. Finally in the case of phenanthrene from Figure 4 we find as the summary of the contributions of the five Kekulé structures to individual rings, (26/5, 18/5, 26/5), which adds to 70/5, again giving a total of 14 π -electrons. As we see for individual rings typically we obtain a fractional π -electron count, which however adds correctly to the total number of π -electrons of the molecule. We observe also a rather uniform partitioning of π -electrons among the three rings of anthracene and a nonuniform partition of π -electrons in the rings of phenanthrene—the result that to a degree parallels Clar’s formulas for anthracene and phenanthrene, respectively.

In Figure 8 we have summarized for a collection of smaller benzenoids the data for the average π -electron distributions of π -electrons in various benzene rings. The numerical formulas in Figure 8 represent the average *algebraic* Kekulé valence structure for each of the benzenoids considered. A close look at Figure 8 shows several regularities for the values of the ring π -counts that parallel other rings indices for local aromaticity.^{18–21} Typically terminal rings have more π -electrons than adjacent nonterminal rings. The same is again often the case with the “kink” rings (in the terminology of Gordon and Davison²²) in the interior part of the catacondensed benzenoids. On the other hand, the rings that Clar’s formula suggests to be “empty” are found to have a rather low π -electron count.

Table 2. Partition of Kekulé Valence Structures of Smaller Benzenoids into Individual Benzene Rings by Dividing Electrons of CC Double Bond Equally between the Adjacent Rings^a

chrysene	picene	triphenylene	pyrene
6, 6, 4, 2	6, 6, 6, 2, 2	6, 6, 6, 0	5, 5, 4, 2
6, 6, 3, 3	6, 6, 5, 3, 2	6, 6, 5, 1	5, 5, 3, 3
6, 5, 4, 3	6, 6, 4, 4, 2	6, 5, 5, 2	5, 4, 4, 3
benzo[ghi]perylene	6, 6, 4, 3, 3	6, 4, 4, 4	pentaphene
5, 5, 5, 3, 3, 1	6, 5, 5, 3, 3	5, 5, 5, 3	6, 6, 4, 4, 2
5, 5, 5, 3, 2, 2	6, 5, 4, 4, 3	benzochrysene	6, 5, 5, 4, 2
5, 5, 4, 4, 4, 0	5, 5, 4, 4, 4	6, 6, 4, 4, 2	6, 5, 4, 4, 3
5, 5, 4, 4, 3, 1	dibenzo[ah]anthracene	6, 5, 5, 4, 2	5, 5, 5, 5, 2
5, 5, 4, 4, 2, 2	6, 6, 5, 3, 2	6, 6, 4, 3, 3	6, 4, 4, 4, 4
5, 5, 4, 3, 3, 2	6, 6, 4, 4, 2	6, 5, 5, 3, 3	5, 5, 5, 4, 3
4, 4, 4, 4, 3, 3	6, 5, 5, 4, 3	6, 5, 4, 4, 3	5, 5, 4, 4, 4
benzo[e]pyrene	6, 5, 5, 3, 3	5, 5, 5, 4, 3	dibenzo[ac]anthracene
6, 5, 5, 4, 0	6, 5, 4, 4, 3	5, 5, 4, 4, 4	6, 6, 6, 4, 0
6, 5, 5, 3, 1	5, 5, 5, 4, 3	benzanthracene	6, 6, 5, 5, 0
6, 5, 5, 2, 2	anthracene	6, 6, 4, 2	6, 6, 5, 4, 1
6, 5, 4, 4, 1	5, 5, 4, 4, 2, 2	6, 5, 5, 2	6, 5, 5, 5, 1
5, 5, 5, 4, 1	5, 5, 4, 3, 3, 2	6, 5, 4, 3	6, 5, 5, 4, 2
5, 5, 5, 3, 2	5, 4, 4, 4, 3, 2	6, 4, 4, 4	6, 4, 4, 4, 4
5, 5, 4, 4, 2	5, 5, 3, 3, 3, 3	5, 5, 5, 3	5, 5, 5, 5, 2
5, 4, 4, 4, 3	5, 4, 4, 3, 3, 3	5, 5, 4, 4	5, 5, 5, 4, 3

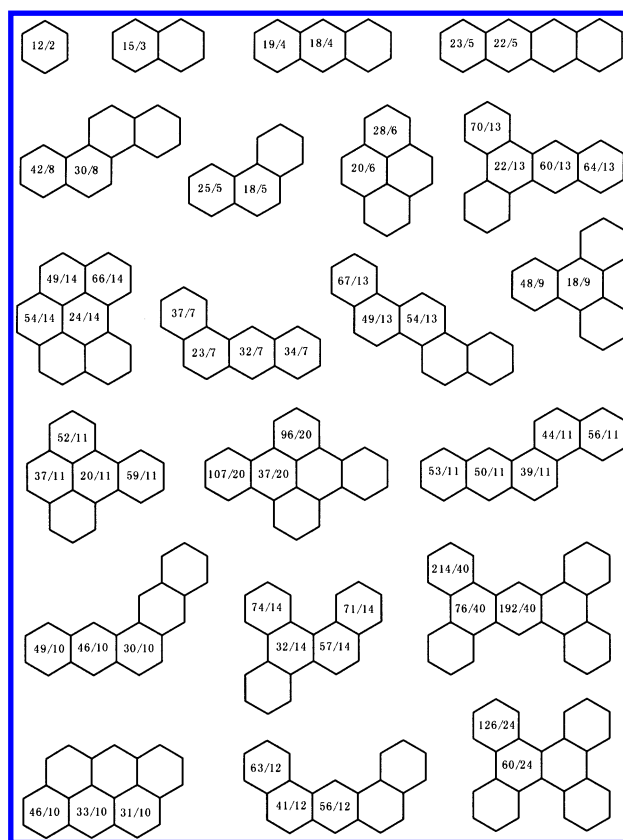
^a If there are several Kekulé structures (symmetry equivalent or not) that have the same π -electron partitioning only one case is shown.

**Figure 7.** The π -electron ring codes for a dozen smaller benzenoid hydrocarbons listed in Table 3.

One can view the average counts of π -electrons belonging to individual benzene rings as novel *ring indices*. A comparison with the graph theoretical ring indices obtained by counting how many times an individual ring is represented by the Kekulé formula of benzene shows a considerable parallelism between the two approaches describing local aromatic features in benzenoids. There are also significant (though minor) differences between the two approaches mentioned. In the case of anthracene the graph theoretical approach assigns the same local magnitudes to all rings. Now a slightly *different* π content is assigned to the central and the peripheral ring, the latter being more benzene-like. Generally in the case of linearly fused rings terminal rings have the largest π -ring index. This parallels the local characterization of rings based on the count of conjugated circuits as used in the calculation of the molecular RE.²³

QUANTITATIVE CLAR FORMULAS FOR BENZENOIDS

One can restrict the partitioning of π -electrons of polycyclic benzenoid hydrocarbons by considering only a selec-

**Figure 8.** The π -electron content for individual benzene rings of polycyclic aromatic compounds obtained by averaging the distributions of π -electrons as given by individual Kekulé valence structures.

tion of Kekulé valence structures. If we consider only Kekulé valence structures of the maximal degree of freedom we will obtain the partitioning of π -electrons between various rings for Clar valence structures. The degree of freedom of a Kekulé valence structure is defined as the smallest number of CC double bonds that, when selected, determines fully the locations of the remaining CC double bonds. In Figure 9 we show three Clar structures of benzo[a]pyrene, each of which has *two* aromatic π -sextets. By decomposition of the

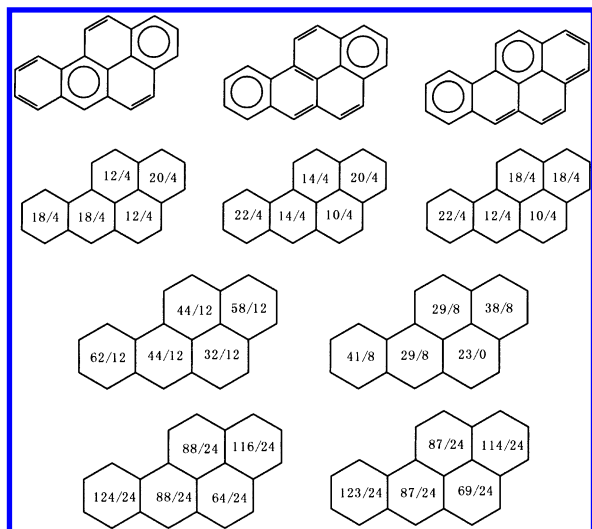


Figure 9. Top: Clar valence structures for benzo[a]pyrene and their representation by algebraic valence formulas. Bottom: The average of the three Clar's formulas and the single Clar's formula based on Kekulé valence structures of maximal degree of freedom. To facilitate the comparison numerical formulas are reduced to a common denominator.

Clar structures in the Kekulé valence structures for this case we obtain *four* underlying Kekulé valence structures. Below each Clar structure we give the count of ring π -electrons, which is the largest value for rings involving π -sextets, intermediate in value for rings sharing several CC double bonds, and the smallest for rings having a single CC double bond. When we superimpose the results for the three Clar structures we obtain the numerical valence structure shown at the left in the lower part of Figure 9, which represents the *average* of the numerical Clar structures of benzo[a]pyrene depicted at the top of Figure 9. However, mathematically the Clar structure is not defined as the *average of possible Clar structures* but as a *superposition of all Kekulé valence structures of the highest degree of freedom*. The difference between the two approaches is that in the first case some Kekulé valence structures appear with multiple integer weights, while in the latter case all Kekulé structures participate in the superposition with the same weight. Observe that in the first case we have to superimpose 12 Kekulé structures, hence some were used more than once. In the second case we use only eight Kekulé structures. In the lower part of Figure 9 at the right we show the numerical Clar structure based on the superposition of eight Kekulé valence structures of the highest *df*. In order to better see the difference between two alternative superposition of Kekulé structures, which is rather small but nevertheless significant, at the bottom of Figure 9 we have transformed the fractions appearing in the two Clar structures to the common denominator. As we see by averaging the contributions of the three Clar structures we gave a slightly greater weight to the terminal rings of benzo[a]pyrene and a lesser weight to the benzene ring with a fixed CC double bond than in fact these rings have. The comparison illustrates that the Clar structure of benzo[a]pyrene 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.

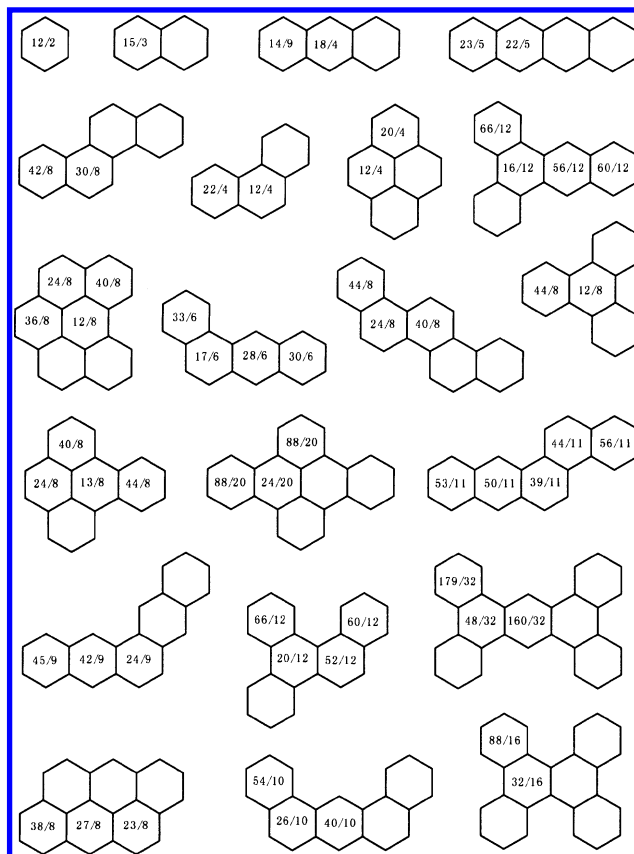


Figure 10. Partitioning of π -electrons into individual benzene rings when only Kekulé structures of the maximal degree of freedom are used.

In Figure 10 we show the average π -electron counts for individual rings for the same collection of benzenoids in Figure 8. As one may expect now the terminal rings and rings associated with π -aromatic sextets have increased their “benzene-character” relative to the “empty” rings of Clar structures when compared with the same rings based on the use of all Kekulé valence structures.

UNIQUE STRUCTURAL FORMULAS OF BENZENOID HYDROCARBONS

The significance of the above result is not only in the fact that we can transform a collection of *geometrical* structural formulas into a *numerical* structural formula but that in doing this we obtain a *single* formula for a molecule that has many Kekulé structures or several Clar structure. This is a novelty that has hitherto been unrecognized. Existence of a *single* and hence *unique* (numerical) structural formula for benzenoid hydrocarbons is a very desirable structural element. This approach also allows construction of a unique numerical formula to represent the Clar structure and the structure obtained by the superposition of any number of Kekulé valence structures. This includes trivially writing the numerical algebraic structure for a molecule based on a single Kekulé valence structure, such as the Fries valence structure²⁴ or the anti-Fries structure²⁵ of a benzenoid. The Fries valence structure of a benzenoid is defined as the Kekulé valence structure having the maximal number of rings with the Kekulé formula of benzene. According to Fries such Kekulé valence structures are the most important valence structures of the polycyclic benzenoid system. Interestingly, there are

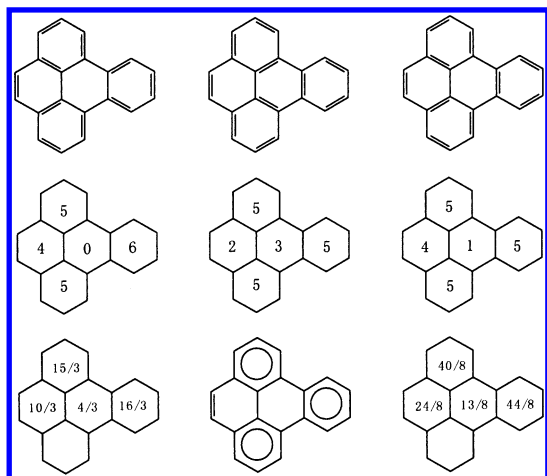


Figure 11. Comparison of *algebraic* or *numerical* Kekulé valence structures of the Fries structures of benzo[e]pyrene and Clar's structure of benzo[e]pyrene.

numerous benzenoids for which one can write two or more Fries structures, but the present approach would in those instances also produce just a single numerical valence structure. The same is true for the anti-Fries valence structures, which are Kekulé structures illustrating "long range" order, that is, valence structures in which the location of a single CC double bond determines the location of most of the other CC double bonds.²⁵

In Figure 11 we illustrate three Kekulé structures of benzo[e]pyrene which qualify as Fries structures. Using the partitioning of π -electrons associated with CC double bonds as the basis for the numerical characterization of Fries structures we arrive at a *single* Fries structure for benzo[e]pyrene as shown at the bottom left of Figure 11. We observe that the numerical Fries structure shows a considerable parallelism with the corresponding Clar structure of benzo[e]pyrene (bottom middle), the numerical value of which is shown at the bottom right. In both cases the rings belonging to the aromatic sextet have a high π -electron content, while the central ring, which corresponds to Clar's "empty" ring, shows a very low π -electron content.

CONCLUDING REMARKS

Novel quantitative algebraic Kekulé structures offer an alternative novel characterization of local properties of benzenoid hydrocarbons. While graph theoretical ring indices are based on the count of R_1 conjugated circuits of the individual rings the partition of π -electrons in a ring considered here includes contributions to a ring from the larger conjugated circuits. Thus not only the novel ring indices were obtained but also the novel interpretation for the contributing conjugated circuits toward the molecular resonance energy of benzenoid systems follow. The focus has shifted now on the distribution of π -electrons among different rings rather than among the different conjugated circuits.

In Figure 12 on the case of benzo[a]pyrene we have summarized the main message of the present paper: NO to QUALITATIVE incorrect formulas of benzenoid structures with "liberally" inscribing "circles" to adjacent rings in benzenoid structures; YES to QUALITATIVE notation of benzenoids using the inscribed " π " as a reminder of

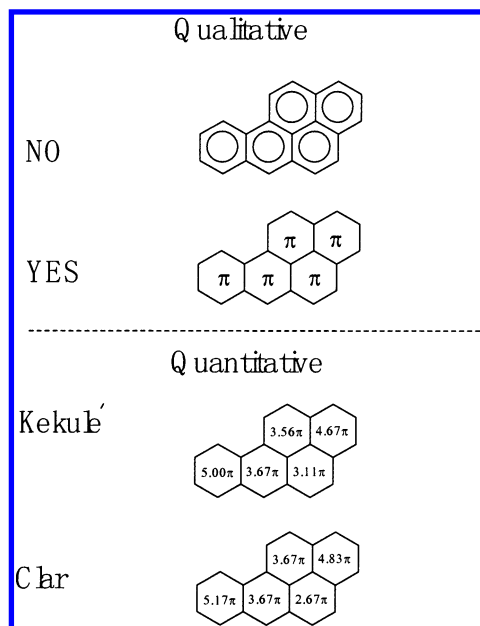


Figure 12. Summary of the present effort to correct an incorrect notational representation of structural formulas of polycyclic aromatic compounds.

the aromatic character of fused benzene rings; YES to QUANTITATIVE numerical structures based on *all* Kekulé valence structures; and YES to QUANTITATIVE numerical structures based on the Clar valence structures or any *selection* of Kekulé valence structures of interest. Elsewhere we describe the extension of the present work to other benzenoids, including cata-condensed, corona-condensed, and peri-condensed benzenoids^{26–28} as well as the discussion of some mathematical properties of the algebraic Kekulé valence structures.^{16,17}

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