

π -Electron currents in fixed π -sextet aromatic benzenoids

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Abstract In view of different patterns of π -electron density currents in benzenoid aromatic compounds it is of interest to investigate the pattern of ring currents in various classes of compounds. Recently such a study using a graph theoretical approach to calculating CC bond currents was reported for fully benzenoid hydrocarbons, that is, benzenoid hydrocarbons which have either π -sextets rings or “empty” rings in the terminology of Clar. In this contribution we consider π -electron currents in benzenoid hydrocarbons which have π -electron sextets and C=C bonds fully fixed. Our approach assumes that currents arise from contributions of individual conjugated circuits within the set of Kekulé valence structures of these molecules.

Keywords Conjugated circuits · Ring currents · CC bond currents · Benzenoid hydrocarbons · Clar structures

1 Introduction

Ring currents in benzenoid and non-benzenoid hydrocarbons received attention in the chemical literature ever since the emergence of NMR spectroscopy in late 1950s. Currently there are three distinct theoretical approaches to such calculations, each having its own merits:

- (1) Calculation of ring currents using MO methods [1–4];
- (2) Calculation of current densities using ab initio methods [5–13];
- (3) Calculation of CC bond currents using graph theoretical methods [14–20].

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For a long time all molecular orbital calculations were based on HMO, the Hückel MO method [21–27], though in principle such calculations could be made by more advanced MO approaches, such as the PPP (Pariser–Parr–Pople) method [28–32]. The Hückel MO method applied to conjugated hydrocarbons having no heteroatoms, when the secular equation can be formally represented by a binary matrix, is tantamount to graph-theoretical spectral theory [33–37]. Hence, such results can therefore be viewed as graph-theoretical in nature, results that follow from molecular connectivity alone.

The recent alternative graph theoretical approach to “the problem of ring currents” emerged for the first time already in mid-1970s [14] and was for most time overlooked, then again outlined about 10 years ago [15] to be again overlooked, and to be resuscitated just a few years ago [16]. This approach is based on the concept of conjugated circuits as the elementary components in the calculation of π -electron bond currents. Conjugated circuits arise within individual Kekulé valence structure as those circuits in the valence structure in which there is alternation of CC single and CC double bonds [38–42]. They are necessarily even, can involve $4n + 2$ or $4n$ π -electrons and contribute diamagnetic (anticlockwise) and paramagnetic (clockwise) currents, respectively. In order to find molecular π -electron current patterns, one has to find contributions to molecular ring currents coming from all conjugated circuits in all Kekulé valence structures; the number of conjugated circuits is $K(K - 1)$, where K is the number of Kekulé valence structures in a molecule [43]. In this graph-theoretical approach the actual computations of CC π -electron bond currents are thus reduced to *enumerating* the participation of individual CC bonds in $4n + 2$ and $4n$ conjugated circuits.

In this contribution we will examine CC π -electron bond currents for a class of benzenoid hydrocarbons which have two or more π -sextets, while the remaining C=C bonds have fixed positions. The smallest representative of this class of benzenoids is phenanthrene.

2 Quest for aromaticity

Before we continue with our graph-theoretical approach to ring current calculations and we use of such results to characterize the aromaticity in benzenoid hydrocarbons with fixed π -sextet aromatic benzenoids we ought to briefly mention other theoretical approaches to the characterization of the elusive concept of aromaticity, which despite its ambiguity remains one of the central notions in organic chemistry. There is no doubt that the first and probably the most significant advancement towards understanding aromaticity was Hückel’s $4n + 2$ and $4n$ Rule, that holds for monocyclic compounds, explaining the difference between aromatic benzene C_6H_6 and non aromatic cyclooctatetraene C_8H_8 , and also the aromatic character of cyclopentadiene anion $C_5H_5^-$, cycloheptatriene cation $C_7H_7^+$, and cyclooctatetraene dianion $C_8H_8^{2-}$. Numerous efforts to generalize this rule to polycyclic conjugated hydrocarbons have failed—till 1976, when it has been shown that conjugated circuits do offer such a generalization [28]. This was recognized by few scientists [44], while apparently many remain unaware of it.

While Kekulé thought that aromaticity should be defined in terms of structural concepts, Erlenmeyer, who was first to propose three Kekulé valence structures for

naphthalene, advocated the determination and characterization of aromaticity on the basis of properties of compounds. Apparently his view prevailed and resulted over the time in numerous proposed criteria for aromaticity, based on molecular energetic properties like the extra stabilization due to delocalization and resonance [45–47], molecular geometric properties such as bond equalization [48,49], molecular spectral properties, i. e., UV spectra as well as NMR spectra [50], molecular magnetic properties based on π electron ring currents induced by an external magnetic field [51–57] besides molecular reactivities. In view of this diversity of approaches to aromaticity, each of which may parallel some of multitude of aspects of aromaticity, Klein and Babić recently described aromaticity as an n -dimensional molecular feature [58]. What this implies is that aromaticity cannot be characterized by a single (numerical) entry, but rather as n -dimensional vector. With more recent advancements of quantum chemistry and the emergence of ab initio computations, theoretical and computational properties started to play an increasing role in discussions of aromaticity and bridging the gap between different theoretical models of aromaticity. Of particular significance is also the revival of interest in valence bond (VB) calculations [59–61] and VB ab initio calculations [62–65], which form a bridge between the quantum-chemical and the graph-theoretical calculations.

However, because aromaticity is a non-observable quantity, there is considerable latitude in relating it to various molecular properties, whether experimental or equally non-observable concepts, such as molecular orbitals, resonance energies, or ring currents. This is well reflected in a variety of approaches for calculation of molecular resonance energy (RE) or delocalization energies, such as: the Dewar's method [65], the method of Hess and Schaad [66], several topological or graph-theoretical methods [67–70] π electron conjugated circuit theory of Randić [38–40,42], Simpson–Herndon's semi-empirical VB method [71,72], and the block-localized wave function method [73–75]. Besides having different methodologies these approaches differ in how they define the extra stabilization energy. Most approaches calculate the extra stabilization energy as a difference between the total energy of the molecule and a hypothetical "reference" system lacking delocalization. In this respect Randić's π electron conjugated circuit theory [38–40,42], is an exception, because in this approach RE is defined naturally by the count of the contributing conjugated circuits, the approach that holds also for benzene.

Before closing this short outline of diverse approaches to aromaticity we would like to mention that, while most chemist agree that aromaticity is one of the central concepts of organic chemistry, questions remain concerning the characterization of aromaticity, its elusive definition, and even the possibility that no definition of aromaticity may be unique [76] or even possible. Clearly if it is difficult to characterize and define aromaticity for conjugated hydrocarbons, one can only think of additional difficulties that are to accompany extending the concept of aromaticity to heterocyclic molecules and even inorganic structures.

Be it as it may, the recent advancement in ab initio calculations of π -electron density currents and ab initio calculations of ring currents and chemical shifts as developed by Schleyer et al. may turn out to present currently useful standards for discussion of aromaticity and a testing ground for alternative theoretical and experimental approaches.

3 Clar's structural formulas of benzenoid hydrocarbons

In Fig. 1 we have illustrated Clar's structural formulas for a dozen benzenoid hydrocarbons. These formulas in the current version in which selected benzene rings are represented by π -aromatic sextets, may have originated by Crocker [77], rather than with Armit and Robinson [78], but it was Clar [50] who fully developed the notion of π -aromatic sextets and supported the model with spectral experimental data, including NMR data. One of the remarkable results of Clar's model of benzenoid hydrocarbons is his conclusion that benzenoid hydrocarbons having $6n$ π -electrons (molecules in the upper half of Fig. 1), will display unusual stability. This rule, which is by far more general than the Hückel $4n + 2$ rule for monocyclic conjugated systems, because it applies to polycyclic benzenoid hydrocarbons that are more general than monocyclic systems of the Hückel Rule, may not be so widely known. It is interesting to observe, for example, that giant benzenoids of Klaus Müllen [79], known for their extraordinary stability are all $6n$ π -electron systems. The Clar theory, as shown by Balaban [80], can be extended also to 3-dimensional systems.

All benzenoids of Fig. 1 have rings with fixed locations for their π -electron sextets, which are represented by inscribed circles that signify benzenoid rings, the six π -electrons of which are represented in Kekulé valence structures by three C=C bonds. The difference between the five structures in the upper part of Fig. 1 and the seven structures in the lower part of Fig. 1 is that benzene rings in molecules in the upper part of Fig. 1 either contain a π -sextet or, in the terminology of Clar have "empty" rings. Such benzenoids have been called by Clar "fully benzenoid hydrocarbons," and by Balaban and Klein "claromatic" [81–83]. The benzene rings in the seven benzenoid hydrocarbons in the lower part of Fig. 1 either contain π -sextet or, in their rings have a *single* C=C bond, hence, are not "empty."

There is yet another class of benzenoid hydrocarbons, illustrated in Fig. 2, in which some benzene rings have *two* C=C bonds and which have no unique Clar's formula.

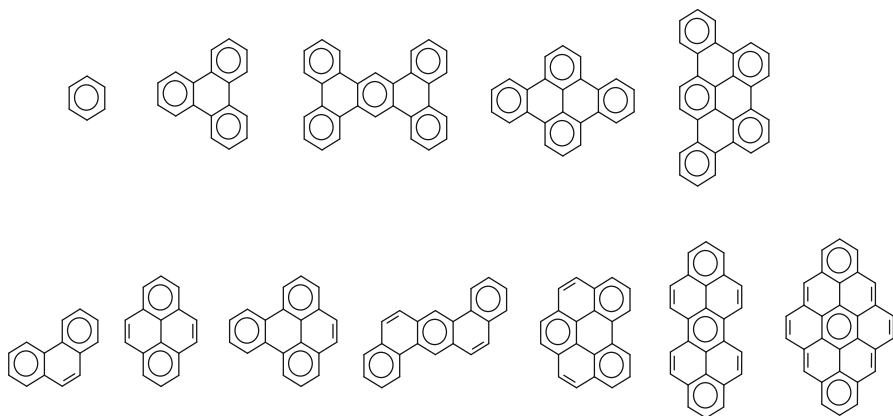


Fig. 1 Benzenoid hydrocarbons with a single Clar Structure. In the *first row* are fully benzenoid hydrocarbons (having π -sextets and "empty" rings) while benzenoids in the *second row* have π -sextets and ring(s) with one C=C bond

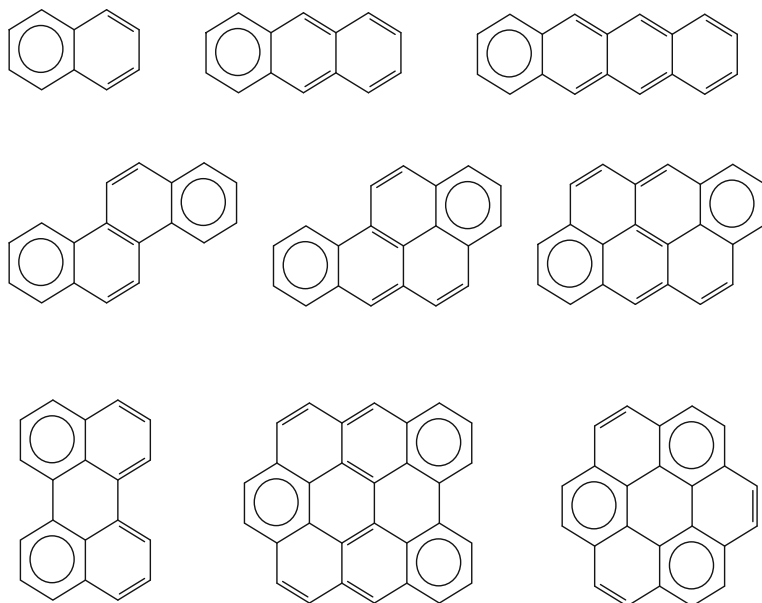


Fig. 2 Smaller benzenoid hydrocarbons having several Clar structures, that is, having “migrating” π -sextets

Clar referred to this class of benzenoid hydrocarbons as benzenoids with “migrating” π -sextets. In view of distinct structural features of the three classes of benzenoid hydrocarbons with respect to π -electron sextets, it is of interest to investigate bond currents and ring currents of these molecules separately. Calculations of CC bond currents using graph-theoretical methods have been recently reported for fully benzenoid hydrocarbons of the upper part of Fig. 1 [17]. In this article we will report on calculations of CC bond currents using a graph-theoretical approach for the seven benzenoid hydrocarbons of the lower part of Fig. 1, having also a unique Clar structure and fixed π -sextets beside aromatic sextet rings and empty rings.

4 Conjugated circuits

The central structure elements in the recently introduced graph-theoretical approach to the calculation of CC bond currents are conjugated circuits. Conjugated circuits are defined within individual Kekulé valence structures as circuits in which C–C and C=C bonds alternate. We will outline the approach on benzo[ghi]perylene $C_{22}H_{12}$, the 14 Kekulé valence structures of which are shown in Fig. 3 and labelled A–N. In Fig. 4 are illustrated all conjugated circuits for the first of the 14 Kekulé structures of benzo[ghi]perylene, six of which have a single component, six of which have two components, and one that has three components. A theorem of Gutman [43] tells that each Kekulé valence structure in a molecule having K Kekulé valence structures has $K - 1$ conjugated circuits, the count of which include, as we see from Fig. 4, individual conjugated circuits as well as disjoint conjugated circuits.

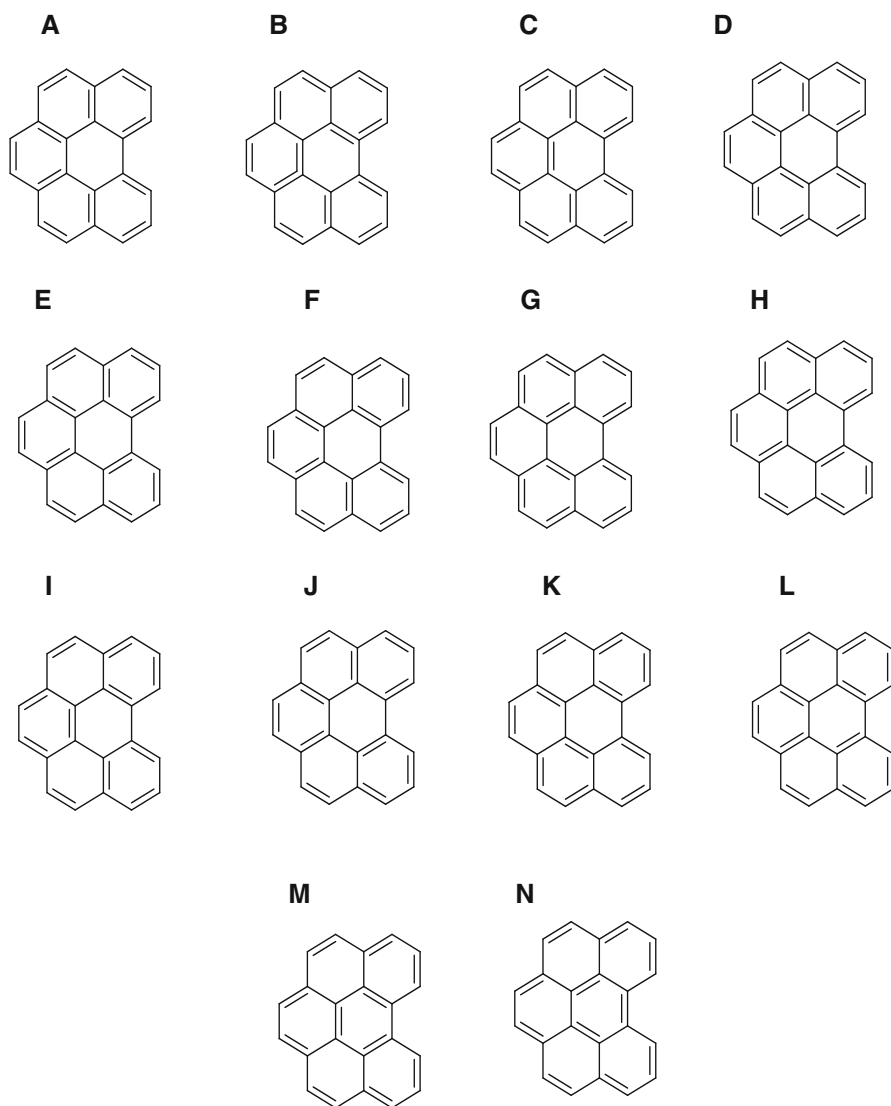


Fig. 3 The 14 Kekulé valence structures of benzo[*ghi*]perylene, labeled **a–n**

If one assigns to each conjugated circuit an anti-clockwise unit current (diamagnetic bond current), which is indicated in Fig. 5 by arrows along CC bonds, one obtains the corresponding π -electron currents. Conjugated circuits are always even, of size $4n + 2$ or $4n$. Conjugated circuits of size $4n + 2$ carry diamagnetic (anti-clockwise) currents, while conjugated circuits of size $4n$ (which occur in non-benzenoid conjugated hydrocarbons) carry paramagnetic (clockwise) currents. In order to find CC bond currents we have first to add contributions from all currents from conjugated circuits in a single Kekulé valence structure, and then add contributions from the remaining Kekulé

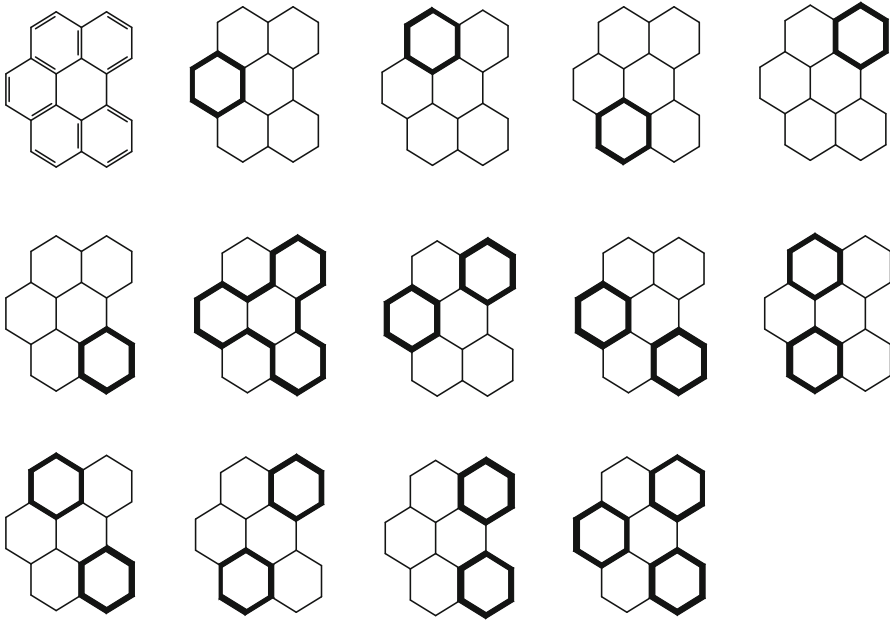


Fig. 4 The 13 conjugated circuits of the first Kekulé valence structure of benzo[*ghi*]perylene of Fig. 3

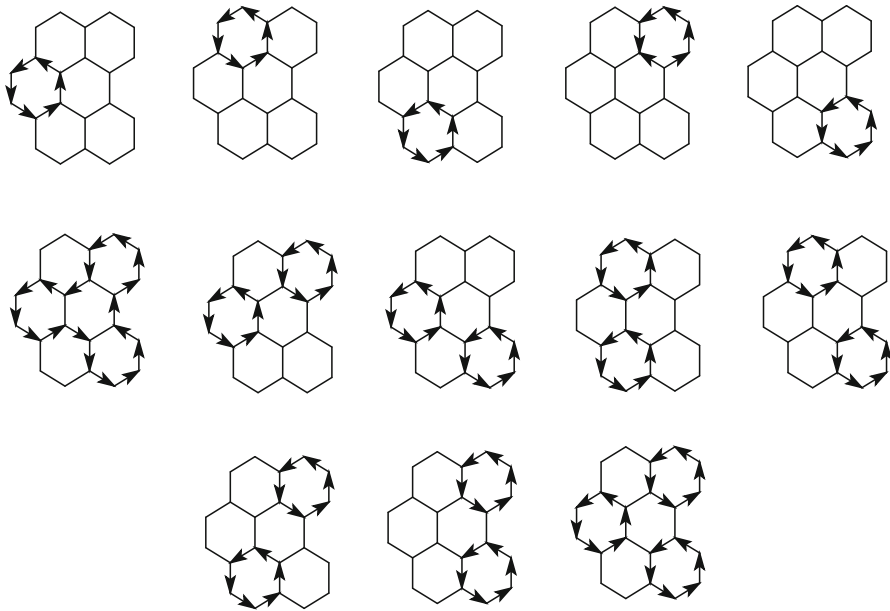


Fig. 5 π -Electron bond currents for the 13 conjugated circuits of Fig. 4

valence structures. Thus if we focus attention on $[ghi]$ CC bonds of benzo $[ghi]$ perylene we can see from Fig. 5 that in bond g in conjugated circuits 1, 6, 7, 8, and 13 the current flows from right to left while in conjugated circuits 2, 9, and 10 current flows from left to right, resulting in an overall current of 2 units in the direction right to left. On the other hand, currents in CC bond h appear only in conjugated circuits 1, 7, 8, and 13 and flows upward, which results in current of strength 4 units flowing upwards. Due to the symmetry the resulting currents in CC bond i is the same as in CC bond g , but flows from left to right. These results and similar results for the remaining CC bonds of benzo $[ghi]$ perylene are summarized in the top left part of Fig. 6.

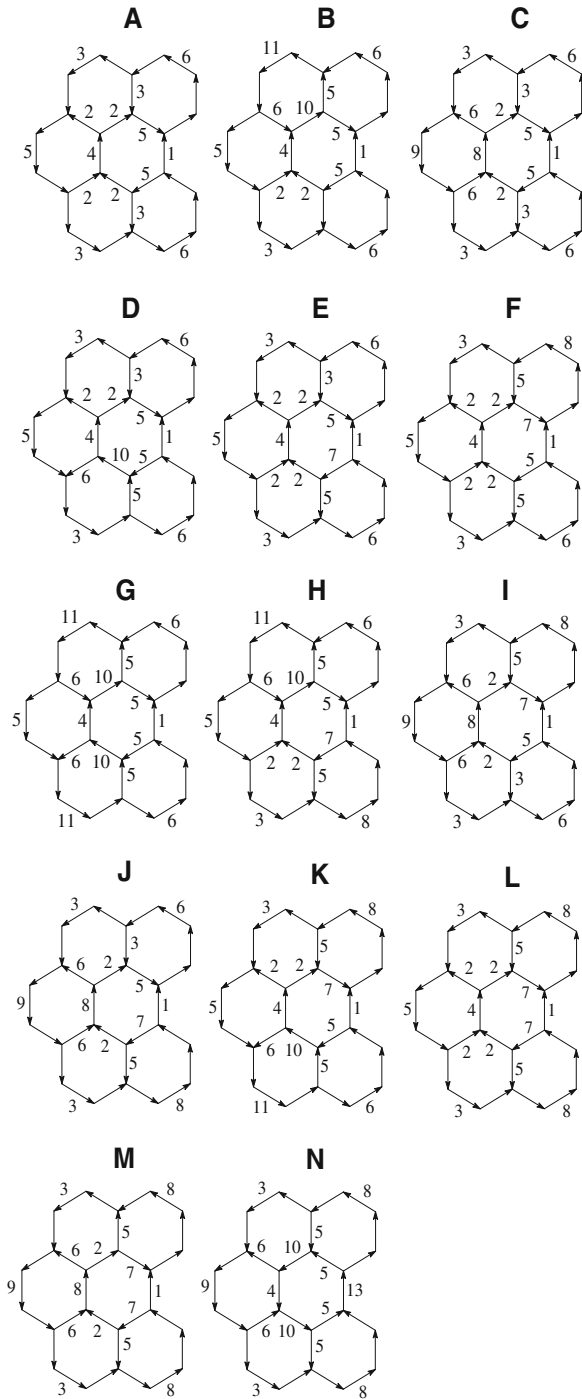
Figure 6 shows CC bond currents for all 14 Kekulé valence structures of benzo $[ghi]$ perylene of Fig. 4. Observe that in all cases Kirchhoff current laws are satisfied at every carbon junction so that the currents coming in and going out of such junction are balanced. The Kekulé valence structures that are symmetrical with respect to a horizontal line bisecting the structure (structures A, C, G, L, M and N) have necessarily the same bond currents in symmetry-related bonds. Asymmetrical structures come in pairs: (B, D), (E, F), (H, K), and (I, J) and their bond currents are symmetrical with respect to reflection across the bisecting horizontal line. As one can see from Fig. 6, in the case of benzo $[ghi]$ perylene each Kekulé valence structure shows a different pattern for π -electron bond currents. However, in a general case two different Kekulé valence structures may result in the same π -electron bond currents. Hence, one cannot reconstruct the corresponding Kekulé valence structure from a given pattern for π -electron bond currents. Superposition of all CC bond currents of all 14 Kekulé valence structure will give the π -electron current pattern for the molecule, to be shown later.

A close look at Fig. 6 shows considerable variations in CC bond currents in different Kekulé valence structures. In the case of benzo $[ghi]$ perylene CC bond, currents can be as small as 1 unit and as high as up to 13 units (which is $K - 1$). Clearly CC bond currents have to be less than K , the number of Kekulé valence structures, because the number of conjugated circuits is $K - 1$, and if a CC bond current is present in all conjugated circuits and maintains the same direction (as is the case with one peripheral CC bond in Kekulé valence structure N of benzo $[ghi]$ perylene) its current amplitude will be $K - 1$. Let us add amplitudes of CC bond currents for all bonds in each Kekulé valence structure separately, when one obtains in the case of benzo $[ghi]$ perylene values in the range from 110 to 186, as shown below:

Structure	A	E, F	C	L	I, J	B, D	M	H, K	G	N
Current sum	110	122	132	134	146	148	158	160	186	178
R_1	5	4	3	3	3	3	3	2	2	1

In the bottom row we show the number of the smallest conjugated circuits R_1 for each Kekulé valence structure. As one can see, the number of R_1 decreases with the increase of the current sum. Thus Kekulé valence structures which make larger contributions to the molecular RE apparently make smaller contributions to π -electron currents, at least in the case of benzo $[ghi]$ perylene.

Fig. 6 CC bond currents for individual Kekule valence structures of benzo[ghi]perylene



5 Construction Of π -electron currents

Calculations of π -electron CC bond currents take place by first constructing all Kekulé valence structures and then finding all conjugated circuits of a molecule, which can be performed by inspection of individual Kekulé valence structures; although if straightforward, this laborious and error-prone already for relatively small molecules. As we have seen, it may be done for smaller molecules, like benzo[ghi]perylene, with $K = 14$. However, as K grows, the total number of all conjugated circuits grows quadratically, and require computer-oriented approaches. Fortunately, it suffices to have a single Kekulé valence structure, from which all conjugated circuits for any benzenoid and non-benzenoid conjugated system can be obtained. Once an arbitrarily *single* Kekulé valence structure is selected, one can construct in a systematic way all other conjugated circuits by superimposing it successively with the $(K - 1)$ remaining Kekulé valence structures. Each time C=C bonds which are not in the same positions in the two Kekulé valence structures, form a conjugated circuit or disjoint conjugated circuits. This algorithm, which has been outlined over 30 years ago [43], illustrates a not-so-widely-known fact that a single (any) Kekulé valence structure of a molecule contains information on all other Kekulé valence structures. That is, by knowing a *single* Kekulé valence structure one can construct *all* Kekulé valence structures of the molecule, and having *all* Kekulé valence structures, by superposition with a single Kekulé valence structures one obtains all conjugated circuits.

One can obtain patterns of π -electron bond currents for a molecule in two ways:

- (1) One considers all Kekulé valence structures separately and superimposes the resulting CC bond currents over a single molecular structure, or
- (2) One constructs all possible conjugated circuits for the molecular graph and enumerates their occurrence for each CC bond.

The first alternative, which we have already seen, gives π -electron bond patterns for individual Kekulé valence structures, while the second alternative appears more efficient, particularly suitable for molecules having large numbers of Kekulé valence structures. We will illustrate now the second approach again on benzo[ghi]perylene. Before showing the remaining conjugated circuits of benzo[ghi]perylene, we show in Fig. 7 half a dozen circuits that one can construct for benzo[ghi]perylene which though even and in isolation can support conjugation (alternation of C–C and C=C bonds) do not represent conjugated circuits—because the remaining part of the molecule has no Kekulé valence structure, that is, one can not assign C=C bonds to the remaining CC bonds so that every carbon atom is incident to one C=C bond.

In the case of proper conjugated circuits, the CC bonds not involved are either C–C or C=C bonds and no carbon atom is left with unpaired π -electron. In Fig. 8 we have illustrated all additional conjugated circuits of benzo[ghi]perylene, besides the 13 conjugated circuits already shown in Fig. 4. Having this construction complete, one enumerates the Kekulé valence structures in which each such conjugated circuit occurs, the number of which is $2K^*$, where K^* is the number of Kekulé valence structures for the molecular *fragment* obtained when the conjugated circuit considered is excised from the molecular graph. The factor 2 comes because each conjugated circuit, just as is the case with benzene ring, can have two Kekulé structures. To obtain

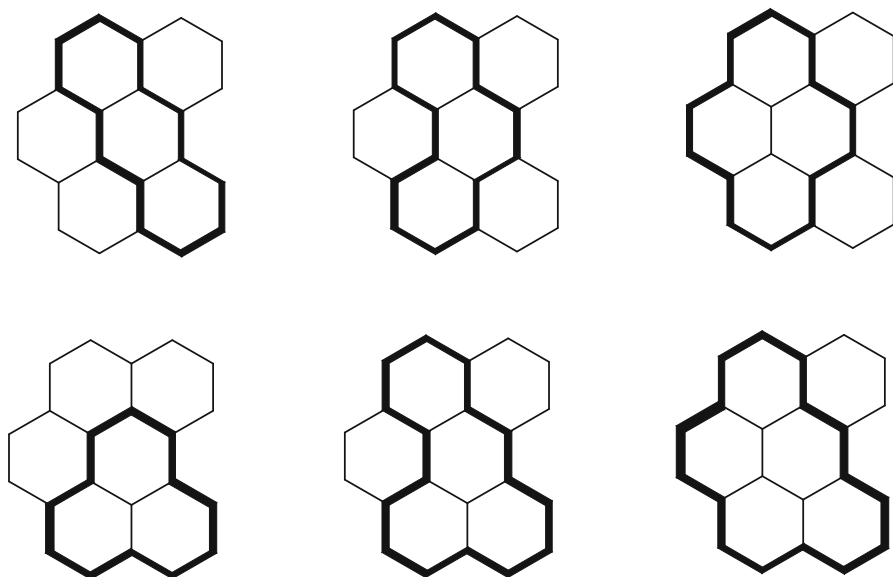


Fig. 7 Molecular fragments that do not qualify as conjugated circuits

π -electron CC bond currents one selects a CC bond and adds $2K^*$ contributions from all conjugated circuits of which the considered CC bond is part. For example, the three peripheral CC bonds of the top left benzene ring of benzo[ghi]perylene occur in three conjugated circuits of the first Kekulé valence structure in Fig. 4 (conjugated circuits 2, 9 and 10) with $K^* = 3, 1,$ and 1 respectively, which add to $2K^* = 10$. In order to obtain CC bond currents for these three peripheral CC bonds we should do the same analysis on the the remaining conjugated circuits of Fig. 8 and add the results.

6 Results

In Fig. 9 we report on the π -electron CC bond currents for the seven benzenoid hydrocarbons of the lower part of Fig. 1. Observe that at all junctions the π -electron bond currents satisfy the Kirchoff currents law, as should be expected. The first finding that follows from Fig. 9 is that benzene rings that involve π -sextets at the molecular periphery of molecules are associated with the largest peripheral CC bond currents. The magnitudes of the currents shown in Fig. 9 are un-normalized, given as the *counting* integers. The magnitudes of the thus calculated currents will clearly increase with the number of Kekulé valence structures because of the quadratic increase in the number of conjugated circuits, and when one is interested in comparing currents in different molecules, one should divide the bond currents of Fig. 9 by the number of conjugated circuits. Of interest may also be a normalization based on K , the number of Kekulé valence structures or a normalization by dividing currents by N , the number of π -electrons.

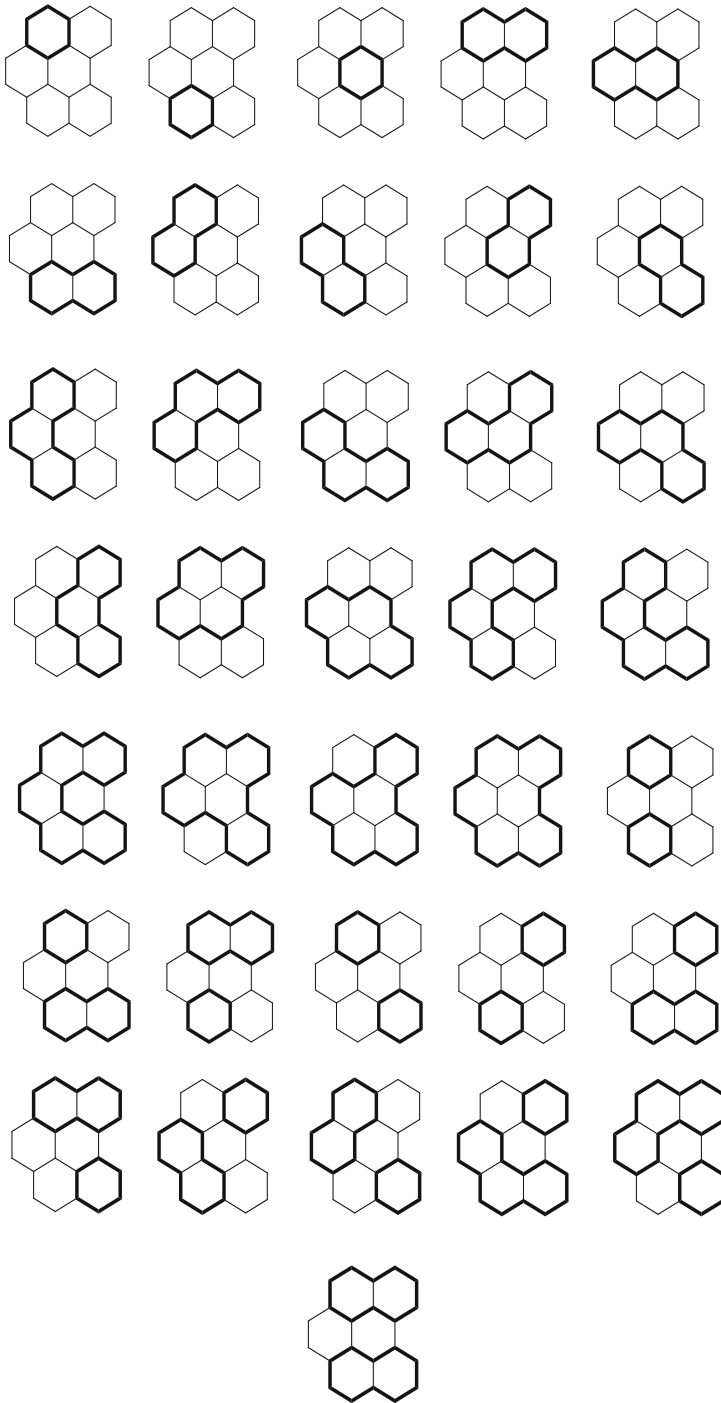


Fig. 8 Additional conjugated circuits of benzo[*ghi*]perylene

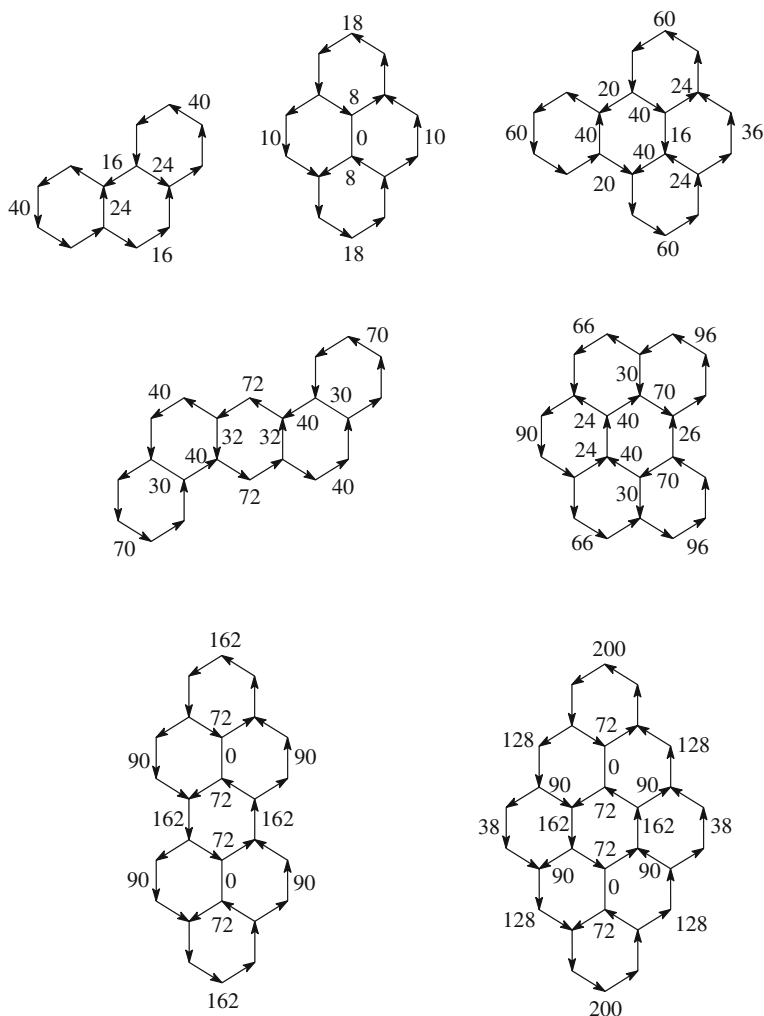
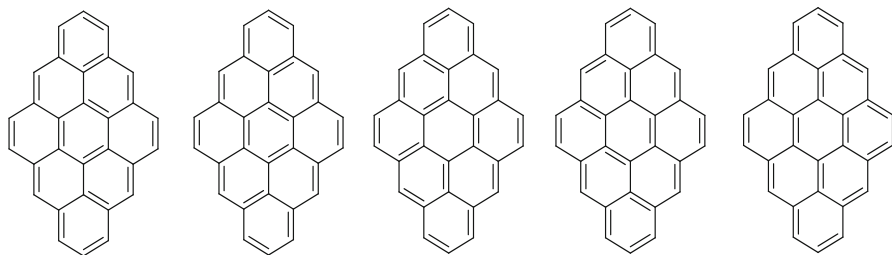


Fig. 9 CC Bond π -electron currents for the seven benzenoid hydrocarbons of the *second row* of Fig. 1

In Table 1 we report the normalized bond currents: the average currents per Kekulé valence structure, as well as the average currents per conjugated circuit, and the average currents per π -electron. As one can see from Table 1, the benzene rings having π -sextets have the largest average currents per conjugated circuit, all in the range 0.4945–0.6000. The benzene rings involving single C=C bond have the average currents per conjugated circuit in the range 0.2942–0.4000, with a few exceptions such as the “equatorial” C=C bonds in dibenzocoronene. Finally, the “empty” rings (the central rings in benzopyrene and benzo[*ghi*]perylene) have the average currents per conjugated circuit of 0.1818 and 0.1429, respectively, being less than half of the the average currents per conjugated circuit for rings involving single C=C bond.

Table 1

CC bond current/ K	Numerical	Per conjugated circuit divided by $K(K - 1)$	Per electron divided by N
Phenanthrene	$K = 5$	$K(K - 1) = 20$	$N = 14$
12/5	2.40000	0.60000	0.17143
8/5	1.60000	0.40000	0.11429
Pyrene	$K = 6$	$K(K - 1) = 30$	$N = 16$
18/6	3.00000	0.60000	0.18750
10/6	1.66667	0.33333	0.10417
Benzopyrene	$K = 11$	$K(K - 1) = 110$	$N = 20$
60/11	5.45455	0.54545	0.27273
36/11	3.27273	0.32727	0.16364
20/11	1.81818	0.18182	0.09091
Dibenzoanthracene	$K = 12$	$K(K - 1) = 132$	$N = 22$
72/12	6.00000	0.54545	0.27273
70/12	5.83333	0.53030	0.26515
40/12	3.33333	0.30303	0.15152
Benzoperylene	$K = 14$	$K(K - 1) = 182$	$N = 22$
96/14	6.85714	0.52747	0.31169
90/14	6.42857	0.49451	0.29221
66/14	4.71429	0.36264	0.21429
26/14	1.85714	0.14286	0.08442
Peropyrene	$K = 18$	$K(K - 1) = 306$	$N = 26$
162/18	9.00000	0.52941	0.34615
90/18	5.00000	0.29412	0.19231
Dibenzocoronene	$K = 20$	$K(K - 1) = 380$	$N = 30$
200/20	10.00000	0.52632	0.33333
128/20	6.40000	0.33684	0.21333
38/20	0.05000	0.10000	0.06333

**Fig. 10** Five Kekulé valence structures of dibenzocoronene having five, four, three, two and one benzene ring with three CC double bonds

Dibenzocoronene apparently is an exception in comparison with other benzenoids with the same or similar number of fused benzene rings, in having an unusually small number of Kekulé valence structures for molecules of this size. In Fig. 10 we show

five of the 20 Kekulé valence structures of dibenzocoronene, starting with the Fries structure, the Kekulé valence structure having the largest number of benzene rings with three CC double bonds (which is in this case equal to five benzenoid rings), followed by structures having four, three, two, and one benzenoid ring with alternating C=C and C–C bonds. As one can see, there are many benzenoid rings in the five Kekulé valence structures of dibenzocoronene that do not involve small conjugated circuits (which is typical of Kekulé structures that contribute to the RE of molecules). Therefore although dibenzocoronene is aromatic (as it has no $4n$ conjugated circuits to decrease its intrinsic aromaticity from the contributing $4n + 2$ conjugated circuits) it is not accompanied by a high RE and REPE (resonance energy per electron).

A close comparison of CC bond currents in peropyrene and dibenzocoronene is instructive: The dominant CC bond currents in dibenzocoronene involve the same benzenoid rings (uppermost and lowermost) as in peropyrene. Thus one can view the CC bond currents in dibenzocoronene as perturbed CC bond currents of peropyrene.

7 Ring currents

Figure 9 and Table 1 summarize the outcome of our calculations on CC bond currents. One can interpret these results in two ways: One can look for the dominant current over the molecular network, and alternatively, one can partition the CC bond currents into ring current contributions. For instance, in the case of coronene as has been shown in Ref. [18] and by ab initio computations of Balaban et al. [13], one can speak of the peripheral diamagnetic current (or current density) as the dominant current and a minor paramagnetic current in the central ring. In the case of non-benzenoid isomers of coronene having five- and seven-membered rings, again one finds dominant peripheral diamagnetic currents, while in the interior there are some variations in patterns of bonds of the central ring and radial CC bonds towards the molecular periphery. In the case of benzenoid hydrocarbons, if one considers the alternative interpretation one can determine the individual ring currents, which are illustrated in Fig. 11. This alternative interpretation is useful if one wishes to compare the results of such computations with the calculations based on the MO approaches, which starts by assuming the existence of ring currents and calculating such ring currents.

Figure 11 shows the decomposition of the π -electron CC bond currents into individual ring currents. Although the decomposition of ring currents is generally not unique, if one selects 6-membered rings in benzenoid hydrocarbons as the ultimate current components, the results are unique. From comparing Fig. 11 with Fig. 1 it is immediately visible that rings containing π -electron aromatic sextets have the maximal ring currents, that benzene rings containing C=C bonds have intermediate ring currents, and that “empty” rings contain the smallest ring currents. Inadvertently, but not unexpectedly, the results of our computations of π -electron current through the model of conjugated circuits, resulted in yet another theoretical support of Clar’s notion of aromatic π -sextets.

It is of some interest to observe that in several instances symmetry-non-equivalent benzenoid rings have the same ring currents, which include also the terminal and the central benzene rings in peropyrene and dibenzocoronene. On the other hand, in

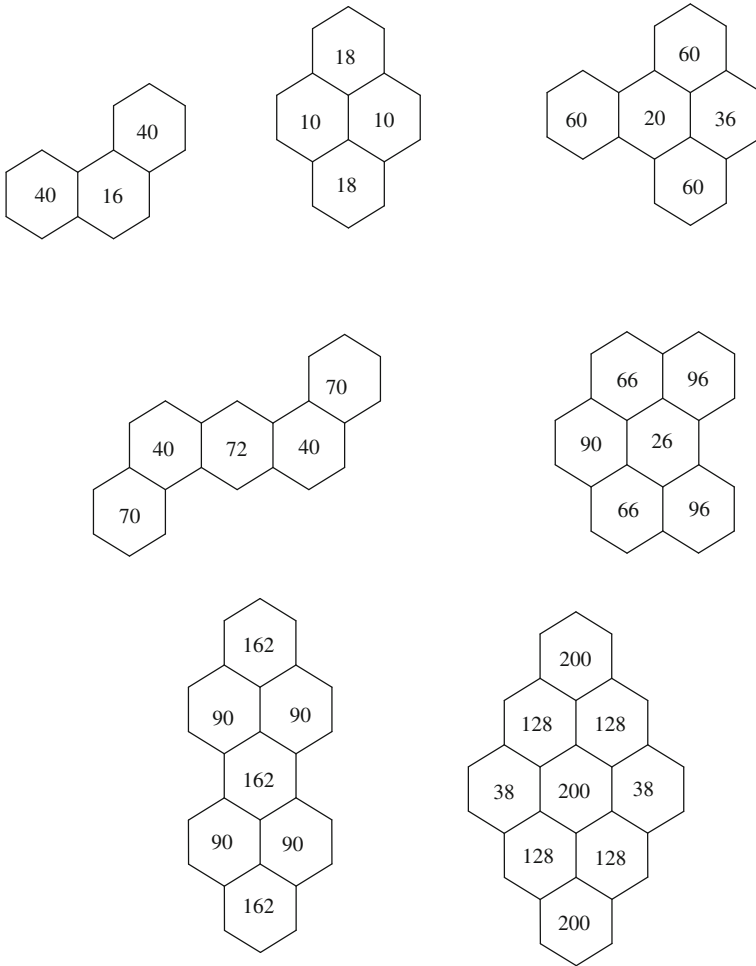


Fig. 11 Decomposition of bond π -electron currents into ring currents for the seven benzenoid hydrocarbons of Fig. 9

cata-condensed dibenzoanthracene the central benzenoid ring has slightly higher ring current than the terminal rings. Interestingly, this parallels the findings via HMO ring current calculations of Malion, the *ab initio* current density calculations of Fowler and collaborators on anthracene and tetracene, as well as calculations based on the model of conjugated circuits [16], all of which show that central rings in these molecules have higher ring currents or higher π -electron ring densities than the terminal rings.

8 Concluding remarks

The essential result of the present calculations of induced currents in benzenoid molecules are not the ring currents of Fig. 11, which reports on π -electron currents in

individual CC bonds, but the CC currents shown in Fig. 9. The reason for this is that CC π -electron currents of Fig. 9 can be related, in principle, to experimentally observable quantities, the π -electron current densities, which in turn relate to the experimentally observable quantities, the π -electron densities. It is true that ring currents relate also to an experimentally observable quantity, the proton chemical shift, but as one can see by comparing Figs. 9 and 11, the CC bond currents for the individual rings on the molecular periphery determine the magnitude of the ring currents of peripheral rings (rings carrying hydrogen atoms). Thus the distinction between CC bond currents and ring currents, at least in benzenoid hydrocarbons, can also be viewed as semantic, but the former allows a direct comparison with quantum chemical calculations, while the latter is to some extent model dependent: not in the part that relates to the calculation of ring currents, but in the part that relates to the calculation of chemical shifts. For example, Ciesielski et al. [12] calculated chemical shifts in selected benzenoid hydrocarbons assuming only contributions from the adjacent benzenoid rings and ignoring contributions of non-adjacent rings. Contributions from non-adjacent rings will affect ring currents calculations but have no effect on CC bond currents, though refined calculations that take into account the role of non-adjacent benzenoid rings need not introduce dramatic changes in numerical values of calculated protein chemical shifts.

In addition, there are, however, two other more significant aspects of π -electron CC bond and ring currents calculations on which we would like draw the attention of readers. The first relates to the fundamental question of normalization of CC π -electron currents (which, of course affects magnitudes of rings currents also) in a class of benzenoid hydrocarbons having essentially single CC bonds. The second relates to the equally important, if not even more fundamental, problem of understanding how can two so distinct theoretical approaches to π -electron currents as are the quantum chemical calculations that are based on calculus, that is mathematics of *continuum*, and the graph theoretical calculations that are based on *enumerations*, that is discrete mathematics, yield apparently comparative results, as has been for the first time observed on isomers of coronene in [16].

Coming to the first problem, it suffices to focus attention on perylene, which in the model for conjugated circuits is equivalent to two independent naphthalene units. So should normalization of CC currents be based on the number of Kekulé structures of naphthalene $K = 3$, or perylene $K = 9$? Are perylene and similar benzenoid systems a case of self-similar systems, which may require a renormalization, as has been the case with self-similar systems in quantum electrodynamics? If this would be the case, then this will be not only the first time that renormalization enters chemistry [84], but probably the simplest case of understanding the nature of renormalization, which after being for the first time introduced in physics it took about a year to be accepted.

The second problem may relate, even if distantly, to occasional overlap of selected partial results of simplified quantum chemical MO calculations with simplified quantum chemical VB calculations, the latter involving some elements of Discrete Mathematics (like Kekulé valence structures). However, in the case of CC π -electron calculations by quantum chemical methods and graph theoretical approaches, the underlying problems are not in the computational details but in the conceptual differences, which appear of paramount magnitude. Hence, it may take years before we

see the light at the end of this tunnel, which may turn out to remain a formidable theoretical chemistry problem.

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