

ARTICLES

Molecules-in-Molecule Estimation of the Extent of Localization of Kekuléan Substructures in Polycyclic Aromatic Hydrocarbons

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This article first revises graph-theoretical (local aromaticity and overall molecular) indices, introduced by M. Randić in 1975, for benzenoid hydrocarbons and somewhat improves them for computer enumeration. This goes beyond total Kekulé structure enumeration, yielding an index calculation useful for the quantitative estimation of localization of different Kekuléan substructures (including ethylene-, benzene-, annulene-, and radialene-units). This may be viewed as a “molecules-in-molecule” approach to polycyclic aromatic hydrocarbons within the context of graph theoretical partitioning.

THE RANDIC INDICES REVISITED

The physical and/or chemical properties of benzenoid hydrocarbons (BHs, Figures 1 and 2) have been well explained classically by Clar's aromatic sextet theory.^{1–3} It seems that the essence of this theory is to partition a given BH into two kinds of disjoint molecular pieces graph-theoretically: benzene rings (Clar sextets or full hexagons inscribed by circles) and carbon–carbon double bonds. Such examples are shown in IX, XI, and XII of Figure 2. In each of these BHs, two full hexagons are never adjacent, nor are two isolated double bonds conjugated, while every vertex of the BH is covered by a full hexagon or a double bond. This method of *total covering* (or partitioning) identifies a so-called “Clar structure” (or “Clar formula”) (as in ref 4). In other words, the benzene rings and/or carbon–carbon double bonds taken as the building blocks of the BH are interconnected with one another solely by means of only single bonds in an associated Kekulé (valence) structure. We consider an index quantitatively related to such graph theoretical partitioning in polycyclic aromatic hydrocarbons (PAHs).

Let us denote by $K (> 0)$ the total number of Kekulé structures of a given PAH. First partition the PAH into two pieces, a *base* substructure (unit) and the remnant. This base substructure is set to be Kekuléan. Let S and R be the numbers of Kekulé structures of the Kekuléan base substructure and of the remnant, respectively. Here every bond that connects between the two pieces is fixed to be single in the Kekulé structure counting of S and R . An index for the Kekuléan base substructure is defined as the ratio of the product $S \times R$ to K , i.e., as SR/K . Clearly this local index reduces to the Pauling bond order^{5–7} P , if an ethylene unit

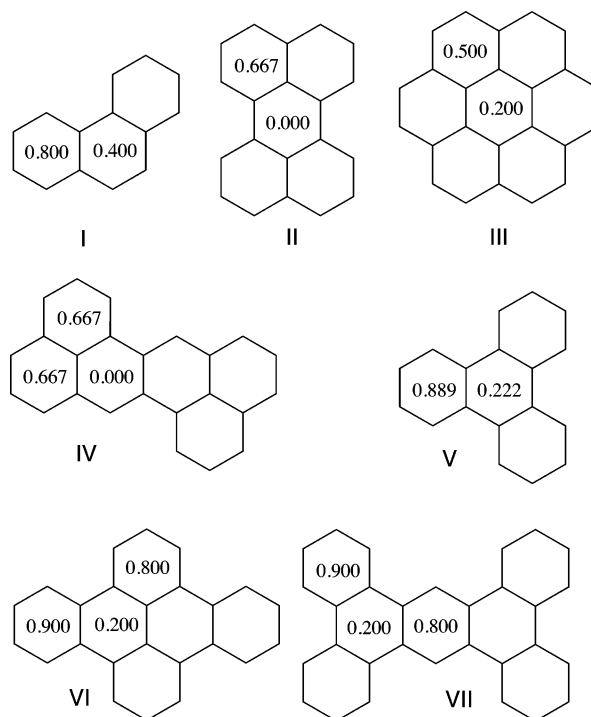


Figure 1. Calculations of the six-membered ring localization index $2R/K$ for phenanthrene I ($K = 5$), perylene II ($K = 9$), coronene III ($K = 20$), zethrene IV ($K = 9$), triphenylene V ($K = 9$), dibenzo-*[fg,op]*naphthalene VI ($K = 20$), and tetrabenzo-*[a,c,h,j]*anthracene VII ($K = 40$).

(a double bond) is chosen as the Kekuléan base substructure; then, $S = 1$, and $P = R/K$. Note that R is set to be 1 in the trivial case when the Kekuléan base substructure is the whole PAH. A general computationally efficient scheme is noted in the Appendix.

A natural case of interest occurs when the Kekuléan base substructure in a BH is a hexagonal ring. There are two Kekulé structures in the hexagon unit, in each of which triples

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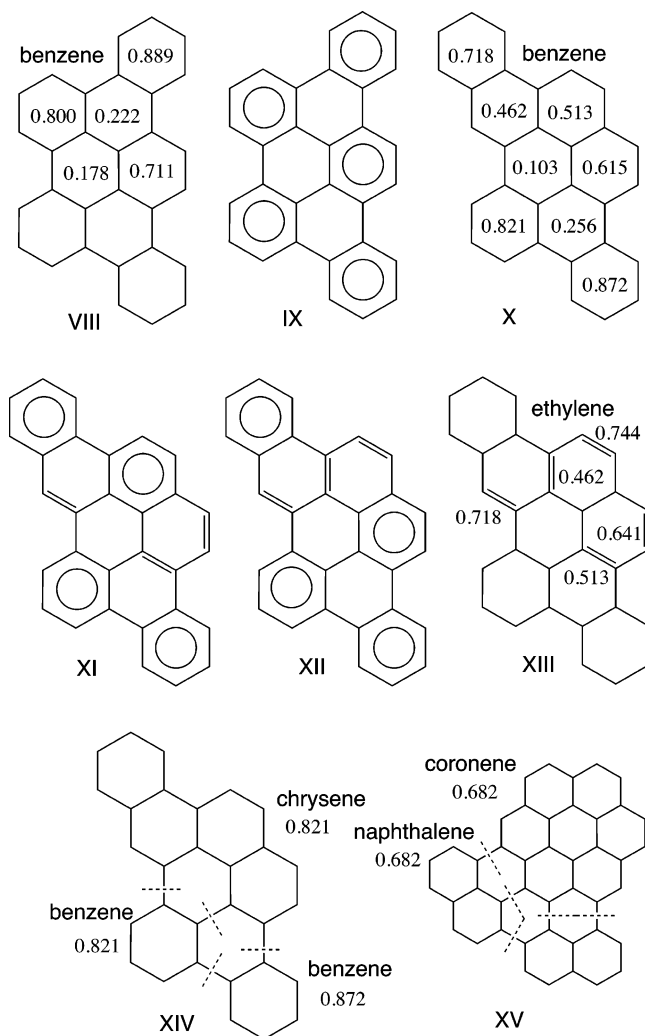


Figure 2. Isomeric tribenzoperylenes VIII–XIV and a hexagonoid hydrocarbon XV.

of single and double bonds alternate, so that $S = 2$. The Kekulé structure counting of R then begins after the removal of the hexagon and of all the edges that meet with the hexagon; note that this remnant substructure is not necessarily a benzenoid graph. This $2R/K$ has been introduced⁸ by Randić in 1975 as “index of local aromaticity” (or “local ring index”). Randić counts the number of Kekulé structures having the single-double alternation in the hexagonal ring and divides it by K . The remnant, if the BH is of large size, is influential in the sextet localization index $2R/K$.

There are many further choices for the Kekuléan base substructure. If it is taken as naphthalene, then $S = 3$; e.g., as for perylene II of Figure 1. It is to be noted that in the definition of SR/K , the Kekuléan base substructure need not necessarily be connected. For example, three sextets in XIX of Figure 3, each of which is far away from the others, can be chosen as the Kekuléan base substructure; $S = 2^3 = 8$ in this example.

Summation of $2R/K$ for all hexagonal ring units defines an overall molecular index. Such sum indices are calculated⁸ as 2.0000 for phenanthrene I, 2.6667 for perylene II, 3.2000 for coronene III, and 2.6667 for zethrene IV. For example, the sum, $4/5 + 2/5 + 4/5$, in the Randić overall index for phenanthrene I ($K = 5$) equals $10/5$, where the counted number of Kekulé structures appears in the numerator. Such

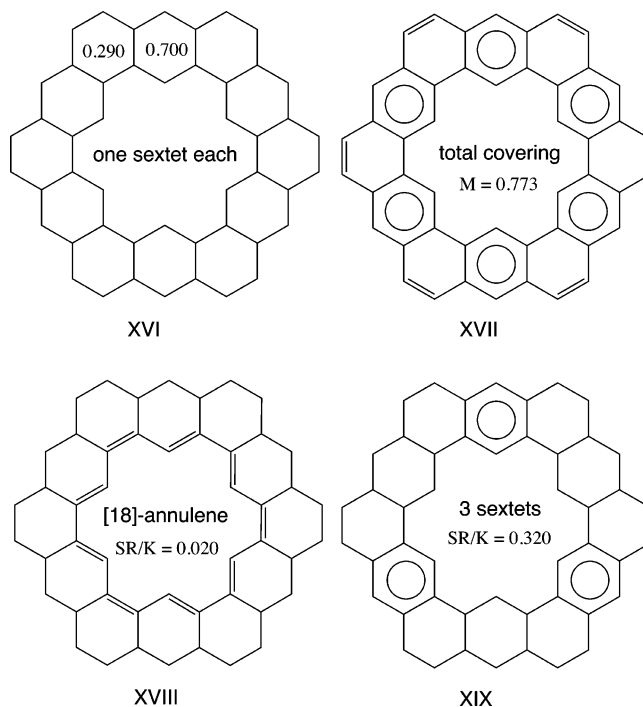


Figure 3. The localization index calculation for one sextet (left top), total covering (right top), [18]-annulene (left below), and 3 sextets (right below) in kekulene.

counts were described by Herndon⁹ and have been used¹⁰ in an explication of resonance energies earlier obtained via a relatively complicated semiempirical SCF-MO computation.¹¹

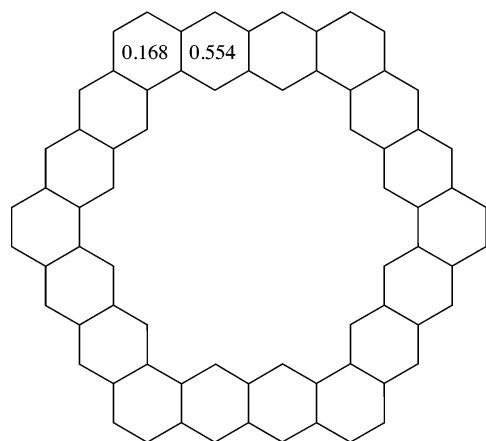
Another meaningful summation is possible as follows. A PAH is given, which may be totally covered by a *base* set of Kekuléan units (substructures), the number of entries being N . Here the total covering of the base set means that two Kekuléan units share no common site and that every vertex of the PAH is included in the base set. We then calculate a series of local indices, $S_1 \times R_1/K$, $S_2 \times R_2/K$, ..., and $S_N \times R_N/K$. The mean value of the indices $S_i R_i/K$, i.e., $\sum S_i R_i / (K \times N)$, is hereafter denoted by M . Note that for each Kekuléan unit, remnant i satisfies $R_i \geq (S_1 \times S_2 \times \dots \times S_N) / S_i$, $i = 1, 2, \dots, N$, so that

$$M \geq (S_1 \times S_2 \times \dots \times S_N) / K$$

Equality here for M holds only when every Kekuléan unit in the base set is “essentially disconnected” (refer to the following section) with one another in the base set. For instance, if one ethylene and two hexagon units in phenanthrene I are chosen as the base set, then N counts 3. One then has $S_1 R_1/K = 1 \times 4/5$ for the ethylene unit inside the center hexagon, and $S_2 R_2/K = 2 \times 2/5$ and $S_3 R_3/K = 2 \times 2/5$ for the two terminal hexagon units. Hence, M for this base set chosen in phenanthrene I is equal to $4/5$; refer to the Randić overall index $10/5$. The total covering by use of the base set of Kekuléan units is implicit in the above-mentioned definition of M .

CALCULATIONS AND DISCUSSION

The calculation of $2R/K$ for hexagonal rings is shown inside the hexagons of Figures 1–4. We have $2R/K = 0.00$ for the center rings in perylene II and zethrene IV; these



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Figure 4. The localization index $2R/K$ in a PAH homologue of kekulene.

rings are said^{8,12} to be “empty”. It is to be noted, however, that each of the center hexagons in zethrene IV has one “essential¹³” or “fixed²” double bond in Kekulé structure counting. If this essential double bond (i.e., full ethylene) is chosen as the Kekuléan base substructure, then P equals 1, because such an ethylene unit exists in every Kekulé structure. The value $2R/K = 0$ implies that no alternation of single and double bonds is possible inside the hexagonal ring; in other words, a hexagonal ring, even if $2R/K = 0$, is not necessarily empty.

The mean value M approaches 1 as the extent of localization for the base set of Kekuléan units increases, because the limit of each local index is at most 1. At this limit, one has the equality

$$S_1 \times S_2 \times \dots \times S_N = K$$

Then $M = 1$ for the base set. A BH, where this equality holds, is called¹⁴ “essentially disconnected”. In zethrene IV, for the two naphthalene units or for the two ethylene units in the center region, $S_i R_i/K = 1$; then, one has $M = 1$ for this base set. The above calculation suggests that the zethrene molecule can be decomposed into two naphthalene and two ethylene (or one butadiene) units and that the connection between them as a π -electron system is very weak.¹⁵ The Kekuléan base substructure, where $SR/K = 0, 1$, in BHs may be termed “essential” in general.

However, two concepts, empty (or quasi-empty) and complete delocalization, may be distinguished by use of SR/K . Complete delocalization of π -electrons occurs in bulk graphite, P being equal to $1/3$ everywhere.^{5,16} It is expected that $2R/K$ for every hexagonal ring in graphite is the same. A question arises as to what extent such a hexagon in graphite is like that in a benzene ring, and hence whether $2R/K$ in the range from 0 to 1 might be used as an aromaticity index. The n -circumscribed hexagon graph as a two-dimensional graphite model^{17,18} is constructed as follows. Circumscribing one hexagon by 6 hexagons, one gets the 1-circumscribed hexagon graph (i.e., coronene); circumscribing the 1-circumscribed hexagon by 12 hexagons, one gets the 2-circumscribed hexagon graph (i.e., circum-coronene); such a procedure is repeated n times. We calculate two series of $2R/K$ for the center and the adjacent hexagons in the

n -circumscribed hexagon graph; refer to Table 1. Here the total number of carbon atoms in the n -circumscribed hexagon is equal to $6(n+1)^2$, which is expressible as either $4(6k^2 + 12k + 6)$ if $n = 2k + 1$ or $4(6k^2 + 6k + 1) + 2$ if $n = 2k$. From the associated data, the index $2R/K$ in the n -circumscribed hexagon seems to approach somewhere in the range 0.28–0.30 as n increases. Indeed a more exact result for graphite may be obtained; the value 0.1450142 for a single conjugated 6-circuit¹⁹ has been reported, and twice the value (for each conjugated 6-circuit around a given hexagon) gives 0.2900284 for $2R/K$. Graphite (with $2R/K = 0.290$) is exceptional as compared to finite fully benzenoid structures in that such finite structures have exactly one Clar structure, which selects particular hexagons as “aromatic” and remnant others as “nonaromatic”. Whereas graphite has three Clar structures, with all hexagons being equivalent, so that whatever aromaticity there might be is delocalized among all the hexagons. (Note: That graphite has 3 Clar structures may be understood if first one considers that such a Clar structure is uniquely determined given any full ring ρ : the adjacent rings are then empty and the 6 rings at the ends of the radialenic bonds radiating from ρ , and then each of these full rings similarly determines its environment, etc. Second, granted any site in graphite one may choose any one of the three rings incident there to be the initiating full ring ρ .) In any event the unique nature of graphite suggests its use as a reference, with rings in the BH being “subgraphitic” if $2R/K < 0.29$, and with rings in the BH being “supergraphitic” and also “aromatic” if $2R/K > 0.29$. The deviations from 0.29 indicate relatively greater localizations of either nonaromatic rings (for deviations below 0.29) or of aromatic rings (for deviations above 0.29). Thus, $2R/K$ in the range from 0 to 1 may be termed a “localization index” (as distinguished from an “aromaticity index”, though $2R/K$ certainly indicates a contribution to the local aromaticity).

Four examples, V–VII of Figure 1 and IX of Figure 2, are termed¹² “fully benzenoid” hydrocarbons (FBHs). These are covered totally by full hexagons, as the graph IX indicates. We can observe the index values of $2R/K$ between 0.7 and 0.9 for the full hexagons in the FBHs of small size; and the hexagonal rings with about $2R/K = 0.20$, by which the full hexagons are separate,²⁰ are called “quasi-empty” by Clar and Zander.¹² The small value of SR/K does not mean the “quasi-empty” hexagonal ring, as the previous paragraph has discussed. We obtain M for the base set of full hexagons in the FBHs as 0.889 in V, 0.850 in VI, 0.880 in VII, and 0.818 in IX.

Clar and Zander¹² in 1958 compared two isomeric compounds $C_{30}H_{16}$, VIII (tribenzo[*fg,ij,rst*]pentaphene, $K = 45$) and X (benzo[*qr*]naphtho[2,1,8,7,*fghi*]pentacene, $K = 39$), in Figure 2, and attributed the physical and/or chemical properties to the difference between IX and XI. The molecule IX is totally covered by 5 aromatic sextets, while in XI, at least three double bonds remain outside the benzene rings. The calculated values of $2R/K$ for hexagonal rings are indicated in VIII and X of Figure 2, respectively. We can observe a good correspondence between VIII and IX; each of the 5 sextets with 0.711–0.889 corresponds to the hexagon on which a circle is inscribed, and the 3 hexagonal rings with 0.178–0.222 separate the 5 full hexagons. The formula XI for the isomer X has been written by Clar and Zander in 1958. However, the calculation of X suggests that another

Table 1. Calculation of $2R/K$ for n -Circumscribed Hexagons

n	1	3	5	7	9	11	13	15	17
center	0.2000	0.2363	0.2518	0.2604	0.2659	0.2696	0.2724	0.2745	0.2761
adjacent	0.5000	0.3432	0.3197	0.3106	0.3057	0.3027	0.3007	0.2992	0.2981
n	2	4	6	8	10	12	14	16	18
center	0.4082	0.3526	0.3325	0.3221	0.3158	0.3116	0.3086	0.3063	0.3045
adjacent	0.2633	0.2708	0.2751	0.2778	0.2797	0.2811	0.2822	0.2830	0.2837

formula XII is more appropriate than XI, when the sextet with 0.615, instead of 0.513, is chosen as the fourth sextet. This choice is supported by the calculation of SR/K for the other Kekuléan base substructure, e.g., the ethylene unit. In Figure 2, XIII shows the calculation of P for the isomer; $P = 0.744$ in XII is greater than $P = 0.641$ in XI. Both XI and XII are totally covered by 4 aromatic sextets and 3 ethylene units as the Kekuléan base substructure, so that SR/K is the same, where $S = 16$, $R = 1$, and $K = 39$. We further calculate M for quantitative estimation of the difference between XI and XII. The mean values M for XI and XII, respectively, are given as

$$(28 + 20 + 32 + 34 + 28 + 20 + 25)/(39 \times 7) = 0.685$$

$$(28 + 24 + 32 + 34 + 18 + 29 + 28)/(39 \times 7) = 0.707$$

This calculation suggests that XII is more dominant than XI.

The above-mentioned calculation of the values of $2R/K$ for hexagonal rings (and P for ethylene units) suggests how to choose the base set of Kekuléan units for M in a given PAH. The local index $2R/K$ for each hexagonal ring is the same in a given acene; hence, the whole molecule is chosen as the base set. No two hexagonal rings with 0.103 or 0.259 in X can be chosen as full hexagons. The isomer X can then be considered as a composite of one chrysene and two benzene units; refer to XIV in Figure 2. Here the two hexagonal rings that are not included in the base set are denoted by dotted lines. This choice is also supported by the fact that the local indices SR/K for the three units, respectively, are calculated as 0.821, 0.872, and 0.821; and the mean value M for the base set of the three units is equal to 0.838.

Other choices for the Kekuléan base substructure may be of interest. For instance, the naphthalene units in perylene II being connected by essential single bonds give $3R/K = 1$, whereas in pyrene, $3R/K = 0.500$ for the naphthalene units. Analogically one may define²¹ a PAH to be “fully naphthalenoid” if its sites are fully covered by disjoint naphthalene units. There are 10 such fully naphthalenoid²² hydrocarbons, each of which is partitioned into three naphthalene substructures (units). A choice of one naphthalene unit in each naphthalenoid hydrocarbon decomposes the rest into two disjoint naphthalene units; hence one has $S = 3$, and $R = 3 \times 3$ for each naphthalene base substructure in the 10 fully naphthalenoid hydrocarbons. In the 10 fully naphthalenoid hydrocarbons, K therefore determines the local index $27/K$ for the naphthalene unit. Other types of “fully arenoid” categorizations and testings are also possible. The molecule XV ($K = 264$) of Figure 2 indicates a “hexagonoidal” partitioning.²³ That is, we can regard XV as a composite of one (hexagonoidal) coronene and two naphthalene units, for each of which $SR/K = 0.682$ and $M = 0.682$ for this base set.

The six-membered index $2R/K$ calculations for kekulene ($K = 200$, a benzo-fused macrocycle of benzenes) and a homologue²⁴ of kekulene are respectively indicated in XVI of Figure 3 and XX of Figure 4. In kekulene, we have $2R/K = 0.290$, 0.700 for the corner and side hexagons (XVI), respectively, and $P = 0.845$ for the bond inside the corner hexagon in XVII of Figure 3. Comparing the sextet indices between phenanthrene I and kekulene XVI, we can observe that kekulene includes phenanthrene units as the Kekuléan base substructure. This kekulene molecule XVII has $M = 0.773$ for the base set of 6 side benzene rings and 6 corner ethylene units. In addition, for the [18]-annulene inside annulus of kekulene, one finds SR/K to be $2 \times 2/200 = 0.020$ in XVIII of Figure 3; the value of $R = 2$ is equal to that for the [30]-annulene exterior macrocycle. Note that each of these two annulene substructures has $(4n + 2)$ π -electrons. The total number of C–C bonds in the [18]-annulene base substructure equals 18, and another 18-bond choice for the Kekuléan base substructure could be the three sextets in example XIX in Figure 3; then $SR/K = 0.320$, because $S = 8$, $R = 8$, and $K = 200$. Note that $SR/K = 0.320$ if the 6 sextets in XVII are chosen as a Kekuléan base substructure, because $S = 64$ and $R = 1$. Comparing 2×2 for [18]-annulene with 8×8 for three sextets suggests why the latter is more stable than the former. The above observations agree well with the experimental fact²⁵ that the benzenoid is far more stable than the annulenes in kekulene. Even without explicit resonance energy calculations,²⁶ we can say that there is no superaromaticity in kekulene, because the contribution of either [18]-annulene or [30]-annulene is very small. This benzenoid character for kekulene becomes clearer in the calculation of SR/K for the compound²⁴ XX ($K = 1300$) in Figure 4. One has $2R/K = 0.168$, 0.554 in the corner and the side hexagons, respectively; and $M = 0.873$ for the base set of 6 ethylene and 6 naphthalene units. We can hence observe the overlapping of 6 pentaphene units in this compound.

Comparison of the locality for [5]-radialene becomes possible by use of the index SR/K , where $S = 1$. The [5]-radialene-like substructure has 5 double bonds that meet with the five-membered ring; SR/K for the [5]-radialene base substructure is denoted by R_5/K . Figure 5 shows the calculation of R_5/K in two fluoranthrene series.¹ Fluoranthrene XXI is composed into a naphthalene and a benzene unit. As the number of hexagonal rings increases as naphthalene, anthracene, and tetracene, the index decreases; refer to XXI–XXIII. While as the number of hexagonal rings increases as benzene, naphthalene, and anthracene, the index increases; refer to XXI, XXIV, and XXV. The difference between the indices of the two series is due to the sides (zigzag and the other) of acene units, to which the radialene unit is attached.

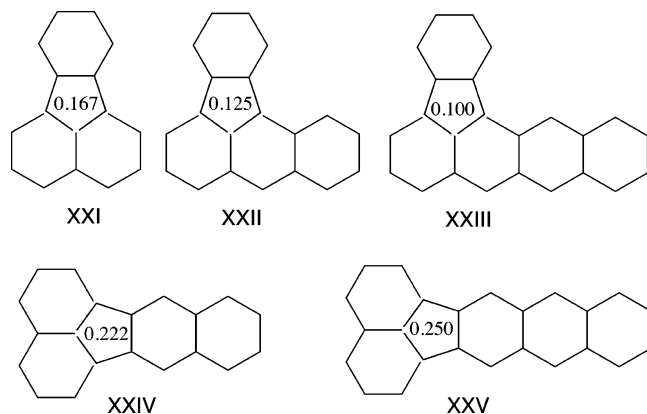


Figure 5. The localization index calculation for [5]-radialene substructures.

Let us consider an edge e and the hexagon including e in Figures 1 and 2, where the hexagon is fused with the remnant by at most two adjacent hexagons. It is then clear that, if e fuses the hexagon and the remnant, then $2R/K$ for the hexagon is equal to $2P$, because the choice of the ethylene unit e inside the fused hexagon determines the alternation of single and double bonds inside the hexagon.

It is concluded (in the preceding notation) that $S \times R/K$ and M are good indices for estimation of the extent of localization of different Kekuléan base substructures in PAHs. We term this scheme the “molecules-in molecule” approach for PAHs.

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APPENDIX

We note a computational scheme for the index SR/K for benzenoid hydrocarbons. Indeed if G denotes the structure remaining when a Kekuléan fragment is deleted from a benzenoid B , then the number of Kekulé structures of G is given by a determinantal formula

$$S = |\det(\mathbf{A})|^{1/2}$$

where \mathbf{A} is the adjacency matrix of G . Basically this relation is well-known if G were itself to be a benzenoid, as early established by Dewar and Longuet-Higgins²⁷ in 1952. Also see the discussion in section 2.5.3 of the monograph²⁴ by Cyvin et al. Thence this gives a scheme to compute K (the parent structure being benzenoid). But this simple result also applies for other structures G arising in our construction. For a benzenoid B the proof depends on the expression of the determinant as a sum over permutations P of terms $\pm \prod_i A_{i,P_i}$, so that each term can be viewed as corresponding to a G -spanning directed graph G_P (with an edge directed from i to P_i , if $P_i \neq i$). The components of G_P are either directed cycles or undirected isolated edges (each corresponding to a neighbor pair of transposed sites). Further these G_P correspond to superpositions of pairs of Kekulé structures, two oppositely directed cycles corresponding to the two orders to superpose two different conjugation patterns around the given cycle. The parity sign \pm occurs as the permutation is even or odd, and the sign is the product of those for the

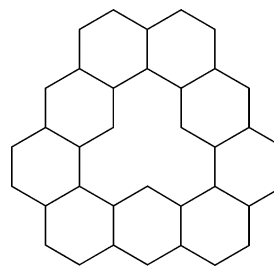


Figure 6. $C_{36}H_{18}$, cyclononakisbenzene.

components. Since the resultant cyclic components of G_P for a benzenoid are of size $4m+2$, every such component has a negative parity and involves an odd number of edges into starred sites. A term, say $A_{ij}A_{ji}$, corresponding to an isolated edge component $i-j$ of G_P has negative parity and also may be viewed to involve an odd number of edges into a starred site. Thus (for a benzenoid) the parity of each component is negative and may be viewed as the parity of the number of edges into a starred site of the component. Thus the overall parity is just $(-1)^{n/2}$ (n being the total number of vertices) for every permutation giving a nonzero contribution in $\det(\mathbf{A})$. Thus $(-1)^{n/2}\det(\mathbf{A})$ is just the number (S^2) of superposition pairings for Kekulé structures of B . But now for G resulting from the deletion of a Kekuléan structure G' from a benzenoid B , either one has $S = 0$ or else there is a Kekulé structure on G as well as G' such as to correspond precisely to that represented for the parent B by the superposition of those of G & G' together. For $S = 0$ there are no superposition diagrams giving a contribution to the determinant, so that $\det(\mathbf{A}) = 0$. On the other hand, for $S \neq 0$ all the parity considerations for the parent benzenoid carry over to G , and the simple result follows.

Though $K(G) = |\det(\mathbf{A}(G))|^{1/2}$ carries over to structures beyond benzenoids it is noted that there are many other (even interesting) structures to which it does not apply. That kekulene may be viewed as the remnant structure upon deletion of the center ring of circum-circum-coronene, which means that the formula applies to kekulene. However, for the triangle-shaped coronoid obtained by fusing three anthracenes together at their end rings the formula does not hold (as may be surmised because this is only viewed as a remnant structure from a benzenoid by deletion of a non-Kekuléan single site from the center of a circum-perinaphthyl portion); refer to Figure 6. To handle the general situation for a planar graph, there is a general method²⁸ available which however requires as special anti-symmetrically “signed” adjacency matrix.

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