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A Special Form of Numerical Self-Similarity of Kekulé Counts of Benzenoid Hydrocarbons

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> *Such a strange world is luckily not our world,*
> *but it is a conceivable world. It is a frightful*
> *world, and the theories describing it have a*
> *frightfully techical name;*
> *non-renormalizable*
>
> *Q. HO-Kim, N. Kumar and C. S. Lam*

Previously defined equivalence relation, ℓ, on Kekulé counts, K(B)'s of catacondensed benzenoids, classifies Kekulé structures according to the number of their terminal conjugated circuits. The function ℓ, is an enumeration method which uncovers the less transparent combinatorial properties of K(B)'s, such as their numerical self-similarity[1], graph generation,[2,4] modeling quasicrystals[3] and modeling of Feigenbaum's theory of chaos[5]. Here, we consider two benzenoid system; B_0, an all-kinked unbranched benzenoid, and B_3, an all-kinked benzenoid which has one branched hexagon and for which all branches are equal which are characterized by the peculiar property that the statistical distribution of the hypercubes (vertices, edges, squares, ...) which constitute their Kekulé spaces remains invariant under the effect of the ℓ function. For these two systems, ℓ is analogous to a percolation process. This property leads to a diagonal equality of conjugated circuit counts of members of the B_0 series, which is scaled down by the powers of the golden-mean in the case of the B_3 series. $K(B_0)$'s and/or $K(B)_3)$'s are shown to model a one-dimensional quasicrystal.

INTRODUCTION

In previous papers,[1–6] an equivalence relation, ℓ, has been defined on the Kekulé space, $\kappa(\mathrm{B})$, of a catacondensed benzenoid, B, where;

$$\kappa(\mathrm{B}) = [k_1, k_2, ..., k_K], \tag{1}$$

k_i is an i^{th} Kekulé structure $\in$ B and K is the Kekulé count $\equiv K(\mathrm{B}) = |\kappa(\mathrm{B})|$

The relation, ℓ, simply partitions $\kappa(\mathrm{B})$ into a set of equivalent classes, each class containing those Kekulé structures which possess the same number of terminal conjugated circuits[7] of type R_1. This surprisingly simple operation uncovered several important combinatorial properties of Kekulé counts of catacondensed systems, *viz.*,

a) For any catacondensed benzenoid hydrocarbon, its $K(\mathrm{B})$ can be expressed as a sum of j-cubes,[2,4] namely

$$K(\mathrm{B}) = \sum_{J=0}^{t} 2^j K(2^j) \tag{2}$$

where $K(2^j)$ is the number of Kekulé structures of the resonating part of B after fixation of some of its terminal R_1 circuits, *viz.*,

$$K(2^j) = sK(\mathrm{B}(2^j)) \tag{3}$$

where $\mathrm{B}(2^j)$ is the resonating part of B in which j terminal R_1 circuits are fixed so that it generates a j-cube, and s is a symmetry factor (see *e.g.* (9–11) or (15–18) below where the corresponding $\mathrm{B}(2^j)$ parts are shaded). The value of j determines the size of the hypercube.[2,4] For example, $j = 0$ leads to a 0 – cube (or simply a vertex) while $j = 1$ corresponds to a 1 – cube (an edge), $j = 2$ generates a 2-cube (*i.e.* a square), $j = 3$ is the (traditional 3-) cube, $j = 4$ gives a 4-cube (tessaract), and so on. In Eq. (2), t is the maximum possible number of terminal R_1 circuits in a Kekulé structure $\in$ B. Then, this ℓ relation showed how to use Kekulé structures as graph generators, a topic of both graph and chemical interest.[8] Indeed, the resulting hypercubes have both biochemical and stereochemical implications.[9]

b) Operation ℓ enables one to study (and demonstrate) the numerical self-similarity of homologous series of benzenoid hydrocarbons[1,3] and thus show fractal properties[3] in cases of non-deterministic fractals.[10]

c) The ℓ relation demonstrated that all-kinked benzenoids[11] (branched and/or unbranched) can be made to generate sequences like the one shown below;[3]

$$1011010110110... \tag{4}$$

which are neither random nor truly aperiodic and whence it models a new state of matter called quasicrystal which shares the properties of both crystalline and amorphous substances, such as the Al_6Mn alloy discovered by Shechtman *et al.*[12] This point will be further elaborated in this paper. Indeed, because of this property, c), the name quasicrystalline benzenoids has been suggested for the class of branched and/or unbranched all-kinked benzenoid hydrocarbons.

The general results make the study of ℓ relation a worthy task.

Here, we demonstrate that ℓ is indeed similar to a percolation process[13] and we present two rare cases of a special form of what might be called statistical self-similarity.

Percolation Process[13]

When a structure changes from a collection of many disconnected parts into basically one big cluster, it is said that percolation has occured. This process can be analyzed using renormalization methods in physics; Imagine a triangular lattice the sites of which are to be colored black or white and let the original sites be labelled as 1,2,3,4,5,6,... Then, during renormalization process, these sites become supersites {1,2,3}, {2,3,4}, {3,4,5}, {4,5,6},..so that the »origins« of supersites »overlap«. If 2 or 3 of original sites are black, then the supersite will be black, otherwise it will be white. More details may be found elsewhere.[13,14] When the probability $p = 0$, one gets nothing, when $p = 1$, one obtains a solid (black) triangle. Then, only intermediate density values are of interest. Now, renormalize the lattice by replacing each three neighboring sites by a supersite. There are three possible outcomes according to the starting value of p;

i. If p is low, then there are only a few isolated occupied sites and the resulting density p' will be $< p$.

ii. when p is large, many more supersites will be generated, and in this case $p' > p$.

iii. At the percolation threshold, at critical density, p_c (calculated to be 0.5),[14] one has the interesting situation; $p = p'$, in which case one is dealing with a nontrivial configuration which, after renormalization, remains statistically the same!.

How is this related to our ℓ equivalence relation? First, one recalls that renormalization is a procedure to re-express a fundamental physical law in an effective form appropriate to a certain scale in terms of some parameters. Analogously, ℓ is an operation where K(B) is re-expressed as a sum of hypercubes. Indeed, ℓ is a combination of vertex-, edge-, square-, ..., *i.e.*

$$\ell = \ell(2^0) \cup \ell(2^1) \cup \ldots \cup \ell(2^t) \tag{5}$$

(see *e.g.* Eqs. 9–11), where $\ell(2^j)$ is that part of ℓ which fixes j terminal R_1's in B and hence generates a j-cube.

Then, one might say the ℓ »percolates« $\kappa(B)$. Formally, ℓ may be envisaged as an operator, $\hat{\ell}$, in the following way;

$$\begin{aligned}
&\widehat{\ell(2^0)}B_L \rightarrow (B(2^0))_L,\\
&\widehat{\ell(2^1)}\, B_L \rightarrow (B(2^1))_L,\\
&\quad\vdots \qquad\qquad \vdots\\
&\widehat{\ell(2^t)}\, B_L \rightarrow (B(2^t))_L
\end{aligned} \tag{6}$$

where L indicates the position of a given B in its homologous series and $(B(2^j))_L$ is a subset of B (*cf.* Eq. 3). Then, we define B to be statistically self-similar if the combination of Kekulé spaces of the set of resonating benzenoids, $\cup_j^t\ \kappa(B(2^j))_L$, corresponds to the Kekulé spaces of an earlier member of the B series. This is detailed in Theorem 2 and exemplified by Table III. In such a (rare) case, B defines a threshold connectivity which remains statistically invariant under the ℓ operation.

THE MAIN RESULT

Considering catacondensed benzenoids containing no more than one branched hexagon, only the B_0 and B_3 homologous series (shown in Figure 1) are statistically self-similar and obey;

Theorem 1

(In Ref. 1 K_k is equivalent to our $K(2^k)$ notation, *cf.* Eq.,8), Ref. 1).

A. For the L^{th} member of a homologous series of the B_0 type (Figure 1), the number of Kekulé structures, $K(B_0)_L$, is given by;

$$K(B_0)_L = (K(2^0))_L + 2\ (K(2^1))_L + 4\ (K(2^2))_L\ ; \tag{7a}$$

$$K(B_0)_{L-2} = (K(2^0))_L + (K(2^1))_L + (K(2^2))_L\ . \tag{7b}$$

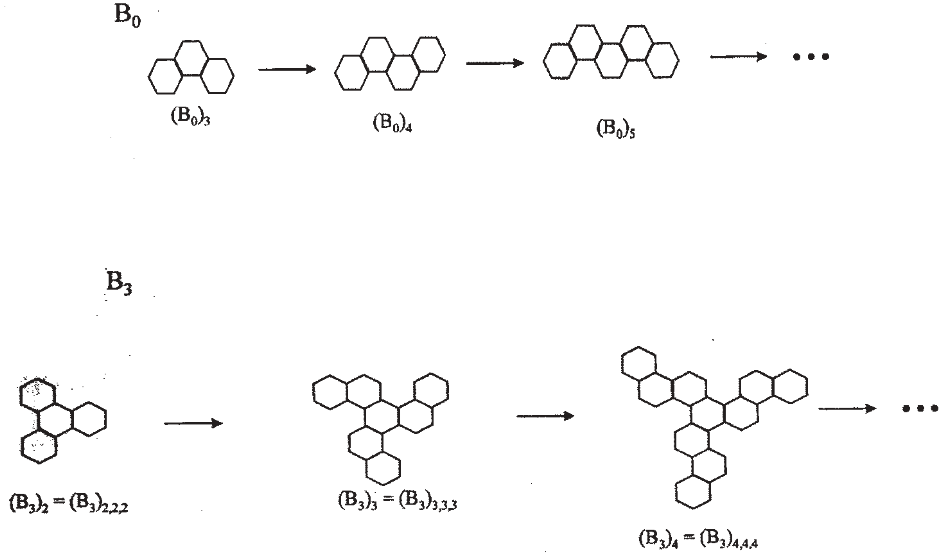


Figure 1. B_0 and B_3 systems considered here. The systems also involve all possible isoarithmic benzenoids, *cf.* Ref. 11.

B. For the L^{th} member of the B_3 type (Figure 1), the corresponding relations are;

$$K(B_3)_L = (K(2^0))_L + 2\ (K(2^1))_L + 4\ (K(2^2))_L + 8\ (K(2^3))_L \tag{8a}$$

$$K(B_3)_{L-1} = (K(2^0))_L + (K(2^1))_L + (K(2^2))_L + (K(2^3))_L \,. \tag{8b}$$

In words: the number of Kekulé structures of the resonating parts of a benzenoid system (B_0 and/or B_3) generated during the operations of ℓ (Eq. (6)) equals the Kekulé count of an earlier member. Then, the distribution of j-cubes (vertices, edges, squares, ...) in the total Kekulé spaces of the corresponding resonating benzenoids is the same as the Kekulé space of an earlier homologous of the series.

Then, the structure of the Kekulé spaces in the B_0 and/or B_3 types is self-similar with respect to the counts of terminal R_1 circuits. Because of this particular property, we suggest the name statistical self-similarity in these two cases.

Before we prove Theorem 1, we give some numerical examples to illustrate this property in Tables I and II.

TABLE I

Partitioning of $\kappa(B_0)_L$. Numbers under the j-cubes are their multiplicities, *i.e.*, the corresponding $(K(2^j))_L$'s, Eq. (7a). The last column corresponds to Eq. (7b).

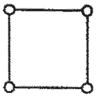
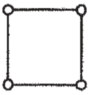
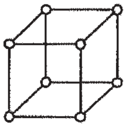
L	○	○—○		K	$\sum_{J=0}^{2} K(2^j))_L$
6	1	4	3	21	$8 = K((B_0)_4)$
7	2	6	5	34	$13 = K((B_0)_5)$
8	3	10	8	55	$21 = K((B_0)_6)$
9	5	16	13	89	$34 = K((B_0)_7)$
10	8	26	21	144	$55 = K((B_0)_8)$
⋮	⋮	⋮	⋮	⋮	

TABLE II

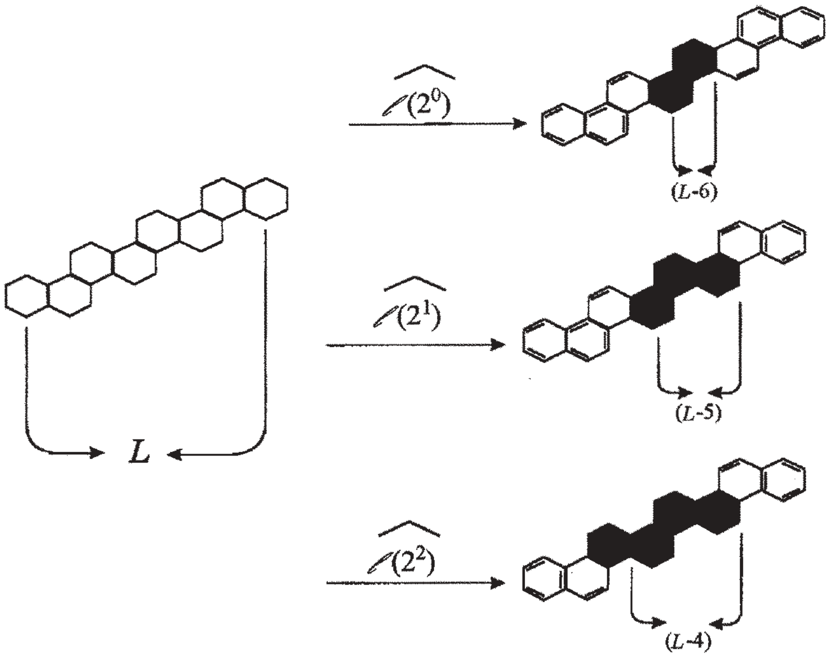
Partitioning of $\kappa(B_3)_L$. Numbers under the j-cubes are thair multiplicities, *i.e.* $(K(2^j))_L$'s, Eq. (8a). The last column is the sum given by Eq. (8b).

L	○	○—○			K	$\sum_{J=0}^{2} K(2^j))_L$
3	1	3	3	2	35	$9 = K((B_3)_2)$
4	2	9	15	9	152	$35 = K((B_3)_3)$
5	9	42	66	35	637	$152 = K((B_3)_4)$
6	35	171	279	152	2709	$637 = K((B_3)_5)$
⋮	⋮	⋮	⋮	⋮	⋮	

Proof of Theorem 1

A. $(B_0)_L$ type;

Here, $\mathcal{A}$ is explicitly stated as $\mathcal{A}(2^0) \cup \mathcal{A}(2^1) \cup \mathcal{A}(2^2)$, *i.e.*, $\kappa(B_0)$ may be clustered out (percolated)[13] into a set of vertices, edges and squares only. No other hypercubes are possible. These generations are demonstrated below in Eqs. (9–11) where in all cases the shaded parts of the benzenoid are the corresponding resonating fragments, $B(2^j)$'s, *cf.* Eq. (3) obtained during the formation of a given j-cube.



(9)

(10)

(11)

Eqs. (9–11) lead, respectively, to;

$$\left.\begin{array}{l} (K(2^0))_L = (K(\mathrm{B}_0))_{L-6} \\[2ex] (K(2^1))_L = 2\ (K(\mathrm{B}_0))_{L-5} \\[2ex] (K(2^2))_L = (K(\mathrm{B}_0))_{L-4} \end{array}\right\} \qquad \begin{array}{r} (9') \\[2ex] (10') \\[2ex] (11') \end{array}$$

where the factor of 2 in (10') is a symmetry factor.

To prove Eq. (7b), we recall[15] for type B_0 the following identity;

$$(K(\mathrm{B}_0))_L = F_{L+1} \tag{12}$$

where F_L is the L^{th} Fibonacci number ($F_0 = F_1 = 1$; $F_2 = 2$, $F_{n+2} = F_{n+1} + \mathrm{F}_n$). *Substituting Eq. (12) into Eqs. (9'–11'), we have;*

$$(K(\mathrm{B}_0))_L = F_{L-5} + 2 \times 2\ F_{L-4} + 4F_{l-3}\ .$$

Then, we would like to prove that;

$$F_{L-5} + 2F_{L-4} + F_{L-3} \equiv (K(B_0))_{L-2} = F_{L-7} + 2 \times 2\, F_{L-6} + 4\, F_{L-5}\ . \tag{13}$$

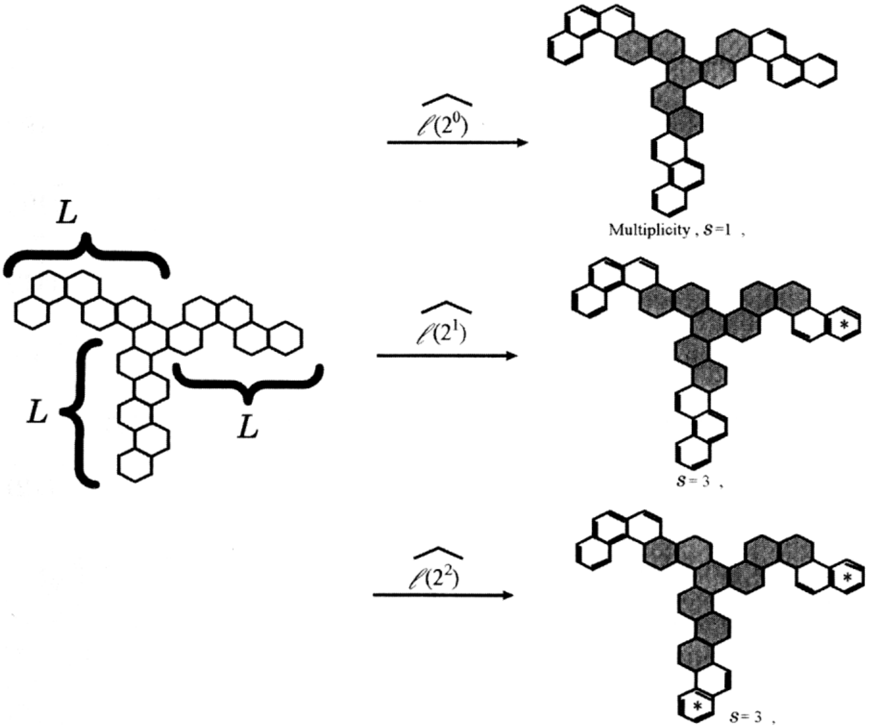
But

$$\left.\begin{aligned} F_{L-5} &= F_{L-6} + F_{L-7}\ ; \\ 2F_{L-4} &= 2F_{L-5} + 2F_{L-6}; \\ F_{L-3} &= F_{L-4} + F_{L-5}\ . \end{aligned}\right\} \tag{14}$$

Adding Eqs. (14) leads to the right – hand side of Eq. (13).

B. $(B_3)_L$ type:

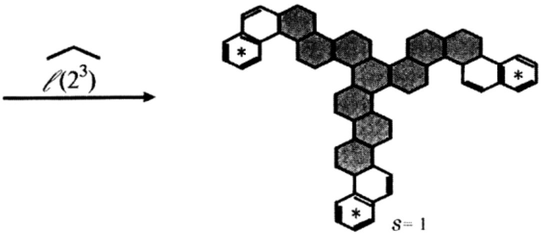
Eq. (8a) is demonstrated by Eqs. (15)–(18) where ℓ is in this case a combination of four operations, *viz.*, $\ell(2^0) \cup \ell(2^1) \cup \ell(2^2) \cup \ell(2^3)$. *I.e.*, the Kekulé space, $\kappa(B_3)$ clusters into a set of vertices, edges, squares as well as cubes, *cf.* Table II.



(15)

(16)

(17)



(18)

Eqs. (15–18) are pictorial illustrations of the following equalities;

$$(K(2^0))_{L,L,L,} = (K(\mathrm{B}_3))_{L-3,L-3,L-3} \tag{15'}$$

$$(K(2^1))_{L,L,L} = 3(K(\mathrm{B}_3))_{L-2,L-3,L-3} \tag{16'}$$

$$(K(2^2))_{L,L,L} = 3(K(\mathrm{B}_3))_{L-2,L-2,L-3} \tag{17'}$$

$$(K(2^3))_{L,L,L} = (K(\mathrm{B}_3))_{L-2,L-2,L-2}\ . \tag{18'}$$

And now we recall[16] the following identity for a member of type $(\mathrm{B}_3)_{L,M,N}$

$$(K(\mathrm{B}_3))_{L,M,N} = F_L F_M F_N + F_{L-1} F_{M-1} F_{N-1}\ . \tag{19}$$

Substituting Eq. (19) into (15')–(18'), we write:

$$\begin{aligned}(K(\mathrm{B}_3))_{L,L,L} &= ({F_{L-3}}^3 + {F_{L-4}}^3) + 2 \times 3({F_{L-3}}^2 F_{L-2} + {F_{L-4}}^2 F_{L-3}) \\ &\quad + 4 \times 3\ ({F_{L-2}}^2 F_{L-3} + + {F_{L-3}}^2 F_{L-4}) + 8({F_{L-2}}^3 + {F_{-3}}^3)\ .\end{aligned} \tag{20}$$

Now to prove (8b) is equivalent to proving that;

$$\begin{aligned}&({F_{L-3}}^3 + {F_{L-4}}^3) + 3({F_{L-3}}^2 F_{L-2} + {F_{L-4}}^2 F_{L-3}) + 3({F_{L-2}}^2 F_{L-3} + {F_{L-3}}^2 F_{L-4}) \\ &\qquad + ({F_{L-2}}^3 + {F_{L-3}}^3) = (K(\mathrm{B}_3))_{L-1,L-1,L-1}\ .\end{aligned} \tag{21}$$

We start with the traditional equalities:

$$\left.\begin{aligned}F_{L-1} &= F_{L-2} + F_{L-3}: \\ {F_{L-1}}^2 &= {F_{L-2}}^2 + {F_{L-3}}^2 + 2\ F_{L-2} F_{L-3}; \\ {F_{L-1}}^3 &= {F_{L-2}}^3 + {F_{L-3}}^3 + 3\ {F_{L-3}}^2 F_{L-2} + 3\ {F_{L-2}}^2 F_{L-3}\ .\end{aligned}\right\} \tag{22}$$

When Eqs. (22) are substituted into the left–hand side of Eq. (21), one obtains (after straghtforward but somewhat tedious algebra);

$$F_{L-4}^{3} + F_{L-5}^{3} + 2\times 3\,(F_{L-4}^{2}F_{L-3} + F_{L-5}^{2}F_{L-4}) + 4\times 3\,(F_{L-3}^{2}F_{L-4} + F_{L-4}^{2}F_{L-5}) + 8(F_{L-3}^{3} + F_{L-4}^{3})\,. \tag{23}$$

But (23) is nothing else but $(K(B_3))_{L-1,L-1,L-1}$ (*cf.* Eq. 20).

Numerical Self-Similarity of B_3 Series

This concept was introduced in Ref. 1 and demonstrated for some dozen types of benzenoid hydrocarbons. Eq. (6) of Ref. 1 defines the conditions required for a series of compounds to possess numerical self-similarity. In terms of Eqs. (7a) and (8a) of this paper, the members of the B_3 (or B_0) series are numerically self- similar if;

$$\lim_{L\to\infty}\frac{K(B_3)_{L-1}}{K(B_3)_L} = \lim_{L\to\infty}\frac{K(2^j)_{L-1}}{K(2^j)_L} \tag{24}$$

for $j = 0,1,2,3$

Indeed, this is almost trivial to show; we start with Eq. (19).

Then, at an infinitely large member, we have the approximate formula;

$$K(B_3)_{L,M,N} \approx 2F_L^{3} \tag{25}$$

and therefore the required limit in Eq. (24) is given by $\gamma^3 \approx (0.618033)^3 \approx 0.236$. This can be verified using even the (early) L values of Table II.

$$(9/35) \cong 0.257 \cong (42/171) \cong 0.245 \cong (66/279) \cong 0.236 \cong (35/152) \cong 0.230 \cong (637/2709) \cong 0.235 \tag{26}$$

Theorem 2

Members of the B_3 series possess statistical self-similarity.

Of course, the B_3 series represents the prototype whose limit is the golden-mean itself. But, what distinguishes members of the B_3 (and B_0) series from the series considered in Ref. 1 is that the former, in addition, possess that might be called statistical self-similarity, which is a special form of numerical self- similarity that exists when the overall (or average) effect of the ℓ function is to regress a given member of the series into an earlier homologue (as in Eqs. (7a) and (8b)). In such a case, the statistical distribution of the hypercubes in the Kekulé space of B remains invariant to the equivalence relation. This propeerty might be casted as;

Corollary of Theorem 1

Eqs. (7b) and (8b) lead, respectively, to;

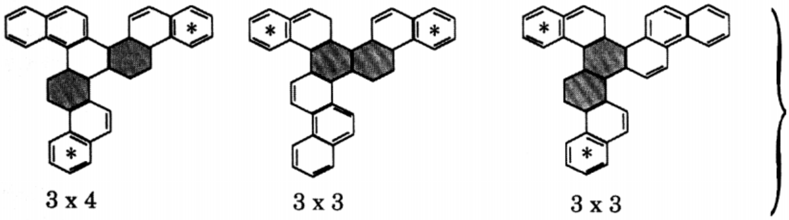
$$\kappa \cup {}^{2}{}_{j=0}(\mathrm{B}_0(2^j))_L = \kappa(\mathrm{B}_o)_{L-2} ; \tag{27a}$$

$$\kappa \cup {}^{3}{}_{j=0} (\mathrm{B}_3(2^j))_L = \kappa(\mathrm{B}_3)_{L-1} . \tag{27b}$$

This corollary is best illustrated by a numerical example: In Table III, we show the set of resonating benzenoids of $(\mathrm{B}_3)_{6,6,6} \equiv (\mathrm{B}_3)_6$ and the distribution of clusters of various sizes in their Kekulé spaces. From the table we see that the resulting distribution is identical to $\kappa(\mathrm{B}_3)_5$, which corresponds to the third row of Table II. A pictorial illustration of Eqs. (27a), (28b) which illustrates the concept of statistical self- similarity is given below:

$$\left.\begin{array}{c} (\mathrm{B}_0)_L \xrightarrow{\ell} (\mathrm{B}_0)_{L-2} \\ \\ (\mathrm{B}_3)_{L,L,L} \xrightarrow{\ell} (\mathrm{B}_3)_{L-1,L-1,L-1} . \end{array}\right\} \tag{28}$$

As an illustration, we consider the number of squares generated from $(\mathrm{B}(2^2))_6$ (which is $3 \times 4 + 3 \times 3 + 3 \times 3$: the third entry in the third row of Table III).



(29)

(where the first number is multiplicity, s, of the fragment).

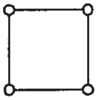
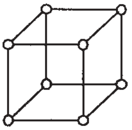
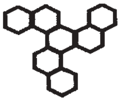
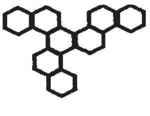
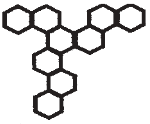
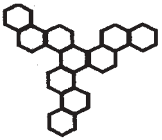
We observe that for both vertex- and cube- generation, the reonating fragment is indeed an earlier homologue of the B_3 series. However, for edge- and square-generations, their overall effect leads to a Kekulé space of an earlier homologue.

Conjugated – Circuit Count[7]

The equivalence relation ℓ is an »auxiliary« combinatorial technique which helps uncover the less trransparent properties of Kekulé counts of benzenoid systems. The technique depends on the classification of Kekulé structures of a benzenoid hydrocarbon according to the number of terminal

TABLE III

The set of resonating benzenoids generated* when $(B_3)_6$ is subject to the equivalence relation. The resulting population of hypercubes (last row) is identical to the distribution of $\kappa(B_3)_5$, as shown in Table II (manifestation of statistical self-similarity of $(B_3)_L$ series).

*s***						
1	 $(B(2^0))_6$	1×1	1×3	1×3	2	
3	 $(B(2^1))_6$	3×1	3×2 + 3×1 + 3×1	3×2 + 3×2 + 3×2	3×3	
3	 $(B(2^2))_6$	3×1	3×2 + 3×2 + 3×2	3×4 + 3×3 + 3×3	3×5	
1	 $(B(2^3))_6$	2×1	3×3	3×5	9	
	Sum	9	42	66	35	*c.f.* third row in Table II

* *cf.*, the shaded fragments in Eqs. (15)–(18)

** Multiplicity of resonating fragment (symmetry factor, *s*).

conjugated circuits. This classification, then, assumes »fixation« of some of the double bonds in terminal hexagons and their immediate neighbors. For example, in cube-generation, three terminal R_1's are fixed while in vertex-generation three terminal R_2's are fixed (*cf.* Eqs. (18) and (15), respectively) in the (all-kinked) B_3 system. This fixation, so-to-speak, of some of the terminal circuits is reminiscent of the technique of counting the total number of conjugated circuits of a benzenoid system. Let $R_j(B_0)_L$ be the number of R_j – type circuits (which contain $4j+2$ pi- electrons) in a system of B_0 of L^{th} position in the homologous series. Then, a »diagonal equality«[17] exists in the form:

$$R_1(B_0)_L = R_2(B_0)_{L+1} = R_3(B_0)_{L+2} = .. \tag{30}$$

For the B_3 system, the counts of the circuits are scaled down by powers of the golden mean, *viz.*,

$$R_1(B_3)_L \cong \gamma^2 R_2(B_3)_{L+1} \cong \gamma^4 R_3(B_3)_{L+2} \cong \ldots \tag{31}$$

Lemma 1

We define two parameters, namely;

$$d_1 = 1 = F_n\gamma^n + F_{n-1}\gamma^{n+1} \tag{32}$$

$$d_2 = \gamma^{-1} = F_n\gamma^{n-1} + F_{n-1}\gamma^n \tag{33}$$

where $\gamma^{-1} = 2^{-1}(\sqrt{5}+1) \approx 1.618033989$; $\gamma = \gamma^{-1}-1$; $F_0 = F_1 = 1$, $F_{n+2} = F_{n+1} + F_n$. The ratio γ is called the golden mean and F_n is an n^{th} Fibonacci number. This Lemma is proved by induction in the Appendix.

Modeling Quasicrystals

Kekulé counts of B_0 and B_3 series can be made to model a typical 1-dimensional quasicrystal. In Figure 2, we demonstrate the idea using $K(B_0)$'s by placing the individual Kekulé structured (represented as vertices) on a straight line such that each 1 (in the sequence given by Eq. (4)) corresponds to an inter atomic distance of γ^{-1} = 1.618... Å and each 0 to a distance of 1 Å. These two values correspond, respectively, to parameters d_2 and d_1. We call this line, with the vertices (*i.e.* Kekulé structures) thus spaced on it, the original lattice. Now, we scale down this lattice by a factor of γ, then the resulting (compressed) lattice will be more dense but all interatomic distances will be scaled down by γ. This process may be repeated and we observe that every vertex in the original lattice coincides precisely with a vertex in the compressed lattice (which demonstrates position – invariance to scaling). The compressed lattice, however, will have some extrapositions with no partners in the original lattice but will match with positions in crystal generated at higher stages. Thus, the one-dimensional lattices thus constructed are position (scale) invariant and are self-similar. In Figure 3, a magnified portion of Figure 2 is shown to demonstrate the scaling invariance of positions of the vertices resulting from d_1 and d_2 defined in Lemma 1 ($d_1 = 1$; $d_2 = 1 + \gamma$). In stage 1, d_1 is subdivided into two intervals, in stage 2, d_1 becomes the sum of three intervals, in stage 3, d_1 corresponds to five intervals and so on: in the n^{th} stage d_1 is a sum of F_{n+1} intervals. Analogously, d_2 is subdivided into F_n intervals at the nth stage of compression of the original lattice. In Table IV, we illustrate the initial stages of partitions of d_1 and d_2 which lead to position-invariance to scaling and whence to self-similarity.

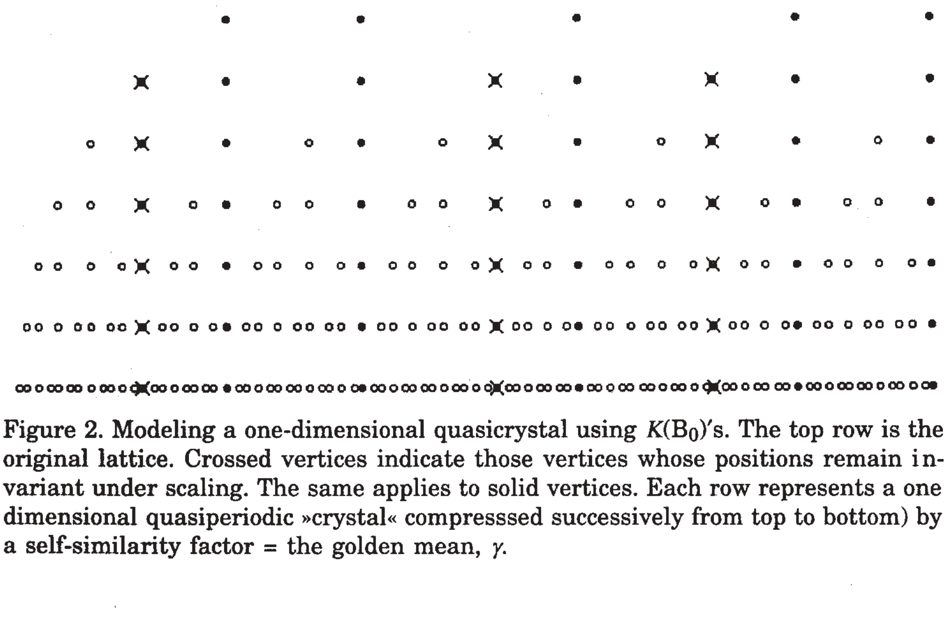


Figure 2. Modeling a one-dimensional quasicrystal using $K(B_0)$'s. The top row is the original lattice. Crossed vertices indicate those vertices whose positions remain invariant under scaling. The same applies to solid vertices. Each row represents a one dimensional quasiperiodic »crystal« compresssed successively from top to bottom) by a self-similarity factor = the golden mean, γ.

TABLE IV

Position-invariance to scaling illustrating the self-similarity of a 1-dimensional quasicrystal modeled by the Kekulé counts of B_0 (or B_3) series.

Stage	$d_2 \equiv 1$	$d_1 \equiv 0$
0	γ^{-1}	1
1	$1 + \gamma$	1
2	$2\gamma + \gamma^2$	$\gamma + \gamma^2$
3	$3\gamma^2 + 2\gamma^3$	$2\gamma^2 + \gamma^3$
⋮	⋮	⋮
n	$F_n\gamma^{n-1} + F_{n-1}\gamma^n$	$F_n\gamma^n + F_{n-1}\gamma^{n+1}$

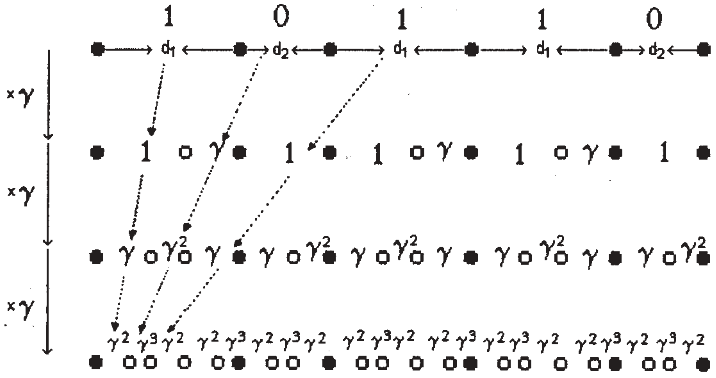
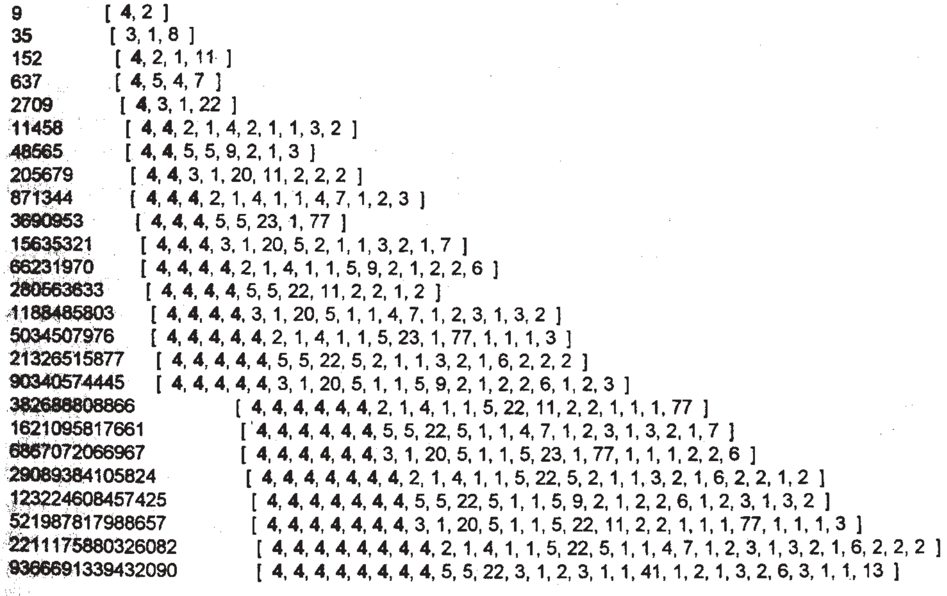


Figure 3. A magnified portion of Figure 2 illustrating the structure of Table IV and d_1 and d_2 distances of Lemma 2.



9	[4, 2]
35	[3, 1, 8]
152	[4, 2, 1, 11]
637	[4, 5, 4, 7]
2709	[4, 3, 1, 22]
11458	[4, 4, 2, 1, 4, 2, 1, 1, 3, 2]
48565	[4, 4, 5, 5, 9, 2, 1, 3]
205679	[4, 4, 3, 1, 20, 11, 2, 2, 2]
871344	[4, 4, 4, 2, 1, 4, 1, 1, 4, 7, 1, 2, 3]
3690953	[4, 4, 4, 5, 5, 23, 1, 77]
15635321	[4, 4, 4, 3, 1, 20, 5, 2, 1, 1, 3, 2, 1, 7]
66231970	[4, 4, 4, 4, 2, 1, 4, 1, 1, 5, 9, 2, 1, 2, 2, 6]
280563633	[4, 4, 4, 4, 5, 5, 22, 11, 2, 2, 1, 2]
1188485803	[4, 4, 4, 4, 3, 1, 20, 5, 1, 1, 4, 7, 1, 2, 3, 1, 3, 2]
5034507976	[4, 4, 4, 4, 4, 2, 1, 4, 1, 1, 5, 23, 1, 77, 1, 1, 1, 3]
21326515877	[4, 4, 4, 4, 4, 5, 5, 22, 5, 2, 1, 1, 3, 2, 1, 6, 2, 2, 2]
90340574445	[4, 4, 4, 4, 4, 3, 1, 20, 5, 1, 1, 5, 9, 2, 1, 2, 2, 6, 1, 2, 3]
382686808866	[4, 4, 4, 4, 4, 4, 2, 1, 4, 1, 1, 5, 22, 11, 2, 2, 1, 1, 1, 77]
1621095817661	[4, 4, 4, 4, 4, 4, 5, 5, 22, 5, 1, 1, 4, 7, 1, 2, 3, 1, 3, 2, 1, 7]
6867072066967	[4, 4, 4, 4, 4, 4, 3, 1, 20, 5, 1, 1, 5, 23, 1, 77, 1, 1, 1, 2, 2, 6]
29089384105824	[4, 4, 4, 4, 4, 4, 4, 2, 1, 4, 1, 1, 5, 22, 5, 2, 1, 1, 3, 2, 1, 6, 2, 2, 1, 2]
123224608457425	[4, 4, 4, 4, 4, 4, 4, 5, 5, 22, 5, 1, 1, 5, 9, 2, 1, 2, 2, 6, 1, 2, 3, 1, 3, 2]
521987817988657	[4, 4, 4, 4, 4, 4, 4, 3, 1, 20, 5, 1, 1, 5, 22, 11, 2, 2, 1, 1, 1, 77, 1, 1, 1, 3]
2211175880326082	[4, 4, 4, 4, 4, 4, 4, 4, 2, 1, 4, 1, 1, 5, 22, 5, 1, 1, 4, 7, 1, 2, 3, 1, 3, 2, 1, 6, 2, 2, 2]
9366691339432090	[4, 4, 4, 4, 4, 4, 4, 4, 5, 5, 22, 3, 1, 2, 3, 1, 1, 41, 1, 2, 1, 3, 2, 6, 3, 1, 1, 13]

Figure 4. Continued fractions[1] corresponding to $K(B_3))_{L-1}/K(B_3))_L$ values. Observe that the values of the first column represent the number of Kekulé structures of the members of the B_3 series (*cf.* Figure 1).

Observe that the value of $(d_1 + d_2)$ at stage $(j-1)$ leads to d_2 at stage j when scaled down by γ. *E.g.*, at stage 0, $d_1 + d_2 = 1 + \gamma^{-1}$ which when multiplied by γ becomes $1 + \gamma$ which is d_2 at stage 1. While $1 + \gamma + 1 = 2 + \gamma = d_1 + d_2$ at stage 1 which when scaled by γ becomes $2\gamma + \gamma^2 = d_2$ at stage 2 and so on, which accounts for the scaling – invariance of this model.

Continued Fractions of B_3 Series

In Ref. 1, we demonstrate how self-similarity (as uncovered by the $\diagup$ relation) is reflected when K_{L-1}/K_L for a homologous series of benzenoids is expressed in the form of continued fractions.[1] The B_0 type (Figure 1) represents a rare case of exact self-similarity. For example $(K(B_0))_1/(K(B_0))_2 = 2/3 \equiv [1,1,1]$; $(K(B_0))_2/(K(B_0))_3 = 3/5 \equiv [1,1,1,1]$, ... Indeed, as $L \rightarrow \infty$ $(K(B_0))_{L-1}/K(B_0))_L = [1,1,1,...,1] \equiv [1]$ and that is why such expressions are sometimes described as a fixed point of the hyperbolic map.

In Figure 4, we expressed $(K(B_3))_{L-1}/(K(B_3))_L$ in their continued fraction forms. For this series, there is some degree of self-similarity manifested as strings of 4′s. However, these strings are followed by seemingly random numbers ordered in a chaotic fashion.

DISCUSSION AND CONCLUSIONS

The equivalence relation introduced earlier and reconsidered here is an »artificial« device to uncover some of the hidden properties of Kekulé counts of benzenoids, such as graph generation[2,6,8] (in which K(B) can be expressed as a sum of hypercubes for any catacondensed B), numerical self-similarity[1,3] and modeling of quasicrystals.[3,12] Here, we have presented two peculiar cases where the structure of the homologous series does not change under the equivalence relation, (*cf.* Eqs. (27a), (27b). Instead, a system is simply regressed to an earlier member of the same homologous series, Eq. (28). We »borrowed« an »elementary« argument from renormalization theorems in physics to propose that the B_0 and B_3 systems represent a »threshold structure« analogous to the critical percolation density,[13] which remains self-similar under a renormalization operation:[14] we claim here that B_0 and B_3 are the only two benzenoid systems containing no more than one brnached hexagon whose Kekulé counts obey Eqs. (27a), (27b). Although not explicitly stated, the chemical graph theory has »renormalized« unbranched benzenoids into caterpillar trees and the branched ones as Clar graphs![18] Analogously, when B is catacondensed, the relation $\diagup$ renormallizes K(B) as a sum of hypercubes! If the statistical distribution of these hypercubes remains self-similar under the $\diagup$ operation (as in B_0 or B_3 series), the system is defined here to be statistically self-similar. It is conjectured that B_0 and B_3 are the only two systems which possess statistical self- similarity in catacondensed benzenoids with no more than one branched hexagon.

Appendix

Inductive proof of Lemma 1
we start with Binet formula.[19]

$$F_n = \frac{1}{\sqrt{5}}\left[\left(\frac{1+\sqrt{5}}{2}\right)^{n+1} - \left(\frac{1-\sqrt{5}}{2}\right)^{n+1}\right]. \qquad \text{(A–1)}$$

Now,

$$\gamma^n = \left(\frac{\sqrt{5}-1}{2}\right)^n . \qquad \text{(A–2)}$$

Then

$$F_n\gamma^n + F_{n-1}\gamma^{n+1} = \frac{2}{\sqrt{5}(\sqrt{5}-1)}\left[1-\left(\frac{\sqrt{5}-3}{2}\right)^{n+1}\right] + \frac{\sqrt{5}-1}{2\sqrt{5}}\left[1-\left(\frac{\sqrt{5}-3}{2}\right)^{n}\right]. \qquad \text{(A–3)}$$

Let

$$A = \frac{\sqrt{5}-3}{2}, \; B = \frac{2}{\sqrt{5}(\sqrt{5}-1)}, \; C = \frac{\sqrt{5}-1}{2\sqrt{5}} . \qquad \text{(A–4)}$$

We assume that Lemma is true for $(n-1)$ and (n), *i.e.*,

$$\begin{aligned} B(1-A^n) + C(1-A^{n-1}) &= 1 \\ B(1-A^{n+1}) + C(1-A^n) &= 1 \end{aligned} \qquad \text{(A–5)}$$

and it is required to prove the Lemma for $(n+1)$ *i.e.*,

$$B(1-A^{n+2}) + C(1-A^{n+1}) = 1 .$$

Now,

$$\begin{aligned} (1-A^n)(1+A) &= 1 - A^n + A - A^{n-1} \\ &= 1 - A^{n+1} + A(1-A^{n-1}) \end{aligned}$$

$$\therefore\ (1-A^{n}) = \frac{1-A^{n+1}+A(1-A^{n-1})}{(1+A)} \qquad \text{(A–6)}$$

$$(1-A^{n+1}) = \frac{1-A^{n+2}+A(1-A^{n})}{(1+A)} .$$

Hence, using (A–6) in (A–5), we obtain;

$$B((1-A^{n+2}) + A(1-A^n)) + C((1-A^{n+1}) + A(1-A^{n-1})) = (1+A)$$

$$B(1-A^{n+2}) + C(1-A^{n+1}) + BA(1-A^n) + CA(1-A^{n-1}) = 1+A$$

$$B(1-A^{n+2}) + C(1-A^{n+1}) = 1 + A - A(B(1-A^{n}) + C(1-A^{n-1})) = 1 + A - A = 1$$

which proves Lemma for $(n+1)$.

Glossary of Important symbols

$(K(\mathrm{B}))_L$	Kekulé structure of the L^{th} benzenoid system B in a homologous series.
$\kappa(\mathrm{B})$	Kekulé space of a benzenoid system B, Eq. (1).
$K(\mathrm{B}(2^j))$	The number of Kekulé structures of the resonating part of B in which j terminal R_1 circuits are fixed. *C f.* Eqs. (9)–(11) or (15)–(18).
s	Symmetry factor *e.g.* $s = 2$ in Eq. (10') $s = 3$ in Eq. (16), (17). See also Table III, first column.
$K(2^j)$	An abbreviation for $sK(\mathrm{B}(2^j))$. *Cf.* Eqs. (2), (3), (7a), (8a).
$(K(2^j))_L$	The value of $K(2^j)$ for the L^{th} member of a given homologous series. *Cf.* Eq. (7a), (8a), Figure 1.
ℓ	An equivalence relation which expresses $K(\mathrm{B})$ as a sum of hypercubes. *cf.* Eqs. (7a) and (8a) are examples of the application of ℓ on a given series of benzenoids.
F_n	n^{th} Fibonacci number.
γ	$\lim\limits_{n\to\infty} F_n/F_{n+1}\ 2^{-1}(\sqrt{5}-1)$ = the golden mean.

Acknowledgment. – The author's son, Islam El-Basil, designed the models of 1-dimensional quasicrystals (Figures 2,3) and computed continued fractions of Figure 4.

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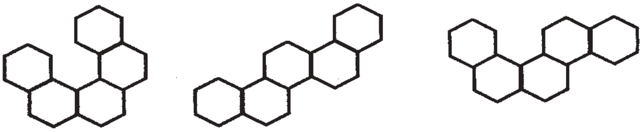
7. The conjugated circuit model was introduced in: M. Randić, *Chem. Phys. Lett.* **38** (1976) 68; *J. Am. Chem. Soc.* **99** (1977) 444; *Int. J. Quantum Chem.* **17** (1980) 549. By a terminal R_1 circuit, an R_1 circuit is meant which is entirely located in a terminal hexagon, *i.e.* a hexagon which shares only one edge with an adjacent hexagon in the benzenoid system. An R_1 circuit contains $4j + 2$ pi – elelctrons. (see Ref. 4).
8. The concept of graph-generation is considered in: M. Randić, W. L. Woodworth, A. F. Kleiner, and H. Hosoya, *J. Comput. Chem.* **8** (1987) 522.

9. For example, some of three-connected transition-metal clusters exist in the form of a (3-)cube [D. M. P. Mingos, and D. J. Wales, *Introoduction to Cluster Chemistry*, Prentice Hall, Englewood Cliffs, 1990, pp. 76–77], *e.g.* $Ni_8(PPH)_6(CO)_8$ possessing 120 valence electrons. The 3-cube and the tessaract have been used in the field of organometallic chemistry to describe certain symmetry operations related to six-coordinate complexes [M. Gielen, in; A. T. Balaban (Ed.), *Chemical Applications of Graph Theory*, Academic Press, London, 1976, pp. 289–290]. In the field of enzymes, the ferrodoxin system is mentioned which contains the Fe_4S_4 »cubane« cluster unit and similarly the dimeric anions $[Fe_6Mo_2S_8(SR)_9]^{3-}$ have two Fe_3MoSO_4 »cubane« linked by SR bridges [D. M. P. Mingos and D. J. Wales, *Introduction to Cluster Chemistry*, Prentice Hall, Englewood Cliffs, 1990, pp. 24, 27, 62, 76]. The graph generation uncovered by the ℓ-operation also led to an analogy with Feigenbaum's theory of chaos [see Ref. 5, and M. Feigenbaum, *J. Stat. Phys.* **19** (1978) 25].
10. On the other hand, deterministic fractals have been considered by D. J. Klein, J. J. Cravey, and G. E. Hite, *Polycyclic Aromat. Compd.* **2** (1991) 165; D. Plavšić, N. Trinajstić, and D. J. Klein, *Croat. Chem. Acta* **65** (1992) 279.
11. All-kinked benzenoids include, in addition to the polyphenanthrenoid polyphenes (which are traditionally called zigzag polyacenes such as phenanthrene, chrysene, pentacene,...), all possible isoarithmic benzenoids: See *e.g.* S. J. Cyvin and I. Gutman, *Lecture Notes in Chemistry* **46** (1988) 29. Isoarithmicity is considered in; A. T. Balaban and I. Tomescu, MATCH, **14** (1983) 155. For instance, there are three isoarithmic all-kinked benzenoids (the *K* values of any of which is 13). The molecular graphs of these benzenoids are shown below.



12. D. Sechtman, I. Blech, D. Gratias, and J. W. Cahn, *Phys. Rev. Lett.* **53** (1984) 1951. See also Refs. 2, 3.
13. D. Stauffer, *Introduction to Percolation Theory*, Taylor and Francis, London, 1985.
14. See, *e.g.*, H.-O. Peitgen, H. Jürgens, and D. Saupe, Chaos and Crystals, Springer-Verlag, New York, 1992, p. 471.
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SAŽETAK

Poseban oblik numeričke samosličnosti Kekuléovih brojeva benzenoida ugljikovodika

Sherif El-Basil

Ranije definirana relacija ekvivalencije, označena s ℓ, Kekuléovih brojeva, označenih s K(B), katakondenziranih benzenoidnih ugljikovodika klasificira Kekuléove strukture prema broju njihovih krajnjih konjugiranih krugova. Relacija ekvivalencije ℓ omogućuje otkrivanje manje uočljivih kombinatoričkih svojstava brojeva K(B), kao što su numerička samosličnost, generiranje grafova, modeliranje kvazikristala i modeliranje Feigenbaumove teorije kaosa. U ovom su radu razmatrana dva benzenoidna sustava: B_0 – benzenoidni cik-cak sustav bez grana, i B_3 – benzenoidni cik-cak sustav s jednakom granom. Takve benzenoidne sustave karakterizira posebno svojstvo, a to je da statistička raspodjela hiperkocki (čvorovi, bridovi, kvadrati...), koje čine njihov Kekuléov prostor, ostaje invarijantna na djelovanje relacija ekvivalencije ℓ. To svojstvo omogućuje jednostavno prebrojavanje konjugiranih krugova B_0 i B_3 benzenoidnih sustava. Pokazano je također da $K(B_0)$ i $K(B_3)$ modeliraju jednodimenzijski kvazikristal.