Benzenoids with Maximum Kekule Structure Counts for Given Numbers of Hexagons[†]

Alexandru T. Balaban,[‡] Xiaoyu Liu,[§] Sven J. Cyvin,[⊥] and Douglas J. Klein[*,§]

Department of Organic Chemistry, Polytechnic University, Splaiul Independentei 313, 77206 Bucharest, Romania, Department of Marine Sciences, Texas A&M University at Galveston, Galveston, Texas 77553-1675, and Division of Physical Chemistry, Norwegian Institute of Technology, University of Trondheim, N-7034 Trondheim, Norway

Polycyclic aromatic hydrocarbons with the maximal numbers of Kekule structures for any number h of benzenoid rings are shown to be branched cata-condensed systems. Their structures present regularities with periodicities of three and four in terms of h. An analysis of their structures is presented, and the recurrences are highlighted.

INTRODUCTION AND DEFINITIONS

The number of Kekule structures (or the Kekule structure count) has served for a long time as an indicator for resonance energies of polycyclic aromatic hydrocarbons (PAH's), for computing Pauling bond orders, and for other properties. From the rich bibliography, one may note a few books,[1-6] book chapters,[7-11] and papers.[11-24] Of course there are some qualifications in using Kekule structures: the more elaborate theoretical methods indicate, in agreement with experimental findings for enthalpies of formation, that triphenylene (**1**) and chrysene (**2**) have approximately equal stabilities, despite the higher Kekule structure count of the former;[23-28] this is probably due to the slight nonplanarity of triphenylene.[26]

Alternative names for PAH's are *polyhexes* or *benzenoids*. The latter term, however, has sometimes been used in a restricted sense[1,29] to denote only those PAH's which can be obtained from the graphite lattice by selecting a connected array of hexagons ("graphite-connected PAH's"[27]). Under such a restricted acceptance, helicenes with six or more hexagons would be excluded, yet they are stable and interesting compounds because of their nonplanar geometry and inherent chirality. [Nonplanar geometry is different from graph-theoretical nonplanarity, which is not relevant in the present context.] Herndon and co-workers[26-28] have shown, moreover, that most PAH's are geometrically nonplanar. Trinajstic[30] restricted further the term "benzenoid" to those PAH's whose Kekule structure counts are nonzero. In the present paper we shall use the term benzenoid as a synonym for "polyhex", including also geometrically nonplanar PAH's, i.e. ignoring any restriction (actually, it so happens that all systems which will be presented here have nonzero Kekule structure counts).

The number of hexagons in the benzenoid system will be denoted by h and the number of Kekule structures by K (or K with some subscript such as K_h). A simple means of computing the value of K_h for any given benzenoid structure is via its adjacency matrix and its determinant or via its characteristic polynomial. In graph theory, the Kekule structure count is called the number of perfect matchings of the Huckel graph.

Benzenoids are of three types: (i) cata-condensed (catafusenes), in which no carbon atom is common to three hexagons or whose dualist graph (inner dual) is acyclic [dualist graphs have vertices corresponding to the centers of benzenoid rings,

and edges connecting vertices which correspond to condensed rings; unlike usual graphs, in dualist graphs the angles between the edges do matter[31-33]]; (ii) peri-condensed (perifusenes) which have some carbon atoms common to three hexagons, or whose dualist graphs have 3-membered rings;[32] (iii) coronoids (coronafusenes) whose dualist graphs have larger rings which are not the periphery of fused 3-membered rings.[3] Benzenoids which have the same K_h values are called isoarithmic.[34] The most interesting ones are isomeric benzenoids with the same numbers h of hexagons. In the dualist graph, directions of "kinks" differentiate isoarithmic systems. Thus chrysene (**2**) and benzo(c)phenanthrene (**3**), or picene (**4**), naphtho(2,1-c)phenanthrene (**5**), and naptho(1,2-c)-phenanthrene (**6**) are isoarithmic.

All the previously displayed benzenoids have dualist graphs with no triple of linearly annelated benzenoid rings. This corresponds to the absence of zeroes in their codes[31-33] obtained as a sequence of digits 0, 1, 2 denoting "no kink", "left-kink", and "right-kink", respectively, appearing in their dualists.[31] If in the dualist graph one codes only for the existence, but not for the direction of a kink, one obtains the "L-transform"[35] or the "LA-sequence",[36] which is the same for all isomeric isoarithmic catafused chains, but does not discriminate among their structures.

BENZENOIDS WITH MAXIMUM K VALUES FOR GIVEN NUMBER h OF HEXAGONS

Gutman published formulas (1) and (2) for the h and K_h values of maximally branched catafusenes with trigonal symmetry, whose dualist graphs have only vertices of degree 1 and 3. He denoted these systems as series X_k with $k = 1$,
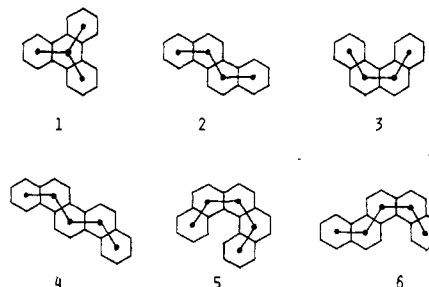
2, etc.[37] Formulas (3) and (4) by the same author apply to series Y_k with bilateral symmetry, such that the dualist graph has, in addition to two maximally branched identical portions with vertices of degree 1 and 3, a single central vertex of degree 2. In the
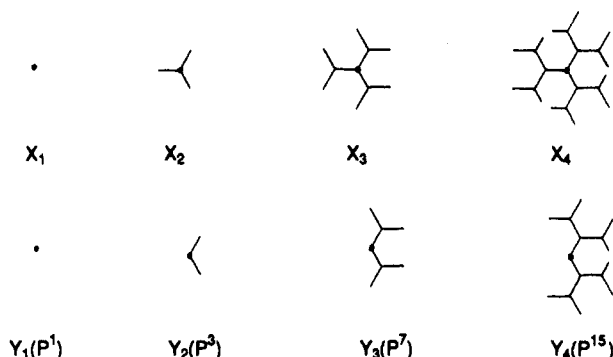
430 *J. Chem. Inf. Comput. Sci., Vol. 33, No. 3, 1993*

BALABAN ET AL.

present paper, for the latter series we shall also use the notation P^h (h being, as always, the number of benzenoid rings); for the case P^3 the superscript may be omitted. These two series are labeled as

X_1 X_2 X_3 X_4

$Y_1(P^1)$ $Y_2(P^3)$ $Y_3(P^7)$ $Y_4(P^{15})$

and the associated counts of hexagons and Kekule structures are given by

$$h(X_k) = 3(2^{k-1}) - 2 \qquad (1)$$

$$K(X_k) = K(Y_{k-1})^3 + K(Y_{k-2})^6 \qquad (2)$$

$$h(Y_k) = 2^k - 1 \qquad (3)$$

$$K(Y_k) = K(Y_{k-1})^2 + K(Y_{k-2})^4 \qquad (4)$$

Recurrences 2 and 4 with initial values $K(Y_{-1}) = K(Y_0) = 1$ allow the calculation of K for certain h values given by (1) and (3); such h values become increasingly sparse as h increases.

Gutman,[37] as well as John and Sachs,[38,39] investigated asymptotic bounds for K_{max} in catafusenes with given h values. A "brute force approach" taken here shows that among all benzenoids with h as in (1), the catafusenes in the X_k series have the largest K values. Among the initial structures with small h values, a few terms of the Y_k series appear. However, little more has been known about the structures of all benzenoids with maximal K values for arbitrary numbers h of hexagons. It is the purpose of the present paper to solve this problem by induction: starting from a purposefully designed computer program, the structures of benzenoids with maximum K_h values are here reported for up to $h = 60$ hexagons. The 3- and 4-periodicity in terms of h revealed for the resulting structures is then postulated to hold also for higher h values.

COMPUTER PROGRAM FOR OBTAINING POLYHEXES WITH K_{max}

A generalized Gordon–Davison algorithm[12] for computing the Kekule structure count of branched catafusenes is presented below, using dualist graphs.

For an acenic subgraph with h benzenoid rings (7), the number of Kekule structures is $h + 1$. When a kink appears in a nonbranched benzenoid subgraph, as in pentaphene (8),

7   8A   8B
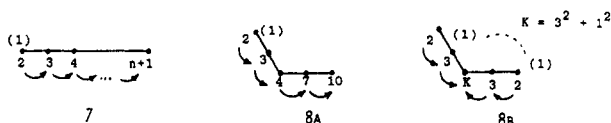
one may compute K either proceeding from one end to the other by incrementing each hexagon by the value preceding the last kink (having begun with an initial off-chain prekink

value of 1) or else considering the hexagon at the kink as a branching point with two branches and summing the product of K values for the hexagons connected to the branching point with the product of pre-Kekule counts (at the ends of the acenic strings). This last approach may be generalized for two or three branches.

In general,[19] K_1', K_2' denote the pre-kink Kekule counts, and K_1, K_2, the Kekule counts adjacent to the branching hexagon in a catafusene with two branches at a kinked angle as in 9 or 10. Then we have

9   10   11

(B)

12   13

(A)
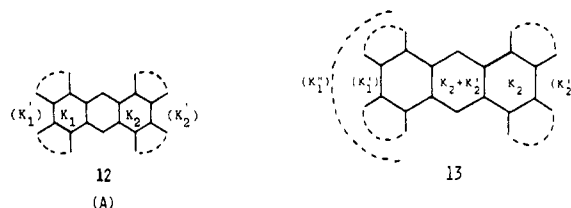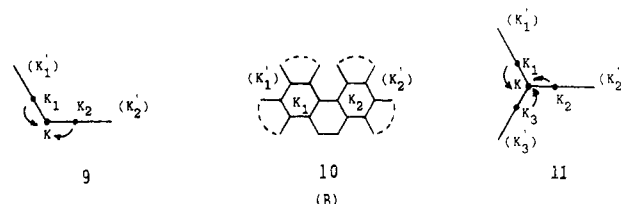
$$K = K_1 K_2 + K_1' K_2'$$

and, for a catafusene with three branches (11) coming together at a single hexagon, likewise

$$K = K_1 K_2 K_2 + K_1' K_2' K_3'$$

Here we utilize especially the construction of 9. We let (h, K', K) represent a so-called building benzenoid (BB) with h catafused hexagons, a Kekule structure count K, and a pre-Kekule count K' at the root kink point of its dualist graph. Of course there are other fusion patterns possible, such as the anthracenic fusion (12). To find the number of Kekule structures in this case, one may utilize the kinked recursion if we realize the equivalence of 12 to 13, where recursion is imagined to the center ring from the right (K_2) ring solely before recursion into the ring marked with K_1 in 12. To have obtained K_1 in 12, it must have a Kekule structure count K_1' added to an earlier prekink count K_1'', so that $K_1'' = K_1 - K_1'$, and one is prepared to make the recursion for the circumstance of 13, as

$$K_A = K_1'(K_2 + K_2') + K_1'' K_2' + K_1' K_2 + K_1 K_2'$$

Now comparing this Kekule structure count K_A to that K_B for the kinked addition as in 10, we find

$$K_B - K_A = (K_1 K_2 + K_1' K_2') - (K_1' K_2 + K_1 K_2')$$
$$= (K_1 - K_1')(K_2 - K_2') > 0$$

Therefore we have proved the following result.

Theorem. On fusing two building benzenoids on one benzenoid ring, the number of Kekule structures in the result is smaller when the fusion is linear than when it is kinked (i.e. $K_A < K_B$).

If we admit the 0- and 1-hexagon building benzenoids with labels $(0,1,1)$ and $(1,1,2)$, then all catafusenes are obtainable via recursion with kinked fusion as in 10 or with anthracenic fusion as in 12. But in seeking catafusenes with maximal Kekule structure counts the preceding theorem allows us to consider only the kinked fusion (foregoing all catafusenes with an anthracene subgraph).

Thence one may build up all building benzenoid catafusenes in a recursive manner and simultaneously keep track of Kekule

structure counts. Two building benzenoids, with labels (h_1, K_1', K_1) and (h_2, K_2', K_2), may be combined by kinked fusion of the two roots at a new root as in **10**, thereby obtaining a new (larger) building benzenoid with label

$$(h_1 + h_2 + 1, K_1K_2, K_1K_2 + K_1'K_2')$$

If the two fused building benzenoids are identical, then one may recover the recursions of eqs 3 and 4 for the Y_i or P^h sequence.

A program was devised to accomplish the construction of all "relevant" building benzenoids up to some maximum count h_{max} of hexagonal rings. Here by relevant we mean either those of maximal Kekule structure count for the associated number of rings or those which might be a component in building up a larger structure of maximal Kekule structure count, K_{max}. A simple test for "irrelevance" of a structure S_1 with label (h, K_1', K_1) is that there exists another structure S_2 with label (h, K_2', K_2) such that $K_1' < K_2'$ and $K_1 < K_2$, so that any larger structure S using S_2 in place of S_1 (via a kinked fusion) leads to a larger Kekule structure count for S. Retaining only the results for relevant building benzenoids then allows computer time and space available to be expended on proceeding to larger systems.

The logical detail of the program is conveniently expressed with some little additional notation. We let $\{h\}$ denote the ordered collection of ring counts for all building benzenoids retained, that is, the ith component of $\{h\}$ is the number of rings in the ith (relevant) building benzenoid. Similarly $\{K\}$ and $\{K'\}$ are the corresponding ordered sets of Kekule structure counts and pre-Kekule structure counts, respectively, while $\{H\}_h$, $\{K\}_h$, and $\{K'\}_h$ are the subsets with ring count h. In forming structures of ring count h, we look at subsets $\{...\}_{h1}$ and $\{...\}_{h2}$ for various possible values of h_1 and h_2 satisfying $h = h_1 + h_2 + 1$; one needs only to allow h_1 to cover no more than half the range since h_2 jointly covers the remaining range. That is, h_1 is taken to range from 0 to $[(h - 1)/2]$, while simultaneously h_2 ranges from $h - 1$ down to $[(h - 1)/2]$, where $[x]$ generally denotes the integer part of x. The pseudocode for our program is

```
initialization
    (h₁, K₁', K₁) = (0, 1, 1); (h₂, K₁', K₂) = (1, 1, 2)
    h = 2
iteration
    10 While h ≤ hmax, do
        {h} = φ; {K'}h = φ; {K}h = φ
        for h₁ = 0, to [(h - 1)/2], do
            h₂ = h - h₁ - 1
            for all i ε {h₁}, j ε {h₂}, do
                K' = KiKj; K = K' + Ki'Kj'
                if K' > Kβ' or K > Kα for all
                    Kα ε {K}h, Kβ' ε {K'}h
                then
                    {h} = {h} ∪ {h₁ + h₂ + 1}
                    {K}h = {K}h ∪ {K}
                    {K'}h = {K'}h ∪ {K'}
                end if
            end do
        end do
        output h, Kmax = max{K}h
        h = h + 1; go to 10
    end do
stop
```

As it can be seen from the pseudocode algorithm above, the computation becomes costly as h increases. Because the sizes of the preceding sets of building benzenoids $\{h - 1\}$, $\{h - 2\}$, ..., become larger and larger for greater h's, more CPU time

Table I. Numbers K_{max} of Kekule Structures of Polyhexes for Given Numbers h of Hexagons

h	K_{max}	h	K_{max}	h	K_{max}
1	2	21	49,913	41	1,319,360,447
2	3	22	84,546	42	2,210,390,934
3	5	23	138,170	43	3,669,617,993
4	9	24	231,117	44	6,100,902,003
5	14	25	386,222	45	10,104,225,566
6	24	26	640,830	46	17,012,572,857
7	41	27	1,061,039	47	27,963,021,326
8	66	28	1,785,078	48	46,730,211,414
9	110	29	2,931,008	49	77,723,628,299
10	189	30	4,927,011	50	129,649,151,874
11	305	31	8,176,976	51	214,222,610,438
12	510	32	13,562,472	52	359,261,197,551
13	863	33	22,512,977	53	592,810,520,174
14	1,425	34	37,891,224	54	993,399,265,662
15	2,345	35	62,212,949	55	1 645,851,650,042
16	3,987	36	104,076,573	56	2 742,311,644,086
17	6,515	37	173,169,326	57	4 539,590,744,474
18	10,905	38	288,667,101	58	7 627,440,899,358
19	18,254	39	476,880,266	59	12 575,135,816,912
20	30,135	40	800,699,454	60	20 988,331,387,026

is thus needed to exhaust all possible fusions to construct the succeeding set $\{h\}$. On the other hand, however, the exhaustive algorithm does guarantee that the reported benzenoid of K_{max} is indeed the (all-kinked) cata-condensed benzenoid of ring count h with the maximum Kekule structure count. The algorithm was tested out successfully on an IBM RISC/6000 computer with h going from 2 to 60, and the resulting h and K_{max} values are presented in Table I.

If we label the benzenoids in sets $\{0\}$, $\{1\}$, $\{2\}$, ..., $\{h - 1\}$, $\{h\}$ consecutively as the iteration proceeds, we can fairly easily back-track all the building benzenoids from which the cata-condensed benzenoid of maximum Kekule structure count is constructed. The implemented generalized algorithm is actually a binary scheme in that two building benzenoids of smaller sizes are put together to form a third one in each construction step during the iteration. The following two array structures are then defined to record the genealogy of the complete construction process:

BB1(I) the label of the first building benzenoid from which the Ith is built

BB2(I) the label of the second building benzenoid from which the Ith is built, or if there is no second, then 0

Initially

$$BB1(1) = 0 \quad BB1(2) = 0$$

$$BB2(1) = 0 \quad BB2(2) = 0$$

where BB1(1) and BB2(1) are the labelings for the building benzenoids from which the benzenoid of zero ring is constructed, whereas BB1(2) and BB2(2) are the labelings for the building benzenoids from which the benzenoid of one ring is built. The above initial labelings are based on the fact that the zero-ring system and the benzene ring are themselves the initial building benzenoids and their predecessors do not exist.

The pseudocode algorithm is now slightly modified to keep track of the iterative construction process:

```
initialization
    ......
    I = 2
Iteration
    ......
```

if K' > K_{β}' or K > K_{α} for
all $K_{\alpha} \in \{K\}_h$, $K_{\beta}' \in \{K'\}_h$
then

......

I = I + 1
BB1(I) = i; BB2(I) = j
end if

......

Stop

where I is the labeling index, while i and j are the labels for the first and second building benzenoids from which the Ith is built. Thence once the maximum value K_{max} is located, the corresponding binary construction tree is readily laid out, as shown in Figure 1. For example, at $h = 16$ the K_{max} value is equal to 3987. The binary construction tree is depicted in Figure 2. The dualist graph of the benzenoid is also shown in Figure 2. In this case the BB denoted by (0/1) does not appear in the dualist graph of the final benzenoid because it is the abstract precursor, with zero rings, of benzene. However, when the BB's have $h = 1$, as in all other end points of the above binary construction tree, they do appear.

3- AND 4-PERIODICITY OF BENZENOIDS WITH K_{max} IN TERMS OF h

The output of the computer program allows the retrieval of benzenoid structures with K_{max} values but does not discriminate among isomeric isoarithmic systems. Therefore when by out-of-plane rotation around a line in the dualist graph a different benzenoid results, both these structures which are isoarithmic will be solutions of the problem. The smallest system which exemplifies this occurrence has $h = 9$ hexagons, and the next one has $h = 13$ hexagons; all are illustrated in Figure 3.

The 4-periodicity in terms of h, observed in the above systems, holds for all $h \equiv 1 \pmod 4$ values ($h > 9$) which, as shown in Table II, indicate that such systems have K_{max} values corresponding to more than one benzenoid structure.

Table II presents for each h value one (namely, the least overcrowded) structure for a benzenoid with K_{max}. A few remarkable facts emerge on considering this table.

(1) All structures in Table II are highly branched catafusenes. If, instead of the number h of hexagons, we had considered as the independent variable the number of carbon atoms (which is equal to the number of π-electrons in the benzenoid), then perifusenes would have surpassed the branched catafusenes for h values higher than about 12: indeed, as seen in Table I, the catafusene with $h = 13$ and 54 carbon atoms has $K = 863$, but circumcoronene (a perifusene with the same number of carbon atoms and with $h = 19$) has $K = 980$.

As a consequence of the fact that all K_{max} polyhexes which will be discussed henceforth are cata-condensed, it results that dualist graphs which are presented in Table II and subsequent ones are acyclic (trees) with maximal degree equal to 3.

(2) The 4-periodicity in terms of h is easily perceived in the structures of the dualist graphs presented in Table II. An even better appreciation of this periodicity is made possible by denoting a phenanthrene unit annelated at the central 9,10-bond as a P^3 subgraph (corresponding to Y_2); the superscript in P^3 indicates the number of hexagons in the subgraph, i.e. the number of vertices in the dualist graph. Such a subgraph is actually the second term in the series Y_k which will be renamed $P^1-P^3-P^7-P^{15}-P^{31}-P^{63}-...$ consisting of a central vertex with degree 2 connected to two identical
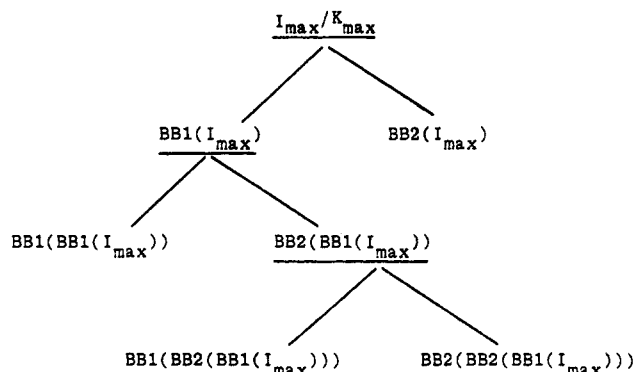

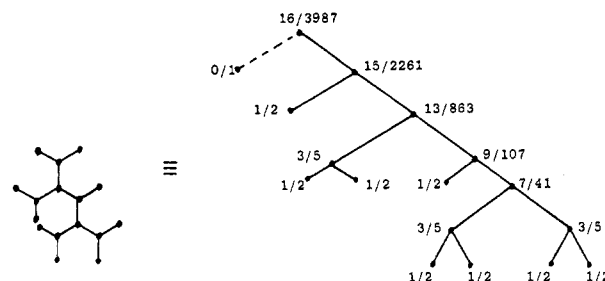**Figure 1.** Partial binary construction tree.

Figure 2. Binary construction tree for the cata-condensed benzenoid with $h = 16$ and $K_h = 3987$.
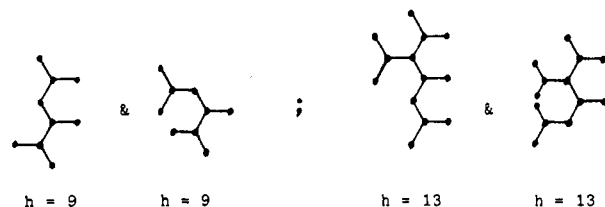

Figure 3. Dualist graphs of pairs of isoarithmic cata-condensed benzenoids with K_{max}, having $h = 9$ and 13.

subgraphs preceding in the series. Therefore the number of hexagons in this series has the recurrence

$$h_{i+1} = 2h_i + 1 \qquad (5)$$

Table III presents the same data from Table II in a different form, emphasizing the presence of P^3 subgraphs (denoted for brevity by P) in all structures. It is evident that systems belonging to the most symmetrical, last column with $h \equiv 2 \pmod 4$ have a core graph totally surrounded by P^3 subgraphs, and that this core is identical to the sequence of dualist graph structures contained sequentially in Table II. In other words, disregarding the letters in Table III and examining the core graphs vertically in any column, we obtain the same sequence as when we follow horizontally row after row in Table II. Indeed, the dualist graphs in the last column of Table III have, for each value $h = 4k + 2$, a core with $h' = k - 1$ points surrounded by $k + 1$ P^3 subgraphs so that each point of the core graph has degree 3. Thus, by taking sequentially all dualist graphs from Table II, adding two lines at 120° angles to each point with degree 1 and one line to each point with degree 2, and surrounding the resulting tree by P^3 subgraphs, one obtains the last column of Table III. The number h' of points in the core graph obeys the relationship

$$h' = (h - 6)/4$$

(3) It can be seen from Table III that the cores of all other columns repeat the core of the last column stepping down from right to left diagonally. For each of these other columns, we use a different abbreviation (X, Y, Z) for a particular

BENZENOIDS WITH MAXIMUM KEKULE STRUCTURE COUNTS

J. Chem. Inf. Comput. Sci., Vol. 33, No. 3, 1993 **433**

Table II. Dualist Graphs of Benzonoids with Maximum Numbers of Kekule Structures for a Given Number h of Hexagon[a]

$h \equiv 3 \pmod 4$	$h \equiv 0 \pmod 4$	$h \equiv 1 \pmod 4$	$h \equiv 2 \pmod 4$

[a] Asterisks indicate systems which have two or more isoarithmic isomers: their dualist graphs differ by rotation around edges with angles of 180°.

subgraph having three points plus 1, 2, or 3 subgraphs P^3, respectively. This indicates a 3-periodicity in h, because a subgraph P^3 has three hexagons.

One can also observe that the unique subgraph X, Y, or Z for any h value is alternately connected to points of the core graph with degrees 1 and 2. On examination of the core

Table III. Dualist Graphs of K_{max} Catafusenes with Their Core Graphs Surrounded by P, X, Y, Z Subgraphs

$h \equiv 3(\mathrm{mod}\ 4);\ Z =$	$h \equiv 0(\mathrm{mod}\ 4);\ Y =$	$h \equiv 1(\mathrm{mod}\ 4);\ X =$	$h \equiv 2(\mathrm{mod}\ 4);\ P =$
			10 • P_3
		13 • P_2X	14 P_2 •—• P_2
	16 • P_2Y	17 P_2 •—• PX	18 P_2 •—<P, P_2
19 • P_2Z	20 P_2 •—• PY	21 P_2 •—<X, P_2	22 P_2 •—<P_2, P_2
23 P_2 •—• PZ	24 P_2 •—<Y, P_2	25 P_2 •—<P_2, PX	26 P_2 •—<P_2, P, P_2
27 P_2 •—<Z, P_2	28 P_2 •—<P_2, PY	29 P_2 •—<P_2, X, P_2	30 P_2 •—<P_2, P, P_2
31 P_2 •—<P_2, PZ	32 P_2 •—<P_2, Y, P_2	33 P_2 •—<P_2, PX, P_2	34 P_2 •—<P_2, P, P_2
35 P_2 •—<P_2, Z, P_2	36 P_2 •—<P_2, PY, P_2	37 P_2 •—<P_2, X, P_2	38 P_2 •—<P_2, P, P_2
39 P_2 •—<P_2, PZ, P_2	40 P_2 •—<P_2, Y, P_2	41 P_2 •—<P_2, PX, P_2	42 P_2 •—<P_2, P, P_2
43 P_2 •—<P_2, Z, P_2	44 P_2 •—<P_2, PY, P_2	45 P_2 •—<P_2, X, P_2	46 P_2 •—<P_2, P_2
47 P_2 •—<P_2, P_{PZ}, P_2	48 P_2 •—<P_2, Y, P_2	49 P_2, PX •—<P_2, P_2	50 P_2, P_2 •—<P, P_2
51 P_2 •—<P_2, Z, P_2	52 P_2 •—<P_2, P_2; PY, P_2	53 P_2, P_2 •—<X, P_2	54 P_2, P_2 •—<P_2, P_2
55 P_2, P_2 •—<P_2, P_2; PZ	56 P_2, P_2 •—<Y, P_2	57 P_2, P_2 •—<PX, P_2	58 P_2, P_2 •—<P, P_2, P_2
59 P_2, P_2 •—<Z, P_2	60 P_2, P_2 •—<PY, P_2	61 P_2, P_2 •—<X, P_2, P_2	62 P_2, P_2 •—<P, P_2, P_2

graphs diagonally from the upper right corner as they repeat themselves throughout all four columns, it is evident that the X, Y, and Z subgraphs are attached always to the same point of the core subgraph; when this point has degree 2, the position is strictly determined as there is just one point with degree 2; when this point has degree 1, it is the one closest to the tree center. The core is then surrounded by P^3 subgraphs just those as for the last column. Thus, all four columns of Table III can be easily deduced recursively from Table II.

(4) Table IV shows how one can predict the constitution of the dualist graphs for the catafusenes in the last column of Table III; by deleting from them the peripheral P^3 subgraphs, one obtains the core graphs which are common to all columns

and structures in Table III. The idea on which Table IV is based is that the dualist graphs from the last column of Table II may be represented as resulting from joining together two, three, or four P^h subgraphs (series Y_k) as seen in Figure 2.

The same constitution of a single dualist graph may generally be represented in several ways. There is no ambiguity in joining together two or three subgraphs. However, on joining four subgraphs $P^i - P^m$, there are three possibilities for pairing geminally the four subgraphs if all are different (Figure 4). An example will serve to illustrate this situation. For $h = 58$, one may add a P^3 subgraph to the dualist graph having $h = 54$ in two different positions, as shown by dualist graphs a and b from Figure 5 (a third one with P^3 geminally flanked by P^7

BENZENOIDS WITH MAXIMUM KEKULE STRUCTURE COUNTS

J. Chem. Inf. Comput. Sci., Vol. 33, No. 3, 1993 **435**

Table IV. Constitutions of Dualist Graphs for $K_{max} \equiv 2(\text{mod } 4)$ versus the Number h of Hexagons by Joining Together, as in Figure 4, k Subgraphs P^i, Verified for $h \leq 58$ and Predicted for $h \geq 62$

h	P³	P⁷	P¹⁵	P³¹	d
6	2	-	-	-	2
10	1	1	-	-	2
	3	-	-	-	3
14	-	2	-	-	2
	2	1	-	-	3
	4	-	-	-	4
18	1	-	1	-	2
	1	2	-	-	3
	3	1	-	-	4
22	-	1	1	-	2
	2	-	1	-	3
	-	3	-	-	3
	2	2	-	-	4
26	1	1	1	-	3
	1	3	-	-	4
	3	-	1	-	4
30	-	-	2	-	2
	-	2	1	-	3
	-	4	-	-	4
	2	1	1	-	4
34	1	-	-	1	2
	1	-	2	-	3
	1	2	1	-	4
36	-	1	-	1	2
	2	-	-	1	3
	-	1	2	-	3
	2	-	2	-	4
42	1	1	-	1	3
	1	1	2	-	4
	3	-	-	1	4

h	P³	P⁷	P¹⁵	P³¹	P⁶³	k
46	-	-	1	1	-	2
	-	2	-	1	-	3
	-	-	3	-	-	3
	2	2	-	-	-	4
50	1	-	1	1	-	3
	1	-	3	-	-	4
54	-	1	1	1	-	3
	2	-	1	1	-	4
	-	3	-	1	-	4
58	1	1	1	1	-	4
62	-	-	-	2	-	2
	-	-	2	1	-	3
66	1	-	-	-	1	2
	1	-	-	2	-	3
	1	-	2	1	-	4
70	-	1	-	-	1	2
	-	1	-	2	-	3
	2	-	-	-	1	3
	2	-	-	2	-	4
	-	1	2	1	-	4
74	1	1	-	-	1	3
	1	1	-	2	-	4
	3	-	-	-	1	4
78	-	-	1	-	1	2
	-	-	1	2	-	3
	-	2	-	-	1	3
	-	-	3	1	-	4
	-	2	-	2	-	4
	2	1	-	-	1	4

Figure 4. Construction of catafusenes with K_{max} from 2, 3, and 4 different subgraphs P^h.

$$K_a = (18254)(41)(8143397) + (5^3)(2306^3)$$

$$K_b = (5)(136571)(8143397) + (2^2)(41)(2306^3)$$

Figure 5. Two of the three possibilities of constructing catafusenes with K_{max} from 4 subgraphs P^h with different numbers h of hexagons, and finding their corresponding K values via the generalized Gordon–Davison algorithm.

cannot be derived from the system with $h = 54$, and moreover it has the smallest K value). Simple calculations outlined in the bottom part of Figure 5, using the generalized Gordon–Davison algorithm, lead to the K values for subgraphs shown on the formulas in Figure 5. It results that $K_b < K_a = 76276\,440\,899\,358$.
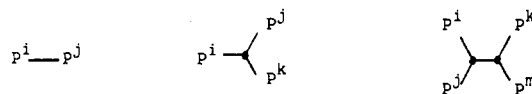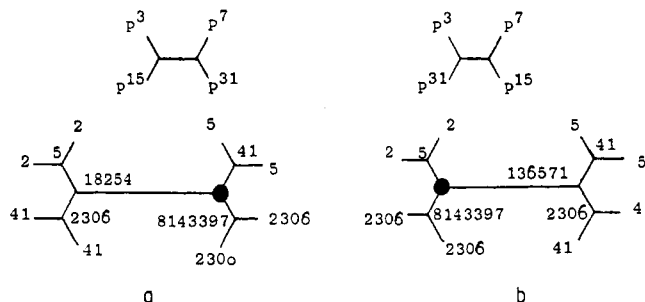
When two of the four subgraphs are identical, as for $h = 22, 30, 34, 38, 42, 46, 70, 74,$ and 78, there are only two possibilities; in such cases, these subgraphs are placed geminally and not vicinally; only the former situation corresponds to K_{max}.

CONSTITUTION OF DUALIST GRAPHS FOR K_{max} POLYHEXES

The constitution of dualist graphs of polyhexes with K_{max} (Table II), which are identical to the core graphs surrounded by P^3 and/or X, Y, Z subgraphs (Table III), obeys certain rules which will be briefly discussed below. All points of these graphs have degrees 1 and 3 for the columns $h \equiv 0(\text{mod } 4)$ and $h \equiv 2(\text{mod } 4)$ in Table II; in addition, for columns $h \equiv 1(\text{mod } 4)$ and $h \equiv 3(\text{mod } 4)$, there is a single point of degree 2.

It was shown earlier that given the constitution of dualist graphs (corresponding to L-transforms, or LA-sequences of catafusenes[11,12] for the last column $h \equiv 2(\text{mod } 4)$ in Tables II and III, it is easy to obtain all remaining columns of those tables. Therefore in the following we shall discuss only K_{max} systems with $h \equiv 2(\text{mod } 4)$.

The dualist graphs are trees with points of degree 1 and 3 having as high a symmetry and branching as possible for each

h value. Whenever possible, trigonal D_3 symmetry around the tree center is achieved ($h = 10, 22, 46, 94,$ etc.). Bilateral D_2 symmetry is, however, more common ($h = 2, 6, 14, 18, 30, 34, 38, 62, 70, 78,$ etc.).

For all other h values, consider the core graph obtained by ignoring the letters in the last column of Table III; in every second such graph, a single point of degree 2 is present. Such core graphs with one point of degree 2 can be obtained by a simple procedure from the preceding core graph in the same column, which has only points of degrees 1 and 3: one creates a point of degree 2 on the most central edge (except for $h = 58$; cf. Figure 3).

To obtain the other half of core graphs in the last column of Table III, possessing only points of degree 1 and 3, there are two rules instead of one; namely, (i) trigonal or bilateral symmetry takes precedence, whenever possible, by joining together identical subgraphs P^3, P^7, P^{15}, P^{31}, etc., according to Table IV, and (ii) otherwise, one adds an edge ending in a vertex of degree one to the vertex of degree 2 of the preceding core graph in the same column.

CONCLUSION

We have shown that for any number h of hexagonal rings in condensed benzenoids, the maximum number of Kekule structures corresponds to cata-condensed benzenoids. These are one or more isoarithmic benzenoids with the same L-transform, whose dualist graphs have points of degree 1 and 3, and zero or one point of degree 2. The constitution of such K_{max} catafusenes obeys interesting recurrences with periodicities of three and four evidenced by the dualist graphs presented in Tables II and III. The 4-periodicity corresponds to the columns in these tables, while the 3-periodicity corresponds to constancy of core graphs seen on diagonals from upper right to lower left in Table III.

REFERENCES AND NOTES

(1) Cyvin, C. J.; Gutman, I. *Kekule Structures in Benzenoid Hydrocarbons*; Lecture Notes in Chemistry No. 46; Springer: Berlin, 1988.
(2) Gutman, I.; Cyvin, C. J. *Introduction to the Theory of Benzenoid Hydrocarbons*; Springer: Berlin, 1989.
(3) Cyvin, S. J.; Brunvoll, J.; Cyvin, B. N. *Theory of Coronoid Hydrocarbons*; Lecture Notes in Chemistry No 54; Springer: Berlin, 1989.

436 *J. Chem. Inf. Comput. Sci., Vol. 33, No. 3, 1993*

BALABAN ET AL.

(4) Trinajstic, N. *Chemical Graph Theory*, 2nd ed.; CRC Press: Boca Raton, FL, 1992; Chapter 8, p 161.

(5) Knop, J. V.; Muller, W. R.; Szymanski, K.; Trinajstic, N. *Computer Generation for Certain Classes of Molecules*; Union of Chemists and Technologists of Croatia: Zagreb, 1985.

(6) Dias, J. R. *Handbook of Polycyclic Hydrocarbons*, Part A; Elsevier: Amsterdam, 1987.

(7) Rouvray, D. H. In *Chemical Applications of Graph Theory*; Balaban, A. T., Ed.; Academic Press: London, 1976; p 175.

(8) Randic, M.; Nikolic, S.; Trinajstic, N. In *Graph Theory and Topology in Chemistry*; King, R. B., Rouvray, D. H., Eds.; Elsevier: Amsterdam, 1987; p 429. See also: Chapter 9 of ref 4. Plavsic, D.; Nikolic, S.; Trinajstic, N. *J. Math. Chem.* **1981**, *8*, 113.

(9) Randic, M.; Klein, D. J. In *Mathematical and Computational Concepts in Chemistry*; Trinajstic, N., Ed.; Ellis Horwood-Wiley: Chichester, U.K., 1986; p 274.

(10) Herndon, W. C. In *Polynuclear Aromatic Compounds*; Ebert, L., Ed.; Advances in Chemistry Series No. 217; American Chemical Society: Washington, D.C., 1988.

(11) Balaban, A. T.; Tomescu, I. In *Applications of Graphs in Chemistry and Physics*; Kennedy, J. W., Quintas, L. V., Eds.; North Holland: Amsterdam, 1988; p 5 (reprinted from *Discr. Appl. Math.* **1988**, *19*, 5).

(12) Gordon, M.; Davison, W. H. T. *J. Chem. Phys.* **1952**, *20*, 428.

(13) Cvetkovic, D.; Gutman, I. *Croat. Chem. Acta* **1974**, *46*, 15.

(14) Gutman, I. *Math. Chem. (MATCH)* **1982**, *13*, 173.

(15) Cyvin, S. J. *Math. Chem. (MATCH)* **1986**, *20*, 165.

(16) Balaban, A. T.; Brunvoll, J.; Cyvin, B. N.; Cyvin, S. J. *Tetrahedron* **1988**, *44*, 221.

(17) Cyvin, B. N.; Brunvoll, J.; Cyvin, S. J.; Gutman, I. *Math. Chem. (MATCH)* **1986**, *21*, 428.

(18) Sachs, H. *Combinatorics* **1984**, *4*, 89.

(19) Klein, D. J.; Seitz, W. A. *J. Mol. Struct. (THEOCHEM)* **1988**, *169*, 167.

(20) Cyvin, S. J.; Brunvoll, J.; Cyvin, B. N. *Z. Naturforsch.* **1986**, *41a*, 1429.

(21) Brunvoll, J.; Tosic, R.; Kovacevic, M.; Balaban, A. T.; Gutman, I.; Cyvin, S. J. *Rev. Roum. Chim.* **1990**, *35*, 85.

(22) Knop, J. V.; Szymanski, K.; Jericevic, Z.; Trinajstic, N. *J. Comput. Chem.* **1980**, *1*, 149.

(23) Rongsi, C.; Cyvin, S. J. *Math. Chem. (MATCH)* **1987**, *22*, 175.

(24) Cyvin, S. J. *Chem. Phys. Lett.* **1991**, *181*, 431.

(25) Herndon, W. C. *Thermochim. Acta* **1974**, *8*, 225.

(26) Herndon, W. C.; Nowak, P. C.; Connor, D. A.; Lin, P. *J. Am. Chem. Soc.* **1992**, *114*, 41.

(27) Herndon, W. C. *J. Am. Chem. Soc.* **1990**, *112*, 4546.

(28) Herndon, W. C.; Connor, D. A.; Lin, P. *Pure Appl. Chem.* **1990**, *62*, 435.

(29) Balaban, A. T.; Brunvoll, J.; Cioslowski, J.; Cyvin, B. N.; Cyvin, S. J.; Gutman, I.; He, W. C.; He, W. J.; Knop, J. V.; Kovacevic, M.; Muller, W. R.; Szymanski, K.; Tosic, R.; Trinajstic, N. *Z. Naturforsch.* **1987**, *42a*, 863.

(30) Trinajstic, N. *J. Math. Chem.* **1990**, *5*, 171.

(31) Balaban, A. T.; Harary, F. *Tetrahedron* **1968**, *24*, 2505.

(32) Balaban, A. T. *Tetrahedron* **1969**, *25*, 2949.

(33) Balaban, A. T. *Pure Appl. Chem.* **1982**, *54*, 1075.

(34) Balaban, A. T.; Tomescu, I. *Math. Chem. (MATCH)* **1983**, *14*, 155.

(35) Balaban, A. T. *Rev. Roum. Chim.* **1977**, *22*, 45.

(36) Gutman, I. *Theor. Chim. Acta* **1977**, *45*, 309.

(37) Gutman, I. *J. Serb. Chem. Soc.* **1988**, *53*, 607.

(38) John, P.; Sachs, H. In *Advances in the Theory of Benzenoid Hydrocarbons*; Gutman, I., Cyvin, S. J., Eds.; Topics in Current Chemistry; Springer: Berlin, 1990; Vol. 153, p 145.

(39) John, P. *Z. Phys. Chem. (Leipzig)* **1990**, *271*, 941.