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AROMATIC PROPERTIES OF FULLY-BENZENOID HYDROCARBONS[1]

MILAN RANDIĆ[*], DOUGLAS J. KLEIN, HONGYAO ZHU, NENAD TRINAJSTIĆ[**] and TOMISLAV ŽIVKOVIĆ[**]

Theoretical Chemical Physics Group, Texas A & M University at Galveston, Galveston, TX 77553-1675, U.S.A.
[*]*Department of Mathematics and Computer Science, Drake University, Des Moines, IA 50311, U.S.A.*
[**]*Rugjer Bošković Institute, Bijenička c. 54, 41001 Zagreb, Croatia*

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We consider a family of structurally closely related fully-benzenoid hydrocarbons of increasing number of fused benzene rings. Local and global aromatic properties of such molecules are investigated with a particular interest in investigating the role of the finite size of such molecules in modelling the high-polymer or even graphite. An interesting alternation of local properties for benzene rings in a similar environment was observed.

1. *Introduction*

Realistic models of infinite systems usually require extensive computation and are often sparse in offering simple interpretation of the results of computation. An illustration of this are *ab initio* calculations, which, when possible, produce an overwhelming amount of detail about the wave function of the system from which it is difficult to extract information that can be visualized. On the other hand, simple models while not necessarily presenting computational difficulties and offering simple interpretations, often lead to numerical results which are unreliable or do not correlate well with experimental data. An illustration of this is the tight-binding model, such as exemplified by the Hückel MO computations, that is easy to visualize but often of meager quantitative significance.

There is yet another relatively simple, yet not overly simplistic, approach to the study of large systems. If one wishes to develop a realistic but simple model, one pays a price through restrictions imposed by the model. In such modelling one can often obtain quantitative results of a satisfying quality but for selected properties only. If the interest of a study is restricted to a limited number of questions about the system, one can obtain very reliable results with a relatively simple model. This is the case of the conjugated-circuit model [1-7] which leads to surprisingly reliable and accurate predictions for aromatic stabilities of polycyclic conjugated systems, particularly those having no $4n$-membered rings. If properly parametrized [8,9], the conjugated-circuit model can reproduce molecular resonance energies of SCF MO accuracy (say for a Pariser-Parr-Pople-like model [10,11] treated by Dewar's MO methodology [12]).

In this contribution we apply the conjugated-circuit model and consider a family of fully-benzenoid systems of increasing size illustrated in Fig. 1.

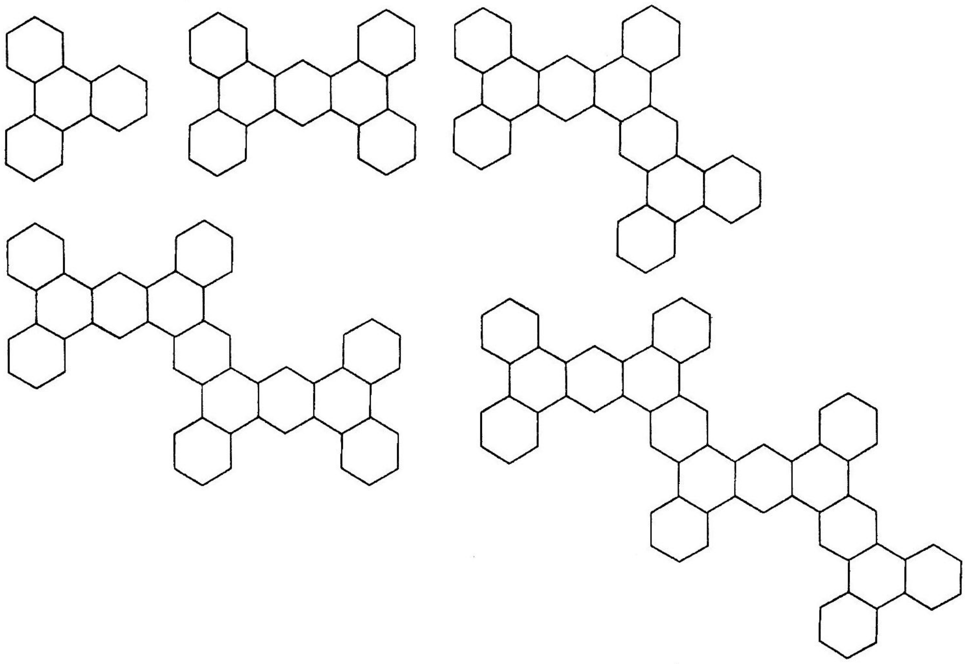

Fig. 1. The initial five members of the fully-benzenoid family investigated.

Our motivation is to learn about the role of the end groups of carbon atoms on the local properties in more distant areas and to see how well finite models can simulate properties of infinite polymers and eventually the properties of graphite.

2. *Conjugated-circuit model*

This model is based on the set of Kekulé valence structures as the basis for a representation of polycyclic conjugated systems built from sp^2 carbon atoms. Numbers of (especially smaller) conjugated circuits averaged over all Kekulé valence structures are to be enumerated. The graph-theoretical analysis of Kekulé structures produced the notion of conjugated circuits. A conjugated circuit is the circuit within the individual Kekulé structure in which there is a regular alternation of formal single and double carbon-carbon bonds. Hence, the conjugated circuits are necessarily of even length. The circuit decomposition of individual Kekulé structure of a benzenoid hydrocarbon gives only conjugated circuits of sizes $4n + 2$ (n=integer). Linearly independent, linearly dependent and disjoint conjugated circuits are possible. Linearly independent conjugated circuits are those that cannot be represented as a superposition of circuits of smaller size. Linearly dependent conjugated circuits are those which can be expressed as a linear combination of circuits of smaller size. Disjoint conjugated circuits are composites of two or more single circuits, no pair of which share a site. We consider only linearly independent conjugated circuits. Conjugated circuits of sizes $4n + 2$ are denoted by R_n. For example, the conjugated-circuit count for two isomeric benzenoids, anthracene and phenanthrene, is: $6R_1 + 4R_2 + 2R_3$ and $10R_1 + 4R_2 + 2R_3$, respectively.

Efficient algorithms for enumeration of conjugated circuits have been described in the literature. They are based on the transfer-matrix approach [13] in which individual Kekulé valence structures are represented by a product of various possible matrices that connect the repeating cells of fused benzenes (utilizing erasure of a fragment as a benzene ring or several fused such rings) from the full graph [7], or they are based on a "many body" scheme [14], utilizing an antisymmetric adjacency matrix S with the count of conjugated circuits obtained from subdeterminants (corresponding to various cycles) of the inverse S^{-1}.

In this report we use the latter approach. After all conjugated circuits of different sizes were enumerated, one can write down an expression for the molecular resonance energy (RE) as the parametrized size-weighted average of conjugated circuits:

$$RE = \sum_{n\geq 1} r_n R_n / K,$$

where K is the Kekulé-count for a benzenoid hydrocarbon, R_n is the parameter corresponding to $4n + 2$ conjugated circuits and r_n is the total count of R_n. The above formula is valid only for benzenoids, because in this class of conjugated systems only $4n+2$ circuits appear. This formula gives the overall molecular resonance energy. However, one can restrict attention to an individual ring and count only conjugated circuits involving the selected ring. In this way one arrives at a description of local aromaticity associated with individual benzene rings [15]. To obtain numerical values, one has to select a parametrization which establishes the relative role of conjugated circuits of different sizes [8] and, if desired, of different shape [16].

Since the smaller conjugated circuits give the major contributions to the molecular RE, we consider only the two smallest circuits, that is R_1 and R_2. Hence, the above formula reduces to a rather simple form:

$$RE = (r_1 R_1 + r_2 R_2)/K.$$

We should also add that the conjugated-circuit model is similar to the differently motivated resonance theory model of Herndon [17], as pointed by Schaad and Hess some time ago [18]. Herndon's model can be viewed as an extension of the early work of Simpson [19]. The conjugated-circuit model follows classical chemical bonding ideas such as exemplified in the work of Clar [20]. Finally we should mention that the conjugated-circuit model (as well as Herndon's resonance theory) can be related to standard quantum-mechanical models [16,21].

3. Triphenylene - tetrabenzanthracene family

In Fig. 1 we show several smaller members of a family of fully-benzenoid systems which can be viewed as higher members of a family that starts with triphenylene and tetrabenzanthracene. Individual symmetry-nonequivalent rings in these molecules have been labeled as shown in Fig. 2, beginning with A as the terminal ring.

In Fig. 3 we illustrate a few initial steps of the count of conjugated circuits (for rings A and B) for the next member in the sequence triphenylene, tetrabenzanthracene.

We start with the ring A which is labeled as "1" (corresponding to conjugated circuits R_1 or $n = 1$). After removal of this ring, the remaining structure consists of a benzene ring ($K = 2$) and tetrabenzanthracene ($K = 40$) connected by an essentially single carbon-carbon (CC) bond (structure **a** in Fig. 3). Here K is the number of Kekulé valence structures for the indicated fragments. Essentially, single bonds are CC bonds which are single in all Kekulé valence structures (like the central bonds in perylene). Such bonds can be deleted and we obtain the count of the Kekulé valence structures for the fragment $K = 80$. This has to be multiplied by two, since the benzene ring A itself has two Kekulé structures. Thus we obtain $\mathrm{A}(R_1) = 160$ for the count of the conjugated circuits R_1 for the ring A.

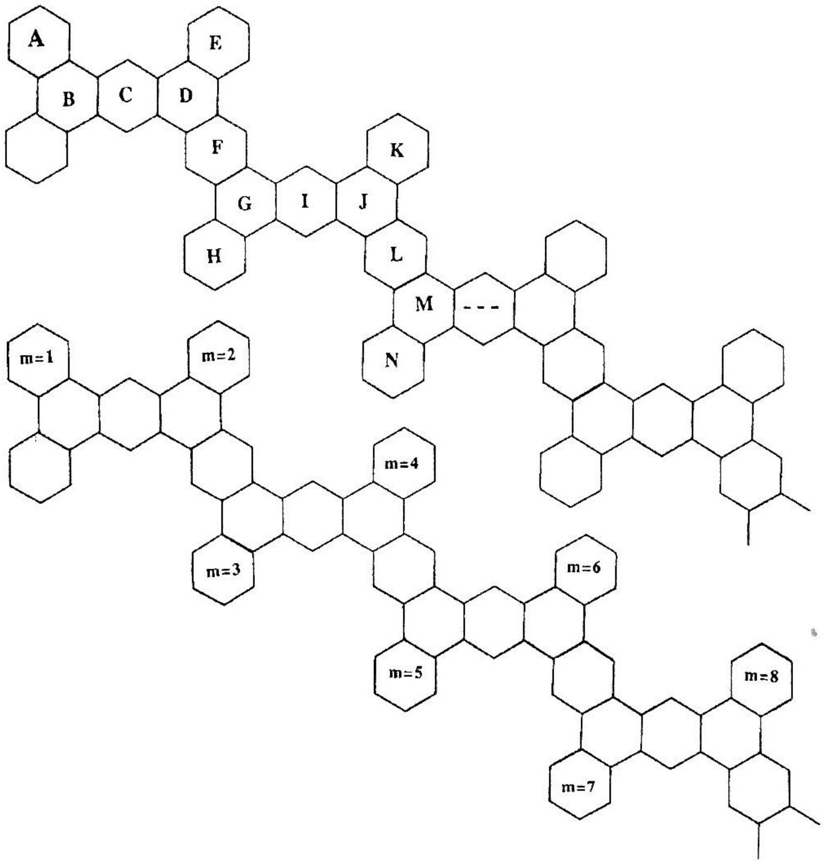

Fig. 2. Two alternative ways of labeling the individual rings in polymer extension of the family of fully-benzenoids considered.

Next we inscribe "2" in the ring A which implies label "1" for the ring B as only in this way the terminal ring A can be involved in a conjugated circuit R_2. This step permits the assigment of CC double bonds in the other two rings adjacent to ring B. When one deletes the assigned CC bonds, one obtains a subgraph with a benzene ring connected by an essentially single CC bond to triphenylene (structure **b** in Fig. 3). This gives $\mathrm{A}(R_2) = 18$ for the R_2-count at A.

The process continues untill all symmetry-nonquivalent rings have been considered. In the next step one considers $\mathrm{B}(R_1)$, and we can immediately conclude (see structure **c** in Fig. 3) that $\mathrm{B}(R_1) = 2\ \mathrm{A}(R_2)$, with the factor of two coming from the two Kekulé structures for the B-ring.

Table 1 shows the data for the first six members of the family having 18, 30, 42, 54, 66 and 78 carbon atoms, respectively. The table gives the count of linearly independent conjugated circuits. The largest possible conjugated circuits for the family are R_6.

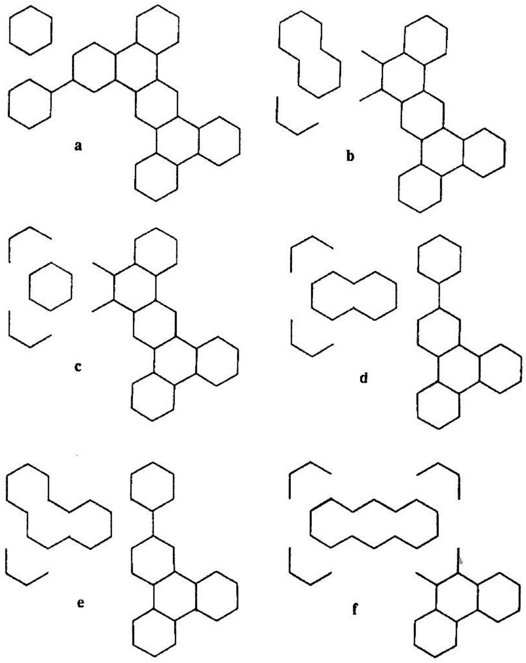

Fig. 3. Illustration of graphical enumeration of the smallest conjugated circuits in one of fully-benzenoid system studied (the third structure in Fig. 1).

TABLE 1.
The contributions of different rings to the molecular resonance energy for the six initial members of the fully-benzenoid family considered.

		R_1	R_2	R_3	R_4	R_5	R_6			R_1	R_2	R_3	R_4	R_5	R_6
$N = 1$								$N = 5$							
	A	8	1						A	3 168	356				
	B	26	6	3	1				B	712	1 068	1 148	516	80	
$N = 2$									C	2 848	676				
	A	36	4						D	640	960	1 112	624	170	18
	B	8	12	13	6	1			E	3 204	320				
	C	32	8						F	2 880	644				
$N = 3$									G	648	972	1 116	612	160	16
	A	160	18						H	3 200	324				
	B	36	54	58	26	4		$N = 6$							
	C	144	34						A	14 096	1 584				
	D	32	48	56	32	9	1		B	3 168	4 752	5 108	2 296	356	
	E	162	16						C	12 672	3 008				
$N = 4$									D	2 848	4 272	4 948	2 776	756	80
	A	721	80						E	14 256	1 424				
	B	160	240	258	116	18			F	12 816	2 864				
	C	640	152						G	2 880	4 320	4 964	2 728	716	72
	D	144	216	250	140	38	4		H	14 240	1 440				
	E	720	72						I	12 800	2 880				
	F	648	144												

TABLE 1. (cont.)

$N = 1$

$$\mathrm{RE} = (3A + B)/9 = (26R_1 + 6R_2 + 3R_3 + R_4)/9$$
$$\mathrm{REPE} = 0.16049R_1 + 0.037037R_2 = 0.1486eV$$

$N = 2$

$$\mathrm{RE} = (4A + 2B + C)/40 = (192R_1 + 48R_2 + 26R_3 + 12R_4 + 2R_5)/40$$
$$\mathrm{REPE} = 0.16R_1 + 0.04R_2 = 0.1489eV$$

$N = 3$

$$\mathrm{RE} = (4A + 2(B + C) + D + E)/178 = (1994R_1 + 292R_2 + 172R_3 + 84R_4 + 17R_5 + R_6)/178$$
$$\mathrm{REPE} = 0.159711R_1 + 0.039058R_2 = 0.1484eV$$

$N = 4$

$$\mathrm{RE} = (4A + 2(B + C + D + E) + F)/792 = (6824R_1 + 1824R_2 + 1016R_3 + 512R_4 + 112R_5 + 8R_6)/792$$
$$\mathrm{REPE} = 0.1595585R_1 + 0.0426487R_2 = 0.1492eV$$

$N = 5$

$$\mathrm{RE} = (4A + 2(B + C + D + E + F) + G + H)/3524$$
$$\mathrm{RE} = (37088R_1 + 10056R_2 + 5636R_3 + 2892R_4 + 660R_5 + 52R_6)/3524$$
$$\mathrm{REPE} = 0.1594607R_1 + 0.0432360R_2 = 0.1493eV$$

$N = 6$

$$\mathrm{RE} = (4A + 2(B + C + D + E + F + G + H) + I)/15680$$
$$\mathrm{RE} = (189760R_1 + 53376R_2 + 30040R_3 + 15600R_4 + 3656R_5 + 304R_6)/15680$$
$$\mathrm{REPE} = 0.1551543R_1 + 0.0436421R_2 = 0.1456eV$$

4. *Global molecular properties*

From the information in Table 1 we can extract molecular RE by summing the contributions of the individual rings. For the first few members (N=1 being triphenylene) we obtain the following simple expressions:

- N=1 RE = {3 Re(A)+ Re(B)}
- N=2 RE = {4 Re(A)+ 2 Re(B) + Re(C)}
- N=3 RE = {4 Re(A)+ 2 Re(B) + 2 Re(C) + Re(D) + Re(E)}
- N=4 RE = {4 Re(A)+ 2 Re(B) + 2 Re(C) + 2 Re(D) + 2 Re(E) + Re(F)}
- N=5 RE = {4 Re(A)+ 2 Re(B) + 2 Re(C) + 2 Re(D) + 2 Re(E) + Re(F)}
- N=6 RE = {4 Re(A)+ 2 Re(B) + 2 Re(C) + 2 Re(D) + 2 Re(E) + 2 Re(F) + 2 Re(G) + 2 Re(H) + Re(I)}.

Here RE signifies total molecular resonance energy and Re signifies a local (ring) contribution to the molecular resonance energy. When the results from the count of conjugated circuits are substituted in the above expressions we obtain the resonance energies as shown in Table 1, which also include the resonance energy per electron REPE, corresponding to the resonance energy per site in benzenoid polymers.

5. *Local aromatic properties*

It is of considerable interest to see how the benzenoid character of corresponding individual rings varies with molecular size. One expects that as the molecule increases in size, the role of the terminal rings, i.e., the boundary, will be less and less pronounced. From Table 2 in which the resonance energies of individual rings are listed we see indeed that the changes in the resonance contributions of the individual rings decrease. Here m is the position of the terminal ring starting with $m = 1$ in A, $m = 2$ in E, etc. (see Fig. 2).

TABLE 2.
The resonance energy of the individual rings for higher members of the fully-benzenoid family considered. N stands for a higher member of a fully-benzenoid family and m for the terminal ring in the benzenoid studied.

	m						
N	1	2	3	4	5	6	7
6	0.89897959	0.90918367	0.90816327				
7	0.89897948	0.90918473	0.90815274	0.90826740			
8	0.89897949	0.90918462	0.90815380	0.90825688			
9	0.89897949	0.90918463	0.90815369	0.90825794	0.90824636		
10	0.89897949	0.90918463	0.90815370	0.90825784	0.90824742		
11	0.89897949	0.90918463	0.90815370	0.90825785	0.90824732	0.90824899	
12	0.89897949	0.90918463	0.90815370	0.90825785	0.90824733	0.90824838	
13	0.89897947	0.90918463	0.90815370	0.90825785	0.90824733	0.90824839	0.90824827
14	0.89897949	0.90918463	0.90815370	0.90825785	0.90824733	0.90824839	0.90824828

One can clearly differentiate three kinds of rings: the terminal rings which show the highest content of R_1, the "central" rings (of successive anthracene units) which also have a high albeit lesser R_1 content, and the branching rings with little R_1 content and consequently much reduced local aromatic character. The first two rings are the so-called Clar rings, signifying localized π-sextets, while the last are the so-called "empty" rings of Clar [20].

A closer look at Table 2 indicates an oscillatory behaviour of the local aromatic character of successive terminal rings. For example, when we increase a molecule by a single triphenylene unit and consider the sequence of terminal rings A, E, H, etc. (see Fig. 2), we see that the successive terminal rings give smaller and larger contributions to the molecular RE. The difference between the individual successive rings decrease, the largest increase in Re is between the A rings and E rings. The oscillatory behaviour of the local ring Re suggests a relatively fast convergence for the contributions of the individual rings, a phenomenon that has already been used in theoretical computations such as the modeling of graphite by structures with torus-like boundary conditions [22]. In order to judge better the degree of such oscillatory behaviour within a family of compounds, we extend the computations but only for selected rings.

6. *Recursions*

In order to extend the considerations to much larger systems we need expressions for the ring Re in a recursive manner. One of the present authors [23] has derived general recursive expressions for the count of conjugated circuits in polymeric structures or within family of structurally related molecules. For the R_1 we obtain the following relation:

$$\partial K_{N+1} = 2a\partial K_N + (2b - a^2)\partial K_{N-1} - 2ab\partial K_{N-2} - b^2\partial K_{N-3}.$$

Here a and b are the coefficients occurring in the recursion for Kekulé valence structure count: $K_{N+1} = aK_N + bK_{N-1}$ and ∂ is the graph-theoretical equivalent of the differential operator, e.g., the operator of deleting rings. The above recursion formula for ∂K_{N+1} is obtained from the coefficients of its "characteristic" polynomial:

$$\{f(x)\}^2 = x^4 - 2ax^3 + (a^2 - 2b)x^2 + 2abx + b^2$$

where $f(x)$ is characteristic polynomial of the recursion $K_{N+1} - aK_N - bK_{N-1} = 0$, that is, $f(x) = x^2 - ax - b$.

A similar intriguing and interesting relationship between the calculus (as it involves differentiation) and the discrete graphs (fragment erasure) has already been reported by Clarke [24] between the characteristic polynomial of the adjacency matrix of a graph and the characteristic polynomials for its Ulam subgraphs. It allows the construction of the characteristic polynomials of some cyclic graphs [25].

For our family of graphs we have already seen that Kekulé numbers form the sequence:

$$40,\ 178,\ 792,\ 3524,\ 15680, ...$$

which satisfy the recursion:

$$K_N = 4K_{N-1} + 2K_{N-2}$$

with $K_1 = 9$ and $K_2 = 40$. Hence in our case $a = 4$ and $b = 2$. In fact one can start with benzene $K_0 = 2$ and triphenylene $K_1 = 9$ and continue the recursion. Note that the above recursion formula is a special case of a recursion formula for the matching polynomial derived by Babić et al. [26]. The Kekulé structures are the constant terms in the matching polynomial. However, in this special case our method is much faster then the method proposed by Babić et al. In Table 3 we list the K-values for the first 15 members of the series.

TABLE 3.
The Kekulé-structure count for the initial members of the fully-benzenoid family considered.

K_0	=	*2*	K_6	=	*15 680*	K_{12}	=	*121 676 672*
K_1	=	*9*	K_7	=	*69 768*	K_{13}	=	*541 399 104*
K_2	=	*40*	K_8	=	*310 432*	K_{14}	=	*2 408 949 760*
K_3	=	*178*	K_9	=	*1 381 264*	K_{15}	=	*10 718 597 248*
K_4	=	*729*	K_{10}	=	*6 145 920*	K_{16}	=	*47 692 288 496*
K_5	=	*3 524*	K_{11}	=	*27 346 208*			

The recursion for K can be derived directly by considering consecutive members of the family, or alternatively, it can be derived using the regression analysis. We know in advance that the recursion is linear and involves only two consecutive smaller members, because there are only two possible ways of distributing CC double bonds across the connecting bonds between successive members in the family. In other words the transfer matrix has only two rows.

In Table 4 we list all the recursion relations for individual rings for the first six members of the family.

TABLE 4.
The recursions for the ring contributions of various conjugated circuits expressed in terms of the Kekulé-structure counts.

Ring A	R_1	$K_n = 4K_{n-1}$	Ring E	R_1	$K_n = 18K_{n-2}$
	R_2	$K_n = 2K_{n-2}$		R_2	$K_n = 8K_{n-3}$
Ring B	R_1	$K_n = 4K_{n-2}$	Ring F	R_1	$K_n = 72K_{n-3}$
	R_2	$K_n = 6K_{n-2}$		R_2	$K_n = 8K_{n-3} + 36K_{n-4}$
	R_3	$K_n = 6K_{n-2} + 2K_{n-3}$			
	R_4	$K_n = 2K_{n-2} + 2K_{n-3}$	Ring G	R_1	$K_n = 36K_{n-4}$
	R_5	$K_n = 2K_{n-3}$		R_2	$K_n = 108K_{n-4}$
				R_3	$K_n = 116K_{n-4} + 36K_{n-5}$
Ring C	R_1	$K_n = 16K_{n-2}$		R_4	$K_n = 44K_{n-4} + 72K_{n-5}$
	R_2	$K_n = 2K_{n-2} + 8K_{n-3}$		R_5	$K_n = 8K_{n-4} + 44K_{n-5}$
				R_6	$K_n = 8K_{n-5}$
Ring D	R_1	$K_n = 16K_{n-3}$			
	R_2	$K_n = 24K_{n-3}$	Ring H	R_1	$K_n = 80K_{n-3}$
	R_3	$K_n = 26K_{n-3} + 8K_{n-4}$		R_2	$K_n = 36K_{n-4}$
	R_4	$K_n = 12K_{n-3} + 16K_{n-4}$			
	R_5	$K_n = 2K_{n-3} + 10K_{n-4}$			
	R_6	$K_n = 2K_{n-4}$			

This Table clearly indicates to several regularities of the relative contributions of individual rings to the molecular resonance energy within a single molecule, or between corresponding rings in molecules of different size. The regularities allow one to write a general formula for the number of 6-membered conjugated circuits in terminal rings for a molecule of arbitrary size:

$$\mathrm{Re}(\text{ring } m) = 2K_{m-1}K_{N-m}.$$

For the first few rings this gives:

$$m = 1 \quad \mathrm{Re}(A) = 2K_0K_{N-1}$$

$$m = 2 \quad \mathrm{Re}(E) = 2K_1K_{N-2}$$

$$m = 3 \quad \mathrm{Re}(H) = 2K_2K_{N-3}$$

$$m = 4 \quad \mathrm{Re}(K) = 2K_3K_{N-4}$$

$$m = 5 \quad \mathrm{Re}(N) = 2K_4K_{N-5}.$$

The recursion for the central rings is slightly different. Except for the constant factor $2(K_0)^2$, it combines the product of the Kekulé valence counts for two non-consecutive members:

$$m = 1 \quad \mathrm{Re}(A) = 2(K_0)^2K_0K_{N-2}$$

$$m = 2 \quad \mathrm{Re}(E) = 2(K_0)^2K_1K_{N-3}$$

$$m = 3 \quad \mathrm{Re}(H) = 2(K_0)^2K_2K_{N-4}$$

$$m = 4 \quad \mathrm{Re}(K) = 2(K_0)^2K_3K_{N-5}$$

$$m = 5 \quad \mathrm{Re}(A) = 2(K_0)^2K_4K_{N-6}.$$

It is not difficult to see that for all N, the $K_m\ K_{N-(m-1)}$ product is always smaller then the product $K_{m-1}\ K_{N-m-1}$. Hence the π-sextets of the terminal rings show a greater local aromaticity than the central π-sextets.

In Table 5 we show the numerical results for the relative aromaticity of the terminal rings by extending calculations to $N = 15$.

TABLE 5.
The numerical results for the relative aromaticities of the terminal rings.

			N		
m	6	7	8	9	10
1	14 096	62 720	279 072	1 241 728	5 525 056
2	14 256	63 432	282 240	1 255 824	5 587 776
3	14 240	63 360	281 920	1 254 400	5 581 440
4		63 368	281 952	1 254 544	5 582 080
5				1 254 528	5 582 016
			N		
m	11	12	13	14	15
1	24 583 680	109 384 832	486 706 680	2 165 596 416	9 635 799 040
2	24 862 752	110 626 560	492 231 744	2 190 180 096	9 745 183 872
3	24 834 560	110 501 120	491 673 600	2 187 696 640	9 734 133 760
4	24 837 408	110 513 792	491 729 984	2 187 947 520	9 735 250 048
5	24 837 120	110 512 512	491 724 288	2 187 922 176	9 735 137 280
6	24 837 152	110 512 640	491 724 864	2 187 924 736	9 735 148 672
7			491 724 800	2 187 924 480	9 735 147 520
8					9 735 147 648

Table 5 clearly shows the oscillatory behavior of terminal rings as one moves from the periphery towards the central region of the molecule.

7. Discussion

Benzenoid polymers continue to receive considerable attention in the literature [27]. One can think of at least two important reasons for this continuing interest. Computations on such polymers offer insights on models for graphite and other closely related structures, such as recently discussed bucky tubes [28] and elemental benzenoids [29,30]. On the other hand, such polymers may include cases of unusual conductive properties and may become important for potential applications. Recently Seitz and Schmalz [27] examined 30 different benzenoid polymers built by fusing four or fewer hexagons per monomer unit. These are all possible polymers of that size according to the proposed graph-theoretical classification scheme for fused benzenoid polymers [31,32]. They reported resonance energies per electron (REPE). Only two of the polymers considered, T(1,2)-phenanthrene (Fig. 4) and $T(1,1)$-tetracene (Fig. 5) which has also been called also polyphenanthrenophenanthrene [33] are fully-benzenoid. Their REPE values are 0.152 and 0.155 eV, respectively. These numerical values are based on the exact count of 6 and 10-membered conjugated circuits and the use of the standard values of parameters R_1 (0.869 eV) and R_2 (0.247 eV) [1-4]. The above values compare well with the REPE values reported here for the fully-benzenoid systems that we considered.

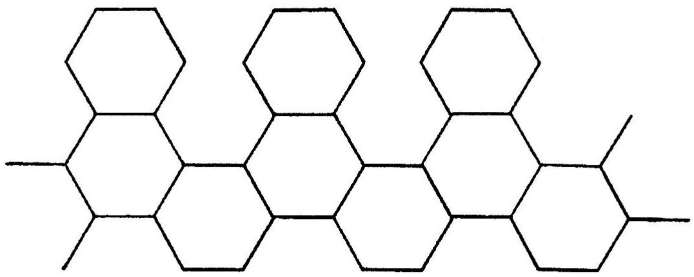

Fig. 4. Diagram of $T(1,2)$-phenanthrene.

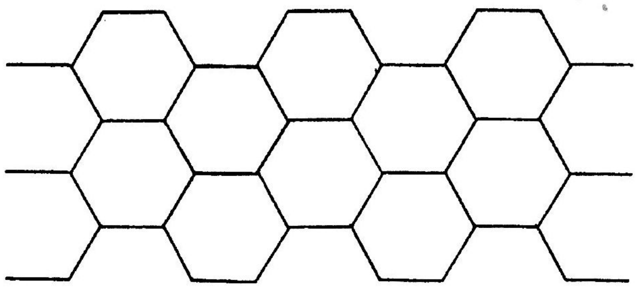

Fig. 5. Diagram of $T(1,1)$-tetracene.

Recently Zhu and Klein [34] examined a dozen benzenoid polymers among several nonbenzenoid and nonalternant polymers. Of those considered only polyphenanthreno-phenanthrene was fully-benzenoid, i.e., having only rings to which π-sextets are assigned and no CC double bonds appear separately. It is interesting to see that this benzenoid polymer among all reported has the largest REPE value (0.1553 eV). From the results of Zhu and Klein one can also obtain local ring aromaticities:

exposed ring A $\qquad \mathrm{Re} = 2\,\{\,0.34929\,R_1 + (0.10757\,R_2 + 2\cdot 0.08863\,R_2)\}$
internal ring B $\qquad \mathrm{Re} = 2\,\{0.10757\,R_1 + 0.10757\,R_2\,\}.$

When the numerical values for the parameters R_1 and R_2 are substituted, we obtain for ring resonance energies the following values: Re(A) = 0.7478 eV and Re(B) = 0.2401 eV, respectively.

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[1]Dedicated to Professor Mladen Paić on the occasion of his 89th birthday.

References

1) M. Randić, Chem. Phys. Lett. **38** (1976) 68;

2) M. Randić, Tetrahedron **31** (1975) 1477;

3) M. Randić, J. Amer. Chem. Soc. **99** (1977) 444;

4) M. Randić, Int. J. Quantum Chem. **17** (1980) 549;

5) S. Nikolić, N. Trinajstić and D.J. Klein, Comput. Chem. **14** (1990) 313;

6) N. Trinajstić, S. Nikolić and D.J. Klein, J. Mol. Struct. (Theochem) **229** (1991) 63;

7) N. Trinajstić, *Chemical Graph Theory*, second revised edition, CRC Press, Boca Raton, FL, (1992) 199;

8) M. Randić and N. Trinajstić, J. Amer. Chem.Soc. **106** (1984) 4428;

9) M. Randić, S. Nikolić and N. Trinajstić, in *Graph Theory and Topology in Chemistry*, edited by R.B. King and D.H. Rouvray, Elsevier, Amsterdam, (1987) 429;

10) R. Pariser and R. G. Parr, J. Chem.Phys. **21** (1953) 767;

11) J. A. Pople, Trans. Faraday Soc. **49** (1953) 1375;

12) M. J. S. Dewar and C. de Llano, J. Amer. Chem.Soc. **91** (1968) 789;

13) D. J. Klein, G. E. Hite and T. G. Schmalz, J. Comput. Chem. **7** (1986) 443;

14) D. J. Klein and X. Liu, J. Comput. Chem. **12** (1991) 1260.

15) M. Randić, D. Plavšić and N. Trinajstić, Gazz. Chim. Ital. **118** (1988) 441;

16) D. J. Klein and N. Trinajstić, Pure Appl. Chem. **61** (1989) 2107;

17) W. C. Herndon, J. Amer. Chem.Soc. **95** (1973) 2404;

18) L. J. Schaad and B. A. Hess, Jr., Pure Appl. Chem. **54** (1982) 1097;

19) W. T. Simpson, J. Amer. Chem.Soc. **75** (1953) 597;

20) E. Clar, *The Aromatic Sextet*, Wiley, New York (1972);

21) D. J. Klein, Topics Curre. Chem. **153** (1990) 57;

22) H. Hosoya, Y. Tsukano, M. Ohuchi and K. Nakada, Comp. Aided Innov. Materials, II, (1993) 155;

23) D. J. Klein, unpublished work;

24) F. H. Clarke, Discrete Math. **3** (1972) 305;

25) M. Randić, J. Comput. Chem. **3** (1982) 421;

26) D. Babić, A. Graovac, B. Mohar and T. Pisanski, Discrete Appl. Math. 15 (1986) 11.

27) W. A. Seitz and T. G. Schmalz, Benzenoid polymers, in *Valence Bond Theory and Chemical Structure*, edited by D. J. Klein and N. Trinajstić, Elsevier, Amsterdam, (1990) 525;

28) D. J. Klein, W. A. Seitz and T. G. Schmalz, J. Phys. Chem. **97** (1993) 1231;

29) E. C. Kirby, Croat. Chem. Acta **66** (193) 13;

30) D.J. Klein, J. Chem. Inf. Comput. Sci. **34** (1994) 453;

31) D. J. Klein, W. C. Herndon and M. Randić, New J. Chem. **12** (1986) 71;

32) N. Trinajstić, S. Nikolić, J.V. Knop, W. R. Müller and K. Szymanski, *Computational Chemical Graph Theory: Characterization, Enumeration and Generation of Chemical Structures by Computer Methods*, Horwood/Simon & Schuster, New York, (1991);

33) G. E. Hite, A. Metropoulos, D. J. Klein, T. G.Schmalz and W. A.Seitz, Theor. Chim. Acta 69, **369** (1986) 369;

34) H. Zhu and D. J. Klein, in preparation.

AROMATIČKA SVOJSTVA POTPUNIH BENZENOIDNIH UGLJIKOVODIKA

MILAN RANDIĆ*, DOUGLAS J. KLEIN, HONGYAO ZHU, NENAD TRINAJSTIĆ**
i TOMISLAV ŽIVKOVIĆ**

Theoretical Chemical Physics Group, Texas A & M University at Galveston, Galveston, TX 77553-1675, U.S.A.

* *Department of Mathematics and Computer Science, Drake University, Des Moines, IA 50311, U.S.A.*

** *Rugjer Bošković Institute, Bijenička c. 54, 41001 Zagreb, Croatia*

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Razmatrana je skupina strukturno vrlo sličnih potpunih benzenoidnih ugljikovodika. Studirana su lokalna i globalna svojstva ovih molekula, a naročita je pažnja posvećena ulozi konačne veličine studiranih molekula u modeliranju benzenoidnih polimera ili čak grafita. Opažena je interesantna pojava da lokalna svojstva benzenskih prstenova alterniraju u sličnom okolišu, iako razlike u veličinama opadaju rastom veličine molekule.