Edge Effets in Very Large Benezenoid Polymers

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Large benzenoid polymers containing monomer units which are mutually connected by two CC bonds are considered. These molecules are treated within the simplified BORT or, equivalently, within a simplified VB approach. A general method for the evaluation of resonance energies and local aromaticity properties, such as contribution of various six- and ten-cycles to the total resonance energy, is described. As an illustration, the tetrabenzanthracene polymer family is considered. Exact expressions for local and global properties of infinite tetrabenzanthracene polymers, as well as highly accurate approximate expressions for finite tetrabenzanthracene polymers, are derived.

INTRODUCTION

In the literature, calculations were reported on a number of benzenoid polymers,[1] including random pi-network polymers, and various graph theoretical models and enumerations.[2] In a recent paper,[3] very large polymer molecules were considered. The prime intention of this paper was to study finite but very large benzenoid systems. Interests in such calculations are manifold:

1) How large do such finite molecule need to be in order to exhibit properties that are the »same« as those of infinite systems?

2) How far into the bulk of the molecule does the edge effect penetrate?

3) What local properties are there, in particular the local properties of cycles not far from the edge of the molecule?

In order to answer these questions, one can treat benzenoid polymers within various semiempirical methods. One possibility is to use the conjugated circuit approach.[4] This model is equivalent to the resonance theory model of Herndon,[5] which, in turn, can be viewed as an extension of the early work of W. T. Simpson.[6] Another possibility is to use a simplified VB approach, and yet another to use a simplified BORT approach.[7,8] However, on this simplified level, the particular framework is not essential. One can show that, subject to appropriate approximations and in the case of benzenoid systems, almost identical formulas are obtained within the VB, the conjugated circuit, and the BORT approaches.[7,8]

In Ref. 3, numerical treatment of very large benzenoid systems was done with the computer program, developed by the author, which can manipulate very large integers.[7] The computations were performed on a PC 386 (33 MHz) computer, and the practical limit was approximately 25000 monomer units. This limit was due to the memory limitations of the PC and it was not inherent to the computer program itself.

In the present paper, we intend to show that one does not need to perform such extensive numerical calculations involving thousands of monomer units in order to obtain the required results. In particular, we will show that the properties of large benzenoid polymers, such as resonance energies, local aromaticity properties, edge effects *etc.*, can be expressed in a close analytical form.

THE METHOD

Let us first formulate a simplified treatment of large benzenoid molecules within the VB and BORT approaches.

In the VB approach, the ground state ψ of a conjugated molecule is represented as a linear combination of VB resonance structures. In a simplified approach, one considers only VB Kekulé structures K_k, and one further assumes that all these structures are contained in the ground state ψ with the same weight, *i.e.* one uses the *ansatz*

$$\psi = \sum_k K_k \, . \tag{1}$$

The expectation value of an operator O in the above state is

$$\langle \psi | O | \psi \rangle = \frac{\sum_{s,p} \langle K_s | O | K_p \rangle}{\sum_{s,p} \langle K_s | K_p \rangle} \tag{2}$$

where $\langle K_s | K_p \rangle$ is the overlap between VB Kekulé structures K_s and K_p, while $\langle K_s | O | K_p \rangle$ is a matrix element of the operator O between these structures.

A similar approximation can be formulated in the BORT approach.[8,9] In this approach, the ground state ψ is first approximated in the spin-separated form

$$\psi = | \phi \, \overline{\phi} \rangle \tag{3}$$

where ϕ and $\overline{\phi}$ are spin-α and spin-β substrates, respectively. In a closed shell system, the state ϕ is identical to a state $\overline{\phi}$, except for a spin. Hence, one can express all spin independent properties in terms of the state ϕ alone. In the case of alternant molecules, the ground state ϕ can be approximated as a linear combination of positive BORT Kekulé structures.[9]

$$\phi = \sum_k K_k^+ \tag{1'}$$

This expression is formally identical to expression (1), except that only positive Kekulé structures are considered. Absence of negative structures is due to the fact that, in the case of an alternant system, the matrix element of the Hamiltonian operator between BORT structures of opposite parity vanishes.[10]

Expectation value of the spin independent operator O in the state ψ is now

$$\langle\psi|O|\psi\rangle = 2\,\frac{\sum\limits_{s,p}\langle K_s^+|O|K_p^+\rangle}{\sum\limits_{s,p}\langle K_s^+|K_p^+\rangle} \tag{2'}$$

This expression is formally identical to expression (2), except for a factor 2 which is due to the spin separation (3), and except for the fact that, in the BORT case, one considers only positive Kekulé structures, while in the VB case one considers all Kekulé structures, positive and negative alike. However, in the case of benzenoid molecules, this latter difference vanishes, since in a benzenoid system all Kekulé structures have the same parity.[8,9]

Relations (2) are quite easy to implement. All one needs is a systematic way for the calculation of overlaps $\langle K_s|K_p\rangle$ and matrix elements $\langle K_s|O|K_p\rangle$. We will consider here the resonance energy RE of benzenoid hydrocarbons. This energy can be represented as the expectation value of the Hamiltonian H. Since resonance energy should measure the extra stabilization due to the resonance between various structures, it is convenient to define the corresponding Hamiltonian in such a way that all Kekulé structures have zero energy.[9] One can show that in the case of benzenoid systems, matrix elements of the BORT Hamiltonian between BORT Kekulé structures are proportional to matrix elements of the VB Hamiltonian between VB Kekulé structures, while the corresponding overlaps are identical.[11] As a consequence, in the case of benzenoid systems, relations (2) and (2') will produce results that differ only ba an unimportant scaling factor. Hence, on this level of approximation, it is not important whether one uses the BORT or VB approach. In order to be more specific, we will consider the BORT approach.

Relations (2') can be further simplified, since the summations over overlaps and matrix elements can be conveniently reformulated in terms of the summations over various superposition diagrams.[7,9] Each superposition diagram is a superposition of two positive Kekulé structures, and, in general, a given superposition diagram corresponds to more than just one pair of Kekulé structures. Superposition diagrams corresponding to distinct Kekulé structures contain isolated cycles which have an even number of vertices, and a diagram contribution depends only on the pattern of these cycles.[7,9] One can, hence, associaate with each cycle pattern a weighted count which equals a number of different superposition diagrams having identical cycle patterns. One easily finds that a weighted count of each cycle pattern equals a number of Kekulé structures in a subgraph which is obtained by removing this cycle pattern from the original graph. Relation (2') can be, thus, expressed in terms of various weighted counts and the corresponding contributions.

We will now make yet another approximation. We will assume that Kekulé structures are orthonormalized, i.e. we will assume[9,10]

$$\langle K_s | K_p \rangle = \delta_{sp} \ .$$

This approximation it not so severe. The only effect of this approximation is to rescale the relative contributions of different terms to the total resonance energy, without affecting either their relative order or their ratios. With this approximation, the denominator in (2') reduces to a Kekulé count.

The resonance energy per carbon atom can be now approximated as:

$$\mathrm{RE} = \sum_s R_s \frac{C_s}{KN} \tag{4}$$

where K is the Kekulé count, N is the number of carbon atoms, C_s is the weighted count of the particular cycle pattern, and R_s is the corresponding contribution of this cycle pattern to the total resonance energy. The summation is performed over all cycle patterns. Each cycle pattern consists of disjoint even cycles,[12] and the weighted count C_s of each partiuclar cycle pattern equals the number of Kekulé structures in the graph which is obtained by removing from the original graph all cycles forming this pattern. One also finds that the contribution R_s of each cycle pattern equals the sum of the contributions of various cycles contained in this cycle pattern.[12] Moreover, the contribution of each particular cycle in a cycle pattern rapidly decreases with the size of this cycle and the number and size of all other cycles.[12] In a crude approximation, one can neglect all smaller terms and retain only the few dominant ones. In the case of benzenoid systems, two most important contributions are due to the cycle patterns containing a single six-cycle and a single ten-cycle, respectively.[8,12] Relation (4) thus reduces to

$$\mathrm{RE} = \frac{C(6)\, R_6 + C(10)\, R_{10}}{KN} \tag{4'}$$

where $C(6)$ and $C(10)$ are global weighted counts of six- and ten-cycles, respectively, while R_6 and R_{10} are the corresponding contributions to the total resonance energy. Weighted count of each particular cycle equals the number of Kekulé structures in the graph which is obtained by removing this cycle,[7] and global weighted count $C(6)$ and $C(10)$ are the sums of such counts over all six- and ten-cycles, respectively. One also finds contributions R_6 and R_{10}[12]

$$R_6 = \frac{3}{2}\,\beta \qquad R_{10} = \frac{3}{4}\,\beta$$

where β is a resonance integral. Up to an unimportant scaling factor, the same result is obtained also within the VB approach.[11]

In the conjugated circuit model[4] and in the case of benzenoid systems, one obtains a relation which is formally identical to the simplified relation (4'). However, in this model, quantities R_6 and R_{10} are adjustable parameters chosen in such a way as to maximize the agreement with experiment. Their recommended values are:[4]

$$R_6 = 0.869 \text{ eV and } R_{10} = 0.247 \text{ eV} .$$

The advantage of BORT is that it produces the exact ratio of contributions R_6 and R_{10}, without introduction of yet another parameter. This advantage is much more pronounced in the case of a more general expression (4) which includes many other terms besides a single six- and a single ten-membered cycle.[7]

LOCAL AND GLOBAL PROPERTIES

As an example, we will consider the tetrabenzanthracene family shown in Figure 1. These molecules can be considered as being derived from the biphenyl by adding additional triphenylene units. Each new triphenylene unit is added to the already existing fragment by introducing two additional CC bonds. We use index n in order to indicate a finite molecule of this family which has n biphenylene units embedded in its structure. Thus, $n=1$ represents biphenylene itself, $n=2$ represents tetrabenzanthracene, *etc.* (Figure 1).
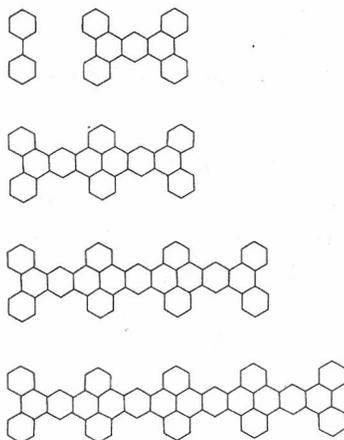
Figure 1.

According to (4') the resonance energy per carbon atom for this family is

$$\text{RE}_n = \frac{C_n(6)\,R_6 + C_n(10)\,R_{10}}{K_n N_n} = \text{RE}_n(6)\,R_6 + \text{RE}_n(10)\,R_{10} \qquad (4")$$

where index n refers to the n-th member of the family, and where $\text{RE}_n(6)$ and $\text{RE}_n(10)$ are contributions of six- and ten-membered cycles to the total resonance energy RE_n, respectively.

In the case of the tetrabenzanthracene family, Kekulé counts K_n satisfy recursive relations[3]

$$K_{n+1} = 10\,K_n - K_{n-1}$$

with the initial conditions $K_0 = 0$ and $K_1 = 4$.

In general, in the case of an arbitrary benzenoid polymer whose monomer units are mutually connected with two CC bons, the Kekulé count satisfies the recursive relation

$$K_{n+1} = \alpha\,K_n - \beta\,K_{n-1}$$

where coefficients α and β depend on a particular polymer family. In order to derive these quantities, it is sufficient to establish Kekulé counts K_1, K_2, K_3 and K_4 for the first four members of the family. This gives two equations in tow unknowns, α and β

$$K_3 = \alpha\,K_2 - \beta\,K_1$$

$$K_4 = \alpha\,K_3 - \beta\,K_2$$

which are trivial to solve.

Hence, the Kekulé count can be expressed in terms of quantities U_n satisfying the same recursive relation

$$U_{n+1} = \alpha\,U_n - \beta\,U_{n-1} \qquad (5)$$

and with the initial values $U_0=0$ and $U_1=1$

In particular, in the case of the tetrabenzanthracene family, one finds

$$K_n = 4\,U_n \qquad (6)$$

where

$$U_{n+1} = 10\,U_n - U_{n-1}\,. \qquad (5')$$

In the case of other benzenoid polymers consisting of identical monomer units mutually connected with two CC bonds, the Kekulé count K_n can be generally expressed as a linear combination

$$K_n = K_1\,U_n + (K_2 - \alpha\,K_1)\,U_{n-1} \qquad (7)$$

where K_1 and K_2 are Kekulé counts of the first two members of a polymer family, respectively.

According to Eq. (7), Kekulé counts can be expressed in terms of quantities U_n. However, not only Kekulé counts, but also all weighted cycle and weighted cycle pattern counts can be expressed in terms of quantities U_n. This follows from the fact that each weighted count equals the Kekulé count of the graph which is obtained

by removing from the initial graph all cycles contained in the superposition pattern, and from relation (7) which expresses Kekulé counts in terms of quantities U_n.

For example, in the case of the tetrabenzanthracene family, there are three types of six-cycles and two types of ten-cycles (Figure 2), weighted cycle count C_{nk} of a six-cycle X_k in the n-th tetrabenzanthracene polymer (Figure 2a) equals the Kekulé count of the graph which is obtained by removal of this cycle. However, by removing the six-cycle X_k, one essentially obtains two tetrabenzanthracene polymers, one containing k and the other containing $n-k$ units. Hence, the resulting graph has $K_k K_{n-k}$ Kekulé structures. Using relation (6) one obtains $C_{nk} = 16 \, U_k \, U_{n-k}$.
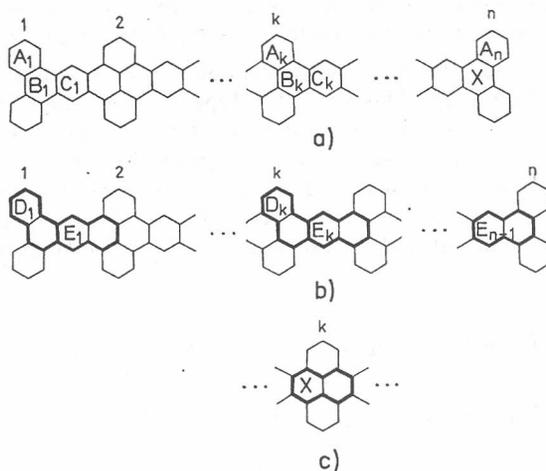
Figure 2.

Removal of a single cycle from a tetrabenzanthracene polymer does not necessarily result in graphs corresponding to the same polymer family. This is, for example, the case of the removal of cycle A_k in Figure 2a. However, the resulting graphs are members of another polymer family which differs from the initial polymer family only in terminal atoms. The Kekulé count for this other polymer family satisfies the same recursive relation (5') as the original tetrabenzanthracene family, only the initial conditions K_1 and K_2 differ. Hence, one can again express the weighted cycle count A_{nk} in terms of quantities U_n. In this way, all cycle counts can be ultimately expressed in terms of quantities U_n.

This is a general result. The Kekulé count as well as all six- and ten-cycle weighted counts can be always expressed in terms of quantities U_n. For different polymer families, one obtains only different parameters α and β. But the final result is always the same: there is a finite number of six- and ten-membered types, such as A, B, X, Δ and E in Figure 2, and for each cycle type the weighted count of the particular cycle can be expressed in terms of quantities U_n.[7] In the case of the tetrabenzanthracene family, the weighted counts of six-cycles are

$$A_{nk} = 2 \; (U_k - U_{k-1}) \; (U_{n-k+1} - U_{n-k}) \quad k = 1, \ldots, n$$

$$B_{nk} = 4 \; (U_k - U_{k-1}) \; U_{n-k} \qquad\qquad k = 1, \ldots, n-1 \qquad (8)$$

$$C_{nk} = 16 \; U_k \, U_{n-k} \qquad\qquad\qquad k = 1, \ldots, n-1 \, .$$

Relations (8) include the weighted counts of all six-cycles. For example, by symmetry the weighted count of six-cycle $\mathcal{Z}$ in Figure 2a equals $B_{n,1}$. Also by symmetry, $A_{n,k} = A_{n,n-k-1}$ and $C_{n,k} = C_{n,n-k}$.

On this level of approximation, the above weighted counts are the same in the BORT, VB, and the conjugated circuits approach.[7] In fact, relations (8) were first reported, without derivation, within the framework of the conjugated circuit model.[3]

In a similar way, one derives weighted counts for various ten- cycles.[7] These cycles are shown in Figure 2b. There are two types of ten-cycles, type $\varDelta$ and type E. Formally, one can draw yet another cycle type, shown as type $\mathcal{Z}$ in Figure 2c. However, this ten-cycle isolates two subgraphs containing three vertices. Since no Kekulé structure can be drawn on an odd number of vertices, this ten-cycle has no contribution.[7] One finds that types $\varDelta$ and E include all possible ten-cycle types that have a nonvanishing contribution to the total resonance energy.[7] Weighted counts of these cycles are

$$D_{nk} = 4 \; (U_k - U_{k-1}) \; U_{n-k} \qquad k = 1, \ldots, n-1$$

$$\hspace{8cm} (8')$$

$$E_{nk} = 4 \; (U_{n-k} - U_{n-k-1}) \; U_k \qquad k = 1, \ldots, n-1 \, .$$

Relations (8') differ from the corresponding relations in Ref. 3. In this reference, the weighted counts of ten-membered conjugated circuits are given. In the case of the tetrabenzanthracene family, there are three types of ten-membered conjugated cycles. These types are associated with cycle types A, B, and X in Figure 2a, respectively. There are, hence, three corresponding formulas for weighted counts.[3] There are, however, only two types of ten-membered cycles, types $\varDelta$ and E in Figure 2b, and hence only two expressions (8') are needed.

One can express weighted counts (8) in a more compact form in terms of quantities $X_{n,k}$

$$X_{n,k} = U_k \, U_{n-k} \qquad k = 0, 2, \ldots, n \qquad\qquad (9)$$

which satisfy $X_{n,k} = X_{n,n-k}$ and $X_{n0} = X_{nn} = 0$. *One obtains*

$$A_{nk} = 2 \; (X_{n+1,k} + X_{n-1,k-1} - X_{n,k} - X_{n,k-1})$$

$$B_{nk} = 4 \; (X_{n,k} - X_{n-1,k-1}) \qquad\qquad\qquad\qquad (10)$$

$$D_{nk} = 4\,(X_{n,k} - X_{n-1,k-1})$$

(10')

$$E_{nk} = 4\,(X_{n,k} - X_{n-1,k})$$

In order to obtain relative contributions of various cycles to the total resonance energy, one has to normalize the above weighted counts to the Kekulé count

$$a_{nk} = \frac{A_{nk}}{K_n}, \quad b_{nk} = \frac{B_{nk}}{K_n}, \quad c_{nk} = \frac{C_{nk}}{K_n}$$

(11)

$$d_{nk} = \frac{D_{nk}}{K_n}, \quad e_{nk} = \frac{E_{nk}}{K_n}$$

(11')

Relations (11) refer to local properties, *i.e.* to the properties of a particular six- or ten-cycle. For example, a_{nk} is a relative contribution of a six-membered cycle A_k in a tetrabenzanthracene polymer containing n embedded biphenyl units. Since this is a contribution to the total resonance eneergy, one can associate a_{nk} with the local aromaticity of the six- cycle A_k, *etc.*

In order to obtain the contribution of all cycles of a particular type (A, B, X, $\varDelta$ or E), one has to sum the above weighted counts over all allowed cycle positions indicated by index k. In this way, one obtains the properties which refer to the entire molecule and which are global. One can define other global properties, such as the total contribution of all six-cycles, total contribution of all ten-cycles, as well as an appropriate linear combination of these contributions, which represents the total resonance energy. All these global quantities can be expressed in terms of the global counts W_n:

$$W_n = \sum_{k=1}^{n-1} X_{n,k} = \sum_{k=1}^{n-1} U_k\,U_{n-k}\,.$$

(12)

For exmaple, the global weighted count of all six-membered A- type cycles is

$$A_n = 2\sum_{k=1}^{n} A_{nk} = 4\,(W_{n+1} - 2W_n + W_{n-1})\,.$$

One similarly obtains all other global weighted counts

$$A_n = 4\,(W_{n+1} - 2W_n + W_{n-1})$$

$$B_n = 8\,(W_n - W_{n-1})$$

(13)

$$C_n = 16W_n$$

$$D_n = 16 \, (W_n - W_{n-1})$$

$$(13')$$

$$E_n = 8 \, (W_n - W_{n-1})$$

In order to obtain the relative contributions of various cycle types to the total resonance energy, one has to normalize the above weighted counts with the Kekulé count. Moreover, we are not interrested in the total resonance energy but rather in the resonance energy per carbon atom. The corresponding relative contributions per carbon atom are

$$a_n = \frac{A_n}{K_n N_n}, \quad b_n = \frac{B_n}{K_n N_n}, \quad c_n = \frac{C_n}{K_n N_n} \tag{14}$$

$$d_n = \frac{D_n}{K_n N_n}, \quad e_n = \frac{E_n}{K_n N_n} \tag{14'}$$

where $N_n = 18n - 6$ is the number of carbon atoms in the tetrabenzanthracene polymer containing n embedded biphenylene units.

Quantities A_n, B_n etc. are weighted counts of all six- and ten-cycle types, while quantities a_n, b_n etc. are the corresponding contributions to the total resonance energy, normalized per one carbon atom. All these quantities are expressed in terms of global counts W_n and Kekulé counts. We have above given expressions for the case of the tetrabenzanthracene family. However, one obtains similar expressions for all other benzenoid polymers, provided these polymers consist of identical monomer units which are mutually connected by two bonds.[7] In each case, there is a finite number of different six-cycle and ten-cycle types, and the global weighted counts of these cycle types can be always expressed in terms of quantities W_n.

Finally, in the case of the tetrabenzanthracene family, the global six- and ten-cycle weighted counts are:

$$C_n(6) = 4 \, (W_{n+1} + 4W_n - W_{n-1})$$

$$(15)$$

$$C_n(10) = 24 \, (W_n - W_{n-1})$$

and hence

$$RE_n(6) = \frac{4\,(W_{n+1} + 4W_n - W_{n-1})}{K_n N_n}$$

$$(15')$$

$$RE_n(10) = \frac{24\,(W_n - W_{n-1})}{K_n N_n}$$

Table I shows a few initial values for the key quantities U_k and W_n. These quantities are needed to express all the above local and global properties.

TABLE I

Initial values for the key quantities U_k and W_n which are required to express the local and global properties of the tetra-benzanthracene family

n	U_n	W_n
0	0	0
1	1	0
2	10	1
3	99	20
4	980	298
5	9701	3940
6	96030	48803
7	050599	580120
8	9409960	6702996
9	93149001	75859800
10	922080050	845044005
11	9127651499	9296660300
12	90354434940	101249210494
13	894416697901	1093549879580
14	8853812544070	11728666283207
15	87643708742799	125046925496560
16	867583274883920	1326384297425192

EDGE EFFECTS IN AN INFINITE BENZENOID POLYMER

Let us now investigate the edge effect in an infinite benzenoid polymer. As an illustration, we again consider the tetrabenzanthracene family shown in Figure 1, and we take n to be infinite. We would like to estimate the contribution of the first few cycles A_1, B_1, X_1, A_2, B_2,... to the total resonance energy. We would also like to estimate how far the edge effect penetrates into the bulk of the molecule.

As n increases, the contribution of a particular cycle, such as cycle A_k ($k=1,2,3,...$), converges to some limit value. This limit value is associated with an infinite polymer. Further, as k increases, the limit values associated with a particular cycle type converge to some bulk value. Thus, far enough from the edge of an infinite

polymer the contributions of the cycles A_k stabilize to some bulk value a, the contributions of the cycles B_k stabilize to some bulk value b, *etc.* We will now derive closed expressions for all these limit values, as well as for the corresponding bulk values.

From relations (9), (10) and (11), one finds for a finite tetraabenzanthracene polymer

$$a_{nk} = \frac{1}{2}\left\{x_{n+1,k} + x_{n-1,k-1}\frac{U_{n-2}}{U_n} - x_{n,k}\frac{U_{n-1}}{U_n} - x_{n,k-1}\frac{U_{n-1}}{U_n}\right\}$$

$$b_{nk} = x_{n,k}\frac{U_{n-1}}{U_n} - x_{n-1,k-1}\frac{U_{n-2}}{U_n}$$

$$c_{nk} = 4x_{n,k}\frac{U_{n-1}}{U_n} \tag{16}$$

$$d_{nk} = x_{n,k}\frac{U_{n-1}}{U_n} - x_{n-1,k-1}\frac{U_{n-2}}{U_n}$$

$$e_{nk} = x_{n,k}\frac{U_{n-2}}{U_n} - x_{n-1,k}\frac{U_{n-2}}{U_n}$$

where x_{nk} is the normalized quantity

$$x_{n,k} = \frac{X_{n,k}}{U_{n-1}} = \frac{U_k U_{n-k}}{U_{n-1}} \tag{17}$$

which satisfies $x_{n,k} = x_{n,n-k}$ and $x_{n,1} = 1$.

In order to evaluate the contribution of various cycles to the resonance energy of an infinite polymer, one has to evaluate the limit of the above quantities as $n \to \infty$, that is, one has to evaluate quantities $a_{k\infty} = \lim\limits_{n \to \infty} a_{nk}$, $b_{k\infty} = \lim\limits_{n \to \infty} b_{nk}$, *etc.* From Eq. 17, one finds

$$a_{k\infty} = \frac{1}{2}\left\{x_k - \frac{x_k + x_{k-1}}{\lambda} + \frac{x_{k-1}}{\lambda^2}\right\}, \quad b_{k\infty} = \frac{x_k}{\lambda} - \frac{x_{k-1}}{\lambda^2}, \quad c_{k\infty} = 4\frac{x_k}{\lambda}$$

$$d_{k\infty} = \frac{x_k}{\lambda} - \frac{x_{k-1}}{\lambda^2}, \quad e_{k\infty} = \frac{x_k}{\lambda} - \frac{x_k}{\lambda^2} \tag{18}$$

where

$$\lambda = \lim_{n \to \infty} \frac{U_{n+1}}{U_n} \quad \text{and} \quad x_k = \lim_{n \to \infty} x_{n,k} \tag{19}$$

Quantity $a_{k\infty}$ is, thus, the resonance energy contribution of cycle A_k in an infinite polymer, quantity $b_{k\infty}$ is the resonance energy contribution of cycle B_k in an infinite polymer, *etc.*. One can associate local aromaticity with these contributions, and one can study the edge effect in terms of a change of these contributions as k increases. As one penetrates more and more into the bulk of a molecule, these cycle contributions converge to some bulk values $a = \lim_{k \to \infty} a_{k\infty}$, $b = \lim_{k \to \infty} b_{k\infty}$ *etc.* It is convenient to define a limit bulk quantity x:

$$x = \lim_{k \to \infty} x_k . \tag{20}$$

Bulk quantities a, b, c, d and e are now

$$a = \frac{x}{2}\left\{1 - \frac{2}{\lambda} + \frac{1}{\lambda^2}\right\}, \quad b = x\left\{\frac{1}{\lambda} - \frac{1}{\lambda^2}\right\}, \quad c = \frac{4x}{\lambda}, \quad d = e = x\left\{\frac{1}{\lambda} - \frac{1}{\lambda^2}\right\} . \tag{21}$$

Our derivation is almost complete. It remains to evaluate quantities x, λ, and x_k. We will evaluate these quantities for a general case, and not just for the tetrabenzanthracene family.

Let us first evaluate the quantity λ. From Eq. (7), it follows

$$\frac{U_{n+1}}{U_n} = \alpha - \beta \frac{U_{n-1}}{U_n} .$$

Since this relation holds for each n, taking the limit $n \to \infty$, one finds

$$\lambda^2 - \alpha \lambda + \beta = 0 . \tag{22}$$

This equation is identical to the transfer matrix equation.[13] Quantity λ is, hence, the root of the transfer matrix equation. According to definition (19), of the two possible roots it must be the larger one. Hence

$$\lambda = \frac{\alpha + \sqrt{\alpha^2 - 4\beta}}{2} . \tag{23}$$

Let us now evaluate bulk quantity x and limit quantities x_k, From Eqs. (17) and (19), one finds

$$x_k = \frac{U_k}{\lambda^{k-1}} \tag{24}$$

in particular, $x_1 = 1$ and $x_2 = \alpha/\lambda$.

We will now prove by mathematical induction that

$$x_k = x(1 - y^k) \tag{25}$$

where
$$x = \frac{\lambda}{2\lambda - \alpha} = \frac{\alpha + \sqrt{\alpha^2 - 4\beta}}{2\sqrt{\alpha^2 - 4\beta}}, \quad y = \frac{\alpha - \lambda}{\lambda} = \frac{\alpha - \sqrt{\alpha^2 - 4\beta}}{\alpha + \sqrt{\alpha^2 - 4\beta}}. \tag{25'}$$

First, one can easily verify that relation (25) holds for $k=1$ and $k=2$. Assume now that this relation holds for $k-1$ and $k-2$. We will show that this implies the validity of Eq. (25) for k.

Using Eqs. (5) and (24), one finds

$$x_k = \frac{\alpha}{\lambda} x_{k-1} - \frac{\beta}{\lambda^2} x_{k-2}.$$

By assumption, relation (25) holds for $k-1$ and $k-2$, which implies

$$x_k = \frac{\lambda}{2\lambda - \alpha} \left\{ \frac{\alpha}{\lambda} - \frac{\beta}{\lambda^2} - \frac{\alpha}{\lambda} y^{k-1} + \frac{\beta}{\lambda^2} y^{k-2} \right\}.$$

Using Eq. (22), the first two terms in the brackets evaluate into one. Using Eqs. (22) and (25'), the remaining two terms evaluate into $-y^k$. This proves that x_k satisfies relation (25), provided this relation is satisfied by x^{k-1} and x^{k-2}. Since this relation is satisfied for $k=1$ and $k=2$, by mathematical induction it is satisfied for each k.

According to Eq. (25), llimit quantities x_k converge exponentially to a bulk value x. Since the edge effect decreases by $(1/y)$ whenever k increases by one, quantity $(1/y)$ can be considered as a damping factor. One can also define the penetration index γ with the relation

$$y = e^{-1/\gamma}$$

that is

$$\gamma = -\frac{1}{\ln y}.$$

The penetration index determines how far the edge effect penetrates into the bulk of a polymer. The larger this index, the further is the penetration.

All six- and ten-cycle contributions in an infinite tetrabenzanthracene polymer are now expressed in a closed analytical form. These contributions are given by relations (18), where quantities λ and x_n are given by relations (23) and (25), respectively. Using $\alpha=10$ and $\beta=1$, one finds

$$\lambda = 5 + \sqrt{24} = 9.898979485566, \quad y = \frac{5 - \sqrt{24}}{5 + \sqrt{24}} = 0.0102051443364$$

$$x = \frac{5 + \sqrt{24}}{2\sqrt{24}} = 1.0103103630799 \ , \qquad \gamma = 0.218109009153$$

In particular, from Eq. (21), six- and ten-cycle bulk contributions are

$$a = c = \frac{1}{\sqrt{6}} = 0.408248290464 \ , \qquad b = \frac{2 + \sqrt{6}}{\sqrt{24}\,(5 + \sqrt{24})} = 0.0917517095361$$

$$\text{(21')}$$

$$d = e = \frac{2 + \sqrt{6}}{\sqrt{24}\,(5 + \sqrt{24})}\, 0.0917517095361 \ .$$

Comparing the three six-cycles, one finds that cycles A and X have the same bulk contribution to the total resonance energy, while cycle B has a substantially smaller bulk contribution. This contribution determines the relative bulk aromaticity of six-cycles. As regards the two ten-cycles, they have the same bulk contribution to the total resonance energy and, hence, they are equally aromatic.

These contributions are only relative, that is one can compare only the contributions of the cycles of the same size, six-cycle to six- cycle and ten-cycle to ten-cycle. In order to compare six- to ten- cycle contributions, one should multiply six-cycle contributions with R_6 and ten-cycle contributions with R_{10}. Here one can use either BORT or conjugated-circuit values for these quantities.

In a similar way, one can obtain explicit expressions for all other local properties. All the dependence on index k, which determines the distance from the edge of an infinite polymer, is contained in quantity x_k. As k increases, x_k exponentially approaches to a bulk value x. The rate of this change is mainly determined by the damping factor $1/y = 97.98979482$.

In the same way, one can analyze all the other linear benzenoid polymers containing identical monomer units which are mutually connected by two CC bonds. In general, in the limit of an infinite polymer, all six- and ten-cycle contributions can be expressed in terms of the quantities x_k and λ *via* some relations similar to relations (18) above. In each case, quantity λ is given by Eq. (23) while quantities x_k are given by Eq. (25). The penetration of the edge effect into the bulk of the molecule is determined by quantity x_k, which exponentially approaches the bulk value x. Ultimately, all these expressions depend on only two quantities, α and β. These quantities depend on a particular benzenoid family and can be very easily obtained. The rate at which the edge effect decreases from the edge of the polymer into the bulk of the polymer is determined by the damping factor $1/y$. This damping factor equals the ratio of the larger to the smaller root of Eq. (22). The smaller this ratio, the further the edge effect penetrates into the bulk of the molecule.

Another problem is how reliable are the limit quantities Eq. (18) which are valid for an infinite tetrabenzanthracene polymer, as an approximation for the quantities Eq. (16) valid for a finite tetrabenzanthracene polymer. According to relations (16), (17) and (18), this question reduces to the problem of how reliable is the bulk quan-

TABLE II

Convergence of x_{nk} to limit values x_k for the case of the tetrabenzanthracene fa-
mily. These limit values correspond to an infinite tetrabenzanthracene polymer. As
k increases, limit values x_k in the last row converge to the bulk value x.

n	x_{n2}	x_{n3}	x_{n4}	x_{n5}
3	1.010101010101			
4	1.010204081633			
5	1.010205133491	1.010308215648		
6	1.010205144226	1.010309278351		
7	1.010205144335	1.010309289200	1.010310341164	
8	1.010205144336	1.010309289306	1.010310352010	
9	1.010205144336	1.010309289307	1.010310352121	1.010310362856
10	1.010205144336	1.010309289307	1.010310352122	1.010310362967
11	1.010205144336	1.010309289307	1.010310352122	1.010310362968
∞	1.010205144336	1.010309289307	1.010310352122	1.010310362968

tity x_k as an approximation of the quantity $x_{n,k}$. This is illustrated in Table II. In
this Table, quantities x_{nk} for $k=2$, 3, 4 and 5 are given. Each column contains the
values x_{nk} for a fixed k. As n increases, these values converge to a limit quantity x_k
at the bottom of each column. For each value of k, only those values of n which sat-
isfy $n \geq 2k - 1$ are shown. For smaller values of n, one can use the symmetry relation
$x_{nk} = x_{n,n-k}$.

Convergence of each x_{nk} to a limit quantity x_k is very fast. Thus, already x_{71} ap-
proximates the limit quantity x_1 up to twelve significant figures. while already x_{82}
approximates the limit quantity x_2 up to twelve significant figures, *etc.* Since all
limit quantities Eq. (18) are expressed in terms of limit quantities x_k, this illus-
trates how reliable limit quantities $a_{k\infty}$, $b_{k\infty}$ *etc.* are as an approximation of quan-
tities a_{nk}, b_{nk} *etc.* in the case of a finite tetrabenzanthracene polymer. As illus-
trated by Table II, for all tetrabenzanthracene polymers except very small ones,
one can reliably approximate exact quantities Eq. (11) with the corresponding
limit quantities Eq. (18). In the case of small polymers, direct numerical calcu-
lation is not so involved and one can use exact expressions Eq. (11) instead of
approximate expressions Eq. (18).

Similar results are obtained for all other benzenoid polymers containing mono-
mer units which are mutually connected by two CC bonds. In general, one has to
estimate the convergence of quantities x_{nk} to the limit quantity x_k. This convergence
depends on the damping coefficient $1/y$: the larger this damping coefficient, the
faster is the convergence.

GLOBAL PROPERTIES

Let us now consider global properties, such as the global cycle contributions
of a particular cycle type, global six-cycle and ten- cycle contributionas and, fi-
nally, the global resonance energy. We will derive formulas for global proper-
ties in the limit $n \to \infty$, and we will compare these formulas with the exact results
for some finite n.

Let us first define normalized quantities w_n as average quantities x_{nk}.

$$w_n = \frac{W_n}{U_{n-1}(n-1)} = \frac{1}{n-1} \sum_{k=1}^{n-1} x_{nk} \tag{26}$$

As n increases, x_{nk} converges to x_k. Thus, for a big enough n and for $k \le n/2$, one can approximate x_{nk} with x_k, while for $k \ge n/2$ one can use symmetry $x_{n,k} = x_{n,n-k}$ and approximate x_{nk} with x_{n-k}. Hence, and from Eqs. (19) and (25), the global quantity w_n can be approximated as

$$w_n \approx \frac{2}{n-1} \sum_{k=1}^{n/2} x_k = x \left\{ 1 - \frac{2}{n-1} \sum_{k=1}^{n/2} y^k \right\}.$$

The last sum equals $(y - y^{n/2})/(1-y)$. For a big enough n, one has $y^{n/2} \approx 0$, and, hence, finally

$$w_n \approx x \left\{ 1 - \frac{2}{n-1} \frac{y}{1-y} \right\}. \tag{27}$$

One can now approximate all global contributions Eq. (14) in terms of quantities w_n

$$a_n \approx w_{n+1} \frac{n}{18n-6} - 2 \frac{w_n}{\lambda} \frac{n-1}{18n-6} + \frac{w_{n-1}}{\lambda^2} \frac{n-2}{18n-6}$$

$$b_n \approx 2 \left\{ \frac{w_n}{\lambda} \frac{n-1}{18n-6} - \frac{w_{n-1}}{\lambda^2} \frac{n-2}{18n-6} \right\}$$

$$c_n \approx 4 \frac{w_n}{\lambda} \frac{n-1}{18n-6} \tag{28}$$

$$d_n \approx 4 \left\{ \frac{w_n}{\lambda} \frac{n-1}{18n-6} - \frac{w_{n-1}}{\lambda^2} \frac{n-2}{18n-6} \right\}$$

$$e_n \approx 2 \left\{ \frac{w_n}{\lambda} \frac{n-1}{18n-6} - \frac{w_{n-1}}{\lambda^2} \frac{n-2}{18n-6} \right\}$$

where quantities λ and w_n are given by relations (23) and (27), respectively.

TABLE III

Comparison of the exact six- and ten-cycle global contributions with these contributions calculated approximately using relation (29)

n	$RE_n(6)$ approx.	$RE_n(6)$ exact	$RE_n(10)$ approx.	$RE_n(10)$ exact.
1	0.0824564191455	0.8333333333333	0.0000000000000	0.0000000000000
2	0.0799872435695	0.0800000000000	0.0199914957131	0.0200000000000
3	0.0793349625984	0.0793350168350	0.0239902244094	0.0239898989898
4	0.0790352499271	0.0790352504638	0.0257885004374	0.0257884972217
5	0.0788639855435	0.0788639855489	0.0268160867391	0.0268160867068
6	0.0787531674129	0.0787531674130	0.0274809955226	0.0274809955222
7	0.0786755947215	0.0786755947215	0.0279464316710	0.0279464316710
8	0.0786182583844	0.0786182583844	0.0282904496937	0.0282904496937
9	0.0785741535097	0.0785741535097	0.0285550789420	0.0285550789420
10	0.0785391737814	0.0785391737814	0.0287649573113	0.0287649573113
100	0.0782654193867	0.0782654193867	0.0304074836799	0.0304074836799
1000	0.0782389476379	0.0782389476379	0.0305663141723	0.0305663141723
10000	0.0782363091990	0.0782363091990	0.0305821448058	0.0305821448058
∞	0.0782360161369	0.0782360161369	0.0305839031787	0.0305839031787

Similarly, one approximates the total six- and ten-cycle contributions

$$RE_n(6) \approx w_{n+1} \frac{n}{18n-6} + 4 \frac{w_n}{\lambda} \frac{n-1}{18n-6} - \frac{w_{n-1}}{\lambda^2} \frac{n-2}{18n-6}$$

$$RE_n(10) \approx 6 \left\{ \frac{w_n}{\lambda} \frac{n-1}{18n-6} - \frac{w_{n-1}}{\lambda^2} \frac{n-2}{18n-6} \right\}.$$

(29)

In the limit $n \to \infty$, one obtains

$$RE_\infty(6) = \frac{x}{18} \left\{ 1 + \frac{4}{\lambda} - \frac{1}{\lambda^2} \right\}, \quad RE_\infty(10) = \frac{x}{3\lambda} \left(1 - \frac{1}{\lambda} \right).$$

(30)

Table III gives a comparison of the exact values $RE_n(6)$ and $RE_n(10)$ with these values calculated according to relations (29). Formally, approximations Eq. (29) shoud be valid for a large n. However, as shown in Table III, these approximations are extremely good also for quite a small n. Already for the polymer containing only seven units, relations (29) approximate exact global six- and ten-cycle contributions up to twelve significant figures. Relations (29) are quite acceptable even for very small polymers. Thus, in the case of tetrabenzanthracene, which is the the second member in this polymer family, these relations reproduce exact six- and ten-cycle contributions up to three and four significant figures, respectively.

Another point which should be emphasized is that values $RE_n(6)$ and $RE_n(10)$ converge quite slowly to the respective limit values $RE_\infty(6)$ and $RE_\infty(10)$ for an infinite polymer. As shown in Table III, in the case of the tetrabenzanthracene polymer containing as many as 1000 monomer units, the six-cycle contribution $RE_{1000}(6)$ approximates the exact limit value $RE_\infty(6)$ only up to four significant figures, while the

ten-cycle contribution $RE_{1000}(10)$ approximates the exact limit value $RE_{\infty}(10)$ only up to three significant figures. In view of this slow convergence, and in order to estimate the behaviour of these quantities for very large polymers, various extrapolation techniques were attempted in Ref. 14, such as expansion in a geometric series, polynomial optimal curve fitting, orthogonal optimal curve fitting, *etc.* All these approximations are far less accurate than the closed relations (29) obtained here.

CONCLUSIONS

Benzenoid polymer systems containing monomer units which are mutually connected by two CC bonds were considered. These molecules were treated within a simplified BORT or equivalently[11] within a simplified VB approach. This simplified approach relies on the ansatz Eq (1), and in the resulting expression Eq. (4') for the total resonance energy all terms are neglected, except two dominant terms corresponding to a single six- and a single ten-cycle, respectively. On this level of approximation, and in the case of benzenoid systems, the resulting relations are quite similar to the conjugated circuit model.[4]

As an illustration, the tetrabenzanthracene polymer family was explicitly considered. Closed expressions for local and global contributions to the total resonance energy were derived. Exact bulk values for various cycle types were also obtained. As regards global properties, highly accurate approximate expressions which describe finite polymers were also obtained. It was shown that the influence of the edge effect decreases exponentially as one enters the bulk of the molecule. The damping coefficient which determines how much this influence decreases as one moves a single monomer unit inside a polymer equals the ratio of the larger to the smaller root of the characteristic equation (22). In the case of the tetrabenzanthracene family, one has $\alpha = 10$ and $\beta = 1$. In the case of other polymer families, these quantities have some other values, producing some other damping coefficients. In each particular case, coefficients α and β can be very easily determined, for example, from the Kekulé counts of the first four members of a polymer family.

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SAŽETAK

Rubni efekti u vrlo velikim benzenoidnim polimerima

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U radu su razmatrani vrlo veliki benzenoidni polimeri čiji su monomeri međusobno pove-
zani sa po dvije veze CC. Račun je proveden u okviru pojednostavnjenog BORT, tj. pojedno-
stavnjenog VB postupka. Opisan je općeniti postupak za račun rezonancijskih energija i svoj-
stava lokalne aromatičnosti, kao što su npr. doprinosi šestero- i deseteročlanih prstenova
ukupnoj rezonancijskoj energiji. Za ilustraciju postupka razmatrani su tetrabenzantracenski
polimeri. Izvedeni su točni izrazi za lokalna i globalna svojstva beskonačno dugih polimera toga
tipa, kao i vrlo dobri približni izrazi kada takovi polimeri imaju konačnu duljinu.