Theor Chim Acta (1995) 90: 1–26

Theoretica Chimica Acta

Comparative study of large molecules. Highly accurate calculation of a limit for infinite systems from data on finite systems

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Received April 29, 1994/Accepted June 8, 1994

Summary. We have initiated a comparative study of several families of structurally closely related large benzenoid hydrocarbons of increasing number of fused benzene rings. Local and global properties of such molecules have been studied with a particular interest in investigating the closeness of finite-size molecules for modelling infinite polymeric structures having the same structural patterns. We focus in this report on two questions: (1) how large is a finite molecule which well approximates an infinite system? and (2) how do terminal groups influence local properties in the central part of the molecule as we approach the infinite system. Emphasis in this report is on extraction of high-accuracy limiting values for selected molecular properties from limited data on a few smaller members of structurally related molecules.

Key words: Polymers – Oligomers – Benzenoids – Resonance – Conjugation

1 Introduction

Polymers are idealized as infinite systems with a regularly repeating structural unit. Much very useful information on polymers has been derived from a close study of the unit cell employing various theoretical models. However, strictly speaking infinite systems do not exist; they are an idealization. The question can then be posed: How large should a finite molecular system be such that, for practical purposes, the system behaves as an infinite system? This is the question addressed in this study.

In the literature there are numerous reports in which infinite benzenoid polymers of finite width were compared with the limiting structure of graphite [1]. Although such studies have been of considerable interest they do not answer the above question which pertains to finite molecules. It has been stated [2] that in

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order to approach the properties of graphite realistically, one would have to consider molecular systems having 10^5 carbon atoms. However, with judicious lesser computation we might be able to estimate or guess answers.

In this paper we consider large but finite molecules having a "repeating" unit which if extended to ever larger size would asymptotically approach a polymer. We outline a general scheme which is concerned with a comparison of results for finite molecules with similar calculations for infinite systems. This will be illustrated for one particular property, that of the molecular stability as reflected in the conjugated-circuit resonance energy per electron (REPE). The numerical parameterization adopted is from SCF MO-type calculations. In cases where each site corresponds to a single carbon atom each contributing a single pi-electron to the overall molecular network the REPE is the same as the resonance energy per carbon atom (or per site).

Recently [3], we have examined in some detail a particular family of large benzenoids in order to see how the finite-size influence selects molecular parameters. The molecules considered belong to the triphenylene-tetrabenzanthracene family of Fig. 1. Each successive member is obtained by fusion of a phenanthrene unit at the benzene ring of an end group. Molecules involving up to $n = 6$ "repeating" units were examined and convergence of local molecular properties was observed.

Here we present more ambitious calculations on several similar finite benzenoid structures of increasing size. In particular, we consider structures having a single "repeating" unit but different end groups (Fig. 2). In this way we hope to obtain more insight as to the role of end groups on the properties of large systems. It is already known [4] that the asymptotic rates of convergence for long polymers having the same repeating unit but different end groups are generally (i.e., for those associated with the same long-range spin-pairing order) the same. The rate of convergence depends only on the eigenvalue properties of the corresponding transfer matrix. For example, the leading "correction" term governing the

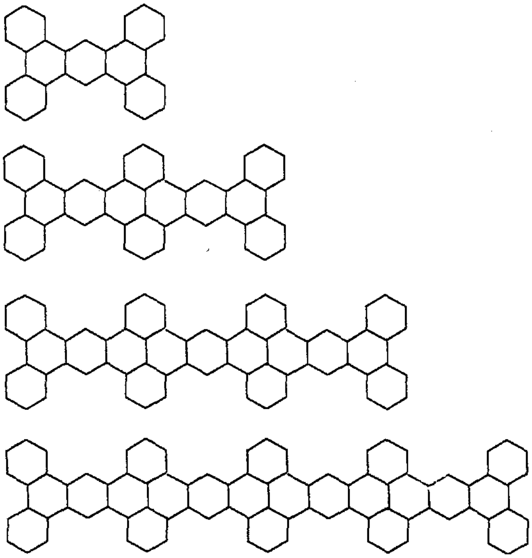
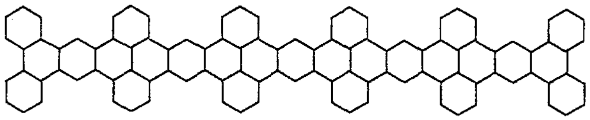


Fig. 1. The smaller members of the tetrabenzanthracene family

Family I



Family II

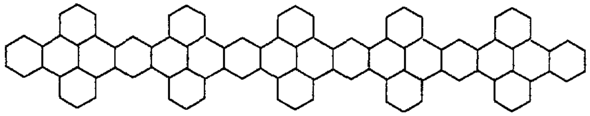


Fig. 2. The families considered which differ only in their end groups but have the same repeating monomer unit

convergence for the Kekule structure count is the length power of the ratio of the second largest magnitude to the maximum eigenvalue of the transfer matrix. Since polymers with the same repeating unit generally have the same transfer matrix there should be no difference in this aspect of the convergence behavior. One expects that the sort of behavior will generally occur when sequences of finite molecules model infinite systems. The transfer matrix approach applies best to regular systems, either infinite, or finite with a single repeated monomer unit. With cyclic boundary conditions the ends are “eliminated”. The latter are illustrated by more symmetric fullerenes including buckminster fullerene [5], and there are also numerous statistical mechanical applications [6] of the technique. But more generally not even regularity is required [7].

2 Conjugated circuit model

Before we proceed we have to outline briefly the conjugated circuits approach to calculate the molecular resonance stability. Although the model is based on examination of the set of Kekule valence structures it is intimately related to some valence–bond-type calculations of molecular electronic properties. Within each Kekule valence structure one enumerates conjugated circuits, and usually restricts the enumeration only to smaller conjugated circuits, since only such make a significant contribution to the molecular stability. Efficient algorithms for enumeration of conjugated circuits are based on the transfer matrix approach [4], involving examination of relevant substructures derived by erasure of even cycles of various sizes [8], or they are based on the so-called “many-body” scheme [9]. In this report we use the latter approach, which has been implemented for computer use.

After one enumerates conjugated circuits of different sizes, one can write down the expression for the molecular resonance energy (RE) which is given in terms of the contributions of conjugated circuits of different sizes averaged over the Kekulé valence structures [10–12]. One can even restrict attention to individual rings and only consider conjugated circuits involving a selected ring. In this way one obtains local aromaticity characteristics for distinct individual benzene rings in a molecule [13]. To obtain numerical values, one can select a parameterization which gives the RE based on SCF MO resonance energies [14].

Since the smaller conjugated circuits make the major contributions to the molecular RE, we decided to count only conjugated circuits of size six (benzene fragments) and size ten (naphthalene periphery). We should reiterate that the model of conjugated circuits is equivalent to the resonance theory model of Herndon [15], although the two schemes are motivated in different ways. Herndon's model can be viewed as an extension of the early work of Simpson [16]. The conjugated circuit model follows VB theory and can be viewed as an extension of the early work of Pauling and others involving "islands" [17]. Finally, we should mention that both approaches, the conjugated circuits theory [10, 11] and Herndon's resonance theory [15], can be derived within the standard quantum chemical framework [18, 19].

3 Tetrabenzanthracene family

In Fig. 1 we have shown several smaller members of a family of fully benzenoid systems which are derived by augmenting the parent structure tetrabenzanthracene with a triphenylene unit at the end of a molecule. In Fig. 2 are illustrated larger members of the family of tetrabenzanthracene and closely related molecules which differ only in their ending (or initial) groups. Both molecules not only have the same "repeating" unit, but also both represent examples of Clar's fully benzenoid hydrocarbons [20]. These are hydrocarbons for which one can write, but a single, Clar structure in which all benzene rings are either assigned to a pi-sextet or are "empty" (i.e., seemingly devoid of innate contribution to the overall aromatic properties of the system). We will focus in this report on two questions:

(1) How large is a finite molecule which well approximates an infinite system?
(2) How do terminal groups influence local properties in the central part of the molecule as we approach the infinite system?

In order to obtain insight into the convergence of the results for finite molecules to the properties of an infinite system, we have collected in Tables 1 and 2 the REPE values for the smaller members of the first family of tetrabenzanthracene-based polymers. We consider the first 12 members of each family, i.e., molecules from two dozen carbon atoms up to molecules containing over 200 carbon atoms and having over 30 fused benzene rings.

Table 1

N	n	$\#R_1/nK$	$\#R_2/nK$	REPE (eV)
1	30	0.1600000	0.04000000	0.14888
2	48	0.1586700	0.04797980	0.14969
3	66	0.1580705	0.05157700	0.15005
4	84	0.1577280	0.05363217	0.15026
5	102	0.1575063	0.05496199	0.15039
6	120	0.1573512	0.05589286	0.15049
7	138	0.1572365	0.05658090	0.15056
8	156	0.1571483	0.05711016	0.15061
9	174	0.1570783	0.05752991	0.15065
10	192	0.1570215	0.05787097	0.15069
11	210	0.1569744	0.05815355	0.15072
12	228	0.1569347	0.05839152	0.15074
Limit	∞	0.1564720	0.06116781	0.15102

Table 2

N	n	$\# R_1/nK$	$\# R_2/nK$	REPE
1	24	0.1583333	0.05000000	0.14989
2	42	0.1575277	0.05483406	0.15038
3	60	0.1572109	0.05673469	0.15057
4	78	0.1570404	0.05775773	0.15068
5	96	0.1569338	0.05839712	0.15074
6	114	0.1568609	0.05883459	0.15079
7	132	0.1568079	0.05915276	0.15082
8	150	0.1567676	0.05939406	0.15084
9	168	0.1567359	0.05958455	0.15086
10	186	0.1567104	0.05973777	0.15088
11	204	0.1566893	0.05986395	0.15089
12	222	0.1566717	0.05996967	0.15090
Limit	∞	0.1564720	0.06116781	0.15102

We see from Tables 1 and 2 that the convergence of the R_1 and R_2 coefficients, which indicate contributions of six-membered and ten-membered conjugated circuits to REPE, varies quite slowly as we consider larger systems. The coefficients of R_1 and R_2 shown in Tables 1 and 2 were obtained using a computer program prepared in this laboratory [21]. The entries in the two tables are the ratios $\# R_1/nK$ and $\# R_2/nK$ where K is the number of the Kekule valence structures in the molecule, and n is the number of carbon atoms. $\# R_1$ and $\# R_2$ are the counts of six- and ten-membered conjugated circuits in a molecule, respectively.

That finite molecules show a slow convergence as they approach an infinite system representing a polymer has been generally known. Tables 1 and 2 should display convergence to the same limit, because they both have the same "repeating" unit. However, it may sometimes be difficult to estimate the limit by viewing the behavior of finite molecules even if they appear large. When we approach molecules having some 200 carbon atoms the molecules show but a small increase in REPE. The changes in the coefficients evidently affect only the fifth decimal place. But, as the sequence $1/N$ well illustrates, small changes need not ensure convergence, and even if an upper bound exists we may be far from the limit for even moderate values of N.

To illustrate the very slow convergence we have evaluated exact values, using the analytical approach to molecular RE [22], for $\# R_1/nK$ for several large N which are shown below:

N	$\# R_1/nK$
200	0.1565012
300	0.1564915
500	0.1564837
1000	0.1564779
1500	0.1564759
2000	0.1564748
2500	0.1564744
3000	0.1564740

The analytical approach allows one to continue the calculation for even larger N values. The slow convergence is illustrated by recording the N values for which each successive digit in the limit 0.1564720 appears, as is illustrated below:

Digit	N
2	2
3	11
4	251
5	1001
6	6101

Having the results for very large N, one can extrapolate and find limits to high accuracy. Our prime purpose, however, here is to outline how one can obtain an accurate limit when calculations are not available for very large N, as often will be the case.

4 Expansion of REPE in reciprocal power series $1/N^k$

In Table 3, instead of listing R_1 and R_2 coefficients we computed their ratio. Since the R_1 coefficient decreases and the R_2 coefficient increases with N, the ratio is a more sensitive function of N than either considered separately. Thus, while in Tables 1 and 2 already when $N = 12$ the difference in the coefficients for R_1 is about 0.000018, the ratio $\#R_1/\#R_2$ shows a much greater difference, i.e. 0.012. Even when we know the limit (as in the last row in Tables 1 and 2), inspection of the entries in these tables may give but a misleading impression that one is not too far from reaching the limit. In this respect, Table 3 better reflects the reality, that we have a long way to go in order to approach the limit, i.e., to reduce the ratio $\#R_1/\#R_2$ from about 2.60 down to 2.56.

Table 3

N	Family I	Family II
1	4.00000000	3.16666667
2	3.30707543	2.87280702
3	3.06476820	2.77098321
4	2.94092074	2.71895021
5	2.86573197	2.68735558
6	2.81522864	2.66613387
7	2.77896814	2.65089706
8	2.75166998	2.63942626
9	2.73037686	2.63047881
10	2.71330363	2.62330457
11	2.69930897	2.61742395
12	2.68762904	2.61251600
13	2.67773343	2.60835782
14	2.66924228	2.60478981
15	2.66187640	2.60169463
16	2.65542600	2.59898415
17	2.64973042	2.59659083
∞	2.55807821	2.55807752

4.1 Expansion

In order to get a more reliable estimate to the limit of REPE for an infinite system we will examine the regression of our coefficients for R_1 against powers of $1/N$. Since both families of finite molecules of Tables 1 and 2 are indistinct in the $N \to \infty$ limit, we will focus attention on Table 2, in which the initial values for N are smaller than for the corresponding N in Table 1. We will expand the coefficients in the R_1 column in a power series in $(1/N)^k$ and then extrapolate the expansion for larger values of the number N of "repeating" units of fused triphenylenes. In particular, we will consider $N = 100$, $N = 1000$, $N = 10\,000$ as finite molecules which may suffice to approximate infinite systems sufficiently well.

First we have to select the degree of the polynomial for the fit. In Fig. 3 we give the residuals of the plot for a linear, a quadratic, a cubic, a quartic and a quintic polynomial. By comparison of these different results of the figures, one can immediately see that there is little improvement in going beyond a quadratic correction. In the case of quadratic regression the residuals might be interpreted to reflect a cubic dependence on $1/N$. Similarly, regular patterns might also be seen for residuals of cubic and quartic regressions and only when we reach a quintic regression does the residual start to appear as noise rather than reflecting a pattern of a higher polynomial.

In Table 4 we give the information for the coefficients of the multiple regression equations based on quadratic and higher polynomials for the entries of Table 2 under the column $\# R_1/nK$. In the last column we show the Fisher F ratio which suggests the quality of the regressions. We see an enormous increase in F when going from the linear regression to the quadratic, and even larger increase in F when introducing the cubic term. After the cubic term there is no increase in F; this suggests that our best equation is

$$R_1 = 0.15647218 + 0.00245947(1/N) - 0.00079578(1/N^2) + 0.00019747(1/N^3).$$

By using the above cubic equation we derive the extrapolated values for $\# R_1/nK$ as shown in Table 5. N is the number of "repeating" units and n gives the approximate number of carbon atoms in the corresponding finite systems. All the values for R_1 are given in units of $R_1 = 1$. Since R_1 is usually listed in eV units to three digits we see that already a finite molecular model having 10^3 carbon atoms will give a very adequate approximation for the resonance stability of the infinite polymer system which the finite system approaches.

By considering molecules having large numbers of carbon atoms we can increase the accuracy of the model should other conditions warrant such expansions. The limiting value is given by the constant term of the cubic expansion, which quite well approaches the exact limit base on an "infinite" polymer model.

4.2 Limit

We obtain the exact limiting value for R_1 (and R_2) for the infinite system having the same "repeating" unit by using another program in which, with employment of translational symmetry, a numerical single integration is performed. For molecules considered here cyclic conditions on polymers of much smaller length already give the limiting value for R_1. In Table 6 we give the output of the count and the conjugated circuits R_1 and R_2 for the infinite (cyclic periodic) strip. The count of

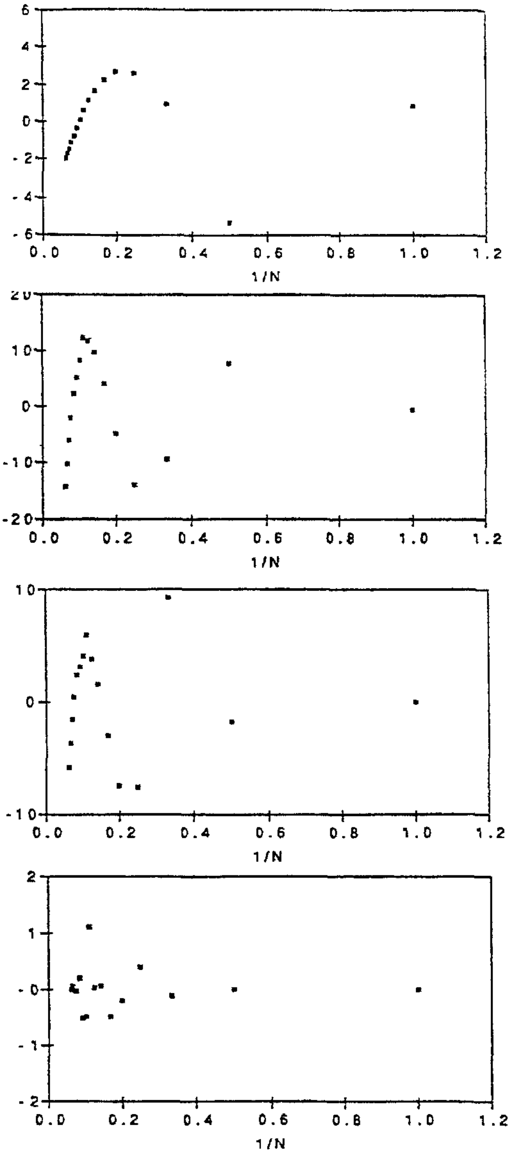


Fig. 3. The residuals of quadratic, cubic quartic and quintic fitting of the data in terms of the polynomials in $1/N$

conjugated circuits is normalized by dividing the count by the corresponding number of Kekule valence structures for the repeating "cell".

In order to extract the correct contributions to R_1 and R_2 we have to identify rings which belong to the periodic cell. We illustrate in Fig. 4 the contributing rings for R_1 and R_2, respectively. In Table 6 the 10-cycle contributing conjugated circuits have been indicated by a " + " sign. In our case all ten-membered conjugated circuits either make an equal contribution of 0.0917511 (which in Clar's terminology equals the contribution of 6-membered "empty" rings), or make no contribution. Hence, some of Clar's "empty" rings are not really "empty" (i.e., are not actually devoid of contribution to the molecular resonance stability), but are

Table 4

	$m=2$	$m=3$	$m=4$	$m=5$
constant	0.15647919	0.15647218	0.15647212	0.15647203
$1/N$	0.00236172	0.00245947	0.00246061	0.00246293
$1/N^2$	− 0.00050845	− 0.00079578	− 0.00080208	− 0.00082201
$1/N^3$		0.00019747	0.00020941	0.00028027
$1/N^4$			− 0.00000673	− 0.00011183
$1/N^5$				0.00005195
F	3.1×10^3	2.8×10^5	2.1×10^8	1.9×10^8

Orthogonal expansion

Constant	0.15653557	F
$1/N$	0.00185594	2.5×10^3
$1/N^2$	− 0.00050845	3.1×10^5
$1/N^3$	0.00019635	2.8×10^8
$1/N^4$	0.00001415	2.1×10^8
$1/N^5$	0.00026478	1.9×10^8

Correlation matrix

	R_1	Ω_1	Ω_2	Ω_3	Ω_4	Ω_5
R_1	1	0.997	− 0.074	0.005	0.000	0.000
Ω_1		1	0	0	0	0
Ω_2			1	0	0	0
Ω_3				1	0	0
Ω_4					1	0
Ω_5						1

Table 5

$N = 10$	$R_1 = 0.15671215$	$n \sim 1.8 \times 10^2$
$N = 100$	$R_1 = 0.15649670$	$n \sim 1.8 \times 10^3$
$N = 1000$	$R_1 = 0.15647464$	$n \sim 1.8 \times 10^4$
$N = 10\,000$	$R_1 = 0.15647233$	$n \sim 1.8 \times 10^5$
Limit $N \to \infty$	$R_1 = 0.15647218$	
Exact $N \to \infty$	$R_1 = 0.15647203$	

"almost empty". This has been observed earlier [10–12]. The count of Kekule valence structures for triphenylene, which is the repeating unit in our molecules, is 9; hence, the final result is obtained by summing the ring contributions and dividing the sum by 9. Thus, we obtain as the limiting contribution of 6-membered rings 1.408248288/9 = 0.156472032.

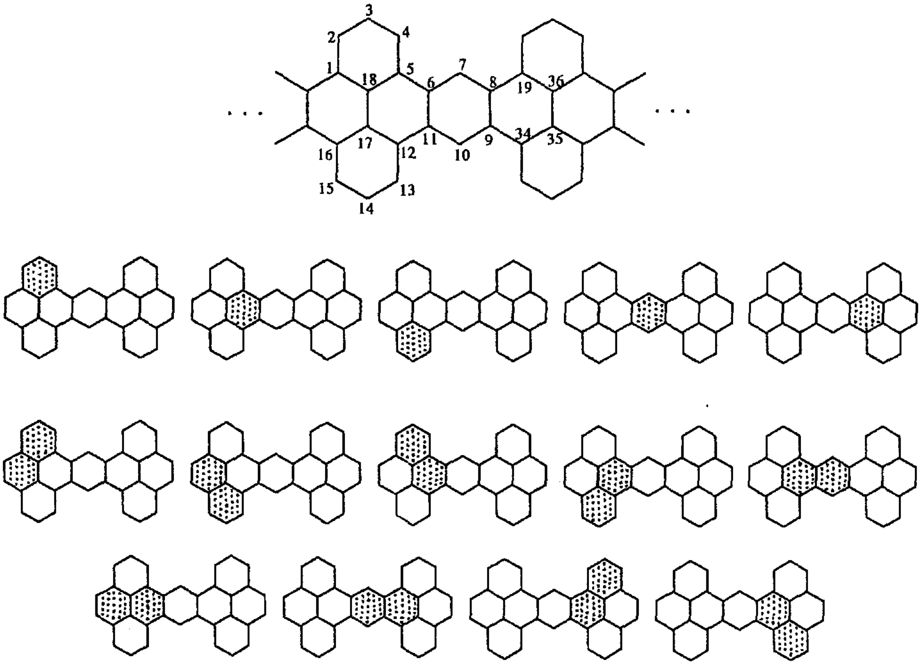


Fig. 4. Numbering of carbon atoms for Table 6; all distinct rings contributing to six membered conjugated circuits (middle) and all pairs of adjacent rings contributing to ten-membered conjugated circuits

Table 6. Contributions of all 6-cycle conjugated circuits

Carbon atoms							R_1 contribution
1	2	3	4	5	18	C	0.40824829
1	18	17	16	45	44	B	0.09175171
5	6	11	12	17	18	D	0.09175171
6	7	8	9	10	11	E	0.40824829
8	9	34	35	36	19	A	0.09175171
12	13	14	15	16	17	C′	0.40824829

Contribution of all 10-cycle conjugated circuits Contributions of triphenylene "cell" are indicated by +

Carbon atoms											R_2 contributions
1	2	3	4	5	6	11	12	17	18	+	0.09175171
1	2	3	4	5	18	17	16	45	44	+	0.09175171
1	18	5	6	11	12	17	16	45	44	+	0
1	18	17	12	13	14	15	16	45	44	+	0.09175171
1	18	17	16	45	46	47	42	43	44		0.09175171
5	6	7	8	9	10	11	12	17	18	+	0.09175171
5	6	11	12	13	14	15	16	17	18	+	0.09175171
6	7	8	19	36	35	34	9	10	11	+	0.09175171
8	9	34	33	32	31	30	35	36	19		0.09175171
8	9	34	35	30	29	24	23	36	19		0
8	9	34	35	36	23	22	21	20	19		0.09175171

4.3 *Very accurate estimate of the limit*

We have already seen that the extrapolation gave a very good value for the limiting contributions R_1 and R_2. The question is whether the "approximate" limit was fortuitously so good? In this section we want to study this question and will try, on the one hand, to obtain some insights into factors that can "spoil" the accuracy and, on the other hand, will consider alternative routes to the limit. The importance of such study is for the cases of limiting processes for which no cyclic boundary conditions apply that would facilitate "exact" calculations. In this class would belong the so-called "fractal benzenoids" [23], and closely related dendritic systems which form patterns of self-similar substructure. While only a few of the smaller members of such molecules may exist or are likely to be prepared, the model of fractal and dendritic benzenoids is of interest for a better understanding of important amorphous systems, which locally and globally may have, statistically speaking, self-similar structure.

Yet another recent interesting use of dendritic systems built from smaller benzenoids is concerned with the reversal of the traditional approximation of an infinite planar system (e.g., graphite) simulated by smaller systems having cyclic boundary conditions. In the reversed problem the opposite is considered: approximating finite systems having cyclic boundary conditions by infinite systems. An application of such is in the domain of fullerenes and other caged carbon structures where by representing such by dendritic structures of ever increased size one can obtain some insight of the roles and contributions of the 12 "pentagons" in those systems, which are absent in the associated dendritic benzenoids [24].

In Table 7 we listed several schemes of establishing or approximating the limiting contributions of R_1 to the unit cell resonance energy. There are three distinct models considered.

(1) Expansion in a geometric series.
(2) Polynomial optimal curve fitting.
(3) Orthogonal optimal curve fitting.

The first approach which we have labeled as "perturbation method", is suggested from a knowledge of properties of transfer matrix for deriving the Kekule structure count (K) and the count of conjugated circuits [4]. For any finite molecule which is a member of a family that is based on a repeating monomer unit,

Table 7. The limiting values for R_1 contribution

Method	Limit
$A + B/N + C\mu^N + D\mu^N/N$	0.15649542
Quadratic fit	0.15647919
Residuals quadratic	0.15647919
Slopes (tangent at the "end")	0.15647531
Slopes (limits of tangents)	0.15647236
Cubic fit	0.15647218
Residuals cubic	0.15647222
Quartic fit	0.15647212
Residual quartic	0.15647235
Quintic fit	0.15647203
Residual quintic	0.15647189

one can obtain K from an expression like

$$K_N = A\lambda_1^N + B\lambda_2^N, \tag{1}$$

where the constants A and B depend on the form of the "end" groups, while λ_1 and λ_2 are the latent roots of the transfer matrix depending only on the monomer unit. Index N indicates the number of the repeating units in a finite molecule M_N. In general, there are further eigenvalues and further terms for each eigenvalue added into the equations for K_N, but for "doubly connected" polymers (i.e., those not wider than one ring at some point in the unit cell) there are but two relevant eigenvalues.

The contributions of 6-cycle conjugated circuits may heuristically be identified by taking "formal" derivative of the above expression (conjugated circuit counts being a "derivative" of K_N in some formal sense):

$$\begin{aligned}\partial K_N &= \partial(A\lambda_1^N + B\lambda_2^N)\\ &= NA\lambda_1^{N-1}\partial\lambda_1 + NB\lambda_2^{N-1}\partial\lambda_2 + \lambda_1^N\partial A + \lambda_2^N\partial B\\ &= (\alpha N + \alpha')\lambda_1^N + (\beta N + \beta')\lambda_2^N,\end{aligned} \tag{2}$$

where $\alpha, \alpha', \beta, \beta'$ are appropriate new constants, e.g., with $\alpha = A(\partial\lambda_1)/\lambda_1$ and $\alpha' = \partial\lambda_1$. The per-cell contribution for R_1 follows by dividing the above by NK_N:

$$\frac{\partial K_N}{NK_N} = \frac{(\alpha + \alpha'/N)\lambda_1^N + (\beta + \beta'/N)\lambda_2^N}{A\lambda_1^N + B\lambda_2^N}. \tag{3}$$

Finally, introducing the symbol μ for the eigenvalue ratio λ_2/λ_1, with λ_1 being identified as the maximum (magnitude) eigenvalue, and then dividing both the numerator and the denominator by $A\lambda_1^N$ we obtain

$$\frac{\partial K_N}{NK_N} = \frac{(\alpha + \alpha'/N)/A + ((\beta + \beta'/N)/A)\mu^N}{1 + (B/A)\mu^N}. \tag{4}$$

The expansion of

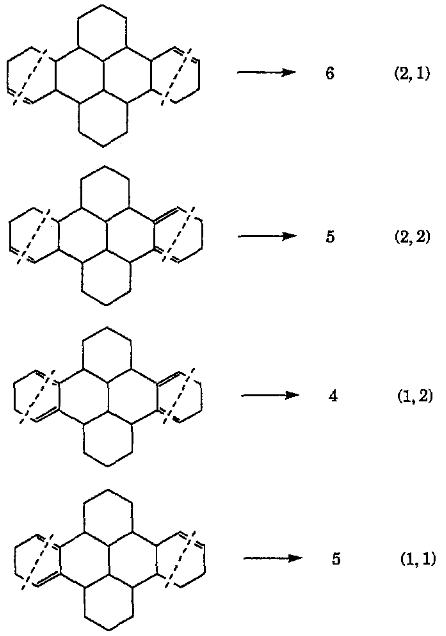
$$1/(1 + B/A\mu^N) \tag{5}$$

in a geometric series yields the final expression

$$\frac{\partial K_N}{NK_N} = (A_1 + A_1'/N) + (B_1 + B_1'/N)\mu^N + O(\mu^{2N}). \tag{6}$$

Here A_1, B_1 and μ should be independent of the end group parameters, while A_1', B_1' should be dependent on the end groups and can in general be derived exactly by knowing the end groups and the transfer matrix. In Fig. 5 we illustrate the four elements of a 2×2 transfer matrix, the determinant of which leads to the quadratic secular polynomial $x^2 - 10x + 1$ which has roots $\lambda_1 = 5 + \sqrt{24} \cong 9.898979486$ and $\lambda_2 = 5 - \sqrt{24} \cong 0.101020514$, giving for $\mu \cong +0.010251443$.

The curve fitting of the expansion in terms of $1/N$, μ^N and μ^N/N for $N \leqslant 12$ gives the limit for R_1 of 0.156491 as compared to the "exact" value of 0.156472. In view that R_1 takes the value of 0.869 eV the difference is 0.000020 eV. Nevertheless, in this paper we are interested in formulating procedure which can eventually give the limit to ever increasing accuracy. This, of course, is well below the accuracy of the model. The error here is due to truncation of the mixed power-geometric series. Of course, fitting to the form in Eq. (4) using an ever larger range of N should yield, in principle, exact asymptotic results.



$$\mathbf{T} = \begin{pmatrix} 5 & 4 \\ 6 & 5 \end{pmatrix}$$

Fig. 5. Construction of the transfer matrix for the repeating monomer unit

The remaining results listed in Table 7 are based on curve fitting with high-degree polynomials in $1/N$ using the information on the first $N = 16$ members of the family. The constant terms of the power expansion represent the limiting values

$N = 1$	0.1565357
$N = 2$	0.1564892
$N = 3$	0.1564722
$N = 4$	0.1564721
$N = 5$	0.1564720
$N = 6$	0.1564720
$N = 7$	0.1564720
$N = 8$	0.1564721
$N = 9$	0.1564720
$N = 10$	0.1564718

Clearly, with $N = 5$ we achieved the accuracy of the fittings sufficient to get the limit at 0.1564720. The fitting of even higher polynomials (particularly for $N = 8$ and above) already show numerical oscillations due to statistically "unfair" adjustments to numerical data to minimize the residuals.

In summary, the results of Table 7 convincingly suggest that the limit for the coefficient of R_1 can be obtained fitting with the polynomials of fifth degree in $1/N$ using the data on the initial $N = 16$ molecules. The only problem that we have to consider is how reliable are the numbers so derived. The polynomial fit (derived by Statworks Macintosh software) is identical to a stepwise multiple regression in which various powers of $1/N$ are taken as variables. Stepwise regression does not necessarily identify the optimal combination of descriptors. For example, if we decide to use the regression of 5th power but consider first the highest power and then the two highest powers and so on, instead of the limiting values shown above for $N = 1$–5, we would obtain (using the abbreviation $x = 1/N$) the following:

Polynomial terms	Limit (constant term)
x^5	0.15682893
x^5, x^4	0.15675137
x^5, x^4, x^3	0.15666556
x^5, x^4, x^3, x^2	0.15656975
x^5, x^4, x^3, x^2, x	0.15647203

Although we have reached the same limit, since the final equation is based on the same five variables, from the above we could not so convincingly claim that we have reached very good approximation for the limit! If one is to add x^6 we would confirm that we have reached the limit, but only a posteriori, since the above results do not suggest that we are even close to the limit. It is only when the same limit is obtained by using additional powers (in whatever order) that some confidence in the above result would follow.

The reason that we have obtained very good limit truncating a power expansion at $N = 5$ is that the power expansion effectively parallels the mixed power-geometric expansion which, as we have seen from the introductory comments on limits, is the natural expansion in this case; but in the general case we need not know that. Moreover, for polymer strips of a "wider" form, larger, or for "higher-order" models even for the studied polymer transfer matrices would arise with several eigenvalues. All this makes the convergence of the constant terms less apparent in the corresponding power expansion and multiple regressions.

4.4 *Orthogonal expansion*

The constant term and other coefficients in multiple regression are sensitive to truncation of an expansion. To avoid the "instabilities" of the coefficients, which can change dramatically with inclusion of a higher power or an additional descriptor, or exclusion of some descriptors even if their role was marginal, one makes the variables involved in the expansions mutually orthogonal. The general procedure for this has been outlined [25, 26]. The advantage of the orthogonal descriptors is in their interpretability. Since they remain constant as new variables are added they signify the contributions of already used descriptors and as such can be transfered or compared to similar results from other studies.

We have applied the procedure to derive "stable" regression equations by first constructing the orthogonalized variables (Table 8). Our first descriptor Ω_1 is $1/N$. The next descriptor Ω_2 is the part of $1/N^2$ which does not correlate with $1/N$. By definition this is the residual in the regression of $1/N^2$ against $1/N$. Similarly, we obtain Ω_3 by first finding the residual (from the regression of $1/N^3$ against $1/N$) and then following with a regression of this residual against the residual of the regression of $1/N^2$ against $1/N$, which we already labeled as Ω_2. The process continues with additional descriptors which are gradually made orthogonal to each of the already introduced descriptor. The software Statworks allows one to construct orthogonal descriptors easily as it makes possible to save and store residuals of various regressions as needed.

Table 8

	$^1\Omega$	$^2\Omega$	$^3\Omega$	$^4\Omega$	$^5\Omega$
1	1.0000000	0.1164032	0.0044002	0.0000708	0.0000006
2	0.5000000	−0.1362157	−0.0267850	−0.0014014	−0.0000325
3	0.3333333	−0.1092778	0.0048286	0.0028111	0.0001814
4	0.2500000	−0.0750252	0.0129148	0.0009758	−0.0001520
5	0.2000000	−0.0477871	0.0132782	−0.0003967	−0.0001398
6	0.1666667	−0.0268837	0.0112079	−0.0010498	−0.0000478
7	0.1428571	−0.0105780	0.0084356	−0.0012348	0.0000299
8	0.1250000	0.0024451	0.0055722	−0.0011488	0.0000743
9	0.1111111	0.0129930	0.0028817	−0.0009274	0.0000918
10	0.1000000	0.0216892	0.0004283	−0.0006384	0.0000891
11	0.0909091	0.0290060	−0.0017998	−0.0003144	0.0000706
12	0.0833333	0.0352461	−0.0038138	0.0000215	0.0000413
13	0.0769231	0.0405853	−0.0056108	0.0003482	0.0000071
14	0.0714286	0.0452414	−0.0072381	0.0006673	−0.0000317
15	0.0666667	0.0492592	−0.0086760	0.0009612	−0.0000696
16	0.0625000	0.0528990	−0.0100242	0.0012557	−0.0001127

In this way, we obtain for the polynomial of degree five with orthogonalized variables:

$$R_1 = 0.15653572 + 0.00185594\Omega_1 - 0.00050845\Omega_2 + 0.00019635\Omega_3 + 0.00001415\Omega_4 + 0.00026478\Omega_5.$$

If one is interested in approximations using lower-degree polynomials, one can truncate the above polynomial, the remaining coefficients will remain the same.

Two multiple regressions, one based on powers of $1/N$ variables and the other on the corresponding orthogonalized variables are associated with the same regression coefficients and the same standard errors of prediction. The difference is in the interpretability of the coefficients of the regression equation. From Table 4 (the row belonging to $1/N^2$), for example, one would think that the contribution of $1/N$ is close to 0.002462. However, since $1/N$ (over the finite domain given by $N = 16$) involves a constant (although small) contribution the independent part of $1/N$ is not given by 0.002462. It is smaller and is given by the corresponding coefficient in the orthogonal expansion: 0.001856.

We are, however, interested in the limiting behavior of the expansion. The constant term in the orthogonal expansion 0.15653572 is visibly inferior as an approximation to the limit than the constant term in non-orthogonal expansion 0.15647203. How can that be? Hence, it appears that while by orthogonalization we get an insight into the role of the contributing factors, apparently we "lost" on the accuracy of our prediction. But that cannot be, because both expansions, the orthogonal and the non-orthogonal, are, from the point of view of chemical information, fully equivalent. The reason for the apparent discrepancy lies in the variables. While powers of $1/N$ can be neglected when considering the limit $N \to \infty$, they do not go to zero as $N \to \infty$ in the case of orthogonal expansion. When expanding Ω_2 in power series of $1/N$ the contribution is not zero but 0.111163. Hence, the correction of the constant term of the orthogonal regression equation is given by the product of $(-0.00050844) \times (0.111163) = -0.00005652$.

Thus, at this level (the quadratic approximation) we obtain as the limit for R_1 0.15647919, precisely the value reported in Tables 4 and 5 for non-orthogonal quadratic power expansion.

Such parallelism extends to higher-degree polynomials, although because of the effects of rounding errors that gradually accumulate in the iterative construction of orthogonal descriptors some numerical differences will appear reflecting the effects of rounding errors on the highest decimal places. The exceptional good behavior of $1/N$ expansion when searching for the limit is due to the fact that all variables in the limit make no contribution so that constant term carries the desired information.

The plot of data points (Fig. 6) shows that linear expansion cannot account for the slight "bending" of the data points. The quadratic expansion obviously does better job, but will nevertheless be associated with some error.

Instead of fitting higher polynomials to the set of data points we could make a good estimate of the limit even by using a linear expression if we could determine the slope to the curve near the "end" points of the graph that approach $N \to \infty$, or $1/N \to 0$.

If we select the end point $N = 16$ ($x_1 = 0.0625$ and $y_1 = 0.15662282$ and use the slope as determined by two close points ($m = -0.00236016$), then the slope-point equation of a line

$$y - y_1 = m(x - x_1)$$

for $x = 0$ immediately gives for the limit of the R_1 contribution: 0.15647531. This is indeed a very good estimate.

One can do even better by taking the limiting value for the slope as we gradually cut the number of points associated with small N (Table 9). In the case of the quadratic fit the limiting slope is $m = 0.0024069321$ (see the lower part of Table 9) which leads to the correction $0.0625\,m = -0.000150433$ and the limit for R_1 is 0.15647236, which is a significant improvement when using the estimated slope.

Finally, an even better result is obtained when one seeks the limit for the constant term by reducing the number of data points by eliminating information on smaller members of the series of molecules. As we can see from Table 9, at the bottom of the right column, the cubic approximation (and higher) when constant terms are expanded in powers of $1/N$ gives extremely good limits.

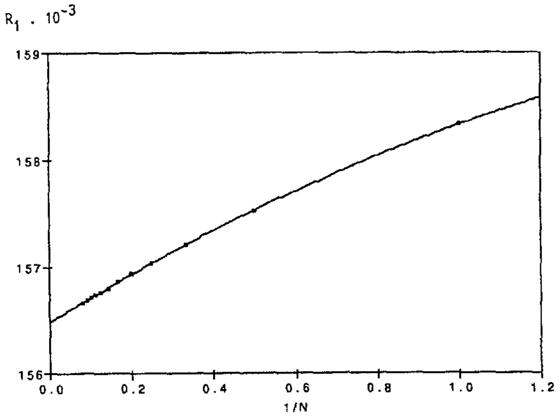


Fig. 6. Plot of $\#R_1/nK$ against $1/N$

Table 9. The change in the coefficient of $1/N$ and the constant term as the number of data points corresponding to smaller members of the series are eliminated from polynomial fit

# Points	Coefficients $1/N$	Constant
16	0.0018559372	0.15635710
15	0.0020935366	0.15601890
14	0.0021875361	0.15649076
13	0.0022372449	0.15648554
12	0.0022682676	0.15648256
11	0.0022896494	0.15648065
10	0.0023053844	0.15647932
9	0.0023175064	0.15647834
8	0.0023271742	0.15647760
7	0.0023350610	0.15647702
6	0.0023416791	0.15647654
5	0.0023473241	0.15647615
4	0.0023521668	0.15647583
3	0.0023564039	0.15647555
2	0.0023601598	0.15647531
Limits		
Linear		0.15647032
Quadratic	0.0024069321	0.15647135
Cubic	0.0024047024	0.15647213
Quartic	0.0024165578	0.15647214
Quintic	0.0024151768	0.15647215

5 Local aromatic properties

It is of interest to see how benzenoid character of individual rings approach the limiting values as the size of a molecule increases. As molecular size increases the role of the terminal rings, i.e., the boundary, will be less and less pronounced. From Table 8 in which the resonance energies of individual rings are listed we see that indeed the changes in the resonance contributions of the individual rings decrease. We can differentiate two types of Clar-sextet rings and the "central" rings which Clar classifies as "empty" rings [20]. However, even the two Clar rings are not equivalent. The "peripheral" rings have a higher R_1 content, which is slightly less pronounced in the "bridge" rings. The so-called "empty" rings are not strictly empty (of contributions to R_1) but have much reduced local aromatic character [10, 13, 27, 28].

6 Recursions

We can extend the above considerations to much larger finite systems using expressions for ring RE in a recursive manner. When the Kekulé-structure count follows a recursion

$$K_{n+1} = aK_n + bK_{n-1}$$

within a family of structurally related molecules, then the conjugated-circuit counts follow a related recursion:

$$\partial K_{n+1} = 2a\partial K_n + (2b - a^2)\partial K_{n-1} - 2ab\,\partial K_{n-2} - b^2\partial K_{n-3},$$

where as earlier ∂ is a graph-theoretical "differential" operator, e.g., the operator of deleting rings.

For our families of graphs we have already seen that Kekule numbers form the sequence

Family I	20;	198;	1960;	19402; ...
Family II	40;	396;	3920;	38804; ...

Each molecule in the second family has twice as many Kekule valence structures than the corresponding member in the first family. One way to find the recursion is to take these initial values and solve the corresponding equations for a and b. We can write the corresponding system of equations as

$$\begin{pmatrix} K_3 \\ K_4 \end{pmatrix} = \begin{pmatrix} K_2 & K_1 \\ K_3 & K_2 \end{pmatrix} \begin{pmatrix} a \\ b \end{pmatrix},$$

which (using Sarus rule) immediately gives for a and b,

$$a = \frac{K_3K_2 - K_4K_1}{K_2K_2 - K_3K_1} = 10,$$

$$b = \frac{K_2K_4 - K_3K_3}{K_2K_2 - K_3K_1} = -1.$$

Hence, we obtain the recursion

$$K_n = 10K_{n-1} - K_{n-2}.$$

Here for the first family $K_1 = 20$ and $K_2 = 198$ are the initial values, while twice those values of K_1 and K_2 are initial values for the second family. In fact, one can easily verify that we could have started the recursions by including benzene with $K_0 = 2$ as the first member of the first family and then continue with $K_1 = 20$, to recur to K values for the higher members of the family.

The recursions for K can also be derived directly by examining smaller members of each family. We know that the recursion involves only two successive members, because the corresponding transfer matrix which gives possible distributions of bonds across the repeating cell has only two rows. However, while the recursion expression does not depend on the end groups construction a direct construction of the recursion may be seemingly hindered by the presence of "awkward" end groups. This is illustrated for the first family when one assigns CC double and CC single bonds to the exposed CC bonds in the last benzene ring. One then obtains successively:

$$K_1 = 2 + 2 \times 9,$$

$$K_2 = 9K_1 + 2 \times 9,$$

$$K_3 = 9K_2 + 8K_1 + 2 \times 9,$$

$$K_4 = 9K_3 + 8K_2 + 8K_1 + 2 \times 9,$$

The above recursion also has a simple mathematical form, but differencing successive expressions here reveals that the above can be reduced to the earlier recursion involving only two consecutive members of the family.

The recursion relations for individual rings for R_1 as well as all higher R_n conjugated circuits are given by the same recursion valid for the Kekule valence structures:

$$X_{n+1} = 10X_n - X_{n-1}.$$

The regular increase in the coefficients allows one to generate the contributions of 6- and 10-membered conjugated circuits in the formulas for the RE of rings for which initial coefficients are known.

7 Going beyond R_1 and R_2 contributions

Although contributions from higher conjugated circuits to the molecular resonance energy decreases in larger benzenoids the number of higher conjugated circuits also increases. In order to estimate the role of such higher conjugated circuits, we will now consider contributions of 14-membered conjugated circuits R_3.

The enumeration of higher conjugated circuits is not prone to simple calculation, since contributions arise from conjugated circuits of both, different relative orientation and of different shape, although in any case recursions as in the second equation of Sect. 6 continue to hold. For molecules considered in this paper we were, however, able to arrive at the exact counts of R_3 being able to extrapolate the count of conjugated circuits for new rings (not occurring in smaller molecules) from "old" rings of a molecule of a same size. Once the initial coefficients for the "new" rings are found, we can use the recursion $X_{n+1} = 10X_n - X_{n-1}$ and derive the coefficients that enumerate the contributions of these "new" rings for molecules of even greater size. The count of the conjugated circuits R_1, R_2 and R_3 for initial members of our family of structures is listed in Table 10.

Since we obtained the count of conjugated circuits of R_1 and R_2 using the computer we will here only outline the exact count of conjugated circuits R_3. Fig. 7 illustrates labeling of individual symmetry non-equivalent rings for one of the families considered. The Clar sextet rings, A, C, E, G, I, etc., are indicated as hexagons with an inscribed circle. These hexagons do not contribute towards R_3. So we have to consider only rings B, D, F, H, J, L, N, etc. To find the contributions of the rings near the "ends" of the molecules, the rings B, D, F, one can apply the recursion. These rings appear in smaller members of the family and since the counts of conjugated circuits for smaller molecules are known, one can continue with recursion and generate coefficients for these rings for arbitrary large members of the family.

The problem is to determine the contributions from the "inside" rings, rings which appear for the first time in the sequence of family members, and which cannot be determined from the recursion. In Fig. 8 we show that there is a one-to-one correspondence for the count of R_3 conjugated rings of the shape of "phenanthrene" and the count of R_2 conjugated circuits. Since the count of the latter is already found (using our computer program), we need only to find the count of 14-membered conjugated circuits of the "pyrene" perimeter. The molecules that we consider do not have 14-membered conjugated circuits of the "anthracene" shape.

Figure 9 shows how a count of R_3 conjugated rings of a shape defined by the periphery of pyrene for a "deeper" ring, i.e., a ring away from the periphery,

Table 10

Ring	R_1	R_2	RE	REPE
A	0.450000	0.100000	3.325200	
B	0.100000	0.300000	0.642800	
C	0.400000	0.200000	0.793600	
			4.761600	0.158720
A	0.449495	0.101010	3.323680	
B	0.101010	0.303030	0.649292	
C	0.404040	0.191919	1.593292	
D	0.090909	0.181818	0.494908	
E	0.409091	0.181818	1.600908	
			7.662080	0.159627
A	0.449495	0.101020	3.500816	
B	0.101020	0.303061	0.649356	
C	0.404082	0.191837	1.593356	
D	0.090815	0.271449	0.582780	
E	0.408673	0.182653	3.200552	
F	0.091837	0.275510	0.590328	
G	0.408163	0.275510	0.844938	
			10.962130	0.166093
A	0.449490	0.202041	3.522472	
B	0.101021	0.303062	0.649364	
C	0.404082	0.191834	1.593352	
D	0.090815	0.272446	0.583760	
E	0.408670	0.182662	3.200552	
F	0.091846	0.275539	0.590388	
G	0.408205	0.183587	1.599588	
H	0.091743	0.275229	0.589724	
I	0.408257	0.183486	1.599652	
			13.938850	0.165820

becomes equivalent to the count of R_1 conjugated circuits for the "inner" ring, i.e., a ring which is one "periodic unit" close to the molecular "end". Moreover, the count pertains to a molecule which is also one periodic unit smaller. So formally we can write for the count of R_3 conjugated circuits of "pyrene" shape for the top molecule of Fig. 8:

Count of R_3 in molecule M_n	Count of R_1 in molecule M_{n-1}
D, F	C
H, J	G
L, N	K
P, R	O
T, V	S
X, Z	W

and so on.

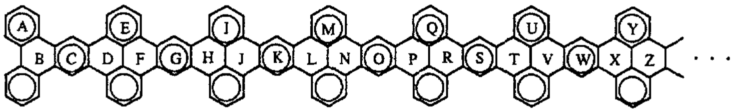


Fig. 7. Labeling of individual benzene rings. Clar sextet rings are shown by inscribed circles

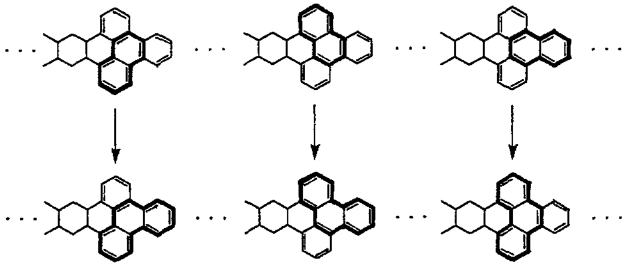


Fig. 8. One-to-one correspondence between the count of R_2 conjugated circuits and R_3 conjugated circuits of the "phenanthrene" shape

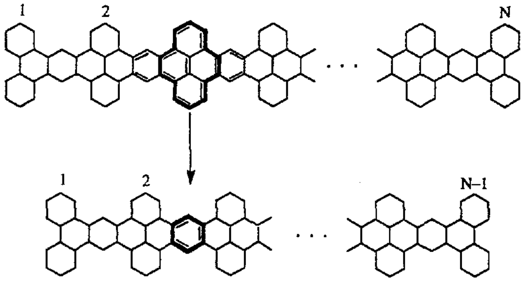


Fig. 9. Equivalence of the count of 14-membered conjugated circuit of "pyrene" shape in a molecule with N monomer units to the count of 6-membered conjugated circuits in a molecule of size $N-1$

Since the coefficients for the rings to the left and of smaller molecules are already known, one can continue with the recursion indefinitely. Before we can write the final result for the count of R_3 in molecule M_n, we have to find contributions of 14-membered conjugated circuits of "anthracene" and "phenanthrene" shape. In our molecules the former do not exist, while the latter give the same count as the count R_2, as one can easily verify. Therefore, to obtain the contributions of the count of R_3 in molecule M_n, we have to add to the already known count of R_2 the count of R_1 in preceding molecule and the corresponding lexicographically relevant "preceding" ring.

In Table 10 we have included contributions for smaller members of the family that starts with tetrabenzantracene.

8 Discussion

Benzenoid polymers continue to receive considerable attention in the literature [29]. One can think of at least two important reasons for this continuing interest. On the one hand, computations on such polymers offer insights on models for graphite and other closely related structures, such as recently discussed buckytori [30, 31], and fullerene cones [32]. On the other hand, such polymers may

Table 11

Structure	Ring	R_1	R_2	R_3
$n = 30$	A	18	4	
$K = 40$	B	4	12	12
	C	16	8	
$n = 48$	A	178	40	
$K = 396$	B	40	120	120
	C	160	76	
	D	36	108	124
	E	162	72	
$n = 66$	A	1762	396	
$K = 3920$	B	396	1188	1188
	C	1584	752	
	D	356	1068	1228
	E	1602	716	
	F	360	1080	1240
	G	1600	720	
$n = 84$	A	17442	3920	
$K = 38804$	B	3920	11760	11760
	C	15680	7444	
	D	3524	10572	12156
	E	15858	7088	
	F	3564	10692	12276
	G	15840	7124	
	H	3560	10680	12280
	I	15482	7120	
$n = 102$	A	172658	38804	
$K = 384120$	B	38804	116412	116412
	C	155216	73688	
	D	34884	10465	120332
	E	156978	70164	
	F	35280	105840	121520
	G	156800	70520	
	H	35240	105720	121400
	I	156818	70484	
	J	35244	105732	121572
	K	156816	70488	
$n = 120$	A	1709138	384120	
$K = 3802396$	B	3837280	1152360	1152360
	C	1536480	729436	
	D	345316	1035948	1191164
	E	1553922	694552	
	F	349236	1047708	1202924
	G	1552160	698076	
	H	348840	1046520	
	I	1552698	697720	
	J	348880	1046640	
	K	1552320	697756	
	L	348876	1046628	
	M	1552322	697752	

include cases of unusual conductive properties and may become important for potential applications. Graovac et al. [33] discussed the structural conditions on the periodic unit that secures zero energy gap (i.e., no energy gap at all) for the HMO model with the restriction to singly connected polymers, while Klein et al. [34] as well as Hosoya et al. [35] discussed it more generally. Recently, Seitz and Schmalz [36] examined 30 different polymers built by fusing four or fewer fused hexagons per monomer unit and reported the resonance energies relative to graphite, as well as the resonance energies per site or resonance energies per electron (REPE). Such polymers of such size are all possible according to a proposed graph-theoretical classification scheme for fused polyhex polymers [37].

In Table 11 we first give the numerical values for the resonance energy contributions based on the exact count of 6-membered conjugated rings and 10-membered conjugated rings. We used the following parameters [11]: $R_1 = 0.869$ eV and $R_2 = 0.246$ eV. In the last two columns of Table 11 we give the contributions of R_3 which as we see makes some, even if not, dramatic change for the computed REPE. The numerical value for the contribution of 14-membered conjugated circuits is also $R_3 = 0.100$ eV [11].

As we see the values that we derived compare well with the REPE reported in the literature for similar benzenoid systems. For example, Zhu et al. [8] examined a fully benzenoid polyphenanthrene, i.e., benzenoid polymer having all non-adjacent rings can be assigned pi-sextets. This benzenoid polymer, among all reported, has the largest REPE 0.1553 eV, and is most similar to molecules studied in this report.

9 Cluster expansion

Another simple extrapolative approach with some chemical appeal is to use an (additive) cluster expansion [39]. In our present case we can view each monomer unit as an overall "site" or supersite and an oligomer as a linear chain of such (super) sites. We then write the resonance energy for an N-site chain as

$$E_N = \varepsilon_0 + N\varepsilon_1 + (N-1)\varepsilon_2 + \cdots + \varepsilon_N,$$

where ε_m is an m-site cluster term, the coefficient $(N - m + 1)$ of ε_m is the number of such m-site clusters in an N-site chain, and ε_0 is an end correction. It is straightforward to show

$$\begin{aligned}
\varepsilon_1 &= E_1 - \varepsilon_0 \\
\varepsilon_2 &= E_2 - 2E_1 + \varepsilon_0 \\
\varepsilon_3 &= E_3 - 2E_2 + E_1 \\
&\vdots \\
\varepsilon_m &= E_m - 2E_{m-1} + E_{m-2}, \quad m \geqslant 3
\end{aligned}$$

What we identify as an end may appear as a little bit ambiguous, as illustrated in Fig. 10, where alternative choices for the repeating unit for the same polymer are depicted. One thing that can be done is first to note that the $N = 1$ species contain $n = 30$ atoms, while only 18 atoms are added with any increase of N by 1, so that

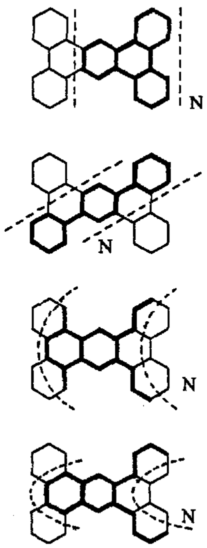


Fig. 10. The "ambiguity" in selecting end groups

we might associate 12 atoms with the end correction (as also indicated in Fig. 7) and simply take

$$\varepsilon_0 = (12/30)E_1.$$

Then from the data in Table 1, one obtains

N	E_N	ε_N
0		1.78656
1	4.46640	2.67984
2	7.18512	0.03888
3	9.90033	0.00054

Evidently, fairly rapid convergence here is observed. Again the interpretation here is that ε_0 is an end energy, ε_1 a monomer energy, ε_2 a monomer–monomer (or dimer correction) interaction, etc. For the second family of polymers in Table 2 a similar analysis now with $\varepsilon_0 = (6/24)E_1$ can be done to yield

N	E_N	ε_N
0		0.8934996
1	3.5973998	2.7039002
2	6.3159898	− 0.0146898
3	9.0343800	− 0.0001998
4	11.7527662	− 0.0000004

Again convergence is quite rapid. And we note (as has been done before) that the addition of higher terms does not change the earlier ones (much as with orthogonal descriptors) – in fact, the addition of more data points E_N does not change the earlier descriptors ε_N. Finally, in terms of the asymptotic expansion coefficients of Sect. 4 one may show $\varepsilon_N \sim \mu^N$.

Acknowledgements. Support for the research is acknowledged to the donors of the Petroleum Research Fund, administrated by the American Chemical Society, and to The Welch Foundation of Houston, TX.

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