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Original Scientific Paper

Resonance in Large Benzenoid Hydrocarbons*

Milan Randić,[a,**] *Douglas J. Klein,*[b] *Sherif El-Basil,*[c] *and Patricia Calkins*[a]

[a]*Department of Mathematics and Computer Science, Drake University, Des Moines, Iowa 50311, USA*

[b]*Department of Marine Sciences, Texas A&M, Galveston, Texas 77553, USA*

[c]*School of Pharmacy, University of Cairo, El-Aini Str., Cairo, Egypt*

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Pi-sextet resonance between Kekulé valence structures of benzenoid hydrocarbons are depicted by benzenoid resonance graphs. We outline the construction of the resonance graphs for families of benzenoid compounds. For the compounds considered the resonance graphs are built from fused n-dimensional cubes. We report the leading eigenvalue of the resonance graphs (λ) and two different bounds to the leading eigenvalue. Correlation between λ and RE is examined.

INTRODUCTION

Direct ambitious quantum chemical calculations on large benzenoid hydrocarbons are limited by computational restrictions. Even approximate MO calculations are often limited to systems of intermediate size. For example, the largest systems for which the MINDO type calculations of Dewar[1] were made have some half a dozen fused benzene rings.[2] The HMO calculations were routinely applied to benzenoid hydrocarbons having a dozen fused benzene rings.[3] However, with the available software even rather modest computers allow the treatement, *via* the HMO, of benzenoids up to 100 rings, while more serious computers would go, one could guess, beyond 500 rings.

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* Dedicated to the memory of Professor Stanko Borčić.

** Author to whom correspondence should be addressed.

Nevertheless, if one is interested in more sophisticated approaches, or if one is interested in systems that would approach properties of a bulk, alternative approaches have to be developed. It is estimated that the size of system that will simulate bulk properties is around 10^5 carbon atoms.[4]

Graph theory, has made it possible to extend the quantitative examination of large benzenoid hydrocarbons. Moreover, with suitable parametrization graph theoretic computational schemes approach SCF MO methods in their accuracy. The procedure of choice for large benzenoid hydrocarbons is the Method of Conjugated Circuits.[5–12] Conjugated circuits are defined within individual Kekulé valence structures as those circuits in which there is a regular alternation of CC single and CC double bonds. In the case of benzenoid hydrocarbons the conjugated circuits that occur within the set of Kekulé valence structures are all of the type $4n + 2$, with $n = 1, 2, 3, \ldots$.[5–7] The molecular resonance energy (RE) is given as the average weighted contribution of the conjugated circuits per Kekulé valence structure:

$$\mathrm{RE} = (aR_1 + bR_2 + cR_3 + \ldots)/K.$$

Here K is the number of Kekulé valence structures for the benzenoid considered and R_1, R_2, R_3, are the empirical parameters that give the relative contributions of the conjugated circuits of sizes 6, 10, and 14, respectively. The parameters R_1, R_2, R_3, were selected to reproduce the RE for smaller benzenoid hydrocarbons. The contributions from the larger conjugated circuits are neglected since they are very small. When the following parameters are used:[10]

$$R_1 = 0.869 \text{ eV}$$
$$R_2 = 0.247 \text{ eV}$$
$$R_3 = 0.099 \text{ eV}.$$

one obtains the molecular RE of benzenoids of satisfactorily quality. The coefficients a, b, c give the number of conjugated circuits of the size 6, 10, and 14, respectively. In the above scheme the count of the conjugated circuits of size 14 is limited to the minimal set of linearly independent conjugated circuits.

Enumeration of Kekulé Valence Structures

To obtain the molecular RE we need to enumerate conjugated circuits. For smaller benzenoids enumeration of Kekulé valence structures and the enumeration of conjugated circuits is straightforward. One first constructs all Kekulé valence structures and then by brute force finds K, a, b, and c. An algorithm for a systematic construction of all Kekulé valence structures has been outlined some time ago.[13]

For larger systems the enumeration of K, and the enumeration of conjugated circuits requires an efficient algorithm. Both problems have been considered in the literature. For K some approaches are applicable to special families of compounds,[11,14–16] some are more general.[17] For benzenoids K can also be obtain by computer,[18] the number of Kekulé structures being given as the square root of the determinant of the adjacency matrix. Hence, it can be obtained from the constant term of the characteristic polynomial.[11] Finally the enumeration of Kekulé valence structures has also been extended to benzenoid tori.[4] Some work has also been reported on enumeration of the so called higher energy Kekulé valence structures, the count of which is given by the coefficients of the Wheland polynomial[19] and the generalized Wheland polynomial.[20–22]

Enumeration of Conjugated Circuits

Enumeration of conjugated circuits is more involved. In some cases it is possible to obtain the count of conjugated circuits using the transfer-matrix method.[23] The transfer-matrix method may be viewed as a repeated use of recursions. This method often allows one to consider the limiting case of a molecule (polymer) when the number of carbon atoms in a system increases to infinity. Alternatively, it can be applied to a system with some periodicity, as is the case with buckminsterfullerene. The brute force approach can also be extended to large systems if they belong to a family of structurally related benzenoid hydrocarbons. One can then establish regularities in the pattern of a, b, c for smaller benzenoids, which extend to larger benzenoids.[24] Molecules of intermediate complexity (*i.e.*, those having up to dozen fused benzene rings and at most few hundreds of Kekulé valence structures) can be generated and examined exhaustively.[25–27] For the very large benzenoids one can also consider the statistical approach in which one examines only a sample of Kekulé valence structures in greater detail.[28,29] Rigorous enumerations of conjugated circuits are possible for structurally related hydrocarbons of increasing size that have a regular repeating unit.[30–32] The recursions arising in such calculations were carried out by computer program that works with integers of any size, in order to avoid errors that may arise by the iterative nature of the calculations.[33]

There is yet another powerful method for making conjugated-circuit computations. The method is based on the inversion of an antisymmetrically signed adjacency matrix.[34] That the approach is efficient and applies to large systems is witnessed by being used on a few thousand fullerenes, including over 1800 fullerenes with 180 carbon atoms.[35,36] Equally this approach has been applied to numerous polymer chains[37] as well as a larger number of 2-dimensional lattices[38].

The enumeration of conjugated circuits in an arbitrary benzenoid of large size may become computationally intensive, since the system may not belong to a recognized family of structures. Consider, for example, the benzenoid shown in Figure 1. To which family of benzenoids does it belong? Can

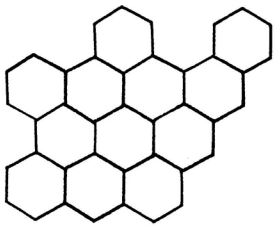


Figure 1. One of the benzenoid hydrocarbons considered in this article.

we derive the count of the conjugated circuits R_1, R_2 and R_3 for this benzenoid from the information on smaller benzenoids? Which smaller benzenoids should we consider? Is the exhaustive approach for enumeration of conjugated circuits the only available route for such molecules? It appears that the mentioned technique involving the inversion of an antisymmetrically signed adjacency matrix may give an answer for benzenoids of an arbitrary form and size.

Resonance Energy for Large Benzenoids

As discussed recently from the number of Kekulé structures and the number of the smallest conjugated circuits R_1, we can estimate the molecular RE.[39–42] In this paper we will show how using the benzenoid resonance graphs we can derive the count of K, and enumerate the smallest R_1 conjugated circuits for large benzenoids. The conjugated circuits R_2 and R_3 influence the regression equation of the first eigenvalue of the resonance graphs against the RE and are therefore indirectly taken into consideration.

The advantage of the present approach which uses the first eigenvalue of the resonance graph is that it avoids lengthy analysis of a large number of Kekulé structures. Resonance graphs of large systems can often be derived from the known forms for the resonance graphs of smaller benzenoids as illustrated in the next section. Moreover, we will show that there is very good correlation between the first eigenvalue of the resonance graphs and selected lower bounds for the first eigenvalue that can be derived. The simplest lower bound for the first eigenvalue is given by $2E/V$, where E is the number of edges in the resonance graph and V is the number of vertices. Hence, one can derive REs of large benzenoid by simply counting the edges and the vertices of its resonance graph.

BENZENOID RESONANCE GRAPHS

The resonance graph depict pi-sextet couplings between Kekulé valence structures. The vertices of the resonance graph represent the Kekulé valence structures and the edges connect those Kekulé structures in which all CC double bonds are at the same locations except for the bonds in a single benzene ring. In Figure 2 we illustrate the resonance graph for the nine Kekulé valence structures of benz[*a*]pyrene. We start with Kekulé structure 1 and superimpose it on all the remaining structures as illustrated in Figure 3. As we see only the combination 1,2 and 1,3 give a structure in which all CC double bonds remain fixed except for a single benzene ring, a single π-sextet. Hence vertex 1 belonging to Kekulé structure 1 is connected only to vertices 2 and 3 corresponding to the Kekulé valence structures 2 and 3. Next we repeat the process with valence structure 2 to find that it can be comined only with structure 4 to produce a single π-sextet. We contiue with the rest of the structures and thus obtain the resonance graph shown at the bottom part of Figure 2.

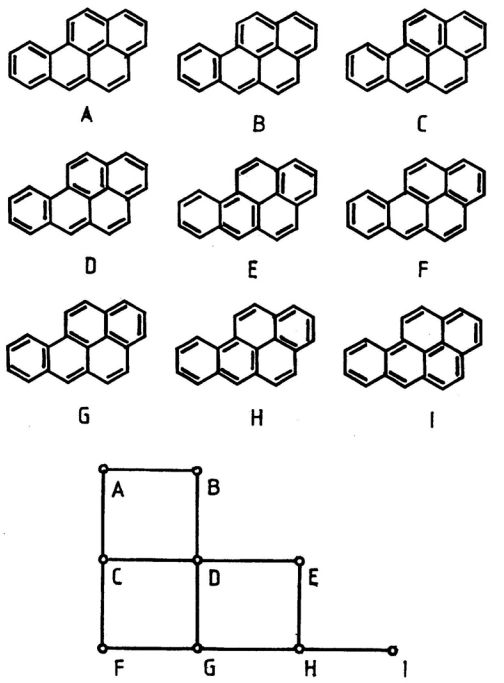


Figure 2. The nine Kekulé valence structures of benz[*a*]pyrene and the corresponding resonance.

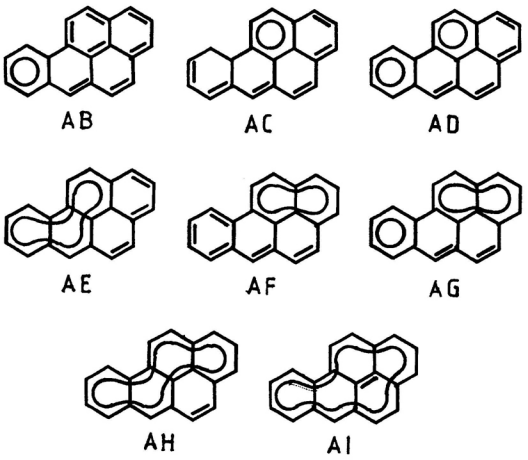
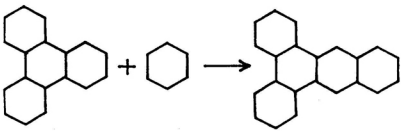


Figure 3. The superposition of the first Kekulé valence structures of benz[*a*]pyrene (of Figure 2) with the remaining eight valence structures to illustrate the resonance relationship among Kekulé valence structures that generate the resonance graph.

While the count of the vertices of the resonance graph give K, the sum of the valences of all the vertices, which equals $2E$ (E = the number of edges), gives the count of the smallest conjugated circuits R_1.

In Figure 4 we illustrate smaller benzenoids used to construct, *via* hexagon-fusion, larger benzenoids studied in this report. Figure 5 illustrates their resonance graphs drawn somewhat arbitrarily but so that the presence of n-dimensional cubes (n = 1 line segment, n = 2 square, n = 3 cube, n = 4 hyper-cube, *etc.*) is apparent. The resonance graphs for individual families shows common characteristics that allow construction of the resonance graphs for still larger members of families of benzenoids. In the top part of Figure 6 we illustrate the construction of the resonance graphs for dibenz[*a*,*c*]anthracene from the resonance graph of triphenylene. When we augment triphenylene by fusing a benzene ring linearly



the resonance graph for dibenz dibenz[*a*,*c*]anthracene is obtained by first doubling the edges of a square face of the cube. After we drew the copy of the fragment we then connect the copy of the fragment (here a square face of the cube) with the »original« fragment in the parent resonance graph. The resulting graph is the resonance graph of the next member of the family.

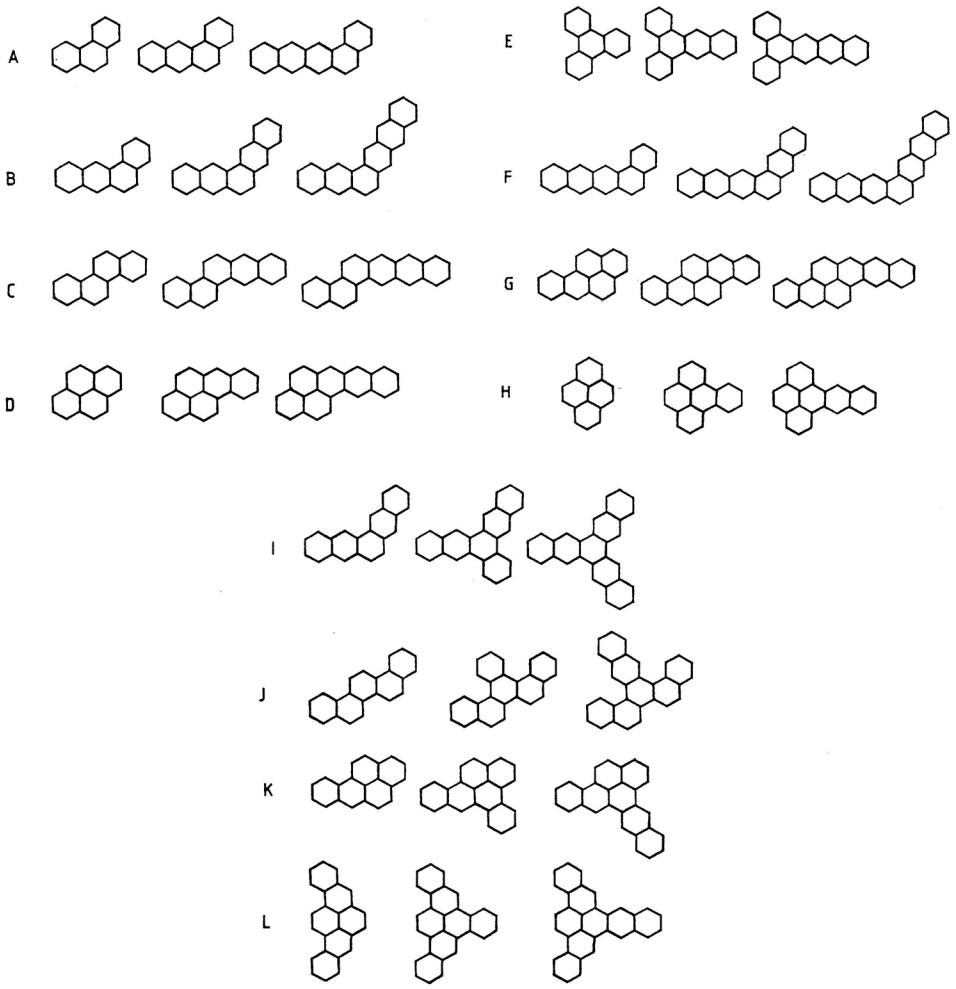
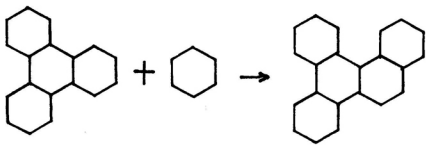


Figure 4. The parent benzenoid hydrocarbons considered in this article. Observe that several structures apper in more than one family. Hence there is some cross-labeling, *e.g.*, $B_1 = A_2$, $F_1 = A_3$, $F_2 = B_3$, $D_2 = G_1$, *etc.*

If we augment triphenylene by fusing a benzene ring angularly:



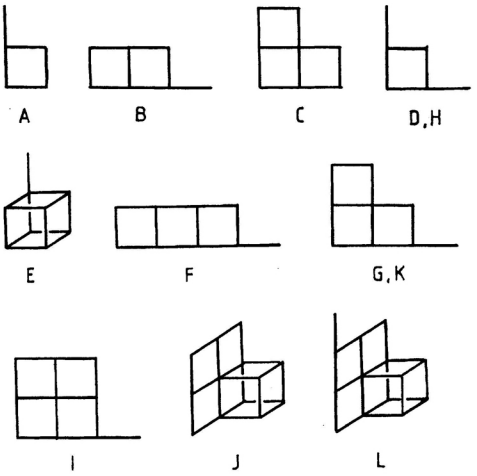
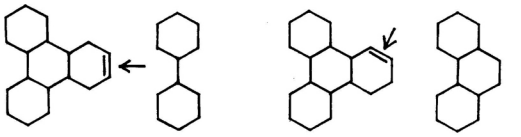


Figure 5. The resonance graphs for the parent benzenoid hydrocarbons of Figure 3.

the resonance graph for the derived dibenzphenanthrene is constructed by first doubling the edges of the periphery of the cube that involves the exocyclic edge. After we drew the square with the pending edge we connect this fragment with the corresponding vertices same fragment in the parent resonance graph (bottom part of Figure 6). The resonance graphs for the higher members for each family considered are obtained by repeating the outlined procedure.

One can determine the »face« of the parent resonance graph that has to be duplicated in order to obtain the resonance graph of the larger benzenoid without an inspection of the resonance graphs of the smaller benzenoids. We need only know the parent resonance graph and its Kekulé valence structures. In order to decide which »face« of the parent graph will be duplicated we need to know the Pauling bond orders for the parent benzenoid.[43] Pauling bond orders for smaller benzenoids can be obtained as the quotient K'/K, where K is the number of Kekulé valence structures and K' is the number of the Kekulé valence structures for the subgraph G' obtained from the molecular graph G of the benzenoid considered by deleting the selected bond and bonds next to it.[44] In the case of triphenylene we obtain for the two peripheral CC bonds of interest the following bond orders:



G $K = 9$ G' $K' = 4$ Bond order 4/9

G $K = 9$ G' $K' = 5/9$ Bond order 5/9

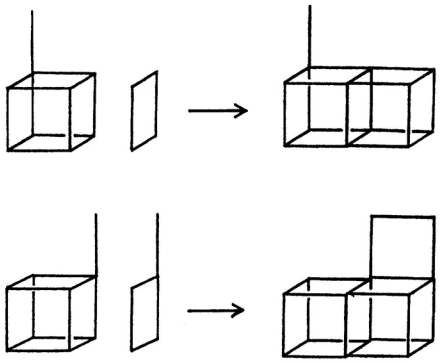


Figure 6. Construction of resonance graph for a larger benzenoid from that of the parent structure.

If we fuse a benzene ring to the bond with $K' = 4$ we should duplicate the »face« having four vertices, and if we fuse a benzene ring to the bond with $K' = 5$ we should duplicate the »face« having five vertices. It is not difficult to see the reason for such choices. All the nine Kekulé valence structures of triphenylene upon fusion of an additional benzene ring will give rise to a Kekulé structure for the augmented benzenoid whether the particular site of fusion is C=C or C–C. However, in addition to these Kekulé structures, the Kekulé structures which have CC double bonds at the site of fusion give rise to additional valence structures for the augmented benzenoid. These Kekulé valence structures are obtained by replacing C=C by a single C–C bond and two exocyclic C=C bonds.

The Kekulé structure count for the augmented benzenoid is given by $K + 2K'$, with $K + K'$ Kekulé valence structures of the first type and K' Kekulé valence structures of the second type. Hence, K' new vertices have to be introduced in the resonance graph of the parent benzenoid hydrocarbon to obtain the resonance graph of the augmented benzenoid. Such considerations will often suffice to indicate the »face« of the resonance graph of the parent benzenoid that need to be duplicated in order to derive the resonance graphs for the larger system.

RESONANCE GRAPHS OF LARGE BENZENOIDS

In Figure 7 we depict the resonance graphs for the families of the benzenoid hydrocarbons considered here. The resonance graphs are shown only for the leading members of each family. The resonance graphs of benzenoid hydrocarbons have very regular structural features. The resonance graphs

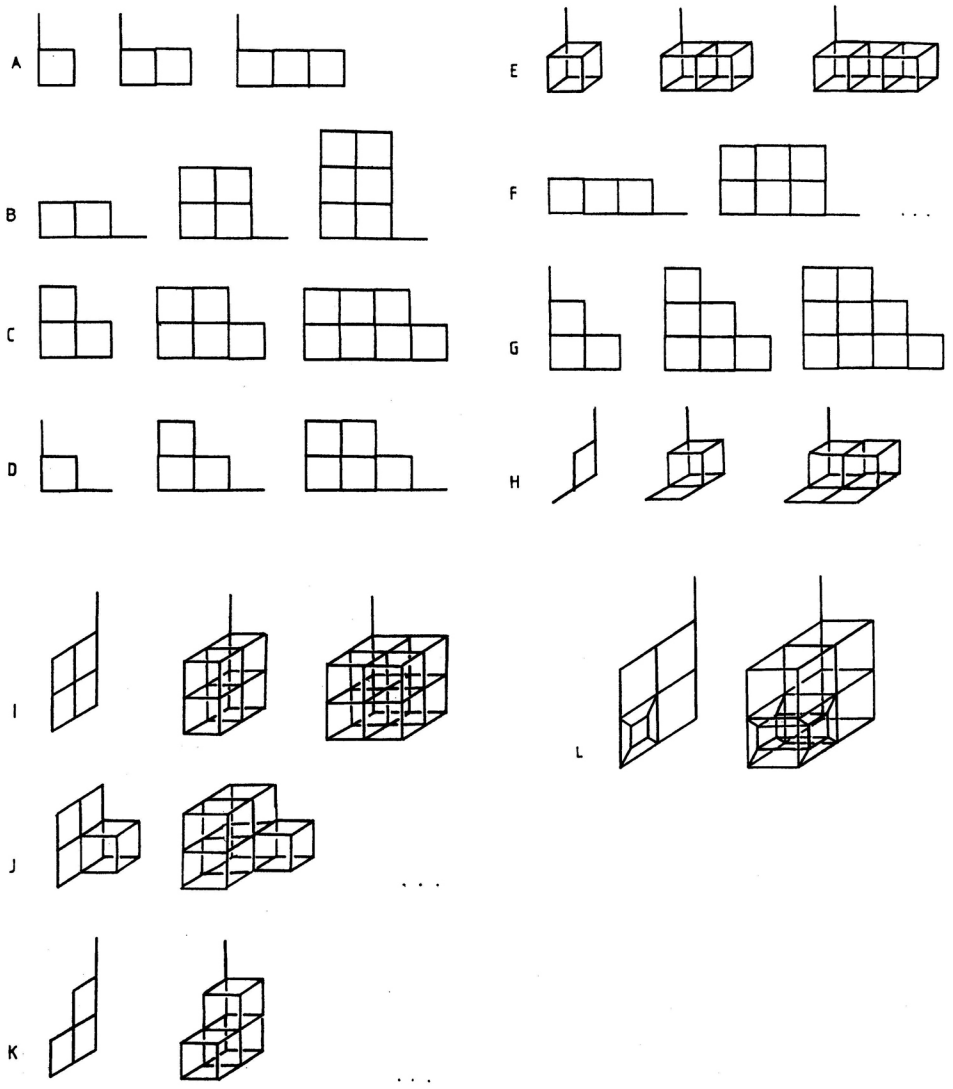


Figure 7. The resonance graphs for families of benzenoid hydrocarbons considered in this article. Only the graphs for few leading members of each family are shown.

are bipartite, and if cyclic their minimal cycles are 4-membered – indeed every site in a cycle seems to be in at least one 4-cycle. We will refer to such graphs as augmented n-cubes, since n-cubes arise as their subgraphs. Each family is defined by a single parent structure and the CC bond selected for fusion of an additional benzene ring. The higher members of each family are

obtained by successive linear (*i.e.*, polyacenic) fusion of additional benzene rings to the last fused benzene of the preceding member in the family. Each family is characterized by a constant ΔK, the increment in the number of Kekulé valence structures. In Table I we list the first eigenvalue (λ) of the derived resonance graphs.

The Lower Bounds for the First Eigenvalue

The resonance graph G has a $V \times V$ adjacency matrix, and it is its maximum eigenvalue λ which we seek. Since all its matrix elements are non-negative so that the Frobenius-Perron theorem (see *e.g.* Ref. 45), applies to imply that associated to λ there is an eigenvector which is »nodeless«. Indeed since the adjacency matrix $\boldsymbol{A}$ represents a connected graph G, $\boldsymbol{A}$ also is irreducible (in the sense that there is no permutation of row and column indices so as to bring $\boldsymbol{A}$ into reduced or block-diagonal form), and it follows that λ is non-degenerate and the associated eigenvectors are such that all components may be chosen to be positive. Thence a reasonable ϕ is a column vector all of whose elements are 1. Then $\phi^+ \boldsymbol{A} \phi = 2E$ and $\phi^+ \phi = V$, so that the Raleigh quotient for ϕ is

$$\frac{\phi^+ \boldsymbol{A} \phi}{\phi^+ \phi} = \frac{2E}{V}$$

and $2E/V$ is a lower bound to λ. This bound is essentially just that of the conjugated 6-circuit count.[46,47]

If one takes a trial vector θ with i^{th} element $\sqrt{\mathrm{d}_i}$ with d_i the degree of the i^{th} node of G, then one has

$$\lambda \geq \frac{\theta^+ \boldsymbol{A} \theta}{\theta^+ \theta} = \frac{\Sigma \sqrt{\mathrm{d}_i \mathrm{d}_j}}{E} = \frac{\chi_1}{E}$$

where the quantity $\chi_1 = \Sigma \sqrt{\mathrm{d}_i \mathrm{d}_j}$ is some sort of »inverse« molecular connectivity index, the usual connectivity index ${}^1\chi$ being defined the same[48] but with a summand that is inverse of that of χ_1.

Another bound is obtained with a columm vector Ψ whose i^{th} element is d_i,

$$\lambda = \frac{\Psi^+ \boldsymbol{A} \Psi}{\Psi^+ \Psi} = \frac{2 \Sigma \mathrm{d}_i \mathrm{d}_j}{\Sigma \mathrm{d}_i^2}$$

This bound is generally better than $2E/V$, because $\Psi = \boldsymbol{A}\phi$ and application of $\boldsymbol{A}$ to any trial vector increases the relative weights of the larger eigenvalue eigenvectors. Indeed one could continue with ever higher powers of $\boldsymbol{A}$, though for very large systems the evaluation of such bound is more involved.

TABLE I

The resonance graph characteristics for families of benzenoids considered: The lower bounds to the first eigenvalue $2E/V$ (where E is the number of edges and V the number of vertices of the resonance graph) and $2EE/VV$ (see text for symbols), and λ (the first eigenvalue)

	size	$2E/V$	numerical	θ	λ
A_1	5 x 5	10/5	2.0000	2.0909	2.1889
A_2	7 x 7	16/7	2.2857	2.4500	2.4737
A_3	9 x 9	22/9	2.4444	2.6207	2.6491
A_4	11 x 11	28/11	2.5454	2.7105	2.7503
A_5	13 x 13	34/13	2.6154	2.7660	2.8135
A_6	15 x 15	40/15	2.6667	2.8036	2.8556
limit			6/12 = 3.0000	54/8 = 3.0000	
B_1	7 x 7	16/7	2.2857	2.4500	2.4737
B_2	10 x 10	26/10	2.6000	2.8378	2.8536
B_3	13 x 13	36/13	2.7692	3.0185	3.0452
B_4	16 x 16	46/16	2.8750	3.1127	3.1538
B_5	19 x 19	56/19	2.9474	3.1705	3.2209
B_6	22 x 22	66/22	3.0000	3.2095	3.2652
limit			10/3 = 3.3333	116/34 = 3.4118	
C_1	8 x 8	20/8	2.5000	2.6667	2.6762
C_2	11 x 11	30/11	2.7273	2.9318	2.9476
C_3	14 x 14	40/14	2.8571	3.0656	3.0957
C_4	17 x 17	50/17	2.9412	3.1410	3.1839
C_5	21 x 21	60/20	3.0000	3.1895	3.2403
C_6	24 x 24	70/23	3.0435	3.2232	3.2784
limit			10/3 = 3.3333	116/34 = 3.4118	
D_1	6 x 6	12/6	2.0000	2.1429	2.2361
D_2	9 x 9	22/9	2.4444	2.6667	2.7058
D_3	12 x 12	32/12	2.6667	2.9149	2.9594
D_4	15 x 15	42/15	2.8000	3.0469	3.1017
D_5	18 x 18	52/18	2.8889	3.1235	3.1873
D_6	21 x 21	62/21	2.9524	3.1735	3.2424
limit			10/3 = 3.3333	116/34 = 3.4118	
E_1	9 x 9	26/9	2.8889	3.0250	3.0455
E_2	13 x 13	42/13	3.2308	3.2500	3.4343
E_3	17 x 17	58/17	3.4118	3.4808	3.6285
E_4	21 x 21	74/21	3.5238	3.6029	3.7382
E_5	25 x 25	90/25	3.6000	3.6786	3.8058
E_6	29 x 29	106/29	3.6552	3.7300	3.8504
limit			16/4 = 4.0000	256/64 = 4.0000	

TABLE I, Cont.

	size	$2E/V$	numerical	θ	λ
F_1	9 x 9	22/9	2.4444	2.6207	2.6491
F_2	13 x 13	36/13	2.7692	3.0185	3.0452
F_3	17 x 17	50/17	2.9412	3.2025	3.2427
F_4	21 x 21	64/21	3.0476	3.2981	3.3539
F_5	25 x 25	78/25	3.1200	3.3566	3.4224
F_6	29 x 29	92/29	3.1724	3.3961	3.4674
limit			14/4 = 3.5000	180/50 = 3.6000	
G_1	9 x 9	22/9	2.4444	2.6667	2.7058
G_2	13 x 13	36/13	2.7692	3.0000	3.0333
G_3	17 x 17	50/17	2.9412	3.1772	3.2252
G_4	21 x 21	64/21	3.0476	3.2788	3.3401
G_5	25 x 25	78/25	3.1200	3.3411	3.4123
limit			14/4 = 3.5000	180/50 = 3.6000	
H_1	6 x 6	12/6	2.0000	2.1429	2.2361
H_2	11 x 11	32/11	2.9091	3.1373	3.1690
H_3	16 x 16	52/16	3.2500	3.5326	3.5646
H_4	21 x 21	72/21	3.4286	3.7143	3.7614
H_5	26 x 26	92/26	3.5385	3.8103	3.8723
H_6	31 x 31	112/31	3.6129	3.8698	3.9405
limit			20/5 = 4.0000	338/82 = 4.1220	
I_1	10 x 10	26/10	2.6000	2.8378	2.8536
I_2	19 x 19	68/19	3.5789	3.8140	3.8373
I_3	28 x 28	110/28	3.9286	4.2096	4.2466
I_4	37 x 37	152/37	4.1081	4.3891	4.4485
I_5	46 x 46	194/46	4.2174	4.5271	4.5617
I_6	55 x 55	236/55	4.2909	4.5790	4.6311
limit			42/9 = 4.6667	480/200 = 4.8000	
J_1	13 x 13	40/13	3.0769	3.1212	3.3175
J_2	22 x 22	82/22	3.7273	3.9689	3.9903
J_3	31 x 31	124/31	4.0000	4.0881	4.3136
J_4	40 x40	166/40	4.1500	4.2853	4.4836
J_5	49 x 49	208/49	4.2449	4.3970	4.5823
J_6	58 x 58	250/58	4.3103	4.4688	4.6442
limit			42/9 = 4.6667	480/200 = 4.8000	
K_1	9 x 9	22/9	2.4444	2.6667	2.7028
K_2	17 x 17	58/17	3.4118	3.6604	3.6864
K_3	25 x 25	94/25	3.7600	4.0635	4.0949
K_4	33 x 33	130/33	3.9394	4.2426	4.2966
K_5	41 x 41	166/41	4.0488	4.3380	4.4097
K_6	49 x 49	202/49	4.1224	4.3973	4.4791
limit			36/8 = 4.5000	386/166 = 4.6506	

TABLE I, Cont.

	size	$2E/V$	numerical	θ	λ
L_1	14 x 14	42/14	3.0000	3.1387	3.3237
L_2	27 x 27	108/27	4.0000	4.2795	4.3198
L_3	40 x 40	174/40	4.3500	4.6384	4.7327
L_4	53 x 53	240/53	4.5283	4.8727	4.9361
L_5	66 x 66	306/66	4.6364	4.9289	5.0499
L_6	79 x 79	372/79	4.7089	4.9924	5.1196
limit			66/13 = 5.0769	906/344 = 5.2647	

In Table I we list for all the 65 benzenoids considered the lower bound $2E/V$ and the bound $2 \Sigma d_i d_j / \Sigma d_i^2$ which we will abbreviate as $2EE/VV$. The latter bound, as we see from Table I is considerably better than $2E/V$, even though in a few cases the two bounds have the same limit. For such cases as N increases the distinction between the two bounds becomes less important.

Since the vector whose elements are given by d_i can be obtained by multiplying $\boldsymbol{A}$ with a vector with all entries equal one, we can view this bound as derived from the matrix $\boldsymbol{A}^2$ applied to the vector with all entries equal one. Still better bounds would follow if we consider higher powers of the adjacency matrix $\boldsymbol{A}^n$ applied to the vector with all entries equal one. However, as we will see, the two bounds here considered, $2E/V$ and $2EE/VV$, respectively, correlate equally well with λ and RE, so there is no incentive to search for better bounds for the first eigenvalue. A justification for the use of the simple bounds instead of λ in regressions for RE is that they elminate the need to diagonalize large matrices.

For special cases, like polyphenanthrenes (angularly fused benzene rings) there is some analytic work on the maximum eigenvalue λ of such resonance graphs.[49] Indeed, the »graph« there (represented as an adjacency matrix, identified as a Hamiltonian matrix) is allowed to have a second set of edges corresponding to changes around conjugated 10-circuits. The two type of edges are given different weights (R_1 and R_2), and exact analytic results are obtained for $R_2/R_1 = 1/\sqrt{8}$, though approximate but very good (size-consistent) bounds for λ are obtained otherwise.

Correlations of λ and Its Lower Bounds

A good correlation between λ and $2E/V$ would allow one to obtain RE without knowing λ. In Figure 8 we show the linear regression between λ and $2E/V$ and in Figure 9 we show the linear regression between λ and $2EE/VV$. The regression coefficients and the standard errors for the two regressions are $r = 0.9984$, $r = 0.9975$ and $s = 0.0406$, $s = 0.0503$, respectively. The cor-

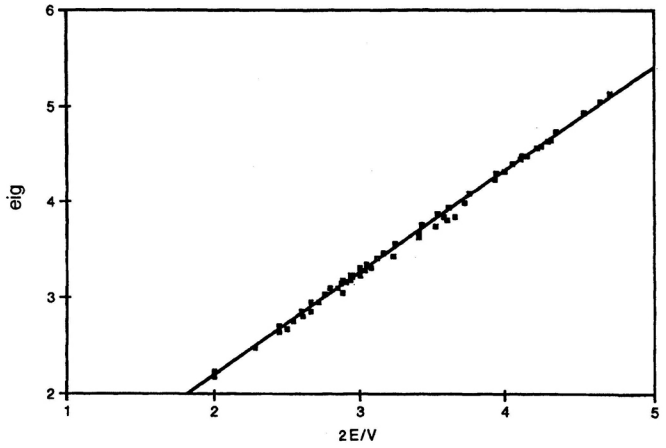


Figure 8. The correlation between the first eigenvalue λ *and* $2E/V$ for the 65 compounds of Table I.

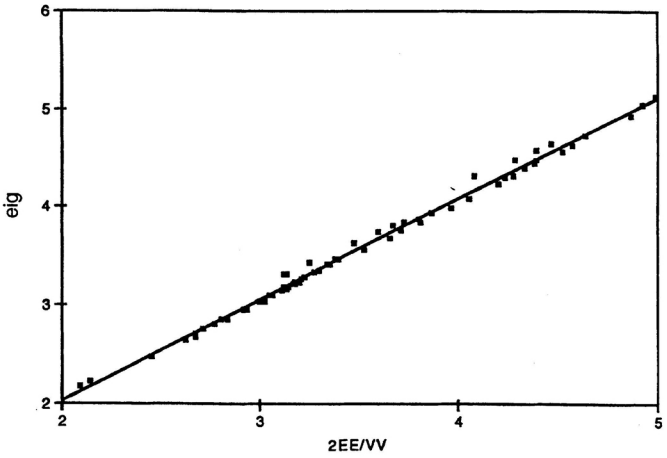


Figure 9. The correlation between the first eigenvalue λ and $2EE/VV$ for the 65 compounds of Table I.

responding Fisher ratios are: F = 19,112 and F = 12,404 respectively. Hence, both regressions are of very high quality with the regression involving $2E/V$ being slightly superior. This is somewhat surprising, even paradoxical, since $2EE/VV$ is a considerably better lower bound for λ. The reason for this unexpected behaviour is not quite clear. In Figure 10 in which we depicted the residuals for the two regressions we can discern different behavior of different families of the benzenoids. What will happen when individual families

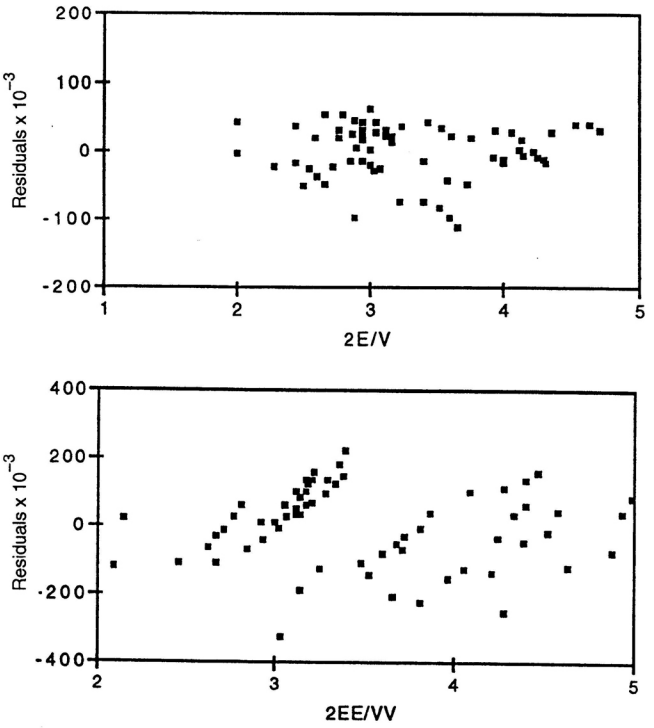


Figure 10. The residuals of the correlations in Figure 8 and Figure 9. One can discern different behaviors of the residuals for different families of the benzenoids.

of benzenoids are considered separately? Will the residuals then better reflect the distinction between different lower bounds?

In Table II we re-examined the benzenoids of the first family. We considered higher members of this family of benzenoids involving molecules having up to 15 fused benzene rings. Again, however, we see the paradoxical situation in which the better lower bound $2EE/VV$ has somewhat worse correlation statistics than the bound $2E/V$, which is not as close to λ.

BENZENOID RESONANCE ENERGIES

In Table III we list the expressions for the resonance energies of the 72 benzenoids listed in Table I (There are only 65 different molecules among the 12 families listed). The calculated resonance energies are given in eV, and are based on somewhat revised values for R_1, R_2 and R_3. We decided to include in the enumeration of conjugated circuits all conjugated circuits of

TABLE II

Illustration of the convergence of the lower bounds $2E/V$ and $2EE/VV$ for the first family of the benzenoids (phenanthrene, benzanthracene, ...)

	$2E/V$	numerical	θ	λ
A_1	10/5	2.0000	2.0909	2.1358
A_2	16/7	2.2857	2.4500	2.4737
A_3	22/9	2.4444	2.6207	2.6491
A_4	28/11	2.5454	2.7105	2.7503
A_5	34/13	2.6154	2.7660	2.8135
A_6	40/15	2.6667	2.8036	2.8556
A_7	46/17	2.7059	2.8308	2.8849
A_8	52/19	2.7368	2.8514	2.9061
A_9	58/21	2.7619	2.8675	2.9220
A_{10}	64/23	2.7826	2.8804	2.9342
A_{11}	70/25	2.8000	2.8911	2.9437
A_{12}	76/27	2.8148	2.9000	2.9513
A_{13}	82/29	2.8276	2.9076	2.9575
A_{14}	88/31	2.8387	2.9141	2.9626
A_{15}	94/33	2.8485	2.9198	2.9668
limit		6/2 = 3.0000	54/18 = 3.0000	?

size 14. As mentioned earlier in most applications of the Conjugated Circuit Method only linearly independent conjugated circuits were considered. However, as recently discussed,[41] a more consistent procedure requires use of all conjugated circuits. In large benzenoids the number of linearly dependent conjugated circuits of size 14, that are usually ignored, can be large. For example, in benzo[*s*]picene (the compound J_2 in Figure 4.) there are only nine linearly independent conjugated circuits R_3 but the number of all conjugated circuits of size 14 is twice that number.

We used the following values for the parameters required to evaluate RE:

$$R_1 = 0.822 \text{ eV}$$
$$R_2 = 0.3355 \text{ eV}$$
$$R_3 = 0.058 \text{ eV}$$

These values were based on the best linear fit of RE for selected twenty smaller benzenoids.[50] The values can be compared to the values usually adopted in the calculation of RE: $R_1 = 0.869$ eV; $R_2 = 0.247$ eV; and $R_3 = 0.099$ eV recommended in the literature.[10] As we see when all conjugated circuits of size 14 are included their individual contributuion was reduced almost to half of the previous value, but that should not be surprising because in many molecules the number of R_3 conjugated circuits doubles. We also see slightly

TABLE III

The expressions for the resonance energy and calculated RE for the benzenoids of Table I

	Resonance Energy	RE/eV	REPE
A_1	$(10\ R_1 + 4\ R_2 + 2\ R_3)/5$	1.936	0.1383
A_2	$(16\ R_1 + 8\ R_2 + 4\ R_3)/7$	2.295	0.1275
A_3	$(22\ R_1 + 12\ R_2 + 8\ R_3)/9$	2.508	0.1140
A_4	$(28\ R_1 + 16\ R_2 + 12\ R_3)/11$	2.644	0.1017
A_5	$(34\ R_1 + 20\ R_2 + 16\ R_3)/13$	2.737	0.0912
A_6	$(40\ R_1 + 24\ R_2 + 20\ R_3)/15$	2.806	0.0825
B_1	$(16\ R_1 + 8\ R_2 + 4\ R_3)/7$	2.295	0.1275
B_2	$(26\ R_1 + 16\ R_2 + 6\ R_3)/10$	2.709	0.1231
B_3	$(36\ R_1 + 24\ R_2 + 12\ R_3)/13$	2.949	0.113
B_4	$(46\ R_1 + 32\ R_2 + 18\ R_3)/16$	3.100	0.1033
B_5	$(56\ R_1 + 40\ R_2 + 24\ R_3)/19$	3.202	0.094
B_6	$(66\ R_1 + 48\ R_2 + 30\ R_3)/22$	3.277	0.0862
C_1	$(20\ R_1 + 10\ R_2 + 4\ R_3)/8$	2.503	0.1391
C_2	$(30\ R_1 + 18\ R_2 + 8\ R_3)/11$	2.833	0.1288
C_3	$(40\ R_1 + 26\ R_2 + 14\ R_3)/14$	3.030	0.1165
C_4	$(50\ R_1 + 34\ R_2 + 20\ R_3)/17$	3.157	0.1052
C_5	$(60\ R_1 + 42\ R_2 + 26\ R_3)/20$	3.246	0.0955
C_6	$(70\ R_1 + 50\ R_2 + 32\ R_3)/23$	3.312	0.0872
D_1	$(12\ R_1 + 8\ R_2 + 4\ R_3)/6$	2.130	0.1331
D_2	$(22\ R_1 + 14\ R_2 + 8\ R_3)/9$	2.583	0.1291
D_3	$(32\ R_1 + 22\ R_2 + 12\ R_3)/12$	2.865	0.1194
D_4	$(42\ R_1 + 30\ R_2 + 18\ R_3)/15$	3.042	0.1087
D_5	$(52\ R_1 + 38\ R_2 + 24\ R_3)/18$	3.160	0.9876
D_6	$(62\ R_1 + 46\ R_2 + 30\ R_3)/21$	3.245	0.0901
E_1	$(26\ R_1 + 6\ R_2 + 6\ R_3)/9$	2.637	0.1465
E_2	$(42\ R_1 + 14\ R_2 + 8\ R_3)/13$	3.053	0.1388
E_3	$(58\ R_1 + 22\ R_2 + 16\ R_3)/17$	3.293	0.1267
E_4	$(174\ R_1 + 30\ R_2 + 24\ R_3)/21$	3.442	0.1147
E_5	$(90\ R_1 + 38\ R_2 + 32\ R_3)/25$	3.543	0.1042
E_6	$(106\ R_1 + 46\ R_2 + 40\ R_3)/29$	3.617	0.0952
F_1	$(22\ R_1 + 12\ R_2 + 8\ R_3)/9$	2.508	0.1140
F_2	$(36\ R_1 + 24\ R_2 + 12\ R_3)/13$	2.949	0.1134
F_3	$(50\ R_1 + 36\ R_2 + 22\ R_3)/17$	3.203	0.1068
F_4	$(64\ R_1 + 48\ R_2 + 32\ R_3)/21$	3.360	0.0988
F_5	$(78\ R_1 + 60\ R_2 + 42\ R_3)/25$	3.467	0.0912
F_6	$(92\ R_1 + 72\ R_2 + 52\ R_3)/29$	3.545	0.0844
G_1	$(22\ R_1 + 14\ R_2 + 8\ R_3)/9$	2.583	0.1291
G_2	$(36\ R_1 + 24\ R_2 + 12\ R_3)/13$	2.949	0.1229
G_3	$(50\ R_1 + 34\ R_2 + 24\ R_3)/17$	3.171	0.1132
G_4	$(64\ R_1 + 44\ R_2 + 34\ R_3)/21$	3.302	0.1032

TABLE III, Cont.

	Resonance Energy	RE/eV	REPE
G_5	(78 R_1 + 54 R_2 + 44 R_3)/25	3.391	0.0942
G_6	(92 R_1 + 64 R_2 + 54 R_3)/29	3.456	0.0864
H_1	(12 R_1 + 8 R_2 + 4 R_3)/6	2.130	0.1331
H_2	(32 R_1 + 14 R_2 + 12 R_3)/11	2.882	0.1441
H_3	(52 R_1 + 28 R_2 + 14 R_3)/16	3.309	0.1379
H_4	(72 R_1 + 42 R_2 + 26 R_3)/21	3.561	0.1272
H_5	(92 R_1 + 56 R_2 + 38 R_3)/26	3.716	0.1161
H_6	(112 R_1 + 70 R_2 + 50 R_3)/31	3.821	0.1061
I_1	(26 R_1 + 16 R_2 + 6 R_3)/10	2.709	0.1231
I_2	(68 R_1 + 30 R_2 + 10 R_3)/19	3.502	0.1347
I_3	(110 R_1 + 60 R_2 + 12 R_3)/28	3.973	0.1324
I_4	(152 R_1 + 90 R_2 + 30 R_3)/37	4.240	0.1247
I_5	(194 R_1 + 120 R_2 + 48 R_3)/46	4.402	0.1159
I_6	(236 R_1 + 150 R_2 + 66 R_3)/55	4.512	0.1074
J_1	(40 R_1 + 20 R_2 + 10 R_3)/13	3.090	0.1405
J_2	(82 R_1 + 40 R_2 + 18 R_3)/22	3.721	0.1431
J_3	(124 R_1 + 70 R_2 + 26 R_3)/31	4.094	0.1365
J_4	(166 R_1 + 100 R_2 + 34 R_3)/40	4.299	0.1265
J_5	(208 R_1 + 130 R_2 + 42 R_3)/49	4.429	0.1166
J_6	(250 R_1 + 160 R_2 + 50 R_3)/58	4.519	0.1076
K_1	(22 R_1 + 14 R_2 + 8 R_3)/9	2.583	0.1291
K_2	(58 R_1 + 26 R_2 + 16 R_3)/17	3.372	0.1405
K_3	(94 R_1 + 52 R_2 + 22 R_3)/25	3.840	0.1371
K_4	(130 R_1 + 78 R_2 + 42 R_3)/33	4.105	0.1283
K_5	(166 R_1 + 104 R_2 + 62 R_3)/41	4.267	0.1185
K_6	(202 R_1 + 130 R_2 + 82 R_3)/49	4.376	0.1094
L_1	(42 R_1 + 24 R_2 + 16 R_3)/14	3.107	0.1295
L_2	(108 R_1 + 46 R_2 + 430 R_3)/27	3.924	0.1401
L_3	(174 R_1 + 92 R_2 + 42 R_3)/40	4.408	0.1378
L_4	(1240 R_1 + 138 R_2 + 78 R_3)/53	4.681	0.1300
L_5	(306 R_1 + 184 R_2 + 114 R_3)/66	4.847	0.1212
L_6	(372 R_1 + 230 R_2 + 150 R_3)/79	4.958	0.1127

reduced contributions of R_1 and somewhat increased contributions of R_2. Although numerically the two sets of parameters differ for most molecules the numerical values for the resonance energies have changed very little. For example, in the case of benzo[*g*]picene instead of 3.854 eV we now have the value 3.721 eV, the difference being within the standard error of the regression used to derive the parameters for R_1, R_2 and R_3.

In Figure 11. we show the regression of RE against λ. The linear regression is given by:

$$\mathrm{RE} = 0.9471\,\lambda + 0.0388$$

with r (coefficient of correlation) = 0.9865; s (standard error of estimate) = 0.1113 and F (Fisher ratio) = 2288. Again one can discern the presence of separate clusters on points belonging to different families suggesting that a better regression can be developed when individual families are considered separately.

The corresponding regression using instead of λ the descriptors $2E/V$ and $2EE/VV$, respectively, gives the following:

$$\mathrm{RE} = 1.0078\ (2E/V) + 0.1057$$

with r = 0.9804; s = 0.1338 and F = 1563 and

$$\mathrm{RE} = 0.9700\ (2EE/VV) + 0.0266$$

with r = 0.9852; s = 0.1165 and F = 2080. We see that both regressions are quite satisfactory, with the one using $2EE/VV$ being slightly better.

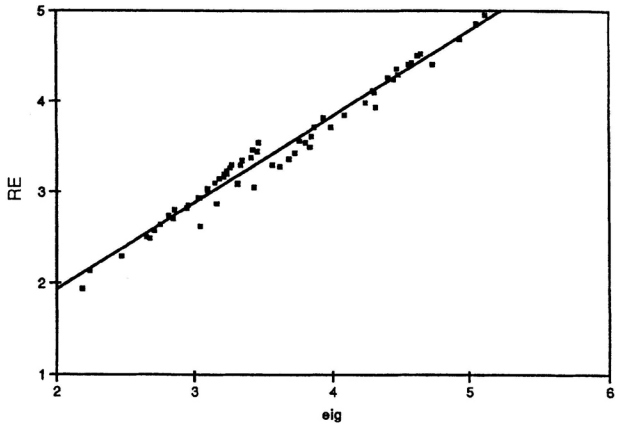


Figure 11. Linear regression of the resonance energy against the first eigenvalue of the resonance graph for the 65 structures considered.

CONCLUDING REMARKS

We have shown that the molecular resonance graphs, which only reflect the relationship between the smallest conjugated circuits (R_1), allow one to derive the RE for large graphs either through using the first eigenvalue of such graphs or alternatively by using information on lower bounds of λ, such as the number of vertices and edges. So derived RE provides very good es-

timate of the molecular stability as it indirectly (through the correlation of λ with RE for selected smaller benzenoids) also includes contributions of the higher conjugated circuits R_2 and R_3.

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SAŽETAK

Rezonancija u velikim benzenoidnim ugljikovodicima

Milan Randić, Douglas J. Klein, Sherif El-Basil i Patricia Calkins

Rezonancija pi-seksteta između Kekuléovih valentnih struktura benzenoidnih ugljikovodika prikazana je benzenoidnim rezonantnim grafom. Opisana je izrada rezonantnog grafa za skupinu benzenoidnih spojeva. Za razmatrane spojeve rezonantni grafovi izgrađeni su iz spojenih n-dimenzijskih kocki. Prikazana je glavna vlastita vrijednost grafa (λ) i dvije granice za glavnu vlastitu vrijednost. Proučavana je korelacija između λ i RE.