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Resonance Energy of Conjugated Hydrocarbons Derived by Cluster Expansion

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Resonance energy of conjugated hydrocarbons is considered through the cluster expansion concept. For the first time it is applied in its exact form and fullness. A comparison with previous results, which were obtained by a truncation of the expansion, indicates a high sensitivity of the result to the extent of truncation. The result, which greatly reduces the computation and simplifies implementation, is presented in the paper.

The reference structure is defined in graph-theoretical terms, but the application of the model is not confines to any particular method for electron energy evaluation. σ–electrons can be also accounted for. The final expression is parameter free and requires a knowledge of electron energies of the molecule and of its certain acyclic fragments.

The model is examined within the framework of the Hückel π–electron approximation. The results obtained for a number of molecules show unexpected disagreement with commonly accepted values. However, these results qualitatively agree with the recent results of Shaik *et al.* by which π–electron delocalization is interpreted as a generally destabilizing effect.

INTRODUCTION

Evaluation of the resonance energy (RE) of conjugated molecules is still a subject of interest in theoretical chemistry; for some recent results see Ref. 1. The cause and consequences of π–electron delocalization are controversially interpreted even for simple molecules like benzene.[2]

There is a plethora of models developed for the evaluation of RE, with a varying degree of sophistication and relying on various definitions of the reference energy.[1–4] All these models could be grouped according to whether a delocalization is considered in terms of only π–electrons, or if also σ–electrons are accounted for. Both concepts find their confirmation in experimental facts but nevertheless, recent results[1b] show that any model based solely on π–electrons is questionable. For example, (in)stabilities

of atomic clusters X_6 and X_4(X=Li,Na,H,F), which are isoelectronic species with p–systems of benzene and cyclobutadiene, respectively, contradict the Hückel modulo 4 rule.

Essentially, we pursue the idea exposed by Schmalz *et al.*,[5] who used the cluster expansion (CE) to get an insight into the relations between various topological models of the RE. They have shown that the models proposed by Hess and Schaad[6], Jiang, Tang and Hoffmann,[7] and some others, can be regarded as particular approximations of the CE concept, mutually differing in the number of retained terms in the expansion. Truncation was necessary due to a large (although finite) number of expansion terms. One would expect to obtain better results if the truncation were omitted, *i.e.* if all expansion terms were included. This expectation has motivated the present research. We have derived a result which greatly reduces computation and enables accounting for all fragments involved in the expansion. Thus, for the first time, cluster expansion is applied to the evaluation of the RE in its fullness.

An important characteristic of the CE concept in the evaluation of the RE is that it is not confined to either of the two mentioned views on the role of σ– and π–electrons, *i.e.* it can be applied with either assumption. Here, we report the results obtained within the framework of the Hückel method. The obtained results are quite unexpected and it is interesting to see that they conform to the results[1] obtained by using much more sophisticated computational methods.

CLUSTER EXPANSION OF THE RESONANCE ENERGY

Before we describe the use of cluster expansion for the resonance energy evaluation, let us briefly review the basis of the cluster expansion concept. We use mainly the graph-theoretical concepts and terminology since these are appropriate for structural relations considered here. More details about the chemical graph theory can be found in Ref. 8. A molecule is represented by a graph, usually denoted by G, with atoms and bonds being represented by vertices and edges, respectively. Each molecular fragment corresponds to a certain connected subgraph of the molecular graph. A subgraph relation is denoted by the symbol $\subseteq$. The chemical nature of the fragment corresponding to a given subgraph needs to be separately defined. Two possibilities arise: that broken bonds result from radicals, or that they are appropriately saturated (*e.g.* by hydrogen atoms). Both of these options seem to be consistent and worth trying. However, since here we present the results obtained by accounting for only π–electrons, this question is left open.

The CE concept starts by expressing any molecular property, X(G), as a sum of contributions from all possible fragments G′:[9]

$$X(G) = \sum_{G' \subseteq G} x(G') \qquad (1)$$

The sum goes over all connected subgraphs, including also G. x(G′) is the contribution of a fragment G′ to the property X. x(G) can be calculated recursively from Eq. (1) if x(G′), G′⊂G are already known, and if X(G) is available. However, the Möbius inversion of Eq. (1) yields a more practical expression:[10]

$$X(G) = \sum_{G' \subseteq G} \mu[G',G] \cdot X(G') \tag{2}$$

$\mu[G',G]$ denotes the Möbius function[10] with G′ and G as its arguments. An implied partially ordered set (shortly called poset) consists of G and all of its subgraphs with an order relation established through subgraph property: $G' \leq G \Leftrightarrow G' \subseteq G$. Möbius function for this poset is known:[11]

$$\mu[G',G] = \left\{ \begin{array}{c} 0 \text{ if there is e} \in \varepsilon(G \backslash G') \text{ not incident to } G' \\ (-1)^{|\varepsilon(G \backslash G')|} \end{array} \right\} \tag{3}$$

$\varepsilon(G\backslash G')$ denotes a set of edges in G *not* included in G′.

If one is interested in the evaluation of $X(G)$, Eq. (1) is of no use, since $x(G)$ requires $X(G)$ to be known. A practical significance of the cluster expansion concept in that case comes through an approximate expression:

$$X(G) = \sum_{G' \subseteq G}^{s(G') \leq S} x(G') \tag{4}$$

in which the number of terms is reduced by applying some size function $s(G')$. Only those fragments having $s(G')$ less or equal to some chosen limit S are accounted for. The size function, $s(G')$, can be defined in various ways[9] (*e.g.* as the number of atoms, or the number of bonds, or a diameter of an appropriate graph, *etc.*) and for a certain property X, it is a matter of convenient choice. Contributions arising from larger fragments are ignored in Eq. (4), but, nevertheless, if these are small, a good estimate of $X(G)$ can be obtained. Besides, the quantity $x(G')$ establishes some scale of importance for fragments G′ and, thus, enables exploring of a relation between the molecular topology and the property X. For some recent applications of CE in chemistry see Ref. 12 and the references therein.

For evaluation of the resonance energy, cluster expansion is used in a specific way: for the definition of a reference energy and for its evaluation. To define the reference energy, first we rewrite Eq. (1) giving to X a meaning of the molecular energy $E(G)$:

$$E(G) = \sum_{G' \subseteq G} e(G') \tag{5}$$

$e(G')$ denotes the energy contribution of G′. Theoretical considerations of the resonance energy[3,4] are widely based on the assumption that the resonance effect is produced by cycles present in the π–carbon skeleton. Thus, to define a reference energy one seeks a way to eliminate energy contributions coming from the presence of cycles.[13] These contributions are usually identified in a scheme chosen for the evaluation of electronic energy. In the present concept, this idea is naturally realized by removing from expansion Eq. (5) all terms that correspond to cyclic fragments:

$$E_{ref}(G) = \sum_{G'_{ac} \subseteq G} e(G'_{ac}) \tag{6}$$

and retaining only those, G'_{ac}, which do not possess any cycle. The resonance energy, RE, is then defined by:

$$RE(G) = E(G) - E_{ref}(G) \tag{7}$$

If G is acyclic, one expects to get RE(G) = 0, disregarding the model used, and this is obviously fulfilled in the present model: in that case Eq. (6) gives $E_{ref}(G) = E(G)$.

In further text, we assume that G is cyclic, *i.e.* that it contains at least one cycle. Relation (6) enables one to calculate $E_{ref}(G)$ when all $e(G'_{ac})$ are determined by using Eqs. (2) and (3). However, although simple, this is a time consuming task and it is difficult to organize computation efficiently. This was probably the reason why this appealing concept was not examined before in more detail. An important shortcut is achieved by the following consideration.

Let us express $e(G)$ from Eq. (5) as:

$$e(G) = E(G) - \sum_{G' \subseteq G} e(G') \tag{8}$$

By substituting Eq. (6) into Eq. (7), one obtains a formally similar expression:

$$RE(G) = E(G) - \sum_{G'_{ac} \subset G} e(G'_{ac}) \tag{9}$$

A comparison of Eqs. (8) and (9) reveals that RE(G) equals $e(G)$, the contribution of G itself, if expansion Eq. (5) is carried out in acyclic fragments only. Therefore, the Möbius inversion can be applied again, but now on a different poset. The partially ordered set involved now consists of G and its acyclic subgraphs only. An expression for $e(G)$ can be written in advance, by analogy with Eq. (2), as:

$$RE(G) = e_{ac}(G) = E(G) + \sum_{G'_{ac} \subset G} \mu[G'_{ac}, G] \cdot E(G'_{ac}) \tag{10}$$

where $E(G)$ is separately written and already multiplied by $\mu[G,G]$, which is always equal to 1.[10]

There remains to find $\mu[G'_{ac},G]$, the Möbius function on the poset consisting of a cyclic graph G and its acyclic subgraphs. In the Appendix, we prove the following result:

$$\mu[G'_{ac}, G] = - \prod_{v_i \in G \setminus G_{ac}} (1 - d_i) \tag{11}$$

The product goes over all vertices v_i in G which are not in G'_{ac}, and d_i denotes the number of edges by which v_i is linked to G'_{ac}. The use of Eqs. (10) and (11) is advantageous over Eq. (9) since no previous calculation of $e(G'_{ac})$ is required, and since Eq. (11) enables ignoring of those G'_{ac} for which $\mu[G'_{ac},G] = 0$. It is obvious from Eq.

(11) that $\mu[G'_{ac},G]\neq 0$ if and only if $d_i\neq 0$) for all $v_i \in G\backslash G'_{ac}$. A reader wishing to have a look at $e(G'_{ac})$ values is referred to Table II of Ref. 5.

It should be pointed out that a similar result for the evaluation of RE has already been reported in Ref. 4. However, it was obtained by using completely different arguments, and it is confined to the Hückel approximation. It was derived as the limiting case of the TRE* model introduced by Jiang, Tang and Hoffmann.[7] The coincidence is not surprising because the scheme from Ref. 7 was already recognized as the special case of cluster expansion.[5]

RESULTS AND DISCUSSION

The advantages of the introduced model for the evaluation of the RE are the following: (i) the resulting expression is parameter free, and (ii) there is a freedom to use any method for the calculation of molecular and fragment electron energies. It means that, at least in principle, σ–electrons can be also included. Nevertheless, one should observe that the reference »structure« is defined only in topological terms. Thus, the geometry of the involved fragments and their chemical nature remain undetermined. The disadvantage of the method relates to the large number of terms involved in the expansion Eq. (10). Although this number is significantly reduced in comparison with the initial expression Eq. (9), it still increases very rapidly with the size of the molecules, and soon surpasses any computationally acceptable limit.

TABLE I

The considered molecules and their calculated REPE(CE) together with REPE(Hess-Schaad) values (in β–units)

REPE(CE)	REPE(H&S)	REPE(CE)	REPE(H&S)	REPE(CE)	REPE(H&S)
-0.190	0.065	-0.009	-0.010	-0.711	-0.021
-0.403	0.055	0.003	-0.002	-0.597	0.009
-0.882	0.047	-0.534	-0.027	-0.298	0.023
-1.047	0.055	-1.086	0.027	-0.314	-0.004
-2.107	0.042	-1.084	-0.012	-1.141	-0.019
-2.937	0.053	-0.903	0.007	-3.351	-0.011
-2.984	0.051	-1.154	-0.070	-1.191	-0.036
-0.346	0.060	-1.029	-0.060	-2.720	-0.036
-0.124	0.046	0.022	-0.002	-1.064	0.018
0.006	0.005	0.001	-0.002	-2.688	-0.002
-0.067	0.027	-0.063	-0.100	-2.762	0.021
-0.907	0.039	0.037	0.043	-2.818	-0.014
-3.108	0.019	-0.084	-0.033	-0.079	0.012
0.053	0.005	-0.048	0.022		
-0.644	-0.268	-0.107	-0.014		
-0.030	-0.028	-0.374	-0.018		

To get some insight into the quality of the results which it gives, the model is used to evaluate the RE's of a number of conjugated molecules, by considering only π–electrons and using the Hückel method for the calculation of π–electron energies. Acyclic fragments of a given molecule were generated by the computer program which also supplied the appropriate $\mu[G'_{ac},G]$ values by Eq. (11). There is a real possibility for some fragments G'_{ac} to be isomorphic. Fortunately, the corresponding acyclic graphs can be easily coded and checked for isomorphism. Thus, after acyclic fragments were generated and coded by the method presented in Ref. 15, they were sorted out and reduced to nonisomorphic representatives. Significant computational time was saved in this way. Further saving was achieved in the evaluation of the Hückel energy spectra. As the acyclic graph is bipartite, the square of its adjacency matrix can be brought into a block-diagonal form. Then, to get the spectrum of an adjacency matrix, it is sufficient to diagonalize any of the two diagonal blocks.[16] The diagonalization procedure was thus approximately 8 times reduced. However, the method remains of limited applicability due to the explosive growth of fragments to be considered. For example, the molecule of triangulene (the smallest benzenoid with an even number of carbon atoms and without Kekule structure, having 22 vertices and 27 edges in 6 cycles) could not be processed on the PC AT microcomputer because of its nonrealistic memory and time requirements.

The considered molecules and the calculated values of RE per electron (REPE) are listed in Table I, together with the values obtained by Hess and Schaad.[6] The Hess-Schaad values have been chosen for comparison for two reasons: (i) they are commonly accepted as properly reflecting aromatic properties, and (ii) the underlying concept can

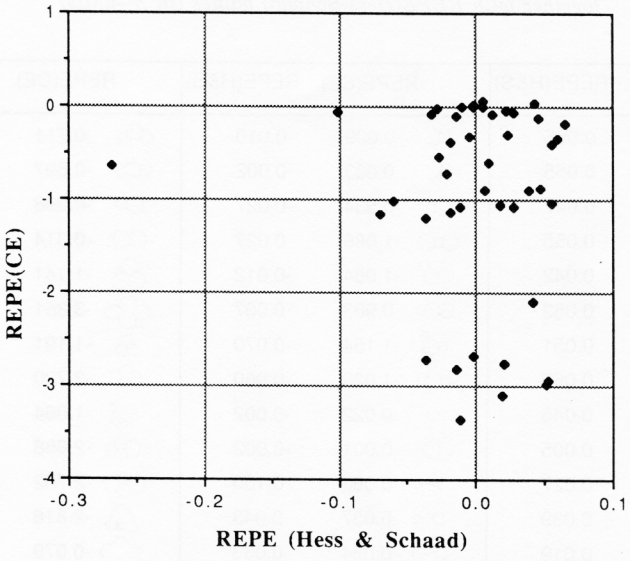

Figure 1. Resonance energies obtained by the cluster expansion approach (in the framework of the Hückel approximation) *vs.* their Hess-Schaad resonance energies (in β units), for molecules listed in Table I.

be regarded as an approximate cluster expansion in the truncated set of fragments;[5] thus, the effect of truncation can be also examined.

The two sets of REPE values are graphically compared in Figure 1. There is an obvious absence of correlation between the two sets. Values obtained by the cluster expansion for annulenes are depicted separately in Figure 2 in order to demonstrate contradiction with the Hückel rule too: the destabilization effect of electron delocalization is assigned to both 4n and 4n+2 annulenes.

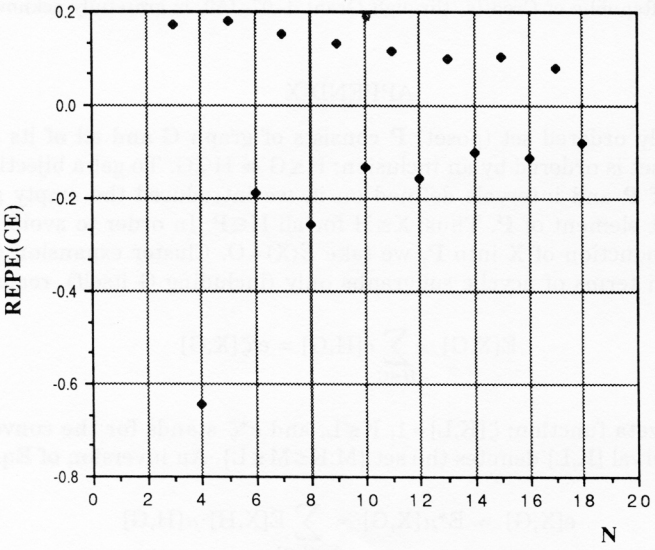

Figure 2. Resonance energies obtained by the cluster expansion approach (in the framework of the Hückel approximation, in β units) for annulenes *vs.* the ring size N.

Having in mind the concordance between the Hess and Schaad RE values and empirical facts, as well as the acceptance of the Hückel rule, the values obtained by cluster expansion seem to be absurd. However, in the light of recent, but not entirely new,[4] results about the role and effect of π–electron delocalization, a reinterpretation is possible. Namely, the values obtained by rather sophisticated techniques[1] suggest that π–electrons are generally reluctant to delocalize, and that the σ–electrons are responsible for delocalization in a molecule. Thus, the resonance energy is viewed as related to both σ– and π–electrons, and the effect of the π–electrons is estimated as generally negative. This finding seems to be in good agreement with the results presented here. From Figure 1 it can be seen that the REPE(CE) values are mainly negative.

As another interesting fact, a large discrepancy between REPE(CE), as exact, and REPE(H&S), as approximate cluster expansion values should be observed. Since a similar discrepancy between the exact and approximate values is found also in Ref. 4, we concluded that the cluster expansion of the RE is very sensitive to truncation of the complete set of fragments. Perhaps, it is related to the RE as a result of subtraction of the two usually close values of the molecular and reference electronic energies.

In conclusion, the usefulness of the complete cluster expansion for the evaluation of the resonance energy remains an open question. It would be very interesting to answer whether the agreement with the recent results[1] is only accidental. If it is not, the cluster expansion concept could be useful in understanding the controversy between the two general views of the evaluation of RE.[3,4] It would be meaningful to examine how the results are affected by the choice of the method for the evaluation of molecular and fragment electron energies.

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APPENDIX

The partially ordered set (poset) **P** consists of graph G and all of its acyclic subgraphs. The poset is ordered by an inclusion: $H \leq G \Leftrightarrow H \subseteq G$. To get a bijection between the elements of **P** and intervals defined on it, we introduced the empty graph X, as the unique least element of **P**. Thus: $X \leq H$ for all $H \in \mathbf{P}$. In order to avoid any side effect of the introduction of X into **P**, we take $E(X) = 0$. Cluster expansion (5), when it is carried out in terms of acyclic subgraphs only (including G itself), reads as:

$$E[X,G] = \sum_{H \leq G} e[H,G] = e^{*}\zeta[X,G] \tag{A1}$$

where ζ is the zeta function: $\zeta[K,L] = 1$, $K \leq L$, and $e^{*}\zeta$ stands for the convolution of e and ζ.[10] An interval [K,L] denotes the set $\{M : K \leq M \leq L\}$. An inversion of Eq. (A1) gives:

$$e[X,G] = E^{*}\mu[X,G] = \sum_{X \leq H \leq G} E[X,H] \cdot \mu[H,G] \tag{A2}$$

The Möbius function, μ, is defined by:

$$\mu^{*}\zeta[K,L] = \delta[K,L] = 1 \text{ if } K = L, \text{ and } 0 \text{ otherwise} \tag{A3}$$

From Eq. (A3), it immediately follows that $\mu[G,G] = 1$; thus, in deriving the expression for $\mu[H,G]$, we consider only the case $H \neq G$. First, we derive a recursive relation (A5):

$$\mu^{*}\zeta[H,G] = \sum_{H \leq M \leq G} \mu[H,M] = \mu[H,G] + \sum_{H \leq M \leq G} \mu[H,M] = 0 \tag{A4}$$

$$\mu[H,G] = -\sum_{H \leq M \leq G} \mu[H,M] \tag{A5}$$

We proceed by considering a particular subset of **P**. Vertices to which H, a subgraph of G, is linked in G are called the attachment vertices of H [17], and denoted as $a_1, a_2, \cdots, a_n$. They are connected with H by $d_1, d_2, \cdots, d_n$, edges, respectively. $e_j^{(i)}$ denotes the j-th edge which links a_i with H. The following two cases will be separately treated: H = X and H = spanning tree of G. Until then, we assume that neither one is the actual case.

The subposet $\mathbf{R} \subset \mathbf{P}$ contains H and the subgraphs obtained by extending H onto one or more of its attachment vertices. It should be noted that the elements of **R** are the least in the interval [H,G], *i.e.* for $H', H'' \in \mathbf{R}$, there is no $K \notin \mathbf{R}$, such that $H' < K < H''$. The subposet **R** is order isomorphic to the Cartesian product (denoted by X) of posets:

$$\mathbf{Q} = \bigtimes_{i=1}^{n} \mathbf{Q}_i = \bigtimes_{i=1}^{n} \{\varnothing, e_1^{(j)}, e_2^{(j)}, \cdots, e_{d_i}^{(j)}\} \tag{A6}$$

with $\varnothing$ meaning an empty set. Bijection between elements of **R** and **Q** is provided by the edges between H and the attachment vertices present in elements of **R**. $\mathbf{Q}_i$ are ordered also by inclusion. According to the Theorem on the Möbius function of a product of posets:[10]

$$\mu[p,q] = \prod_{i=1}^{n} \mu_i[p(i),q(i)] \tag{A7}$$

where p and q are the elements of **Q**, $p(i)$ and $q(i)$ denote their components in $\mathbf{Q}_i$, and μ_i is the Möbius function defined on $\mathbf{Q}_i$, whose values are, due to the simple structure of $\mathbf{Q}_i$, easy to obtain: $\mu_i[p(i),q(i)] = 1$, if $p(i) = q(i)$; and -1, if $q(i) > p(i)$.[10] Let o denote the element of **Q** with $o(i) = \varnothing$, $i = 1 \cdots n$; by bijection it corresponds to H in **R**. Now, we may express the part of the summation in Eq. (A5) which runs over the elements of **R**:

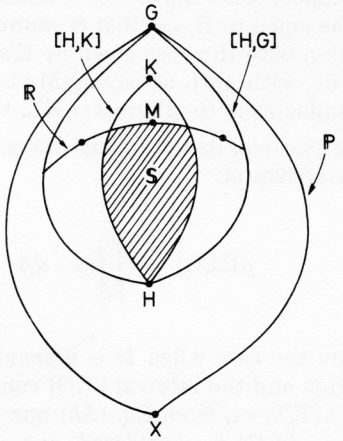

Figure 3. An arrangement of the Hasse diagram[10] of the poset **P** and its subposets [H,G], **R**, [H,K] and **S**.

$$\sum_{M\in\mathbf{R}} \mu[H,M] = \sum_{q\in\mathbf{Q}} \mu[o,q] =$$

$$= \sum_{q\in\mathbf{Q}} \prod_{i=1}^{n} \mu_i[o(i),q(i)] = \prod_{i=1}^{n} \sum_{q(i)\in\mathbf{Q}(i)} \mu_i[o(i),q(i)] = \prod_{i=1}^{n}(1-d_i) \tag{A8}$$

To show that each term $\mu[H,K]$, $K\notin R$, is zero, we consider the intersection $S=[H,K]\cap\mathbf{R}$. The diagram given in Figure 3 could be helpful to get a picture of the relations between different subposets. First, we prove that **S** contains a unique element M greater than all the others. Let us assume the opposite: that **S** contains two incomparable elements M and N, with no elements greater than they are. If they, taken together, contain two different edges linked to the same attachment vertex, then K should contain a cycle closed by H and the edges. By definition K is acyclic; hence, this option must be abandoned. However, if M and N do not contain different edges linked to the same attachment vertex, then the subgraph being a union of M and N must be also in **S**. But it is greater than both M and N, and thus M and N are not the greatest. We conclude that there is only one maximal element in **S**.

Now, for $K\notin R$, we may write:

$$\mu[H,K] = -\sum_{H\le L<K} \mu[H,L] = -\sum_{H\le L\le M} \mu[H,L] - \sum_{M<L<K} \mu[H,L] =$$

$$= -\mu^*\zeta[H,M] - \sum_{M<L<K} \mu[H,L] = -\sum_{M<L<K} \mu[H,L] \tag{A9}$$

The first summation term in Eq. (A9) vanishes because it is identical to $\delta[H,M]$, being zero for $H\neq M$ (compare with Eq. (A4)). It should be clear from definitions of **R** and **S** that M cannot be equal to H, *i.e.* that **S** cannot be just a single element. The proof proceeds by induction with the base given by K's having an »empty« remaining summation in Eq. (A9), *i.e.* with no L satisfying $M<L<K$. For such K, $\mu[H,K]$ is obviously zero. It extends inductively to all greater K's, too.

Then, except for the two mentioned special cases, from Eqs. (A5), (A8) and the above consideration, one arrives at:

$$\mu[H,G] = -\prod_{i=1}^{n}(1-d_i) \tag{A10}$$

Now, we will examine the case when H is a spanning tree, T, of G. T does not have any attachment vertex and the interval [T,G] contains only the two elements: T and G. Having in mind: $\mu[T,T]=1$, from Eq. (A5) one gets $\mu[T,G]-1$. Taking all $d_i=0$ as a natural choice when $\mu[T,G]$ is considered, one sees that Eq. (A10) is also applicable when H=T.

When H=X, the meaning of attachment vertices and numbers of edges linking them to H becomes elusive. It can be shown that $\mu[X,G]=-C$, with C being the

cyclomatic number of G.[8] However, this value is quite irrelevant for the present consideration since E(X) is taken to be zero. The proof is, therefore, omitted.

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SAŽETAK

Rezonancijska energija konjugiranih ugljikovodika izvedena razvojem u fragmente

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Rezonancijska energija konjugiranih ugljikovodika razmatrana je pomoću razvoja u fragmente. Koncepcija je po prvi puta primijenjena točno i potpuno. Usporedba s ranijim rezultatime, koji su dobiveni kraćenjem razvoja, pokazuje visoku osjetljivost rezultata na stupanj kraćenja. U radu je prikazan rezultat koji uvelike smanjuje računanje i pojednostavnjuje primjenu.

Referentna struktura definirana je graf-teorijskim pojmovima, ali primjena modela nije ograničena na posebnu metodu za izračunavanje elektronske energije. σ–elektroni mogu se također uzeti u obzir. Konačan izraz nema parametara, a zahtijeva poznavanje elektronskih energija molekule i nekih njezinih acikličkih fragmenata.

Model je ispitan u okviru Hückelove π–elektronske aproksimacije. Rezultati dobiveni za niz molekula pokazuju neočekivano neslaganje s uobičajeno prihvaćenim vrijednostima. Međutim, ovi rezultati kvalitativno se slažu s nedavnim rezultatima Shaika i dr. koji π–elektronsku delokalizaciju prikazuju kao općenito destabilizirajući efekat.