

On the Cycle-Dependence of Topological Resonance Energy[†]

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The topological resonance energy (TRE) was conceived in the 1970s. From the very beginning, it was known that TRE is equal to the collective energy-effect of all cycles present in a conjugated molecule. Also in the 1970s a theory of cyclic conjugation was elaborated, by means of which it was possible to compute the energy-effect $ef(Z)$ of each individual cycle Z present in a conjugated molecule. Yet, the connection between TRE and the $ef(Z)$ -values was, until now, not studied. We now show that TRE and the sum of the $ef(Z)$ -values are closely correlated but that a certain correction needs to be made by taking into account the energy-effects of pairs, triplets, quartets, etc. of cycles.

INTRODUCTION

The idea that the “aromaticity” and “antiaromaticity” of unsaturated conjugated molecules is related to and, perhaps, caused by, the energy-effects of cyclic interactions of π -electrons emerged slowly in theoretical chemistry and can be traced back to the works of Armit and Robinson,^{1,2} Breslow and Mohácsi,³ Dewar,^{4,5} and Clar.⁶ Of crucial importance was Dewar’s new concept of resonance energy^{4,5,7–10} which (contrary to earlier approaches) was defined so that the resonance energy of acyclic systems was as close to zero as possible. Inspired by Dewar’s works are also the two early papers^{11,12} by Nenad Trinajstić and his first graduate students.¹³

A new breakthrough in the same direction occurred after the mathematical apparatus of graph spectral theory, and especially the Sachs theorem, was applied to molecular orbital theory.^{14–17} Within the formalism of Sachs theorem^{14–18} it became possible to precisely characterize all structural features of a conjugated molecule that influence its total π -electron energy and to quantitatively determine the effect of each such structural feature.^{19,20} In particular, a method was elaborated for the calculation of the energy-effect of each individual cycle^{21–23} and another for assessing the collective effect of all cycles present in a conjugated molecule.^{24–27} The effect of all cycles on total π -electron energy was named^{26,27} “topological resonance energy” (TRE).

Although the TRE concept was conceived more than a quarter of century ago (independently by Trinajstić and co-workers²⁴ and Aihara²⁵), its relation to the energy-effects of individual cycles (which became calculable soon^{21,22} after the discovery of TRE) was not investigated until now. The present paper is aimed at filling this gap.

SACHS THEOREM AND ENERGY-EFFECTS OF CYCLIC CONJUGATION

The role of cycles and cyclic conjugation in molecular orbital theory was analyzed in detail in several earlier

works.^{28–30} Therefore we repeat here only the basic details of the respective theory.

Let G be a molecular graph, representing a conjugated π -electron system,^{15–17} and Z_1, Z_2, \dots, Z_t the cycles contained in it. In what follows we assume that G possesses $n(G)$ vertices and at least one cycle, i.e., that $t \geq 1$. For a characteristic example see Figure 1.

The characteristic polynomial $\phi(G) = \phi(G, \lambda)$ of the graph G is the characteristic polynomial of its adjacency matrix.^{15–17} The eigenvalues of G , denoted by $\lambda_1, \lambda_2, \dots, \lambda_{n(G)}$, are the solutions of the equation $\phi(G, \lambda) = 0$. Within the framework of the simple HMO theory, these eigenvalues are, in a linear manner, related to the π -electron molecular orbital energy levels.^{15–17} Then the total π -electron energy of the conjugated molecule corresponding to the graph G is equal to

$$E_\pi = \sum_{i=1}^{n(G)} g_i \lambda_i \quad (1)$$

where g_i is the occupation number of the i th molecular orbital. Here and later the energy terms are, as usual,^{31,32} expressed in units of the HMO carbon–carbon resonance integral β .

From the above it is seen that the total π -electron energy can be computed from the characteristic polynomial of the molecular graph. We denote this fact as

$$E_\pi = F[\phi(G)] \quad (2)$$

where F is a precisely defined, yet analytically quite complicated function. For instance, for conjugated systems in which all bonding molecular orbitals are doubly occupied, and all antibonding molecular orbitals are empty, eq 2, assumes the form^{20,33}

$$E_\pi = \frac{2}{\pi} \int_0^\infty \left[n(G) - \frac{ix\phi'(G, ix)}{\phi(G, ix)} \right] dx \quad (3)$$

A cycle of size k is a connected graph with k vertices, in which every vertex is of degree 2 (i. e., has exactly two neighbors). By K_2 we denote the connected 2-vertex graph (possessing a single edge). Sachs graphs are graphs whose

[†] Dedicated to Professor Nenad Trinajstić on the occasion of his 70th birthday.

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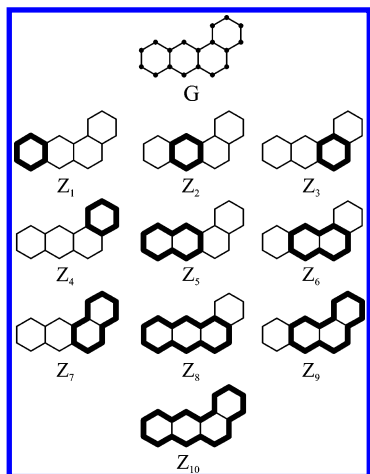


Figure 1. The molecular graph G of benzoanthracene and the cycles Z_1, Z_2, \dots, Z_{10} contained in it (indicated by heavy lines). Note that the following pairs of cycles (Z_1, Z_3), (Z_1, Z_4), (Z_1, Z_7), (Z_2, Z_4), and (Z_4, Z_5) are disjoint and that in G there are no triplets, quartets, etc. of mutually disjoint cycles.

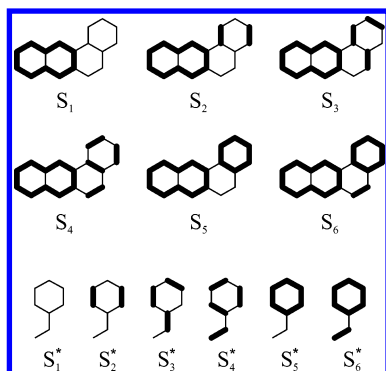


Figure 2. Heavy lines indicate the Sachs graphs S_1, S_2, \dots, S_6 contained in the molecular graph G of benzoanthracene and $S_1^*, S_2^*, \dots, S_6^*$ contained in the subgraph $G - Z_5$, cf. Figure 1. The Sachs graphs S_1, S_2, \dots, S_6 are chosen so that the cycle Z_5 is one of their components; the total number of Sachs graphs of G is 11 371, and 46 of these contain the cycle Z_5 . The one-to-one correspondence between the Sachs graphs of G containing a cycle Z_a , and the Sachs graphs of $G - Z_a$ should be self-evident by comparing S_i with S_i^* , $i = 1, 2, \dots, 6$.

components are either cycles or K_2 -graphs. The number of vertices, components, and cyclic components of a Sachs graph S is denoted by $n(S)$, $p(S)$, and $c(S)$, respectively. By definition, also the empty graph, for which $n(S) = p(S) = c(S) = 0$, is considered as a Sachs graph. Examples of Sachs graphs are found in Figure 2.

The set of all Sachs graphs that is, as subgraphs, contained in the graph G is denoted by $S(G)$. If G is the graph representation of a polycyclic conjugated molecule, then the number of elements of $S(G)$ is usually enormously large. For instance, the molecular graph of benzoanthracene has a total of 11 371 Sachs graphs.

The Sachs theorem relates the structure of the graph G with its characteristic polynomial. It reads^{14–17}

$$\phi(G, \lambda) = \sum_{S \in S(G)} (-1)^{p(S)} 2^{c(S)} \lambda^{n(G) - n(S)} \quad (4)$$

where the summation embraces all elements S of the set $S(G)$.

Combining eqs 2 and 4, one concludes¹⁹ that E_π is uniquely determined by the set $S(G)$ of all Sachs graphs of the molecular graph G . In view of this we shall write

$$E_\pi = f[S(G)] \quad (5)$$

where f is another precisely defined, yet analytically quite complicated function.

Each Sachs graph of a molecular graph G can be viewed as representing a certain structural feature of the corresponding conjugated molecule that influences its total π -electron energy. Because some Sachs graphs contain cycles, formula 5 is convenient for analyzing the effects of cycles on E_π i.e., the energy-effects of cyclic conjugation. This is done in the following manner.

If we are interested in the energy-effect of an individual cycle Z_a , then we construct the set $S(G; Z_a)$ consisting of those Sachs graphs from $S(G)$ which possess Z_a as a component. (For instance, the Sachs graphs S_1, S_2, \dots, S_6 in Figure 2 are elements of $S(G; Z_5)$; in addition, S_5 and S_6 belong also to $S(G; Z_4)$.) Then the difference $S(G) \setminus S(G; Z_a)$ represents all structural features of a conjugated molecule influencing its total π -electron energy, except those containing the cycle Z_a . Consequently, the energylike quantity

$$f[S(G) \setminus S(G; Z_a)]$$

includes the energy-effects of all structural features, except the energy-effect of the cycle Z_a . Then the difference

$$ef(Z_a) = ef(G; Z_a) = f[S(G)] - f[S(G) \setminus S(G; Z_a)] \quad (6)$$

is just the energy-effect of the cycle Z_a .

Following the same way of reasoning, let Z_a and Z_b be two disjoint cycles of the molecular graph G , and let $S(G; Z_a, Z_b)$ be the set of Sachs graphs of G containing both Z_a and Z_b . (For instance, the Sachs graph S_5 depicted in Figure 2 is an element of $S(G; Z_4, Z_5)$.) Then

$$ef(Z_a, Z_b) = ef(G; Z_a, Z_b) = f[S(G)] - f[S(G) \setminus S(G; Z_a, Z_b)]$$

is the collective energy-effect of the of the cycles Z_a and Z_b .

Note that the cycles Z_a and Z_b must be disjoint (i.e., must not possess common vertices). If Z_a and Z_b are not disjoint, then $S(G; Z_a, Z_b)$ is an empty set and, consequently, $ef(Z_a, Z_b) = 0$.

In full analogy to the above, the energy-effects of triplets, quartets, etc. of mutually disjoint cycles contained in the molecular graph G conform to the expressions

$$\begin{bmatrix} ef(Z_a, Z_b, Z_c) & = & ef(G; Z_a, Z_b, Z_c) = \\ & & f[S(G)] - f[S(G) \setminus S(G; Z_a, Z_b, Z_c)] \\ ef(Z_a, Z_b, Z_c, Z_d) & = & ef(G; Z_a, Z_b, Z_c, Z_d) \\ & = & f[S(G)] - f[S(G) \setminus S(G; Z_a, Z_b, Z_c, Z_d)] \\ \vdots & & \vdots \end{bmatrix}$$

In the subsequent section we show how $ef(Z_a)$, $ef(Z_a, Z_b)$, $ef(Z_a, Z_b, Z_c)$, etc. can be effectively calculated.

The so-called “topological resonance energy” is in fact the energy-effect of all cycles present in the conjugated molecule. In line with the above elaborated symbolism, its definition is

$$\text{TRE} = f[S(G)] - f[S(G) \setminus S_{\text{cyc}}(G)]$$

where $S_{\text{cyc}}(G)$ is the set of all Sachs graphs contained in G that possess at least one cyclic component, i.e., for which $c(S) > 0$. The actual calculation of TRE goes via the formula

$$\text{TRE} = \sum_{i=1}^{n(G)} g_i(\lambda_i - \lambda_i^*)$$

in which the notation is the same as in eq 1, whereas λ_i^* , $i = 1, 2, \dots, n(G)$, are the zeros of the polynomial

$$\phi^*(G, \lambda) = \sum_{S \in S(G) \setminus S_{\text{cyc}}(G)} (-1)^{p(S)} 2^{c(S)} \lambda^{n(G)-n(S)}$$

constructed in analogy with the Sachs theorem, eq 4. We mention in passing that $\phi^*(G, \lambda)$ is just the matching polynomial.^{34–36}

SOME OLD AND SOME NEW RESULTS

A result equivalent to Lemma 1 was proven a long time ago.²¹ We nevertheless offer here a new proof of it, because then the (new) Lemmas 2–4 follow immediately.

Lemma 1. If Z_a is a cycle of the graph G , then, bearing in mind eq 2

$$ef(G; Z_a) = F[\phi(G)] - F[\phi(G) + 2\phi(G - Z_a)]$$

Proof. Consider eq 6. That the term $f[S(G)]$ is equal to $F[\phi(G)]$ is clear from eqs 2 and 5. In view of (4), the term $f[S(G) \setminus S(G; Z_a)]$ corresponds to a polynomial $\phi(G; Z_a) = \phi(G; Z_a, \lambda)$ defined as

$$\phi(G; Z_a, \lambda) = \sum_{S \in S(G) \setminus S(G; Z_a)} (-1)^{p(S)} 2^{c(S)} \lambda^{n(G)-n(S)}$$

Then

$$\begin{aligned} \phi(G; Z_a, \lambda) &= \sum_{S \in S(G)} (-1)^{p(S)} 2^{c(S)} \lambda^{n(G)-n(S)} - \\ &\quad \sum_{S \in S(G; Z_a)} (-1)^{p(S)} 2^{c(S)} \lambda^{n(G)-n(S)} \\ &= \phi(G, \lambda) - \sum_{S \in S(G; Z_a)} (-1)^{p(S)} 2^{c(S)} \lambda^{n(G)-n(S)} \quad (7) \end{aligned}$$

Each element of the set $S(G; Z_a)$ is in an obvious one-to-one correspondence with an element of $S(G - Z_a)$, where $G - Z_a$ is the subgraph obtained by deleting the cycle Z_a from the graph G . For illustrative examples of this correspondence see Figure 2. Now, if $S \in S(G; Z_a)$ corresponds to $S^* \in S(G - Z_a)$, then $p(S) = p(S^*) + 1$, $c(S) = c(S^*) + 1$, and $n(S) = n(S^*) + |Z_a|$, where $|Z_a|$ denotes the size (number of vertices) of the cycle Z_a . Recall that $G - Z_a$ possesses $n(G) - |Z_a|$ vertices. Bearing these relations in mind, we have

$$\begin{aligned} \sum_{S \in S(G; Z_a)} (-1)^{p(S)} 2^{c(S)} \lambda^{n(G)-n(S)} &= \\ \sum_{S^* \in S(G - Z_a)} (-1)^{p(S^*)+1} 2^{c(S^*)+1} \lambda^{n(G)-n(S^*)-|Z_a|} \\ &= \phi(G - Z_a, \lambda) \end{aligned}$$

$$= -2 \sum_{S^* \in S(G - Z_a)} (-1)^{p(S^*)} 2^{c(S^*)} \lambda^{n(G - Z_a) - n(S^*)}$$

Substituting the above result back into eq 7, we obtain

$$\phi(G; Z_a, \lambda) = \phi(G, \lambda) + 2\phi(G - Z_a, \lambda)$$

which immediately implies

$$f[S(G) \setminus S(G; Z_a)] = F[\phi(G) + 2\phi(G - Z_a)]$$

and Lemma 1 follows.

In a fully analogous manner we deduce expressions for the energy-effects of pairs, triplets, etc. of mutually disjoint cycles. We sketch the proof of Lemma 2 and state Lemmas 3 and 4 without proof.

Lemma 2. Let Z_a and Z_b be two disjoint cycles of the graph G . Then

$$ef(G; Z_a, Z_b) = F[\phi(G)] - F[\phi(G) - 4\phi(G - Z_a - Z_b)]$$

Proof. This time there is a one-to-one correspondence between the elements of $S(G; Z_a, Z_b)$ and $S(G - Z_a - Z_b)$. If $S \in S(G; Z_a, Z_b)$ and $S^* \in S(G - Z_a - Z_b)$, then $p(S) = p(S^*) + 2$, $c(S) = c(S^*) + 2$, and $n(S) = n(S^*) + |Z_a| + |Z_b|$. Therefore

$$\begin{aligned} \phi(G; Z_a, Z_b, \lambda) &:= \sum_{S \in S(G) \setminus S(G; Z_a, Z_b)} (-1)^{p(S)} 2^{c(S)} \lambda^{n(G)-n(S)} \\ &= \phi(G, \lambda) + 4\phi(G - Z_a - Z_b, \lambda) \end{aligned}$$

and Lemma 2 follows.

Lemma 3. Let Z_a, Z_b , and Z_c be three mutually disjoint cycles of the graph G . Then

$$ef(G; Z_a, Z_b, Z_c) = F[\phi(G)] - F[\phi(G) + 8\phi(G - Z_a - Z_b - Z_c)]$$

Lemma 4. Let Z_a, Z_b, Z_c , and Z_d be four mutually disjoint cycles of the graph G . Then

$$ef(G; Z_a, Z_b, Z_c, Z_d) = F[\phi(G)] - F[\phi(G) - 16\phi(G - Z_a - Z_b - Z_c - Z_d)]$$

It is easy to envisage how the analogous expressions for the collective energy-effects of more than four mutually disjoint cycles look alike. These, however, occur only in very large polycyclic conjugated systems and are usually negligibly small.

By means of Lemmas 1–4 the calculation of the energy-effects of cycles is reduced to the finding of certain graph polynomials and the zeros thereof. For the conjugated system for which eq 3 holds, by means of the Coulson–Jacobs formula³⁷ the calculation of the ef -values can be further simplified, viz.

$$ef(G; Z_a) = \frac{2}{\pi} \int_0^\infty \ln \left| \frac{\phi(G, ix)}{\phi(G, ix) + 2\phi(G - Z_a, ix)} \right| dx \quad (8)$$

$$ef(G; Z_a, Z_b) = \frac{2}{\pi} \int_0^\infty \ln \left| \frac{\phi(G, ix)}{\phi(G, ix) - 4\phi(G - Z_a - Z_b, ix)} \right| dx \quad (9)$$

$$ef(G; Z_a, Z_b, Z_c) =$$

$$\frac{2}{\pi} \int_0^\infty \ln \left| \frac{\phi(G, ix)}{\phi(G, ix) + 8 \phi(G - Z_a - Z_b - Z_c, ix)} \right| dx \quad (10)$$

$$ef(G; Z_a, Z_b, Z_c, Z_d) =$$

$$\frac{2}{\pi} \int_0^\infty \ln \left| \frac{\phi(G, ix)}{\phi(G, ix) + 16 \phi(G - Z_a - Z_b - Z_c - Z_d, ix)} \right| dx \quad (11)$$

The integrals occurring on the right-hand side of eqs 8–11 can be relatively easily evaluated by standard numerical methods. Whereas eq 8 is a previously known^{21,22} and much applied²³ result, the formulas 9–11 are reported here for the first time.

The numerical results outlined later in this paper (see Figures 4 and 5) were obtained by using formulas 8–11.

In Figure 3 are given the *ef*-values of all cycles as well as pairs and triplets of mutually disjoint cycles of dibenz[*a,c*]anthracene. This benzenoid molecule does not contain quartets of mutually disjoint cycles. As seen from Figure 3, the energy-effects of pairs and triplets of cycles are small but by no means negligible.

RELATING TRE AND THE ENERGY-EFFECTS OF INDIVIDUAL CYCLES

In view of the fact that TRE is the energy-effect of all cycles, whereas *ef*(*Z*) is the analogous effect of a single cycle *Z*, the obvious question is what is the relation between them. Curiously, however, this property of the topological resonance energy as well as some other elementary problems of this kind^{38,39} have eluded the attention of theoretical chemists over more than a quarter of century.

The first guess would be to look for correlations between TRE and the sum of the *ef*(*Z*)-values, namely

$$ef_1 = \sum_{a=1}^t ef(Z_a) \quad (12)$$

Indeed, there exists a reasonably good linear correlation of this kind, as exemplified in Figure 4.

However, a more careful consideration reveals that in *ef*₁ the collective energy-effects of cycles are not correctly represented. Indeed, if *Z*_{*a*} and *Z*_{*b*} are mutually disjoint cycles, then their collective energy-effect is included both in *ef*(*Z*_{*a*}) and *ef*(*Z*_{*b*}) and is therefore included two times in the term *ef*₁.

In order to correct for this duplication one needs to use the difference *ef*₁ – *ef*₂, where⁴⁰

$$ef_2 = \sum_{a < b} ef(Z_a, Z_b) \quad (13)$$

This time, however, the collective effects of triplets of mutually disjoint cycles are not correctly accounted for. Namely, if *Z*_{*a*}, *Z*_{*b*}, and *Z*_{*c*} are disjoint cycles, then their collective energy-effect is included in both *ef*(*Z*_{*a*}), *ef*(*Z*_{*b*}), and *ef*(*Z*_{*c*}) and also in *ef*(*Z*_{*a*}, *Z*_{*b*}), *ef*(*Z*_{*a*}, *Z*_{*c*}), and *ef*(*Z*_{*b*}, *Z*_{*c*}). Consequently, in the difference *ef*₁ – *ef*₂ the energy-effects

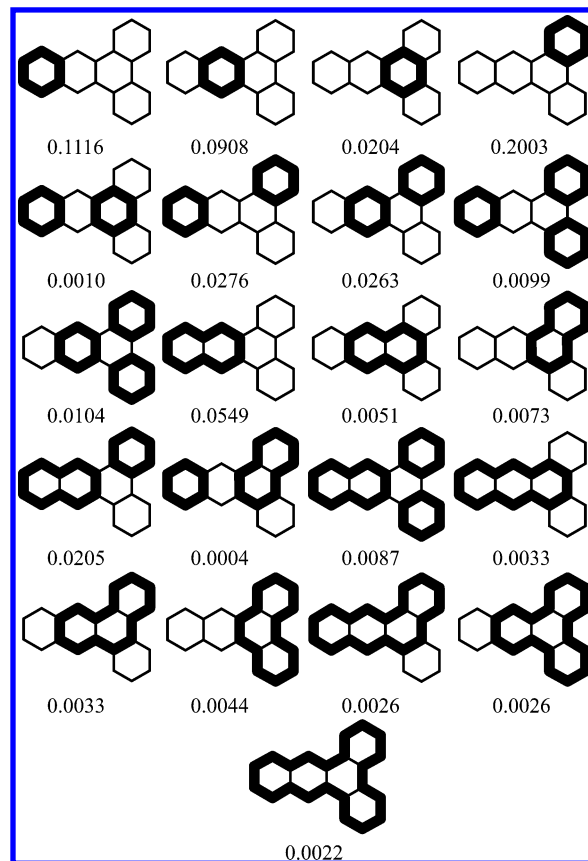


Figure 3. The energy-effects of cycles of dibenz[*a,c*]anthracene, calculated according to eqs 8–10. Only the symmetrically non-equivalent cases are shown. For details see text.

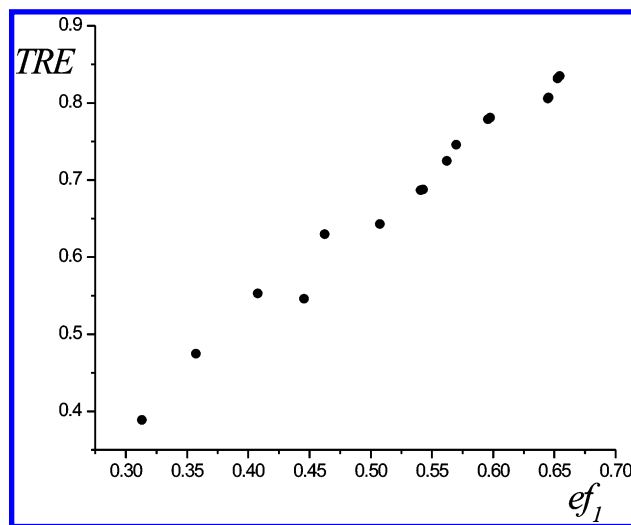


Figure 4. Correlation between topological resonance energy (TRE) of unbranched catacondensed benzenoid hydrocarbons with 6 and fewer hexagons and the sum *ef*₁, eq 12, of the individual energy-effects of all cycles present in the respective molecules, cf. Figure 1. For this data set and for the regression line $TRE \approx Aef_1 + B$ one gets $A = 1.24 \pm 0.04$, $B = 0.02 \pm 0.02$, and correlation coefficient $R = 0.9918$.

of triplets of cycles are completely cancelled out. In order to compensate for this, we need to add the term⁴⁰

$$ef_3 = \sum_{a < b < c} ef(Z_a, Z_b, Z_c) \quad (14)$$

i.e., to consider *ef*₁ – *ef*₂ + *ef*₃.

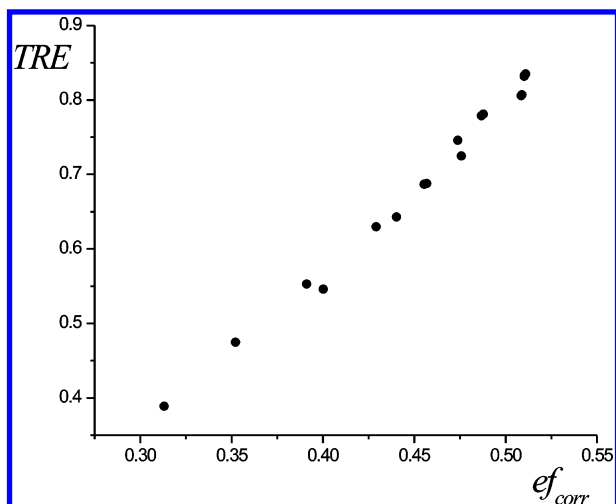


Figure 5. Correlation between topological resonance energy (TRE) and the corrected sum ef_{corr} , eq 15, of the individual energy-effects of all cycles present in the respective molecules for the same set of molecules as in Figure 3. For the regression line $TRE \approx Aef_{\text{corr}} + B$ one gets $A = 2.26 \pm 0.06$, $B = -0.33 \pm 0.03$, and correlation coefficient $R = 0.9949$. For this data set, $ef_4 = ef_5 = \dots = 0$.

Continuing this reasoning we arrive at the conclusion that the correct expression, representing the sum of energy-effects of all cycles of the polycyclic conjugated molecule considered, is

$$ef_{\text{corr}} = ef_1 - ef_2 + ef_3 - ef_4 + ef_5 - ef_6 + \dots \quad (15)$$

where the quantities ef_4, ef_5, \dots (corresponding to the energy-effects of quartets, quintets, etc. of cycles) are defined analogously to eqs 12–14. In practically all chemically relevant examples, the terms ef_4, ef_5, \dots are either equal to zero or are negligibly small.

The linear correlation between TRE and ef_{corr} is remarkably good and is, of course, better than the correlation between TRE and ef_1 . A characteristic example is shown in Figure 5.

CONCLUDING REMARKS

The sum of energy-effects of individual cycles present in a polycyclic conjugated molecule is in a good linear correlation with topological resonance energy, TRE. Bearing in mind that TRE is just the total energy-effect of all cycles, such a linear correlation is something that one could expect. Yet, whereas both TRE and the individual energy-effects were studied already in the 1970s, the relations between them are reported now for the first time.

Although each term $ef(Z)$ correctly accounts for the energy-effect of the cycle Z , the sum of these terms over all cycles, namely ef_1 , eq 12, overestimates the collective effect of pairs, triplets, etc. of (mutually disjoint) cycles. We showed how this needs to be corrected, via the term ef_{corr} , eq 15.

Our findings imply that one needs to express TRE as a linear combination of contributions coming from both single cycles and pairs, triples, quadruples, etc. of cycles. This result clearly reflects the complexity of the problem, in which the simple sum of the parts does not make the whole.

Studies of correlations between TRE and ef_{corr} for polycyclic conjugated molecules other than catacondensed benzenoids are underway and will be reported elsewhere.

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- It is worth mentioning that ref 12 is Ivan Gutman's first scientific publication, and the first of his 55 joint scientific papers with Nenad Trinajstić.
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- (40) In formulas 11 and 12 the summation may embrace all pairs and triplets of cycles, because the energy-effects of pairs and triplets of cycles that are not mutually disjoint are equal to zero.

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