

Effect of Cycles on Topological Resonance Energy*

I. Gutman

Faculty of Science, P. O. Box 60, 34000 Kragujevac, Yugoslavia

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Two basic properties of the topological resonance energy (*TRE*) are established: 1. *TRE* represents the joint effect of all cycles on total π -electron energy (*E*) of a conjugated system; 2. The effect of a particular cycle on *TRE* is equal to the effect of the same cycle on *E*. An approximate formula is derived, which enables one to express *TRE* as a linear combination of contributions of single cycles.

INTRODUCTION

Topological resonance energy (*TRE*) is a new concept in theoretical organic chemistry, which was recently introduced by the Zagreb group¹ and, independently, by Aihara². *TRE* was thereafter extensively used in chemical applications by various authors.³⁻⁶ The commonly accepted¹⁻⁶ definition of topological resonance energy is

$$TRE = \sum_{j=1}^n g_j (x_j - x_j^R) \quad (1)$$

where x_j and x_j^R ($j = 1, 2, \dots, n$) are the zeros of the characteristic and matching⁷ polynomial, respectively, of the molecular graph, while g_j is the pertinent occupation number.

We shall use the following graph-theoretical notation and terminology.¹⁴ The molecular graph of the conjugated system considered is G ; it possesses n vertices. The characteristic polynomial of G is denoted by $\Phi(G) = \Phi(G, x)$. Its zeros are $x_1 \geq x_2 \geq \dots \geq x_n$. The matching polynomial $\alpha(G) = \alpha(G, x)$ is defined via

$$\alpha(G, x) = \sum_{k=0}^{[n/2]} (-1)^k p(G, k) x^{n-2k} \quad (2)$$

where $p(G, k)$ is the number of distinct k -matchings in the graph G . (A k -matching in a graph is a selection of $2k$ vertices which are pairwise joined by k edges.¹³) The zeros of $\alpha(G)$ are real numbers^{9,12,15} and will be denoted by $x_1^R \geq x_2^R \geq \dots \geq x_n^R$.

Let C_a ($a = 1, 2, \dots$) be a cycle contained in G . Then the subgraph $G - C_a$ is obtained by deletion of C_a from G . If C_a and C_b are disjoint cycles (i. e. have no common vertices), then $G - C_a - C_b = (G - C_a) - C_b$. The subgraphs $G - C_a -$

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$-C_b-C_c$ etc. are defined analogously, provided the cycles C_a, C_b, C_c are mutually disjoint.

The following relation exists between the characteristic and the matching polynomial.^{11,16}

$$\begin{aligned} \Phi(G) = & \alpha(G) - 2 \sum_a \alpha(G - C_a) + 2^2 \sum_{a,b} \alpha(G - C_a - C_b) - \\ & - 2^3 \sum_{a,b,c} \alpha(G - C_a - C_b - C_c) + \dots \end{aligned} \quad (3)$$

with the summations going over all pairs, triplets etc. of mutually disjoint cycles.

Further details about the graph theoretical background of the present considerations can be found elsewhere.^{13,14}

ON THE CHEMICAL AND MATHEMATICAL INTERPRETATION OF *TRE*

All the applications¹⁻⁶ of the *TRE* concept are based on the belief that

(a) the greater is the value of *TRE*, the greater is the chemical stability of the pertinent compound;

(b) conjugated systems with positive (resp. negative) *TRE* can be classified as aromatic (resp. antiaromatic).

These assumptions have been tested on numerous examples^{1-6,17} and can be nowadays considered as firmly established. Thus in the present moment *TRE* should be accepted as one of the most reliable theoretical measures of the aromaticity of conjugated molecules having a non-degenerate ground state.

There exist, however, certain classes of conjugated systems in *degenerate* ground and excited state where the *TRE* concept should be applied with caution and where a non-critical usage of eq. (1) may result in apparent difficulties. As a characteristic example we consider benzene, which has a doubly degenerate highest bonding MO. Therefore in the benzene monocation one may assume $g_1 = g_2 = 2, g_3 = 1$ (which gives $TRE = -0.210$) or $g_1 = g_3 = 2, g_2 = 1$ (which gives $TRE = +0.687$). Similarly, for cyclobutadiene we can compute $TRE = -1.226$ or $TRE = +0.304$, depending on the choice of the occupation numbers g_j .

There is a simple way out of the above type of artifacts of the *TRE* method, namely eq. (1) should be slightly modified as

$$TRE = \sum_{j=1}^n (g_j x_j - h_j x_j^R)$$

where now the h_j 's are the occupation numbers of the reference structure and h_j is not necessarily equal to g_j .

We emphasize once again that the *TRE* method gives good results for the great majority of the chemically interesting conjugated compounds and that the only cases where modifications of the method are necessary are the conjugated radicals, polyradicals, radical ions and excited states. The difficulties which occur when *TRE* is applied to these latter compounds were discussed elsewhere.¹⁸

In the following we present a formal demonstration of the fact that (from a mathematical point of view) *TRE* reflects the simultaneous effect of all cycles of the molecule on total π -electron energy.

Within the Hückel molecular orbital model the total π -electron energy (E) of a conjugated molecule can be calculated from the zeros of the characteristic polynomial of the molecular graph. This polynomial, on the other hand, can be determined from the set S of all Sachs graphs of the molecular graph.¹⁴ Hence there exists a mapping f such that

$$E = \sum_{j=1}^n g_j x_j = f(S) \quad (4)$$

The crucial idea of the TRE concept is^{1,2} to construct the reference energy E^R by applying the same mapping f to the set S^R of those Sachs graphs (of the molecular graph) which do not contain cycles.

$$E^R = \sum_{j=1}^n g_j x_j^R = f(S^R) \quad (5)$$

Eqs. (4) and (5) imply $TRE = f(S) - f(S^R)$. Therefrom, the following conclusion is evident.

Proposition 1. TRE is the joint effect of all cycles of the conjugated system on total π -electron energy.

The fact that TRE can be calculated from the set S will be symbolized by the function F , viz. $TRE = F(S)$.

Let C be a cycle in the molecular graph G . Then some Sachs graphs of G contain C as a component. Let S/C be the set of all Sachs graphs (of G) which do not contain the cycle C . Then $F(S) - F(S/C)$ is the effect of the cycle C on TRE , while $ef(G, C) = f(S) - f(S/C)$ is the effect of the same cycle on the total π -electron energy.^{19,20}

Proposition 2. The effect of a particular cycle C on TRE is equal to $ef(G, C)$.

Proof is based on the fact that by deletion of the cyclic Sachs graphs from either S or S/C one obtains the same subset, namely $S^R = (S/C)^R$. Then

$$\begin{aligned} F(S) - F(S/C) &= f(S) - f(S^R) - [f(S/C) - f((S/C)^R)] = \\ &= f(S) - f(S^R) - [f(S/C) - f(S^R)] = f(S) - f(S/C) = ef(G, C) \end{aligned}$$

The $ef(G, C)$ function was calculated for a large number of conjugated systems¹⁹ and recently also various its mathematical properties have been determined.²⁰ Because of the above proposition, these former results apply equally well to TRE . They will not be reproduced here once again.

Proposition 3. If G represents a monocyclic conjugated system, then $ef(G, C) = TRE$.

Proof. If C is the unique cycle of G , then $S/C = S^R$ and $TRE = f(S) - f(S^R) = f(S) - f(S/C) = ef(G, C)$.

AN APPROXIMATE LINEAR FORMULA FOR TRE

According to Proposition 1, TRE results from a simultaneous action of all cycles in a conjugated system. It would be desirable to express this effect as an additive function of the contributions arising from single cycles. According to Proposition 2, there is no exact solution of this problem. However, it is

possible to derive an approximate formula for TRE , which is a linear function of terms being associated with cycles of the molecular graph.

Let us consider alternant conjugated systems having doubly occupied bonding and unoccupied antibonding MO's (note, however, that all the obtained conclusions are valid for non-alternants as well). Then the following integral expression for TRE holds^{1,14}

$$TRE = \left\langle \log \frac{\Phi(G, ix)}{\alpha(G, ix)} \right\rangle \quad (6)$$

Substituting eq. (3) back into (6) and taking into account the definition (2) of matching polynomials, one obtains

$$TRE = \left\langle \log [1 - 2 \sum_a (-1)^{|C_a|/2} (G - C_a) + 2^2 \sum_{a,b} (-1)^{(|C_a| + |C_b|)/2} (G - C_a - C_b) - \dots] \right\rangle$$

with $|C_a|$ being the size of the cycle C_a and

$$(G - C_a) = \frac{\sum_p (G - C_a, k) x^{n - |C_a| - 2k}}{\sum_p (G, k) x^{n - 2k}}$$

$$(G - C_a - C_b) = \frac{\sum_p (G - C_a - C_b, k) x^{n - |C_a| - |C_b| - 2k}}{\sum_p (G, k) x^{n - 2k}}$$

etc. It is important to note that the functions $(G - C_a)$, $(G - C_a - C_b)$ etc. are positive for all values of the variable x ($x \neq 0$) and may vanish only for $x = 0$.

In addition, it can be shown that

$$(G - C_a) \geq (G - C_a - C_b) \geq (G - C_a - C_b - C_c) \geq \dots$$

and

$$2(G - C_a) \leq 1$$

for all values of the variable x . Assuming that the terms $(G - C_a - C_b)$, $(G - C_a - C_b - C_c)$ etc. are negligibly small with respect to $(G - C_a)$, and that $2(G - C_a)$ is much smaller than unity, we arrive to the following approximate expression.

$$TRE \doteq \sum_C I(G, C) \quad (7)$$

where $I(G, C) = -2(-1)^{|C|/2} \langle (G - C) \rangle$. Eq. (7) has the desired linear form. If we interpret the term $-2(-1)^{|C|/2} \langle (G - C) \rangle$ as an *approximate* contribution of the cycle C to TRE , then we immediately obtain the following conclusions.

(a) If the cycle C is of the size $4m + 2$, then $I(G, C) > 0$. If the cycle C is of the size $4m$, then $I(G, C) < 0$. Hence, we have reproduced the well-known fact that $(4m + 2)$ -membered cycles increase and $(4m)$ -membered cycles decrease TRE .

(b) If the cycle C is odd, then $(G - C)$ is an odd function and $I(G, C) = 0$. Consequently, within the validity of eq. (7), odd-membered cycles have no

effect on *TRE*. This means that the actual effect of odd cycles on *TRE* is rather small and usually of no chemical significance.¹⁹

(c) The function $(G-C)$ is bell-shaped and has the following asymptotic behaviour.

$$(G-C) \sim \begin{cases} x^{-|C|} & \text{for large } |x| \\ \frac{K(G-C)}{K(G)} & \text{for small } |x| \end{cases}$$

where $K(G)$ and $K(G-C)$ are the numbers of Kekulé structures of the systems G and $G-C$, respectively. Therefore²¹, the greater is the size of the cycle C , the smaller is the contribution of C to *TRE*. The greater is the ratio $K(G-C)/K(G)$, the greater is the contribution of C to *TRE*.

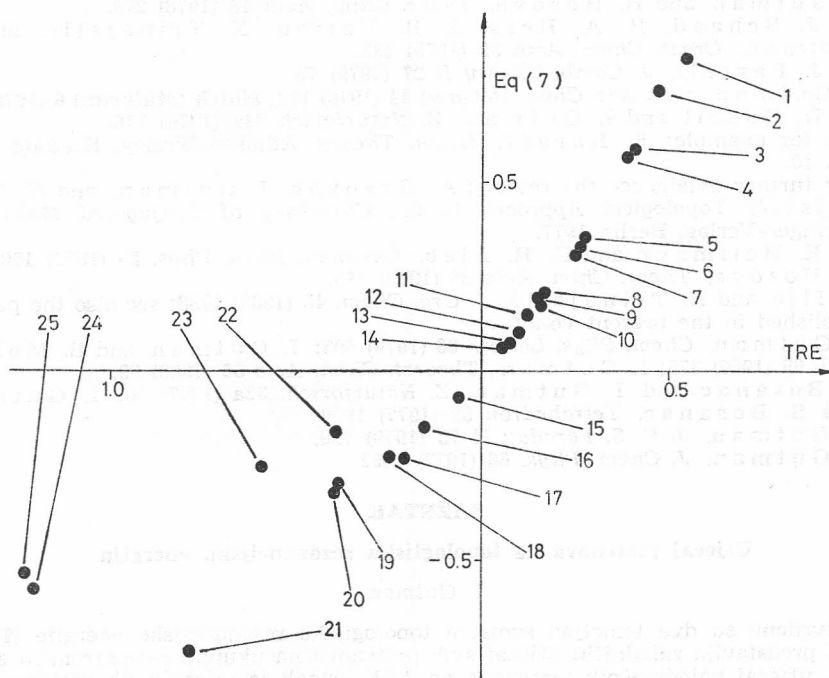


Figure 1. Correlation between eq. (7) and exact *TRE* values. 1. phenanthrene 2. anthracene 3. acenaphthenyl radical 4. naphthalene 5. benzene 6. 2-phenyl-allyl radical 7. styrene 8. [10]-annulene 9. azulene 10. benzyl radical 11. biphenylene 12. *m*-xylylene 13. *p*-xylylene 14. *o*-xylylene 15. [4]-radialene 16. 1,2-dimethylene-cyclobutadiene 17. pentalene 18. 1,3-dimethylene-cyclobutadiene 19. benzocyclobutadiene 20. methylene-cyclobutadiene radical 21. dicyclobuta(a,c)benzene 22. [12]-annulene 23. cyclooctatetraene 24. dicyclobuta(a,d)benzene 25. cyclobutadiene

The validity of eq. (7) was tested on a number of conjugated systems, both alternant and non-alternant, monocyclic and polycyclic. Some typical results are presented in *Figure 1*. As it can be seen, the relation between the approximation (7) and the exact *TRE* is apparently not linear. The correlation is relatively good for systems having positive and small negative values of *TRE*. However, considerably high violations exist in the case of antiaromatic molecules, especially (4*m*)-annulenes.

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SAŽETAK

Utjecaj prstenova na topologijsku rezonancijsku energiju

I. Gutman

Utvrđena su dva temeljna svojstva topologijske rezonancijske energije (TRE): 1. TRE predstavlja zajednički utjecaj svih prstenova na ukupnu π -elektronsku energiju; 2. utjecaj pojedinačnih prstenova na TRE jednak je utjecaju tih prstenova na ukupnu π -elektronsku energiju. Izvedena je približna formula koja prikazuje TRE kao linearnu kombinaciju doprinosa pojedinačnih prstenova.