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Structural Normalization of Topological Resonance Energy*

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Topological resonance energy method, derived as a variant of Dewar resonance energy concept, and expressed by adjacency algebra formalism, has been for years applied for successful prediction of aromatic properties of conjugated organic and inorganic species. In this work a numerical value of TRE has been discussed in light of its physical meaning. Normalization method of this value has been proposed, and numerical boundary values for evaluation of the degree of aromaticity were given. The method is new and quite different from all other known methods which has been proposed and employed for TRE normalization. Versatility and stability of our normalization procedure has been shown on numerous examples.

INTRODUCTION

Certain prominent chemical phenomena are difficult to give a sufficient and unique physical characterization. Nevertheless, salient features of their phenomenology may be abstracted and given a representation suitable for mathematical treatment. Such an approach is exerted in graphtheoretical analysis of the aromaticity of conjugated hydrocarbons. The elements of this treatment are briefly reviewed in following lines;

(*i*) a collection of nuclei in a molecule (see Note a) is represented by a class of points or vertices, $\{V(G)\}$,

(*ii*) separations between pairs of nearest-neighbour nuclei are given lines or edges, $\{E(G)\}$.

Set $\{G(V, E)\}$ composed of a class $V(G)$ and an incidence relation $E(G)$ has been recognized as molecular graph (Ref. 1). Adjacency of nuclei is critical

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Note a: nuclei heavier than hydrogen atom nuclei are commonly being considered and given a representation.

in a molecules, so is the adjacency of points v_i, v_i ε V (G). The algebra associated to these structures is usually recognized as adjacency algebra (Ref. 2). By use of appropriate combinatorial procedure spectra of a graph are obtained (Ref. 3). One spectrum is associated with a combinatorial procedure that stresses on most remarkable patterns in a graph. Following the widely respected ideas and facts on the aromaticity (Ref. 4) circles have been chosen as the most salient graph elements (Ref. 5). The second spectrum of the same graph is obtained so as to reflect more closely the pairwise incidence relation $\{E (G)\}$. In most of the chemical graph representation this relation has been taken as nontransitive.

A pairwise, weighted difference between, generally, halves of two spectra of a molecular graph (see Note b):

$$\Delta = a_1x_1 - b_1y_1 + a_2x_2 - b_2y_2 + \ldots + a_kx_k - b_ky_k \tag{1}$$

produces a number disclosed as topological resonance energy, TRE (Ref. 5b). Brief inspection reveals a similarity among TRE values and the corresponding Hückel MO energies. The mutual resemblance in two series of numbers is probably due to the nontransitivity of the relation $\{E (G)\}$ and is rather incidental.

The exploitation of topological resonance energy values, gauged with respect to thermodynamic stability of a respective conjugated compound has proved many times the elegancy and usefulness of the method (Ref. 6). Normalization of TRE values has been given an early if not proper concern, however. By dividing a TRE value with a »number of π-electrons« the aromaticity index TRE(PE) has been introduced. The index has been conferred certain meaning of quantitativness by defining reference values for aromatic nonaromatic and antiaromatic conjugated compounds (Ref. 7). The relative success of this index has probably been due to the close dependance of TRE values on the number of π-electrons, expressed either as modulo 4 or, trivially, as modulo 1. The fact that essential step in calculating TRE values relies on a number, size and organization of circles in a molecular graph was to lead some authors to suggest a normalization procedure based on a number of edges, e_i ε $\{E (G)\}$, making circles. The aromaticity index thus introduced — topological resonance energy per bond TRE(PB) (Ref. 8) or, more consistently, topological resonance energy per ring bond TRE(PRB) (Ref. 9) — has not come to be of any advantage over the TRE(PE) index yet in use. More pragmatic normalization procedures but of significantly lower generality have since been introduced (Ref. 10, 6f). Theoretical and practical validity of some of normalization procedures has been discussed to certain extent (Ref. 9), however, no serious attempt to quantify the topological resonance energies has ever been made.

THEORY

A question of whether the topological resonance energy, defined by (1) should be normalized at all seems to be at place. This is essentially the question of whether TRE is an intrinsic or an extrinsic property. The intrinsic quality of TRE is expressed by the fact that TRE of a chain is zero while TRE of a circle is different from zero. How much it is different should be irrelevant.

Note b: weights in the expression (1) are equal to orbital occupancy numbers; therefore TRE is not always obtained by subtracting exactly the halves of two spectra.

However, within the formulism of associated adjacency algebra, the applied combinatorial procedure does not discern circles of different size as sole homeomorphs of a bounded surface — the corresponding TRE values differ markedly. Furthermore, topological resonance energies of structurally homogeneous larger systems show strong dependance on a size of a system. We think that besides its intrinsic quality TRE does manifest extrinsic contributions too. It is therefore to be normalized.

In the present paper we offer a method to normalize TRE values. The method issues out of the combinatorial procedure of graph spectral decomposition. In that sense it is general and unique yet some of its characteristics allow for arbitrariness in application (vide infra). We introduce the concept of a detachment of a graph:

$$d: \{V(G), E(G)\} \rightarrow \{V(F), E(F)\} \tag{2}$$

Formally, "F is detachment of G if $E(F) = E(G)$ and there exists a function p from $V(F)$ into $V(G)$ such that, for each $\lambda \, \varepsilon \, E(G)$, the vertices joined by λ in G are the images under p of the vertices joined by λ in F", (Ref. 11). Detachment of a typical molecular graph is illustrated in Figure 1.

Figure 1
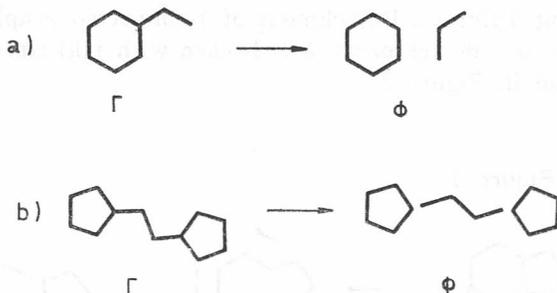
Detachment obviously leaves relation $E(G)$ unchanged while acting on a class $V(G)$; each vertex $v_i \, \varepsilon \, V(G)$ splits into $b(v_i)$ vertices, $b(v_i) \, \varepsilon \, V(F)$, $b \geq 1$. The map p is therefore surjective and (in general sense) strictly noninjective. Detachment of molecular graphs produces trees and circles, the latter of which we recognize as homeomorphic eulerian graphs. We impose a restriction on a detachment that all possible eulerian graphs be produced. The rationale of the normalization method is to count the elements of $F(V, E)$ and to compare these with $G(V, E)$. »Counting« is to be based on respective TRE values of F and G. The consequence immediately following is that only circular components of graph F are observed. Graph F is generally a disconnected graph, composed of a collection of circles. Recollecting the partition function formulism for a disconnected graph (Ref. 12),

$$Z(G) = \prod_i Z(G_i) \tag{3}$$

and the Coulson-type formula for TRE (Ref. 6b),

$$\text{TRE} = \left(\ln \frac{\varphi(G; x)}{\alpha(G; x)} \right) \qquad (4)$$

we get for a topological resonance energy of a detachment graph F the expression;

$$\text{TRE}(F) = \sum_j \text{TRE}(F_j) \qquad (5)$$

where the summation index runs over circular components. The quantities to compare then are TRE (G) and TRE (F). It is important at this stage to observe the ways circles are connected in molecular graphs. They are mutually joined either by an edge (»essentially single« or »essentially double« bond, (Ref. 13)) or they are fused together (cata- and/or pericondensed). The »contact element« in the first case is a vertex and an edge in the second case, respectively. Using the classical topological terminology we classify molecular graphs or parts of these as o-connected and 1-connected (Ref. 14), respectively. To obtain the TRE (F) value one detaches molecular graph G into as many as possible circular components, calculates TRE values of all components and sums these up. Single detachment of an o-connected graph produces j circular components, $j \geq 1$; concerning TRE numerics more than one detachment would not give anything different. Detachment of 1-connected graph, however, produces a sequence of k detachments, $k \geq 1$, each with $j(k)$ circular components. This is illustrated in Figure 2.

Figure 2
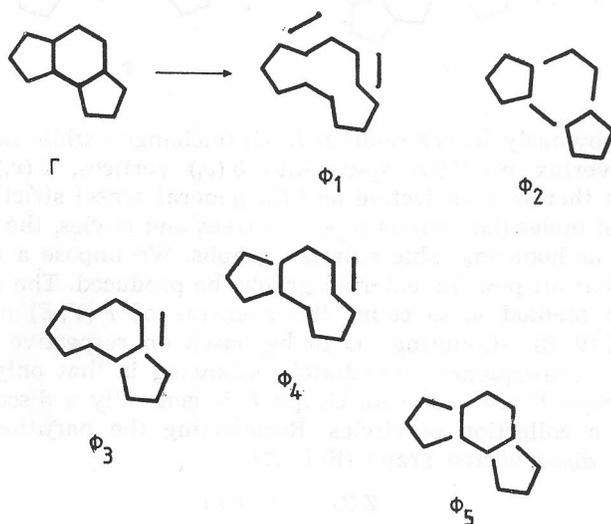
To include all detachment components simultaneously is combinatorially meaningless and to treat them separately and piecewisely is representatively insufficient. We therefore associate an exponential weight function, exp $[-(k-1)]$, to the sequence of k detachments. Topological resonance energy of a detachment graph F is then calculated according to formula:

$$\text{TRE}(F) = \sum_k \sum_j \text{TRE}(F_{jk}) \exp[-(k-1)] \qquad (6)$$

where the summation indices run over all detachments k, each containing j circular components. The relation thus obtained is proportional to the combinatorial entropy function associated with graph covering (Ref. 15).

Finally, normalized topological resonance energy of a molecular graph G is to be computed by the following formula;

$$\text{NTRE}(G) = \sigma(F) \cdot |\text{TRE}(G)| \cdot \text{nf} \qquad (7)$$

where

$\sigma(F)$ denotes the signum function, $\sigma(F) = \text{sgn}(F)$ and

$$\text{sgn}(F) = \text{sgn}\left\{\sum_k \sum_j \text{TRE}(F_{jk}) \exp[-(k-1)]\right\} \text{ (see Note c),}$$

$|\text{TRE}(G)|$ is absolute value of TRE (G),

nf — »normalization« function.

The normalization function is to quantify a comparison between the TRE (G) and the TRE (F) values. The constraints imposed on it require that it has to,

(*i*) be continuous,

(*ii*) have a finite range,

(*iii*) be positive,

(*iv*) be smooth, and

(*v*) produce NTRE values numerically conformable to the many TRE values yet calculated and analyzed.

The function we used is of the form (Ref. 16):

$$\text{nf} = \left\{ \exp[-\sigma(\Delta)|\Delta|^{1/\varepsilon}] \right\}^{\sigma(\Delta) \cdot 1} \qquad (8)$$

where,

$$\sigma(\Delta) \text{ is defined as } \text{sgn}(\Delta) = \frac{\Delta}{|\Delta|} \qquad ,$$

$$\Delta = \frac{\text{TRE}(G) - \text{TRE}(F)}{\text{TRE}(F)}$$

Normalized topological resonance energy of a molecular graph G detached into k detachment graphs F_k, each containing j circular components, is then calculated by formula:

$$\text{NTRE}(G) = \sigma(F) |\text{TRE}(G)| \left\{ \exp\left[-\sigma(\Delta) \cdot \left| \frac{\text{TRE}(G) - \text{TRE}(F)}{\text{TRE}(F)} \right|^{1/e} \right] \right\}^{\sigma(\Delta) \cdot 1}$$

Note c: By convention, sgn (TRE $(F) = 0$) = $+$

RESULTS AND DISCUSSION

In Table are given molecular graphs, topological resonance energies and normalized topological resonance energies, G, TRE and NTRE, respectively. Prior to an analysis of a meaning of sequences of these numbers some general remarks are necessary. These concern TRE numerics. Topological resonance energies of most of common finite molecular graphs are values in the range from —2.5 to +1.0. Topological or A-II resonance energies (Ref. 5d) are not electronic energies, however, these are proportional (Refs. 6b, 4b) to

TABLE

	G	TRE	NTRE	TRE(F)
1)		0.276	0.276	R6
'2)		— 1.060	— 0.657	R4
3)		0.433	$-0.133^{a)}$ $0.200^{b)}$	R5 + R3 $(R5)^- + (R3)^+$
4)	$\left\{ \right\}^{\oplus}$	0.821	$0.454^{a)}$ $-0.182^{b)}$ $0.097^{c)}$	$(R3)^+ + R6 + R6$ $(R6 + R6)^+ + R3$ $(R6 + R3 + R6)^+$
5)		— 0.393	$-0.192^{a)}$ $-0.097^{b)}$	R8, R6, R4 R6, R8, R4
6)		0.151	$0.032^{a)}$ $0.051^{b)}$	R10, R7, R5 R10, $(R7)^+$, $(R5)^-$
7)		0.475	$0.257^{a)}$ $0.159^{b)}$	(R6+R6), R6 R14, R10, R6
8)		0.217	$-0.026^{a)}$ $-0.071^{b)}$ $0.188^{c)}$	$\Phi_1,\ \Phi_6$ $\Phi_6,\ \Phi_{13}$ $\Phi_7,\ \Phi_8$
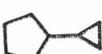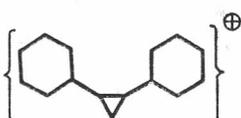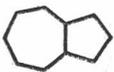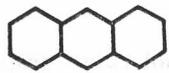
certain observables, the heats of atomatization of conjugated compounds being the most notable one. The NTRE values in Table are given a meaning by setting up reference values. These can be set by observing the mathematical structure of the LCAO model (Ref. 17), by some other theoretical work (Ref. 18) or else. We are inclined, on grounds of experimental works (Ref. 19) and earlier work (Ref. 20) to treat [18] annulene as a borderline conjugated compound. Thus all NTRE values are gauged with respect to the TRE values of either neutral or doubly charged [18] annulene. Therefore,

(*i*) compounds having NTRE $\geq$ + 0.088 are aromatic.

(*ii*) compounds having NTRE $\leq$ — 0.258 are antiaromatic,

It is nevertheless not to be forgotten that,

(*iii*) NTRE scale is not linear.

According to (*iii*) naphthalene, with NTRE = 0.284 is not three times more aromatic (whatever it means) than the diphenylcyclopropenyl cation with NTRE = 0.097, however it certainly is more aromatic.

Comparing the numbers in the two columns in Table, TRE and NTRE, respectively, we see that the NTRE values are more or less different from the progenitorial TRE values. With the help of picturesque graph representation we can reveal that,

(*i*) NTRE equals TRE in annulenes,

(*ii*) normalization is reciprocally dependent on a size of a graph,

(*iii*) normalization is sensitive to a charge on a conjugated compound.

The first property is a result of a convention that TRE of simple annulenes be left unchanged by normalization. The second property is only roughly valid but it can be shown it is valid in a proper way (Ref. 16). The third observation deserves more attention. It is evident that most graphs in Table are given more than one NTRE value. This multiplicity is due to possible variations in the procedure for calculating TRE $(F) = \sum_k \sum_j$ TRE (F_{jk}) exp [— — $(k-1)$] expression, as is shown in the rightest column in Table. Figure 3

Figure 3
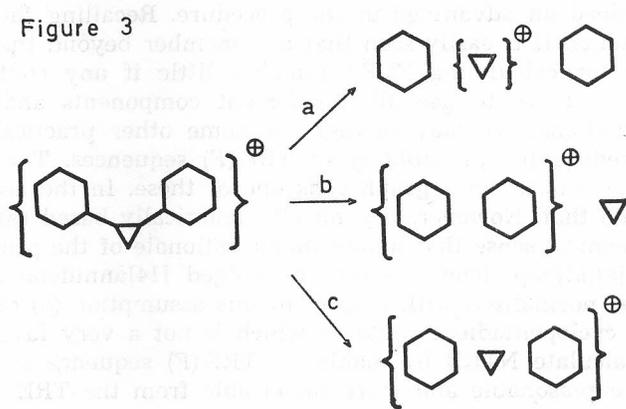
is to help to clarify tehnical intricacies of the procedure and to explain the symbols in the righthand column in Table (Ref. 21).

Obviously, TRE (F) of diphenylcyclopropenyl cation can be calculated with charge localized on cyclopropenyl ring (a), on benzene(s) ring(s) (b), or with charge dispersed over all three circular components of the compound (c). The first value, (a), though reduced by normalization is still too high positive value. The second NTRE value, (b) is, however, too low one; besides, it has been arrived at making not very plausible assumptions. Therefore the (c) value, indicating weak aromaticity, is quite in line with the observed chemistry of pertinent conjugated compound (Ref. 22). We may thus make a further observation,

(iv) NTRE can be used to localize charge in calculating »resonance energy« of conjugated ions.

The ways to calculate TRE (F) expression are supposedly many in case of 1-connected compounds. Azulene graph, for example, can be detached into [10]annulene, [7]annulene and [5]annulene. The TRE (F) is then calculated according to,

$$\text{TRE } (F) = \text{TRE } (R10) \, e^0 + \text{TRE } (R7) \, e^{-1} + \text{TRE } (R5) \, e^{-2} \tag{10}$$

We may, however, assume that, following the principle of maximal positive TRE value, the compound is more stable as ionic structure (Ref. 19) and calculate the TRE (F) term according to,

$$\text{TRE } (F) = \text{TRE } (R10) \, e^0 + \text{TRE } (R7)^+ \, e^{-1} + \text{TRE } (R5)^- \, e^{-2} \tag{11}$$

In this way we get sligthly more positive NTRE values for azulene (b). Another observation then is that,

(v) NTRE procedure allows to include ionic structure contributions.

The possibility of multiple detachments of 1-connected graphs is particularly striking with larger systems. bis(cyclopenta)[ef,kl]heptalene is one of these. It can be vertex-split into 13 detachments which cover a graph, as seen in Figure 4.

To calculate TRE (F) for such a system one could use all the 263 combinations which is certainly not a very appealing procedure for exploitation. This variety, however, is indeed an advantage in the procedure. Recalling the property of the weight function it is easily seen that any member beyond the fourth term in a sequence for calculating TRE (F) makes little if any contribution. No practical need is there to use all detachment components and make them into all combinations. We may further use some other practical, reasonable principles to reduce the multiplicity of TRE (F) sequences. The principle of covering all the vertices in a graph G is one of these. In the above example Φ_1, Φ_6 would do that. However, beyond all numerically based rationalizations is a general chemical sense that makes major rationale of the procedure. Thus bis(cyclopenta)[ef,kl]heptalene is either a bridged [14]annulene and its TRE value should be normalized with respect to this assumption (a) or it is heptalene with two cyclopentadiene units — which is not a very favourable topology — and calculate NTRE by making a TRE (F) sequence of Φ_6, Φ_{13} (see Figure 4). More reasonable and more favourable from the TRE standpoint is

Figure 4
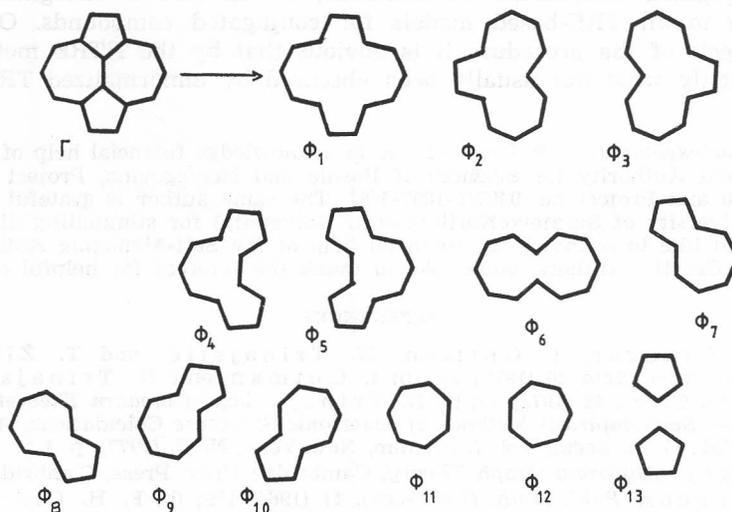
to assume combination of two azulene units or even two [10]annulenes, like and Φ_7, Φ_8 (see Figure 4). This combination gives the highest positive NTRE value, (c). IR spectra, on the other hand, suggest existence of azulene constitutional elements in the heptalene derivative (Ref. 23). We may thus state still another property of the NTRE procedure,

(vi) by the NTRE procedure certain, deliberately chosen, parts of molecular graph can be more expressed on TRE scale.

The suggested normalization method is not without deficiencies, however. Thus, for instance, it is claimed that charge localization is perceived through the procedure; examples (3) and (5) in Table. The effect is usually too small on numerical scale and does not make sufficient distinction between, for example, completely polarized azulene and nonpolarized azulene. Furthermore, the normalization function is reciprocally size-dependant but not much so. For instance, TRE value of anthracene is reduced by normalization (see Table, (7)), particularly in the case when an emphasis has been given to larger rings that cover the graph of anthracene, (b). Nevertheless, even so diminished TRE value may appear still too high indicating more of aromatic character than is commonly ascribed to anthracene. Both of these deficiences, however, are numerical consequences of properties of the used normalization function (Ref. 16) and can be easily cured. What cannot be cured are effects resulting from the fact that molecular graph, however dissected, is nothing but a nonmetric representation of an idealized molecular connectivity.

CONCLUSION

Normalization method is suggested to rationalize TRE values and make these more into quantitative relations. The method is based on a simple, zero-order dissection of a molecular graph. It is shown to be applicable to graphs differing in (i) overal size, (ii) number of circles, and (iii) type of con-

nections among circles. It can as well be used to normalize charged and polarized conjugated compounds. Furthermore, the method is straightforwardly applicable to all TRE-based models for conjugated compounds. Observing major effects of the procedure it is obvious that by the NTRE method one gets explicitly what has usually been obscured by unnormalized TRE calculations.

REFERENCES

1. (a) A. Graovac, I. Gutman, N. Trinajstić, and T. Živković, *Theoret. Chim. Acta* 26 (1972) 67; (b) I. Gutman and N. Trinajstić, *Topics Curr. Chem.*, 42 (1973) 49; (c) N. Trinajstić, in *Modern Theoretical Chemistry — Semiempirical Methods of Electronic Structure Calculations*. A. Techniques«, Ed., G. A. Segal, Vol. 7, Plenum, New York, N. Y. (1977), p. 1.
2. N. Biggs, *Algebraic Graph Theory*, Cambridge Univ. Press, Cambridge, (1974).
3. (a) H. Sachs, *Publ. Math. (Debrecen)*, 11 (1964) 119; (b) F. H. Clarke, *Discrete Math.*, 3 (1972) 305; (c) E. J. Farrell, *Discrete Math.*, 39 (1982) 31.
4. (a) R. Breslow and E. Mohacsi, *J. Amer. Chem. Soc.*, 85 (1963) 431; (b) M. J. S. Dewar and C. de Llano, *J. Amer. Chem. Soc.*, 91 (1969) 789; (c) B. A. Hess, Jr. and L. J. Schaad, *J. Am. Chem. Soc.*, 93 (1971) 305.
5. (a) I. Gutman and N. Trinajstić, *MATCH, Math. Chem.*, 1 (1975) 171; (b) I. Gutman and N. Trinajstić, *Acta Chim. Acad. Sci. Hungaricae*, 91 (1976) 203; (c) I. Gutman, M. Milun, and N. Trinajstić, *Croat. Chem. Acta* 48 (1976) 87; (d) J. Aihara, *J. Amer. Chem. Soc.*, 98 (1976) 2750.
6. (a) A. Graovac, I. Gutman, and N. Trinajstić, *Lecture Notes in Chemistry*, No. 4, Springer, Berlin (1977), pp. 1—123; (b) I. Gutman, M. Milun, and N. Trinajstić, *J. Amer. Chem. Soc.*, 99 (1977) 1692; (c) P. Ilić and N. Trinajstić, *J. Org. Chem.*, 45 (1980) 1738; (d) P. Ilić, B. Sinković, and N. Trinajstić, *Israel J. Chem.*, 20 (1980) 258; (e) J. Aihara, *J. Am. Chem. Soc.*, 101 (1979) 5913; (f) P. Ilić, B. Mohar, J. V. Knop, A. Jurić, and N. Trinajstić, *J. Heterocycl. Chem.*, 19 (1982) 625.
7. N. Trinajstić, *Internat. J. Quantum Chem.*, S11 (1977) 469.
8. J. Aihara, *Bull. Chem. Soc. Japan*, 50 (1977) 3057.
9. (a) P. Ilić, B. Džonova-Jerman-Blažič, B. Mohar, and N. Trinajstić, *Croat. Chem. Acta*, 52 (1979) 35; (b) P. Ilić, *Ph. D. Thesis*, Univ. Zagreb (1979).
10. J. Aihara, *J. Amer. Chem. Soc.*, 103 (1981) 1633.
11. C. St. J. A. Nash-Williams, in *Graph Theory and Combinatorics*, Ed., R. J. Wilson, Pitman, London (1979), pp. 87—97.
12. N. Biggs, *Interaction Models*, London Math. Soc., Lecture Note Series, No. 30, Cambridge Univ. Press, Cambridge (1977), p. 10, formula 1.4.3.
13. (a) M. J. S. Dewar, *The Molecular Orbital Theory of Organic Chemistry*, McGraw-Hill, New York, N. Y. (1969), p. 182, (b) Ref. 4b.
14. P. Alexandroff, *Einfachste Grundbegriffe der Topologie*, Julius Springer, Berlin (1932), Ch. I.
15. (a) A. I. Khinchin, *Uspekhi Math. Nauk*, 8 (1953) 3; (b) P. Ilić et al., work in preparation.
16. P. Ilić and N. Trinajstić, second part of this work, prepared for publication.
17. H. C. Longuet-Higgins and L. Salem, *Proc. Roy. Soc. (London)*, A251 (1959) 172.
18. M. J. S. Dewar, R. C. Haddon, and P. J. Student, *J. C. S. Chem. Commun.*, (1974) 569.

19. (a) P. Garrat and P. Vollhardt, *Aromatizität*, Georg Thieme, Stuttgart, (1971), Ch. 3 and references therein; (b) D. Lewis and D. Peters, *Facts and Theories of Aromaticity* Macmillan, London (1975), Ch. 4 and references therein.
20. I. Gutman, M. Milun, and N. Trinajstić, *Croat. Chem. Acta,* **49** (1977) 441.
21. R10, R7, etc, denote [10]annulene, [7]annulene, respectively, while $\Phi_1 - \Phi_{13}$ correspond to graphs given in Figure 4.
22. R. Breslow, J. Lockhart, and H. W. Chang, *J. Amer. Chem. Soc.,* **83** (1961) 2375.
23. A. G. Anderson, Jr., A. A. McDonald, and A. F. Montana, *J. Amer. Chem. Soc.,* **90** (1968) 2993.
24. J. Aihara, *J. Amer. Chem. Soc.,* **100** (1978) 3339.

SAŽETAK

Strukturalno normiranje topologijske rezonancijske energije

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Metoda topologijske rezonancijske energije, TRE, izveden kao inačica pojma Dewar-ove rezonancijske energije i iskazan formulizmom algebre povezanosti koristi se već niz godina za uspješno predskazivanje aromatičkih osobina konjugiranih organskih i anorganskih spojeva. U radu je raspravljano pitanje vrijednosti brojčane veličine topologijske rezonancijske energije u svjetlu njezina fizikalnog značenja. Predložena je metoda normiranja ovih vrijednosti i date su brojčane granice za ocjenu veličine aromatičnosti pojedinog konjugiranog spoja. Metoda je nova i sasvim različita od svih do sada korišćenih i predloženih metoda za normiranje topologijske rezonancijske energije. Na nizu primjera pokazana je svestranost i postojanost našeg postupka normiranja.