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Note

On Normalization of Topological Resonance Energy

P. Ilić[#], *B. Jerman-Blažič-Džonova**, *B. Mohar**, *and N. Trinajstić*

»Ruđer Bošković« Institute, P.O.B. 1016, 41001 Zagreb, Croatia, Yugoslavia, and
**The Jožef Stefan Institute, P.O.B. 199, 61001 Ljubljana, Slovenia, Yugoslavia*

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Normalization of the topological resonance energy, TRE, with respect to the total number of pi-electrons, TRE(PE), and with respect to the number of ring bonds in a molecule, TRE(PRB), was done. That both indices, TRE(PE) and TRE(PRB), lead to similar predictions concerning stability and aromatic behavior of conjugated species was shown by a comparative analysis of various classes of compounds.

INTRODUCTION

The amount of nonlinearity in the single- and double-carbon bond energies that occurs upon closing a ring has been intimately allied with resonance energy, RE. This idea was implicitly exploited by Dewar[1] in the successful PPP-SCF-LCAO-MO calculations of heats of atomizations of hydrocarbons; it was fully recognized by Hess and Schaad[2] and used explicitly in obtaining the REPE index. Milun et al.[3] used simplified approach with only two parameters, thus obtaining the aromatic stability, A_s, index. The concept of linear reference structure was discussed also in the FEMO approach to cyclic conjugated species.[4] However, the problem of intrinsic impossibility of representing a linear and the corresponding cyclic structure with the same number of atoms and bonds has been common to all these approaches. This problem was avoided by use of graph representation of a framework of conjugated structure.[5] The effect of ring closure with respect to the linear structure composed of the same number of atoms and bonds was quantified by a selective counting of the elements of Sachs graphs[6], thus obtaining Hückel characteristic polynomial and a matching polynomial for the same structure. Pairwise subtraction of two spectral series, running over occupied levels, produces topological resonance energy, TRE.

We have latterly reported the topological resonance energy, TRE, indices of various planar conjugated structures including ions, radicals, and ion-radicals.[7–10] There arises a question of how to normalize the TRE values of a whole gamut of planar conjugated structures in order to obtain the intrinsic topological resonance quantity.[11–13] Several ways are open for doing that but we consider here only two. The first one is to take into account the total

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[#] Permanent address: Faculty of Natural Sciences and Mathematics, University in Sarajevo, 71000 Sarajevo, Bosnia and Herzegovina, Yugoslavia number of pi-electrons in the system,[12] thus obtaining TRE per electron, TRE(PE) index. Dividing topological resonance energy by the total number of pi-electrons present in a system one gets a quantity which in some way averages the effects of species topology and of its pi-electron content; it reflects whether a species is neutral or mono-, bi-, tri-, etc., anion or cation. The second way stems from the idea that the TRE method actually reflects the sigma molecular bonds circuitry. One could thus attempt to normalize TRE values with respect to ring-like components[14] obtaining TRE per bond or, more correctly, TRE per ring bond, TRE(PRB), index. In other words, by the procedure of TRE(PRB) normalization one ignores completely all side chains as well as the actual number of pi-electrons. The same applies both to the homocyclic hydrocarbons and to the heterocyclic ones, containing heteroatoms that contribute more than one pi-electron to the overall pi-electron content. Similar way of normalizing resonance energy was considered by several authors,[11,15] the difference having been in that they had taken into account all bonds in a given molecule.

In the present note we analyze the use of TRE(PE) and TRE(PRB) indices in predicting the aromatic stability of various classes of conjugated systems.

RESULTS AND DISCUSSION

TRE, TRE(PE), and TRE(PRB) in units β are calculated employing the following expressions,

$$\mathrm{TRE} = \sum_{j=1} g_j \, (x_j - x_j^{ac}) \qquad (1)$$

$$\mathrm{TRE(PE)} = \frac{\mathrm{TRE}}{N} \qquad (2)$$

$$\mathrm{TRE(PRB)} = \frac{\mathrm{TRE}}{B_\mathrm{r}} \qquad (3)$$

Symbols in the relations 1—3 have the following meaning:

N — stands for a number of pi-electrons,

B_r — stands for a number of sigma bonds forming ring(s),

x_j, x_j^{ac} — are Hückel energies of a molecule ($\alpha = 0$, $\beta = 1$) and corresponding energy levels of a reference structure, respectively,

g_j — stands for orbital occupancy number.

There are graph-theoretical rules developed for evaluating TRE.[9,16,17]

Since for neutral monocyclic systems C_nH_n ($n = 3, 4, 5, \ldots$), $N = B_\mathrm{r}$, it follows TRE(PE) = TRE(PRB). TRE(PE) or TRE(PRB) values of the first several members of the [N] annulene series are reported in Table I.

As for the cationic and anionic species of these annulenes, their TRE(PE) and TRE(PRB) values given in Table II, seemingly vary in an irregular manner.

A brief inspection shows that the scatter of the results is but a consequence of the interference of a size of a ring and the modulo 4 rule.[18] This is also illustrated in Figure 1, where a plot of absolute values |TRE(PRB)| vs. absolute values |TRE(PE)| for monocycles is given, up to the value 0.100.

TABLE I

Monocyclic Charged Systems

Molecule	TRE(PE) = TRE(PRB)	Reference to the preparative work
Cyclopropenyl	—0.1547	a
Cyclobutadiene	—0.3066	b
Cyclopentadiene	—0.0602	c
Benzene	0.0454	d
Cycloheptatrienyl	—0.0314	e
Cyclooctatetraene	—0.0744	f
Cyclononatetraenyl	—0.0192	

[a] R. Breslow, W. Bahary, and W. Reinmuth, *J. Amer. Chem. Soc.* **83** (1961) 2375; [b] L. Watts, J. D. Fitzpatrick, and R. Petit, *J. Amer. Chem. Soc.* **88** (1966) 623; [c] B. A. Trash, *Nature* **178** (1956) 155; [d] E. Clar, *Polycyclic Hydrocarbons*, Academic Press, London 1964; [e] A. G. Harrison, L. R. Honnen, H. J. Dauben, and F. P. Lossing, *J. Amer. Chem. Soc.* **81** (1960) 5593; [f] R. Willstätter und E. Waser, *Ber. Deut. Chem. Gesell.* **44** (1911) 4323.

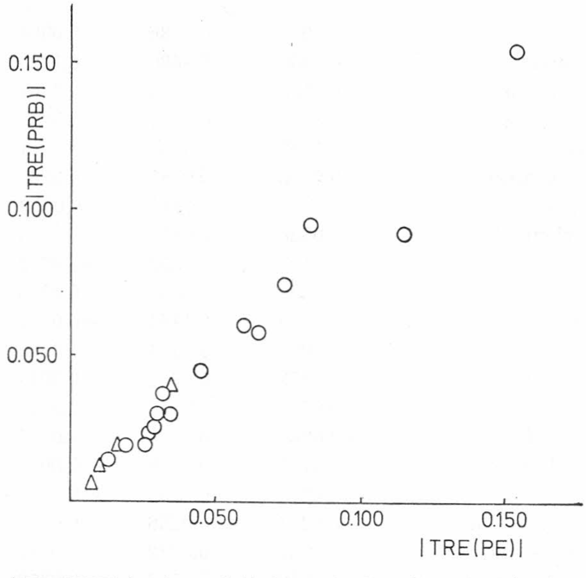

Figure 1. Absolute | TRE(PRB) | values plotted vs. absolute | TRE(PE) | values of the neutral and charged monocyclic systems given in the Tables I and II. For technical reasons only the values up to 0.100 are plotted.

The least-squares method applied to all the values from the Tables I and II, gives the equation:

$$Y = -0.0026 + 0.9932X, \text{ with correlation: } 0.9102.$$

It is to be pointed out that aromatic stability predicted upon both the TRE(PE) and TRE(PRB) values correlate very well with the experimentally observed stabilities of existing species. The quantification of this correlation is not always perfect however, mainly due to the following effects; (*i*) in the case of small rings the TRE values are not counterbalanced by effects such as is ring strain,[19–23] (*ii*) the conjugation is strongly affected by nonplanarity of certain rings, like that of cyclooctatetraene.[24]

In Table III, a comparison between the TRE(PE) and the TRE(PRB) indices of polycyclic systems is reported.
The least-squares method applied to the TRE(PRB) = f (TRE(PE)) relations of the polycyclic species in the Table III, gives the equation:

$$Y = 0.0002 + 0.8747X, \text{ with correlation: } 0.9939.$$

Again we find in virtually no case the TRE(PE), TRE(PRB) — predicted aromatic stability disagrees from the experimental behaviour of the synthesized

TABLE II

Monocyclic Charged Systems

Conjugated Ion	TRE(PE)	TRE(PRB)	Δ^a	Reference to the preparative work
Cyclopropenyl-cation	0.2680	0.1786	0.0984	b
Cyclopropenyl-anion	—0.3660	—0.4880	0.1220	c
Cyclobutadienyl-cation	—0.1536	—0.1152	—0.0384	
Cyclobutadienyl-anion	—0.0922	—0.1152	0.0230	
Cyclobutadienyl-dication	0.1522	0.0761	0.0761	
Cyclobutadienyl-dianion	0.0508	0.0761	—0.0263	d
Cyclopentadienyl-cation	—0.2298	—0.1945	0.0353	e
Cyclopentadineyl-anion	0.0528	0.0634	—0.0104	f
Benzenyl-cation	—0.0420	—0.0350	—0.0070	
Benzenyl-anion	—0.0300	—0.0350	0.0050	g
Benzenyl-dication	—0.1730	—0.1154	—0.0577	
Benzenyl-dianion	—0.0865	—0.1154	0.0289	
Cycloheptatrienyl-cation	0.0373	0.0322	0.0054	h
Cycloheptatrienyl-anion	—0.0831	—0.0950	0.0119	i
Cycloheptatrienyl-dianion	—0.0269	—0.0346	0.0077	j
Cycloheptatrienyl-trianion	0.0181	0.0258	—0.0077	k
Cyclooctatetraenyl-cation	—0.0292	—0.0256	—0.0036	
Cyclooctatetraenyl-anion	—0.0227	—0.0256	0.0029	l
Cyclooctatetraenyl-dianinon	0.0186	0.0232	—0.0046	m
Cyclononatetraenyl-cation	—0.0650	—0.0577	—0.0072	
Cyclononatetraenyl-anion	0.0175	0.0194	—0.0019	n

[a] Δ = TRE(PE) — TRE(PRB); [b] R. Breslow and J. T. Groves, *J. Amer. Chem. Soc.* **92** (1970) 984; [c] R. Breslow and M. Battista, *Chem. Ind.* (London) (1958) 1143; [d] J. S. McKennis, L. Brener, J. R. Schweiger, and R. Petit, *J. Chem. Soc. Chem. Comm.* (1972) 365; [e] K. Ziegler and B. Schnell, *Justus Liebigs Ann. Chem.* **445** (1925) 266; [f] J. Thiele, *Ber. Deut. Chem. Ges.* **33** (1900) 660; [g] M. B. Yim and D. E. Wood, *J. Amer. Chem. Soc.* **98** (1976) 2058; [h] W. von E. Doering and H. Knox, *J. Amer. Chem. Soc.* **76** (1954) 3203; [i] H. J. Dauben and M. R. Rifi, *J. Amer. Chem. Soc.* **85** (1963) 3041; [i] P. J. Garratt and M. V. Sargent, in *Adv. Org. Chem.*, E. C. Taylor and H. Wynberg (Ed.), Wiley, New York, N. Y., 1969, vol. 6, p. 29; [k] J. J. Bahl, R. B. Bates, W. A. Beavers, and C. R. Launer, *J. Amer. Chem. Soc.* **99** (1977) 6126; [l] T. J. Katz, *J. Amer. Chem. Soc.* **82** (1960) 3785; [n] G. Boche and F. Heidenhain, *Angew. Chem.* **90** (1978) 290.

TABLE III

Polycyclic Neutral and Charged Systems

Species	TRE(PE)	TRE(PRB)	Δ[b]	Reference to the preparative work
Naphtalene	0.0389	0.0353	0.0036	c
Naphthalenyl-cation	0.0138	0.0113	0.0025	d
Naphtalenyl-anion	0.0113	0.0113	0.0000	e
sym-diCOTbenzenyl-dianion[a]	—0.0019	—0.0019	0.0000	f
sym-diCOTbenzenyl-tetraanion	0.0108	0.0119	—0.001	f
8,9-benzobicyclo(5.2.0)nona-tetraenyl-cation	0.0075	0.0060	0.0015	g
8,9-benzobicyclo(5.2.0)nona-tetraenyl-radical	—0.0064	—0.0056	—0.0008	
8,9-benzobicyclo(5.2.0)nona-tetraenyl-anion	—0.0184	—0.0172	—0.0012	h
Dibenzocyclobutadienyl-dication	—0.0085	—0.0061	—0.0024	i
Dibenzocyclobutadienyl-anion	0.0015	0.0014	0.0001	j
8-H-cyclopent(alpha)ace-naphthalenyl-anion	0.0325	0.0289	0.0036	k
Cyclopent(cd)phenalenyl-anion	0.0346	0.0308	0.0038	l
Cyclohept(cd)phenalenyl-cation	0.0325	0.0260	0.0065	m

[a] COT = cyclooctatetraene; [b] △ = TRE(PE) — TRE(PRB); [c] E. Clar, *Polycyclic Hydrocarbons*, Acad. Press, London, 1964; [d] W. J. Aalbersberg, G. J. Hoijtink, E. L. Mackor, and W. P. Weijland, *J. Chem. Soc.* (1959) 3049; [e] P. Balk, G. J. Hoijtink, and J. W. Schreuss, *Rec. Trav. Chim. Pays-Bas* **76** (1957) 813; [f] L. A. Paquette, G. D. Ewing, S. Traynor, and J. M. Gardlik, *J. Amer. Chem. Soc.* **99** (1977) 6115; [g] L. Lombard and D. Wege, *Tetrahedron Lett.* **48** (1972) 4859; [h] S. W. Staley, F. Heinrich, and A. W. Orvedal, *J. Amer. Chem. Soc.* **98** (1976) 2681; [i] G. A. Olah and G. Liang, *J. Amer. Chem. Soc.* **99** (1977) 6045; [j] N. L. Bauld and D. Banks, *J. Amer. Chem. Soc.* **87** (1965) 128; [k] K. Yamamoto, M. Morioka, and I. Murata, *Tetrahedron Lett.* (1975) 3009; [l] I. Murata, K. Yamamoto, M. Morioka, M. Tamura, and T. Hirotsu, *Tetrahedron Lett.* (1975) 2287; [m] I. Murata, K. Yamamoto, and Y. Kayane, *Angew. Chem.* **86** (1974) 862.

compounds. Slight deficiences in correlation are probably due to the (*i*) incomplete conjugation, i. e., not all rings participate equally in the overall conjugation,[10,25] (*ii*) neglect of a strain in the sigma-framework. There are other effects of minor influences which do not essentially offset the TRE-based predictions.

Bearing in mind the two discussed ways of normalizing TRE, one is to conclude that appreciable difference between the TRE(PE) and the TRE(PRB) indices would appear with structures possessing side chains linked to rings; the longer and more numerous side chains the greater the differences between reported in Table IV.

In Figure 2, a plot of absolute values | TRE(PRB) | vs. absolute values | TRE(PE) | is given.

The least-squares method applied to these values gives the following relation:

$$Y = -0.0070 + 1.4878X, \text{ with correlation: } 0.9836.$$

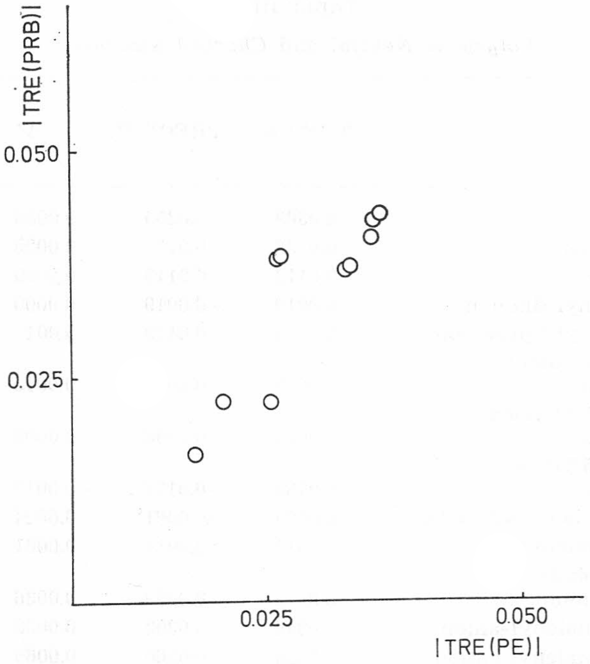

Figure 2. Absolute |TRE(PRB)| values plotted vs. absolute |TRE(PE)| values of the systems containing rings with exocyclic bonds, given in the Table IV. The values of the vinylcyclobutadiene is omitted because of scaling the plot.

TABLE IV

Neutral Systems of Rings with Exocyclic Bonds

Species	TRE(PE)	TRE(PRB)	Δ[a]	Reference to the preparative work
Styrene	0.03115	0.04253	—0.01038	b
Stilbene	0.03435	0.04008	—0.00573	c
1,1-diphenylethylene	0.03598	0.04198	—0.00600	d
Triphenylethylene	0.03619	0.04021	—0.00402	e
m-divinylbenzene	0.02293	0.03821	—0.01528	f
o-divinylbenzene	0.02260	0.03767	—0.01507	g
1-vinylnaphthalene	0.03094	0.03713	—0.00619	h
2-vinylnaphthalene	0.03065	0.03678	—0.00613	i
o-quinododimethide	0.00741	0.00988	—0.00247	j
Fulvadiene	—0.01360	—0.01632	0.00272	
1,2-bicyclopropenylethylene	—0.01656	—0.02208	0.00552	
Vinylcyclobutadiene	—0.17671	—0.26507	0.08836	

[a] Δ = TRE(PE) — TRE(PRB); [b] B. Hibbert, *J. Amer. Chem. Soc.* **47** (1925) 2240; [c] E. Böeseken, *Rec. Trav. Chim.* **47** (1928) 694; [d] B. Schlenk *Justus Liebigs Ann. Chem.* **463** (1928) 25; [e] G. L. Stadnikow, *Ber. Deut. Chem. Ges.* **47** (1914) 2140; [f] W. Johnston, *J. Amer. Chem. Soc.* **69** (1947) 2065; [g] L. Deluchat, *C. R. H. Acad. Sci.* **192** (1931) 1387; [h] Sh. Shorugin, *Chem. Abs.* **29** (1935) 6866; [i] D. Sontag, *C. R. H. Acad. Sci.* **197** (1933) 1130; [j] E. Migirdicyan, *C. R. H. Acad. Sci., Ser. C.* **266** (1968) 756.

It seems, however, that even in this class of structures the two indices generally do not disagree in predicting whether certain species is aromatic, nonaromatic or antiaromatic. Given the TRE method normalized in two ways, that is, as TRE(PE) and/or TRE(PRB), one may conclude that both variants »work« equally well. Firstly, it is to be understood that neither way is in strict terms a normalization of an extensive property; i. e., the capacity characteristic of TRE value in general case remains yet to be proved. TRE divided by a number of pi-electrons gives some rough average value corresponding to the arithmetic mean of half a series — usually, obtained by pairwise subtraction of two graph spectra. However, every TRE(PE) value contains a bit of information concerning the proper molecular topology of a system and the exact number of pi-electrons. The other way exploited here is TRE(PRB). The effects of this »normalization« could be illustrated in the example of fulvadiene. Taking the complete molecular carbon-carbón bonds skeleton, the TRE value is obtained by filling in levels obtained by pairwise subtraction of the Hückel and the matching spectra, with the number of pi-electrons corresponding to that system, that is, twelve. This value is then divided by the number of bonds closing a circle, that is, ten. Obviously, certain information concerning the molecular topology is lost. Take the fulvadiene cation now; TRE is obtained by filling the same levels with eleven electrons. This value is then divided by the same number as in the previous case, that is, ten. A bit of information concerning the exact number of pi-electrons is lost in such a way. In other words, TRE(PRB) is a quantity that reflects the improper molecular topology and the inexact number of π-electrons. The identical choice of elements making up a divisor of a TRE value is made two times, thus the effects are roughly cancelled. Hence the good correlation with the TRE(PE) values. However, this holds for common conjugated systems treated in this note; had we chosen a compound with much more exocyclic bonds, the TRE(PE) and the TRE(PRB) would be quite diverse values.

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SAŽETAK

O normiranju topološke rezonancijske energije

P. Ilić, B. Jerman-Blažič-Džonova, B. Mohar i N. Trinajstić

Topološka rezonancijska energija, TRE normirana je obzirom na ukupni broj pi-elektrona, TRE(PE), i obzirom na broj veza u prstenastom dijelu molekule, TRE(PRB). Analiza provedena u različitim klasama konjugiranih sustava pokazuje da TRE(PE) i TRE(PRB) indeksi vode istim predviđanjima o stabilnosti i aromatičkom ponašanju molekula.

INSTITUT »RUĐER BOŠKOVIĆ«, 41001 ZAGREB,
HRVATSKA I
INSTITUT »JOŽEF STEFAN«, LJUBLJANA,
SLOVENIA

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