On the Relationship between π-Electron Energy and Topological Resonance Energy

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Within series of isomeric benzenoid hydrocarbons there is a very good linear correlation between the topological resonance energy (TRE) and the total π-electron energy (E_π). Furthermore, the slope of the TRE vs. E_π regression line is almost independent of the benzenoid isomers considered, and (for all sets of isomers) is nearly equal to 0.5. This implies that comparison of benzenoid isomers with regard to their aromaticity can be made, with equal success, by using both TRE and E_π. However, E_π is computed significantly simpler than TRE, and thus advantage should be given to the former. Correlations between TRE and E_π exist also in the case of non-benzenoid isomers (both alternant and non-alternant), but are of much inferior quality.

Key words: Total π-Electron Energy; Topological Resonance Energy; Aromaticity; Benzenoid Hydrocarbons.

1. Introduction

The concept of topological resonance energy (TRE) has been independently introduced years ago by two research groups [1 – 4]. It is defined as the difference between the total π-electron energy (E_π) and the energy of a conveniently designed reference structure E_{ref}:

$$TRE = E_\pi - E_{\text{ref}}, \tag{1}$$

where E_π and E_{ref} are given by

$$E_\pi = \sum_{i=1}^{n} g_i x_i, \tag{2}$$

$$E_{\text{ref}} = \sum_{i=1}^{n} g_i y_i. \tag{3}$$

The meaning of the symbols in (2) and (3) is: n is the number of π-electrons in the conjugated molecule, g_i the occupation number of the i-th molecular orbital, $x_1, x_2, \ldots, x_n$ are the eigenvalues of the molecular graph [5, 6] associated with the conjugated molecules under consideration, and $y_1, y_2, \ldots, y_n$ the zeros of the matching polynomial of the molecular graph, representing the reference structure.

The crucial quantity in the TRE-model is E_{ref}. It is defined in a manner fully analogous to E_π, except that any effect resulting from the presence of cycles is disregarded. (From such a definition it immediately follows that for any acyclic conjugated system $TRE = 0$.) By appropriate algebraic considerations [1 – 4] it can be shown that, whereas E_π is computed from the characteristic polynomial and its zeros $x_1, x_2, \ldots, x_n$, E_{ref} is computed from the matching polynomials and its zeros $y_1, y_2, \ldots, y_n$. For the theory and applications of the TRE it is of paramount importance that the zeros of the matching polynomial, and therefore also E_{ref} are real-valued numbers [7].

TRE found considerable use in studies on aromaticity of conjugated compounds and its details can be found in several books (e. g., [5], Vol. II, pp. 1 – 28, [8], pp. 14 – 19) and review articles [9, 10]. Various aspects of the TRE concept have been studied, such as the dependence on the number of Kekulé structures and the number of rings in the benzenoid hydrocarbons [11, 12], its applicability to conjugated ions, radicals, ion-radicals, excited states, fullerenes, and Möbius structures [13 – 17], its relationship to other types of resonance energies [9, 18], and most recently, its relation to the Clar theory [18, 19], as modeled by means of the Zhang-Zhang polynomial [20]. There

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Table 1. The correlation coefficient (R) and standard deviation (SD) for the correlation between the topological resonance energy (TRE) and total π-electron energy (E_π) of sets of benzenoid isomers with h six-membered rings and n_i internal carbon atoms. Each set consisted of all possible Kekuléan isomers, whose number is $N.I.$ The respective regression line is of the form $TRE = aE_\pi + b$. One should note that all regression lines have nearly equal slopes, i. e., they are almost parallel.

h	n_i	$N.I.$	R	SD	a	b
4	0	5	0.9991	0.0034	0.533 ± 0.013	-12.75 ± 0.33
5	0	12	0.9989	0.0032	0.522 ± 0.008	-15.32 ± 0.24
6	0	36	0.9987	0.0036	0.521 ± 0.005	-18.13 ± 0.17
7	0	118	0.9982	0.0041	0.520 ± 0.003	-20.95 ± 0.12
6	2	13	0.9981	0.0034	0.558 ± 0.010	-18.07 ± 0.36
7	2	62	0.9977	0.0042	0.542 ± 0.005	-20.52 ± 0.19
7	4	9	0.9938	0.0058	0.528 ± 0.022	-18.63 ± 0.83
9	6	46	0.9966	0.0049	0.524 ± 0.006	-22.90 ± 0.30

were also critical remarks on TRE, such as comments of its non-physicality since its reference structure is hypothetical [21].

It is interesting to note that, to our knowledge, nobody investigated the relationship between the π-electron energy and topological resonance energy. Therefore, we set to investigate this relationship. To our surprise, we found that there is a high-quality linear correlation between TRE and E_π for both cata- and pericondensed benzenoids. The respective details are given in the subsequent section.

2. Numerical Work

In Figs. 1 and 2 two characteristic plots of TRE vs. E_π are shown, one for cata- and one for pericondensed benzenoid isomers. The correlations are evidently linear.

A carbon atom of a benzenoid hydrocarbon is said to be internal if it simultaneously belongs to three six-membered rings, i. e., if it does not lie on the perimeter; the number of internal carbon atoms is denoted by n_i. Benzenoid molecules are classified as catacondensed and pericondensed [22] if $n_\mathrm{i} = 0$ and $n_\mathrm{i} > 0$, respectively.

We have examined a total of 8 sets of benzenoid isomers, all consisting of all possible Kekuléan species. Of these, 4 were catacondensed and 4 pericondensed systems. (Recall that all catacondensed benzenoids are Kekuléan, whereas some pericondensed benzenoids are non-Kekuléan.) The structures of the benzenoid molecules examined were taken from [23].

The results of our statistical analysis are shown in Table 1. These indicate that in all studied cases there exists an excellent and perfectly linear correlation between TRE and E_π.

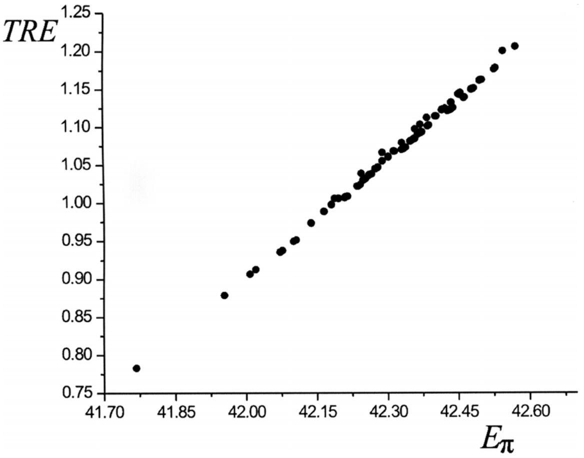

Fig. 1. The topological resonance energies (TRE) of the heptacyclic catacondensed benzenoids with formula $C_{30}H_{18}$ plotted vs. their total π-electron energies (E_π). All possible isomers (118) have been taken into account. For statistical data on this correlation see Table 1.

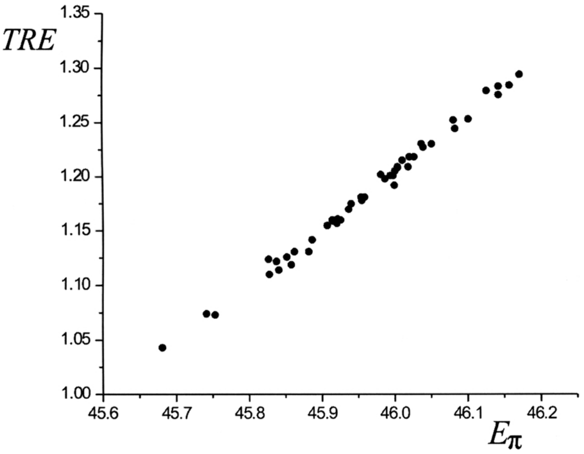

Fig. 2. Same data as in Fig. 1 for the nonacyclic pericondensed benzenoid isomers with formula $C_{32}H_{16}$. All possible Kekuléan isomers (46) have been taken into account.

In order to see whether the regularity discovered can be extended beyond benzenoid isomers, we have examined also three sets of alternant non-benzenoid isomers. These consisted of all possible [24] non-branched [h]-phenylenes, with $h = 4, 5, 6$. (Recall that a [h]-phenylene contains h six-membered rings, separated by $(h-1)$ four-membered rings [24, 25].) As seen from Fig. 3 and the data given in Table 2, the correlation between TRE and E_π, although still linear, is significantly weaker than in the case of benzenoids.

Table 2. Same data as in Table 1 for non-branched [h]-phenylenes. In the case of these alternant non-benzenoids the correlations are significantly weaker than those shown in Table 1.

h	$N.I.$	R	SD	a	b
4	4	0.984	0.008	0.55 ± 0.07	-18.5 ± 2.4
5	10	0.955	0.011	0.53 ± 0.06	-22.9 ± 2.5
6	25	0.944	0.011	0.50 ± 0.04	-25.8 ± 1.9

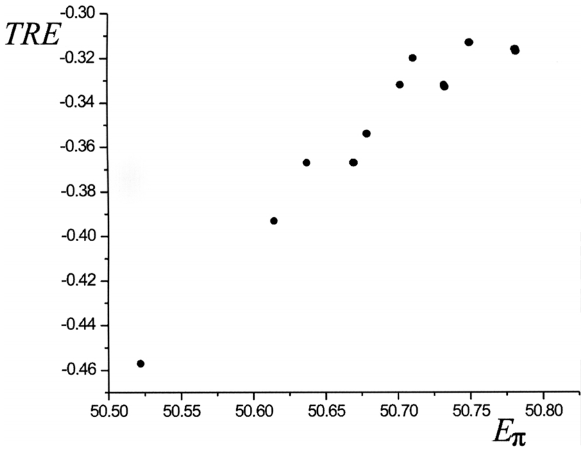

Fig. 3. Same data as in Fig. 1 for the non-branched phenylenes consisting of 6 six-membered and 5 four-membered rings, with formula $C_{36}H_{16}$. All the 25 possible isomers have been taken into account [24].

Preliminary investigations of non-alternant non-benzenoid conjugated systems (benzo-azulenes, $C_{14}H_{10}$, and dibenzo-azulenes, $C_{18}H_{12}$) indicated that the correlation between TRE and E_π is weak. Therefore studies along these lines were not further pursued.

3. Discussion and Concluding Remarks

The results outlined in the previous section would probably upset people whose efforts were dedicated to development of reliable resonance energy index for assessing the aromatic behavior of conjugated systems. A good summary of these efforts is given in [8] and [9]. The (near) linearity of the plots TRE vs. E_π indicates that both quantities are similarly dependent on the structure of benzenoid hydrocarbons. This conclusion is corroborated by the fact that the slopes a of all regression lines in Table 1 are nearly the same ($a \approx 0.5$). Whether this particular value of a has any further implication is not clear at the moment.

There are several consequences of this result. One concerns the nature of the TRE concept. Since E_π is an observable that serves well in the interpretation of many physical and chemical properties of conjugated systems [6, 26 – 28], it is gratifying that it correlates so well with TRE. In this sense the TRE is not an ad hoc quantity, but the quantity with quantum-chemical background.

Another consequence is related to the question whether to use TRE or E_π to predict the degree of aromaticity of a conjugated species? Indeed, if we are interested in comparing (or ordering) benzenoid isomers with respect to their degrees of aromaticity, then we can safely use E_π instead of TRE. However, we may do this only as long as we compare isomers. Besides, it seems that the usage of E_π instead of TRE is limited to benzenoids. Of course, wherever it is possible to use E_π instead of TRE, preference should be given to the former because its computation is much simpler than that of TRE.

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