

COMPARING ENERGY AND RANDIĆ ENERGY

Boris Furtula, Ivan Gutman

Faculty of Science, University of Kragujevac,

P. O. Box 60, 34000 Kragujevac, Serbia

furtula@kg.ac.rs, gutman@kg.ac.rs

The recently conceived Randić energy (RE) is examined, and its relation to the (earlier much studied) total π -electron energy (E) is investigated. Within classes of molecular graphs, there exists a relatively good (increasing) linear correlation between RE and E . However, several significant differences between the structure-dependencies of RE and E have been discovered, the most striking of which is their dependence on the number m of edges of the underlying graph. Whereas, with increasing m , the average value of E increases, reaches a maximum and then decreases, the average value of RE monotonically decreases. The structure of the connected graph with a fixed number of vertices and maximal RE value was established.

Keywords: total π -electron energy; Randić energy; molecular graph; energy (of graph)

СПОРЕДУВАЊЕ НА ЕНЕРГИЈАТА И РАНДИЌЕВАТА ЕНЕРГИЈА

Истражувана е неодамна воведената Рандиќева енергија (RE), како и нејзината врска со порано многу испитуваната вкупна π -електронска енергија (E). Кај класите молекуларни графови постои релативно добра (растечка) линеарна корелација помеѓу RE и E . Најдени се неколку значајни структурни разлики меѓу RE и E , од кои најважна е зависноста на страните m од соодветниот граф. Најдено е дека при зголемувањето на m средната вредност на E се зголемува и достигнува максимум и потоа се намалува, додека средната вредност на RE монотонно опаѓа. Исто така е проценета структурата на поврзаните графови со фиксен број на темиња и максималната вредност на RE .

Клучни зборови: вкупна π -електронска енергија; Рандиќева енергија; молекуларен граф; енергија (на графот)

1. INTRODUCTION

The fact that the total π -electron energy (E), as calculated by methods of chemical graph theory, gives a reliable description of the thermodynamic properties and aromaticity of conjugated molecules, was established and well-documented long ago [1–5]. In the last few years, several other graph-based “energies” have been put forward [6], of which the so-called “Randić energy” (RE) has recently attracted much attention [7–13]. The reason for

this is a strong algebraic parallelism between E and RE (see below), that suggests that these two energies might possess analogous and/or very similar properties. Curiously, however, in none of the several published studies devoted to Randić energy [7–13] has there been any attempt to compare it with the total π -electron energy. Even worse, none of these papers (except [13], see below) report numerical calculations of RE , offering only a variety of mathematical results.

In view of the above, we have undertaken

a detailed numerical study of Randić energy and compared the results thus obtained with corresponding results for total π -electron energy.

The rest of this paper is organized in the following manner. In Section 2, we provide the necessary mathematical definitions and outline some relevant properties of the adjacency and Randić matrices and their eigenvalues. In Section 3, we briefly describe the details of our calculations. In Section 4, we report on the properties of E and RE that make these two “energies” closely analogous. In Section 5, we point out cases where the structure-dependency of E and RE drastically differ.

2. GRAPH ENERGY AND RANDIĆ ENERGY

The usual matrix representation of molecular graphs [2] is the *adjacency matrix*.

Let G be a molecular graph and let v_1, v_2, \dots, v_n be its vertices. Then, the (i, j) -element of the adjacency matrix $\mathbf{A}(G)$ of G is defined as:

$$a_{ij} = \begin{cases} 1 & \text{if the vertices } v_i \text{ and } v_j \text{ are adjacent} \\ 0 & \text{otherwise} \end{cases} \quad (1)$$

Thus, $\mathbf{A}(G)$ is a symmetric square matrix of order n . Let its eigenvalues be $\lambda_1, \lambda_2, \dots, \lambda_n$, forming the A -spectrum of the graph G . As is well-known [2, 14], these eigenvalues are real numbers, their sum is equal to zero, and the relations $\lambda_i = -\lambda_{n-i+1}$ hold for all $i = 1, 2, \dots, n$, if and only if the graph G is bipartite (which is the case with the vast majority of molecular graphs).

The total π -electron energy (expressed, as usual, in the units of the HMO carbon-carbon resonance integral β , see [1, 2, 4, 15, 16]) satisfies the relation:

$$E = E(G) = \sum_{i=1}^n |\lambda_i|. \quad (2)$$

To be more precise, expression (2) holds if all bonding MOs are doubly occupied, and all antibonding MOs are empty [4]. Note that in mathematics, the quantity defined via Equation 2 is referred to as the *graph energy* [6].

In order to understand the motivation for introducing the concepts Randić matrix and Randić energy, recall that in the 1970s Milan Randić conceived a molecular structure descriptor [17] that nowadays is known under the name *connectivity index* or *Randić index*. This topological index found countless chemical and pharmacological applications [18–21], and its mathematical theory has been elaborated in due detail [22–24].

If the degree (= number of first neighbors) of the vertex v_i of the graph G is denoted by $\deg(v_i)$, then the Randić index is defined as:

$$R = R(G) = \sum_{i,j} \frac{1}{\sqrt{\deg(v_i)\deg(v_j)}}, \quad (3)$$

where the summation goes over all pairs of vertices that are adjacent in G .

In view of formula (3), and bearing in mind Eq. (1), it is purposeful to conceive the *Randić matrix* $\mathbf{R}(G)$ of the graph G so that its (i, j) -element is defined as:

$$r_{ij} = \begin{cases} \frac{1}{\sqrt{\deg(v_i)\deg(v_j)}} & \text{if the vertices } v_i \text{ and } v_j \text{ are adjacent} \\ 0 & \text{otherwise} \end{cases}$$

Consequently, $\mathbf{R}(G)$ is also a symmetric square matrix of order n . Let its eigenvalues be $\rho_1, \rho_2, \dots, \rho_n$, forming the R -spectrum of the graph G . It can be easily shown [7, 9] that these eigenvalues are real numbers, their sum is equal to zero, and the relations $\rho_i = -\rho_{n-i+1}$ hold for all $i = 1, 2, \dots, n$, if and only if the graph G is bipartite.

The matrices \mathbf{A} and \mathbf{R} have many other analogous properties. For instance, both matrices have the same number of positive, negative, and zero eigenvalues; this causes the

clustering of the data points seen in Figure 1. In addition,

$$\det \mathbf{R}(G) = \frac{1}{\deg(v_1)\deg(v_2)\cdots\deg(v_n)} \det \mathbf{A}(G)$$

Now, in parallel to Eq. (2), we define the *Randić energy* as:

$$RE = RE(G) = \sum_{i=1}^n |\rho_i|.$$

For reasons that are irrelevant for the present considerations, Randić energy is sometimes referred to as “normalized Laplacian energy” [9, 13].

As one could expect, many aspects of the Randić energy are analogous to the total π -electron energy. Two simple examples are (i) and (ii), whereas a number of chemically more relevant examples are found in Section 4.

- i. Let the graph G consist of two disconnected components G_1 and G_2 . Then, $E(G) = E(G_1) + E(G_2)$ and $RE(G) = RE(G_1) + RE(G_2)$.
- ii. $E(G) = RE(G) = 0$ only if the graph G has no edges (which cannot occur in chemical applications).

3. NUMERICAL WORK

Numerical calculations of Randić energy were reported by Silvia and Davis [13] and Cavers et al. [9]. They systematically examined all connected graphs with a fixed number n of vertices, but limited this to the chemically uninteresting case $n \leq 8$. In order to fill this gap, we have undertaken a detailed computational investigation into Randić energy, directing it towards chemically interesting (molecular) graphs. In all studied cases, the respective total π -electron energies were also calculated, so that we could compare RE with E .

The software used for obtaining these results was written in the *Python* programming language. In it, several Python modules were employed that can be freely downloaded from

the internet. In particular, the *NumPy* module [25] has been used for calculating the Randić and total π -electron energies, and the *NetworkX* module [26] for converting the graphs into a format suitable for calculating the energies. In order to construct all connected graphs and all trees with a given number of vertices, the *Nauty* package [27] was utilized. For constructing all catacondensed benzenoid hydrocarbons with a given number of hexagons, we used the *CaGe* software [28].

Initially, we calculated RE for connected graphs up to $n = 10$ vertices, whose number exceeds 11×10^6 . For general graphs with $n > 10$, it was impossible to continue this kind of investigation, and we restricted it to trees. All trees (= connected acyclic graphs) until $n = 21$ were analyzed. In addition, we made a program that constructs graphs with a given number of vertices by randomly adding new edges (see Section 5). To develop this Python program, we used the built-in *Random* module.

The other task was to examine the correlation between the Randić energy and the total π -electron energy within classes of chemically relevant graphs. We did this for chemical trees with a fixed number n of vertices (up to $n = 20$), and for catacondensed benzenoid hydrocarbons with h hexagons (up to $h = 8$, i.e. up to $n = 34$).

4. AGREEMENTS BETWEEN E AND RE

Within various classes of molecular graphs, a reasonably good (increasing) linear correlation between Randić energy and total π -electron energy could be established. As characteristic examples, we present here such correlations for chemical trees (Figure 1) and catacondensed benzenoid hydrocarbons (Figure 2). From Figures 1 and 2 (as well as from the analogous computational results not presented here), we conclude that the main structural factors that influence the total π -electron energy also influence (in the same sense) the Randić energy. Recall that in the case of chemical trees,

this is the degree of branching, whereas for benzenoid hydrocarbons, the main factor is the number of Kekulé structures [4].

Although at first glance one may get an impression that the structure-dependencies of E and RE fully coincide, this is only “statistically” correct. A more detailed examination of Figures 1 and 2 reveals that there exist numerous pairs of molecular graphs G_1, G_2 (especially

chemical trees), such that $E(G_1) < E(G_2)$, but $RE(G_1) > RE(G_2)$. This implies that the fine details of the structure-dependency of Randić energy differs from that of total π -electron energy. However, some much more pronounced differences in the properties of these two energies were established; we outline these in the subsequent section.

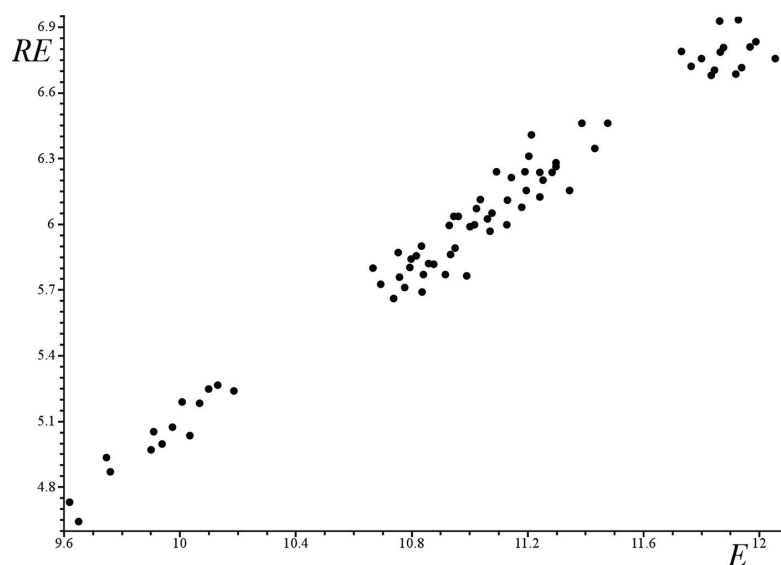


Fig. 1. Randić energy (RE) versus total π -electron energy (E) of chemical trees with $n = 10$ vertices (75 data points). The data points are clearly separated into three clusters, corresponding to number of zero eigenvalues (of both \mathbf{A} and \mathbf{R}) equal to 0 (top, right), 2 (middle), and 4 (bottom, left)

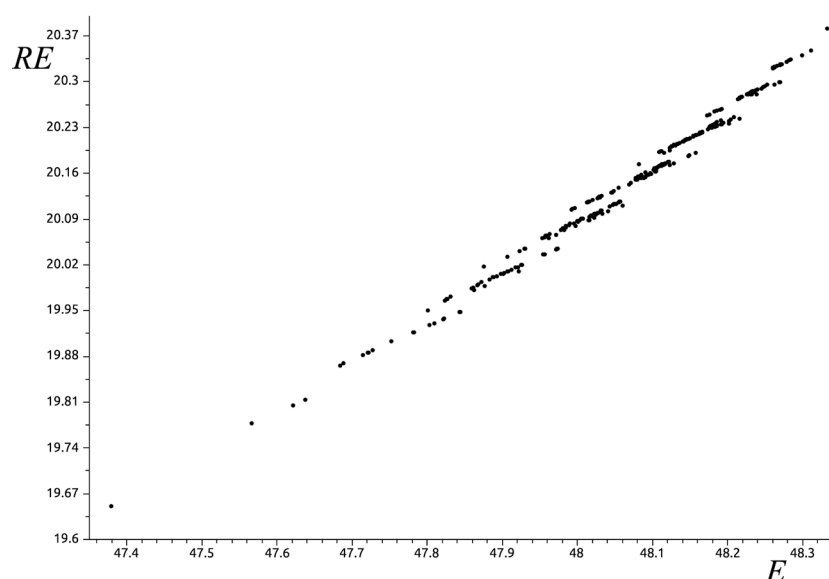


Fig. 2. Randić energy (RE) versus total π -electron energy (E) of catacondensed benzenoid hydrocarbons with $h = 8$ hexagons (411 data points). The data points belong to several near-lying, mutually parallel regression lines, depending on the number of bay regions [29, 30]

5. DISAGREEMENTS BETWEEN E AND RE

One of the classical results of the theory of total π -electron energy is that, in the case of molecular graphs, E is an increasing function of the number m of carbon-carbon bonds (i.e. the number of edges of the molecular graph) [4, 31]. In fact, E is predicted to be approximately proportional to \sqrt{m} . In order to see how far this m -dependence of E goes, a pertinent numerical experiment was designed [32]. In it, we started with a n -vertex graph without edges and added new edges to it (one-by-one) in a random manner. Thus, the E -value increased, reached a maximum and decreased, but in a somewhat

irregular manner. A typical result of this kind is shown in Figure 3(a). By repeating these numerical experiments several hundred times, and calculating the average, an almost perfectly smooth curve was obtained; see Figure 3(b).

We have now performed the analogous numerical experiments with Randić energy for $n \leq 30$. The results obtained indicate a completely different m -dependence of RE , clearly seen from the examples depicted in Figures 3(c) and 3(d). To our surprise, RE was found to be an almost monotonically decreasing function of m (except for $m < n - 1$, when the underlying graphs are necessarily disconnected and thus chemically irrelevant).

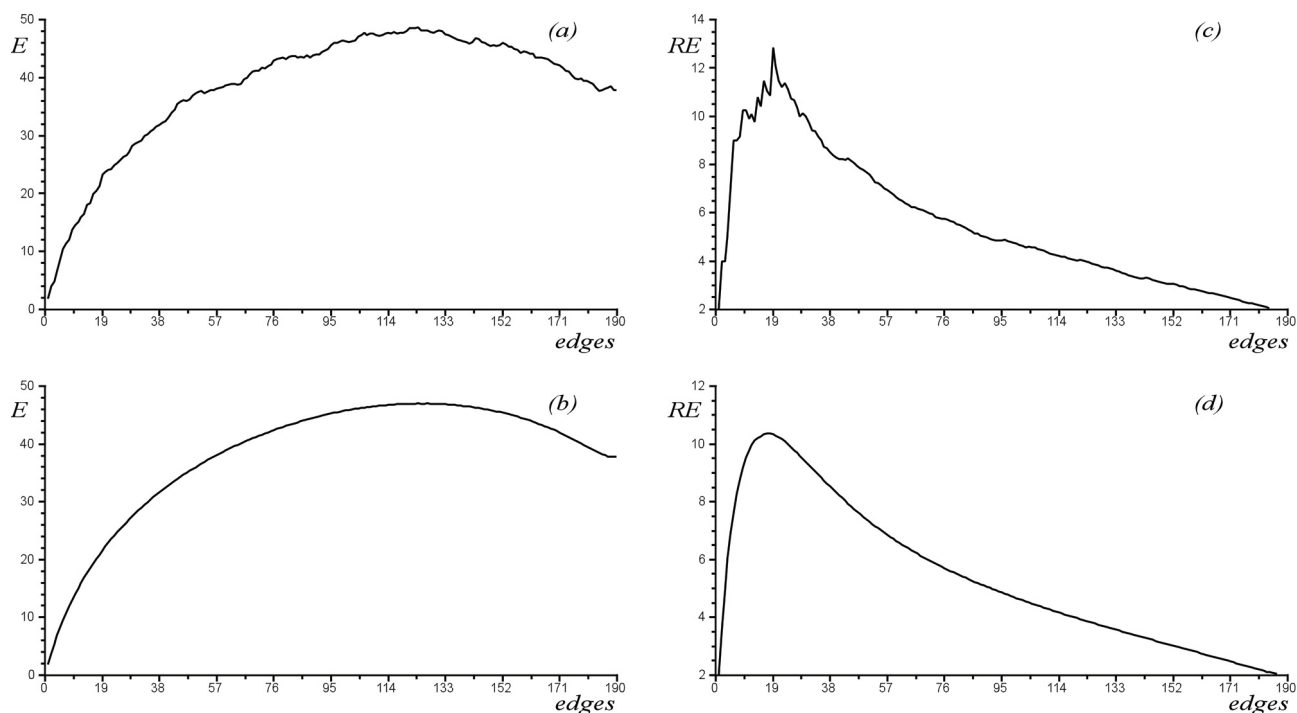


Fig. 3. Diagram (a): Change in total π -electron energy (E) when edges are inserted at random to a graph consisting of $n = 20$ isolated vertices. Diagram (b): The average of 1000 repetitions of the same experiment [32]. Diagrams (c) and (d): Analogous results for Randić energy (RE)

It should be mentioned that by adding new edges to a graph, the Randić energy will increase in most cases, but not always. This property of RE was previously reported in [9, 13], and is clearly seen from the numerous humps on the “curve” in Figure 3(c).

Based on such an m -dependence of RE , it may be expected that the connected graph with maximal Randić energy will have as few edges as possible, i.e. will be a tree. The tree with maximal total π -electron energy is the path graph P_n [33]. Silvia and Davis [13] conjectured

that P_n is also the connected n -vertex graph with maximal RE . However, Cavers et al. [9] have found counterexamples for this conjecture. As in [9], we found that $RE(P_n)$ is maximal only for $n \leq 6$, and that for greater values of n , the maximal- RE tree has a completely different structure; see Figure 4. Note that in [9], it was explicitly stated that the structure of maximal- RE graphs is not known.

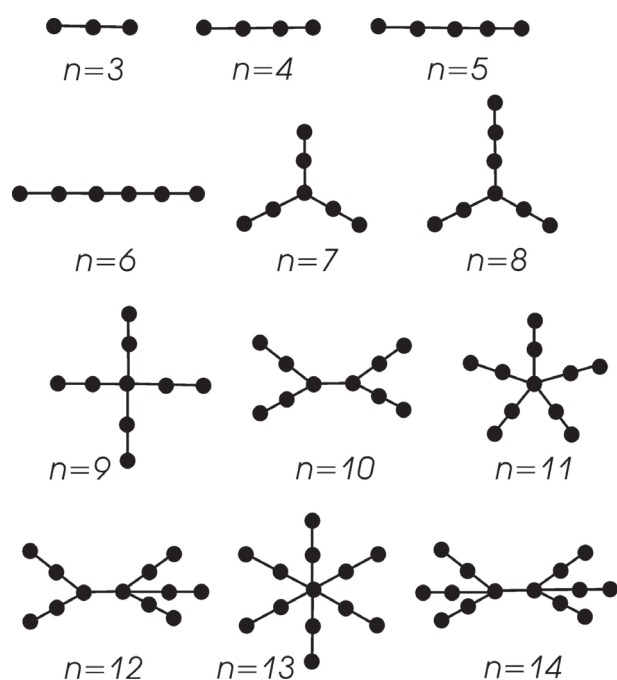


Fig. 4. The first few connected graphs with maximal Randić energy. Note that these are trees, and are path graphs only up to $n = 6$, thus violating the Silvia-Davis conjecture

From the examples depicted in Figure 4, as well as from the analogous results obtained for n up to 21, by means of extensive numerical search, the general form of the connected n -vertex graph with maximal Randić energy can be envisaged, as shown in Figure 5. A mathematical proof of our claim remains a task for the future. At this point, it is worth noting that the structure of the connected n -vertex graph with maximal graph energy is not known [6], which provides one more major difference between E and RE .

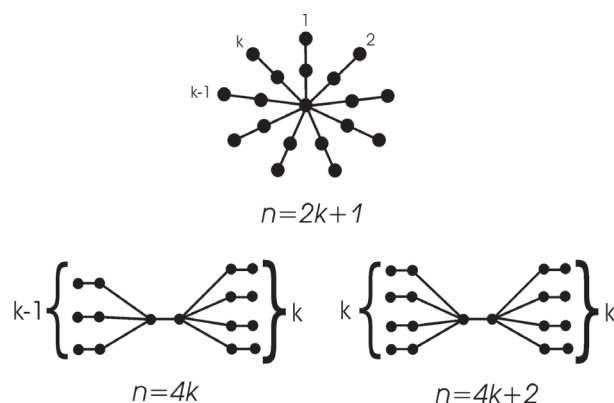


Fig. 5. The general form of connected graphs with n vertices whose Randić energy is maximal. The trees with $2k + 1$ vertices were studied by Cavers et al. [9] who calculated their Randić energies, but failed to recognize that these Randić energies are maximal

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