Topological Resonance Energy of Fullerenes

Darko Babić*

Institute "Rugjer Bošković", HR-10001 Zagreb, PO Box 1016, Croatia

Gunnar Brinkmann and Andreas Dress

Department of Mathematics, University of Bielefeld, D-33501 Bielefeld, Germany

A new algorithm for computation of a matching polynomial is outlined. It has been successfully applied for evaluation of the topological resonance energy (TRE) of all fullerene isomers with up to, and including, 70 carbon atoms. The obtained results indicate a high correlation between TRE values and π-electronic energies (E_π), which was found to be a consequence of the invariance of the reference energy values for a given size of isomers. A similar high correlation was established between TRE and E_π values normalized to a number of carbon atoms, thus extending over different sizes of fullerene isomers. These results show that the resonance energy does not bring any new insight into stabilities of different fullerene isomers which is not already achieved by consideration of E_π.

1. INTRODUCTION

Twelve years after their discovery[1] and seven years after the successful preparation,[2] fullerenes are still among the most studied objects in chemistry. Among the most important questions provoked by their discovery is a mechanism of their formation which is not yet completely understood.[3] A similar question was raised by a rather limited selection of isomers which could be prepared so far. Among 1812 isomers of C_{60} and 8149 isomers of C_{70}, only one C_{60} (buckminsterfullerene) and one C_{70} isomer could be obtained so far. In these two cases the selectivity can be explained by the isolated pentagon rule (IPR)[4] since these are the only two isomers satisfying this rule. Indeed, so far only IPR isomers have been produced,[5,6] but there are also many other IPR isomers which are mysteriously absent, for example those with 72 or 74 carbon atoms.

Since fullerenes are being prepared in high-energy conditions, it is reasonable to assume that thermodynamic (and possibly reactivity) factors are responsible for the exhibited selectivity. A particular aspect of thermodynamic stability of conjugated molecules is their resonance energy. It has been defined in several different ways, and most of the proposed schemes are based on a tight-bonding model for π-electrons such as the Hückel model. The topological resonance energy (TRE) model[7,8] is distinguished from others by not including any adjustable parameter. It has been already applied in several studies of fullerenes[9−15] and fullerene-like molecules,[16] but its use was limited by computational difficulties. The biggest difficulty was a computation of a matching polynomial for which an efficient algorithm did not exist. In this paper we describe an algorithm with the remarkably greater efficiency which allowed us to compute topological resonance energies for all fullerene isomers up to 70 carbon atoms. This systematic study provided a deeper insight into the relation between TRE and π-electronic energy and into their dependence on the size of fullerene molecules.

2. COMPUTATION OF THE TRE OF FULLERENES

TRE is defined as[7,8]

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

where E_π stands for the Hückel π-electronic energy and E_{ref} is the reference energy obtained from the matching polynomial of the corresponding molecular graph. The matching polynomial represents the characteristic polynomial of the implicitly defined reference structure. Generally, the reference structure is only implicitly defined and cannot be fully specified.

Evaluation of the TRE for fullerenes turned out to be a great challenge,[9−15] mostly due to the highly demanding computation of the matching polynomial for fullerenes with more than 50 atoms. In several papers TRE values were reported for isomers with up to 50 atoms[9−11] and for a small number of selected isomers with 60 atoms and their derivatives.[12−15] For fullerenes with more than 60 atoms, TRE was computed only for the best known C_{70} isomer.[15] The CPU times needed for computation of matching polynomials for a few representative fullerenes illustrate the difficulties associated with evaluation of TRE. Balasubramanian[9] reported that more than 7 h was needed for fullerene isomer with 50 atoms, and "a very conservative estimate of the CPU time required for computing of the matching polynomial of the Bucky ball as 113 h on IBM RS6000/560". The algorithm he used for evaluation of the matching polynomial is described in ref 17. By using the algorithm proposed by Herndon et al.,[18] the matching polynomial of C_{70} has been computed in 3 days and 18 h on a DEC Station 3000 Alpha AXP 400 with precision extended to 27 decimal digits.[16] Only 2 h and 11 min were needed for the same task by applying smaller precision provided by integer*8 variables (19 digits). In this case the smaller precision was sufficient, but it was certain only after the computation with safe precision was performed. The algorithm used in ref 16 seems to be more efficient, yet it only slightly shifts the practical limits of the TRE model. Massive calculation for fullerenes remained an open and challenging problem.

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3. ALGORITHM FOR COMPUTATION OF MATCHING POLYNOMIALS

In order to compute TRE for bigger fullerenes, a new algorithm was needed, as pointed out also by Balasubramanian.[9] A remarkable efficiency of the transfer matrix method for matching polynomials of polymer graphs and polygraphs[19,20] led us to develop a new algorithm based on the *divide and conquer* strategy.[21] It has proven to be much more efficient than all known general algorithms.[17,18,22] The above mentioned computation for C_{70}, with the extended precision, needed less than 14 min on a common PC 486/66 MHz. Average and maximum CPU times, on HP-800/G60 9000, for isomers with 64, 66, 68, and 70 atoms, are tabulated as follows:

N	no. of isomers	CPU time/s	
		av	max
64	3464	17.9	32.4
66	4478	18.1	70.5
68	6332	30.0	58.9
70	8149	33.9	96.7

The divide and conquer algorithm is based on successive splitting of the molecular graph into smaller subgraphs until they become either acyclic or sufficiently small that their matching polynomial can be efficiently computed in some straightforward way. Dividing the problem into smaller parts is enabled by the well-known recurrence relation[23]:

$$\alpha(G) = \alpha(G - e) - \alpha(G - u - v) \qquad (2)$$

where e stands for an edge of a graph G with u and v being its incident vertices. We divide vertices of G into two disjoint subsets, which induce two subgraphs G_1 and G_2. Systematic application of relation 2 to all edges connecting two induced subgraphs G_1 and G_2 can be compactly written as

$$\alpha(G) = \sum_{S \in M(G_1,G_2)} (-1)^{|S|} \alpha[G_1 - V_1(S)]\,\alpha[G_2 - V_2(S)]$$

$$(3)$$

where $M(G_1,G_2)$ stands for the set of all matchings (including the empty one) of the set of edges connecting vertices from G_1 to vertices in G_2. The summation runs over all subsets S of $M(G_1,G_2)$, and $G_i - V_i(S)$ denote a subgraph of G_i obtained by removing vertices which terminate edges S in G_i.

The efficiency of the algorithm is strongly affected by the way in which decomposition of G is performed, that is, by the choice of G_1 and G_2. Clearly, $M(G_1,G_2)$ should be as small as possible since its cardinality determines the number of terms in identity 3. However, this criterion taken solely commonly leads to a rather disbalanced G_1 and G_2 and frequently reduces one of them to a single vertex. A simple model, in which an exponential complexity of the computational algorithm is assumed, shows that the optimal decomposition is into equally sized subgraphs (if, by assumption, the number of terms in (3) is held fixed). However, in practice, goals of balanced decomposition and small cardinality of $M(G_1,G_2)$ are frequently opposed to each other, thus making the optimal choice a difficult and still open question.
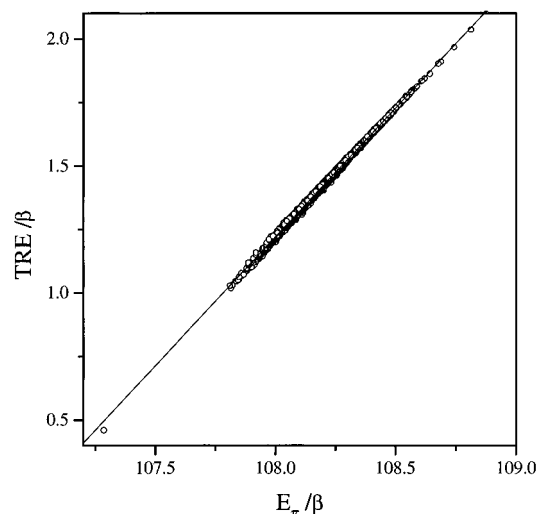

Figure 1. TRE of 8149 isomers of C_{70} drawn vs their E_π.

For the present purpose, we have systematically searched for a decomposition into equally sized G_1 and G_2 while keeping the number of edges connecting them into G, called cutset edges, as small as possible. A target function was defined as a sum of the number of cutset edges and the absolute difference between the sizes of G_1 and G_2. A systematic search was performed for the decomposition producing the minimal target function. In order to make the search more efficient, it was taken that the cutset does not contain adjacent edges.

After the first splitting, the same procedure was applied to each subgraph $G_i - V_i(S)$, and the subgraphs resulting from this second splitting were not decomposed anymore. Instead, the matching polynomial of each of them was computed by, first, successive removal of edges belonging to cycles until acyclic graphs were obtained, and, second, application of the algorithm of Mohar[24] for computation of their characteristic polynomials (which, for acyclic graphs, are identical to their matching polynomials). In this way matching polynomials of graphs obtained by the second splitting were computed similarly to that proposed by Herndon et al.[18] but without paying much attention to the choice of cycle edges to be removed.

Computation of polynomial zeros, which are needed for evaluation of E_{ref}, has been performed by the Laguerre's method as described in *Numerical Recipes*.[25] In order to safely handle large coefficients of matching polynomials, the program has been implemented by using the high-performance multiprecision package developed by Bailey.[26]

4. RESULTS

TRE values of fullerenes show several interesting features. First, there is an excellent linear correlation between TRE and E_π. This has already been noted[16] for fullerene-like isomers with four-membered rings, and the correlation for (proper) fullerenes is even better. Figure 1 shows this relationship for (all) isomers of C_{70}.

Linear regression gives the following relationship between TRE and E_π for C_{70} isomers:

$$\text{TRE} = 1.013684 E_\pi - 108.256556 \qquad r^2 = 0.998 \qquad (4)$$

This excellent correlation can be explained by a small variability of E_{ref} for isomers with a fixed number of atoms.
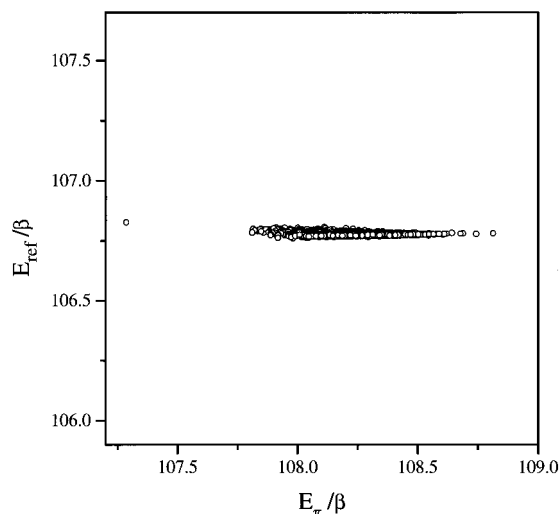
Figure 2. E_{ref} of 8149 isomers of C_{70} drawn vs their E_π. The widths of both axes are deliberately kept the same.

In order to show this, E_{ref} values for the same set of fullerene isomers are drawn in Figure 2 vs E_π, with both axis ranges deliberately chosen to be the same.

Small variability was found not only for E_{ref} values but also for the zeros of the corresponding matching polynomials.[27] Although unexpected, this should not be surprising. Fullerenes are structurally very similar molecules, differing only in the arrangement of the constituent rings: 12 pentagons and some number of hexagons. A matching polynomial was introduced in order to eliminate the effects of the rings present in the conjugated system,[7,8] since the delocalization effects are closely related to the presence of rings. There is no way to explicitly derive a structure implied by the matching polynomial; therefore the "reference" structures of various isomers cannot be compared. Nevertheless, one could expect that in the case of fullerene isomers the implicitly defined reference structures should be even more similar than the parent structures, and this should be reflected in their invariants as well. The small variability of E_{ref} and matching polynomial zeros confirms this reasoning. In this respect the matching polynomial behaves well and indicates that its choice for the definition of a reference structure is good.

The results shown in Figures 1 and 2 indicate that E_π alone suffices for qualitative consideration of π-electronic influence on the stability of fullerenes since TRE can be well-estimated from E_π data. Figure 3 shows average TRE/N values drawn versus average E_π/N for all isomers with between 20 and 70 atoms. The correlation is checked by the linear regression

$$(TRE/N)_{av} = 0.991617(E_\pi/N)_{av} - 1.512148$$
$$r^2 = 0.9998 \quad (5)$$

where the subscript "av" denotes quantities averaged over all isomers of the same size.

This linear relationship is established for average values, and one could doubt whether it holds for individual isomers as well. Figure 4 shows normalized TRE values drawn versus normalized E_π for all isomers of C_{50} and C_{60}. The results of linear regression are

$$TRE/N = 1.024296E_\pi/N - 1.562211 \quad r^2 = 0.998 \quad (6)$$

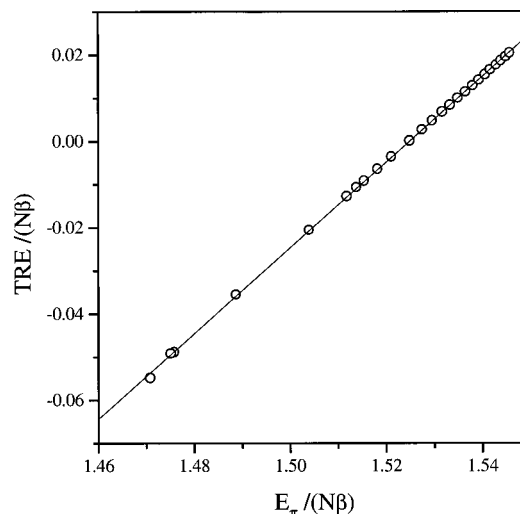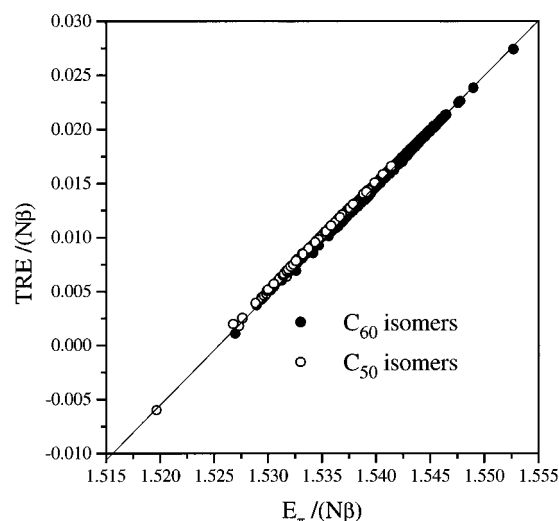**Figure 3.** Average TRE values, normalized to the number of carbon atoms, drawn vs normalized E_π.

Figure 4. Normalized TRE values for all isomers of C_{60} and C_{50} drawn vs normalized E_π.

By comparison with the regression results obtained from Figures 1, 3, and 4, given in eqs 4−6, one can verify that practically the same linear relationship extends to fullerene isomers of different sizes. The values of the first coefficients are close to 1 in all three cases, as should be expected from the invariability of E_{ref}, shown in Figure 2.

Average TRE values, for all considered fullerene isomers normalized to a number of atoms, N, are drawn in Figure 5 versus N. Relation 5 enables one to extrapolate these values to higher isomers if the average E_π values are known. The extrapolated values are also drawn in Figure 5 and denoted by open symbols. The average E_π values for $N = 110$, 120, and 130 are estimated by taking random samples from all of the isomers. Each generated structure was accepted with a pregiven probability such that the expected number of selected isomers was about 140 000. The isomers were generated by the fast algorithm recently reported in refs 28 and 29. Extrapolated TRE/N values for IPR isomers are separately shown in Figure 5 as represented by open circles. One may note that the normalized TRE values increase with size, indicating that bigger fullerenes are more stable. This agrees with the experimental result,[30] which shows that C_{70} is more stable than C_{60}. When size increases, fullerenes become more and more structurally similar to graphite.

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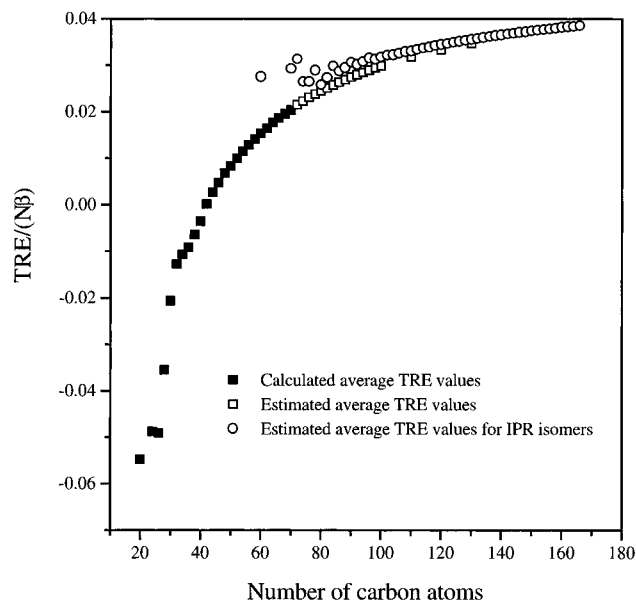*J. Chem. Inf. Comput. Sci., Vol. 37, No. 5, 1997* **923**

Figure 5. Average normalized TRE values, calculated and estimated ones, drawn vs the number of carbon atoms in fullerene isomers.

TRE/N values for graphite are estimated in refs 31 and 32 to be 0.0433 β units and 0.0468 β units, respectively. From the trend shown in Figure 5 one could expect that the TRE/N of fullerenes tend to this value.

5. CONCLUSIONS

Topological resonance energy has been calculated for all fullerene isomers with up to 70 atoms. An exceptionally good correlation between TRE and E_π has been found to exist. The reason for such a good correlation is a very small variability of E_{ref} as compared to E_π within the isomers of a given size. Correlation between TRE and E_π, normalized to a number of atoms, extends through different sizes of fullerene isomers. Average TRE values of isomers of different sizes show that the stability of fullerenes generally increases with size.

All of the results indicate that nothing new can be learned about the stability of fullerenes from their topological resonance energy.

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