

Equienergetic chemical trees

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Abstract: The energy $E(G)$ of a graph G is the sum of the absolute values of the eigenvalues of G . Two graphs, G_1 and G_2 , are said to be equienergetic if $E(G_1) = E(G_2)$. We report here the results of the search for pairs of equienergetic acyclic molecular graphs (chemical trees) with the same number n of vertices. There are very few such pairs. The smallest has $n = 9$ and pertains to 3,3-diethylpentane and 3-methyloctane. Among the chemical trees with $n \leq 18$, only five more such pairs and a triplet were found.

Keywords: energy of graph, total π -electron energy, chemical trees, equienergetic graphs.

INTRODUCTION

The total π -electron energy E , as calculated within the Hückel molecular orbital (HMO) model, is one of the most important and most studied molecular-graph-based quantum mechanical characteristics of conjugated molecules. For the vast majority of (but not all) conjugated molecules, E satisfies the simple expression

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

where G is the molecular graph representing the π -electron system, x_1, x_2, \dots, x_n the eigenvalues, and n the number of vertices of G . Details of the theory of the HMO total π -electron energy are found in the books.^{1–4} A long time ago,⁵ the right-hand side of Eq. (1) was used as a definition of a quantity called *energy of a graph*. By this, the considerations of $E(G)$ need no longer be restricted to molecular graphs of conjugated π -electron systems, but can be extended to all graphs. This not only provided a stimulus for work on the mathematical theory of $E(G)$ (as, for instance, in recent papers^{6–15}), but also made it possible to apply $E(G)$ in the study of the physico-chemical properties of saturated organic compounds^{16–20} and biopolymers.¹⁸

If G_1 and G_2 are two graphs for which the equality $E(G_1) = E(G_2)$ is satisfied, then G_1 and G_2 are said to be *equienergetic*.

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A problem, encountered in chemical graph theory a long time ago, is whether there exist molecular graphs with identical spectra (so called “cospectral molecular graphs”). The answer is affirmative, as was first shown by Balban and Harary²¹ and Herndon.^{22,23} In view of Eq. (1), cospectral molecular graphs are necessarily equienergetic. The question whether pairs of non-cospectral equienergetic molecular graphs pertaining to isomers (thus possessing an equal number of vertices and an equal number of edges) exist remained until now unanswered. In fact, the first examples of non-cospectral equienergetic graphs (which, however, are not molecular graphs) were discovered very recently.^{14,15}

We now show that among chemical trees (*i.e.*, acyclic molecular graphs) pairs of non-cospectral equienergetic species exist and all of them are to be found for $n \leq 18$.

Recall that a connected acyclic graph is called a tree. A chemical tree is a tree in which no vertex has a degree greater than four.^{2,4} An n -vertex tree possesses $n - 1$ edges; thus if two trees have an equal number of vertices, they also have an equal number of edges.

SEARCH FOR EQUIENERGETIC CHEMICAL TREES

In order to detect equienergetic chemical trees, we downloaded from the site²⁴ the files containing all trees with n vertices ($n = 4, 5, \dots, 18$), computed their eigenvalues and energies, and recorded those having equal energies. Recall that there are 205001 trees with $4 \leq n \leq 18$, of which 103444 are chemical trees.⁴

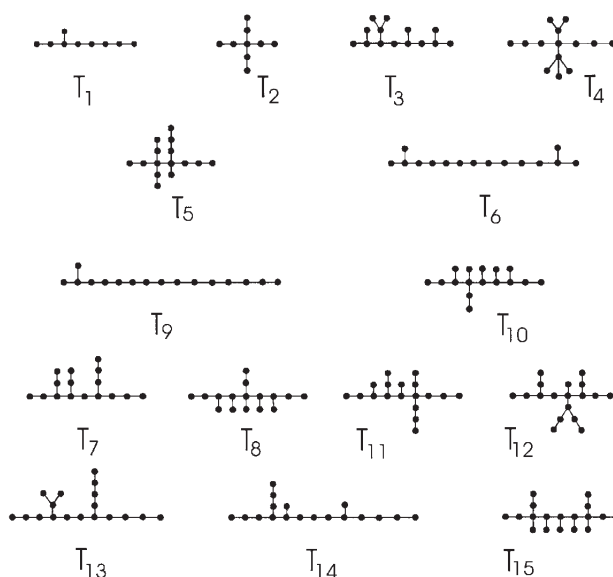


Fig. 1. The six pairs (T_i, T_{i+1}) , $i = 1, 3, 5, 7, 9, 11$, and the triplet (T_{13}, T_{14}, T_{15}) of equienergetic chemical trees. These are the only non-cospectral equienergetic chemical trees with $n \leq 18$ vertices. The three smallest pairs correspond to 3,3-diethylpentane and 3-methyloctane (T_1 and T_2 , both with 9 vertices), 2,5,7-triethyl-3-isopropyloctane and 4-*tert*-butyl-4-isopropyl-heptane (T_3 and T_4 , both with 14 vertices), and 3,3-diethyl-4-methyl-4-propylheptane and 2,12-dimethyltridecane (T_5 and T_6 , both with 15 vertices). The trees T_{13} and T_{14} are cospectral, hence within the triplet (T_{13}, T_{14}, T_{15}) only the pairs (T_{13}, T_{15}) and (T_{14}, T_{15}) are non-cospectral equienergetic.

After abandoning the cospectral species, what remains are the pairs of non-cospectral equienergetic trees. We found a total of 27 such pairs and 5 triplets (two members in each triplet being cospectral). Of them only six pairs and one triplet consisted of chemical trees. These are depicted in Fig. 1.

VERIFYING EQUIENERGETICITY

As the search described in the previous section was based on numerical calculations, there remains a doubt that the pairs of chemical trees detected have not equal, but only very closely lying E -values. In order to verify that these pairs really have equal energies, some further efforts are necessary.

In what follows, the equienergeticity of the three smallest pairs, namely of (T_1, T_2) , (T_3, T_4) and (T_5, T_6) , is demonstrated. In order to do this, the concept of "energy of a polynomial" is used: If $P(x)$ is a polynomial whose zeros are x_1, x_2, \dots, x_n , then the energy of P is defined as $E(P(x)) = |x_1| + |x_2| + \dots + |x_n|$.

Bearing in mind the fact^{1,2} that the eigenvalues x_1, x_2, \dots, x_n of a graph G are the zeros of the characteristic polynomial $\phi(G, x)$ of this graph, it is clear that $E(G) = E(\phi(G, x))$.

It is necessary to first prove two simple auxiliary formulas:

$$E(x^2 - p) = 2\sqrt{p} \quad (2)$$

$$E(x^4 - px^2 + 1) = 2\sqrt{p+2} \quad (3)$$

Formula (2) is obvious, since the roots of $x^2 - p$ are \sqrt{p} and $-\sqrt{p}$.

In order to deduce (3) note that the roots of $x^4 - px^2 + 1$ are:

$$x_{1,2} = \pm \sqrt{\frac{1}{2} \left(p + \sqrt{p^2 - 4} \right)} \quad \text{and} \quad x_{3,4} = \pm \sqrt{\frac{1}{2} \left(p - \sqrt{p^2 - 4} \right)}$$

Therefore

$$E(x^4 - px^2 + 1) = 2(x_1 + x_3) = 2\sqrt{(x_1 + x_3)^2} = 2\sqrt{x_1^2 + x_3^2 + 2x_1x_3}$$

Now,

$$x_1^2 + x_3^2 = \frac{1}{2} \left(p + \sqrt{p^2 - 4} \right) + \frac{1}{2} \left(p - \sqrt{p^2 - 4} \right) = p$$

whereas

$$2x_1x_3 = 2\sqrt{\frac{1}{2} \left(p + \sqrt{p^2 - 4} \right)} \sqrt{\frac{1}{2} \left(p - \sqrt{p^2 - 4} \right)} = \sqrt{p^2 - (p^2 - 4)} = 2$$

from which formula (3) is immediately deduced.

Methods for the calculation of the characteristic polynomials of trees are well elaborated and are relatively easy.^{2,4} Thus, by direct calculation one obtains:

$$\phi(T_1, x) = x(x^2 - 1)(x^2 - 4)(x^4 - 3x^2 + 1)$$

$$\phi(T_2, x) = x(x^2 - 1)^3(x^2 - 5)$$

Therefore, in view of Eqs. (2) and (3).

$$E(T_1) = E(\phi(T_1, x)) = E(x) + E(x^2 - 1) + E(x^2 - 4) + E(x^4 - 3x + 1) = \\ = 0 + 2\sqrt{1} + 2\sqrt{4} + 2\sqrt{3} + 2$$

$$E(T_2) = E(\phi(T_2, x)) = E(x) + 3E(x^2 - 1) + E(x^2 - 5) = \\ = 0 + 3 \times 2\sqrt{1} + 2\sqrt{5}$$

From these results it is evident that $E(T_1) = E(T_2)$. The fact that the polynomials $\phi(T_1, x)$ and $\phi(T_2, x)$ are not identical implies that T_1 and T_2 are not cospectral.

In the case of the trees T_3 and T_4 as well as T_5 and T_6 the calculation is somewhat more evolved and yields

$$\phi(T_3, x) = x^4 (x^2 - 2)^2 (x^2 - 5) (x^4 - 4x + 1)$$

$$\phi(T_4, x) = x^4 (x^2 - 2)^2 (x^2 - 6) (x^4 - 3x + 1)$$

$$\phi(T_5, x) = x^3 (x^2 - 1)^3 (x^2 - 2) (x^2 - 3) (x^2 - 6)$$

$$\phi(T_6, x) = x^3 (x^2 - 1) (x^2 - 2) (x^2 - 3) (x^2 - 4) (x^4 - 4x^2 + 1)$$

from which, using Eqs. (2) and (3), it follows

$$E(T_3) = 2 \times 2\sqrt{2} + 2\sqrt{5} + 2\sqrt{4+2}$$

$$E(T_4) = 2 \times 2\sqrt{2} + 2\sqrt{6} + 2\sqrt{3+2}$$

$$E(T_5) = 3 \times 2\sqrt{1} + 2\sqrt{2} + 2\sqrt{3} + 2\sqrt{6}$$

$$E(T_6) = 2\sqrt{1} + 2\sqrt{2} + 2\sqrt{3} + 2\sqrt{4} + 2\sqrt{4+2}$$

Comparing the above expressions, it can be concluded that $E(T_3) = E(T_4)$ and $E(T_5) = E(T_6)$. In addition, the polynomials $\phi(T_3, x)$ and $\phi(T_4, x)$ are different, and so are $\phi(T_5, x)$ and $\phi(T_6, x)$. Therefore, neither T_3 and T_4 nor T_5 and T_6 are cospectral.

The proof of the equienergeticity of the other pairs of trees depicted in Fig. 1 is analogous, yet still more cumbersome.

DISCUSSION

The importance of equienergetic molecular graphs lies in the difference in their structure. Namely, if the energies of two molecular graphs are equal, then whatever is the difference in their structure it is either irrelevant as far as energy is concerned, or the effects of different structural features cancel out each other. In both cases, examination of the structure of equienergetic molecular graphs reveals valuable information on the structure-dependency of the energy.

As an example, consider the chemical trees T_9 and T_{10} , depicted in Fig. 1. It is evident that T_{10} is much more branched than T_9 . As in chemical trees branching is known^{25,26} to have a decreasing effect on E , there evidently must exist another structural feature: either a stabilizing one in T_{10} (absent in T_9) or a destabilizing one in T_9 (absent in T_{10}). It might be that, in this particular example, this extra effect comes from the number of non-bonding molecular orbitals²⁷ – whereas T_9 has two non-bonding MOs, T_{10} has none.

ИЗВОД

ЕКВИЕНЕРГЕТСКА ХЕМИЈСКА СТАБЛА

ВЛАДИМИР БРАНКОВ^а, ДРАГАН СТЕВАНОВИЋ^а и ИВАН ГУТМАН^б^аПриродно-математички факултет у Нишу и ^бНишу и Природно-математички факултет у Крагујевцу

Енергија $E(G)$ графа G је збир апсолутних вредности сопствених вредности графа G . За два графа, G_1 и G_2 , каже се да су изоенергетски ако је $E(G_1) = E(G_2)$. У раду су саопштени резултати тражења парова еквиенергетских ацикличних молекулских графова (хемијских стабала) са истим бројем n чворова. Има веома мало таквих парова. Најмањи има $n = 9$ и одговара 3,3-диетилпентану и 3-метилоктану. Међу хемијским стаблима са $n \leq 18$ нађено је још само пет таквих парова као и једна тројка.

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