Quest for Molecular Graphs with Maximal Energy: A Computer Experiment

Ivan Gutman* and Dušica Vidović

Faculty of Science, University of Kragujevac, P.O. Box 60, YU-34000 Kragujevac, Yugoslavia

If λ_1, λ_2, ..., λ_n are the eigenvalues of a graph G, then the energy of G is defined as $E(G) = |\lambda_1| + |\lambda_2| + ... + |\lambda_n|$. If G is a molecular graph, representing a conjugated hydrocarbon, then $E(G)$ is closely related to the respective total π-electron energy. It is not known which molecular graph with n vertices has maximal energy. With the exception of $m = n - 1$ and $m = n$, it is not known which molecular graph with n vertices and m edges has maximal energy. To come closer to the solution of this problem, and continuing an earlier study (*J. Chem. Inf. Comput. Sci.* **1999,** *39,* 984−996, ref 7), we performed a Monte Carlo-type construction of molecular (n,m)-graphs, recording those with the largest (not necessarily maximal possible) energy. The results of our search indicate that for even n the maximal-energy molecular graphs might be those possessing as many as possible six-membered cycles; for odd n such graphs seem to prefer both six- and five-membered cycles.

1. INTRODUCTION

The total π-electron energy of a conjugated hydrocarbon, as calculated within the Hückel molecular orbital (HMO) approximation, has a simple algebraic form

$$E_\pi = \alpha n + 2\beta \sum_{i=1}^{n/2} \lambda_i$$

where n is the number of carbon atoms (equal to the number of π-electrons), α and β are the standard HMO parameters, and λ_1, λ_2, ..., λ_n are the eigenvalues of a pertinently constructed molecular graph.[1−5] The nontrivial part of the above expression is

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

a quantity which is usually referred to as the total π-electron energy. For almost all conjugated systems it can be rewritten as

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

where G stands for the molecular graph. The vast majority of results known for $E(G)$ holds under the assumption that eq 1 is satisfied. In view of this, eq 1 is used as the definition of the *energy of the graph G*;[3,6,7] this definition is applicable to all graphs.

Because β is negative-valued, the greater is $E(G)$ the lower is E_π and the higher is the thermodynamic stability of the underlying compound. Consequently, molecular graphs with maximal $E(G)$ pertain to maximally stable π-electron systems.

* Corresponding author phone: 381 34 331876; fax: 381 34 335040; e-mail: gutman@knez.uis.kg.ac.yu.

Research on the mathematical properties of $E(G)$ started more than half a century ago[8] and is still going on;[6,7,9] for more details see refs 3, 10, and 11.

If a graph G possesses n vertices, then we say that G is an (n)-graph. If G possesses n vertices and m edges then it is is referred to as an (n,m)-graph.

A tantalizing unsolved problem in the theory of total π-electron energy is the characterization of the (n)- and (n,m)-graphs having maximal energy. There is an almost complete lack of knowledge of the structure of maximal-energy molecular (n)- and (n,m)-graphs.

The few known results along these lines are the following.

Among connected acyclic graphs (trees, $m = n-1$) the path P_n has maximal energy;[12] P_n is also the maximal-energy molecular ($n,n-1$)-graph, cf. Figure 1.

It has been recently conjectured[7] that among connected (n,n)-graphs the circuit C_n has maximal energy for $n = 3$, 4, 5, 6, 7, 9, 10, 11, 13, and 15, whereas for all other values of n the maximal-energy graph is $C_6 \cdot P_{n-6}$, see Figure 1. The same graphs would then be the maximal-energy monocyclic molecular graphs.
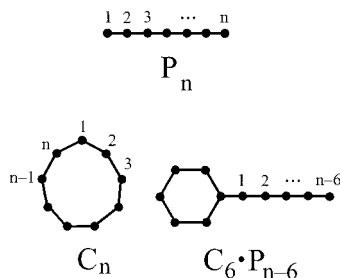
Graphs and molecular graphs with maximal and minimal energy have been determined within several other classes of graphs.[7,13−16] Yet, the structure of bicyclic, tricyclic, etc. maximal-energy graphs and molecular graphs remained completely obscure.

The aim of this work is to shed some light on the structure of the polycyclic molecular graphs with maximal energy. Because theoretical considerations seem to be of little help, our strategy was to use a computer-aided, Monte Carlo-type construction of molecular graphs and to identify those with greatest energy. There is no guarantee that by this procedure we arrive at the true maximum, but— at least—we may come closer to our targets.

2. THE ALGORITHM

The molecular (n,m)-graphs considered by us were required to satisfy the following conditions: (i) to have no

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Figure 1. Acyclic and monocyclic molecular graphs with maximal energy; according to Caporossi et al.,[7] and in full agreement with the present work, the maximal-energy monocyclic graph is $C_6 \cdot P_{n-6}$ (the molecular graph of α-phenyl-polyenes), except for $n = 3, 4, 5, 6, 7, 9, 10, 11, 13, 15$, when the circuit C_n (the molecular graph of annulenes) has the greatest energy.

vertex degree greater than 3, (ii) to be connected, and (iii) to have no triangles.

Conditions (i) and (ii) are self-evident properties of molecular graphs representing conjugated π-electron systems.[3,4] Condition (iii) was imposed in order to avoid the occurrence of highly strained and chemically unrealistic structures.

Step 1. First the value of n is fixed ($10 \leq n \leq 20$). We start with a graph on n isolated vertices. By using the high-quality Haas random number generator[17] a pair of vertices is selected uniformly at random and connected by an edge; for details see refs 6, 18, and 19. The selection of vertex pairs and their connecting by new edges is then continued until a total of $n-1$ edges has been added to the graph. After adding each edge to the graph, the vertices whose degrees became equal to 3 are identified and, by a suitable renumbering, eliminated from the subsequent selection. Thus at each stage the next vertex pair is selected, uniformly at random, among vertices whose degree is less than three.

After an $(n,n-1)$-graph is constructed, its eigenvalues are computed. Then the existence of triangles is checked by means of the relation

$$\sum_{i=1}^{n} \lambda^3 = 6 \times \text{number of triangles}$$

If the graph possesses triangles, the construction is interrupted and started anew. If the graph is triangle-free (and thus obeys condition (iii)), then its connectedness is checked by computing the Laplacian eigenvalues.[20-22] If the second Laplacian eigenvalue is nonzero, then the graph is connected; otherwise it is disconnected. If the graph is found to be connected (thus obeying condition (ii)), then its energy is calculated and compared with the greatest known energy of a molecular $(n,n-1)$-graph. If the new energy exceeds the greatest known, then this E-value is recorded together with the corresponding graph (via its adjacency matrix). After that the random selection of a new edge is restarted. If the graph is found to be disconnected or if its E-value does not exceed the greatest known energy, then nothing is done, and the procedure of selecting a new edge is restarted.

At each stage, the newly constructed graph is checked for triangles and connectedness.

The construction is ended after a sufficiently large number of edges is added to the graph. In this paper we report the results obtained for $(n,n-1+k)$-graphs, $k = 0, 1, 2, 3, 4$.
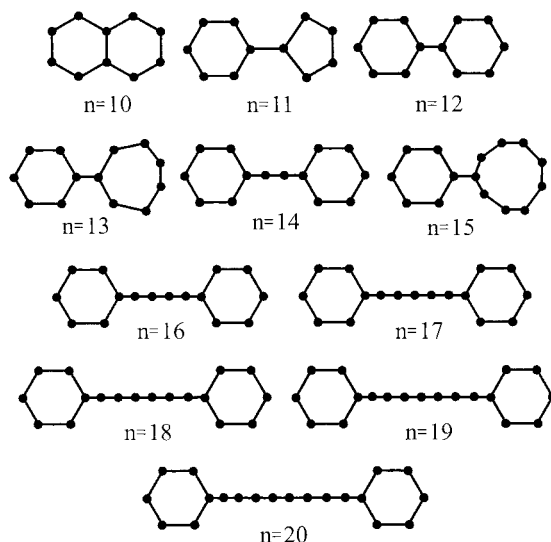
Figure 2. Bicyclic molecular graphs ($m = n+1$) that might have maximal energy; for $n \geq 16$ a simple regularity emerges: we conjecture that (with the exception of $n \leq 13$ and $n = 15$) the maximal-energy bicyclic n-vertex species are the molecular graphs of α,ω-diphenyl-polyenes.
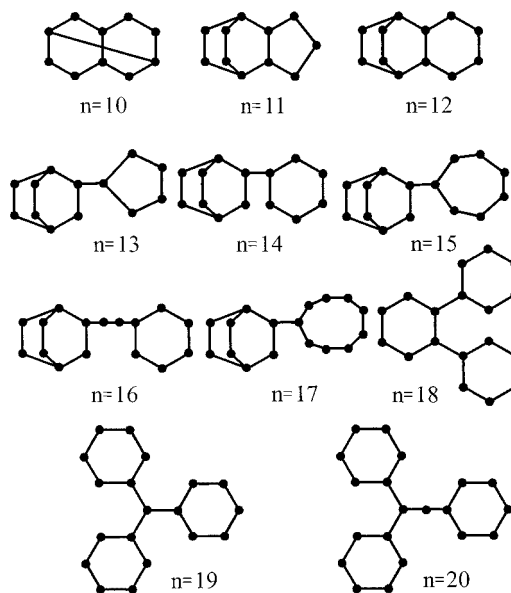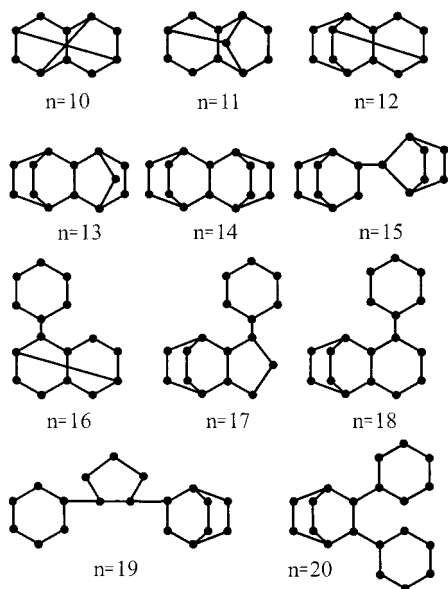

Figure 3. Tricyclic molecular graphs ($m = n + 2$) that might have maximal energy; notice that with increasing n the awkward and sterically impossible structural features are no more encountered.

The entire procedure was repeated a large number of times (50 000 times for $n = 10, 11, ..., 16$, 100 000 times for $n = 17, 18, 19$, and 150 000 times for $n = 20$). By this the maximum-energy or a nearly maximum-energy molecular graphs had a reasonably large probability to be constructed.

Step 2. Every graph obtained in Step 1 was further refined by deleting an edge from it and inserting another edge in all possible ways (always checking for connectedness and the presence of triangles). If a better graph was obtained (having greater energy than the staring one), then the refinement was repeated with the latter graph. The procedure ends when no deletion/insertion of an edge could increase the energy.

Both in Step 1 and in Step 2, the structure of only a single graph has been recorded, the one with maximal energy.

Figure 4. Tetracyclic molecular graphs ($m = n + 3$) that might have maximal energy; the sterically impossible structural features seem to disappear at $n > 20$.

G_1	G_2	G_3
n=10	n=11	n=14
m=9	m=14	m=13
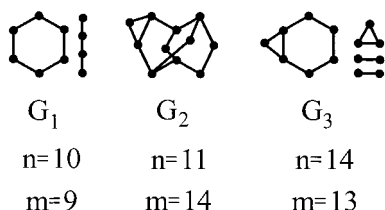
Figure 5. Disconnected and triangle-containing graphs having energies greater than the graphs found by our method: $E(G_1) = 12.4721$, $E(G_2) = 16.1321$, and $E(G_3) = 17.6569$, whereas the energies of the corresponding (10,9)-, (11,14)-, and (14,13)-graphs from Figures 1 and 4 are 12.0533, 16.0185, and 17.1335, respectively.

3. RESULTS

The search for acyclic ($m = n - 1$) and monocyclic ($m = n$) molecular graphs with greatest energy was done only to check the reliability of our method. Indeed, in all the examined cases (that is, for $10 \leq n \leq 20$), the graphs found by us were the same as the previously known[7] maximal-energy species, see Figure 1.

The bicyclic, tricyclic, and tetracyclic molecular graphs found by our search are depicted in Figures 2−4.

At this point it is worth noting that the restriction to connected and triangle-free graphs was justified, because there exist (quite numerous) disconnected and/or triangle-containing graphs having energies greater than the graphs displayed in Figures 1−4. Three such examples are given in Figure 5.

4. DISCUSSION

By inspection of Figures 2−4 we observe that the main structural feature common to all graphs found by our search procedure is a large number of six-membered cycles.

If n is even, then only 6-cycles are present (plus, of course, the larger cycles resulting from the partial overlap of the 6-cycles). In not a single case have odd-membered cycles been encountered.

If n is odd, then in addition to 6-cycles, also odd-membered cycles are encountered, with a preference to 5-cycles. With increasing n, however, more and more graphs without odd-cycles (thus composed exclusively of 6-cycles) are found.

The first few graphs in Figure 3 and all graphs in Figure 4 contain cycles joined in a manner that is "chemically impossible". For evident steric reasons such "molecular" graphs cannot represent chemically sound conjugated hydrocarbons. Fortunately, however, with increasing n this awkward situation seems to completely disappear.

It is plausible to expect that when n is large enough, the maximal-energy molecular graphs are composed exclusively of hexagons. Whenever possible, these hexagons are disjoint, that is, represent phenyl groups. In the case of bicyclic systems the results shown in Figure 2 clearly point toward the following:

Conjecture. If $n = 14$ and $n \geq 16$ the maximal-energy bicyclic molecular graph is the molecular graph of the α,ω-diphenyl-polyene $C_6H_5(CH)_{n-12}C_6H_5$.

For tricyclic and tetracyclic species it would be premature to state such conjectures, although α,α,ω-triphenyl- and $\alpha,\alpha,\omega,\omega$-tetraphenylpolyenes seem to be the most obvious candidates.

As a kind of surprise, benzenoid molecules (such as acenaphthylene, $n = 13$, $m = 15$ or phenanthrene $n = 14$, $m = 16$) are not found among the conjugated systems with the greatest possible total π-electron energy (with the single exception of naphthalene, cf. Figure 2). This may imply that the remarkable stability of benzenoid hydrocarbons comes from a fortuitous combination of the stabilization caused by the numerous 6-cycles (a π-electron effect which, although strong, is not maximally strong) with planarity and lack of steric strain (a σ-electron effect).

Concluding this paper we express our conviction that we have, at least to a limited extent, contributed toward the understanding of the structural features influencing the total π-electron energy (and thus the stability) of conjugated molecules. Our calculations were done on a Pentium PC, and thus could not go beyond $n = 20$. We hope that this limitation will be overcome sometime in the future.

Addendum. After this work has been submitted for publication, thanks to a donation from DAAD, we acquired a stronger PC (with an Athlon 550 MHz processor), which enabled us to extend our calculations up to $n = 30$. These confirmed all our conjectures, namely that the bicyclic, tricyclic, and tetracyclic species with maximal energy are the α,ω-diphenyl-, α,α,ω-triphenyl-, and $\alpha,\alpha,\omega,\omega$-tetraphenylpolyenes, respectively. For bicyclic species this regularity holds for all $n \geq 16$, for tricyclic for $n \geq 19$, and for tetracyclic for $n \geq 26$.

REFERENCES AND NOTES

(1) Graovac, A.; Gutman, I.; Trinajstić, N. *Topological Approach to the Chemistry of Conjugated Molecules*; Springer-Verlag: Berlin, 1977.
(2) Coulson, C. A.; O'Leary, B.; Mallion, R. B. *Hückel Theory for Organic Chemists*; Academic Press: London, 1978.
(3) Gutman, I.; Polansky, O. E. *Mathematical Concepts in Organic Chemistry*; Springer-Verlag: Berlin, 1986.
(4) Trinajstić, N. *Chemical Graph Theory;* CRC Press: Boca Raton, FL, 1983; 2nd ed. 1992.
(5) Dias, J. R. *Molecular Orbital Calculations Using Chemical Graph Theory*; Springer-Verlag: Berlin, 1993.

(6) Gutman, I.; Soldatović, T.; Vidović, D. The Energy of a Graph and Its Size Dependence. A Monte Carlo Approach. *Chem. Phys. Lett.* **1998**, *297*, 428−432.

(7) Caporossi, G.; Cvetković, D.; Gutman, I.; Hansen, P. Variable Neighborhood Search for Extremal Graphs. 2. Finding Graphs with Extremal Energy. *J. Chem. Inf. Comput. Sci.* **1999**, *39*, 984−996.

(8) Coulson, C. A. On the Calculation of the Energy in Unsaturated Hydrocarbon Molecules. *Proc. Cambridge Philos. Soc.* **1940**, *36*, 201−203.

(9) Walikar, H. B.; Ramane, H. S.; Hampiholi, P. R. On the Energy of a Graph. in *Graph Connections*; Balakrishnan, R., Mulder, H. M., Vijayakumar, A., Eds.; Allied Publishers: New Delhi, India, 1999; pp 120−123.

(10) Gutman, I. Total π-Electron Energy of Benzenoid Hydrocarbons. *Topics Curr. Chem.* **1992**, *162*, 29−63.

(11) Gutman, I. The Energy of a Graph: Old and New Results. in *Algebraic Combinatorics and Applications*; Betten, A., Kohnert, A., Laue, R., Wassermann, A., Eds.; Springer-Verlag: Berlin, 2001; pp 196−211.

(12) Gutman, I. Acyclic Systems with Extremal Hückel π-Electron energy. *Theor. Chim. Acta* **1977**, *45*, 79−87.

(13) Li, H. On Minimal Energy Ordering of Acyclic Conjugated Molecules. *J. Math. Chem.* **1999**, *25*, 145−169.

(14) Zhang, F.; Li, H. On Acyclic Conjugated Molecules with Minimal Energies. *Discr. Appl. Math.* **1999**, *92*, 71−84.

(15) Zhang, F.; Li, H. On Maximal Energy Ordering of Acyclic Conjugated Molecules. In *Discrete Mathematical Chemistry*; Hansen, P., Fowler, P., Zheng, M., Eds.; Am. Math. Soc.: Providence, 2000; pp 385−392.

(16) Gutman, I.; Hou, Y. Bipartite Unicyclic Graphs with Greatest Energy. *Commun. Math. Chem. (MATCH)* **2001**, *43*, 17−28.

(17) Haas, A. The Multiple Prime Random Number Generator. *ACM Trans. Math. Software* **1987**, *13*, 368−381.

(18) Gutman, I.; Vidović, D.; Soldatović, T. Modeling the Dependence of the π-Electron Energy on the Size of Conjugated Molecules. A Monte Carlo Approach. *ACH Models Chem.* **1999**, *136*, 599−608.

(19) Fripertinger, H.; Gutman, I.; Kerber, A.; Kohnert, A.; Vidović, D. The Energy of a Graph and Its Size Dependence. An Improved Monte Carlo Approach. *Z. Naturforsch.* **2001**, *56a*, 342−346.

(20) Merris, R. Laplacian Matrices of Graphs: A Survey. *Lin. Algebra Appl.* **1994***, 197−198*, 143−176.

(21) Merris, R. A Survey of Graph Laplacians. *Lin. Multilin. Algebra* **1995**, *39*, 19−31.

(22) Trinajstić, N.; Babić, D.; Nikolić, S.; Plavsić, D.; Amić, D.; Mihalić, Z. The Laplacian Matrix in Chemistry. *J. Chem. Inf. Comput. Sci.* **1994**, *34*, 368−376.