CROATICA CHEMICA ACTA CCACAA **69** (3) 883–897 (1996)

ISSN-0011-1643
CCA–2349

Conference Paper

Complexity of Some Interesting (Chemical) Graphs*

Sonja Nikolić,[a,**] *Nenad Trinajstić,*[a] *Albin Jurić,*[b] *Zlatko Mihalić,*[c] *and Goran Krilov*[d]

[a]*Rugjer Bošković Institute, P.O.Box 1016, Bijenička 54, 10001 Zagreb, The Republic of Croatia*

[b]*Department of Chemistry, Agricultural Institute, 43260 Križevci, The Republic of Croatia*

[c]*Faculty of Science and Mathematics, The University of Zagreb, 10001 Zagreb, The Republic of Croatia*

[d]*Drake University, Des Moines, Iowa 50311, USA*

Received July 26, 1995; revised October 23, 1995; accepted November 3, 1995

Complexity of some interesting polycyclic graphs is expressed in terms of the corresponding spanning trees. Graphs considered were a selection of all connected graphs with four and five vertices, graphs composed of two parts, or more parts, connected by a single edge, the Petersen graph, the Blanuša graph, the Desargues-Levy graph and the Schlegel graph of buckminsterfullerene.

INTRODUCTION

Complexity of (molecular) structures is a difficult concept to quantify. Futhermore, the concept of complexity is also difficult to define.[1] Nevertheless, the contemporary chemical literature contains a number of attempts to define and to quantify molecular complexity.[2]

---

* Reported in part at the MATH/CHEM/COMP 1995, an International Course and Conference on the Interfaces between Mathematics, Chemistry and Computer Science, Dubrovnik, Croatia: June 26 – July 1, 1995.

** Author to whom correspondence should be addressed.

There are two predominant approaches to quantification of molecular complexity. One is based on the information-theoretic concepts and the other on the graph-theoretical concepts. A typical information-theoretic approach to molecular complexity involves the use of the Bertz index $C(n)$:[2a]

$$C(n) = 2n \log_2 n - \sum n_i \log_2 n_i \quad (1)$$

where n can represent any graph invariant. The choice of the specific invariant is dictated by the problem at hand. Note that $n = \sum n_i$. The Bertz index is based on the reasonable assumption that the complexity of a molecular graph should increase with the size, branching, vertex- and edge-weights, *etc.*

The graph-theoretical approach to the complexity of graphs is based on the concept of a spanning tree,[3] that is, the complexity of a molecular structure can be given in terms of the number of the corresponding spanning trees:[4] The most complex structure possesses the highest number of spanning trees. A spanning tree of a graph G is a connected acyclic subgraph containing all the vertices of G.[5] In the case of trees, the spanning tree is identical to the tree itself. Therefore, the number of spanning trees can only be used as a quantitative measure of complexity for polycyclic graphs.

We have selected to study the complexity of several graphs that appear to be of interest also in chemistry. Thus, the present report nicely fits into the MATH/CHEM/COMP 1995, where mathematics, chemistry and computer science meet. This is so because the concept of the spanning tree belongs to mathematics, counting of the spanning trees is a non-trivial computational problem, especially for larger graphs, and belongs to computer science, whilst the comparison between the numbers of spanning trees can be used in chemistry to classify the corresponding molecular graphs according to their structural complexity expressed as the number of spanning trees.

COMPUTATION OF SPANNING TREES

There are several methods available for computing the number of spanning trees. Here, we will review three closely related methods.

(i) Computation based on the Laplacian matrix of a graph

The Laplacian matrix $\boldsymbol{L} = \boldsymbol{L}(G)$ of a graph G is defined as the following matrix:[4,6]

$$\boldsymbol{L} = \boldsymbol{V} - \boldsymbol{A} \quad (2)$$

where $\boldsymbol{V}$ is the degree matrix which is a diagonal matrix whose entries are the vertex degrees and $\boldsymbol{A}$ is the adjacency matrix of G. The Laplacian matrix is a real symmetric matrix. The diagonalization of the Laplacian matrix of G with N vertices produces N real eigenvalues $\{\lambda_i\}_{i=1,\ldots,N}$. The set of Laplacian eigenvalues is usually referred to as the Laplacian spectrum[6c] and denoted by $\lambda_i(\boldsymbol{L})$. The smallest member of the Laplacian spectrum is always zero. This is a consequence of the special structure of the Laplacian matrix.

The number of spanning trees t(G) of G is given by:[4]

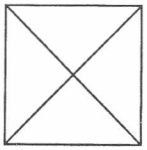
$$t(\mathrm{G}) = (1/N) \prod_{i=2}^{N} \lambda_i(\boldsymbol{L}) \ . \tag{3}$$

The use of the above procedure for computing the number of spanning trees is illustrated in Table I.

TABLE I

Computing the number of spanning trees for graph G

(1) Graph G



(2) The Laplacian matrix of G

$$\begin{bmatrix} 3 & -1 & -1 & -1 \\ -1 & 3 & -1 & -1 \\ -1 & -1 & 3 & -1 \\ -1 & -1 & -1 & 3 \end{bmatrix}$$

(3) The Laplacian spectrum of G

{ 0, 4, 4, 4 }

(4) The number of spanning trees of G

t(G) = 16

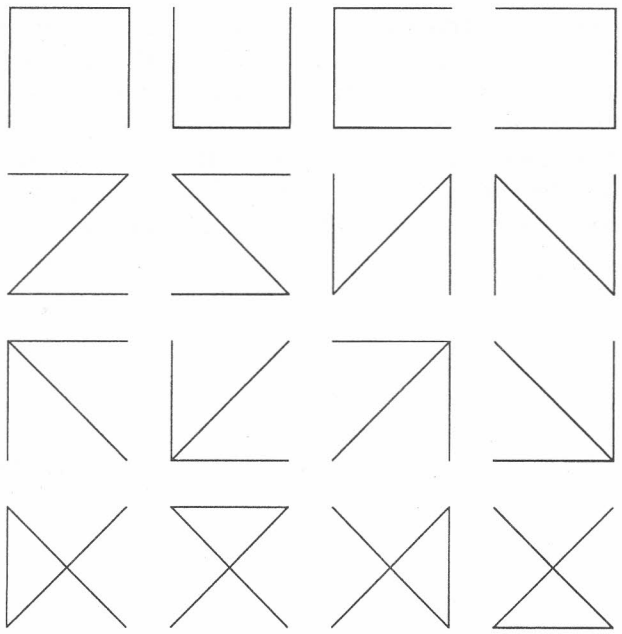


Figure 1. Spanning trees belonging to G depicted in Table I, which is the complete graph K_4.

All spanning trees belonging to graph G in Table I, which is the complete graph K_4, are depicted in Figure 1.

(ii) Computation based on the characteristic polynomial of the inner dual of a graph

This is a rather elegant method for computing the number of spanning trees of G and is based on the work by Gutman *et al.*[7] It consists of the following steps:

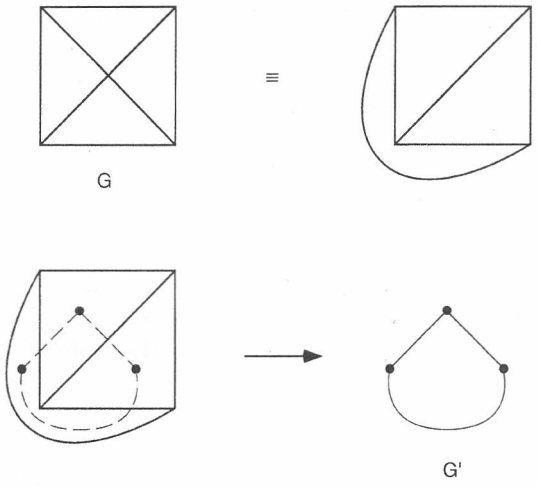
(1) Construction of the inner dual G' of G.
(2) Computation of the characterictic polynomial of G'.
(3) Substitution of the ring sizes into the characteristic polynomial of G'.

The above procedure for computing the number of spanning trees for the same graph G (K_4) from Table I is illustrated in Table II.

This procedure is computationally much simpler than the one based on the Laplacian matrix because the inner dual is always much smaller than the original graph.

TABLE II

Computing the number of spanning trees for G based on the inner dual G' of G



$$P(G';\lambda) = \lambda^3 - 3\lambda - 2$$

$$t(G) = P(G';\lambda = 3) = 3^3 - 3 \cdot 3 - 2 = 16$$

(iii) Computation based on the simple relationship between the number of spanning trees and the coefficient of λ of the Laplacian polynomial of G

The relationship between the number of spanning trees and the absolute value of the coefficient of λ of the Laplacian polynomial of G is given by:[8]

$$t(G) = |\text{Coefficient of } \lambda| \,/\, N \,. \tag{4}$$

The origin of this simple formula is related to the fact that the coefficient at the λ term in the Laplacian polynomial must be equal to the product of all non-zero Laplacian eigenvalues:

$$\text{Coefficient of } \lambda = \prod_{i=2}^{N} \lambda_i(\boldsymbol{L}) \,. \tag{5}$$

This result can be straightforwardly proved.[8] The use of formula (4) is illustrated in Table III.

TABLE III

Computation of the number of spanning trees using formula (4)

(i)	The Laplacian polynomial of G (already depicted in Tables I and II)
	$P(G; \lambda) = \lambda^4 - 12\,\lambda^3 + 48\,\lambda^2 - 64\,\lambda$
(ii)	The number of spanning trees
	$t(G) = \lvert\text{Coefficient of } \lambda\rvert / N = 64/4 = 16$

Since Laplacian polynomials are known for some fullerenes,[9] one can promptly compute the corresponding numbers of spanning trees by means of formula (4). For example, the coefficient at λ in C_{24} fullerene with D_{6d} symmetry, which is –2921536800, produces the following value $t(G)$ = 121730700 for the number of spanning trees.

COMPLEXITY OF SELECTED (CHEMICAL) GRAPHS

In Figure 2, we give all the three possible connected cyclic graphs with four vertices, starting with C_4 (which could serve as a graph-theoretical representation of cyclobutadiene or cyclobutane) and ending with K_4.

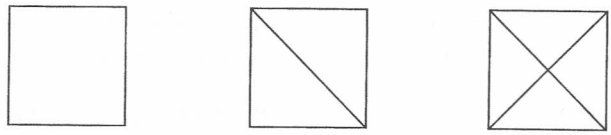


Figure 2. All connected cyclic graphs with four vertices. Underneath each graph, its number of spanning trees is given.

The numbers of spanning trees (given below each graph) follow the intuitive feeling about the complexity of these structures by considering C_4 to be the least complex and K_4 the most complex structure among them. The complexity of these structures follows the exponential increase with base 2, that is 2^2, 2^3 and 2^4.

Next, we consider all the possible connected cyclic graphs with five vertices. There are eight of them, starting with C_5 and ending with K_5. These graphs are depicted in Figure 3.

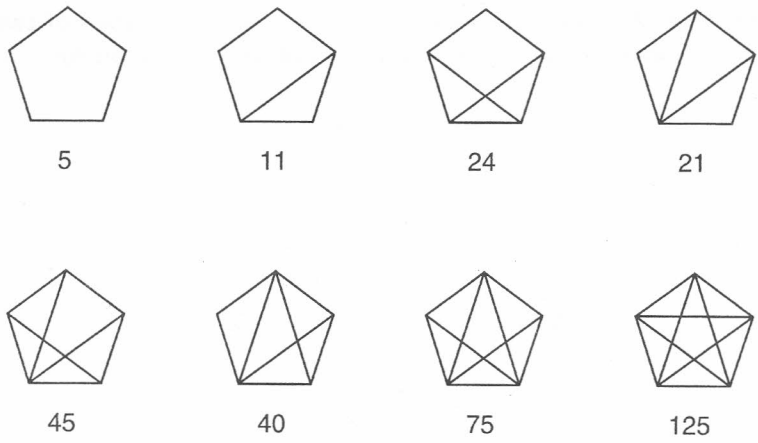


Figure 3. All connected cyclic graphs with five vertices. Underneath each graph, its number of spanning trees is given.

In this case, like in the previous one, the complexity in terms of the spanning trees increases with the intuitive appraisal, that is, the increasing number of edges leading to a complete graph K_5 increases the complexity of a structure. There is also a polynomial relationship between the number of spanning trees S and the number of edges M in the connected cyclic graph with five vertices. This is shown in Figure 4.

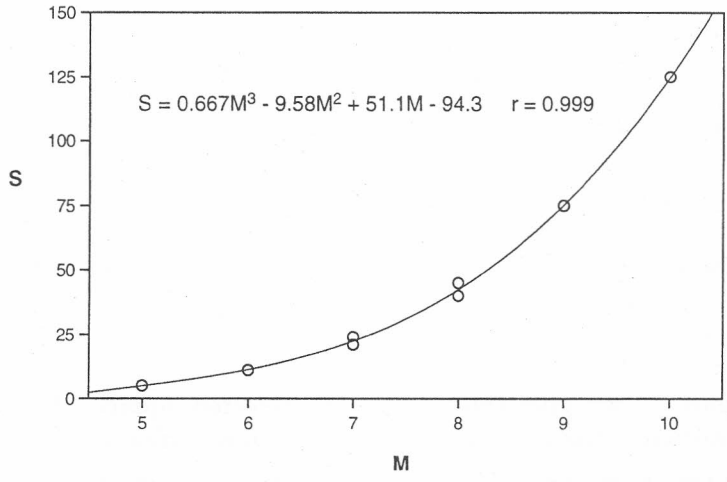


Figure 4. A polynomial relationship between the number of spanning trees S and the number of edges M in connected cyclic graphs with five vertices.

The number of spanning trees for graph G, which consists of two parts G_1 and G_2 connected by a single edge (see Figure 5) is given by:

$$t(G) = t(G_1) \cdot t(G_2) \ . \tag{6}$$

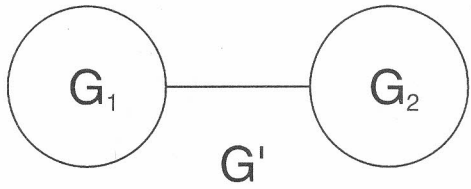


Figure 5. Graph G consisting of two parts, G_1 and G_2 connected by a single edge.

Thus, for example, the biphenyl graph, sequifulvalene graph, heptafulvalene graph and binaphthyl graph have the following values for the number of spanning trees: 36, 35, 49 and 1225, respectively.

Formula (6) may be generalized for chains of graphs (see Figure 6), each connected by a single edge:

$$t(G) = t(G_1) \cdot t(G_2) \cdot \ldots\ldots \cdot t(G_n) \ . \tag{7}$$

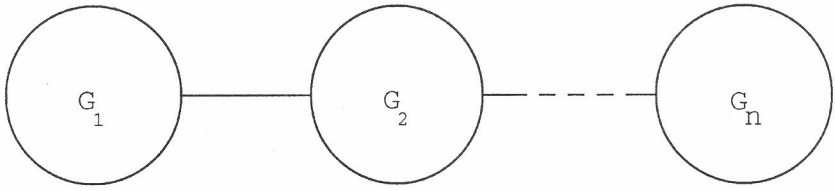


Figure 6. Graph G consisting of several parts, G_1, G_2,...,G_n, all connected by a single edge.

In Figure 7, we give three randomly selected square-cell configurations,[10,11] known in discrete mathematics as square animals.[12]

It is interesting to note than another (surgical) approach to complexity of square-cell configurations[13] gives a reverse order of complexity for the two simply connected square-cells in Figure 7.

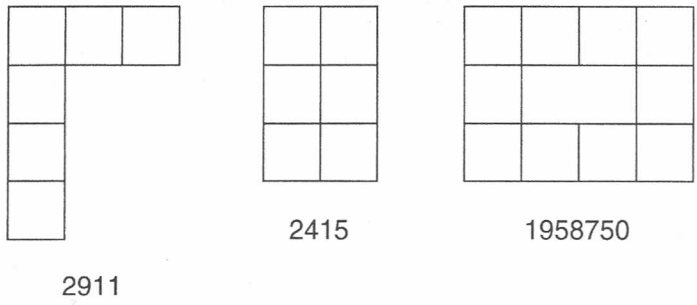


Figure 7. Three square-cell configurations. The first two are simply-connected and the third one is a multiple-connected square-cell configuration.

Several polyhexes and the correspoding numbers of spanning trees are given in Figure 8.

There is no surprise in this case. Isomeric structures show similar counts of spanning trees. The number of spanning trees is the largest for the biggest polyhex.

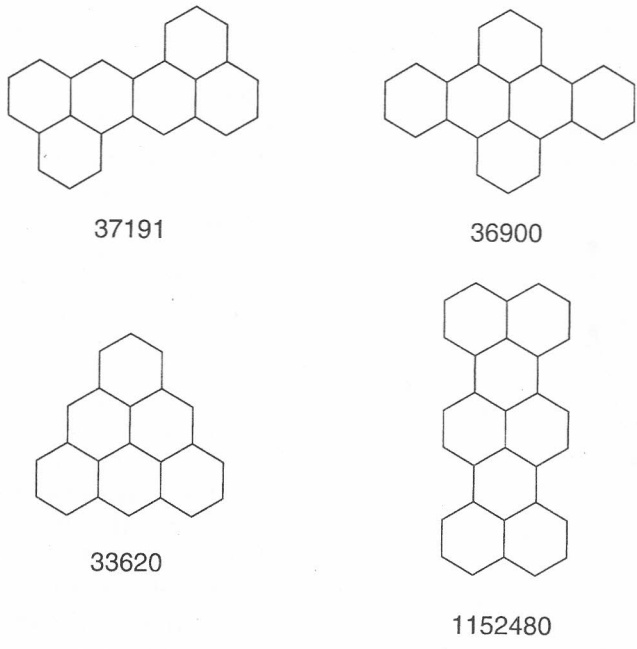
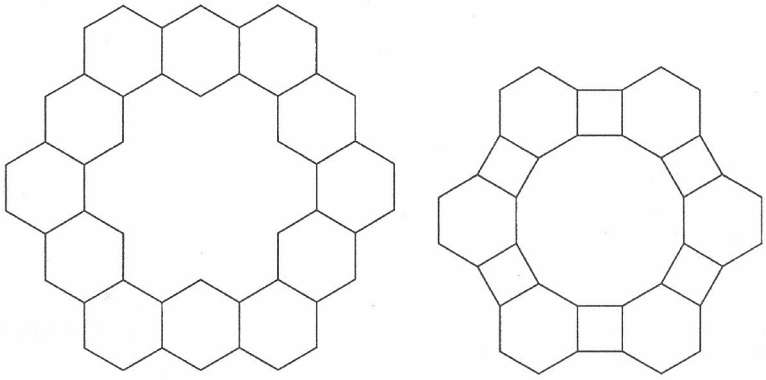


Figure 8. Four randomly selected polyhexes and the corresponding numbers of spanning trees.

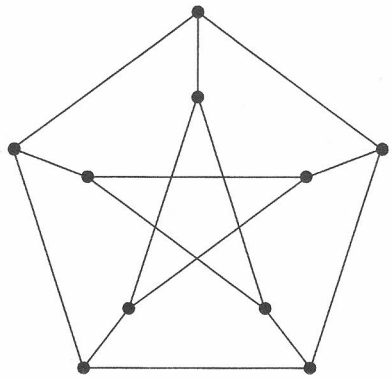


16712665200 873434016

Figure 9. Kekulene and antikekulene.

Figure 9 presents kekulene and antikekulene. Kekulene was prepared in 1983[14,15] while the preparation of antikekulene is optimistically expected to be accomplished soon.[16]

Stability studies indicate that kekulene is much more stable than antikekulene.[17] On the other hand, kekulene appears to be a much more complex structure than antikekulene. The reason for this is related to the fact that our criterion, that is, the number of spanning trees, is strongly correlated with the number of edges in a molecular graph. Thus, a bigger structure in terms of bonds has a bigger number of spanning trees. This is also a week point of this criterion, although one can intuitively expect bigger structures to be more complex. On the other hand, complexity and stability need not be opposite effects, but are more likely unrelated.



1805

Figure 10. The Peterson graph.

Figure 10 shows the Peterson graph.[18] It has been introduced into mathematics to provide a counter example to the Tait conjecture concerned with resolving the four colour problem.[19] It has been found important in discussions of various mathematical problems[20] and it appears to be one of the important graphs in chemistry where it depicts possible routes for the isomerization of trigonal bipyramidal

complexes with five different ligands.[21] The rearrangement graph for the trigonal bipyramid was first discussed by Balaban and co-workers.[22] The Peterson graph is also an incidence graph for the 10 lines and 10 planes resulting from 5 general points in 5-dimensional space, as noted by Cayley in 1878.

The Blanuša graph, which was derived in 1943 and published in 1946, can be obtained by combining two copies of the Peterson graph.[23]

Danilo Blanuša (Osijek, 1903-Zagreb, 1987) was professor of mathematics at the University of Zagreb. His main interest were diferential greometry and special functions.[24] His work on the Blanuša graph, as we call it now, was related to the problem of four colours.[25] Several isomorphic representations of the Blanuša graph are shown in Figure 11.

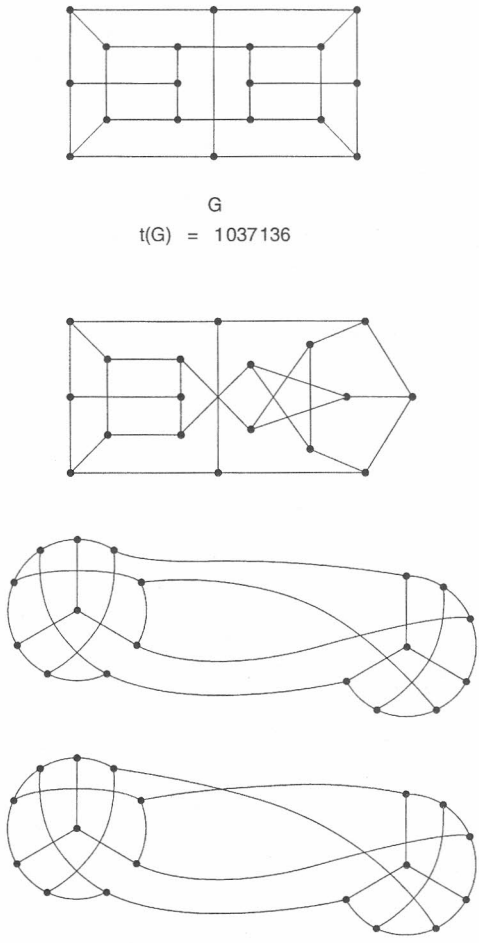
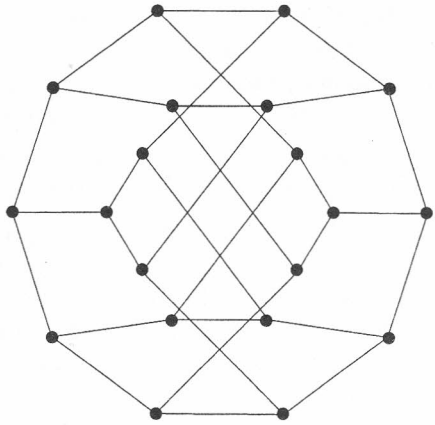


Figure 11. Various representations of the Blanuša graph.

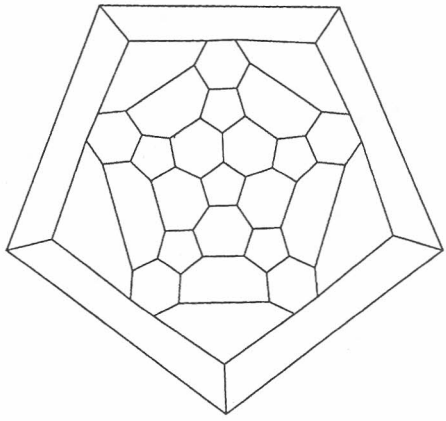


6144000

Figure 12. The Desargues-Levy graph.

The second picture of the Blanuša graphs has been used as a logo for several of the MATH/CHEM/COMP meetings.

The Deasargues-Levy graph (see Figure 12) is another interesting graph that has found use in chemistry to describe a whole set of isomerisations.[22,26,27] Živković has used the Deasargues-Levy graph in his work on characterization of the bullvalene graph.[28]



375,291,866,372,898,816,000

Figure 13. The Schlegel graph of buckminsterfullerene.

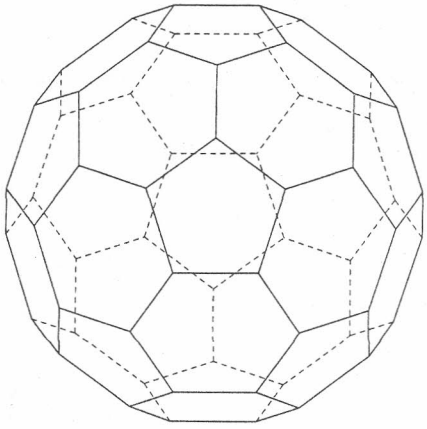


Figure 14. A model of buckminsterfullerene as a truncated icosahedron.

Finally, we considered the Schlegel graph of buckminsterfullerene (Figure 13), a pure carbon molecule consisting of 60 atoms. Buckminsterfullerene is modeled as a truncated icosahedron (see Figure 14).

This molecule has many interesting physical, chemical and practical properties,[29] including highly interesting mathematical properties.[30] There are several reports on the number of spanning trees of the Schlegel graph of buckminsterfullerene.[31] This number is rather astronomical: 375,291,866,372,898,816,000. According to the complexity criterion based on the number of spanning trees, buckminsterfullerene appears to be the most complex structure of all studied in this report.

CONCLUDING REMARKS

Complexity of a number of interesting graphs has been expressed in terms of the corresponding spanning trees. In most cases, the number of spanning trees follows the intuitive feeling about the complexity of a set of related graphs. For some classes of graphs, such as for all connected graphs with five vertices, there is a polynomial relationship between the number of spanning tress and the number of edges in the graph. The same was also found to be valid for all connected graphs with six and seven vertices. Among all the graphs considered, which include the Peterson graph, the Blanuša graph, the Desargues-Levy graph, *etc.*, the Schlegel graph of buckminsterfullerene appears to be the most complex structure, that is, the structure with the highest number of spanning trees.

Acknowledgment. – SN, NT and ZM were supported in part by the Ministry of Science and Technology of the Republic of Croatia through Grants 1-07-159 and 1-07-185. We thank the referees for their constructive comments.

REFERENCES

1. M. M. Waldrop, *Complexity*, Touchstone/Simon&Schuster, New York, 1992.
2. (a) S. H. Bertz, *J. Amer. Chem. Soc.* **103** (1981) 3599.
   (b) S. H. Bertz, *J. Org. Chem.* **50** (1985) 3585.
   (c) B. L. Mil'man, *J. Struct. Chem.* **29** (1989) 957.
   (d) I. Gutman and R. B. Mallion, *Z. Naturforsch.* **48a** (1993) 1026.
   (e) N. Trinajstić, S. Nikolić, and Z. Mihalić, *Bull. Chem. Technol. Macedonia* **13** (1994) 61.
   (f) A. V. Luzanov and E. N. Babich, *J. Mol. Struct. (Theochem)* **333** (1995) 279.
   (g) P. E. John and R. B. Mallion, *Int. J. Quantum. Chem.*, in press.
   (h) T. J. N. Brown, R. B. Mallion, P. Pollak, and A. Roth, *Discrete Appl. Math.* **67** (1996) 51.
3. R. J. Wilson, *Introduction to Graph Theory*, Oliver and Boyd, Edinburgh, 1972, p. 46.
4. (a) B. Mohar, in: *MATH/CHEM/COMP 1988*, A. Graovac (Ed.), Elsevier, Amsterdam, 1989, p. 1.
   (b) B. Mohar, in: *Graph Theory, Combinatorics and Applications*, Y. Alavi, G. Chartrand, O. R. Ollermann and A. J. Schwenk (Eds.), Wiley, New York, 1991, p. 871.
5. S. Nikolić, N. Trinajstić, J. V. Knop, W. R. Müller, and K. Szymanski, *J. Math. Chem.* **4** (1990) 357.
6. (a) D. M. Cvetković, M. Doob, and H. Sachs, *Spectra of Graphs*, 3rd revised and enlarged edition, Johann Ambrosius Barth Verlag, Heidelberg, 1995, p. 27.
   (b) D. M. Cvetković, M. Doob, I. Gutman, and A. Torgašev, *Recent Results in the Theory of Graph Spectra*, North Holland, Amsterdam, 1988, p. 125.
   (c) N. Trinajstić, D. Babić, S. Nikolić, D. Plavšić, D. Amić, and Z. Mihalić, *J. Chem. Inf. Comput. Sci.* **34** (1994) 368.
7. I. Gutman, R. B. Mallion, and J. W. Essam, *Mol. Phys.* **50** (1983) 859.
8. K. Balasubramanian, *J. Phys. Chem.* **99** (1995) 6509.
9. (a) K. Balasubramanian, *Chem. Phys. Lett.* **224** (1994) 325.
   (b) K. Balasubramanian, *Mol. Phys.* **85** (1995) 335.
10. F. Harary and P. G. Mezey, *Theoret. Chim. Acta* **79** (1991) 379.
11. W. R. Müller, K. Szymanski, J. V. Knop, and N. Trinajstić, *Theoret. Chim. Acta* **86** (1993) 269.
12. F. Harary, *Publ. Math. Inst. Hung.* **5** (1960) 63.
13. N. Trinajstić, W. R. Müller, K. Szymanski, and J. V. Knop, *Croat. Chem. Acta* **68** (1995) 91.
14. H. A. Staab and F. Diederich, *Chem. Ber.* **116** (1983) 3487.
15. H. A. Staab, F. Diederich, C. Krieger, and D. Schweitzer, *Chem. Ber.* **116** (1983) 3504.
16. R. H. Schmidt-Radde and K. P. C. Vollhardt, *J. Amer. Chem. Soc.* **114** (1992) 9713.
17. e.g., D. Babić and N. Trinajstić, *J. Mol. Struct. (Theochem)* **314** (1994) 321.
18. J. Petersen, *Acta Math.* **15** (1891) 193.
19. N. L. Biggs, E. K. Lloyd, and R. J. Wilson, *Graph Theory 1736–1936*, Clarendon, Oxford, 1977, Chapter 10.
20. F. Harary, *Graph Theory*, 2nd printing, Addison-Wesley, Reading, MA, 1971, pp. 89–90.
21. (a) J. D. Dunitz and V. Prelog, *Angew. Chem.* **80** (1968) 700.
   (b) M. Gielen and J. Nasielski, *Bull. Soc. Chim. Belges* **78** (1969) 339.
   (c) J. Brocas and M. Gielen, *ibid.* **80** (1971) 207.
   (d) M. Randić, *Croat. Chem. Acta* **49** (1977) 643.

(e) J. Brocas, M. Gielen, and R. Willem, *The Permutational Approach to Dynamic Streochemistry*, McGraw-Hill, New York, 1983.
(f) N. Trinajstić, *Croat. Chem. Acta* **66** (1993) 227.
(g) M. Randić and N. Trinajstić, *Croat. Chem. Acta* **67** (1994) 1.
22. A. T. Balaban, D. Farcasiu, and R. Banica, *Rev. Roum. Chim.* **11** (1966) 1205.
23. D. Veljan, *Combinatorics with the Theory of Graphs* (in Croatian), Školska knjiga, Zagreb, 1989, p. 314.
24. V. Devidé, Academician Danilo Blanuša, Croatian Mathematician of International Reputation (in Croatian), *Radovi Leksikografskog zavoda Miroslav Krleža*, **3** (1993)123.
25. D. Blanuša, The Four Colour Problem (in Croatian), *Glasnik mat.-fiz. i astr.*, ser. 2, **1** (1946) 31.
26. M. Gielen, in: *Chemical Applications of Graph Theory*, A. T. Balaban (Ed.), Academic Press, London, p. 261.
27. M. Randić, D. J. Klein, V. Katović, D. O. Oakland, W. A. Seitz, and A. T. Balaban, in: *Graph Theory and Topology in Chemistry*, R. B. King and D. H. Rouvray (Eds.), Elsevier, Amsterdam, 1987, p. 266.
28. T. Živković, *Croat. Chem. Acta*, in print.
29. (a) W. E. Billups and M. A. Ciufolini (Eds.) *Buckminster-fullerenes*, VCH, New York, 1993.
(b) A. Hirsch, *The Chemistry of the Fullerenes*, Georg Thieme Verlag, Stuttgart, 1994.
30. (a) T. G. Schmalz, W. A. Seitz, D. J. Klein, and G. E. Hite, *J. Amer. Chem. Soc.* **110** (1988) 1113.
(b) N. Trinajstić, *Croat. Chem. Acta* **66** (1993) 227.
(c) F. Chung and S. Sternberg, *Amer. Scientist* **81** (1993) 56.
(d) F. Rioux, *J. Chem. Educ.* **71** (1994) 464.
(e) N. Trinajstić, M. Randić, D. J. Klein, D. Babić, and Z. Mihalić, *Croat. Chem. Acta* **68** (1995) 241.
31. (a) T. J. N. Brown, R. B. Mallion, P. Pollak, B. R. M. de Castro, and J. A. N. F. Gomes, *J. Comput. Chem.* **12** (1994) 1118.
(b) Z. Mihalić and N. Trinajstić, *Fullerene Sci. Technol.* **2** (1994) 89.
(c) N. Trinajstić, Z. Mihalić, and F. E. Harris, *Int. J. Quantum Chem.: Quantum Chem. Symp.* **28** (1994) 525.

SAŽETAK

Kompleksnost nekih interesantnih (kemijskih) grafova

Sonja Nikolić, Nenad Trinajstić, Albin Jurić, Zlatko Mihalić i Goran Krilov

Kao kriterij kompleksnosti građe policikličkih grafova uzet je broj odgovorajućih razapinjajućih stabala. Razmatrani su slijedeći grafovi: svi povezani grafovi s četiri i pet čvorova, grafovi koji se sastoje od dva dijela ili više dijelova povezanih s jednim bridom, Petersonov graf, Blanušin graf, Desargues-Levyjev graf i Schlegelov graf koji predstavlja buckminsterfulleren.