NiceGraph PROGRAM AND ITS APPLICATIONS IN CHEMISTRY

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Abstract

Recently the problem of drawing graphs became a hot subject in mathematical and computer sciences. In the present paper two of the graph drawing algorithms, namely those of Kamada-Kawai and Fruchterman-Reingold are for the first time applied to chemistry in their original two dimensional (2D) versions as well in their generalized three dimensional (3D) version developed by us. In addition, the algorithm based on the adjacency matrix eigenvectors has been also tested.

All three algorithms in their 2D and 3D versions are tested on a series of molecules, especially on fullerenes and toroidal pure carbon cages, the so-called torusenes. The conformations obtained offer a rather good guess of starting geometries for more sophisticated methods. The drawings obtained by the Fruchterman-Reingold algorithm are superior to those generated by Kamada-Kawai algorithm.

In addition, all molecular graphs studied have been also represented by the so-called Schlegel diagrams for whose generation a novel algorithm was developed. Schlegel diagrams are important for identifying and analysing topological properties of large spatial carbon clusters.

INTRODUCTION

When representing molecules with graphs the individuality of constituent atoms and character of chemical bonds is mostly suppressed but the connectivity is emphasised in its pure form.

Atoms are represented by vertices of graphs which are conveniently depicted as points and chemical bonds by edges which are drawn as straight lines. As positions of points are completely arbitrary there is an infinite number of ways to draw a given graph.

However, by imposing some aesthetic or other criterion, the admissible number of ways to draw a graph is reduced. Recently, the problem of drawing graphs became a hot subject in mathematical and computer sciences. A series of international conferences on the subject is being organized annually since 1992 [1]. This topic has important applications in key computer technologies such as software engineering, database design and visual interfaces. Further applications can be found in architectural and circuit design, project management, in mathematical fields such as computational geometry, topological graph theory, ordered sets, and many others. However graph drawing algorithms have been developed primarily for presentations of graphs in plane.

In the present paper two of the graph drawing algorithms [2],[3] are for the first time applied to chemistry in their original 2D version as well as in their generalized three dimensional version developed by us. In parallel, the algorithm bassed on the adjacency matrix eigenvectors has been also tested. Moreover, the algorithm to present so-called Schlegel diagram of a polyhedron is developed.

All the above algorithms belong to the class of so-called spring embedding algorithms [4]. They are all descendants of the Eades' algorithm [5]. Since all of them give aesthetically acceptable drawings we name them NiceGraph models. The methods have been successfully implemented and form a part of the package Vega developed at the IMFM/TCS in Ljubljana.

The methods developed here are not a substitute for more advanced quantum-chemical methods but rather they offer a noble guess of plausible starting geometries for more sophisticated methods. As they are simple to apply, we recommend them for quick determination of molecular geometries, especially when many isomers of a given molecule have to be searched. This is for instance the case in fullerene molecules which are the object of

intense current research in chemistry, physics and material sciences[6].

THE ALGORITHM OF KAMADA AND KAWAI

Let $G = (V, E)$ be a graph with $n = |V|$ vertices and $m = |E|$ edges. The graph-theoretical distance d_{ij} between vertices v_i and v_j is the smallest number of edges between v_i and v_j. The distances d_{ij} are integers ranging from 1 for the first neighbours up to the diameter D, the largest distance in a graph.

Let us make a drawing of graph G in three dimensional Euclidean space. To each vertex v_i a point $\overrightarrow{r_i} = (x_i, y_i, z_i)$ is associated in 3D-space. The Euclidean distance $D_{ij} = |\overrightarrow{r_i} - \overrightarrow{r_j}|$ is associated with a pair of vertices v_i and v_j. The quantity $(D_{ij} - d_{ij})^2$ measures the deviation of the Euclidean from graph-theoretical distance. Overall deviation of Euclidean with respect to graph-theoretical distances in a graph G is given by

$$E = E(\overrightarrow{r_1}, \overrightarrow{r_2}, \ldots, \overrightarrow{r_n}; G) = \sum \frac{1}{2} k_{ij} (D_{ij} - d_{ij})^2$$

where summation goes over all possible pairs of vertices.

According to Kamada and Kawai a graph is modelled as a system of balls and springs. If so, the energy function E could be understood as the elastic energy associated with a particular drawing $(\overrightarrow{r_1}, \overrightarrow{r_2}, \ldots, \overrightarrow{r_n})$ of a graph G. The contribution $k_{ij}(D_{ij} - d_{ij})^2/2$ is the elastic energy of a spring of the force constant k where d plays a role of the equilibrium distance.

The problem of graph drawing is reduced to finding positions of vertices (balls) in such a way that the energy of a system of springs becomes minimal.

It is reasonable to assume that k_{ij} are inversely proportional to d_{ij} :

$$k_{ij} = K/d_{ij}$$

where K is an arbitrary positive constant.

The minimum of E is determined by:

$$\frac{\partial E}{\partial x_i} = 0, \quad \frac{\partial E}{\partial y_i} = 0, \quad \frac{\partial E}{\partial z_i} = 0, \quad i = 1, 2, \ldots, n$$

i.e. by the system of $3n$ non-linear equations. We solve these equations numerically. For each vertex v_i the quantity

$$\Delta_i = \sqrt{\frac{\partial E}{\partial x_i}^2 + \frac{\partial E}{\partial y_i}^2 + \frac{\partial E}{\partial z_i}^2}$$

is calculated.

In each step of the algorithm the vertex v_i with the maximum Δ_i is chosen and E is considered as the function of only three variables x_i, y_i and z_i. By applying the Newton method the related equations become linear and we have to solve the linear system in three variables until Δ_i becomes less than some threshold value ϵ. After that the next maximal Δ_i is found and the procedure is repeated. In another words only one point is moved at each iteration.

By omitting the third coordinate z the two dimensional version of the algorithm is derived. Indeed, the 2D version was first developed. The 2D and 3D versions of the Kamada and Kawai algorithm will be denoted in the further text by KK2 and KK3, respectively.

Time complexity for the calculation of the graph-theoretical distances is $\mathcal{O}(n^3)$. In the first step of the algorithm all Δ_i have to be calculated. Time complexity for this is $\mathcal{O}(n^2)$. Time complexity for each following step is $\mathcal{O}(n)$ since values Δ_i only have to be updated.

THE ALGORITHM OF FRUCHTERMAN AND REINGOLD

In this model graph is again modelled as a physical system. Repulsive forces are calculated between every pair of vertices and attractive forces are calculated between every pair of adjacent vertices. Forces are used to calculate velocity for every time quantum (instead of acceleration as it is usual in physical systems). The aim of the algorithm is to find the static equlibria, i.e. the state with zero resultant forces for all vertices. The 2D and 3D versions of the Fruchterman and Reingold algorithm will be denoted in the further text by FR2 and FR3, respectively.

If d is the distance between the two vertices, then the attractive force f_a is calculated as

$$f_a = d^2/k$$

and the repulsive force f_r is calculated as

$$f_r = k^2/d.$$

Here k denotes the optimal distance between vertices calculated at the beginning of the algorithm as

$$k = C\sqrt{\text{area}/\text{number of vertices}}$$

where the constant C is found experimentally. It is easy to see that for the path of length two k is the distance where the forces would cancel each other out and in a general graph k is the average distance where the resultant forces for all vertices equal zero.

In each step of the algorithm resultant forces of all vertices are calculated and all vertices are moved in the directions of the resultant forces. The displacements are controlled by the temperature parameter T and by the borders of the area. Vertices cannot be displaced outside frame and the size of the displacement δ_v of the vertex v with the resultant force F_v is

$$\delta_v = \min(T, |F_v|).$$

In each step the temperature is reduced using some cooling function.

One step of the algorithm has time complexity $\mathcal{O}(n^2 + m)$.

THE ALGORITHM FOR DRAWING SCHLEGEL DIAGRAMS

Schlegel diagrams are planar representations of polyhedral graphs and therefore they are suitable to represent fullerenes. These diagrams clearly show the connectivity of atoms in fullerenes.

A graph can be modelled as a system of balls and elastic bands where the vertices of the outer face are fixed on regular polygon. We seek for the state of static equlibria. This algorithm is derived from the Fruchterman and Reingold algorithm by deleting all repulsive forces and fixing vertices of an outer face.

Some further modifications were made in order to obtain better figures. If we want to end with approximately equally arranged faces, bands close to the peripheral ring should be stronger than the bands in the middle of

the figure. Otherwise we end with a large number of crowded small faces in the middle and large faces on the border of the figure. For this purpose *peripheriсity* p_v of a vertex v is introduced as the length of the shortest path between the vertex and the outer face.

The size of the attractive force between vertices u and v is calculated as

$$f_a = d^2 \exp(A \frac{2p_{max} - p_u - p_v}{p_{max}})$$

where p_{max} is the maximum peripheriсity in the graph and the constant A is found experimentaly. As in the previous algorithms FR2 and FR3 the resultant forces of all vertices are calculated in each step and vertices are displaced in the directions of the resultant forces for an ammount equal to the minimum of the force size and the temperature T.

The algorithm can be applied to non-planar graphs as long as peripheral ring is specified. In such cases this algorithm often provides a better inside into the connectivity of vertices.

The Schlegel diagram algorithm will be denoted in further text by SCH. One step of the algorithm has time complexity $\mathcal{O}(m)$.

THE ALGORITHM BASED ON THE ADJACENCY MATRIX EIGENVECTORS

Another model being accepted by some fullerene research groups [7], [8],[9] is based on the consideration of the eigenvectors $\overrightarrow{x_1}, \overrightarrow{x_2}, \ldots, \overrightarrow{x_n}$, of the adjacency matrix A of a graph with n vertices. Eigenvalues are ordered as: $\lambda_1 \geq \lambda_2 \geq \ldots$. Three consecutive eigenvectors like $\overrightarrow{x_2}$, $\overrightarrow{x_3}$ and $\overrightarrow{x_4}$ are taken to build $n \times 3$ matrix $B = [\overrightarrow{x_2}\ \overrightarrow{x_3}\ \overrightarrow{x_4}]$. By reading the i-th row of B, (x_{2i}, x_{3i}, x_{4i}) as the 3D-coordinates of vertex i and running over all i's, in many cases a rather decent 3D-drawing of G is achieved. In the case when a graph is not regular, results are generally better if the Laplacean matrix of a graph is taken instead of its adjacency matrix [10].

Adjacency matrix eigenvectors algorithm will be abreviated AME in the further text. Standard numerical algorithms that are available for Mathematica users were employed (`Eigensystem`, `GramSchmidt`).

RESULTS

The basic information on a graph is the connectivity of its vertices. Here it is given by the adjacency matrix of a graph from which the graph-theoretical distances are calculated.

The starting configuration of points in Euclidean space, if not otherwise specified, is given at random. It could be also drawn on the screen by using graphical interface or given by some rule. For instance, the graph G, of snub cube could be depicted [11] as a rotagraph $\omega_4(C_6 + \{\{2,6\},\{3,5\}\};\{\{1,1\}, \{1,2\},\{6,2\},\{6,3\},\{5,3\},\{5,4\},\{4,4\}\})$, i.e. by repeating four times the cycle of length 6 with the connectivity between neighbouring paths given as in Fig. 1. Its SCH, AME, KK2, KK3, FR2 and FR3 drawings are depicted in Fig. 2.

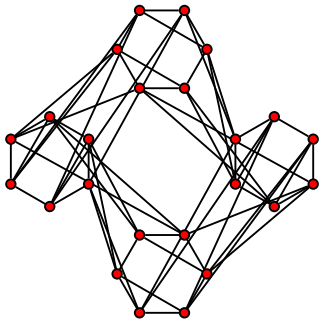
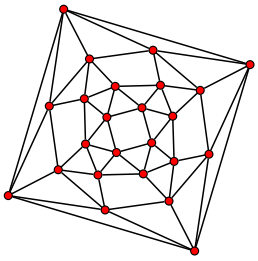
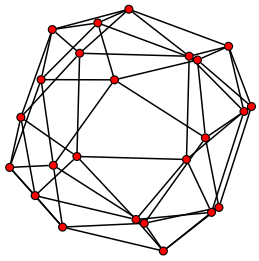


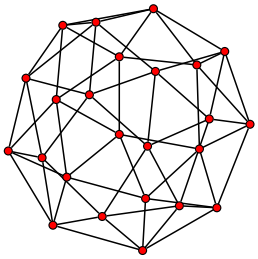
Figure 1. *The graph of snub cube represented as a rotgraph.*



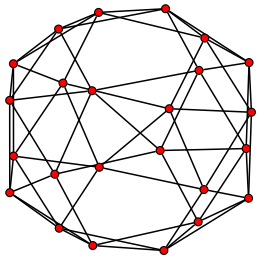
SCH



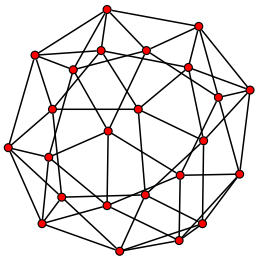
AME



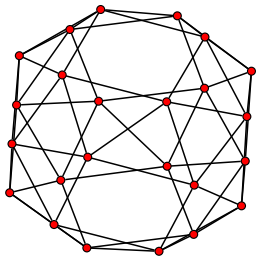
KK2



KK3



FR2

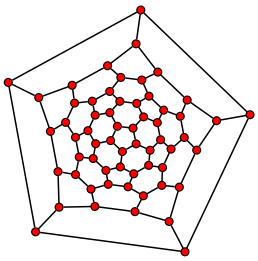


FR3

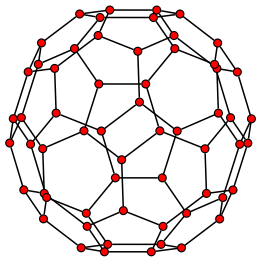
Figure 2. *The Schlegel (SCH), adjacency matrix eigenvectors (AME), Kamada-Kawai 2D (KK2) and 3D (KK3), and Fruchterman-Reingold 2D (FR2) and 3D (FR3) NiceGraph drawings of the snub cube graph.*

Note that the drawings obtained by the optimization in 2D-space look like the 2-dimensional projections of omptimized 3D-drawings. The same applies for other graphs as well.

The starting Schlegel diagram of the celebrated icosahedral I_h : C_{60} fullerene and its NiceGraph drawings are depicted in Fig. 3.



SCH



AME

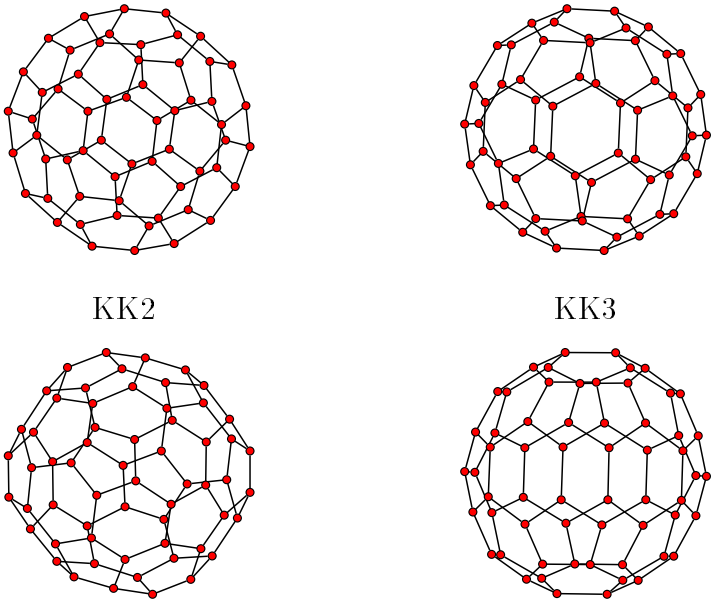
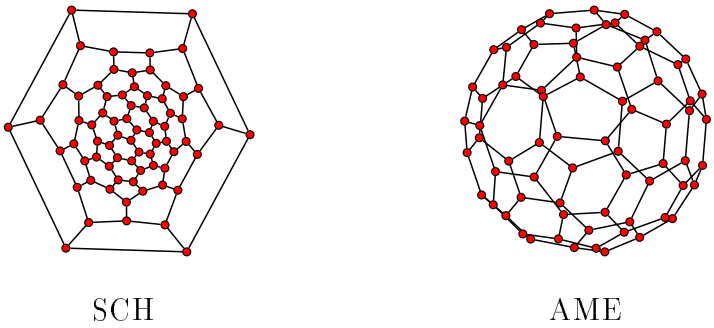


Figure 3. *The Schlegel (SCH), adjacency matrix eigenvectors (AME), Kamada-Kawai 2D (KK2) and 3D (KK3), and Fruchterman-Reingold 2D (FR2) and 3D (FR3) NiceGraph drawings of the buckyball ($I_h : C_{60}$) graph.*

The Schlegel diagram and the NiceGraph drawings of the C_{72} fullerene, a leapfrog[12] of the C_{24} cage are shown in Fig. 4.



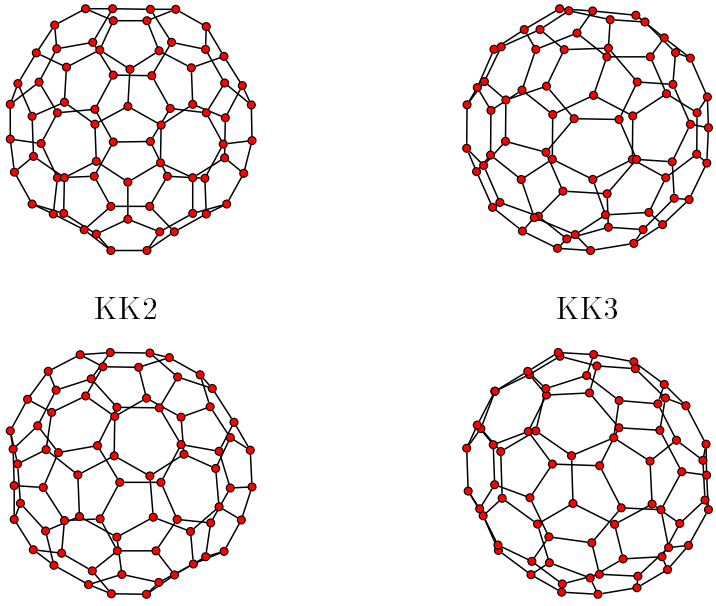


Figure 4. *The Schlegel (SCH), adjacency matrix eigenvectors (AME), Kamada-Kawai 2D (KK2) and 3D (KK3), and Fruchterman-Reingold 2D (FR2) and 3D (FR3) NiceGraph drawings of the C_{72} fullerene, a leapfrog of C_{24}.*

The example depicted in Fig. 5 represents Schlegel and NiceGraph configurations of the C_{28} cage (of T_d simetry) which is the smallest fullerene up to now [13] to form in a substantial abundance.

This cage behaves as a tetravalent species trapping a tetravalent atom inside the cage to make endohedral fullerenes such as $Ti@C_{28}$,$U@C_{28}$, etc. Its tetravalence is exhibited also by reacting at the four tetrahedral vertices on the outside of the $T_d : C_{28}$ cage to make e.g. $C_{28}H_4$.

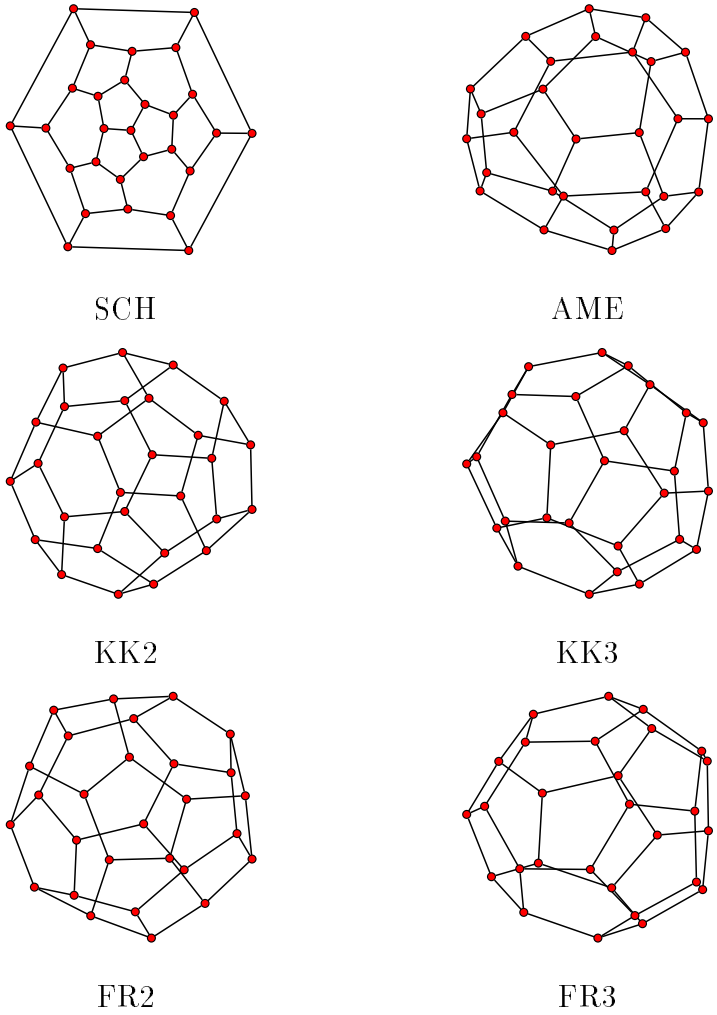


Figure 5. *The Schlegel (SCH), adjacency matrix eigenvectors (AME), Kamada-Kawai 2D (KK2) and 3D (KK3), and Fruchterman-Reingold 2D (FR2) and 3D (FR3) NiceGraph drawings of the $T_d : C_{28}$ fullerene.*

Formally, the fullerenes are defined as 3-valent (3-regular) graphs having only pentagons and hexagons as faces. If the use of heptagons is allowed too, the Euler's polyhedron formula gives:

$$h_5 = h_7 + 12(1 - g)$$

where h_5 and h_7 denotes the number of pentagons and heptagons, respec-

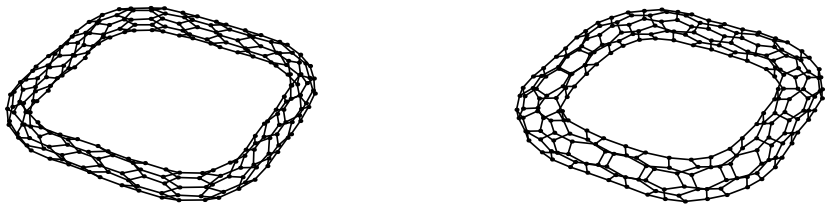
tively. The number of hexagons, h_6, is arbitrary. g denotes the genus of the surface at which G is embedded, i.e. $g = 0, 1$, and 2, for sphere, torus and pretzel, respectively. The toroidal, pure carbon cages recently have received a considerable attention [15],[16].

The above formula for $h_7 = 0, g = 0$ gives $h_5 = 12$, i.e. exactly 12 pentagons are needed to give a spherical fullerene. For a torus ($g = 1$), one has:

$$h_5 = h_7.$$

Two cases are possible. The first in which $h_5 = h_7 = 0$ gives toroidal polyhexes, i.e. the toroidal fullerenes composed solely from hexagons. It is easily to see that: $3n = 2m = 6h_6$. The FR3 NiceGraph drawing of the toroidal polyhex with $h_6 = 120$ is depicted in Fig. 6a.

The second case, $h_5 = h_7 \neq 0$, gives the azulenoid cages. The FR3 NiceGraph drawing of the torus with $h_5 = h_7 = 10$ ($h_6 = 100$) is depicted in Fig. 6b.



(a) (b)

Figure 6. *Fruchterman-Reingold 3D (FR3) NiceGraph drawings of (a) the toroidal polyhex with 120 hexagons and (b) the azelunoid cage with 10 pentagons, 100 hexagons and 10 heptagons.*

In the above cases it is evident that the NiceGraph algorithms are able to recognize the genus of a surface in which the graph has to be embedded.

DISCUSSION

The algorithms presented in this paper are giving reasonable plausible geometries of fullerenes and other molecules graphs. The drawings obtained by the Fruchterman-Reingold algorithm are superior to those generated by the Kamada-Kawai algorithm.

However, the final NiceGraph configuration are not necessarily "nice", i.e. the final drawings do not necessarily exhibit a geometrical symmetry indicated by the automorphisms group of a graph. This is especially true for graphs with large number of vertices. One possible way to remedy for this deficiency would be to make the threshold values in computations smaller but it will increase the computation time. Another approach, which is now under development, is to use the knowledge of the automorphisms group of a graph in building up the proper geometrical symmetry of the final drawing[14].

All algorithms presented here are written in Turbo Pascal and implemented in a system for manipulating discrete mathematical structures Vega [17].

The NiceGraph program in its present form does not discriminate the individuality of atoms and chemical bonds. However, the results for $C_{28}H_4$ cage show that its plausible geometry is nevertheless achieved. The example of biphenyle molecule is instructive too. Its KK NiceGraph drawings where carbon and hydrogen atoms are treated on the equal footing rotates one ring with respect to another but for an incorrect angle of 90^o.

The future developments of the program in which the individuality of the various chemical bonds will be reflected by appropriate changes in graph-theoretical distances are highly desirable. Especially interesting would be to study the changes in geometry of fullerenes in which some number of carbons is substituted by boron, nitrogen, and other atoms.

A systematic comparison of geometries obtained by the mathematical models like the NiceGraph, the eigenvectors of the adjacency matrix, and more realistic, physically based models like molecular mechanics, semiempirical and ab initio quantum-chemical models as well as with the experimental data is under way by the present authors [18].

CONCLUSIONS

The NiceGraph model, proposed here for applications in chemistry, is easy to apply. The only input data are connectivity tables of a molecule and the starting coordinates of atoms are taken at random. The final NiceGraph configuration is aesthetically acceptable and represents a plausible starting geometry to apply some more realistic model like molecular mechanics. The

present model is especially advisable to apply when a large number of isomers has to be searched as it is the case in fullerenes.

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SAŽETAK

NiceGraph program i njegove primjene u kemiji

Tomaž Pisanski, Bor Plestenjak i Ante Graovac

Problem risanja grafova postaje uzbudljiva tema matematike i računarskih znanosti. U ovom radu se po prvi put u kemiji primjenjuju dva postojeća algoritma za risanje grafova, naime, algoritmi Kamada-Kawaija i Fruchterman-Reingolda, i to u njihovom izvornom dvodimenzionalnom (2D), i u od nas poobčenom trodimenzionalnom (3D) obliku. U radu je dalje testiran već poznati algoritam zasnovan na vlastitim vektorima matrice susjedstva.

Sva tri algoritma u njihovim 2D i 3D verzijama su testirana na seriji molekula, posebno na fullerenima i toroidnim čisto ugljikovim kavezima. Dobivene konformacije predstavljaju prilično dobre početne geometrije za točnije račune, s time da su crteži dobijeni Fruchterman-Reingoldovim algoritmom superiorni onima dobijenim Kamada-Kawai algoritmom.

Sve studirane molekularne grafove prikazali smo takodjer tzv. Schlegelovim dijagramima za čije generiranje smo razvili vlastiti algoritam.