

CCA-1677

YU ISSN 0011 1643

UDC 541

Original Scientific Paper

Applications of the Reduced Graph Model. Enumeration of Kekulé Structures for Certain Classes of Large Benzenoid Hydrocarbons*

Pavel Krivka

Department of Mathematics, Institute of Chemical Technology,
53210 Pardubice, Czechoslovakia

and

Sonja Nikolić and Nenad Trinajstić

The Rugjer Bošković Institute, P.O.B. 1016, 41001 Zagreb, Croatia, Yugoslavia

Received October 21, 1985

The reduced graph model is applied to the enumeration of Kekulé structures for several classes of large benzenoid hydrocarbons.

The reduced graph model has been introduced as an alternative way to represent benzenoid-type networks and is used in the various combinatorial problems of benzenoid hydrocarbons.¹⁻⁶ The essence of this model is as follows.

Let G be a connected graph (benzenoid system) in an infinite hexagonal planar lattice H . Three disjunctive sets of parallel edges arranged in rows are present in the lattice H . We can arbitrarily choose one of them and call it vertical and the remaining two we can denote (in two different ways) as left and right diagonal. The hexagonal lattice H with edges assigned as vertical, left diagonal, and right diagonal is named the oriented lattice H . Horizontal rows of hexagons in the oriented lattice H are called levels of the lattice H . The oriented hexagonal lattice H may be transformed into the trigonal planar lattice T according to the following transformation rules:

$$V(T) = \{\text{vertical edges of } H\} \quad (1)$$

$$E(T) = \{(v_1, v_2) \mid \text{either } v_1, v_2 \text{ belong to the same ring in } H \\ \text{or are connected by a diagonal edge}\} \quad (2)$$

$V(T)$ and $E(T)$ are vertices and edges of the trigonal lattice T .

Following rules (1) and (2) each graph G in H is easily transformed into a graph $R(G)$ that is a part of T and is called a reduced graph. We demonstrate in Figure 1 the transformation of a hexagonal network H into a trigonal network T , and simultaneously change the representation of a given

* Reported in part at the IUPAC International Symposium on the Applications of Mathematical Concepts to Chemistry (Dubrovnik, Croatia, September 2—5, 1985).

benzenoid hydrocarbon from the benzenoid graph⁷ G to the reduced graph $R(G)$.

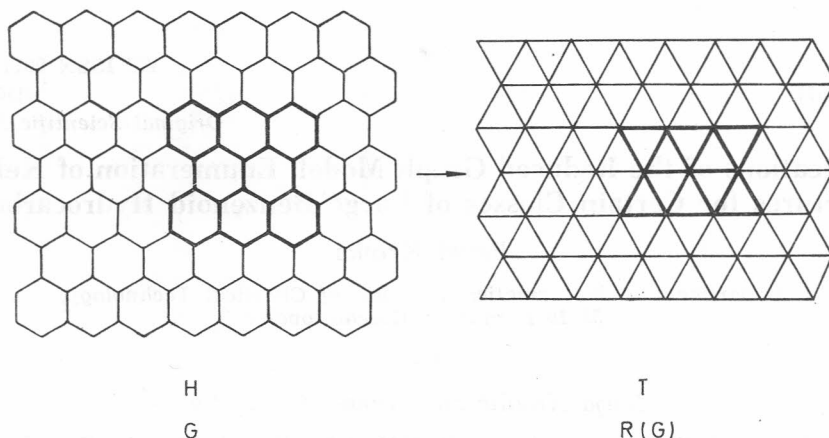


Figure 1. Transformation of a hexagonal network H into a trigonal network T , and the benzenoid graph G into the corresponding reduced graph $R(G)$.

The graph theoretical aspects of the reduced graph model are discussed in detail elsewhere.^{2,8} This model has so far found the greatest use in the enumeration and generation of Kekulé structures of benzenoid and benzenoid-like systems.^{1-5,8} In the present work we wish to report the application of the reduced graph model to the enumeration of Kekulé structures of certain classes of large benzenoid hydrocarbons. There is a continuing interest in counting Kekulé valence structures of large hexagonal systems,⁹⁻¹⁴ because it has been shown that very large benzenoid hydrocarbons can be examined using theories that require only counts of Kekulé structures as input.¹⁵⁻¹⁹

Kekulé structures are conveniently depicted by Kekulé graphs.²⁰ Kekulé graphs are isomorphic to 1-factors.²¹ The 1-factor of G is a graph F such that:

- (i) F is a spanning subgraph of G , i. e. $V(F) = V(G)$.
- (ii) The components of F are only K_2 graphs, i. e. F is a disconnected graph.

We will now consider the 1-factors of G in the oriented lattice H . It appears that whenever we determine which of the vertical edges belong to the 1-factors and which do not, this completely determines the assignment of all other (diagonal) edges. We therefore need to work only with the vertices of the reduced graph $R(G)$. If we have a horizontal edge in $R(G)$ with no triangle above (and/or below), we can add a dummy vertex above (and/or below) and thus create an upper (and/or lower) triangle. After doing the above whenever necessary, we obtain the complete reduced graph of G , $CR(G)$. As an example, we give in Figure 2 the complete reduced graph of pyrene.

A sequence of adjacent edges in T , formed only by diagonal edges, is called a vertical path. The count of (pairwise disjoint) paths over the (labelled) complete reduced graph $CR(G)$ corresponds to the number of

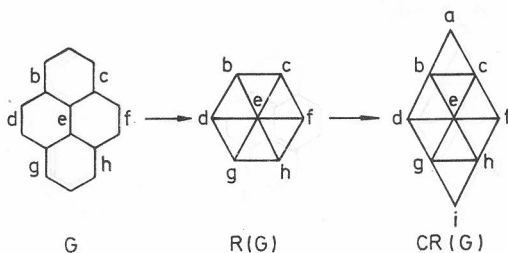


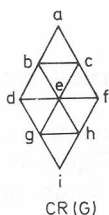
Figure 2. The reduced graph $R(G)$ and the complete reduced graph $CR(G)$ of the pyrene graph G . Dummy vertices in $CR(G)$ are labelled by a and i

1-factors $K(G)$ of G (i. e. the number of Kekulé structures of the corresponding benzenoid hydrocarbon):

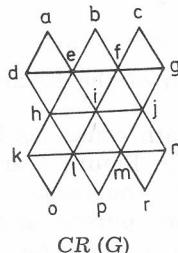
$$K(G) = \text{path count.} \tag{3}$$

We will not consider any other paths in $CR(G)$.

(a) pyrene



(b) bisanthene



Path count

- ab dgi
- ab egi
- ab ehi
- ac egi
- ac ehi
- ac fhi

$$K(G) = 6$$

Path count

- adhko-beilp-cfjmr
- adhko-beilp-cfjnr
- adhko-beilp-cgjmr
- adhko-beilp-cgjnr
- adhko-bfilp-cgjmr
- adhko-bflip-cgjnr
- adhko-bfimp-cgjnr
- adhlo-beimp-cfjnr
- adhlo-beimp-cgjnr
- adhlo-beimp-cfjnr
- adhlo-beimp-cgjnr
- adhko-beimp-cfjnr
- adhko-beimp-cgjnr
- adhko-bfilp-cgjnr
- adhko-bfimp-cgjnr
- adhlo-beimp-cfjnr
- adhlo-beimp-cgjnr

$$K(G) = 16$$

Figure 3. The vertical path count for the complete reduced graph corresponding pyrene and bisanthene

The theorem and its proof on which the above is based is presented elsewhere.⁸ The roots of this procedure can be found in an early piece of work by Gordon and Davison.²²

The reduced graph model strongly reminds that of Sachs²³ who has established a one-to-one correspondence between the set of 1-factors and the set of perfect path systems in hexagonal structures.

We should note that: (i) If G possesses 1-factors, then the number of vertices on the top and bottom levels of $CR(G)$ must be the same and (ii) If G possesses 1-factors, then $CR(G)$ must have at least n vertices on each level, where n = the number of vertices on the uppermost level of $CR(G)$.

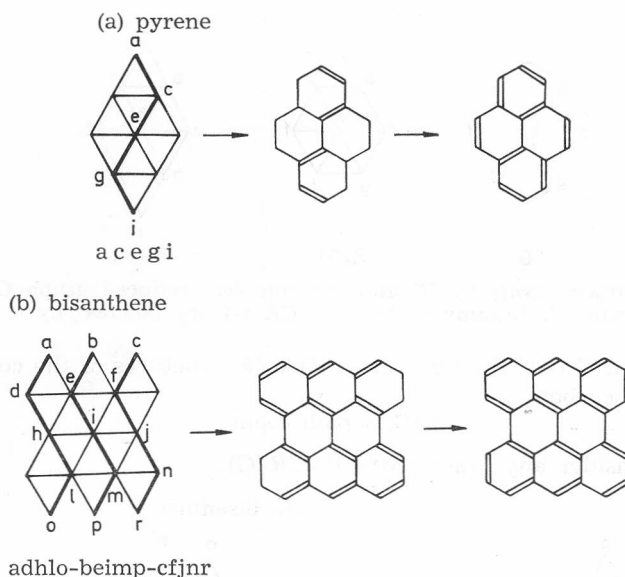


Figure 4. Generation of the Kekulé structures from the vertical paths in $CR(G)$

The vertical path count (and the Kekulé structure count) for two graphs already presented in Figure 1 and Figure 2 is given in Figure 3.

There are many independent methods available for obtaining the Kekulé structure counts for pyrene and bisanthene.²⁴ Both molecules may be found in Tables of benzenoid hydrocarbons published recently,²⁵ and both values from Figure 3 agree with those in these Tables.

Since the (pairwise disjoint) vertical paths in $CR(G)$ correspond to 1-factors, these paths can easily be transformed into Kekulé structures. The generation procedure is based on the following simple rule: The points in the vertical path in $CR(G)$ correspond to single bonds in a given Kekulé structure of a benzenoid hydrocarbon. Examples are given in Figure 4. The generation procedure consists of three steps:

(i) First a given vertical path in $CR(G)$ will be presented.

(ii) $CR(G)$ with a given vertical path will then be transformed into a structure with allocated single bonds corresponding to the position of the particular vertical path in $CR(G)$, and (iii) This structure will be transformed into the corresponding Kekulé structure by adding the missing double bonds.

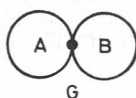
When we try to enumerate 1-factors of a given complex graph, we may use previously determined values of the 1-factors of its constituent graphs. Hence, we partition a complex graph at some convenient vertical path (we can assume that a single vertex represents a path of length one) into two or more fragments with a known number of 1-factors. Then, the total value of the 1-factors of G represents the combination of the known values of the 1-factors of the constituent fragments, from which are excluded those values which correspond to paths having points in common. The procedure can be carried out, of course, only in such cases where there is no path going from one fragment to another.

If we denote by $K(A), K(B), \dots, K(i)$ the total numbers of paths belonging to fragments A, B, \dots, i making up G , and by $P(A), P(B), \dots, P(i)$ the paths passing through the fragmentation points (i. e. path correction), then the expression for calculating $K(G)$ is given by:

$$K(G) = \prod_i K(i) - \text{path correction} \tag{4}$$

The path correction depends on the number of constituent fragments making up the composite benzenoid hydrocarbon. Below we give formulae for several cases of interest. Cases for three and more fragments will be derived by utilizing the formula for the case of two fragments.

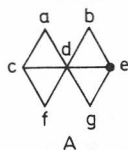
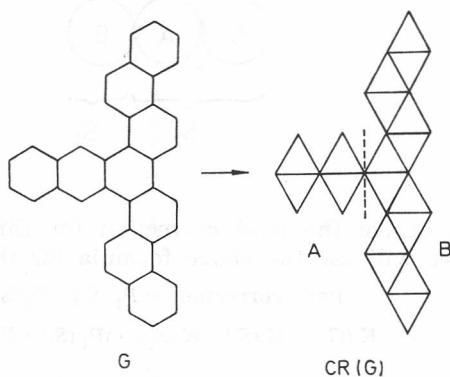
(a) Path correction for the case of two constituent fragments and a single point of connection



$$\text{Path correction} = P(A) \cdot P(B) \tag{5}$$

$$K(G) = K(A) \cdot (K(B) - P(A) \cdot P(B)) \tag{6}$$

An example of this case is shown in Figure 5.



Path count
 acf — bdg
 acf — beg*
 adf — beg*

$$P(A) = 2$$

$$K(A) = 3$$

Figure 5. to be continued

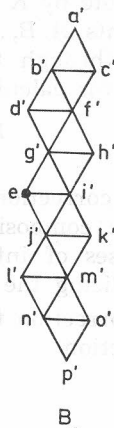
Figure 5. continued

Path count

a'b'd'g'e'j'l'n'p'*	a'b'f'h'i'j'm'n'p'
a'b'd'g'e'j'm'n'p'*	a'b'f'h'i'j'm'o'p'
a'b'd'g'e'j'm'o'p'*	a'b'f'h'i'k'm'n'p'
a'b'd'g'i'j'l'n'p'	a'b'f'h'i'k'm'o'p'
a'b'd'g'i'j'm'n'p'	a'c'f'g'e'j'l'n'p'*
a'b'd'g'i'j'm'o'p'	a'c'f'g'e'j'm'n'p'*
a'b'd'g'i'k'm'n'p'	a'c'f'g'e'j'm'o'p'*
a'b'd'g'i'k'm'o'p'	a'c'f'g'i'j'l'n'p'
a'b'f'g'e'j'l'n'p'*	a'c'f'g'i'j'm'n'p'
a'b'f'g'e'j'm'n'p'*	a'c'f'g'i'j'm'o'p'
a'b'f'g'e'j'm'o'p'*	a'c'f'g'i'k'm'n'p'
a'b'f'g'i'j'l'n'p'	a'c'f'g'i'k'm'o'p'
a'b'f'g'i'j'm'n'p'	a'c'f'h'i'j'l'n'p'
a'b'f'g'i'j'm'o'p'	a'c'f'h'i'j'm'n'p'
a'b'f'g'i'k'm'n'p'	a'c'f'h'i'j'm'o'p'
a'b'f'g'i'k'm'o'p'	a'c'f'h'i'k'm'n'p'
a'b'f'h'i'j'l'n'p'	a'c'f'h'i'k'm'o'p'

$$K(B) = 34$$

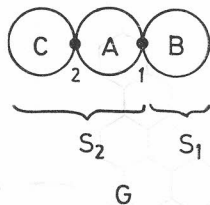
$$K(G) = 3 \cdot 34 - 2 \cdot 9 = 84$$



$$P(B) = 9$$

Figure 5. Application of formula (6)

(b) Path correction for the case of three constituent fragments and two single points of connection



In order to derive the path correction for three constituent fragments making up G , we will use the above formula for the case of two fragments.

$$\text{Path correction} = P_1(S_1) \cdot P_1(S_2) \quad (7)$$

$$K(G) = K(S_1) \cdot K(S_2) - P_1(S_1) \cdot P_1(S_2) \quad (8)$$

Next, we need to substitute convenient expressions for $P_1(S_1)$, $P_2(S_2)$, $K(S_1)$, and $K(S_2)$ to produce the explicit formula for this case.

$$P_1(S_1) = P_1(B) \quad (9)$$

$$P_1(S_2) = P_1(A) \cdot K(C) \quad (10)$$

Then, the path correction is given by:

$$\text{Path correction} = P_1(A) \cdot P_1(B) \cdot K(C) \quad (11)$$

The Kekulé structure counts for fragments S_1 and S_2 are as follows:

$$K(S_1) = K(B) \quad (12)$$

$$K(S_2) = K(A) \cdot K(C) - P_2(A) \cdot P_2(C) \quad (13)$$

By introducing (11), (12) and (13) into (8) we obtain finally:

$$K(G) = K(A) \cdot K(B) \cdot K(C) - P_2(A) \cdot P_2(C) \cdot K(B) - P_1(A) \cdot P_1(B) \cdot K(C) \quad (14)$$

Note, that no vertical path should go through both points 1 and 2 in G . An example illustrating this case is shown in Figure 6.

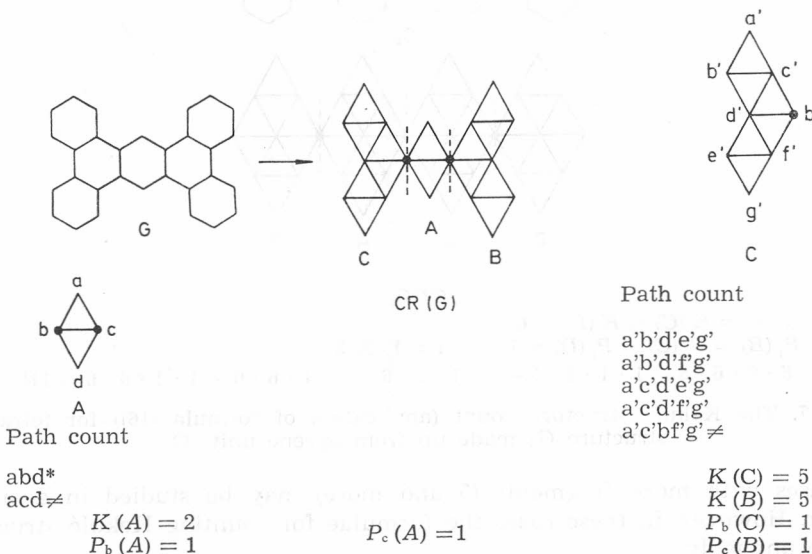
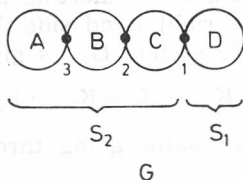


Figure 6. Application of formula (14)

(c) Path correction for the case of four constituent fragments and three single points of connection

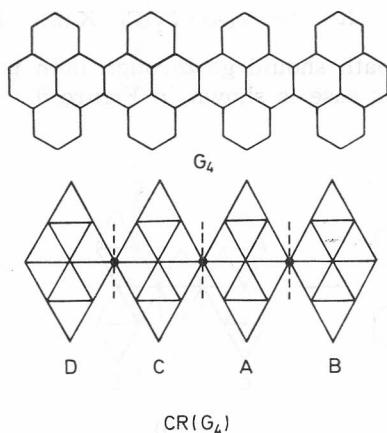


A procedure similar to that outlined above is adopted in this case, although the derivations are somewhat more complicated. The results obtained are as follows:

$$\begin{aligned} \text{Path correction} = & -P_1(A) \cdot P_1(B) \cdot P_3(C) \cdot P_3(D) + P_1(A) \cdot P_1(B) \cdot K(C) \cdot K(D) + \\ & + P_2(A) \cdot P_2(C) \cdot K(B) \cdot K(D) + P_3(C) \cdot P_3(D) \cdot K(A) \cdot K(B) \end{aligned} \quad (15)$$

$$\begin{aligned} K(G) = & K(A) \cdot K(B) \cdot K(C) \cdot K(D) + P_1(A) \cdot P_1(B) \cdot P_3(C) \cdot P_3(D) - \\ & - P_1(A) \cdot P_1(B) \cdot K(C) \cdot K(D) - P_2(A) \cdot P_2(C) \cdot K(B) \cdot K(D) - \\ & - P_3(C) \cdot P_3(D) \cdot K(A) \cdot K(B) \end{aligned} \quad (16)$$

An illustrative example for this case is given in Figure 7.



$$\begin{aligned}
 K(A) &= K(B) = K(C) = K(D) = 6 \\
 P_i(A) &= P_i(B) = P_i(C) = P_i(D) = 1, \quad i = 1, 2, 3 \\
 K(G_4) &= 6 \cdot 6 \cdot 6 \cdot 6 + 1 \cdot 1 \cdot 1 \cdot 1 - 1 \cdot 1 \cdot 6 \cdot 6 - 1 \cdot 1 \cdot 6 \cdot 6 - 1 \cdot 1 \cdot 6 \cdot 6 = 1189
 \end{aligned}$$

Figure 7. The Kekulé structure count (application of formula (16)) for tetrameric structure G_4 made up from pyrene units G .

The cases with more fragments (5 and more) may be studied in a similar manner. However, in these cases the formulae for counting Kekulé structures become unwieldy.

For polymeric systems, such as the tetramer in Figure 7, one may obtain a rather simple enumeration formula. Let S be a structure with one triangle on the top level and one triangle on the bottom level, and two single points of connection (labelled as 1 and 2) on opposite sides of the monomer such that there is no vertical path going through both these points. Let L_N be a chain made out of N copies of S by connecting point 2 of S on the left hand side with point 1 of S on the right hand side. The Kekulé structures count K_N for L_N , i. e. for an N -meric system G_N , is given by:

$$K_N = K_{N-1} \cdot K_1 - K_{N-2} \cdot P_1 \cdot P_2 \quad (17)$$

where P_i is the number of all paths going through point i . If $P_1 = P_2 = 1$, then Eq. (20) reduces to

$$K_N = K_{N-1} \cdot K_1 - K_{N-2} \quad (18)$$

Note that $K_0 = 1$ by definition.

For linear polymers, for example, made up of pyrene units the Kekulé structures count is, because of $K_1 = K(G) = 6$, given by:

$$\begin{aligned}
 K_N &= K_{N-1} \cdot 6 - K_{N-2} \\
 K_1 &= 6 \\
 K_2 &= 6^2 - 1 = 35 \\
 K_3 &= 6^3 - 2 \cdot 6 = 204 \\
 K_4 &= 6^4 - 3 \cdot 6^2 + 1 = 1189 \\
 K_5 &= 6^5 - 4 \cdot 6^3 + 3 \cdot 6 = 6930
 \end{aligned}$$

$$\begin{aligned}
 K_6 &= 6^6 - 5 \cdot 6^4 + 6 \cdot 6^2 - 1 = 40392 \\
 K_7 &= 6^7 - 6 \cdot 6^5 + 10 \cdot 6^3 - 4 \cdot 6 = 235416 \\
 K_8 &= 6^8 - 7 \cdot 6^6 + 15 \cdot 6^4 - 10 \cdot 6^2 + 1 = 1372105 \\
 K_9 &= 6^9 - 8 \cdot 6^7 + 21 \cdot 6^5 - 20 \cdot 6^3 + 5 \cdot 6 = 7997214 \\
 K_{10} &= 6^{10} - 9 \cdot 6^8 + 28 \cdot 6^6 - 35 \cdot 6^4 + 15 \cdot 6^2 - 1 = 46611179 \\
 &\dots\dots\dots
 \end{aligned}$$

As another example let us consider linear polymers made up of 5,6,12.13-dibenzoperopyrene monomeric units. The graph G corresponding to the monomer and the related complete reduced graph, $S(G) = CR(G)$, are shown in Figure 8.

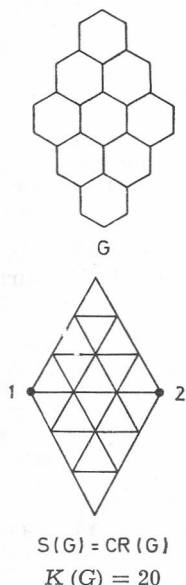


Figure 8. Benzenoid graph and the corresponding complete reduced graph of 5,6,12.13-dibenzoperopyrene

The Kekulé structure counts for this class of linear polymers, because of $K_1 = K(G) = 20$, are given by:

$$\begin{aligned}
 K_N &= K_{N-1} \cdot 20 - K_{N-2} \\
 K_1 &= 20 \\
 K_2 &= 20^2 - 1 = 399 \\
 K_3 &= 20^3 - 2 \cdot 20 = 7960 \\
 K_4 &= 20^4 - 3 \cdot 20^2 + 1 = 158801 \\
 K_5 &= 20^5 - 4 \cdot 20^3 + 3 \cdot 20 = 3168060 \\
 K_6 &= 20^6 - 5 \cdot 20^4 + 6 \cdot 20^2 - 1 = 63202400 \\
 K_7 &= 20^7 - 6 \cdot 20^5 + 10 \cdot 20^3 - 4 \cdot 20 = 1260880128 \\
 K_8 &= 20^8 - 7 \cdot 20^6 + 15 \cdot 20^4 - 10 \cdot 20 + 1 = 25154400256 \\
 K_9 &= 20^9 - 8 \cdot 20^7 + 21 \cdot 20^5 + 20 \cdot 20^4 - 5 \cdot 20 = 501830385664 \\
 K_{10} &= 20^{10} - 9 \cdot 20^8 + 28 \cdot 20^6 - 35 \cdot 20^5 - 15 \cdot 20 + 1 = 10011281457152 \\
 &\dots\dots\dots
 \end{aligned}$$

Acknowledgements. — We thank Professor Milan Randić (Ames), Professor Ivan Gutman (Kragujevac), Professor Douglas J. Klein (Galveston), and Dr Borka Džonova-Jerman-Blažič (Ljubljana) for helpful discussions on the reduced graph model. We also thank the referees for their helpful comments.

REFERENCES

1. B. Džonova-Jerman-Blažič, *Ph. D. Dissertation*, University of Zagreb, 1981.
2. B. Džonova-Jerman-Blažič and N. Trinajstić, *Comput. Chem.* **6** (1982) 121.
3. B. Džonova-Jerman-Blažič and N. Trinajstić, *Croat. Chem. Acta* **55** (1982) 347.
4. S. El-Basil, G. Jashari, J. V. Knop, and N. Trinajstić, *Monat. Chem.* **115** (1984) 1299.
5. S. El-Basil, P. Křivka, and N. Trinajstić, *Croat. Chem. Acta* **57** (1984) 339.
6. S. El-Basil and N. Trinajstić, *Theochem.* **110** (1984) 1.
7. N. Trinajstić, *Chemical Graph Theory*, CRC Press, Boca Raton, Florida 1983, Vol. **I**, Chapter 3.
8. N. Trinajstić and P. Křivka, in: *Mathematics and Computational Concepts in Chemistry*, Edited by N. Trinajstić, Horwood, Chichester, 1986, p. 328.
9. R. L. Brown, *J. Comput. Chem.* **4** (1983) 556; A. Graovac, O. E. Polansky, and N. N. Tyutyulkov, *Croat. Chem. Acta* **56** (1983) 325.
10. A. T. Balaban and I. Tomescu, *Math. Chem. (Mülheim/Ruhr)* **14** (1983) 155; *Croat. Chem. Acta* **54** (1984) 391 and further references therein.
11. W. A. Seitz, D. J. Klein, T. G. Schmalz, and M. Garcia-Bach, *Chem. Phys. Lett.* **115** (1985) 139.
12. S. E. Stein and R. L. Brown, *Carbon* **23** (1985) 105.
13. D. J. Klein, T. G. Schmalz, W. A. Seitz, and G. E. Hite, *Int. J. Quantum Chem.: Quantum Chem. Symp.*, **19** (1986) 707.
14. M. Randić, B. M. Gimarc, and N. Trinajstić, *Croat. Chem. Acta*, in press; A. Graovac and D. Babić, *ibid.*, in press.
15. W. C. Herndon, *Israel J. Chem.* **20** (1980) 270.
16. M. Randić, *Int. J. Quantum Chem.* **17** (1980) 549.
17. W. Gröndler, *Tetrahedron* **38** (1982) 15.
18. S. Kuwajima, *J. Am. Chem. Soc.* **106** (1984) 6496.
19. P. C. Hiberty and G. Ohanessian, *Int. J. Quantum Chem.* **27** (1985) 245.
20. D. Cvetković, I. Gutman, and N. Trinajstić, *Chem. Phys. Lett.* **16** (1972) 614.
21. F. Harary, *Graph Theory*, Addison-Wesley, Reading, MA 1971, second printing, p. 84.
22. M. Gordon and W. H. T. Davison, *J. Chem. Phys.* **20** (1952) 428.
23. H. Sachs, *Combinatorica* **4** (1984) 89.
24. e.g. J. V. Knop, K. Szymanski, N. Trinajstić, and P. Křivka, *Comp. Math. Appls.* **10** (1984) 369.
25. J. V. Knop, W. R. Müller, K. Szymanski, and N. Trinajstić, *Computer Generation of Certain Classes of Molecules*, SKTH, Zagreb 1985.

SAŽETAK

Primjena modela reduciranih crteža. Prebrojavanje Kekuléovih struktura za neke klase velikih benzenoidnih ugljikovodika

P. Křivka, S. Nikolić i N. Trinajstić

Model reduciranog crteža (grafa) upotrijebljen je za prebrojavanje Kekuléovih struktura nekih klasa velikih benzenoidnih ugljikovodika.