Monatshefte für Chemie 115, 1299—1312 (1984)

Monatshefte für Chemie
Chemical Monthly

Note on the Application of the Reduced Graph Model in Conjunction with Search Trees to the Enumeration of *Kekulé* Structures

Sherif El-Basil[a], Gani Jashari[b], Jan V. Knop[c], and Nenad Trinajstić*[,d]

[a] Faculty of Pharmacy, Cairo University, Cairo, Egypt
[b] Department of Physics, University of Prishtinë, YU-38000 Prishtinë, Kosovo, Yugoslavia
[c] Computer Centre, University of Düsseldorf, D-4000 Düsseldorf, Federal Republic of Germany
[d] The Rudjer Bošković Institute, YU-41001 Zagreb, Croatia, Yugoslavia

(Received 31 October 1983. Accepted 16 February 1984)

The reduced graph model, when used in conjunction with the search trees method, provides a novel combinatorial procedure for the enumeration and generation of *Kekulé* structures. The procedure is suited for large benzenoid hydrocarbons consisting of cata- and thin peri-condensed parts.

(Keywords: Benzenoid hydrocarbons; Enumeration of Kekulé structures; Reduced graph model; Search trees)

Zur Anwendung des „Reduced Graph Model" im Zusammenhang mit „Search Trees" zur Ermittlung der Anzahl möglicher Kekulé-Strukturen

Das Modell erlaubt mit der im Titel genannten Kombination eine neuartige Methode zur Ermittlung und Generierung von *Kekulé*-Strukturen. Das Verfahren ist für große benzoide Kohlenwasserstoffe geeignet, die aus cata- und (dünnen) peri-kondensierten Teilstrukturen bestehen.

Introduction

Recently we have proposed a "pencil-and-paper" method for the enumeration of *Kekulé* structures in benzenoid hydrocarbons, BH's[1]. This method is based on the reduced graph model which was introduced as an alternative way to depict hexagonal networks[2,3]. The problem of enumeration (production of the total number) and generating (construction of all possibilities) *Kekulé* structures is continually being

discussed in the literature[1–19]. In addition, the recent interest in *Kekulé* structures is related to their important role in structure-resonance theory[10,19,20] and in the conjugated circuits model[19,21], respectively. Finally, *Kekulé* structures play one of the key role in understanding the mathematical basis for the intimate relationship between resonance theory and the *Hückel* MO model[22–24].

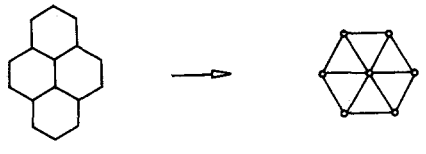
In the present paper we wish to discuss the use of search trees[25] within the reduced graph model, which can be used to generate *Kekulé* structures of BH's and those alternant and non-alternant hydrocarbons which can be reduced or enlarged to BH's by convenient graph-theoretical transformations[18,26]. More specifically, we will be interested in enumerating *Kekulé* structures of large BH's consisting of cata- and peri-condensed subunits. We will consider only thin peri-condensed subunits. Thin peri-condensed benzenoid hydrocarbon (perifusene) does not contain the coronene skeleton[23,24].

Results and Discussion

The reduced graph model and its application to the enumeration problems of BH's have been described elsewhere[1–3]. However, we will review its most salient features in order to clarify the present work.

Every planar BH may be represented as part of an infinite hexagonal planar lattice. Three sets of parallel edges: vertical, left, and right, arranged in rows, are present in the hexagonal lattice. A new infinite trigonal planar lattice may be constructed from the hexagonal lattice. This can be done with the aid of the following information. The vertices of the trigonal lattice correspond to the *vertical* edges of the hexagonal lattice. Two vertices in the trigonal lattice are connected if (a) the corresponding edges belong to the same ring in the hexagonal lattice, or if (b) the corresponding edges are in adjacent rings of the hexagonal lattice, and their distance is unity. The trigonal lattice has two disjunctive sets of edges called "diagonal" and "horizontal" edges. The degree of vertices in the trigonal lattice is 6: two "horizontal" and four "diagonal" edges joining each vertex. Analogous to the transformation from the hexagonal lattice to the trigonal lattice, a given BH may also be transmuted from hexagonal, G, to trigonal, M(G), representation. The trigonal representation of BH, M(G), is called the reduced graph of G. The pyrene graph and the corresponding reduced graph are given in Scheme 1 as an illustration of this procedure.

Scheme 1



The reduced graph M(G) can be colored in a specific way: black vertices correspond to single bonds and white vertices to double bonds in the corresponding structure G. For every bond assignment in G, one coloring of the vertices in M(G) is possible. Every coloring of M(G) is a unique and unambiguous representation of a particular *Kekulé* structure, and hence the number of colorings in M(G) corresponds to the number of *Kekulé* structures that can be assigned to a given BH. The enumeration and display of all possible *Kekulé* structures may be performed by applying a procedure which searches for all reduced graphs which are colored differently[3].

If the set of diagonal edges is empty, the reduced graph takes the form of a chain, otherwise it takes the form of a lattice. Reduced graphs in the form of a lattice may be separated into two groups: reduced graphs in the form of a "whole lattice" and reduced graphs in the form of a fused "whole lattice"[1-3]. A reduced graph in the form of a fused whole lattice can be decomposed into several whole lattices or into whole lattices and chains, respectively.

A fused whole lattice decomposes into whole lattices and/or chains by a path q. Path q is a sequence of vertices and diagonal edges which decompose the complex reduced graph M(G) into subgraphs $M(G_i)$, $M(G_j)$, $M(G_k)$, ... The possible colors of the vertices in path q are given in Table 1.

Table 1. *The colors of the vertices in the path q*

Color of the vertex in $M(G_i)$	Color of the vertex in $M(G_j)$	Color of the vertex in $M(G) = M(G_i)\,M(G_j)$
black	black	∅
black	white	black
white	black	black
white	white	white

We now describe a novel "pencil-and-paper" method for the enumeration and generation of *Kekulé* structures of large fused BH's consisting of cata- and thin peri-condensed fragments. This method makes use of the reduced graph model and *Randić*'s search trees[25]. The method consists of six steps that are now described in detail for 3,4-pentacenopyrene, a sufficiently complex BH to illustrate the method.

Step 1

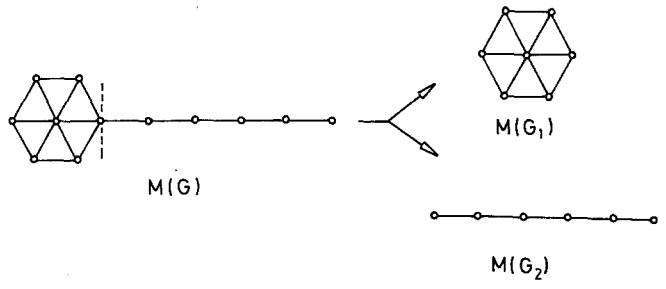
Represent the given BH by a benzenoid graph[18] G and reduced graph M(G) (Scheme 2):

Scheme 2

Step 2

Decompose M(G) (Scheme 3):

Scheme 3



Step 3

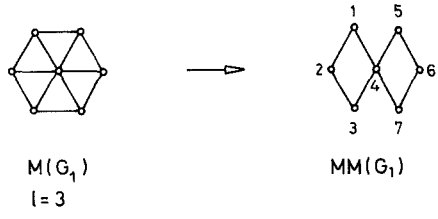
Count the number of levels l in each reduced graph. (Horizontal edges of the reduced graph form levels.)[3] Thus:

$$M(G_1): l = 3$$
$$M(G_2): l = 1$$

Step 4

Construct the modified reduced graph MM(G). A modified reduced graph is obtained by deletion of all horizontal edges from a reduced graph which is in the form of a whole lattice (Scheme 4):

Scheme 4



We do not need to build a modified reduced graph for the chain $M(G_2)$, its coloring is trivial.

Step 5

Make use of search trees.

Here we will describe the procedure for whole lattices when the number of vertices at the first level is equal to two, i.e. $v = 2$. Cases with $v > 2$ will be discussed later.

For $MM(G_1)$ we write,

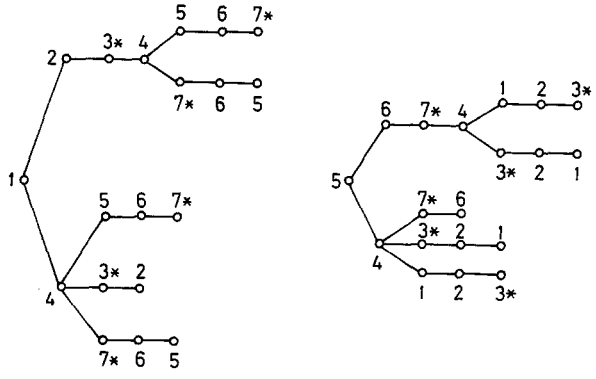
$$K_1 = \sum' p_{13} + \sum' p_{17} + \sum' p_{53} + \sum' p_{57}$$
$$= \text{number of colorings in } M(G_1)$$

where p_{ij} is the number of self-avoiding paths[27] between vertices i and j, whilst $\sum'$ means that the summation is taken *only* over the paths of length $l-1$.

The computation of the p_{ij}'s by hand (adopting the pencil-and-paper method) may be error-prone especially for graphs with large values of l. A *systematic* way of enumerating these paths is via search trees associated with the relevant vertices.

For $MM(G_1)$, search trees for both v_1 and v_5 must be constructed. The self-avoiding paths of length $l-1$ give the number of colorings belonging to the individual reduced graph. Search trees for $M(G_1)$ are depicted in Scheme 5 (vertices belonging to the terminal level of $M(G_1)$ are denoted by asterisks):

Scheme 5



The required self-avoiding paths of length 2 are as follows:

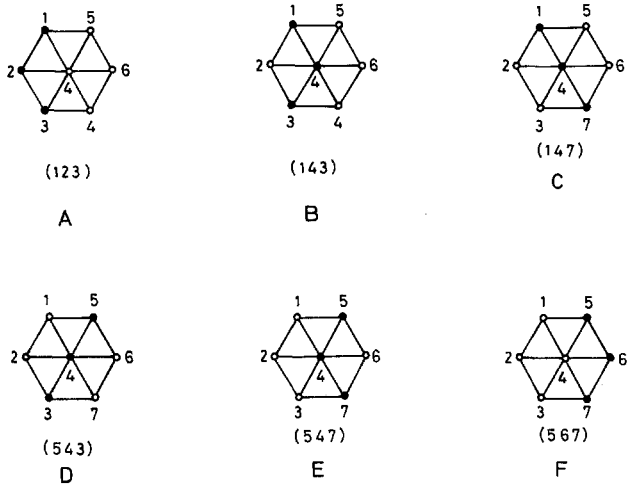
$$\sum' p_{13} = (123) + (143) \qquad = 2$$
$$\sum' p_{17} = (147) \qquad = 1$$
$$\sum' p_{53} = (543) \qquad = 1$$
$$\sum' p_{57} = (547) + (567) \qquad = 2$$

$$K(\text{pyrene}) = K_1 = 6$$

Note that paths such as (1234567) are *not* counted because their lengths are greater than $l-1$.

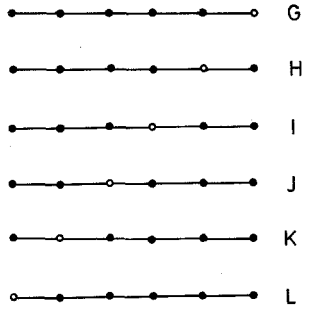
Thus, there are 6 colorings of $M(G_1)$ and these correspond to 6 *Kekulé* structures of pyrene (Scheme 6):

Scheme 6



Reduced graphs in the form of chains can be colored very simply. If M(G) is a chain with v vertices then it can be colored differently v times. The terminal vertices are colored black $v-1$ time and white once. Since $M(G_2)$ is a chain with 6 vertices, there will be six different colorings, corresponding to 6 *Kekulé* structures of pentacene (Scheme 7):

Scheme 7



Step 6

Construct the counting matrix and hence enumerate K(G).

In order to obtain the number of *Kekulé* structures for G, it is necessary to combine $M(G_1)$ and $M(G_2)$. This can be done in a somewhat tedious way by drawing each colored structure $M(G_1) + M(G_2)$ as described in Ref.[1]. A more elegant method makes use of the counting matrix. In constructing the counting matrix it is necessary to obey the rules given in Table 1. The number of *Kekulé* structures is then given by:

$$K(G) = N \times M - \text{the number of zero entries to the matrix}$$

where $N \times M$ is the size of the counting matrix. In our example the counting matrix is of size 6×6 (Scheme 8):

Scheme 8

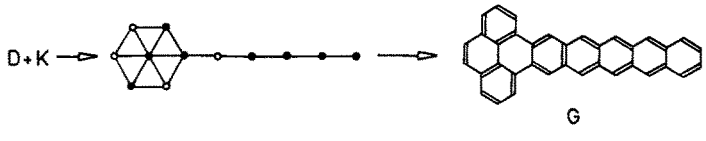
	G	H	I	J	K	L
A	✓	✓	✓	✓	✓	✓
B	✓	✓	✓	✓	✓	✓
C	✓	✓	✓	✓	✓	✓
D	✓	✓	✓	✓	✓	✓
E	✓	✓	✓	✓	✓	✓
F	0	0	0	0	0	✓

Positions in the above matrix with zero entries denote combinations of $M(G_1)$ and $M(G_2)$ which are not possible according to the combination rules given in Table 1. In our example, there are 5 such combinations, hence:

$$K(G) = 6 \times 6 - 5 = 31$$

Thus, 3,4-pentacenopyrene has 31 *Kekulé* structures. Each individual structure may be constructed by considering the superposition of $M(G_1)$ and $M(G_2)$. For example, let us consider the reduced graph consisting of a whole lattices D and a chain K (Scheme 9):

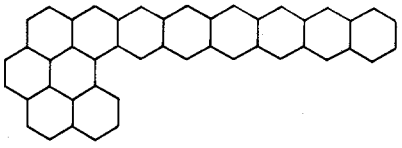
Scheme 9



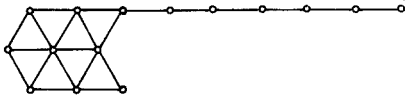
As a further example we consider 1,2-hexaceno-6,7-benzoperylene. This molecule will be treated in the same way as 3,4-pentacenopyrene. The only difference will appear in *Step 5* of the procedure.

Step 1 (Scheme 10)

Scheme 10



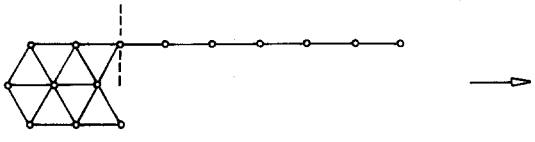
G



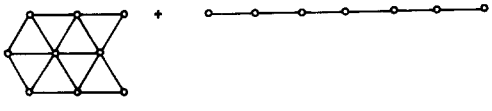
M(G)

Step 2 (Scheme 11)

Scheme 11



M(G)



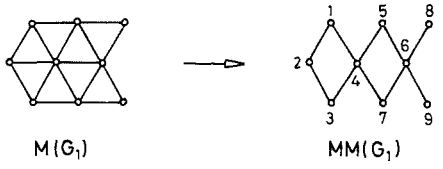
$M(G_1)$ $M(G_2)$

Step 3

$$M(G_1): l = 3$$
$$M(G_2): l = 1$$

Step 4 (Scheme 12)

Scheme 12

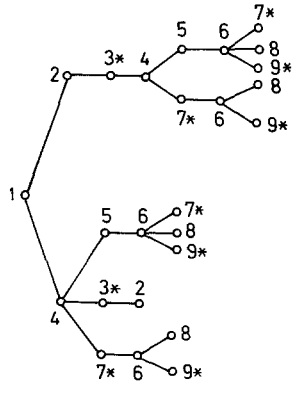


Step 5

(a) $M(G_1)$

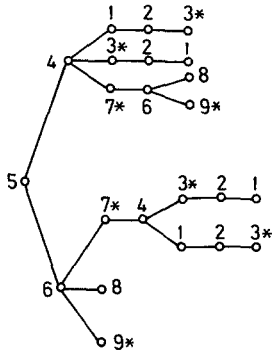
When $v > 2$ vertices appear at the first level of $M(G_i)$, $v - 1$ parallel colorings of whole lattice, corresponding to a given *Kekulé* structure of G_i, must be carried out. This means that, for each self-avoiding path p_{ij}, $v - 1$ parallel self-avoiding paths (paths that do not cross each other) of length $l - 1$ must be found. Note, all parallel paths must end at the starred vertices, i.e. vertices belonging to the last level of $M(G_i)$ (Scheme 13, Scheme 14):

Scheme 13



p_{ij}	parallel self-avoiding paths				
(123)	(547)	(567)	(569)	(867)	(869)
(143)	(567)	(569)	(867)	(869)	
(147)	(569)	(869)			

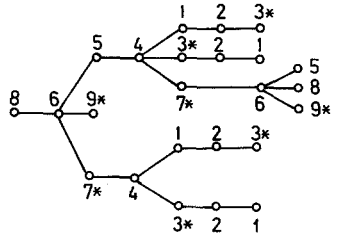
Scheme 14



p_{ij}	parallel paths	
(543)	(867)	(869)
(547)	(869)	

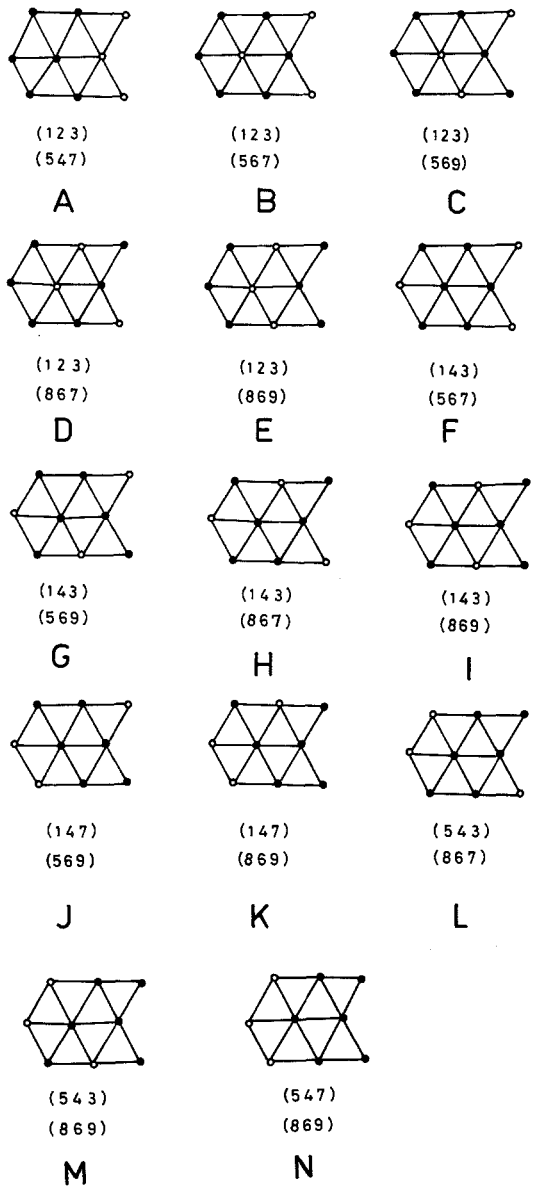
There are no other paths possible; all possible combinations have either been used, or they produce paths that are of length greater than 2. Thus, it is necessary to generate only $v-1$ search trees. The v-th search tree is redundant. In order to illustrate this point we give in Scheme 15 the v-th search tree for our example. It can easily be seen that all legitimate possibilities have been exhausted (see Scheme 15).

Scheme 15



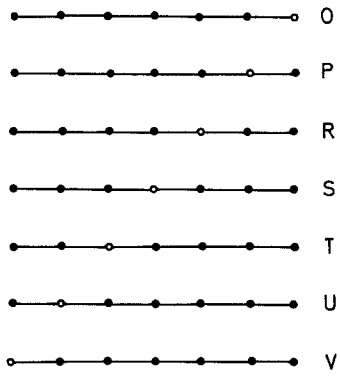
In Scheme 16 we give 14 differently colored whole lattices which correspond to 14 *Kekulé* structures of G_1.

Scheme 16



(b) $M(G_2)$ (Scheme 17)

Scheme 17



Step 6 (Scheme 18)

Scheme 18

	O	P	R	S	T	U	V
A	✓	✓	✓	✓	✓	✓	✓
B	✓	✓	✓	✓	✓	✓	✓
C	✓	✓	✓	✓	✓	✓	✓
D	0	0	0	0	0	0	✓
E	0	0	0	0	0	0	✓
F	✓	✓	✓	✓	✓	✓	✓
G	✓	✓	✓	✓	✓	✓	✓
H	0	0	0	0	0	0	✓
I	0	0	0	0	0	0	✓
J	✓	✓	✓	✓	✓	✓	✓
K	0	0	0	0	0	0	✓
L	0	0	0	0	0	0	✓
M	0	0	0	0	0	0	✓
N	0	0	0	0	0	0	✓

$$K(G) = 14 \times 7 - 48 = 50$$

Thus, 1,2-hexaceno-6,7-benzoperylene has 50 *Kekulé* structures. Individual *Kekulé* structures may be plotted without difficulty by considering the non-vanishing superpositions of $M(G_1)$ and $M(G_2)$.

Acknowledgements

Discussions and correspondence with Professor *A. T. Balaban* (Bucharest), Professor *M. Randić* (Ames) and Dr. *P. Křivka* (Pardubice) on the role of *Kekulé* structures in chemistry and on applicability of the reduced graph model to the chemistry of benzenoid hydrocarbons is gratefully acknowledged.

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