# Binary coding of Kekulé structures of catacondensed benzenoid hydrocarbons

Sandi Klavžar,<sup>a,\*</sup> Aleksander Vesel,<sup>a</sup> Petra Žigert<sup>a</sup>, Ivan Gutman<sup>b</sup>

<sup>a</sup>Department of Mathematics, PEF, University of Maribor, Koroška 160, 2000 Maribor, Slovenia

<sup>b</sup>Faculty of Science, University of Kragujevac, P. O. Box 60, YU-34000 Kragujevac, Yugoslavia

> Received July 2000 Revised January 2001

## Running Title: Coding Kekulé structures of benzenoids

*Key words:* benzenoid hydrocarbons, benzenoid graph, resonance graph, Kekulé structure, algorithm, binary coding

telephone number of corresponding author: +386-1-721-04-02 fax number of corresponding author: +386-1-25-172-81 e-mail address of corresponding author: sandi.klavzar@uni-lj.si

#### Abstract

An algorithm is described by means of which the Kekulé structures of a catacondensed benzenoid molecule (with h hexagons) are transformed into binary codes (of length h). By this, computer-aided manipulations with, and memory-storage of Kekulé structures are much facilitated. Any Kekulé structure can easily be recovered from its binary code.

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#### 1. Introduction

The fact that for some polycyclic conjugated molecules (benzenoid hydrocarbons in particular) more than one classical structural formula can be written fascinates chemists longer than a century. These structural formulae are usually referred to as "Kekulé structures" and a vast amount of theoretical work on them has been done. One major direction of research is finding the number K of Kekulé structures (Cyvin and Gutman, 1988) and trying to relate K with various physico-chemical properties of the underlying compounds (Gutman and Cyvin, 1989). Another direction is the study of individual Kekulé structures and finding relations between them. A famous problem along these lines (never satisfactorily solved) is the identification of the Kekulé structure that provides the most faithful representation of the true bonding in the respective molecule (Friess, 1927; Friess et al., 1935; Graovac et al., 1973). Some authors consider Kekulé structures as quantum-mechanical objects among which some (quantum-mechanical) interactions exist; for detail see in McWeeny and Sutcliffe (1969). In the case of benzenoid molecules the simplest model for such interactions is the following: if two Kekulé structures differ in the position of three double bonds, then they interact (by an unspecified, but constant amount); otherwise their interaction is neglected. Within this model the concept of the so-called "resonance graph" occurs naturally: The vertices of the resonance graph R(G) of the benzenoid hydrocarbon B are the Kekulé structures of B; two vertices of R(G) are adjacent if the corresponding Kekulé structures interact, that is if they differ in the position of just three double bonds.

This model, together with the concept of resonance graphs, was first put forward by Gründler (1982, 1983) and was then re-invented by El–Basil (1993a, 1993b) and, independently, by Randić (Randić et al., 1996, Randić, 1997). In addition to this, without any reference to quantum theory, Zhang, Guo and Chen introduced resonance graphs and established their basic mathematical properties (Zhang et al., 1988a, 1988b; Chen and Zhang, 1997).

For examples illustrating the construction and the basic structural features of resonance graphs see the references quoted as well as Figs. 6, 8, 9 and 10.

Two of the present authors (Klavžar and Zigert, 2000) discovered recently an intriguing property of the resonance graph of catacondensed benzenoid systems, namely that they belong to the class of median graphs. The result was later generalized by Klavžar, Žigert and Brinkmann to the so-called catacondensed even ring systems (Klavžar et. al., 2001). A far-from-obvious consequence of this result is that a unique (and quite short!) binary code can be associated to every Kekulé structure. In this paper we describe an algorithm for the construction of this binary code, as well as for the re-construction of the Kekulé structure from the code.

The advantage of this coding/decoding procedure for computer-aided manipulation with Kekulé structures (in particular, for the construction of the resonance graph) should be obvious. The possibility of storing the complete information on a Kekulé structure by means of a short binary string is another asset that may become indispensable when dealing with benzenoid systems possessing thousands and hundred thousands Kekulé structures (Cyvin and Gutman, 1987). Such benzenoid hydrocarbons have recently been both synthesized (Iyer et al., 1997) and detected in flame (Homann, 1998).

#### 2. Mathematical background of the algorithm

The Cartesian product  $G \Box H$  of graphs G and H (Imrich and Klavžar, 2000) has the vertex set  $V(G) \times V(H)$ , and vertices (a, x) and (b, y) are adjacent in  $G \Box H$ whenever  $ab \in E(G)$  and x = y, or a = b and  $xy \in E(H)$ .

Hypercubes are of utmost importance for our algorithm and are defined as follows. The vertex set of the *n*-cube  $Q_n$  consists of all *n*-tuples  $b_1b_2...b_n$  with  $b_i \in \{0,1\}$ . Two vertices are adjacent if the corresponding tuples differ in precisely one place.  $Q_n$ is also called a *hypercube of dimension* n. Note that  $Q_1$  is the complete graph on two vertices, that is,  $K_2$ , while  $Q_2$  is the 4-cycle  $C_4$  and  $Q_3$  is the ordinary 8-vertex cube. A useful way to represent  $Q_n$  is to take two disjoint copies of  $Q_{n-1}$  and join by an edge pairwise identical vertices in the corresponding copies. In other words,  $Q_n = Q_{n-1} \Box K_2$ .

Recently Klavžar and Žigert (2000) proved that the resonance graph R(G) of a cat-

acondensed benzenoid graph G can be isometrically embedded into the h-dimensional hypercube  $Q_h$ , where h is the number of hexagons of G. In fact, they showed an even stronger statement, namely that R(G) is a median graph; for more details on median graphs see elsewhere (Mulder, 1978, 1980; Klavžar and Mulder, 1999; Imrich and Klavžar, 2000).

The proof outlined by Klavžar and Zigert (2000), as well as the one of Klavžar, Žigert and Brinkmann (2001), gives a (theoretical) indication how R(G) can be embedded into  $Q_h$ . This embedding can be roughly described as follows.

A 1-factor (or perfect matching) of a graph G on n vertices is a selection of n/2mutually independent edges of G. Only graphs with even number of vertices may have 1-factors, and then every vertex is the endpoint of exactly one of the selected edges. The fact that a Kekulé structure of a conjugated molecule is in a one-to-one correspondence with a 1-factor of the underlying molecular graph is well and long known (e. g., Cvetković et al., 1972). In the following considerations we shall, where appropriate, instead of "Kekulé structure" use the equivalent, but somewhat more precise, mathematical term "1-factor".

Let G be a catacondensed benzenoid graph that is obtained from a catacondensed benzenoid graph G' by attaching a hexagon H over an edge e. Suppose that G' contains h - 1 hexagons and that we have already embedded R(G) into  $Q_{h-1}$ . We partition the 1-factors of G into the sets  $\mathcal{F}_e(G)$ ,  $\mathcal{F}_{\overline{e}}^2(G)$ , and  $\mathcal{F}_{\overline{e}}^3(G)$ , where

 $\mathcal{F}_e(G)$  consists of the 1-factors containing the edge e;

 $\mathcal{F}^2_{\overline{e}}(G)$  consists of the 1-factors not containing e, but containing (exactly) two edges of H;

 $\mathcal{F}^{3}_{\overline{e}}(G)$  consists of the 1-factors not containing e, but containing three edges of H.

Then one can embed R(G) into  $Q_h = Q_{h-1} \Box K_2$  in such a way that the 1-factors of  $\mathcal{F}_e(G) \cup \mathcal{F}_{\overline{e}}^2(G)$  lie in one copy of  $Q_{h-1}$ , the 1-factors of  $\mathcal{F}_{\overline{e}}^3(G)$  in the other copy and the 1-factors of  $\mathcal{F}_e(G)$  and  $\mathcal{F}_{\overline{e}}^3(G)$  are pairwise joined by by an edge.

Let us explain this embedding in some more detail.

For a subset X of vertices of a graph G, the subgraph of G induced by X is

denoted by G[X].

We have already observed that the 1-factors of G, that is the vertices of the resonance graph R(G), can be partitioned as follows:

$$V(R(G)) = \mathcal{F}_e(G) \cup \mathcal{F}_{\overline{e}}^2(G) \cup \mathcal{F}_{\overline{e}}^3(G) \,.$$

There is a natural bijective correspondence between the 1-factors of  $\mathcal{F}_e(G)$  and of  $\mathcal{F}_e(G')$ . In addition, a 1-factor from  $\mathcal{F}_e^2(G)$  corresponds to a unique 1-factor from  $\mathcal{F}_{\overline{e}}(G')$ . It follows that the subgraph  $G_1 = R(G)[\mathcal{F}_e(G) \cup \mathcal{F}_{\overline{e}}^2(G)]$  of R(G) is isomorphic to R(G'). Consider now a 1-factor F from  $\mathcal{F}_{\overline{e}}^3(G)$ . In R(G) it is adjacent to a unique 1-factor  $\overline{F}$  of  $G_1$ . We note next that two 1-factors  $F_1$  and  $F_2$  of  $\mathcal{F}_{\overline{e}}^3(G)$  are adjacent if and only if the corresponding 1-factors  $\overline{F_1}$  and  $\overline{F_2}$  are adjacent. Therefore,  $R(G)[\mathcal{F}_e(G)]$  and  $R(G)[\mathcal{F}_{\overline{e}}^3(G)]$  are isomorphic and  $R(G)[\mathcal{F}_e(G)\cup\mathcal{F}_{\overline{e}}^3(G)]$  is a subgraph of R(G) isomorphic to  $R(G)[\mathcal{F}_e(G)]\Box K_2$ .

For further details of this embedding/proof we refer to Klavžar and Žigert (2000) or/and to Klavžar, Žigert and Brinkmann (2001).

#### 3. The algorithm

In the previous section we pointed out that the resonance graph R(G) of a catacondensed benzenoid system G can be (isometrically) embedded into  $Q_h$ . In other words, to each 1-factor of G we can uniquely assign a binary string of length h, such that each bit in the string corresponds to a unique hexagon. In particular, two strings imply the existence of an edge in R(G) if and only if they differ in precisely one position.

Let H be a pendant hexagon of a catacondensed benzenoid graph G. Let G' be the graph obtained from G by removing H (but not e). Suppose that G' contains h-1 hexagons and that we have already embedded R(G') into  $Q_{h-1}$ . Let S(G') be the set of the binary strings of length h-1 corresponding to the embedding of R(G').

In order to establish the embedding of G, we distinguish between three cases with regard to the position of the double bonds, see Fig. 1.

Fig. 1 comes about here

From the discussion in the previous section it follows that 1-factors of the cases a., b., and c. belong to  $\mathcal{F}_e(G)$ ,  $\mathcal{F}_{\overline{e}}^2(G)$ , and  $\mathcal{F}_{\overline{e}}^3(G)$ , respectively.

Since R(G) can be embedded into  $Q_h = Q_{h-1} \Box K_2$  in such a way that the 1factors of  $\mathcal{F}_e(G) \cup \mathcal{F}_{\overline{e}}^2(G)$  lie in one copy of  $Q_{h-1}$  and the 1-factors  $\mathcal{F}_{\overline{e}}^3(G)$  in the other copy of  $Q_{h-1}$ , the corresponding set of strings of length h can be obtained by concatenating the same digit (say 0) to each  $x \in S(G')$  if cases a. and b. occur, and by concatenating the other digit (say 1) to each  $x \in S(G')$  if case c. occurs. G' is obviously a catacondensed benzenoid graph, thus the method described above, can be applied as a recursive procedure that can be repeated till a single hexagon remains.

The two 1-factors (Kekulé structures) of a single hexagon (benzene) are shown in Fig. 2. Their set of strings obviously consists of digits 0 and 1, where one of them (say 0) pertains to the 1-factor on the left-hand side and the other (say 1) to the 1-factor at the right-hand side.

#### Fig. 2 comes about here

In Fig. 3 the three 1-factors (Kekulé structures) of naphthalene are depicted. Based on the procedure described above they are coded with the set of strings  $S(G) = \{00, 01, 10\}$  as shown in the figure.

#### Fig. 3 comes about here

First, the right digit is assigned as 0, 0, and 1, respectively, according to the cases b., a., and c. of Fig. 1. Then, in G', that is, in the left hexagon, the remaining edges correspond to the right, to the left, and to the left case of Fig. 2. Hence the first digits are 1, 0, and 0, respectively.

However, the recursive procedure can be awkward if the graph G has more hexagons. Therefore, an iterative procedure would be more convenient. In order to develop such a procedure we first examine catacondensed benzenoids without branches. Two hexagons of a catacondensed benzenoid have either one common edge (and are then said to be *adjacent*) or have no common vertices. A *hexagonal chain* is an unbranched catacondensed benzenoid graph, that is, the catacondensed system in which no hexagon is adjacent to three other hexagons. The inner dual of a hexagonal chain G with h hexagons is obviously the h-vertex path. Starting from a terminal hexagon  $H_1$  we can assign consecutive numbers to each hexagon to get the ordering  $H_1, H_2, \ldots, H_h$ .

Let  $S_i$  be the set of strings corresponding to the embedding of the resonance graph that corresponds to a hexagonal chain consisting of the hexagons  $H_1, H_2, \ldots, H_i$  and suppose that  $S_{i-1}$  is already known. Then the determination of  $S_i$  depends solely on the previous two hexagons  $H_{i-1}$  and  $H_{i-2}$ . The six possible cases are shown in Fig. 4.

#### Fig. 4 comes about here

According to the positions of hexagons  $H_{i-2}$ ,  $H_{i-1}$ , and  $H_i$  we arrive at two major cases. The hexagons may be linearly arranged, see Fig. 4a or not (then a so called *kink* occurs), see Fig. 4b.

Furthermore, the labeling also depends on the position of the double bonds of  $H_{i-1}$ . Let  $x \in S_{i-1}$ . Then x = y0 or x = y1, where y is a pertinent string of length i-2.

According to the cases in Fig. 4 we get:

a. (Cases without a kink).  $S_i$  can be obtained from  $S_{i-1}$  by inserting strings x0and x1 for each x = y1 and by inserting string x0 for each x = y0.

b. (Cases with a kink).  $S_i$  can be obtained from  $S_{i-1}$  by inserting strings x0 and x1 for each x = y0 and by inserting string x0 for each x = y1.

We are now ready to present the algorithm for the embedding of the resonance graph of s hexagonal chain G with at least two hexagons. Since two previous hexagons are needed at each step of the procedure, we start the algorithm with the embedding of naphthalene, which was already determined to be  $\{00, 01, 10\}$ . The algorithm at *i*-th step builds the new set of strings of length *i* (denoted by S') obtained from the strings of length i - 1 (denoted by S).

### **Procedure** LABELS(G); begin 1. Consecutively number the hexagons of G to get the sequence $H_1, H_2, \ldots, H_h$ ; $S := \{00, 01, 10\};$ For i := 3 to h do begin $S' := \emptyset;$ If $H_i$ induces a kink then begin For each $x \in S$ do begin $S' := S' \cup \{x0\};$ If x = y0 then $S' := S' \cup \{x1\}$ ; end; end else begin For each $x \in S$ do begin $S' := S' \cup \{x0\};$ If x = y1 then $S' := S' \cup \{x1\}$ ; end; end S := S';end; end.

**Remark.** In order to determine whether  $H_i$  induces a kink, the positions of  $H_i$ ,  $H_{i-1}$ , and  $H_{i-2}$  have to be examined.

The procedure for a branched catacondensed benzenoid is a little (but not much!) more involved. The inner dual of a catacondensed benzenoid graph G is an h-vertex tree T. An arbitrary pendant hexagon of G is selected as the root of this tree. The hexagons of G are then numbered such that  $H_i$  is a predecessor of  $H_j$  in T if and only if i < j. Such a numbering can be obtained by the Depth-first search algorithm (DFS) or by the Breadth-first search algorithm (BFS) (Kozen, 1992). Note that the predecessor of every hexagon has to be known in order to determine whether  $H_i$ induces a kink or not.

Based on the discussion above, Step 1 of LABELS should be replaced by the following:

Starting at any pendant hexagon apply the Depth-first search (DFS) algorithm to consecutively visit the hexagons of the graph. At each visited hexagon do the following:

assign a consecutive index to the hexagon, record a predecessor of the hexagon  $H_i$ .

#### 4. Two examples

In this section we present two examples of the algorithm described in the previous section. In addition, at the end we also show the reverse procedure, namely how one can construct the Kekulé structure that corresponds to a given binary code.

As the first example we consider a simple case of the resonance graph of naphthacene. The hexagons are numbered in a natural way as shown in Fig. 5.

#### Fig. 5 comes about here

In Fig. 6 the complete construction of the Kekulé structures, resonance graphs, and the codes for the Kekulé structures are shown, starting from the data for naphthalene.

#### Fig. 6 comes about here

In our second example we consider a more complex benzenoid hydrocarbon – benzo[s]picene, see Fig. 7.

#### Fig. 7 comes about here

In Fig. 8 the first part of the procedure is shown: the generation of the two–, three– and four–digits codes for the vertices of the resonance graphs and the corresponding Kekulé structures.

#### Fig. 8 comes about here

By considering the fifth hexagon of benzo[s]picene, we get the five-digits codes. These codes and the corresponding Kekulé structures are shown in Fig. 9.

#### Fig. 9 comes about here

Finally, considering the sixth hexagon, we derive altogether 22 Kekulé structures, consistent with the fact (Cyvin and Gutman, 1987) that K(benzo[s]picene) = 22. These are too numerous to be drawn. Instead, their codes are given in Table 1 whereas the corresponding resonance graph is shown Fig. 10.

#### Table 1 comes about here

Fig. 10 comes about here

At this point the natural question is how one can reconstruct the Kekulé structure from its binary code. This can be done just by reverting the algorithm. Of course, an input data for such a procedure is also the selected ordering of hexagons with which the codes were constructed.

Instead of describing the reverse procedure in all details, consider, for example, the Kekulé structure  $F_6$  from Table 1. Its binary code is 100101. Recalling the ordering of hexagons from Fig. 7, we can construct the Kekulé structure corresponding to 100101 as it is shown in Fig. 11.

Fig. 11 comes about here

#### Acknowledgements

This work was supported in part by the Ministry of Science and Technology of Slovenia under the grant 101–504.

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Figure 1: Possible arrangements of the double bonds in the hexagon H.



Figure 2: The two Kekulé structures of benzene.



Figure 3: The three Kekulé structures of naphthalene.



Figure 4: Labelling of three consecutive hexagons.



Figure 5: Naphthacene and the labelling of its hexagons.



Figure 6: Kekulé structures, resonance graphs and vertex codes of naphthalene, an-thracene, and naphthacene, cf. Fig. 5.



Figure 7: Benzo[s]picene and the labelling of its hexagons.



Figure 8: Kekulé structures, resonance graphs, and vertex codes of naphthalene, phenanthrene and benzo[c]phenanthrene; note that these consist of the first two, first three and first four hexagons, respectively, of benzo[s]picene, cf. Fig. 7.



Figure 9: Kekulé structures, resonance graphs and vertex codes of benzo[g]chrysene; note that it consists of the first five hexagons of benzo[s]picene, cf. Fig. 7.



Figure 10: The resonance graph of benzo[s]picene, cf. Fig. 7.



Figure 11: Constructing a Kekulé structure of benzo[s]picene from the respective binary code, cf. Fig. 7.

Kekulé		Kekulé		Kekulé	
structure	code	structure	code	structure	code
$F_1$	101001	$F_9$	101000	$F_{17}$	101010
$F_2$	001001	$F_{10}$	001000	$F_{18}$	001010
$F_3$	100001	$F_{11}$	100000	$F_{19}$	100010
$F_4$	000001	$F_{12}$	000000	$F_{20}$	000010
$F_5$	010001	$F_{13}$	010000	$F_{21}$	100110
$F_6$	100101	$F_{14}$	100100	$F_{22}$	000110
$F_7$	000101	$F_{15}$	000100		
$F_8$	010101	$F_{16}$	010100		

Table 1: The binary codes of the Kekulé structures of benzo[s]picene, cf. Figs. 7 and 10.

## Figure and Table Captions

Fig. 1. Possible arrangements of the double bonds in the hexagon H.

Fig. 2. The two Kekulé structures of benzene.

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**Fig. 9.** Kekulé structures, resonance graphs and vertex codes of benzo[g]chrysene; note that it consists of the first five hexagons of benzo[s]picene, cf. Fig. 7.

Fig. 10. The resonance graph of benzo[s]picene, cf. Fig. 7.

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**Table 1.** The binary codes of the Kekulé structures of benzo[s]picene, cf. Figs. 7and 10.