CROATICA CHEMICA ACTA CCACAA 46 (1) 15—23 (1974)

CCA-812

YU ISSN 0011-1643
539.19:516
Original Scientific Paper

Kekulé Structures and Topology. II[1]. Cata-Condensed Systems

*Dragoš Cvetković and Ivan Gutman**

*Faculty of Electrical Engineering, University of Belgrade, 11000 Belgrade, Serbia, Yugoslavia and *Institute »Ruđer Bošković«, 41000 Zagreb, Yugoslavia*

Received February 4, 1974

An algorithm for enumeration of the Kekulé structures of non-branched cata-condensed conjugated systems is described. General formulae for the number of Kekulé structures of several conjugated series are obtained. The Pauling bond orders can be easily calculated using the same algorithm.

The problem of the enumeration of the Kekulé structures was solved for several important benzenoid systems some twenty years ago[2]. Recently, a general solution for all benzenoid systems is obtained[3]. In this paper we would like to present another approach to the same problem covering the class of all non-branched cata-condensed molecules, both alternant and non-alternant. Although in the work of Gordon and Davison[2] there is an elegant and complete enumeration technique for these latter molecules, we think that the formalism developed here might be of interest also.

In the recent years there is a renewed interest for simple resonance theory[4] because of increasing application of ideas of topology in chemistry[5], especially in the field of unsaturated conjugated molecules[6]. Moreover, the notions of the resonance theory appear necessarily in the Hückel molecular-orbital theory (for details and exhaustive references see 1 and 7). Our investigations are timely also because several researchers are currently working on the enumeration of the Kekulé structures[8–11] and related topics[12].

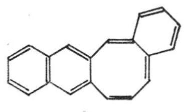
An additional interesting fact is that a problem completely analogous to the enumeration of Kekulé structures, called »the dimer problem«, appears in statistical mechanics of liquid and solid state[13]. For review see[14].

We will use graph-theoretical terminology adopted in our previous work[1,6,7,15]. Thus, a graph corresponding to a cata-condensed (CC) molecule has the following properties[16]:

(i) no vertex is common to three rings

(ii) two rings are either disjoint or possess just one common edge (and then they are adjacent).

We call the graphs having the properties (i) and (ii) »cata condensed«. In general, we need not distinguish between a conjugated molecule and a molecular graph. For example, molecules 1, 2 and 3 are cata-condensed, but 4 is not.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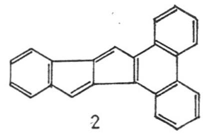
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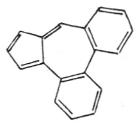
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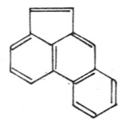
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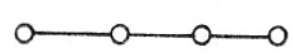
The »ring graph« is constructed[16] as follows: a vertex corresponds to a ring and a pair of such vertices are adjacent if, and only if the corresponding two rings are adjacent. Thus, the ring graphs of the molecules 1—4 are: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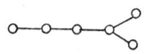
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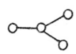
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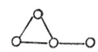
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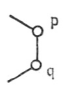
It can be shown that the ring graphs of CC molecules are trees, (*i. e.* they are acyclic). Therefore, CC systems can be understood as »trees of rings«. A CC molecule is non-branched if the corresponding ring graph is non-branched. For example, 1 is a non-branched and 2 and 3 are branched CC molecules.

THE ALGORITHM

For reasons which will be clear later, we consider only alternant molecules here. Let A be a graph of an arbitrary conjugated molecule having

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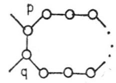
6

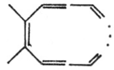
K (A) Kekulé structures. These structures can be either of the type 5 or 6. Let the numbers of these two types be K (5) and K (6), respectively. Of course

$$K(\mathrm{A}) = K(5) + K(6) \tag{1}$$

Let between the vertices p and q a double bond occur D (A) times and a single bond S (A) times in the Kekulé structures of A. One can see immediately that D (A) = K (5) and S (A) = K (6).

Let the graph B be obtained from A by annelation of a new ring (of even size) to the vertices p and q. Three types of Kekulé structures 7—9 can arise, their numbers are K (7), K (8) and K (9), respectively, and


B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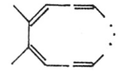
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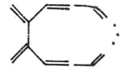
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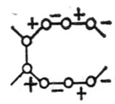
$$K(\mathrm{B}) = K(7) + K(8) + K(9) \tag{2}$$

It is easy to see that

$$K(7) = K(8) = K(5) \tag{3a}$$

$$K(9) = K(6) \tag{3b}$$

We will distinguish two kinds of edges in the considered ring of B and label them successively with two symbols, say + and —:



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This labelling is possible because the ring is of even size. Now let in the Kekulé structures of B on an edge labelled by + a double bond occur D^+ times and a single bond S^+ times. D^- and S^- are the same quantities for the edge labelled with —. Of course

$$D^+ + S^+ = D^- + S = K(\mathrm{B}) \tag{4}$$

From the formulae 7—9 follows

$$D^+ = K(8) \tag{5a}$$

$$D^- = K(7) + K(9) \tag{5b}$$

and substituting this back into eqs. (1)—(4), one obtains:

$$D^+ = D(\mathrm{A}) \tag{6a}$$

$$S^+ = D(\mathrm{A}) + S(\mathrm{A}) \tag{6b}$$

$$D^- = D(\mathrm{A}) + S(\mathrm{A}) \tag{6c}$$

$$S^- = D(\mathrm{A}) \tag{6d}$$

The equations (6) can be written in an operator form:

$$\begin{bmatrix} D^+ \\ S^+ \end{bmatrix} = \mathrm{O}^+ \begin{bmatrix} D \\ S \end{bmatrix} \tag{7a}$$

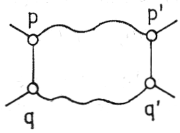
$$\begin{bmatrix} D^- \\ S^- \end{bmatrix} = \mathrm{O}^- \begin{bmatrix} D \\ S \end{bmatrix} \tag{7b}$$

where $\mathrm{O}^+ = \begin{bmatrix} 1 & 0 \\ 1 & 1 \end{bmatrix}$ and $\mathrm{O}^- = \begin{bmatrix} 1 & 1 \\ 1 & 0 \end{bmatrix}$. Therefore, the D and S values (and, hence, the number of Kekulé structures) of a n-cyclic CC molecule can be evaluated from the same quatities of an (n-1)-cyclic system for the bond where the annelation is performed. In other words, the O-operator can be applied to every ring of a non-branched CC-graph, since such a graph can be obtained by successive application of the transformations A → B, beginning with a graph ○——○ for which we have: $\begin{bmatrix} D_0 \\ S_0 \end{bmatrix} = \begin{bmatrix} 1 \\ 0 \end{bmatrix}$

Thus

$$\begin{bmatrix} D_i \\ S_i \end{bmatrix} = \mathrm{O}^{(i)} \begin{bmatrix} D_{i-1} \\ S_{i-1} \end{bmatrix} \tag{8}$$

where $O^{(i)}$ is either O^+ or O^- ($i = 1, 2, \ldots, n$), depending on the topology of the i-th ring. Namely, if the i-th ring is of the form 11, $O^{(i)} = O^+$ if the



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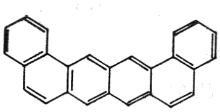
distances between p and p′ and between q and q′ are even and $O^{(i)} = O^-$ if the same two distances are odd. It is unimportant whether $O^{(1)}$ and $O^{(n)}$ are O^+ or O^-.

For an n-cyclic system eq. (8) gives finally

$$\begin{bmatrix} D_n \\ S_n \end{bmatrix} = O^{(n)} O^{(n-1)} \ldots O^{(2)} O^{(1)} \begin{bmatrix} 1 \\ 0 \end{bmatrix} \tag{9}$$

$$K = D_n + S_n \tag{10}$$

The ordered n-tuple of operators $O^{(n)} O^{(n-1)} \ldots O^{(2)} O^{(1)}$ we call an »O-sequence«. An O-sequence, as indicated above, uniquely corresponds to a non-branched CC molecule. For example, the same O-sequence $O^+ O^- O^+ O^+ O^- O^+$ corresponds to molecules 12, 13 and 14, showing that they all have the same K value. Thus



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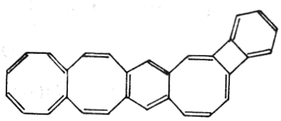

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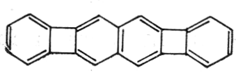

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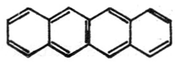
$$O^+ O^- O^+ O^+ O^- O^+ \begin{bmatrix} 1 \\ 0 \end{bmatrix} = O^+ O^- O^+ O^+ O^- \begin{bmatrix} 1 \\ 1 \end{bmatrix} = O^+ O^- O^+ O^+ \begin{bmatrix} 2 \\ 1 \end{bmatrix} =$$

$$= O^+ O^- O^+ \begin{bmatrix} 2 \\ 3 \end{bmatrix} = O^+ O^- \begin{bmatrix} 2 \\ 5 \end{bmatrix} = O^+ \begin{bmatrix} 7 \\ 2 \end{bmatrix} = \begin{bmatrix} 7 \\ 9 \end{bmatrix} \Rightarrow K = 16.$$

This example illustrates the fact that a variety of different non-branched CC molecules may have equal number of Kekulé structures. Particularly, for an arbitrary (alternant n-cyclic non-branched CC molecule an n-cyclic polyacene can be found having the same O-sequence and thus the same K value.

GENERAL FORMULAE FOR THE NUMBER OF KEKULÉ STRUCTURES

In this chapter we present general formulae for K of the CC molecules having the O-sequence of the form a) $O^+ O^+ \ldots O^+$, b) $O^- O^- \ldots O^-$ and c) $O^+ O^- O^+ \ldots O^- O^+$, which will be doneted by P_n, Q_n and R_n, respectively, the index n indicating the number of rings. Molecules 15—21 are examples of O-sequences P_n, Q_n and R_n.



P_4

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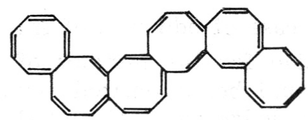
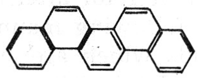


P_6

16

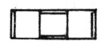


Q_5

17

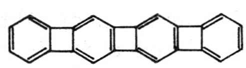
Q_5

18



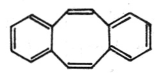
Q_3

19



R_7

20



R_3

21

a) It can be easily proved (*e. g.* by induction) that

$$P_{\mathrm{n}} \begin{bmatrix} 1 \\ 0 \end{bmatrix} = \begin{bmatrix} 1 \\ n \end{bmatrix} \tag{11}$$

and therefore

$$K(P_n) = n + 1 \tag{12}$$

what is the well known formula for linear polyacenes.

b) The equalities

$$\mathrm{O}^{-} \begin{bmatrix} \mathrm{a} \\ \mathrm{b} \end{bmatrix} = \begin{bmatrix} \mathrm{a+b} \\ \mathrm{a} \end{bmatrix}, \quad \mathrm{O}^{-}\mathrm{O}^{-} \begin{bmatrix} \mathrm{a} \\ \mathrm{b} \end{bmatrix} = \begin{bmatrix} \mathrm{2a+b} \\ \mathrm{a+b} \end{bmatrix} \tag{13}$$

lead properly to the recursion relation[2,9]

$$K(Q_n) = K(Q_{n-1}) + K(Q_{n-2}) \tag{14}$$

In the Appendix it is proved that $K(Q_n) = \varphi_1\, x_1{}^n + \varphi_2\, x_2{}^n$ where x_1 and x_2 are the roots of $x^2 = x + 1$. Therefore:

$$K(Q_n) = \varphi_1 \left(\frac{1+\sqrt{5}}{2}\right)^n + \varphi_2 \left(\frac{1-\sqrt{5}}{2}\right)^n \tag{15}$$

and because $K(Q_1) = 2$ and $K(Q_2) = 3$

$$K(Q_n) = \frac{1}{\sqrt{5}}\left[\left(\frac{1+\sqrt{5}}{2}\right)^{n+2} - \left(\frac{1-\sqrt{5}}{2}\right)^{n+2}\right] \tag{16}$$

$$K(R_n) = 2\,K(R_{n-2}) + K(R_{n-4}) \tag{17}$$

c) A similar consideration as for the case of Q_n gives for R_n and

$$K(R_n) = \frac{1}{2\sqrt{2}}\,[(1+\sqrt{2})^{(n+3)/2} - (1-\sqrt{2})^{(n+3)/2}] \tag{18}$$

Note that only the case of odd n is of interest here.

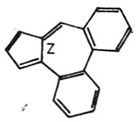
General formulae for the number of Kekulé structures of other series of CC molecules could be, if desired, obtained in an analogous manner. As to the authors' knowledge eqs. (16) and (18) as well as eq. (19) have not yet been obtained, despite of the simple algebraic demands required for their derivation.

EXTENSION TO NON-ALTERNANT MOLECULES

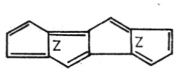
The algorithm derived in the previous chapter for alternant CC-molecules can be extended to non-alternants as in the following manner[2]. In non-alternant CC systems there exist necessarily bonds which are single bonds in all the Kekulé structures (that is, they have a zero Pauling bond order). Obviously, the deletion of such bonds from the molecule cannot change the K-value. It can be shown easily that when all bonds with zero Pauling bond order are deleted from a non alternant CC molecule an alternant CC molecule is obtained.

Moreover, a simple recipe exists to decide whether a bond is of zero bond order. Now, if, and only if there are odd numbers of odd-membered rings from both sides of such a bond, its Pauling bond order is zero..

In examples 22—24 such bonds are indicated by Z. The procedure which we would like to propose is now evident: first delete all Z-bonds and then



22 = 3



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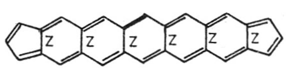

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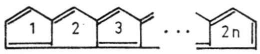
apply the O-sequence algorithm. For instance, $K(22) = 4$, $K(23) = 3$ and $K(24) = 2$.

As another example we give general formulae for K of $2n$-cyclic molecules 25,26 and 27.



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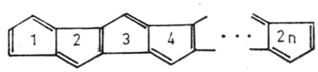

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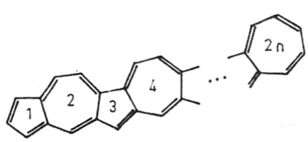

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After the deletion of the Z-bonds it can easily be seen that P_n, Q_n and P_n sequences, respectively, are obtained. Hence

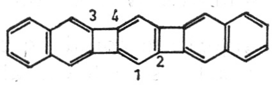
$$K(25) = K(P_n) \tag{19a}$$

$$K(26) = K(Q_n) \tag{19b}$$

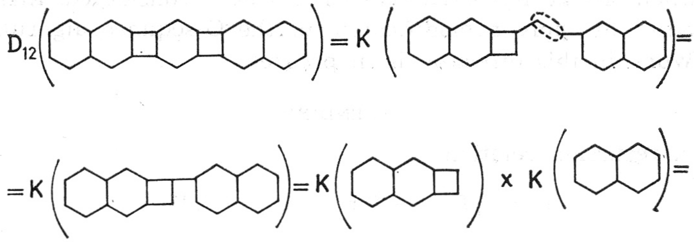
$$K(27) = K(P_n) \tag{19c}$$

CALCULATION OF THE PAULING BOND ORDERS

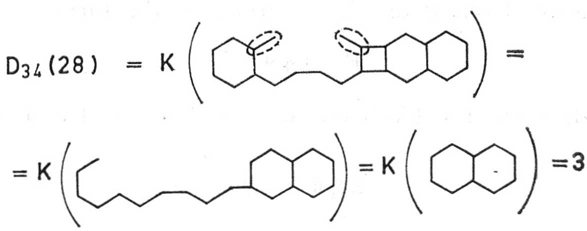
As an additional application we would like to show how the Pauling bond orders[17] can be calculated using the same technique. If among the K Kekulé structures of the molecule there are D_{pq} ones having a double bond between the vertices p and q, the corresponding Pauling bond order is D_{pq}/K. The D_{pq}-value is, in fact, the number of Kekulé structures of the molecule obtained after the deletion of the vertices p and q. Therefore, D_{pq} can be obtained using the above described algorithm. We illustrate this on the examples of bonds 1,2 and 3,4 in 28.



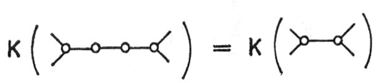
28 K(28) = 24



= 4x 3 = 12



Hence, the corresponding bond orders are 12/24 and 3/24, respectively. Here we have used the relations[2,9]:



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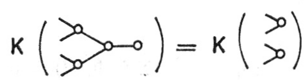
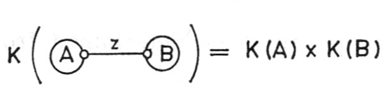


(21)



(22)

CONCLUSIONS

The presented algorithm can be briefly summarized as follows:

step 1: if the molecule is non-alternant, delete all Z-bonds;

step 2: write down the corresponding O-sequence;

step 3: calculate $O \begin{bmatrix} 1 \\ 0 \end{bmatrix}$ and thus the number of Kekulé structures;

step 4: determine, if desired, the Pauling bond orders performing steps 1—3 on the appropriately obtained structures. Eqs. (20)—(22) are to be used for simplification of the calculations.

We note that the whole algorithm could be put in a form convenient for computer calculations. Particularly, step 3 contains n matrix multiplications.

As it is usual in resonance theory[17] the parity of the Kekulé structures[7,8] is not taken into account. However, although a number of additional difficulties arise when the parity of Kekulé structures is considered, there seems to be a possibility to apply a modification of the O-sequnce algorithm for this case also. Work in this direction is in progress.

APPENDIX[18]

Given a recursion relation

$$F_n = f_1 F_{n-1} + f_2 F_{n-2} + \dots + f_t F_{n-t} \qquad \text{(A-1)}$$

or

$$\sum_{j=0}^{t} f_j F_{n-j} = 0 \qquad \text{(A-2)}$$

where $f_0 = 1$, we are looking for the solutions in the form

$$F_n' = \varphi \Phi^n \qquad \text{(A-3)}$$

Substituting (A-3) back into (A-2) one obtains for $\varphi \neq 0$ and $\Phi \neq 0$:

$$\sum_{j=0}^{t} f_j \Phi^{t-j} = 0 \qquad \text{(A-4)}$$

which is an equation of degree t and let its roots be $\Phi_1, \Phi_2, \dots, \Phi_t$. Arbitrary linear combinations of Φ_k $(k = 1, 2, \dots, t)$:

$$F_n'' = \sum_{k=1}^{t} \varphi_k \Phi_k^n \qquad \text{(A-5)}$$

are solutions of (A-2) because of

$$\sum_{j=0}^{t} f_j \left(\sum_{k=1}^{t} \varphi_k \Phi_k^{n-j}\right) = \sum_{k=1}^{t} \varphi_k \Phi_k^{n-t} \left(\sum_{j=0}^{t} f_j \Phi_k^{t-j}\right) = 0$$

The coefficients $\varphi_1, \varphi_2, \dots, \varphi_t$ are to be determined from the knowledge of $F_0, F_1, \dots, F_{t-1}$.

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SAŽETAK

Kekuléove strukture i topologija. II. Kata-kondensirani sistemi

Dragoš Cvetković i Ivan Gutman

Opisan je algoritam za numeriranje Kekuléovih struktura nerazgranatih kata-kondensiranih konjugiranih sistema i dobivene su opće formule za broj Kekuléovih struktura za nekoliko konjugiranih nizova. Paulingov red veze može se lagano izračunati uporabom opisanog algoritma.

ELEKTROTEHNIČKI FAKULTET
UNIVERZITETA U BEOGRADU
11000 BEOGRAD
i
INSTITUT »RUĐER BOŠKOVIĆ«,
41000 ZAGREB

Primljeno 4. veljače 1974.