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Enumeration of Kekulé Structures in One-dimensional Polymers*

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One-dimensional polymer refers here to a polymer with a variable size in only one dimension. A new method for enumeration of Kekulé structures in such polymeric conjugated hydrocarbons is presented. It is quite general, but still efficient and simple to use. It is especially useful for evaluation of the Kekulé structure count, K, in polymers with regular structure, i. e. in those built up of equal monomers with uniform linking. In this case the method gives a recurrence relation and an explicit formula which enable the calculation of K for any number of monomers constituting the given polymer. Systems with more or less complex regularity, as well as those with some defect in structure, may also be successfully treated.

The possibilities of application are demonstrated on several examples, and some specific details, e. g. the lowest order of recursion, are discussed.

INTRODUCTION

The Kekulé structure count, K, is an important piece of information for conjugated polycyclic hydrocarbons[1]. In spite of many other established topological quantities[2], it remains a reliable parameter for the prediction and interpretation of stability and reactivity of a given conjugated compound.

Its evaluation for relatively simple molecules is straight-forward, by counting all different Kekulé structures which can be drawn for a given molecule. This method becomes very impractical for bigger molecules, and various procedures have been developed for the evaluation of K in large molecules[9]. Systems with regularly repeating units, and particularly benzenoid systems, were primarily considered[3–9]. These procedures give explicit formulas for K which depend on the number of monomers involved, or an easy to use recipe for calculation of K, but their application is restricted to particular systems for which they were derived. Recently, a general method[10]

* Dedicated to the memory of the late professor Andrej Ažman.

has been developed for the evaluation of K in any one-dimensional polymer, with full or partial periodicity. For markedly regular systems the result can be expressed as a recursive relation or as an explicit formula with the number of constituting units being the variable.

In this paper this method is described in more detail, partcularly with respect to its potential use. It can be effectively applied in the evaluation of K in systems with more complex regularity, as well as in the study of defect impact on K in respect to its character and position. Attention will be also paid to some specific properties of the method, regarding the minimal order of recursion, treatment of systems with even and odd numbers of carbon atoms in a monomer unit, and others.

The Method

Since the method has been already published elsewhere[10], here we shall only briefly repeat the essentials. By one-dimensional polymer we denote a polymer built up of a finite number of smaller units, not necessarily equal, so that each one is connected with maximally two others, through one or more bonds. In this way, a chain-like or a ring-like form is produced, depending on whether there are two terminal units, or not.

Because the problem of evaluation of K is combinatorial in its nature, the graph-theoretical terminology seems to be appropriate, and we shall use it in the following text. Hydrogen suppressed skeleton of the polymer is represented by a graph which we call a polygraph[11]. It consists of monographs[11] $G_1, G_2, \ldots, G_m$, connected by edge sets $X_1, X_2, \ldots, X_m$ so that each G_i is conected with G_{i+1} by X_i, and G_m is by X_m connected with G_1. The general scheme is depicted in Figure 1. The polygraph with the ring-like form

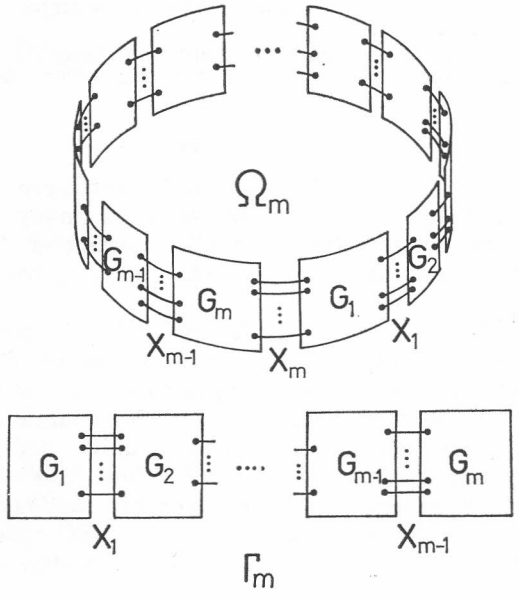

Figure 1.

we denote $\Omega_m = \Omega_m(G_1, G_2, \ldots, G_m;\ X_1, X_2, \ldots, X_m)$, and the case with empty X_m, having the chain-like form, is denoted Γ_m.

Let $M(X_i)$ denote a set of all mathchings in X_i, with elements $W_j^{(i)}$, $j = 1, 2, \ldots, |M(X_i)|$ where $|M(X_i)|$ stands for the cardinality of $M(X_i)$. Each $W_j^{(i)}$ may be also understood as a binary relation with the domain $D(W_j^{(i)})$ among the vertices of G_i, and its range $R(W_j^{(i)})$ among the vertices of G_{i+1}. The matrices $S(G_1)$, $S(G_2), \ldots, S(G_m)$, and $S(\Gamma_m)$ are defined in the following way:

$$[S(G_i)]_{jk} = \begin{cases} K(G_i - R(W_j^{(i-1)}) - D(W_k^{(i)})) & \text{if} \quad R(W_j^{(i-1)}) \cap D(W_k^{(i)}) = \varnothing \\ 0 \text{ otherwise} \end{cases} \tag{1}$$

$$j = 1, 2, \ldots, |M(X_{i-1})|, \quad k = 1, 2, \ldots, |M(X_i)|$$

$$[S(\Gamma_m)]_{jk} = \begin{cases} K(\Gamma_m - R(W_j^{(m)}) - D(W_k^{(m)})) & \text{if} \quad R(W_j^{(m)}) \cap D(W_k^{(m)}) = \varnothing \\ 0 \text{ otherwise} \end{cases} \tag{2}$$

$$j, k = 1, 2, \ldots, |M(X_m)|$$

$G_i - R(W_j^{(i-1)}) - D(W_k^{(i)})$ denotes the subgraph of G_i obtained by removing vertices specified by $R(W_j^{(i-1)})$ and $D(W_k^{(i)})$ out from G_i together with their incident edges. K of the empty graph by definition equals 1.

The following relation holds:

$$S(\Gamma_m) = S(G_1) \cdot S(G_2) \cdot \ldots \cdot S(G_m) \tag{3}$$

It enables the evaluation of all $K(\Gamma_m - R(W_j^{(m)}) - D(W_k^{(m)}))$ specified in $S(\Gamma_m)$ by multiplication of matrices $S(G_i)$ which contain K of monographs G_i and some of their subgraphs. These should be small graphs whose K could be easily calculated.

For $K(\Omega_m)$ we have:

$$K(\Omega_m) = \operatorname{tr}[S(G_1) \cdot S(G_2) \cdot \ldots \cdot S(G_m)] \tag{4}$$

Relations (3) and (4) become extremely useful when all G_i and X_i are equal: $G_1 = G_2 = \ldots = G_m \equiv G$, $X_1 = X_2 = \ldots = X_m \equiv X$. In this case we deal with completely regular, ideally periodical graphs which correspond to ideal polymers in the usual chemical sense. Again, we distinguish two types: one with closed ends, analogous to Ω_m, which is called a rotagraph[12] and is denoted by $\omega_m = \omega_m(G; X)$, and the other with open ends, analogous to Γ_m, called a fasciagraph[12], and denoted by γ_m. Relations (3) and (4) now read as:

$$S(\gamma_m) = S^m(G) \tag{5}$$

$$K(\omega_m) = \operatorname{tr}[S^m(G)] \tag{6}$$

Let us add that $S(\gamma_m)$ is defined as:

$$S(\gamma_m)_{jk} = \begin{cases} K(\gamma_m - R(W_j) - D(W_k) & \text{if} \quad R(W_j) \cap D(W_k) = \varnothing \\ 0 \text{ otherwise} \end{cases} \tag{7}$$

$$j, k = 1, 2, \ldots, |M(X)|$$

having in mind that, in analogy with (2), vertices $R(W_j)$ are removed from the first terminal monograph, and vertices $D(W_k)$ from the last one. Equa-

tions (5) and (6) allow us to calculate $K(\omega_m)$, $K(\gamma_m)$ and K of other subgraphs specified in $S(\gamma_m)$ for any m, once the matrix $S(G)$ is written out.

These two equations provide also the recurrence relations for $K(\psi_m)$, with Ψ_m standing for any of ω_m, γ_m and its subgraphs. Let $\Phi(S;\lambda)$ denote the characterstic polynomial of $S(G)$, defined by:

$$\Phi(S;\lambda) = \det(S - \lambda I) = \sum_{i=0}^{N} a_i \lambda^{N-i} \tag{8}$$

where N stands for $|M(X)|$. According to the Hamilton-Cayley theorem: $\Phi(S;S) = \mathbf{0}$, where $\mathbf{0}$ is the zero matrix of the order N. By equating matrix elements on the left and the right side (one is free to multiply both sides with any power of S), and by taking into account eqns. (5) and (6), the following recursions are derived:

$$\sum_{i=0}^{N} a_i \cdot K(\gamma_{m-i} - R(W_j) - D(W_k)) = 0, \quad m \geq N \tag{9}$$

$$\sum_{i=0}^{N} a_i \cdot K(\omega_{m-i}) = 0, \quad m \geq N \tag{10}$$

To use these recursions for the calculation of K for a particular polygraph ψ_m, it is first necessary to evaluate the coefficients a_i, and to determine the initial values, i. e. K of $\psi_o, \psi_1, \ldots, \psi_{N-1}$. By definition: $K(\omega_o) = N$, $K(\gamma_o - R(W_j) - D(W_k)) = \delta_{jk}$, where δ_{jk} is the Kronecker symbol. The same recursion applies to all ψ_m, and the difference is only in their initial values. One should also note that the characteristic polynomial does not generally give the shortest recursion. The recursion of the lowest order, common to all ψ_m, should be derived from the minimal polynomial of S. Recursions for $K(\gamma_m - R(W_j) - D(W_k))$ may be even of a lower order (and frequently are), but their finding is generally rather difficult, so in most cases the recursion derived from the characteristic polynomial is satisfactory.

The theory of linear recurrence relations[14] makes it possible to express $K(\psi_m)$ in another form: as an explicit formula in terms of the roots $\lambda_1, \lambda_2, \ldots, \lambda_N$ of $\Phi(S;\lambda)$, with m being the variable. Its derivation is a mathematical routine and we shall present it on some characteristic examples.

APPLICATIONS

We begin with some simple cases which may be treated by a straightforward application of the described method.

Example 1. — Figure 2a shows two polygraphs whose K are to be calculated.

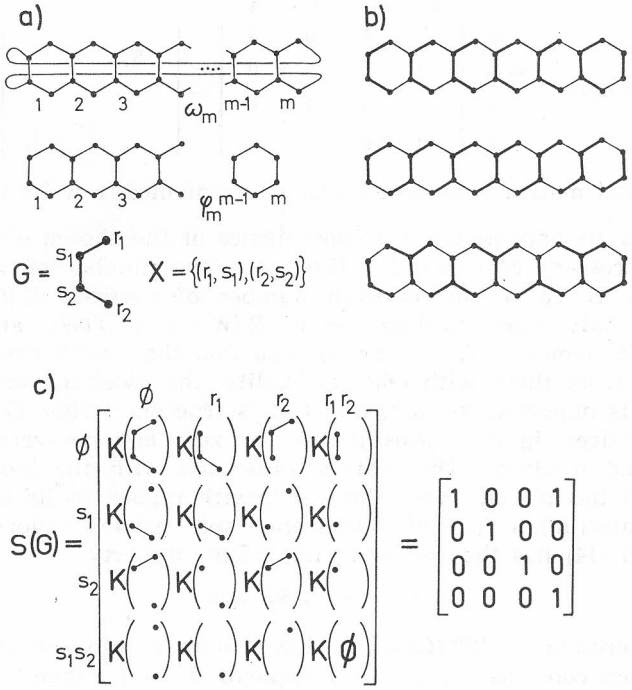

Figure 2.

it is constructed is depicted in Figure 2c. Its characteristic polynomial reads as:

$$\Phi(S;\lambda) = (\lambda - 1)^4 = \lambda^4 - 4\lambda^3 + 6\lambda^2 - 4\lambda + 1 \tag{11}$$

and the recursion relation follows:

$$K(\psi_m) - 4K(\psi_{m-1}) + 6K(\psi_{m-2}) - 4K(\psi_{m-3}) + K(\psi_{m-4}) = 0, \tag{12}$$

with the following initial values for the polygraphs in Figure 2a: $K(\omega_0) = K(\omega_1) = K(\omega_2) = K(\omega_3) = 4$, and $K(\varphi_0) = 0$, $K(\varphi_1) = 1$, $K(\varphi_2) = 2$, $K(\varphi_3) = 3$.

Since $K(\omega_m)$ is equal to the trace of $S^m(G)$, eqn. (6), always holds[13]:

$$K(\omega_m) = \sum_{j=1}^{N} \lambda_i^m \tag{13}$$

where λ_i denote the zeros of the characteristic polynomial of $S(G)$ (not e. g. zeros of its minimal polynomial). In this case $\lambda_1 = \lambda_2 = \lambda_3 = \lambda_4 = 1$ yield $K(\omega_m = 4$, for any m. Before we derive an explicit formula for $K(\varphi_m)$, let us point out a specific property of $S(G)$ when the monograph G has an even number of vertices.

The numbering of the elements of $M(X)$ is arbitrary; so we may take: $W_1 = \varphi$, $W_2 = \{(r_1, s_1), (r_2, s_2)\}$, $W_3 = \{(r_1, s_1)\}$, $W_4 = \{(r_2, s_2)\}$. Rewritten $S(G)$ is given by:

$$S(G) = \begin{array}{c} \\ \varphi \\ s_1 s_2 \\ s_1 \\ s_2 \end{array} \begin{array}{c} \begin{array}{cccc} \varphi & r_1 r_2 & r_1 & r_2 \end{array} \\ \begin{bmatrix} 1 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \end{array} \equiv \begin{bmatrix} S_3 & & & \\ & S_2 & & \\ & & S_1 & \end{bmatrix} \tag{14}$$

A block-diagonal matrix is obtained, and we symbolically write it as: $S(G) = S_1 \dot{+} S_2 \dot{+} S_3$. Its appearence is a consequence of the chosen ordering of W_i, and of the necessary condition for $K(G) \neq 0$: the number of vertices in G must be even. Since G has an even number of vertices, $K(G - R(W_j) - D(W_k)) \neq 0$ only when cardinalities of $R(W_j)$ and $D(W_k)$ are both even or both odd. If elements W_i are arranged so that those with even cardinality are separated from those with odd cardinality, the block-diagonal $S(G)$ will be formed. It is important to note that this is true only when G has an even number of vertices; in the opposite case the zero and non-zero blocks will have exchanged positions. The feature associated with the block-diagonalization of $S(G)$ has already been discussed, with regard to its physical relevance in manifesting a type of »long-range spin pairing order«[15].

$S(G)$ from (14) has the following important property:

$$S^m(G) = S_1^m \dot{+} S_2^m \dot{+} S_3^m \tag{15}$$

If we are interested in $[S^m(G)]_{ij}$, we have to take into consideration only the block which contains the given i,j-element. In our example we want to express $K(\varphi_m) = [S^m(G)]_{1,2}$ (according to the new numbering of W_i); therefore it is sufficient to consider only S_1. Its characteristic polynomial is:

$$\Phi(S_1; \lambda) = (\lambda - 1)^2 = \lambda^2 - 2\lambda + 1 \tag{16}$$

yielding a shorter recursion than (12):

$$K(\varphi_m) - 2K(\varphi_{m-1}) + K(\varphi_{m-2}) = 0, \quad m \geq 2 \tag{17}$$

The initial conditions for $K(\Phi_m)$ are already given by eqn. (12). It must be noted that this recursion is generally valid only for γ_m and its subgraphs related by S_1, and not for others, especially not for $K(\omega_m)$. Quite accidentally, in this example the recurrence relation (17) holds for all elements of $S(\gamma_m)$ and also for its trace, $K(\omega_m)$, because the polynomial in (16) is the minimal polynomial of $S(G)$.

Let us derive now an explicit formula for $K\varphi_m)$. Since $\Phi(S_1; \lambda)$ has degenerate zeros: $\lambda_1 = \lambda_2 = 1$, the following expression holds[14]:

$$K(\Phi_m) = (c_1 + c_2 \cdot m)\lambda_1^m = c_1 + c_2 \cdot m \tag{18}$$

c_1 and c_2 are calculated from the two equations obtained for $K(\varphi_0) = 0$ and $K(\varphi_1) = 1$ They give: $c_1 = 0$, $c_2 = 1$, and finally the well known result[6] is reproduced: $K(\Phi_m) = m$.

Example 2. — The next example is depicted in Figure 3a. The coresponding G and X are given in Figure 3b. Let us recall now that $K(G - R(W_j) - D(W_k)) = 0$ whenever $R(W_j) \cap D(W_k) \neq \varphi$, and $K(G) = 1$ when G is an empty graph, because these situations appear several times in writing down $S(G)$. G has an odd number of vertices, and we do not expect that $S(G)$

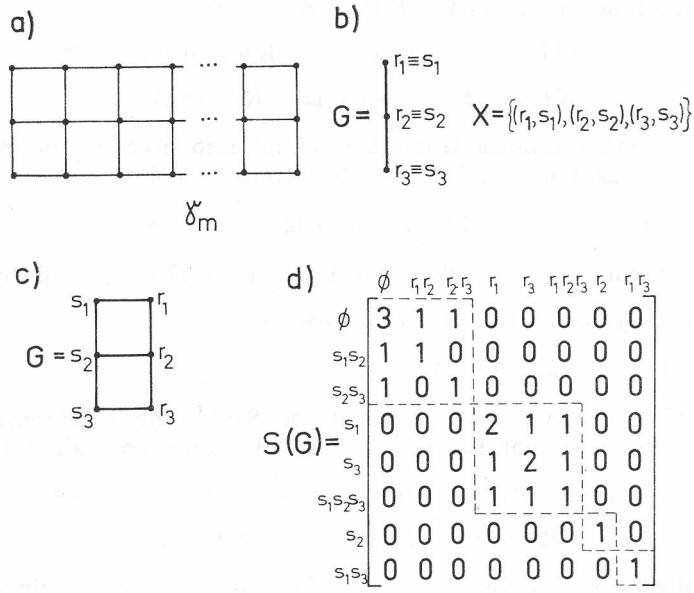

Figure 3.

can have a block-diagonal form (actually it can, but it is a special case, independent of previous considerations). But if we want to evaluate only $K(\gamma_m)$ and $K(\omega_m)$, we may freely take doubled G as the new monograph G_2, shown in Figure 3c. Namely, for odd m $K(\gamma_m)$ and $K(\omega_m)$ are obviously zeros, because the respective polygraphs have an odd number of vertices. So we have to express $K(\gamma_m)$ and $K(\omega_m)$ only for even m, and we rather take G_2 as the monograph. It has an even number of vertices, and consequently it will be possible to present $S(G_2)$ in a preferred block-diagonal form, Figure 3d. $S(G_2)$ may be calculated from $S(G)$ according to: $S(G_2) = S(\gamma_2) = S^2(G)$. We recommend the following procedure to determine all blocks in S matrix: let us understand S as an adjacency matrix of some graph, and let us draw it (weights of its edges and loops are unimportant). It is easy to identify separate components in the drawing, and to carry out the appropriate renumbering of S.

Next, we take G_2 as the monograph, and m in γ_m and ω_m refers to it. The characteristic polynomial of $S(G_2)$ is:

$$\Phi(S(G_2);\lambda) = \lambda^8 - 6\lambda^6 + 10\lambda^4 - 6\lambda^2 + 1 = [(\lambda-1)^2 \cdot (\lambda^2 - 4\lambda + 1)]^2 \qquad (19)$$

Because $S(G_2)$ is a hermitian matrix, it can be transformed to a diagonal form with diagonal values being equal to zeros of $\Phi(S(G_2);\lambda)$ it enables us to write immediately the minimal polynomial for $S(G_2)$[13], and its zeros:

$$\Phi(S(G_2);\lambda) = (\lambda-1)(\lambda^2 - 4\lambda + 1) = \lambda^3 - 5\lambda^2 + 5\lambda - 1$$

Then the recurrence relation for $K(\omega_m)$ reads as:

$$K(\omega_m) - 5K(\omega_{m-1}) + 5K(\omega_{m-2}) - K(\omega_{m-3}) = 0, \quad m \geq 3$$

$$K(\omega_o) = 8, \quad K(\omega_1) = 12, \quad K(\omega_2) = 32 \tag{21}$$

The explicit formula follows from (13) taking into account the degeneracy of λ_1, λ_2 and λ_3 as the roots of the characteristic polynomial:

$$K(\omega_m) = 2[(2 + \sqrt{3})^m + (2 - \sqrt{3})^m] + 4 \tag{22}$$

For $K(\gamma_m)$ we consider only the first block in $S(G_2)$, denoted by S_1. The characteristic polynomial and its zeros read as:

$$\Phi(S_1; \lambda) = \lambda^3 - 5\lambda^2 + 5\lambda - 1, \quad \lambda_1 = 2 + \sqrt{3}, \quad \lambda_2 = 2 - \sqrt{3}, \quad \lambda_3 = 1 \tag{23}$$

Since it is also the minimal polynomial of $S(G_2)$, the recurrence relation for $K(\gamma_m)$ is equal to that for $K(\omega_m)$, but with different initial conditions:

$$K(\gamma_m) - 5K(\gamma_{m-1}) + 5K(\gamma_{m-2}) - K(\gamma_{m-3}) = 0, \quad m \geq 3$$

$$K(\gamma_0) = 1, \quad K(\gamma_1) = 3, \quad K(\gamma_2) = 11 \tag{24}$$

The explicit formula for $K(\gamma_m)$ has the following form[14], since there is no degeneracy in zeros of $\Phi(S_1; \lambda)$:

$$K(\gamma_m) = c_1\lambda_1^m + c_2\lambda_2^m + c_3\lambda_3^m \tag{25}$$

By solving the system of three equations, for $K(\gamma_0)$, $K(\gamma_1)$ and $K(\gamma_2)$, the following result has been obtained: $c_1 = (3 + \sqrt{3})/6$, $c_2 = (3 - \sqrt{3})/6$, and $c_3 = 0$. Substitution into eqn. (25) gives:

$$K(\gamma_m) = 1/6[(3 + \sqrt{3})(2 + \sqrt{3})^m + (3 - \sqrt{3})(2 - \sqrt{3})^m] \tag{26}$$

The fact that $K(\gamma_m)$ can be expressed in terms of only λ_1 and λ_2 means also that the shortest recursion for $K(\gamma_m)$ is not (25), but one derived from the polynomial:

$$(\lambda - \lambda_1) \cdot (\lambda - \lambda_2) = \lambda^2 - 4\lambda + 1 \tag{27}$$

Let us prove it. The general expression for a recursion relation on $K(\psi_m)$ is:

$$\sum_{i=0}^{r} a_i \cdot K(\psi_{m-i}) = 0, \quad m \geq r \tag{28}$$

By the following we want to determine the coefficients a_i. Let us assume:

$$K(\Psi_m) = \sum_{i=0}^{n} c_j \cdot \lambda_j^m, \quad \lambda_i \neq \lambda_j \text{ if } i \neq j, \quad \text{and} \quad c_j \neq 0, \quad \lambda_j \neq 0 \text{ for all } j \tag{29}$$

Substitution into (28) gives:

$$\sum_{i=0}^{r} a_i \cdot K(\psi_{m-i}) = \sum_{i=0}^{r} a_i \sum_{j=1}^{n} c_j \cdot \lambda_j^{m-i} = \sum_{j=1}^{n} c_j \sum_{i=0}^{n} a_i \cdot \lambda_j^{m-i} =$$

$$= \sum_{j=1}^{n} c_j \cdot \lambda_j^{m-r} \sum_{i=0}^{r} a_i \cdot \lambda_j^{r-i} \equiv \sum_{j=1}^{n} \lambda_j^{m-r} \cdot c_j \cdot Q(\lambda_j) = 0 \tag{30}$$

where $Q(\lambda_j)$ stands for the polynomial in λ_j represented by the iner summation part. Let us write the last equation in (30) for $m = r, r+1, \ldots, 2r-1$, treating $c_j Q(\lambda_j)$ as unknowns. The homogenous system of r linear equations is obtained, having a nontrivial solution only if its determinant equals zero. The value of this determinant (also called Vandermonde's determinant) is known[13]:

$$D = \prod_{1 \le j < i \le n} (\lambda_i - \lambda_j) \tag{31}$$

Taking into account the assumptions made in (29), it is clear that D is not equal to zero. Therefore, only the trivial solution remains, and regarding the assumption $c_j \neq 0$, for all j, made also in (29), the final result $Q(\lambda_j) = 0$, for all j, follows. It is actually the only requirement that eqn. (28) puts on $Q(\lambda)$, i. e. on the coefficients a_i. The minimal $Q(\lambda)$ which satisfies this conditions is:

$$Q(\lambda) = \prod_{j=1}^{n} (\lambda - \lambda_j) \tag{32}$$

So we proved that the shortest recursion for $K(\gamma_m)$ indeed derives from the polynomial in (27), and reads as:

$$K(\gamma_m) - 4K(\gamma_{m-1}) + K(\gamma_{m-2}) = 0, \quad m \geq 2 \tag{33}$$

The initial values were given earlier, with eqn. (24). It would be very interesting to know why is some cases (not so rare) the recursions shorter than those obtained from the characteristic and minimal polynomial of S matrix exist, and particularly to devise a simple and straightforward procedure for finding them. Until now it has been found that the symmetry of the monograph, together with the way of its linking, plays a significant role, but the subject is not yet completely understood.

In the next two examples some cases with more complex structure will be considered.

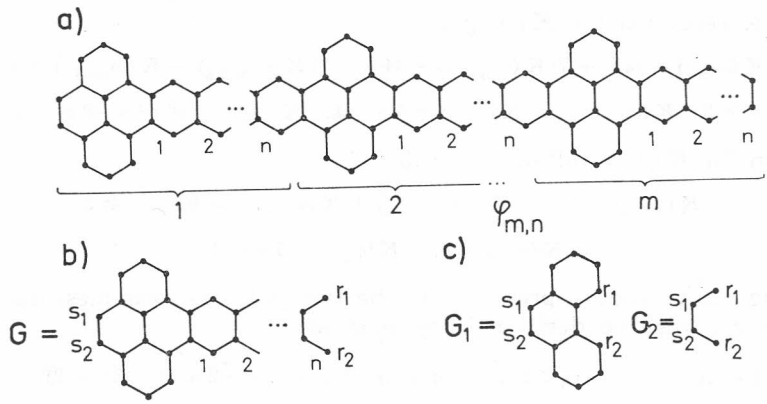

Figure 4.

Example 3. — The polygraph is depicted in Figure 4a. Its monograph, shown in Figure 4b, has a variable length, depending on how many G_2 units it involves. First, we shall deduce $S(G)$. Following eqn. (3) we obtain:

$$S(G) = S(G_1) \cdot S^n(G_2) \tag{34}$$

Extending the results from Example 1, $S^n(G_2)$ is obtained:

$$S^n(G_2) = \begin{array}{c} \\ \varphi \\ s_1 s_2 \\ s_1 \\ s_2 \end{array} \begin{array}{c} \begin{array}{cccc} \varphi & r_1 r_2 & r_1 & r_2 \end{array} \\ \begin{bmatrix} 1 & n & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \end{array} \tag{35}$$

After multiplication by $S(G_1)$, eqn. (34), $S(G)$ follows:

$$S(G) = \begin{array}{c} \\ \varphi \\ s_1 s_2 \\ s_1 \\ s_2 \end{array} \begin{array}{c} \begin{array}{cccc} \varphi & r_1 r_2 & r_1 & r_2 \end{array} \\ \begin{bmatrix} 5 & 5n+1 & 0 & 0 \\ 4 & 4n+1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix} \end{array} = S_1 + S_2 + S_3 \tag{36}$$

The characteristic polynomials we need, and their roots, read as:

$$\Phi(S_1; \lambda) = \lambda^2 - (4n + 6)\lambda + 1$$

$$\lambda_1 = 2n + 3 + 2\sqrt{n^2 + 3n + 2}, \quad \lambda_2 = 2n + 3 - 2\sqrt{n^2 + 3n + 2} \tag{37}$$

$$\Phi(S(G); \lambda) = \lambda^4 - (4n + 8)\lambda^3 + (8n + 14)\lambda^2 - (4n + 8)\lambda + 1 \tag{38}$$

λ_1 and λ_2 are the same as above, $\lambda_3 = \lambda_4 = 1$

A closer look into $S(G)$ reveals that the minimal polynomial of $S(G)$ is:

$$\mu(S(G); \lambda) = \Phi(S_1; \lambda) \cdot \Phi(S_2; \lambda) = [\lambda^2 - (4n + 6)\lambda + 1] \cdot (\lambda - 1) =$$

$$= \lambda^3 - (4n + 7)\lambda^2 + (4n + 7)\lambda - 1 \tag{39}$$

Therefore, recursion for $K(\omega_{m,n})$ is:

$$K(\omega_{m,n}) - (4n + 7)K(\omega_{m-1,n}) + (4n + 7)K(\omega_{m-2,n}) - K(\omega_{m-3,n}) = 0,$$

$$m \geq 3, \quad K(\omega_{0,n}) = 4, \quad K(\omega_{1,n}) = 4n + 8, \quad K(\omega_{2,n}) = 16n^2 + 48n + 36 \tag{40}$$

Recursion for $K(\varphi_{m,n})$ follows from (37):

$$K(\varphi_{m,n}) - (4n + 6)K(\varphi_{m-1,n}) + K(\varphi_{m-2,n}) = 0, \quad m \geq 2,$$

$$K(\varphi_{0,n}) = 0, \quad K(\varphi_{1,n}) = 5n + 1 \tag{41}$$

Following the procedure presented in the two previous examples, the explicit formulas can also be derived. They read as:

$$K(\omega_{m,n}) = (2n + 3 + 2\sqrt{n^2 + 3n + 2})^m + (2n + 3 - 2\sqrt{n^2 + 3n + 2})^m + 2 \tag{42}$$

$$K(\varphi_{m,n}) = (5n + 1)[(2n + 3 + 2\sqrt{n^2 + 3n + 2})^m - (2n + 3 -$$

$$- 2\sqrt{n^2 + 3n + 2})^m]/(4\sqrt{n^2 + 3n + 2}) \tag{43}$$

Example 4. — The polygraph, $H_{m,n}$, considered in this example is depicted in Figure 5a. Figure 5b shows the monographs G_1 and G_2 which

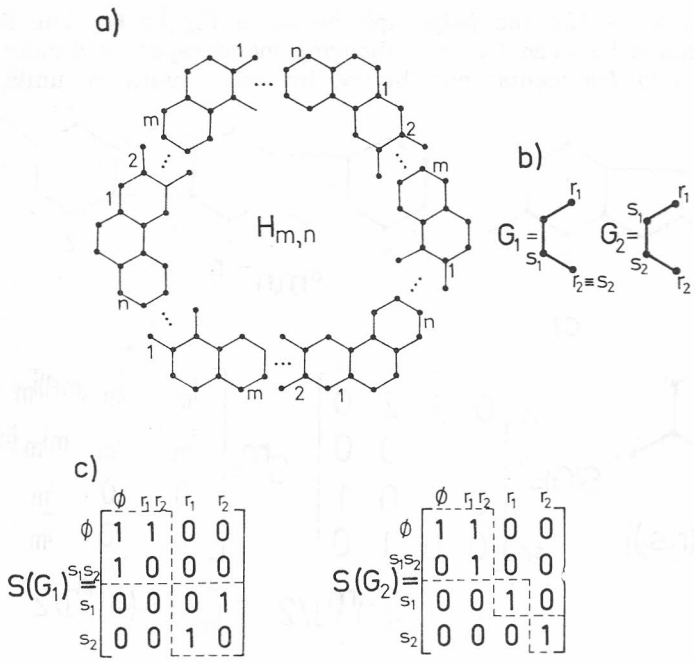

Figure 5.

build up $H_{m,n}$. $S(G_1)$ and $S(G_2)$ are written in Figure 5c. The way of connecting G_1, G_2, and so on, is described by the notation of their linking vertices and by the convention: r_1 of one unit is always linked to s_1 of another, r_2 to s_2, and vice versa. One must consider it when $C(G_1)$ and $S(G_2)$ are created. Following eqn. (4) and the given sequence of monographs G_1 and G_2 in $H_{m,n}$, $K(H_{m,n})$ may be written as:

$$K(H_{m,n}) = \mathrm{tr}\,[S(G_1) \cdot S^m(G_2) \cdot S(G_1) \cdot S^n(G_2)]^3 \tag{44}$$

Using the results from the previous example for $S^m(G_2)$, after the multiplication denoted in square brackets, $K(H_{m,n})$ becomes:

$$K(H_{m,n}) = \mathrm{tr} \begin{bmatrix} m+2 & mn+2n+1 & 0 & 0 \\ m+1 & mn+n+1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}^3 \tag{45}$$

and finally we obtain:

$$K(\varphi_{m,n}) = x^3y^3 + 6x^2y^2 + 9xy + 4, \quad x \equiv m+1, \quad y \equiv n+1 \tag{46}$$

$$K(H_{m,m}) = x^6 + 6x^4 + 9x^2 + 4, \quad x \equiv m+1 \tag{47}$$

As mentioned in the introduction, the method can also serve to examine the effect of eventual defects present in otherwise regular polymers. It is demonstrated by the following example.

Example 5. — Let the polygraph be as in Figure 6a. The defect is a linking inversion between two neighbouring monographs. It divides the polygraph into two fragments: one before inversion, with m units, and the

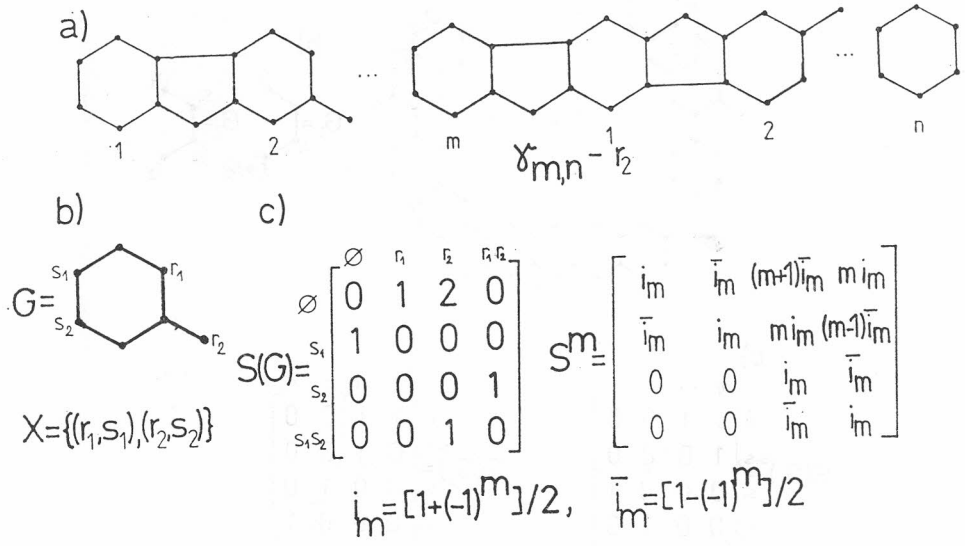

Figure 6.

other after it, with n units. These two parts are strictly regular, but mutually misconnected. G and X are given in Figure 6b, with $S(G)$ and $S^m(G)$ in Figure 6c. If there would be no defect, we could write:

$$S(\gamma_{m,n}) = S^m(G) \cdot S^n(G)$$

To obtain $S(\gamma_{m,n})$ for $\gamma_{m,n}$ with the linking inversion, it is sufficient to exchange the second and the third row in $S^n(G)$ in the above expression. The reason for this is the fact that r_1 and r_2 of the left fragment γ_m are linked to s_2 and s_1, respectively, of the right fragment γ_n. Therefore, X_i describing the linking defect, is: $X_i = \{(r_1, s_2), (r_2, s_1)\}$, and W_2 and W_3 are: $W_2 = \{(r_1, s_2)\}$, $W_3 = \{(r_2, s_1)\}$. $S(\gamma_{m,n})$ equals:

$$S(\gamma_{m,n}) = \begin{bmatrix} i_m & \bar{i}_m & (m+1)\,i_m & m i_m \\ \bar{i}_m & i_m & m i_m & (m-1)\,\bar{i}_m \\ 0 & 0 & \bar{i}_m & i_m \\ 0 & 0 & i_m & \bar{i}_m \end{bmatrix} \cdot \begin{bmatrix} i_n & \bar{i}_n & (n+1)\,\bar{i}_n & n i_n \\ 0 & 0 & i_n & \bar{i}_n \\ \bar{i}_n & i_n & n i_n & (n-1)\,\bar{i}_n \\ 0 & 0 & \bar{i}_n & i_n \end{bmatrix} \tag{48}$$

with $i_m = (1 + (-1)^m)/2$, $\bar{i}_m = (1 - (-1)^m)/2$. Since the polygraph under consideration is in fact $\gamma_{m,n} - r_2$, we read from the above product only its 1,3-element. Here are the results:

$$\begin{aligned} K(\gamma_{m,n} - r_2) &= 0 \quad \text{if} \quad m + n = \text{even} \\ K(\gamma_{m,n} - r_2) &= m + n + 1 \quad \text{if} \quad m = \text{even}, \quad n = \text{odd} \\ K(\gamma_{m,n} - r_2) &= r^2) = mn + n + 1 \quad \text{if} \quad m = \text{odd}, \quad n = \text{even} \end{aligned} \tag{49}$$

The results for even $(m + n)$ can be easily understood when the total number of vertices is counted for $\gamma_{m,n} - r_2$. It is $7(m + n) - 1 =$ odd, and certainly $K = 0$. The result in the next formula shows that the position of the linking inversion has no effect on K if $m =$ even, $n =$ odd, while the last expression shows a quite different result: $K(\gamma_{m,n} - r_2)$ is greatly affected by the position of the inversion when $m =$ odd, $n =$ even.

CONCLUSION

Through the elaborated examples we have shown how the solving of the enumeration problem of Kekulé structures in one-dimensional polymers has become a routine work. The presented method is quite general, efficient and simple to use. It can be used in a variety of systems with more or less complex regularity. Practically, K of all patterns whose size varies in any prescribed way, but in only one dimension, can be successfully evaluated or investigated using this method.

Nevertheless, it has a strong limitation: it is applicable only to one--dimensional polymers. One may try to treat the two-dimensional networks, by gradually increasing the size of the monograph. But, simultaneously, the number of links between them increases and the order of $S(G)$ matrix grows exponentially. Some work on it has already been done [16], but we feel that there should also be an efficient and more general method, similar to the described one. This work is in progress.

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SAŽETAK

Prebrojavanje Kekuléovih struktura u jednodimenzionalnim polimerima

D. Babić i A. Graovac

Prikazana je nova metoda za prebrojavanje Kekuléovih struktura u jednodimenzijskim polimernim ugljikovodicima. Jednodimenzijskim polimerom nazvan je polimer čija veličina, s obzirom na broj monomernih jedinica, varira u samo jednoj dimenziji. Metoda je potpuno općenita, ali i dalje efikasna i jednostavna za upotrebu. Posebno je korisna za određivanje broja Kekuléovih struktura, K, u polimerima s pravilnom strukturom, tj. s jednakim monomerima i uniformnim međusobnim povezivanjem. U tom slučaju metoda daje rekurzivnu relaciju i eksplicitnu formulu koja omogućuje izračunavanje K za zadani polimer s bilo kojim brojem monomera. Složeniji regularni sistemi, kao i oni s nepravilnošću u strukturi, mogu se također uspješno obrađivati.

Mogućnosti primjene pokazane su na nekoliko primjera, a razmotreni su i neki specifični detalji metode, kao npr. najniži red rekurzije.