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Kekulé Structure Counts: General Formulations for Primitive Coronoid Hydrocarbons

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Summary. The Kekulé structure counts (K) for primitive coronoids are treated. The K formula which involves the trace of a matrix product is recalled and supplemented with new findings. In this way a kind of symmetry in the mathematical formulations is restored. Another general formulation for the K number is provided in terms of polynomials which, for a somewhat mysterious reason, are identified as the matching polynomials of cycles.

Keywords. Kekulé structure; Coronoid.

Zählung von Kekulé-Strukturen

Zusammenfassung. Es werden Kekulé-Strukturzählungen (K) für einfache Coronoide behandelt. Die Formel für K wird durch neugefundene Eigenschaften ergänzt. So wird eine Art von Symmetrie in den mathematischen Formulierungen erreicht. Eine andere generelle Formulierung der K-Zahlen wird in Form von Polynomen bereitgestellt, welche aus uneinsichtigen Gründen als die passenden Polynome von Cyclen identifiziert wurden.

Introduction

Coronoid systems (or coronoids) are polyhexes with holes, referred to as corona holes. In the present work it is tacitly assumed that only one corona hole of a system under consideration is present. More precisely, such systems should be referred to as single coronoids. A corona hole, when interpreted as a benzenoid (polyhex without hole) should have a size of at least two hexagons.

The term polyhexes is here used for benzenoids and coronoids taken together. They are geometrically planar systems of congruent regular hexagons. For general treatments of polyhexes, including precise definitions, we cite some recent monographs [1–4].

The present work deals with the enumeration of Kekulé structures [3] for coronoid systems. The notion of Kekulé structures is transferred from chemistry. This is quite natural since coronoid systems have chemical counterparts in conjugated (polycyclic aromatic) hydrocarbons.

For primitive coronoids [5, 6] the studies of Kekulé structure counts (K) have led to interesting classes of polynomials (for references, see below). These results are reviewed concisely and presented for the first time in a general form. They are also supplemented by original results.

Basic Definitions and Notation

A primitive coronoid consists of an even number of segments in a circular arrangement. It has only linearly and/or angularly annelated hexagons. The symbols L and A are used for linear and angular annelation, respectively. The length of a segment, say l, is taken as the number of hexagons between two neighbouring A hexagons inclusive. The sequence of segments associated with a primitive coronoid is written

$$/l_1, l_2, \ldots, l_S/,$$

where S is the number of the segments. Then the number of hexagons is

$$h = -S + \sum_{i=1}^{S} l_i. \tag{1}$$

The number S must be even. It is specifically restricted to $S = 6, 8, 10, 12, 14, \ldots$.

General Formula for Kekulé Structure Count (I)

Consider a primitive coronoid characterized by

$$\mathrm{A} = /a_1 + 1, a_2 + 1, \ldots, a_S + 1/. \tag{2}$$

An elegant formula for the Kekulé structure count is

$$K\{\mathrm{A}\} = \mathrm{Tr}(\mathbf{a}_1\ \mathbf{a}_2 \cdots \mathbf{a}_S) + 2, \tag{3}$$

where

$$\mathbf{a}_i = \begin{bmatrix} a_i & 1 \\ 1 & 0 \end{bmatrix}. \tag{4}$$

This is a slight generalization of a previously given form [7].

The addition of two units in Eq. (3) accounts for the two proper annulenoid [7] Kekulé structures, in which the two perimeters are "in-phase" conjugated circuits.

Units: Definitions and Properties

Definition and Notation

In a primitive coronoid a unit u may be defined as the hexagons between two arbitrary A hexagons inclusive. Hence a unit is characterized by a sequence of segments. It is written symbolically [8]

$$\mathrm{u} = [l_1, l_2, \ldots, l_{s-1}, l_s],$$

where s is the number of segments in the unit.

Fragments of a Unit

A matrix **u** is defined for a unit u as

$$\mathbf{u} = \begin{bmatrix} u_0 & u_1 \\ u_2 & u_3 \end{bmatrix}, \tag{6}$$

where the elements are K numbers for certain fragments of u [8 − 11]. When u is given by Eq. (5), then:

$$u_0 = K\{[l_1 - 1, l_2, l_3, \ldots, l_{s-1}, l_s - 1]\}, \tag{7}$$

$$u_1 = K\{[l_1 - 1, l_2, l_3, \ldots, l_{s-1} - 1]\}, \tag{8}$$

$$u_2 = K\{[l_2 - 1, l_3, \ldots, l_{s-1}, l_s - 1]\}, \tag{9}$$

$$u_3 = K\{[l_2 - 1, l_3, \ldots, l_{s-1} - 1]\}. \tag{10}$$

Proper modifications should be executed by taking into account that no length of a segment may be less than 2. The matrix of Eq. (4) is a special (degenerate) case of **u**, pertaining to one segment ($s = 1$).

Relations

The K number of u is [10, 12]

$$K\{\mathrm{u}\} = \mathrm{Tr}(\mathbf{u}) + \mathrm{Tr}(\mathbf{ju}) = [1 \quad 1]\,\mathbf{u}\begin{bmatrix} 1 \\ 1 \end{bmatrix} = u_0 + u_1 + u_2 + u_3 . \tag{11}$$

Here

$$\mathbf{j} = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}. \tag{12}$$

The determinant of **u** is [9, 10, 12]

$$\det(\mathbf{u}) = \begin{vmatrix} u_0 & u_1 \\ u_2 & u_3 \end{vmatrix} = u_0 u_3 - u_1 u_2 = (-1)^s . \tag{13}$$

General Formula for Kekulé Structure Count (II)

A formula corresponding to Eq. (3) is sound for a primitive coronoid C consisting of n units, $\mathrm{u}_1, \mathrm{u}_2, \ldots, \mathrm{u}_n$ in succession;

$$K\{\mathrm{C}\} = \mathrm{Tr}(\mathbf{u}_1 \ \mathbf{u}_2 \cdots \mathbf{u}_n) + 2 . \tag{14}$$

The total number of segments is

$$S = \sum_{i=1}^{n} s_i , \tag{15}$$

where s_i is the number of segments of the unit u_i. The total number of segments (S) is restricted to the even numbers specified above.

Kekulé Structure Counts for Primitive Coronoids with Repeated Units

Polynomials for the title quantities have been derived during some studies over the last few years and are scattered in different publications [8 – 11, 13]. In the following this material is reviewed for the first time systematically in general terms.

Assume that a primitive coronoid, $\mathrm{C}^{(n)}$, consists of n units u in the above sense and that all of them are identical "up to isoarithmicity". It means that all of them have the same sequence of segments (4). Each unit spans from an A hexagon to another A hexagon inclusive. Only in the degenerate case of one unit ($n=1$) an A hexagon is taken twice, at each end of the unit. This defines the class of primitive coronoids with repeated units. It is clear that a "waffle" [8, 10] has (at least) six repeated units. Fig. 1 shows another example, demonstrating that $\mathrm{C}^{(6)}$ has not necessarily hexagonal symmetry. This system may be interpreted (for instance) as consisting of the six units [4, 3, 2, 2, 2] or [4, 3, 2^3] (when the shaded hexagons in Fig. 1 are taken as common to two neighbouring units).

For the Kekulé structure count we introduce the notation

$$C^{(n)} = K\{\mathrm{C}^{(n)}\}. \tag{16}$$

As a simple corollary of Eq. (14) one has

$$C^{(n)} = \mathrm{Tr}(\mathbf{u}^n) + 2. \tag{17}$$

The total number of segments is

$$S = n s; \tag{18}$$

cf. also Eq. (15).

Polynomial Formulas (I)

The first polynomial formula for the K numbers of primitive coronoids pertains to the class $/a+1,\ a+1,\ a+1,\ a+1,\ a+1,\ a+1/ = /a+1/^6$, of which kekulene [14, 15] is a member (for $a=2$). It reads [16 – 19]

$$K\{/a+1/^6\} = (a^3+3a)^2+4 = (a^2+1)^2(a^2+4) = a^6+6a^4+9a^2+4. \tag{19}$$

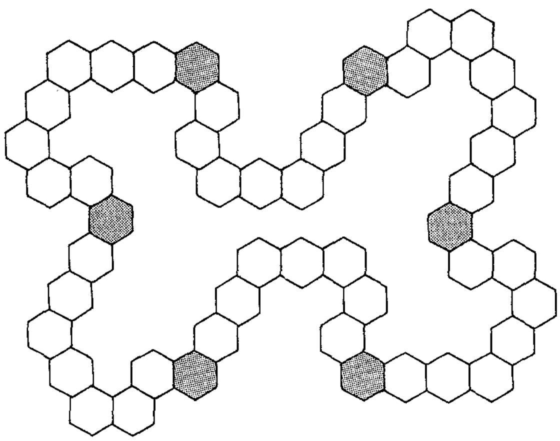

Fig. 1. A primitive coronoid with six repeated units

The formula was generalized to the class of primitive coronoids with six repeated units u, each holding s segments, with the result [9]

$$C^{(6)} = x^6 - (-1)^s 6x^4 + 9x^2 - (-1)^s 2 + 2, \tag{20}$$

where the variable x is

$$x = \mathrm{Tr}(\mathbf{u}) = u_0 + u_3. \tag{21}$$

It is expedient to distinguish between the cases when s is even or odd by the symbols $C^{(n)}_{\text{even}}$ *and* $C^{(n)}_{\text{odd}}$, respectively [9]. Then one has in general terms:

$$C^{(n)}_{\text{even}} = \alpha(C_n | x) + 2, \tag{22}$$

$$C^{(n)}_{\text{odd}} = i^{-n} \alpha(C_n | ix) + 2 = \bar{\alpha}(C_n | x) + 2. \tag{23}$$

The variable x is given by Eq. (21).

The symbol $\alpha\ (C_n | x)$ is used to identify the class of matching polynomials [20, 21] for a cycle C_n, which are closely related to the characteristic polynomials [22, 23] of C_n. The definition of $\bar{\alpha}\ (C_n | x)$ is implied in Eqs. (23). Some authors prefer to define the matching polynomial in this way. The deeper background of Eqs. (22) and (23) is the (generalized) "Hosoya mystery" [13, 18].

Extension to Primitive Non-Coronoids

A primitive coronoid can be constructed for any combination of n units with s segments in each if the total number of segments (18) becomes an even number $S \geqslant 6$ as a necessary condition. However, this condition is not sufficient; many particular cases with acceptable values of n and s cannot be realized unless it is allowed for distorted hexagons when drawn in a plane. Also such coronoid-like systems have well-defined Kekulé structures, of which the numbers follow the pertinent formulas of the above treatment. Then also $S=2$ and 4 are possible values. Such systems, which we may call primitive non-coronoids, have actually been studied in detail in the case of equidistant segments [7, 17], and even the degenerate case of $n=0$ ($S=0$).

Another type of primitive non-coronoids have an odd number of segments in total, which is realized when both n and s are odd. Also in this case there are well-defined Kekulé structures. However, some of our formulas need modifications because of the absence of proper annulenoid Kekulé structures. This fact is understood when realizing that both perimeters are odd-membered cycles.

Generalization of Formulas

In view of the above discussion, Eq. (3) should be generalized to

$$K\{\mathrm{A}\} = \mathrm{Tr}(\mathbf{a}_1\ \mathbf{a}_2 \ldots \mathbf{a}_S) + 1 + (-1)^S, \tag{24}$$

and correspondingly for Eq. (14):

$$K\{\mathrm{C}\} = \mathrm{Tr}(\mathbf{u}_1\ \mathbf{u}_2 \ldots \mathbf{u}_n) + 1 + (-1)^S. \tag{25}$$

The same modification is also necessary for Eq. (17).

The expression of (22) for $C^{(n)}_{\text{even}}$ is valid in general, but $C^{(n)}_{\text{odd}}$ in (23) should be modified as:

$$C^{(n)}_{\text{odd}} = \bar{\alpha}(C_n|x) + 1 + (-1)^n. \tag{26}$$

Listing of Polynomials

In Table 1 we give a comprehensive survey of the $C^{(n)}$ polynomials in the generalized form.

Example

In the case of Fig. 1, when taking

$$\mathrm{u} = [4, 3, 2^3], \tag{27}$$

then:

$$u_0 = K\{[3, 3, 2^2]\} = 27,$$
$$u_1 = K\{[3, 3, 2]\} = 17,$$
$$u_2 = K\{[2^3]\} = 8,$$
$$u_3 = K\{[2^2]\} = 5. \tag{28}$$

Observe that

$$\det(\mathbf{u}) = \begin{vmatrix} 27 & 17 \\ 8 & 5 \end{vmatrix} = -1 \tag{29}$$

Table 1. The polynomials $C^{(n)}$ for $n \leqslant 12$; $C^{(n)}_{\text{even}}$ when s is even, $C^{(n)}_{\text{odd}}$ when s is odd

n	$C^{(n)}$
0	4
1	$x+1+(-1)^s$
2	$x^2-(-1)^s2+2$
3	$x^3-(-1)^s3x+1(-1)^s$
4	$x^4-(-1)^s4x^2+4$
5	$x^5-(-1)^s5x^3+5x+1+(-1)^s$
6	$x^6-(-1)^s6x^4+9x^2-(-1)^s2+2$
7	$x^7-(-1)^s7x^5+14x^3-(-1)^s7x+1+(-1)^s$
8	$x^8-(-1)^s8x^6+20x^4-(-1)^s16x^2+4$
9	$x^9-(-1)^s9x^7+27x^5-(-1)^s30x^3+9x+1+(-1)^s$
10	$x^{10}-(-1)^s10x^8+35x^6-(-1)^s50x^4+25x^2-(-1)^s2+2$
11	$x^{11}-(-1)^s11x^9+44x^7-(-1)^s77x^5+55x^3-(-1)^s11x+1+(-1)^s$
12	$x^{12}-(-1)^s12x^{10}+54x^8-(-1)^s112x^6+105x^4-(-1)^s36x^2+4$

in consistence with Eq. (13) since $s=5$ in our example. In order to compute the K number for the whole system in Fig. 1 we apply Eq. (20), also found in Table 1, with s odd and

$$x = \mathrm{Tr}(\mathbf{u}) = 27 + 5 = 32. \tag{30}$$

The result is:

$$C^{(6)}_{\mathrm{odd}}(32) = 1080042500. \tag{31}$$

Supplementary Developments

The asymmetry of Eq. (21) may seem somewhat disturbing. Why is it possible to express the K numbers of primitive coronoids with repeated units in terms of the two selected elements of the **u** matrix (u_0 and u_3)? We have restored the symmetry by considering units which have linearly annelated hexagons (L) in common, and not only angularly annelated (A) as in the above treatment. It is true that the new considerations are not necessary in a pragmatic sense, since any primitive coronoid has (at least six) A hexagons, while it may or may not have L hexagons. But also this "asymmetry" disappears when the primitive non-coronoids are included. Such systems may very well consist of only L hexagons [17]. In the below treatment the formulas are given in the generalized terms which allow for primitive non-coronoids, including those with an odd number of segments.

Let a unit u of a primitive coronoid, in the generalized sense, consist of any part of the system between two non-neighbouring hexagons, these two hexagons inclusive. As before, we consider sequences of units where each neighbours share one hexagon. Such a pair of units we shall refer to as compressed, and we shall speak about angular (resp. linear) compression, depending on whether the common hexagon is an A (resp. L).

General Formulation for the Kekulé Structure Count

The K formula (25) is a generalization of (14), but still it requires the presence of A hexagon(s). It is not applicable to primitive non-coronoids without A. A remedy of this deficience is achieved by a further generalization where allowance is made for both angularly and linearly compressed units. The only modification which is necessary, is to insert **j** in-between two matrices $\mathbf{u}_i$ and $\mathbf{u}_{i+1}$ if the corresponding units (u_i and u_{i+1}) are linearly compressed.

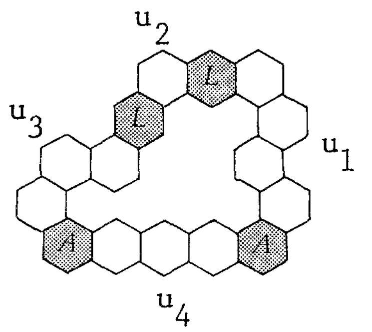

Fig. 2. A primitive coronoid divided into four units

It seems best to illustrate this general algorithm by an example. In Fig. 2a primitive coronoid (C) is divided (arbitrarily) into four units: u_1, u_2, u_3, and u_4. If the units are compressed by A or L hexagons according to the pattern of Fig. 2, then

$$K\{C\} = \mathrm{Tr}(\mathbf{u}_1\mathbf{j}\mathbf{u}_2\mathbf{j}\mathbf{u}_3\mathbf{u}_4) + 1 + (-1)^S. \tag{32}$$

Here $\mathbf{j}$ is the matrix given by Eq. (12). Any cyclic permutation of the factors in the matrix product of (32) will work, and also the reversing of the factors. One has

$$\mathrm{Tr}(\mathbf{u}_1\mathbf{j}\mathbf{u}_2\mathbf{j}\mathbf{u}_3\mathbf{u}_4) = \mathrm{Tr}(\mathbf{j}\mathbf{u}_2\mathbf{j}\mathbf{u}_3\mathbf{u}_4\mathbf{u}_1) = \cdots \text{etc.} \tag{33}$$

and also equal to

$$\mathrm{Tr}(\mathbf{u}_4\mathbf{u}_3\mathbf{j}\mathbf{u}_2\mathbf{j}\mathbf{u}_1) = \mathrm{Tr}(\mathbf{u}_1\mathbf{u}_4\mathbf{u}_3\mathbf{j}\mathbf{u}_2\mathbf{j}) = \cdots \text{etc.} \tag{34}$$

In the particular example of Fig. 2, the numerical values are:

$$\mathbf{u}_1 = \begin{bmatrix} 3 & 2 \\ 2 & 1 \end{bmatrix}, \quad \mathbf{u}_2 = \begin{bmatrix} 2 & 1 \\ 1 & 1 \end{bmatrix},$$

$$\mathbf{u}_3 = \begin{bmatrix} 5 & 3 \\ 3 & 2 \end{bmatrix}, \quad \mathbf{u}_4 = \begin{bmatrix} 4 & 1 \\ 1 & 0 \end{bmatrix}, \tag{35}$$

which yields, according to the alternative in Eq. (32):

$$K = \mathrm{Tr}\begin{bmatrix} 551 & 119 \\ 338 & 73 \end{bmatrix} + 2 = 626. \tag{36}$$

Assume now that n repeated units u (identical up to isoarithmicity) are linearly compressed in a circular arrangement, forming a primitive coronoid or primitive non-coronoid. Then, for the Kekulé structure count one has:

$$C^{(n)} = \mathrm{Tr}[(\mathbf{j}\mathbf{u})^n] + 1 + (-1)^S. \tag{37}$$

Polynomial Formulas (II)

Based on Eq. (37) a set of polynomials for $C^{(n)}$ may be derived in the same way as in the above treatment, but in some sense in a complementary way, as shall be seen from the below result.

It should be noticed that the pre-multiplication of $\mathbf{u}$ by $\mathbf{j}$ only interchanges the rows, i.e.

$$\mathbf{j}\mathbf{u} = \begin{bmatrix} u_2 & u_3 \\ u_0 & u_1 \end{bmatrix}. \tag{38}$$

Therefore, firstly: the variable (x) should now be

$$x = \mathrm{Tr}(\mathbf{j}\mathbf{u}) = u_1 + u_2. \tag{39}$$

Secondly:

$$\det(\mathbf{j}\mathbf{u}) = -\det(\mathbf{u}) = u_1 u_2 - u_0 u_3. \tag{40}$$

If we wish to use polynomials in the same form as they are given in Table 1, we must choose s so that

$$\det(\mathbf{ju}) = (-1)^s \tag{41}$$

in analogy with Eq. (13). Therefore, in the case of linear compression, s should be taken as the number of segments in u off by one (in either direction). In a less restrictive way, it is sufficient to put s equal to an even number for an odd number of segments in u and vice versa.

In conclusion: for n linearly compressed units u, each holding t segments, use the expressions of Table 1 for $C^{(n)}_{\text{even}}$ if t is odd and $C^{(n)}_{\text{odd}}$ if t is even. Insert the variable x according to Eq. (39).

Example

In Fig. 3 the same coronoid as in Fig. 1 is depicted, but with a linear rather than angular compression of units indicated. Now we choose

$$\text{u} = [2^4, 4, 2] \tag{42}$$

and consequently:

$$\begin{aligned} u_0 &= K\{[2^3, 4]\} = 23\,, \\ u_1 &= K\{[2^3, 3]\} = 18\,, \\ u_2 &= K\{[2^2, 4]\} = 14\,, \\ u_3 &= K\{[2^2, 3]\} = 11\,. \end{aligned} \tag{43}$$

In this case

$$\det(\mathbf{u}) = \begin{vmatrix} 23 & 18 \\ 14 & 11 \end{vmatrix} = 1 \tag{44}$$

in consistence with $t=6$. Hence we have to use the expression for $C^{(6)}_{\text{odd}}(x)$, where

$$x = \text{Tr}(\mathbf{ju}) = 18 + 14 = 32 \tag{45}$$

should be inserted. It is seen that the resulting K number is the same as in Eq. (31), as it should be.

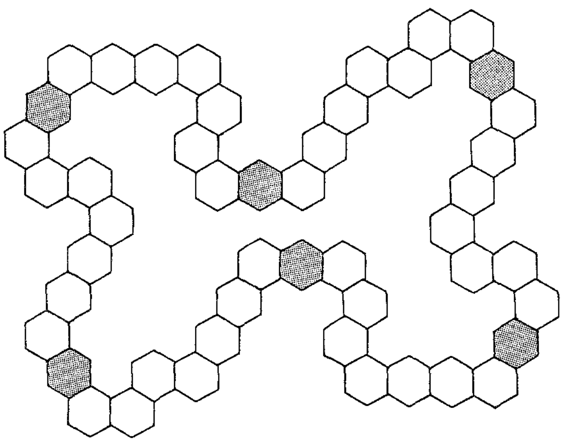

Fig. 3. A primitive coronoid of Fig. 1 with another separation into six repeated units

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