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Enumeration of Kekulé Structures for Some Coronoid Hydrocarbons: "Waffles"

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Summary. Primitive coronoids of hexagonal symmetry (D_{6h} or C_{6h}) are referred to as "waffles". Some theorems about unbranched catacondensed benzenoids are presented and used to derive a general combinatorial formula for the number of Kekulé structures (K) for waffles. The symmetry-adapted method of fragmentation is employed. Several K formulas for special classes of waffles are also reported.

Keywords. Kekulé structures, enumeration of; Coronoid; "Waffle".

Die Anzahl von Kekulé-Strukturen für einige aromatische Coronoid-Kohlenwasserstoffe: „Waffel-Strukturen"

Zusammenfassung. Einfache Coronoide von hexagonaler Symmetrie (D_{6h} oder C_{6h}) werden als „Waffel" bezeichnet. Einige Theoreme bezüglich unverzweigter catakondensierter Benzenoide werden angegeben und zur Ableitung einer generellen Formel für die Anzahl von Kekulé-Strukturen (K) für „Waffel" benutzt. Es wird die symmetrie-adaptierte Methode zur Fragmentierung angewendet. Außerdem werden einige K-Formeln für spezielle Klassen von „Waffeln" angegeben.

Introduction

A number of works on the topological properties of coronoids (for a definition, see below) have appeared during the last years. The recent work on circumkekulene homologs [1] may be consulted for references to previous works, and especially also for the relevance of these studies to organic chemistry. A new class of polycyclic aromatic hydrocarbons, which corresponds to coronoids, has been termed cycloarenes [2].

Several works have appeared on the enumeration of Kekulé structures for coronoids [1, 3–8], but there are still many problems to be solved in this area. In the present work we give a complete solution for the number of Kekulé structures (K) of primitive coronoids with hexagonal symmetry.

A coronoid [9] is a planar system of identical regular hexagons (like a benzenoid [10]), but not simply connected; it has a hole of a size of at least two hexagons. (Only single coronoids with exactly one hole are considered here.) Primitive coronoids, being the catacondensed unbranched systems, are the simplest ones among the coronoids. They consist of a single (circular) chain of hexagons. These hexagons occur only in two modes, linearly and angularly annelated (L and A, respectively).

Table 1. Numbers of primitive coronoids with hexagonal symmetry

h	D_{6h}	C_{6h}
12	1	0
18	2	0
24	2	1
30	5	2
36	5	8
42	12	19
48	13	55
54	31	138
60	33	373
66	80	957

The number of linear segments in a primitive coronoid is equal to the number of the A-mode hexagons. A segment is by definition the linear chain from an A-hexagon to the next A-hexagon, both A-hexagons inclusive.

The only combinatorial K formulas for primitive coronoids of hexagonal symmetry (D_{6h} and C_{6h}) so far available [3–5] concern the classes of systems with equidistant segments. Kekulene [2] is an example.

Another aspect of the studies of coronoids (and benzenoids) is their enumeration for given numbers of hexagons (h) and identification of the forms. This task is usually performed with the aid of computer programming. Primitive coronoids in general (regardless of symmetry) have been enumerated in this way for h values up to 20; see [11] and references cited therein. This does not help much for an effective study of the subsystems with hexagonal symmetry; among the totality of 10 527 nonisomorphic systems ($h \leqslant 20$) there are only 3 with hexagonal symmetry. Fortunately the means for specific generations of coronoids with hexagonal symmetry are available. The systems have been enumerated up to $h = 42$ [7]; notice that the h values for these systems (evidently) can only be multiples of 6. Table 1 shows the numbers of nonisomorphic primitve coronoids with hexagonal symmetry for $h \leqslant 66$. The actual forms for $h \leqslant 36$ are shown elsewhere [7].

For the sake of brevity we shall refer to primitive (single) coronoids of hexagonal symmetry as "waffles".

Results and Discussion

Introductory Remarks

The numbers of Kekulé structures, K, were found numerically in connection with the computer-generation of the waffles. A re-appearance of certain numbers was observed as a striking property. As an example among D_{6h} systems we show five waffles with the same K number; see Fig. 1. This feature is immediately understood for the two bottom systems, which are said to be isoarithmic [12]. Two isoarithmic waffles have the same sequence of segments, which only are kinked in different ways. It is known that this does not affect the number of Kekulé structures. In

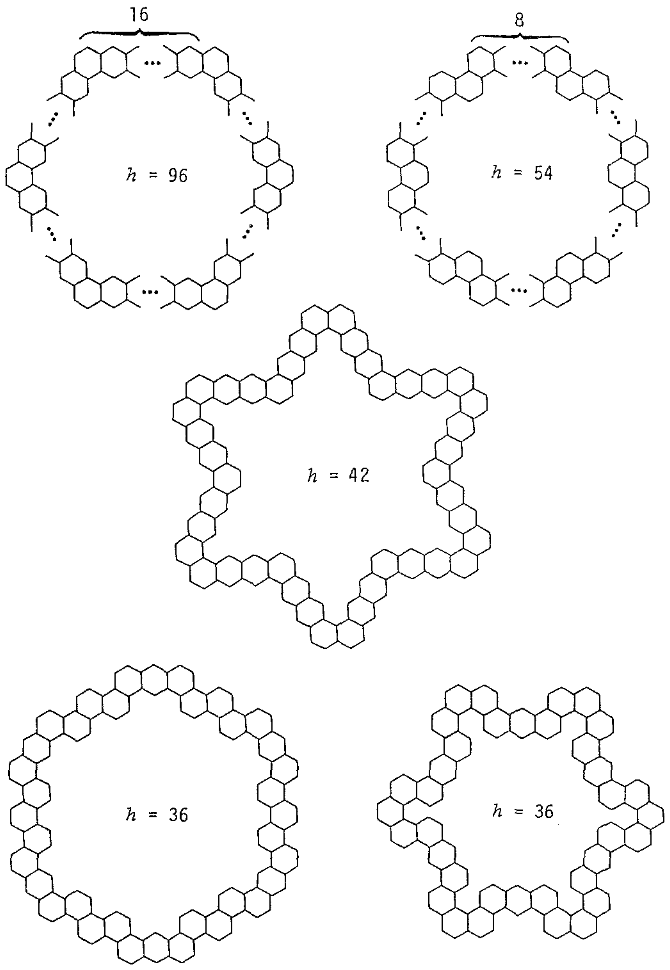


Fig. 1. Five waffles which all have $K = 17172740$. Only the two bottom systems are isoarithmic

our example (Fig. 1) the two isoarithmic waffles have both the segments of the lengths 2, 2, 2, 2, 3 (in terms of the number of hexagons) in the given order and repeated six times. We symbolize this sequence by $/2,2,2,2,3/^6$ or $/2^4,3/^6$. However, Fig. 1 shows forms of different shapes and sizes with the same K, but not (genuinely) isoarithmic. One may speak about accidental isoarithmicity. This puzzling phenomenon was explained in the present work, as is reported in the subsequent sections.

Combinatorial K Formulas for Some Special Classes of Waffles

In Fig. 2 some classes of waffles are defined. Only the portions between two symmetrically equivalent, angularly annelated, hexagons are drawn.

Let the number of hexagons be

$$h = 6\eta; \qquad \eta = 1, 2, 3, \ldots . \tag{1}$$

Here $\eta = 1$ corresponds to a degenerate case represented by coronene, which is a pericondensed benzenoid rather than a primitive coronoid.

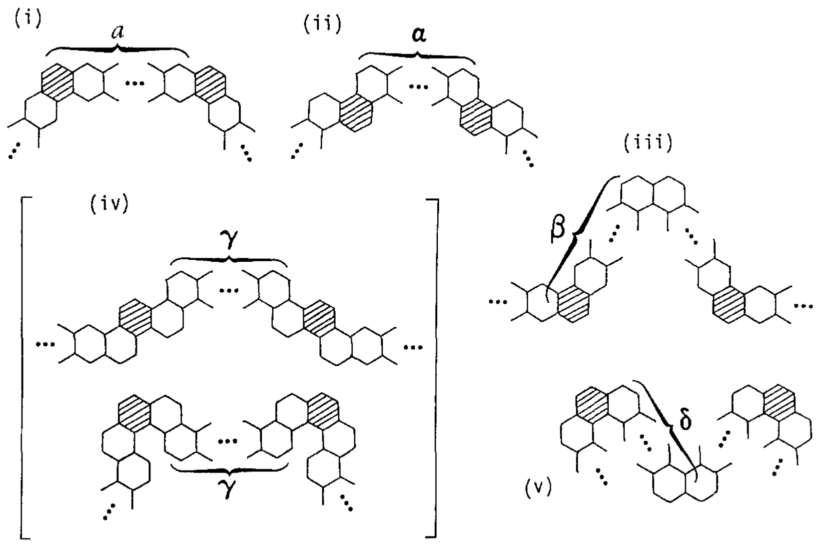


Fig. 2. Classes of waffles. The bracketed systems are isoarithmic

The systems of Fig. 2 were analyzed by the symmetry-adapted method of fragmentation [1, 7, 8, 13], which led to the following combinatorial formulas for the K numbers:

$$\text{(i)} \qquad K = (a^2 + 1)^2 (a^2 + 4); \qquad a = \eta; \qquad \eta = 1, 2, 3, \ldots, \tag{2}$$

where $a = 1$ corresponds to the degenerate case of coronene ($K = 20$). Eq. (2) is consistent with the previous findings [3–5], while the subsequent results are new.

$$\text{(ii)} \qquad K = 4(4a^2 + 1)^2 (a^2 + 1); \qquad a = \eta - 1; \qquad \eta = 2, 3, 4, \ldots, \tag{3}$$

where the system degenerates to kekulene ($K = 200$) for $a = 1$.

$$\text{(iii)} \qquad K = (\beta^4 + 1)^2 (\beta^4 + 4); \qquad \beta = \frac{1}{2}(\eta + 1); \quad \eta = 1, 3, 5, \ldots, \tag{4}$$

where the system with $\beta = 1$ is the degenerate case of coronene.

$$\text{(iv)} \quad K = 5(25\gamma^2 + 10\gamma + 2)^2 (5\gamma^2 + 2\gamma + 1); \quad \gamma = \eta - 3; \quad \eta = 3, 4, 5, \ldots, \tag{5}$$

where the cases of $\gamma = 0$ ($K = 20$) and $\gamma = 1$ ($K = 54\,760$) are degenerate.

$$\text{(v)} \qquad K = 4(2\delta^4 + 4\delta^3 - 2\delta + 1)^2 (4\delta^4 + 8\delta^3 - 4\delta + 5);$$
$$\delta = \frac{1}{2}(\eta - 1); \qquad \eta = 1, 3, 5, \ldots, \tag{6}$$

where $\delta = 0$ ($K = 20$) and $\delta = 1$ ($K = 1\,300$) are degenerate cases.

Generalization of the Combinatorial Formulas

A closer inspection of Eqs. (2)–(6) revealed that they may all be adapted to the general form

$$K = (x^2 + 1)^2 (x^2 + 4) = x^6 + 6x^4 + 9x^2 + 4. \tag{7}$$

In the five cases one has specifically:

$$x = a\,, \tag{8}$$

$$x = 2a\,, \tag{9}$$

$$x = \beta^2\,, \tag{10}$$

$$x = 5\gamma + 1\,, \tag{11}$$

$$x = 2\delta^2 + 2\delta - 1\,. \tag{12}$$

This feature explains the occurrence of accidental degeneracy (see above). But Eq. (7) is more powerful than that. In the following we shall prove that any waffle has a K number which fits the form (7) with integer x. The possible values are $x = 1, 2, 3, \ldots$ when coronene ($x = 1$) is included.

In order to achieve this goal, which amounts to the derivation of a suitable form of a general formula for the K number of a waffle, we shall need some auxiliary results for unbranched catacondensed benzenoids (single chains).

Some Theorems for Single Chains

Assume a single (unbranched) chain, U, with N linear segments. The segments are defined (as in the coronoids) so that they share A-mode hexagons.

Define u_0 by deleting both end hexagons, u_1 and u_2 by deleting one end hexagon and one end segment in the two ways, and finally u_3 by deleting the two end segments.

Let the K numbers be denoted by $U = K\{\mathrm{U}\}$ and $u_i = K\{u_i\}$ $(i = 0, 1, 2, 3)$.

The definition is applicable to all cases with $N > 1$ if we allow for the deleting of all hexagons, in which case $K = 1$.

Theorem 1.

$$U = u_0 + u_1 + u_2 + u_3\,. \tag{13}$$

This relation is a straightforward result from the well-known method of fragmentation [14] for deducing K numbers.

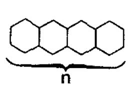
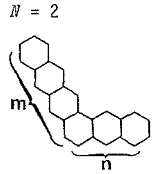
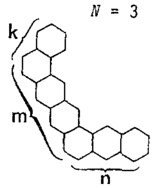
Number of segments / K number	$N = 1$ 	$N = 2$ 	$N = 3$ 
U	$n + 1$	$mn + 1$	$kmn - kn + k + n$
u_0	$n - 1$	$mn - (m + n) + 2$	$kmn - (k + n)m - kn + 2(k + n) + m - 3$
u_1	1	$m - 1$	$km - k - m + 2$
u_2	1	$n - 1$	$mn - m - n + 2$
u_3	0	1	$m - 1$

Fig. 3. K numbers for the single chains of one, two and three segments and their fragments with relevance to the stated theorems

Theorem 2.

$$\begin{vmatrix} u_0 & u_1 \\ u_2 & u_3 \end{vmatrix} = (-1)^N. \quad (14)$$

Proof. In order to prove this theorem we start with $N=2$ and $N=3$. Combinatorial K formulas for such systems are well known [12, 15–17]; they are listed in Fig. 3 for all the systems which are involved in the theorems. By elementary computations both theorems are easily verified for these N values. In particular, when expanding Eq. (14), we find that all parameters (k, m, n) vanish, and the result becomes $+1$ for $N=2$ and -1 for $N=3$. Figure 3 includes the pertinent quantities for $N=1$, which involve degenerate cases and are defined so that they fit into the system.

The rest of this proof is conducted by complete induction. Assume that Theorem 2 holds for a single chain U with N segments. The upper part of Fig. 4 gives an illustration of u_0, u_1, u_2 and u_3 supplied by K values. The indicated systems are the

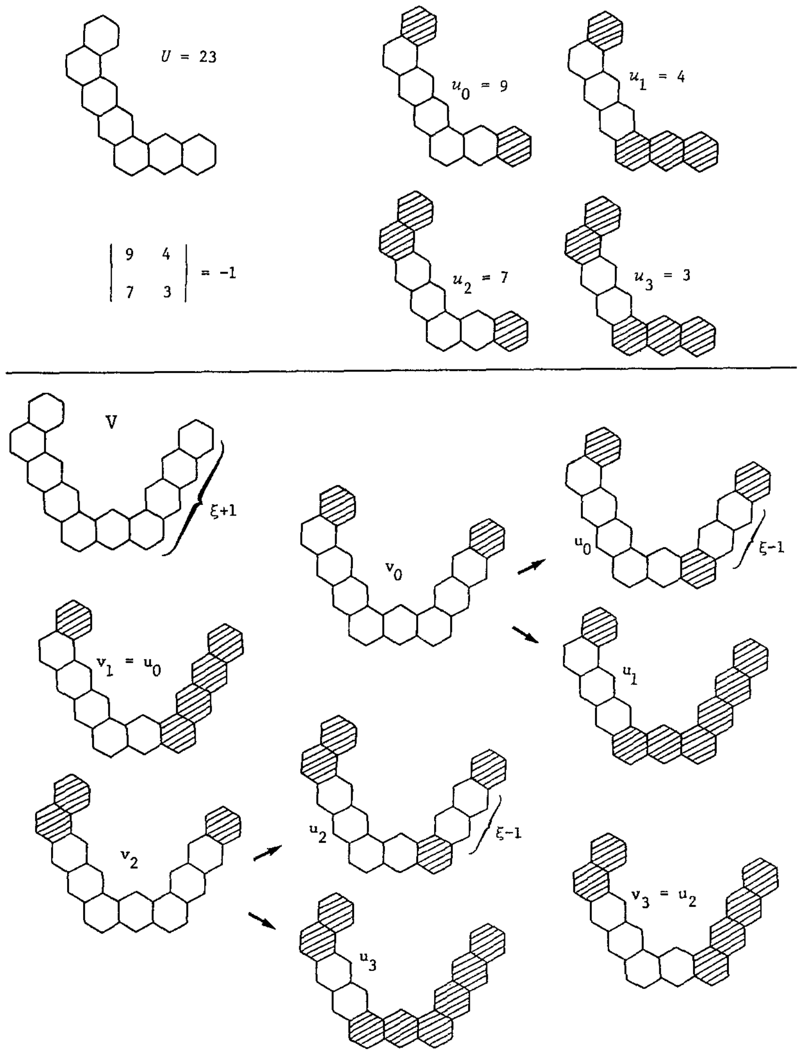


Fig. 4. Illustration to the Proof of Theorem 2

unhatched parts of the drawings. Let the system U be augmented by one segment of $\xi + 1$ hexagons as indicated in Fig. 4, and denote the new system of $N+1$ segments by V. One has for the corresponding fragments:

$$v_0 = \xi u_0 + u_1, \tag{15}$$

$$v_1 = u_0, \tag{16}$$

$$v_2 = \xi u_2 + u_3, \tag{17}$$

$$v_3 = u_2. \tag{18}$$

The relations (15) and (17) were obtained by the method of fragmentation [14]. From (15)–(18) one obtains readily

$$v_0 v_3 - v_1 v_2 = u_1 u_2 - u_0 u_3, \tag{19}$$

where the quantity ξ has cancelled out. Hence

$$\begin{vmatrix} v_0 & v_1 \\ v_2 & v_3 \end{vmatrix} = - \begin{vmatrix} u_0 & u_1 \\ u_2 & u_3 \end{vmatrix} = (-1)^{N+1}, \tag{20}$$

which completes the proof.

Theorem 2 seems to be an interesting result in itself, not only for the subsequent application to waffles. We give one more theorem for the quantities considered.

Let U′ be a single chain consisting of a cyclic permutation of the segments of the single chain U. Define the matrices

$$\mathrm{U} = \begin{bmatrix} u_0 & u_1 \\ u_2 & u_3 \end{bmatrix}, \qquad \mathrm{U}' = \begin{bmatrix} u_0' & u_1' \\ u_2' & u_3' \end{bmatrix}, \tag{21}$$

where the elements are the K numbers of the fragments according to the above definitions. Then the trace and determinant of the matrix is invariant with respect to the permutation:

Theorem 3.

$$\mathrm{Tr}(\mathrm{U}') = \mathrm{Tr}(\mathrm{U}), \qquad \det(\mathrm{U}') = \det(\mathrm{U}). \tag{22}$$

Proof. In order to prove this theorem assume that U is given in terms of segments by $/s_0, s_1, \ldots, s_\omega/$, while U′ is $/s_1, s_2, \ldots, s_\omega, s_0/$. If $s_0 = \xi + 1$ as the number of hexagons in this particular segment, then

$$u_0 = \xi u_1' + u_3', \tag{23}$$

$$u_0' = \xi u_2 + u_3, \tag{24}$$

$$u_1' = u_2. \tag{25}$$

These relations were deduced in the same way as under the proof of Theorem 2. On eliminating u_2 from (23)–(25) also ξ vanishes, and one obtains

$$u_0 + u_3 = u_0' + u_3', \tag{26}$$

which is equivalent to the first part of (22).

The second part of (22) is obvious since both sides of the sign of equality, in accord with Theorem 2, are equal to $(-1)^N$, where N is the same number.

This completes the proof of Theorem 3.

General Combinatorial K Formula for Waffles

Consider a waffle, W, and select six angularly annelated (A) hexagons which are symmetrically equivalent and may be generated by rotations of 60°. The symmetry-adapted method of fragmentation (see above) is to be applied to the free edges of the A hexagons, i.e. the edges between vertices of second degree. Since there are no restrictions on the possibilities for single and double bonds associated with these edges we must take thirteen bonding schemes into account (rather than five [1, 7, 8, 13]); cf. Fig. 5. Let U be the single chain between two neighbouring A hexagons inclusive, and define u_0, u_1, u_2 and u_3 as the K numbers of the fragments as explained in the preceding section. The contributions to the number of Kekulé structures (K) of W from the different bonding schemes were computed with the following result:

$$k_0 = u_0^6 + u_3^6, \tag{27}$$

$$k_1 = (u_0^4 + u_3^4)\, u_1 u_2, \tag{28}$$

$$k_2 = u_0 u_1 u_2 u_3 (u_0^2 + u_3^2), \tag{29}$$

$$k_3 = k_4 = (u_0^2 + u_3^2)(u_1 u_2)^2, \tag{30}$$

$$k_5 = (u_0 u_3)^2 u_1 u_2, \tag{31}$$

$$k_6 = (u_1 u_2)^3 + 1, \tag{32}$$

$$k_7 = u_0 u_3 (u_1 u_2)^2. \tag{33}$$

Taking into account the multiplicity for each bonding scheme (cf. Fig. 5) the total K number is found as

$$K = k_0 + 6k_1 + 6k_2 + 6k_3 + 3k_4 + 6k_5 + 2k_6 + 12k_7. \tag{34}$$

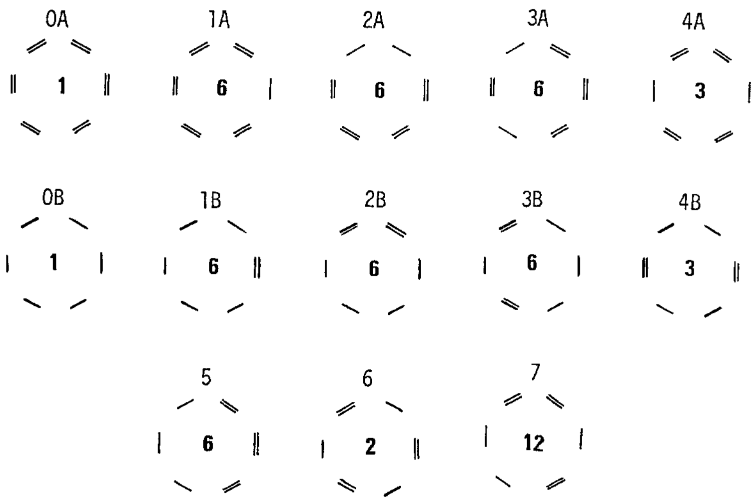


Fig. 5. The thirteen bonding schemes of the symmetry-adapted method of fragmentation. Multiplicities are indicated

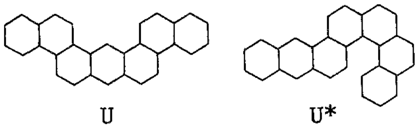


Fig. 6. The single chain between two symmetrically equivalent A hexagons for the bottom-right waffle of Fig. 1, chosen in two different ways

On inserting the expressions (27)–(33) into (34) it was attained at

$$K = u_0^6 + u_3^6 + 6(u_0^4 + u_0^3 u_3 + u_0^2 u_3^2 + u_0 u_3^3 + u_3^4) u_1 u_2 + 3(3u_0^2 + 4u_0 u_3 + 3u_3^2)(u_1 u_2)^2 + 2(u_1 u_2)^3 + 2 . \quad (35)$$

As an example, consider the bottom-right waffle of Fig. 1. Figure 6 shows two different choices of the single chain between A hexagons, viz. U and U*. The corresponding K numbers of fragments are $u_0 = 12$, $u_1 = u_2 = 7$, $u_3 = 4$ and $u_0^* = 13$, $u_1^* = 5$, $u_2^* = 8$, $u_3^* = 3$, respectively. Each set, when inserted into (35), yields $K = 17172740$.

The number of segments in W is obviously a multiple of six. Therefore the number of segments in U as defined in this section must be odd, and by virtue of Theorem 2 one has

$$u_1 u_2 = u_0 u_3 + 1 . \quad (36)$$

With the aid of this substitution Eq. (35) was reduced to the following form by elementary computations,

$$K = (u_0 + u_3)^6 + 6(u_0 + u_3)^4 + 9(u_0 + u_3)^2 + 4 . \quad (37)$$

A cyclic permutation of the segments in U should not affect the K number of W. The fact that $u_0 + u_3$ is invariant with respect to such permutations is actually expressed by Theorem 3. Figure 6 shows an example of two single chains, U and U*, which only differ by a cyclic permutation of the segments. In accord with the theory one has $u_0 + u_3 = u_0^* + u_3^* = 16$. On inserting $u_0 + u_3 = 16$ into Eq. (37) one obtains again $K = 17172740$.

On comparing Eq. (37) with (7) it is proved that the general form (7) always is sound, and the integer x is identified by

$$x = u_0 + u_3 . \quad (38)$$

Systematic Special Combinatorial K Formulas for Waffles

Here we outline a systematic approach to the K formulas for classes of waffles.

Equations (2) and (8) apply to the class of waffles with one segment of $a + 1$ hexagons in U. A member of this class is to be designated $/a + 1/^6$.

Correspondingly $/a + 1, b + 1, c + 1/^6$ symbolizes a waffle with three segments in U. For this class it was derived, as a special case of (38):

$$x = abc + a + b + c . \quad (39)$$

In the two examples of members of this class which are found in Fig. 1, the parameters are $a = c = 1$, $b = 7$ and $a = c = 3$, $b = 1$, respectively. In both cases $x = 16$, leading to the correct K number when inserted into (7).

An extension to five segments in U, viz. $/a + 1, b + 1, c + 1, d + 1, e + 1/^6$, yields

$$x = abcde + abc + bcd + cde + dea + eab + a + b + c + d + e . \quad (40)$$

The K number of the two (isoarithmic) representatives of this class in Fig. 1 is correctly reproduced by inserting $a = b = d = e = 1$, $c = 2$, which again gives $x = 16$.

In this systematic approach a definite pattern of the expressions for x is recognized.

Conclusion

The problem of Kekulé structure counts for primitive coronoids with hexagonal symmetry ("waffles") is considered as completely solved in the present work. A corresponding analysis of primitive coronoids with trigonal symmetry is in progress. In this connection it is relevant to mention the extensive attempts to synthesize the next-smallest primitive coronoid or cycloarene [18], which has $h = 9$ and trigonal symmetry.

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