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The Number of Kekulé Structures for Rectangle-Shaped Benzenoids, Part VIII: Some Perforated Rectangles

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Summary. Classes of coronoids (or degenerate coronoids), r and q are obtained by providing the rectangle-shaped benzenoids $R^j(m, 3)$ with a naphthalenic or pyrenic hole, respectively. The numbers of Kekulé structures (K) are studied. It was found for the K numbers of the classes in question: $r = 4/5\,R$ and $q = 1/5\,R$. The classes r′ and q′ are similar to r and q, respectively, but the naphthalenic or pyrenic hole is oriented in a different way. For these classes it was found: $r' = 3/5\,R$, $q' = 2/5\,R$.

Keywords. Benzenoids; Coronoids; Kekulé structures.

Die Anzahl von Kekulé-Strukturen für hochkondensierte Benzenoide mit rechteckigem Umriß, 8. Mitt.: Einige perforierte benzenoide Rechteck-Strukturen

Zusammenfassung. Es werden Klassen r und q von Coronoiden (oder degenerierten Coronoiden) erhalten, wobei Benzenoide mit rechteckigem Umriß, $R^j(m, 3)$, mit einem Naphthalin- oder Pyren-Loch versehen werden. Die Anzahl von Kekulé-Strukturen (K) wird untersucht; dabei wurde für die untersuchten Klassen $r = 4/5\,R$ und $q = 1/5\,R$ gefunden. Die Klassen r′ und q′ verhalten sich ähnlich, das Naphthalin- oder Pyren-Loch ist jedoch anders orientiert; dafür wurde $r' = 3/5\,R$ und $q' = 2/5\,R$ gefunden.

Introduction

A benzenoid [1, 2] is a planar system of congruent regular hexagons. The benzenoid systems have obvious chemical counterparts in benzenoids hydrocarbons. The Kekulé structures of such systems and especially their numbers (or Kekulé structure counts, K), have been studied intensively. Reference is made to a series of papers of this Journal [3–10] and to the monograph of Cyvin and Gutman [2] with the bibliography therein.

Much less work on the Kekulé structures of coronoid systems [11] is available. A coronoid is, loosely speaking, a benzenoid with a hole. The size of the hole, which is referred to as the corona hole, should not be smaller than two hexagons. Also coronoids have obvious counterparts in conjugated hydrocarbons. The most famous example is $C_{48}H_{24}$ kekulene [12, 13]. Most of the combinatorial K formulas for coronoids pertain to classes of catacondensed systems (i.e. those without internal vertices). Otherwise some K formulas for classes of half essentially disconnected coronoids [14] have been published [15, 16]; the members of these classes are characterized by having only single isolated internal vertices. For classes of regular pericondensed coronoids only two K formulas have been published so far [15, 17], both of them pertaining to systems of the regular hexagonal symmetry.

The aim of the present work was to increase our knowledge of Kekulé structures for pericondensed coronoids. Pericondensed systems are those which possess internal vertices. Many classes of pericondensed benzenoids have been studied with respect to their Kekulé structure counts, and especially the classes of oblate rectangles, $R^j(m, n)$. Most of the findings are summarized in Chapter 12 of the abovementioned monograph [2]. In the present work we concentrated on the oblate rectangles [2, 18–20] with $n = 3$, provided with a naphthalenic (2-hexagon) hole in one of the four-hexagon rows. Some surprising features were detected during these studies.

Fig. 1 shows the coronoid systems obtained by perforating the seven-tier oblate rectangle $R^j(4, 3)$ with a naphthalenic hole in different positions. It was observed that the position of the corona hole is immaterial for the Kekulé structure count. Of course the left- and right-hand systems of Fig. 1 are isomorphic (identical), but the identical K number is not at all trivial for the middle system. The actual K number, viz. 6800 was found to be 4/5 of the Kekulé structure count for the (compact) rectangle, viz. $K\{R^j(4, 3)\} = 8500$.

The naphthalenic holes may be extended to pyrenic (4-hexagon) holes as shown in Fig. 2. Again we find the same K number for the coronoid (or degenerate coronoid) systems. In the present example it is 1700 or 1/5 of $K\{R^j(4, 3)\}$.

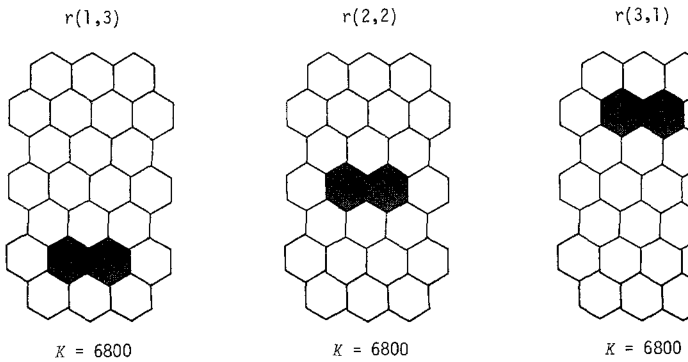

Fig. 1. Members of the class r of coronoids (the left and right system are isomorphic); Kekulé structure counts (K) are indicated

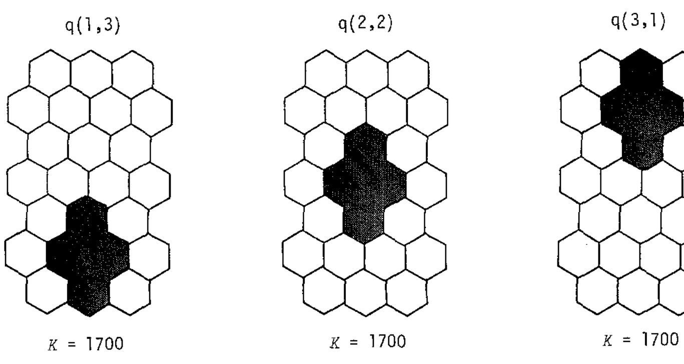

Fig. 2. Members of the class q (coronoid in the middle, isomorphic degenerate coronoids at left and right); Kekulé structure counts (K) are indicated

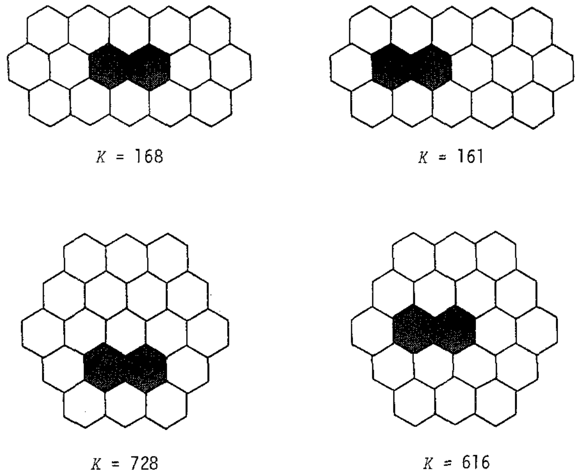

Fig. 3. Two pairs of coronoid systems; K numbers are given

It seems not to be a trivial matter to generalize the observed features. They were unexpected inasmuch as it is not difficult to find examples of coronoids where the position of the hole does matter for the K number. Fig. 3 shows two examples.

Results and Discussion

Definitions of Coronoid Classes

In Fig. 4 the two main coronoid classes under consideration, r and q, are defined. The parameters s and t should have positive integer values. The members of r are coronoids for all $s, t \geqslant 1$, while q are coronoids for $s, t \geqslant 2$. We shall also allow for the degenerate coronoid systems q when $s = 1$ or $t = 1$, viz. q$(1, t)$ and q$(s, 1)$; cf. Fig. 2.

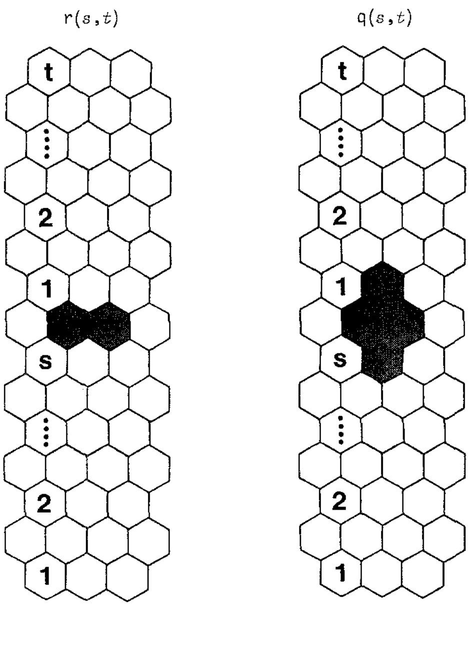

Fig. 4. Definition of the classes r and q

We introduce the following abbreviations for the Kekulé structure counts of the members from r and q,

$$K\{\mathrm{r}(s,t)\} = r(s,t), \tag{1}$$

$$K\{\mathrm{q}(s,t)\} = q(s,t). \tag{2}$$

It is clear that $\mathrm{r}(t, s)$ is isomorphic with $\mathrm{r}(s, t)$, and also that $\mathrm{q}(t, s)$ and $\mathrm{q}(s, t)$ are isomorphic; see Figs. 1 and 2 for examples. Therefore

$$r(t,s) = r(s,t), \qquad q(t,s) = q(s,t). \tag{3}$$

The compact oblate rectangle corresponding to r or q when the hole is filled up, is $\mathrm{R}^{\mathrm{j}}(m, n)$, where $m = s + t$ and $n = 3$. Adhering to the previous notation [2, 21] we write its Kekulé structure count

$$K\{\mathrm{R}^{\mathrm{j}}(s+t, 3)\} = R_3(s+t). \tag{4}$$

Introductory Examples

Ovalene (see Fig. 5) is a hexagon-shaped benzenoid [7], but may as well be interpreted as an oblate rectangle with $m = 2$ and $n = 3$. Its K number is known to be $R_3(2) = 50$. In consistence with the information in Fig. 5 we have

$$R_3(2) = r(1,1) + q(1,1), \tag{5}$$

where

$$r(1,1) = \frac{4}{5}R_3(2), \qquad q(1,1) = \frac{1}{5}R_3(2). \tag{6}$$

This result is easily obtained by the method of fragmentation, which was formulated by Randić [22]. It was employed throughout the present work. In order to derive the results of Fig. 5 the middle bond of ovalene is attacked, assuming that it is single or double, successively.

An even simpler example of systems with K numbers in the ratio 5 : 4 : 1 (actually equal to 5, 4 and 1) is furnished by Fig. 6. Here the method of fragmentation was

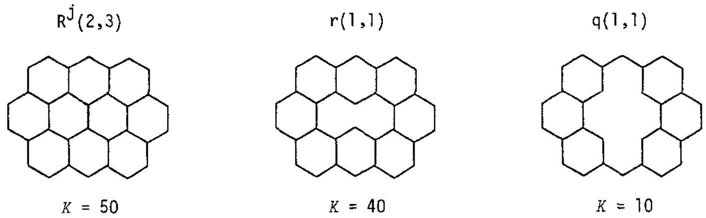

Fig. 5. Three systems with K numbers in the ratio 5 : 4 : 1

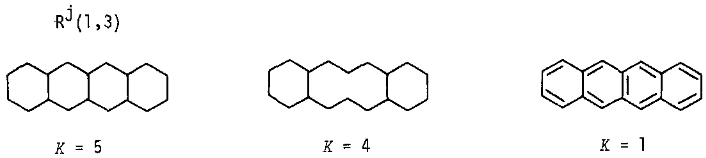

Fig. 6. Three systems with K numbers 5, 4 and 1

applied to naphthacene, which is the degenerate oblate rectangle for $m = 1$ (and $n = 3$). In this case, however, the two fragments can not be identified with members of the classes r and q because $s + t = 1$ has no solution with $s, t \geqslant 1$.

The Main Result

Theorem.

$$r(s,t) = \frac{4}{5} R_3(s+t), \qquad q(s,t) = \frac{1}{5} R_3(s+t). \tag{7}$$

Here it is implied that the K numbers of r and q systems only depend on the sum $s + t$, not the individual values of s and t. That means, in other words, that the hole can be placed in the middle of an arbitrary four-membered row of the rectangle.

It is sufficient to prove one of the equations in (7), since one has

$$R_3(s+t) = r(s,t) + q(s,t). \tag{8}$$

This relation is easily deduced by the method of fragmentation as exemplified in Fig. 5.

The Case of $s = 1$

Let the method of fragmentation be applied to q (1, t) as shown in Fig. 7; the thick arrows indicate the edges to be attacked and assigned to double and single bonds. Thus the system is broken down to known fragments: L (1) is benzene, while B (3, 2 t − 2, 1) and B (3, 2 t − 2, − 1) are members of the well studied and exploited auxiliary benzenoid classes associated with rectangles [2, 10, 19–21, 23–26]. In analytical form the result of this fragmentation scheme is

$$q(1,t) = 2p(1,t), \tag{9}$$

where

$$p(1,t) = 2R_3^{(1)}(t) + R_3^{(-1)}(t), \tag{10}$$

when it is adhered to the previous notation [2, 21].

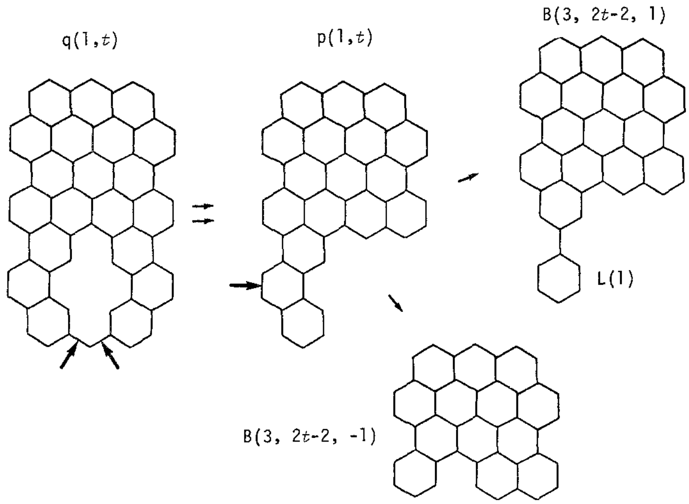

Fig. 7. The method of fragmentation applied to q (1, t); in the depicted example, $t = 3$

With reference to Chapter 12 of [2] (see pp. 214–215 therein) one has

$$R_3^{(1)}(t) = \frac{1}{2} L_t \tag{11}$$

and

$$R_3^{(-1)}(t) = P_{t-1} = 5L_{t-1} - \frac{25}{2} L_{t-2}, \qquad t > 2. \tag{12}$$

Here L_t is used to denote the Kekulé structure count of the rectangle $\mathrm{R}^j(t, 3)$, viz.

$$R_3(t) = L_t. \tag{13}$$

By means of the recurrence relation [2, 19, 27]

$$L_t = 15\,L_{t-1} - 25\,L_{t-2}, \qquad t > 2, \tag{14}$$

we render Eq. (12) into the form

$$R_3^{(-1)}(t) = \frac{1}{2} L_t - \frac{5}{2} L_{t-1}, \qquad t > 1. \tag{15}$$

On inserting (11) and (15) into (10) and subsequently into (9) it is obtained that

$$q(1, t) = 3\,L_t - 5\,L_{t-1}. \qquad t > 1. \tag{16}$$

The recurrence relation (14) is equivalent to

$$L_{t+1} = 15\,L_t - 25\,L_{t-1}, \qquad t > 1. \tag{17}$$

On combining (16) and (17) it is finally obtained that

$$q(1, t) = \frac{1}{5} L_{t+1} \tag{18}$$

which proves the theorem (7) for $s = 1$.

The Case of $s = 2$

The scheme of fragmentation applied to $q(2, t)$ is shown in Fig. 8. Among the smaller fragments L(2) naphthalene, A(3) phenanthrene and two additional single chains are encountered. In the two last cases the systems are supplied with algorithm numerals [2, 28]; the sum of the numerals is the K number for the appropriate single chain. In the analytical form we have

$$q(2, t) = q'(2, t) + q''(2, t), \tag{19}$$

where

$$q'(2, t) = 2\,p'(2, t), \qquad q''(2, t) = 2\,p''(2, t). \tag{20}$$

Furthermore,

$$p'(2, t) = 5\,R_3^{(1)}(t) + 3\,R_3^{(-1)}(t). \tag{21}$$

On inserting from (11) and (15) this yields

$$p'(2, t) = 4\,L_t - \frac{15}{2} L_{t-1}, \qquad t > 1. \tag{22}$$

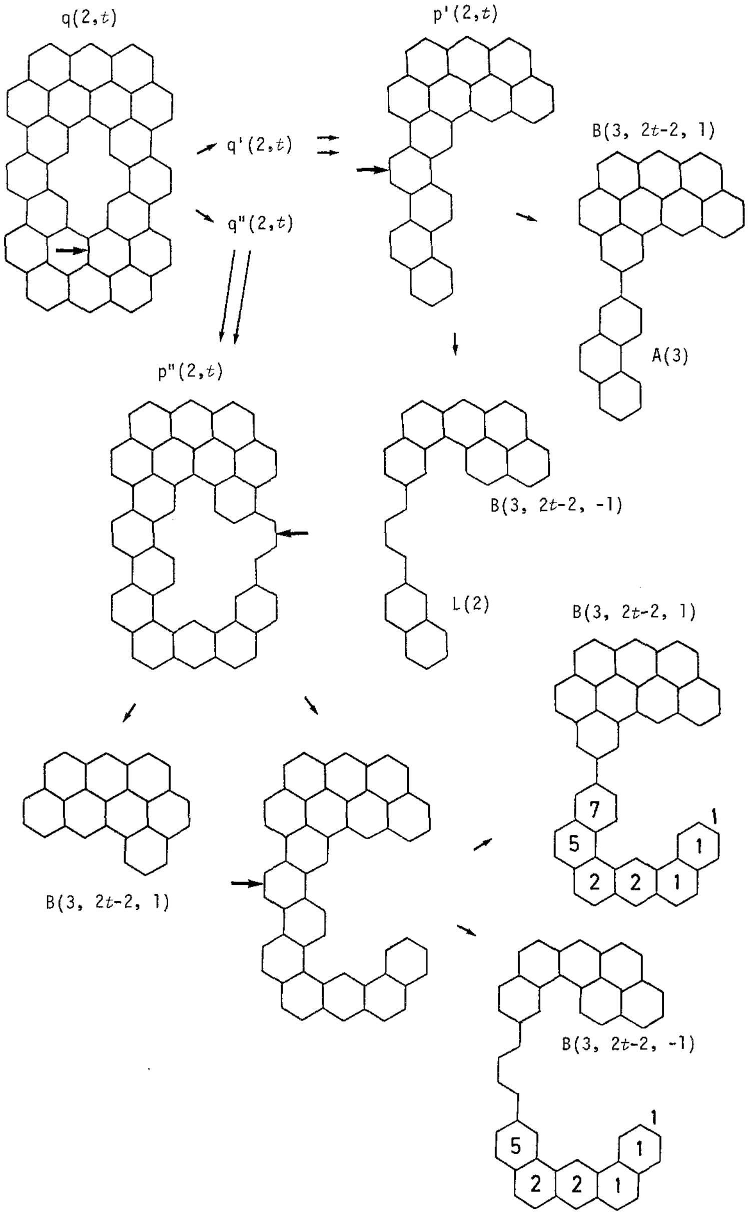

Fig. 8. The method of fragmentation applied to q(2, t); in the depicted example, $t = 2$

On the other hand we have

$$p''(2, t) = R_3^{(1)}(t) + 19\, R_3^{(1)}(t) + 12\, R_3^{(-1)}(t) = 16 L_t - 30\, L_{t-1}, \qquad t > 0. \tag{23}$$

On inserting from (22) and (23) into (20) and subsequently into (19) one obtains

$$q(2, t) = 40\, L_t - 75\, L_{t-1}, \qquad t > 1. \tag{24}$$

Finally by means of the recurrence relations of the form (14) or (17),

$$q(2, t) = 3\, L_{t+1} - 5\, L_t = \frac{1}{5} L_{t+2}. \tag{25}$$

Hence the theorem (7) is also proved for $s = 2$.

The Case of $s = 3$

The procedure applied to the cases $s = 1$ and $s = 2$ above may be extended to higher s values, but the number of fragments increases and the procedure becomes more and more complicated. Still it seems instructive to summarize the application to $s = 3$. Similarly to the preceding case we start with

$$q(3, t) = q'(3, t) + q''(3, t). \tag{26}$$

Altogether we ended up with the nine fragments as shown in Fig. 9, all of them to be taken twice. The "small" fragments now amount to benzenoids with up to thirteen hexagons. Fig. 9 indicates the K numbers of these small fragments, i.e.

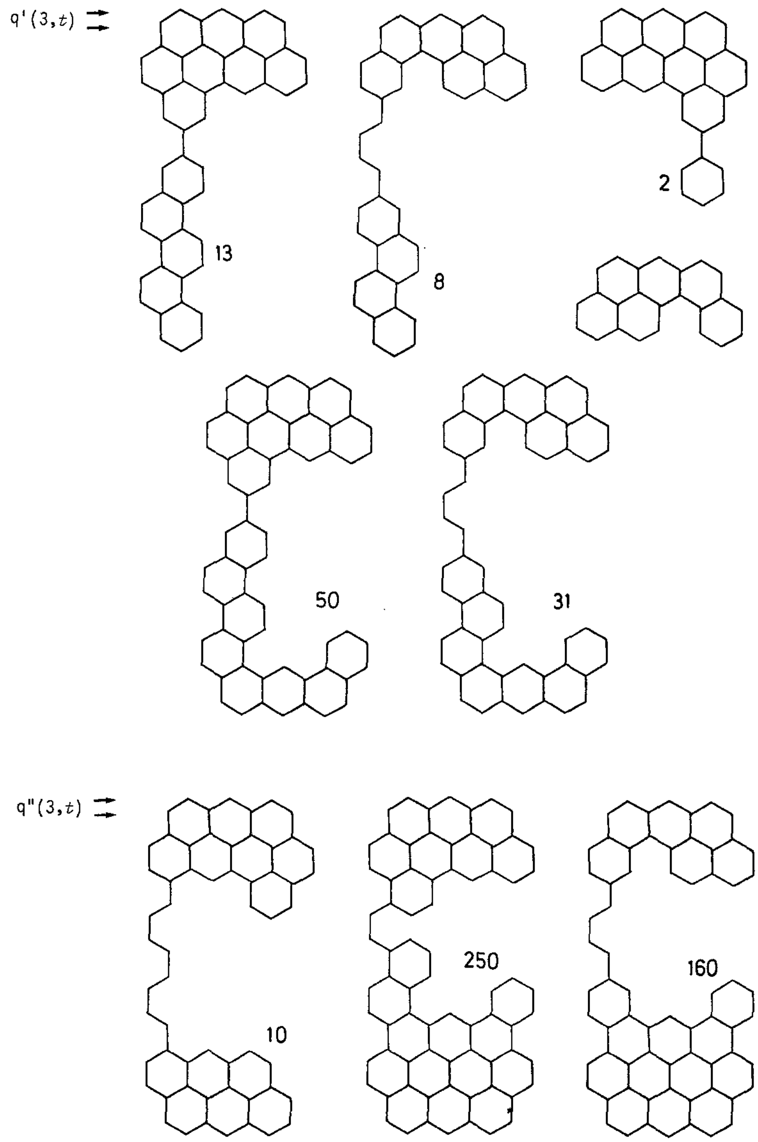

Fig. 9. Fragments obtained from the fragmentation of q(3, t); in this figure, $t = 2$

those different from B (3, $2t-2$, 1) and B (3, $2t-2$, -1). The net analytical results is:

$$q(3,t) = 2(13+2+50+10+250)R_3^{(1)}(t) + 2(8+1+31+160)R_3^{(-1)}(t)$$
$$= 525L_t - 1\,000L_{t-1}, \qquad t>1. \tag{27}$$

Furthermore,

$$q(3,t) = 40L_{t+1} - 75L_t = 3L_{t+1} - 5L_{t+1} = \frac{1}{5}L_{t+3}. \tag{28}$$

General Case

Now we have proved the theorem (7) for $s = 1, 2, 3$. Table 1 shows some numerical values of Kekulé structure counts for members of the r and q classes. The entries form a symmetrical matrix. It is also clear that all sets of r and q numbers (for fixed s values) obey the recurrence relation of the form (14).

The above procedure is not amenable for a generalization to arbitrary s. In order to prove our theorem in general we found a different approach employing the repeated application of the fragmentation method referred to as chopping [2, 10].

The method of chopping has especially been applied to oblate rectangles [2, 19, 20]. Fig. 10 (left column) exemplifies a chopping of R^j (4, 3); see in particular p. 219 of Ref. [2]. The four fragments are shown as obtained from the chopping along the row which is indicated by thick arrows. The right-hand column shows the fragments obtained from the corresponding chopping of r (2, 2). It is observed (see Fig. 10) that the K numbers of each pair of corresponding fragments exhibit the ratio 5:4. We shall find that this property is quite general, thus proving the theorem (7).

The analytical expression corresponding to the chopping of an oblate rectangle reads [2, 19, 20]

$$R_n(s+t) = \sum_{i=0}^{n} R_n^{(-i)}(s+1)\,R_n^{(-i)}(t), \qquad s+t=m. \tag{29}$$

Table 1. Some numerical values of $K\{\mathrm{r}(s,t)\} = r(s,t)$ and $K\{\mathrm{q}(s,t)\} = q(s,t)$

t	$r(1,t)$	$r(2,t)$	$r(3,t)$
1	40	520	6 800
2	520	6 800	89 000
3	6 800	89 000	1 165 000
4	89 000	1 165 000	15 250 000
5	1 165 000	15 250 000	199 625 000
t	$q(1,t)$	$q(2,t)$	$q(3,t)$
1	10	130	1 700
2	130	1 700	22 250
3	1 700	22 250	291 250
4	22 250	291 250	3 812 500
5	291 250	3 812 500	49 906 250

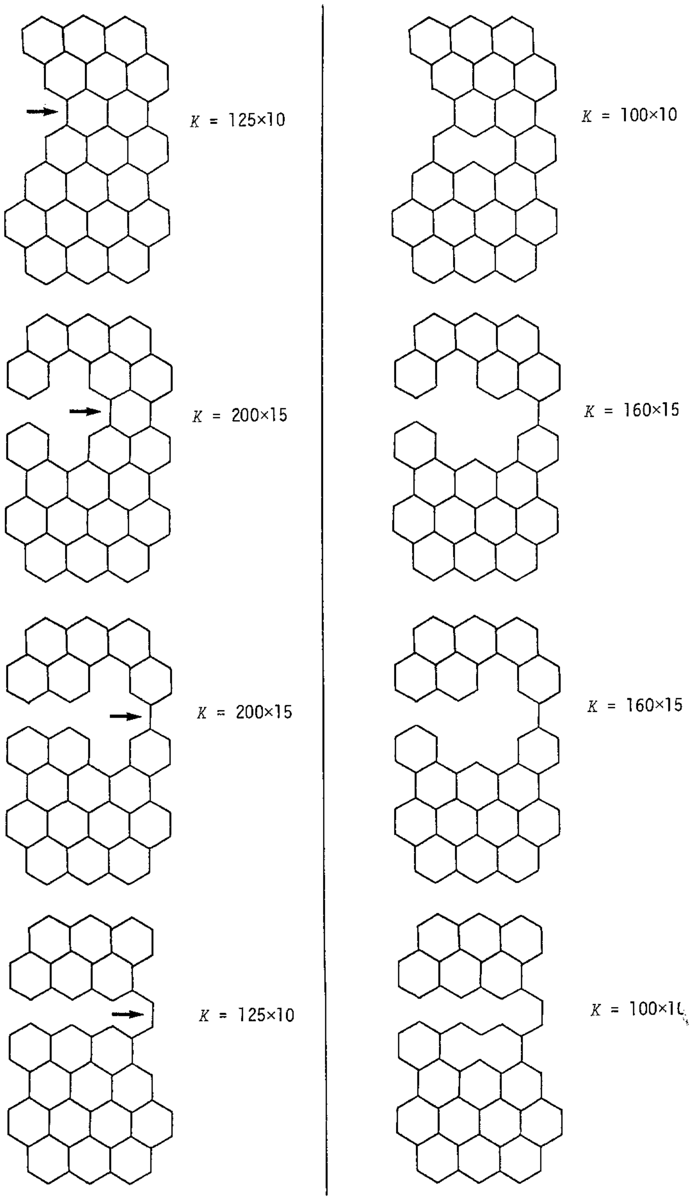

Fig. 10. Fragments obtained from chopping the rectangle R^j (4, 3) (left column) and the coronoid r (2, 2) (right column)

It is emphasized that s and t may assume different integer values if only their sum is m. This is compatible with the fact that the chopping may be executed along an arbitrary three-membered row. Especially for $n = 3$, the case of interest here, Eq. (29) reduces to

$$R_3(s+t) = 2\,R_3^{(0)}(s+1)\,R_3^{(0)}(t) + 2\,R_3^{(-1)}(s+1)\,R_3^{(-1)}(t). \tag{30}$$

Suppose that s and t have such values that the corresponding chopping of $r(s, t)$ occurs in the row just above the corona hole. For this case we find the analytical expression

$$r(s+t) = 2r^{(0)}(s+1)\,R_3^{(0)}(t) + 2r^{(-1)}(s+1)\,R_3^{(-1)}(t), \tag{31}$$

where the systems with $K = r^{(0)}(s + 1)$ and $K = r^{(-1)}(s + t)$ are depicted in Fig. 11 together with the benzenoids having $K = R_3^{(0)}(s + 1)$ and $K = R_3^{(-1)}(s + 1)$. The two latter systems (left column of Fig. 11) belong to the well studied auxiliary classes of incomplete rectangles (see [2] and references cited above). On comparing Eqs. (30) and (31) it is clear that we can prove our theorem if we can demonstrate that

$$r^{(0)}(s + 1) = \frac{4}{5} R_3^{(0)}(s + 1), \qquad r^{(-1)}(s + 1) = \frac{4}{5} R_3^{(-1)}(s + 1). \tag{32}$$

We start with a fragmentation of the degenerate coronoid with $K = r^{(0)}(s + 1)$ as shown in Fig. 12 and obtain

$$r^{(0)}(s + 1) = R_3(s) + R_3^{(0)}(s) + R_3^{(2)}(s). \tag{33}$$

These three fragments are all well known; cf. Chapter 12 of Ref. [2]. Adhering to the notation in this monograph we find

$$R_3^{(0)}(s) = O_{s-1} = \frac{5}{2} L_{s-1} \tag{34}$$

and

$$R_3^{(2)}(s) = M_s = L_s - \frac{5}{2} L_{s-1}, \tag{35}$$

while $R_3(s) = L_s$. The net result, after inserting into (33), becomes

$$r^{(0)}(s + 1) = 2 L_s. \tag{36}$$

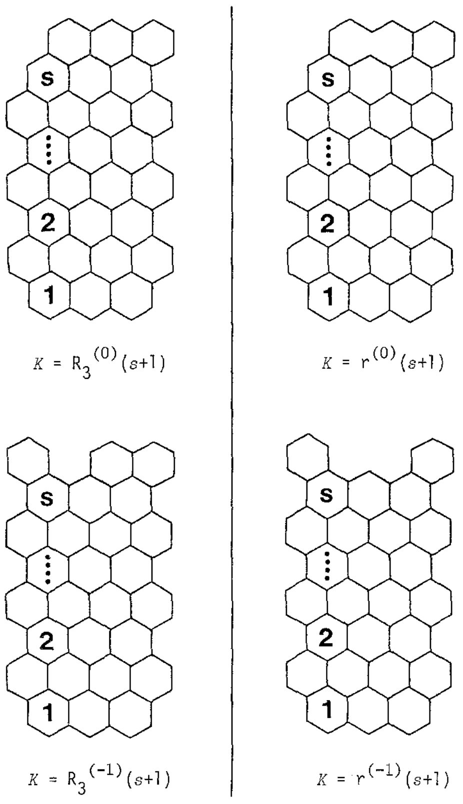

Fig. 11. Definition of three benzenoid classes and one class of degenerate coronoids

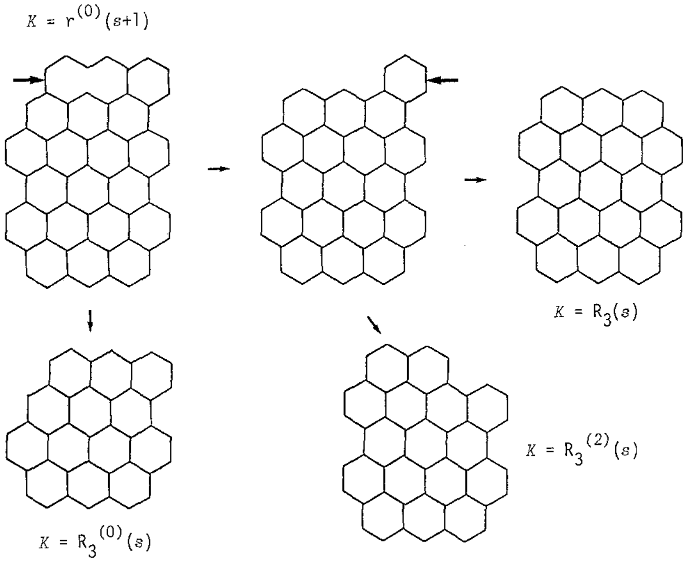

Fig. 12. The method of fragmentation applied to the degenerate coronoid with $K = r^{(0)}(s+1)$; in the depicted example, $s = 3$

Since $R_3^{(0)}(s+1) = \frac{5}{2} L_s$ in consistence with (34), we find immediately that the first part of Eq. (32) is fulfilled.

The proof of the second part of Eq. (32) is easier because of the known classes of rectangles with modifications at an end; cf. again Chapter 12 of Ref. [2]. In the present case we need

$$R_3^{(-1)}(s+1) = P_s = 5L_s - \frac{25}{2} L_{s-1}. \tag{37}$$

Since

$$r^{(-1)}(s+1) = R_s = 4L_s - 10L_{s-1}, \tag{38}$$

we find immediately that also the second part of (32) is fulfilled.

This completes the proof of Theorem (7).

Additional Classes

We have also considered the degenerate coronoids where the oblate rectangle $\mathrm{R}^j(m, 3)$ has a pyrenic hole in a different position than in $\mathrm{q}(s, t)$. A member of this class, viz. $\mathrm{q}'(s, t)$, is shown in Fig. 13 (right-hand drawing). The numbers of Kekulé structures for this class are readily obtained as a corollary of Theorem (7). Consider three edges a, b and c situated in relation to the naphthalenic hole (dotted hexagons) as shown in Fig. 14. The number of Kekulé structures for the oblate rectangle is obtained as the sum of three sets, say (a), (b) and (c), with the bonding schemes indicated on the figure. Here (a) and (b) lead to $\mathrm{q}'(s, t)$ and the mirror image of $\mathrm{q}'(s, t)$, respectively. These two systems are isomorphic. The scheme (c) leads to $\mathrm{q}(s, t)$. Consequently, for the K numbers,

$$R_3(s+t) = 2q'(s,t) + q(s,t). \tag{39}$$

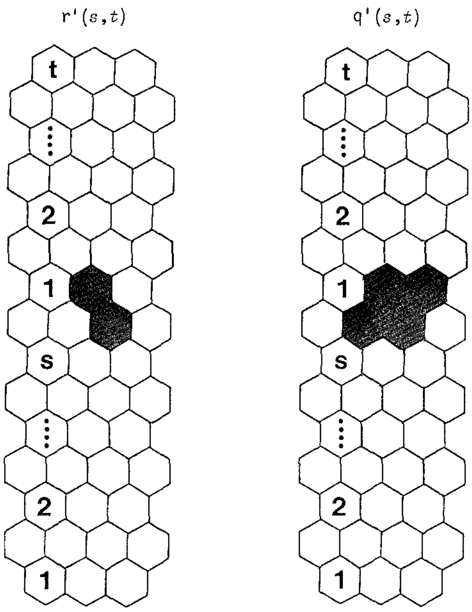

Fig. 13. Definition of the classes r′ and q′

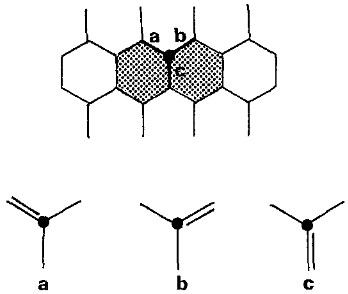

Fig. 14. Fragmentation schemes for an oblate rectangle; see the text for explanation

On inserting for $q\,(s,\,t)$ from (7) one obtains the result

$$q'\,(s,t) = \frac{2}{5}R_3\,(s+t). \tag{40}$$

Here again the position of the hole is immaterial for the number of Kekulé structures; see Fig. 15 (bottom row). Notice that all the three degenerate coronoid systems (in contrast to the systems of Fig. 1 or Fig. 2) are non-isomorphic.

Finally we have considered the class of coronoids (or degenerate coronoids) denoted by $\mathrm{r}'\,(s,\,t)$ and defined in Fig. 13 (left-hand drawing). An obvious fragmentation scheme, analogous to Eq. (8), yields

$$R_3\,(s+t) = r'\,(s,t) + q'\,(s,t). \tag{41}$$

On inserting from (40) it is readily obtained,

$$r'\,(s,t) = \frac{3}{5}R_3\,(s+t). \tag{42}$$

Fig. 15 (top row) shows three non-isomorphic systems belonging to r′ and with the hole in different positions, but having the same K number.

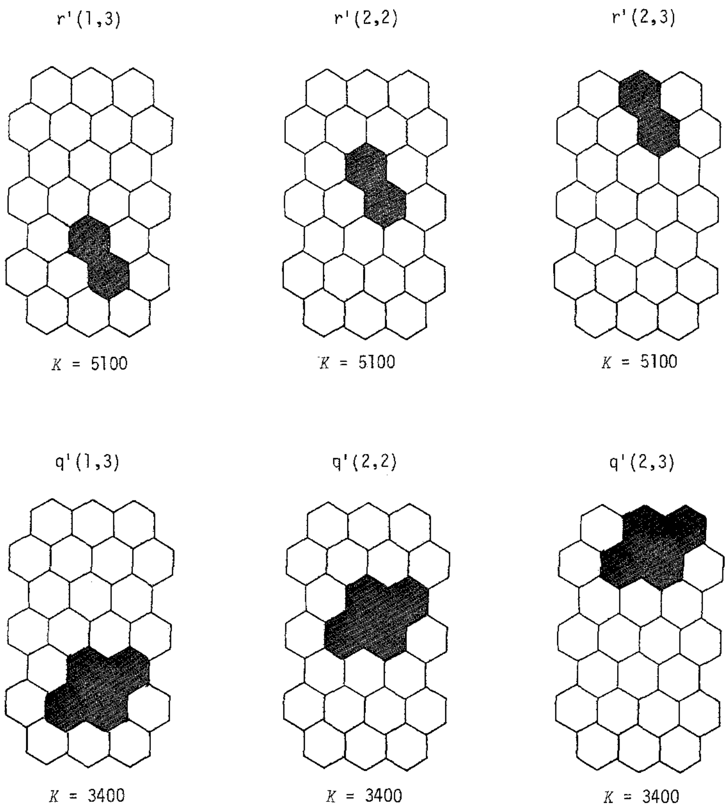

Fig. 15. Members of the classes r' and q'; Kekulé structure counts (K) are indicated

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