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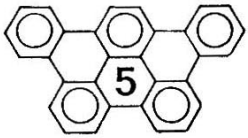

ALL-BENZENOID SYSTEMS: ADDITIONAL CLASSES OF PERICONDENSED CONJUGATED HYDROCARBONS

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(Received: January 1989)

Abstract: Three classes of all-benzenoids and additional seven related benzenoid classes are treated. Three different recurrence relations are detected for the number of Kekulé structures (K), viz.

$$K_n = 5K_{n-1} + \varepsilon; \qquad \varepsilon = 0,\ 1 \text{ or } -1$$

Explicit K formulas are reported for all the ten classes under consideration.

In our systematic studies of Kekulé structure counts (K) for classes of all-benzenoid systems[1-3] we have come to the system with h (the number of hexagons) = 10 and the smallest K, which equals 100; cf. Fig. 3 of Ref. 1. It is defined as a member of a class here denoted by $\Lambda_2(n)$. The present work is devoted to the K numbers for $\Lambda_2(n)$ and several related classes, among which $\Lambda_1(n)$ and $\Lambda(n)$ also consist of all-benzenoid systems. Some members of these three classes are depicted in Fig. 1. The lower members are identified with members of other classes in consistence with previous definitions and notation.[1,4] It should be observed that $\Lambda_1(n)$ and $\Lambda_2(n)$ emerge from $\Lambda(n)$ by a modification on one end or both ends, respectively. Figure 1 is supplied with numerical K values for the benzenoids in question. One observes immediately a regularity for the K numbers of $\Lambda_2(n)$, say $K\{\Lambda_2(n)\}$. It is seen that the value is multiplied by five for every increase in n by one

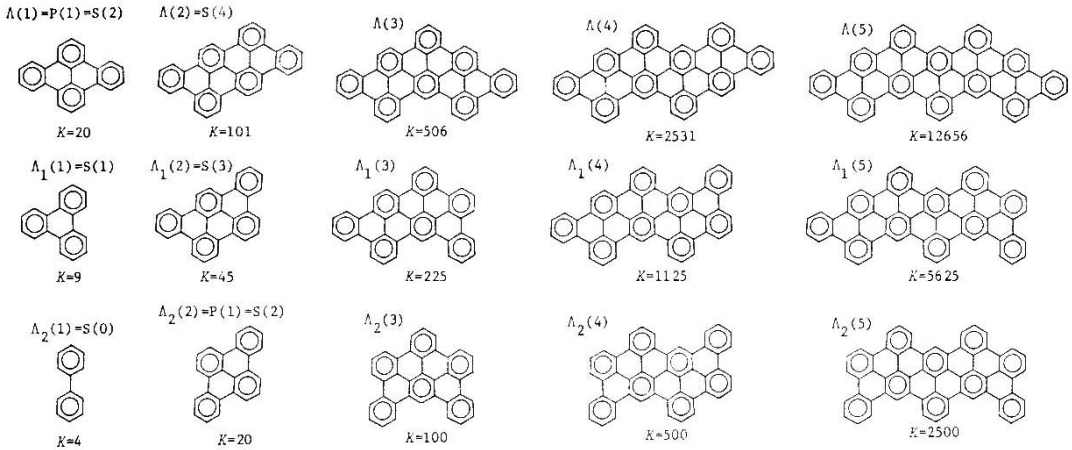
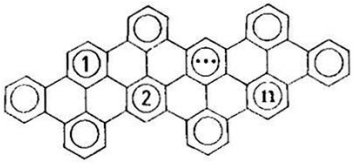


Fig. 1. Members of the classes $A(n)$, $A_1(n)$ and $A_2(n)$. Numbers of Kekulé structures (K) are given.

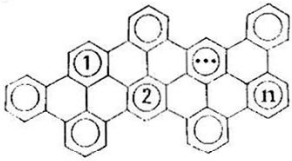
CHART I. Three all-benzenoid classes

$A(n)$



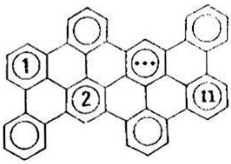
$|A(n)| = \frac{1}{4}(81 \cdot 5^{n-1} - 1)$

$A_1(n)$



$|A_1(n)| = 9 \cdot 5^{n-1}$

$A_2(n)$



$|A_2(n)| = 4 \cdot 5^{n-1}$

For numerical values, see Fig. 1

unit. We shall find that this really is a general rule. The result was obtained by the method of linearly coupled recurrence relations during a somewhat complicated analysis. The simplicity of the result suggests that it could possibly be deduced in an easier way, but we have not succeeded in this task. In our analysis we found that $A_1(n)$ follows the same recurrence property with multiplications by five; cf. the pertinent numbers of Fig. 1. It would be a failure, however, to assume the same property for $A(n)$. From

Fig. 1 it is seen that the multiplication of the first number (K = 20) by five would miss by one; in fact $K\{A(2)\} = 5K\{A(1)\} + 1$. Similarly one has $K\{A(3)\} = 5K\{A(2)\} + 1$, etc. Also this regularity was found to be generally valid.

Definition of Benzenoid Classes. The main classes (cf. Fig. 1) are defined in terms of the parameter n in CHART I. They consist of all-benzenoid systems throughout.

In order to be able to employ the method of linearly coupled recurrence relations we define some additional classes (see CHART II) obtained by deleting one terminal hexagon each time from the members of the main classes. A terminal hexagon shares five edges with the perimeter. In the case of $A_1(n)$ this deletion can be executed in two ways by virtue of the asymmetry of these systems, namely from the modified end and the unmodified end. The different classes thus obtained are denoted $A_1'(n)$ and $'A_1(n)$, respectively. If $A_1(n)$ is oriented as in CHART I, as may be taken as the standard orientation, then $'A_1(n)$ and $A_1'(n)$ refer to the deletion of a hexagon from the left- and right-hand side, respectively. The new classes (CHART II) are no longer all-benzenoid.

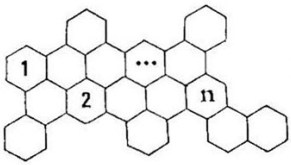
Finally we define the three classes (CHART III) obtained by deleting both terminal hexagons from the members of the respective classes of CHART I.

The Classes $A_1(n)$, $A_2(n)$, $'A_1(n)$ *and* $A_2'(n)$. By the well-known method of fragmentation[5] applied to $A_2(n)$ in two ways one obtains for the numbers of Kekulé structures (K):

$$K\{A_2(n)\} = 2K\{A_1(n-1)\} + K\{A^*(n-2)\} \tag{1}$$

$$K\{A_2(n)\} = 2K\{'A_1(n-1)\} + K\{A^*(n-1)\} \tag{2}$$

Here the auxiliary class $A^*(n)$ is defined by:



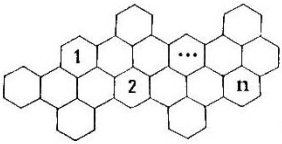
$A^*(n)$

Elimination of A^* from (1) and (2) leads to

$$K\{A_2(n)\} - K\{A_2(n-1)\} = 2K\{A_1(n-1)\} - 2K\{'A_1(n-2)\} \tag{3}$$

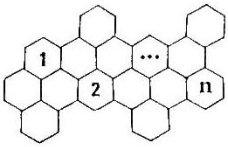
CHART II. Four benzenoid classes related to those of CHART I

$A'(n)$



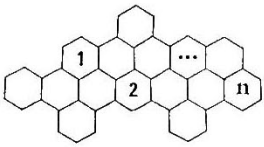
$K\{A'(n)\} = \frac{1}{4}(9 \cdot 5^n - 1)$

$'A_1(n)$



$K\{'A_1(n)\} = 5^n$

$A_1'(n)$

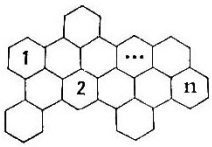


$K\{A_1'(1)\} = 5,$

$K\{A_1'(n)\} = \frac{1}{4}(99 \cdot 5^{n-2} + 1);$

$n > 1$

$A_2'(n)$

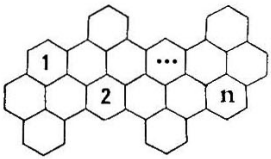


$K\{A_2'(n)\} = 11 \cdot 5^{n-2};\ n > 1$

n	$K\{A'(n)\}$	$K\{'A_1(n)\}$	$K\{A_1'(n)\}$	$K\{A_2'(n)\}$
1	11	5	5	
2	56	25	25	11
3	281	125	124	55
4	1406	625	619	275
5	7031	3125	3094	1375

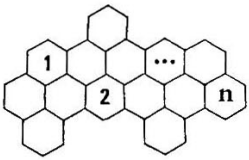
CHART III. Three benzenoid classes related to those of CHART I

$\Lambda''(n)$



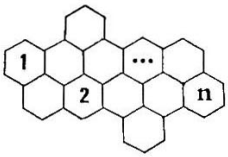
$$K\{\Lambda''(n)\} = \frac{1}{4}(5^{n+1} - 1)$$

$\Lambda_1''(n)$



$$K\{\Lambda_1''(n)\} = \frac{1}{4}(11 \cdot 5^{n-1} + 1)$$

$\Lambda_2''(n)$



$$K\{\Lambda_2''(2)\} = 6,$$

$$K\{\Lambda_2''(n)\} = \frac{1}{4}(121 \cdot 5^{n-3} - 1); \quad n > 2$$

n	$K\{\Lambda''(n)\}$	$K\{\Lambda_1''(n)\}$	$K\{\Lambda_2''(n)\}$
1	6	3	
2	31	14	6
3	156	69	30
4	781	344	151
5	3906	1719	756

Two additional relations for the same fragments were produced, viz.

$$K\{\Lambda_1(n)\} = 2K\{\Lambda_2(n)\} + K\{'\Lambda_1(n-1)\} \tag{4}$$

$$K\{'\Lambda_1(n)\} = K\{\Lambda_2(n)\} + K\{'\Lambda_1(n-1)\} \tag{5}$$

It is found that a substitution from (4) into (3) can be made so that Λ_1 and $'\Lambda_1$ are eliminated at the same time. Hence one arrives at the following recurrence relation.

$$K\{\Lambda_2(n)\} = 5K\{\Lambda_2(n-1)\}; \qquad n > 1 \tag{6}$$

With the initial condition $K\{\Lambda_2(1)\} = 4$ (for biphenyl; cf. Fig. 1) it is attained at the explicit equation for $K\{\Lambda_2(n)\}$ as entered in CHART I.

We shall show that the other title classes obey the same form (6) of the recurrence relation. From (5) the following summation formula emerges.

$$K\{'\Lambda_1(n)\} = K\{'\Lambda_1(1)\} + \sum_{i=2}^{n} K\{\Lambda_2(i)\} \tag{7}$$

On inserting $K\{'\Lambda_1(1)\} = 5$ (for phenanthrene; cf. CHART II) and the explicit K formula (CHART I) for $\Lambda_2(i)$ one arrives at

$$K\{'\Lambda_1(n)\} = 5 + 4\sum_{i=1}^{n-1} 5^i \tag{8}$$

Here the summation is equal to $\frac{5}{4}(5^{n-1} - 1)$. When inserted above one achieves the utterly simple formula given in CHART II.

The explicit formula for $K\{\Lambda_1(n)\}$ is now accessible by inserting the known explicit formulas into the right-hand side of (4).

For the last one of the title classes, viz. $\Lambda_2'(n)$, one finds from an another fragmentation scheme for $\Lambda_2(n)$:

$$K\{\Lambda_2(n)\} = K\{\Lambda_2'(n)\} + K\{\Lambda_1(n-1)\} \tag{9}$$

On inserting the appropriate (already known) explicit formulas from CHART I the explicit K formula of CHART II for $\Lambda_2'(n)$ is achieved (for $n > 1$).

We emphasize that Λ_2 in eqn. (6) may be substituted by Λ_1, $'\Lambda_1$ or Λ_2'.

The Classes $\Lambda(n)$, $\Lambda'(n)$, $\Lambda''(n)$ *and* $\Lambda''(n)$. Similarly to (4) and (5) one has:

$$K\{\Lambda(n)\} = 2K\{\Lambda_1(n)\} + K\{\Lambda'(n-1)\} \tag{10}$$

$$K\{\Lambda'(n)\} = K\{\Lambda_1(n)\} + K\{\Lambda'(n-1)\} \tag{11}$$

From (11) one obtains the summation formula

$$K\{\Lambda'(n)\} = K\{\Lambda'(1)\} + \sum_{i=2}^{n} K\{\Lambda_1(i)\} \tag{12}$$

With $K\{\Lambda'(1)\} = 11$ (for benzo[*e*]pyrene; cf. CHART II) and the explicit formula (CHART I) for $K\{\Lambda_1(i)\}$ one arrives at

$$K\{\Lambda'(n)\} = 11 + 9\sum_{i=1}^{n-1} 5^i \tag{13}$$

and consequently the appropriate explicit formula as given in CHART II.

The explicit K formula for $\Lambda(n)$ is now accessible from (10). The result is entered in CHART 1.

Also the K formulas for the two last title classes, viz. $\Lambda''(n)$ and $\Lambda_2''(n)$ are available with the aid of already known explicit formulas from the following fragmentation schemes.

$$K\{\Lambda'(n)\} = K\{\Lambda''(n)\} + K\{'\Lambda_1(n)\} \tag{14}$$

$$K\{\Lambda_2'(n)\} = K\{\Lambda_2''(n)\} + K\{\Lambda_1'(n-1)\} \tag{15}$$

The results for $K\{\Lambda''(n)\}$ and for $K\{\Lambda_2''(n)\}$ $(n > 1)$ are entered in CHART III.

The following recurrence relation is compatible with the derived K formula for $\Lambda(n)$.

$$K\{\Lambda(n)\} = 5K\{\Lambda(n-1)\} + 1; \qquad n > 1 \tag{16}$$

Here Λ', Λ'' or Λ_2'' may be substituted for Λ. In the case of Λ_2'' the validity is restricted to $n > 3$.

The Classes $\Lambda_1'(n)$ *and* $\Lambda_1''(n)$. We shall find a third type of recurrence properties for these two title classes.

The explicit formula for $K\{\Lambda_1'(n)\}$ is now easily found (for $n > 1$) from the fragmentation scheme

$$K\{\Lambda_1(n)\} = K\{\Lambda_1'(n)\} + K\{\Lambda(n-1)\} \tag{17}$$

The result is entered into CHART II.

The formula for $K\{\Lambda_1''(n)\}$ is found from either of the following two relations.

$$K\{\Lambda_1'(n)\} = K\{\Lambda_1''(n)\} + K\{\Lambda_2'(n)\} \tag{18}$$

$$K\{'\Lambda_1(n)\} = K\{\Lambda_1''(n)\} + K\{\Lambda'(n-1)\} \tag{19}$$

The result is found in CHART III.

The deduced recurrence relation reads

$$K\{\Lambda_1''(n)\} = 5K\{\Lambda_1''(n-1)\} - 1; \qquad n > 1 \tag{20}$$

where Λ_1'' may be substituted by Λ_1', but in that case the validity is restricted to $n > 2$.

Conclusion. The numbers of Kekulé structures (K) in ten related benzenoid classes (see CHARTS I-III) were studied on the basis of the fragmentation technique,[5] as is employed in the method of linearly coupled recurrence relations. We distinguish three groups of the classes, for which the K numbers are mutually linearly dependent, and which obey the same form of recur-

rence relations within each group. The three forms are

$$K_n = 5K_{n-1} + \varepsilon, \qquad \text{where} \qquad \varepsilon = 0,\ 1 \text{ or } -1 \tag{21}$$

We give the following general survey (disregarding the details concerning restrictions on n).

$\varepsilon = 0$ for Λ_1, Λ_2, 'Λ_1, Λ_2' ;
$\varepsilon = 1$ for Λ, Λ', Λ'', Λ_2'' ;
$\varepsilon = -1$ for Λ_1', Λ_1''

From one group to another the K numbers are no longer linearly dependent. An example of a nonlinear dependency of this kind is furnished by

$$K\{\Lambda(n)\} = \frac{1}{4}[9K\{\Lambda_1(n)\} - 1] \tag{22}$$

Acknowledgement: Financial support to BNC from The Norwegian Research Council for Science and the Humanities is gratefully acknowledged.

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