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ALL-BENZENOID SYSTEMS:

SOME CLASSES OF PERICONDENSED CONJUGATED HYDROCARBONS

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Abstract: Nine classes of pericondensed all-benzenoids and three additional (auxiliary) benzenoid classes are treated with respect to the numbers of Kekulé structures (K). Recurrence relations, explicit K formulas and numerical K values are given.

The generation and enumeration of all-benzenoid systems[1] inspired us to the studies of the numbers of Kekulé structures (K) in several classes of all-benzenoids,[2,3] in addition to the previously available material in this area.[4]

Already one of the all-benzenoids with the number of hexagons (h) equal to 9,[1] the one with K=90,[2] calls for a definition of a new all-benzenoid class. Here we employ the method of linearly coupled recurrence equations.[5] Consequently a group of related classes need to be invoked at the same time. Two sets with mutually linearly dependent K numbers were studied in the present work, altogether constituting twelve classes. Within each set the K numbers for every class have the same recurrence properties.

The classes of the present study consist of pericondensed benzenoids. However, they are "thin" in the sense that never more than two connected internal vertices are present. They give rise to the pyrene subunits.

1. Form of the Recurrence Relations: $K_n = 46K_{n-1} - 40K_{n-2}$

In Fig. 1 the main class $\ni(n)$ is defined along with two additional all-benzenoid classes, viz. $\ni_1(n)$ and $\ni_2(n)$, obtained by modifications at one or both ends. Three auxiliary classes (no longer all-benzenoid) are obtained by additional modifications as shown in Fig. 2.

Different schemes of fragmentation[6] lead to the following independent

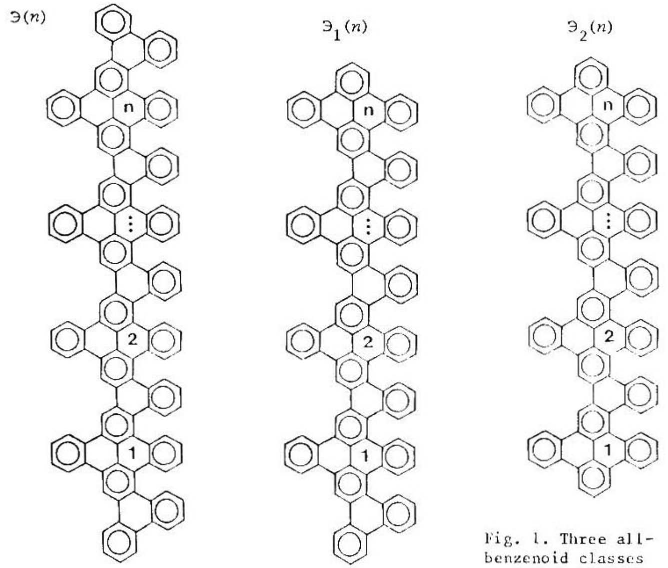


Fig. 1. Three all-benzenoid classes

equations.

$$K\{\text{Э}(n)\} = 4K\{\text{Э}_1(n)\} + 2K\{\text{Э}'(n)\} \tag{1}$$

$$K\{\text{Э}(n)\} = 180K\{\text{Э}_1(n-1)\} + 92K\{\text{Э}'(n-1)\} \tag{2}$$

$$K\{\text{Э}_1(n)\} = 40K\{\text{Э}_1(n-1)\} + 20K\{\text{Э}'(n-1)\} \tag{3}$$

Suitable manipulations yielded the recurrence relation:

$$K\{\text{Э}(n)\} = 46K\{\text{Э}(n-1)\} - 40K\{\text{Э}(n-2)\} \tag{4}$$

In this relation one has primarily the restriction $n \geq 2$ when it is allowed for the degenerate case of $n=0$, represented by triphenylene ($K=9$).

The same form (4) holds for the recurrence relations of $\text{Э}_1(n)$ and $\text{Э}'(n)$. The following linear dependencies for the K numbers of these classes were deduced.

$$K\{\text{Э}_1(n)\} = 10K\{\text{Э}(n-1)\} \tag{5}$$

$$K\{\text{Э}'(n)\} = \frac{1}{2} K\{\text{Э}(n)\} - 20K\{\text{Э}(n-1)\} \tag{6}$$

Two additional equations, which link $K\{\text{Э}_2(n)\}$ and $K\{\text{Э}_1'(n)\}$ to the system of linearly coupled recurrence relations, were obtained by the method of fragmentation and read:

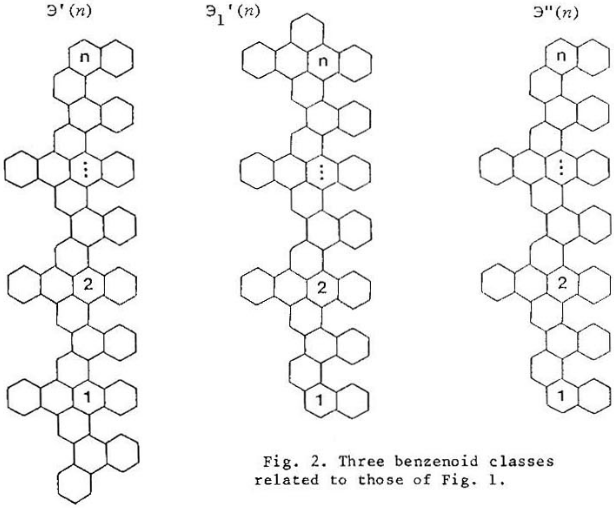


Fig. 2. Three benzenoid classes related to those of Fig. 1.

$$K\{Э_1(n)\} = 4K\{Э_2(n)\} + 2K\{Э_1'(n)\} \tag{7}$$

$$K\{Э_2(n)\} = 40K\{Э_2(n-1)\} + 20K\{Э_1'(n-1)\} \tag{8}$$

Further manipulations yielded

$$K\{Э_2(n)\} = 10K\{Э_1(n-1)\} \tag{9}$$

$$K\{Э_1'(n)\} = 10K\{Э'(n-1)\} \tag{10}$$

and the final linear combinations in terms of the K numbers of the main class:

$$K\{Э_2(n)\} = 100K\{Э(n-2)\} \tag{11}$$

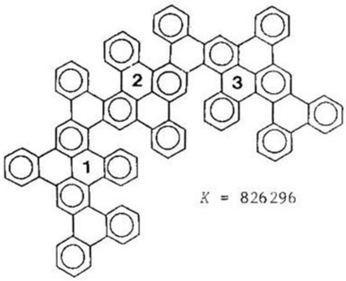
$$K\{Э_1'(n)\} = 5K\{Э(n-1)\} - 200K\{Э(n-2)\} \tag{12}$$

Also the K numbers of the classes $Э_2(n)$ and $Э_1'(n)$ obey recurrence relations of the form (4). With the aid of appropriate initial conditions the following numerical K values were computed for the all-benzenoid classes under consideration (Fig. 1).

n	$K\{Э(n)\}$	$K\{Э_1(n)\}$	$K\{Э_2(n)\}$
0	9	2	½
1	406	90	20
2	18316	4060	900
3	826296	183160	40600
4	37276976	8262960	1831600
5	1681689056	372769760	82629600

The "nominal" value $K\{Э_2(0)\} = \frac{1}{2}$ was obtained by extrapolation.

There are copious possibilities for isoarithmicity among the classes of the present study. Isoarithmic systems are obtained by flipping a subunit of the benzenoid around an edge of fusion.[4,7] As an example we show a system which is isoaritmic with $Э(3)$:



$K = 826296$

By standard methods[4,5] the following explicit formula was deduced for the K numbers of $Э(n)$.

$$K\{Э(n)\} = \frac{1}{10\sqrt{489}}\left[(\sqrt{489} + 22)(23 + \sqrt{489})^{n+1} + (\sqrt{489} - 22)(23 - \sqrt{489})^{n+1}\right] \quad (13)$$

The K numbers for $Э_1(n)$ and $Э_2(n)$ are most easily obtained from $K\{Э(n)\}$ through multiplications by 10 and 100 according to eqn. (5) and eqn. (9) or (11). Therefore it is not necessary to report the explicit equations for $K\{Э_1(n)\}$ and $K\{Э_2(n)\}$ here.

So far the class $Э''(n)$ has not been invoked. The K numbers of this class are coupled to the relations for the other related five classes by:

$$K\{Э'(n)\} = 4K\{Э_1'(n)\} + 2K\{Э''(n)\} \quad (14)$$

$$K\{Э''(n)\} = 10K\{Э_1'(n-1)\} + 6K\{Э''(n-1)\} \quad (15)$$

A table of numerical K values (including nominal values) for the three auxiliary classes (Fig. 2) is given below.

n	$K\{Э'(n)\}$	$K\{Э_1'(n)\}$	$K\{Э''(n)\}$
0	1/2	0	1/4
1	23	5	3/2
2	1038	230	59
3	46828	10380	2654
4	2112568	468280	119724
5	95305008	21125680	5401144

A particularly simple explicit equation for $K\{Э'(n)\}$ was deduced, viz.

$$K\{Э'(n)\} = \frac{1}{4\sqrt{489}}\left[(23+\sqrt{489})^{n+1} - (23-\sqrt{489})^{n+1}\right] \tag{16}$$

From these K numbers those of $Э_1'(n)$ are most easily obtained through the relation:

$$K\{Э_1'(n)\} = 10K\{Э'(n-1)\} \tag{17}$$

For the sake of completeness we report the explicit equation for the K numbers of $Э''(n)$. It reads

$$K\{Э''(n)\} = \frac{1}{8\sqrt{489}}\left[(\sqrt{489}-17)(23+\sqrt{489})^{n} + (\sqrt{489}+17)(23-\sqrt{489})^{n}\right] \tag{18}$$

2. <u>Form of the Recurrence Relations:</u> $K_n = 100K_{n-1} - 20K_{n-2}$

Also the class $И(n)$ was considered (see Fig. 3), together with five additional related classes. They all consist of all-benzenoids. It was achieved to employ the method of coupled recurrence relations without invoking any additional auxiliary class. A plethora of linear dependencies between the pertinent K numbers exist. Firstly:

$$K\{И(n)\} = 2K\{И'(n)\} + K\{И_1(n)\} \tag{19}$$

$$K\{И'(n)\} = 2K\{И''(n)\} + K\{И_1'(n)\} \tag{20}$$

$$K\{И_1(n)\} = 2K\{И_1'(n)\} + K\{И_2(n)\} \tag{21}$$

Then:

$$K\{И(n)\} = 200K\{И'(n-1)\} + 98K\{И_1(n-1)\} \tag{22}$$

$$K\{И'(n)\} = 200K\{И''(n-1)\} + 98K\{И_1'(n-1)\} \tag{23}$$

$$K\{И_1(n)\} = 200K\{И_1'(n-1)\} + 98K\{И_2(n-1)\} \tag{24}$$

Finally:

$$K\{И'(n)\} = 90K\{И'(n-1)\} + 44K\{И_1(n-1)\} \tag{25}$$

$$K\{И''(n)\} = 90K\{И''(n-1)\} + 44K\{И_1'(n-1)\} \tag{26}$$

$$K\{И_1'(n)\} = 90K\{И_1'(n-1)\} + 44K\{И_2(n-1)\} \tag{27}$$

The relations are sufficient for deducing the recurrence relation

$$K\{И(n)\} = 100K\{И(n-1)\} - 20K\{И(n-2)\} \tag{28}$$

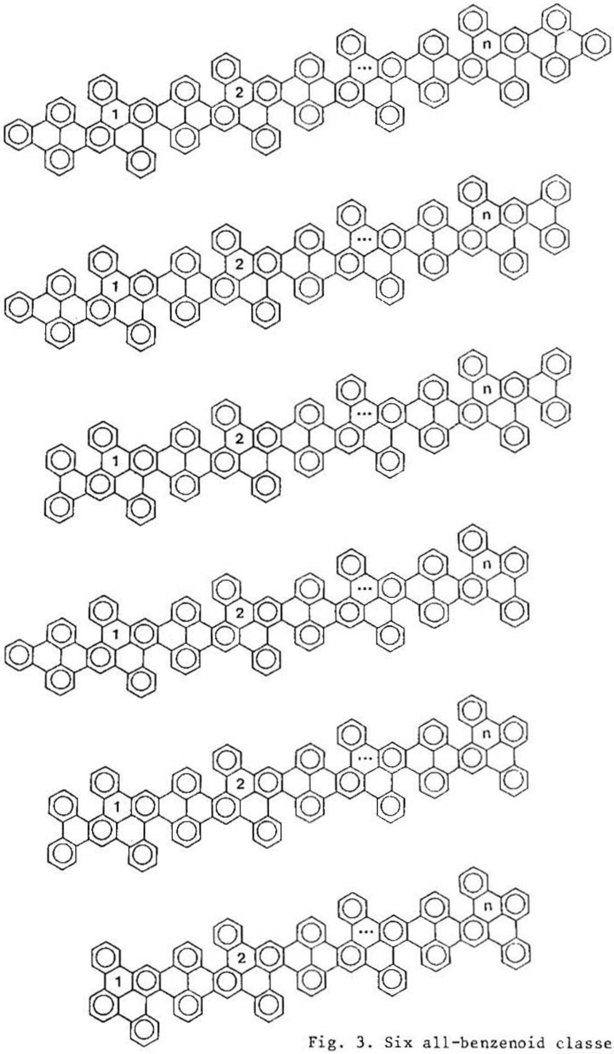
It is also found that $И'$, $И''$, $И_1$, $И_1'$ or $И_2$ may be substituted for $И$ in this relation. Explicit linear combinations:

$$K\{И'(n)\} = \frac{1}{2}K\{И(n)\} - 5K\{И(n-1)\} \tag{29}$$

$$K\{И''(n)\} = 20K\{И(n-1)\} + 20K\{И(n-2)\} = -K\{И(n)\} + 120K\{И(n-1)\} \tag{30}$$

$$K\{И_1(n)\} = 10K\{И(n-1)\} \tag{31}$$

$$K\{И_1'(n)\} = 10K\{И'(n-1)\} = 5K\{И(n-1)\} - 50K\{И(n-2)\} = \frac{5}{2}K\{И(n)\} - 245K\{И(n-2)\} \tag{32}$$



$H(n)$

$H'(n)$

$H''(n)$

$H_1(n)$

$H_1'(n)$

$H_2(n)$

Fig. 3. Six all-benzenoid classes.

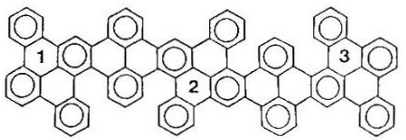
$$K\{И_2(n)\} = 10K\{И_1(n-1)\} = 100K\{И(n-2)\} = -5K\{И(n)\} + 500K\{И(n-1)\} \quad (33)$$

Here we have not imposed any restrictions on the parameter n. That is not necessary if we allow for degenerate cases and nominal K values. Numerical K values are given below.

n	$K\{И(n)\}$	$K\{И'(n)\}$	$K\{И''(n)\}$
0	20	9	4
1	1996	898	404
2	199200	89620	40320
3	19880080	8944040	4023920
4	1984024000	892611600	401585600
5	198004798400	89082279200	40078081600

n	$K\{И_1(n)\}$	$K\{И_1'(n)\}$	$K\{И_2(n)\}$
0	2	1	0
1	200	90	20
2	19960	8980	2000
3	1992000	896200	199600
4	198800800	89440400	19920000
5	19840240000	8926116000	1988008000

Also for these classes there are many possibilities for isoarithmicity. Below we show, as an example, a system which is isoarithmic with $И_2(3)$.



K = 199600

Explicit equations may again be derived by standard methods. For the sake of brevity we give only one of them:

$$K\{И(n)\} = \frac{1}{40\sqrt{155}}\left[(50 + 4\sqrt{155})^{n+2} - (50 - 4\sqrt{155})^{n+2}\right] \quad (34)$$

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