



ALL-BENZENOID SYSTEMS:

CATACONDENSED CONJUGATED HYDROCARBONS

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(Received: August 1988)

Abstract: The material on numbers of Kekulé structures for classes of catacondensed all-benzenoids is supplemented. Two new classes are considered.

In order to fulfil the program which was outlined in the preceding paper on all-benzenoid systems¹ it was found necessary to supplement the existing material on combinatorial K formulas.² Here K is used to designate the number of Kekulé structures. The present paper deals with some classes of catacondensed all-benzenoids. First an introductory section on some topological properties of the systems in question is warranted.

Supplementary Topological Properties of Catacondensed All-Benzenoids. By a *terminal* hexagon in a benzenoid system we understand a hexagon which shares five edges with the perimeter. A terminal hexagon in an all-benzenoid is always full. In a catacondensed all-benzenoid a *backbone* is recognized when the system is stripped for its terminal hexagons. A *segment* of the backbone is defined as the linear chain between two angularly annelated⁵ hexagons inclusive, or between a terminal and an angularly annelated hexagon inclusive. Here it is of course referred to a terminal hexagon of the backbone. An angularly annelated hexagon of the backbone belongs by definition to two neighbouring segments.

As a consequence of the general properties of all-benzenoid systems^{3,4} drastic limitations to the shapes of catacondensed all-benzenoids are present.

1. The catacondensed all-benzenoid systems are highly branched inasmuch as every empty hexagon is a branching hexagon.
2. The backbone has a configuration with alternating empty (E) and full

(K) hexagons: $EEEE \dots E$. Notice that E is always at the ends of an unbranched backbone.

3. The backbone is in general highly kinked: a segment of it never consists of more than three hexagons. We can speak about the 2-segments and 3-segments.

4. A 3-segment has always the configuration EEE (never FEF).

5. The backbone may consist of only 2-segments or only 3-segments. Mixed segmentation is also possible, but between two 3-segments there must be an even number of 2-segments.

6. The backbone may be branched. Then the above rules apply to all subsystems spanning from one end of a branch to an end of another branch. The branching hexagon may be either empty or full.

The contents of the above rules 3 and 4 may be expressed in terms of the LA -sequence⁵ of the backbone. The following patterns are among the possible ones.

- (i) $L \dots AAAAAA \dots L$
- (ii) $LL \dots ALALAL \dots L$
- (iii) $LAAL \dots AAALAAAL \dots L$

On the other hand is, for instance, the following configuration impossible.

$LAL \dots AALAAAL \dots L$

Previous Work. Combinatorial K formulas have been developed² for classes of catacondensed benzenoids corresponding to the LA -sequences (i)-(iii) of the preceding paragraph. They are:

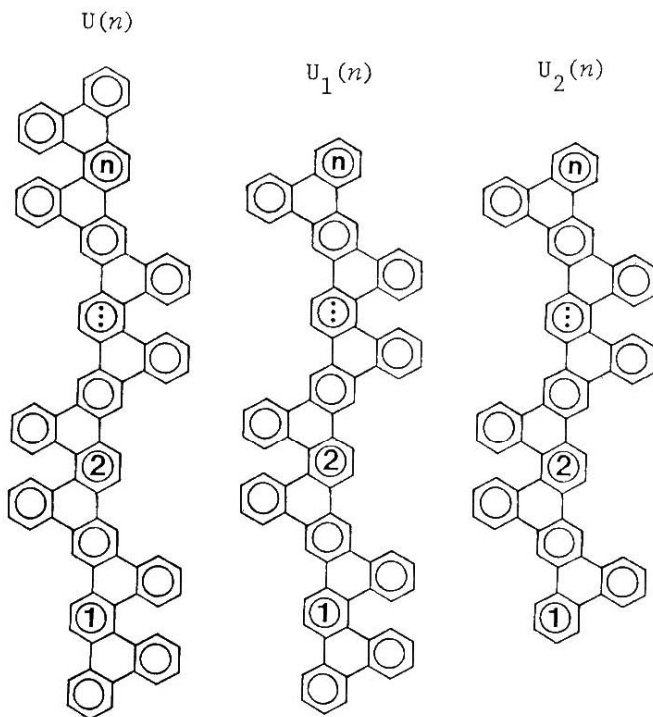
- (i) $\mathcal{U}(n)$: backbone with 2-segments only;
- (ii) $\mathcal{B}(n)$: backbone with 3-segments only;
- (iii) $\mathcal{U}(n)$ "horse-shoes on a string": The sequence of segments in the backbone is 2-2-3-2-2-3-...-2-2.

In addition, the "catacondensed all-benzenoid ladder" $\mathcal{Z}(n)$ was treated; it has a branched backbone for $n > 2$.

The Class of Horse-Shoes on a String and Its Modifications. The benzenoids of the class $\mathcal{U}(n)$ may be modified at one or both ends so that they still are all-benzenoids. It is referred to CHART I, which defines the three classes of catacondensed benzenoids denoted $\mathcal{U}(n)$, $\mathcal{U}_1(n)$ and $\mathcal{U}_2(n)$. They all have the typical sequence of segments -2-2-3-2-2-3-, but terminate in different ways.

The K enumeration problem was solved by the method of linearly coupled recurrence relations. The K numbers of all the three classes in question appear to be linearly dependent so that they obey the recurrence relations of the same form, viz.:

CHART I. Three classes of catacondensed all-benzenoids.



$$K\{U(n)\} = \frac{1}{8\sqrt{26}} \left[(\sqrt{26} - 1)(10 + 2\sqrt{26})^{n+1} + (\sqrt{26} + 1)(10 - 2\sqrt{26})^{n+1} \right]$$

$$K\{U_1(n)\} = \frac{1}{4\sqrt{26}} \left[(\sqrt{26} + 4)(10 + 2\sqrt{26})^n + (\sqrt{26} - 4)(10 - 2\sqrt{26})^n \right]$$

$$K\{U_2(n)\} = \frac{1}{2\sqrt{26}} \left[(10 + 2\sqrt{26})^n - (10 - 2\sqrt{26})^n \right]$$

$$\begin{aligned}
 K\{U(n)\} &= 20K\{U(n-1)\} + 4K\{U(n-2)\} \\
 K\{U_1(n)\} &= 20K\{U_1(n-1)\} + 4K\{U_1(n-2)\} \\
 K\{U_2(n)\} &= 20K\{U_2(n-1)\} + 4K\{U_2(n-2)\}
 \end{aligned}$$

The linear dependencies were explicitly found to be:

$$\begin{aligned}
 K\{U_1(n)\} &= \frac{1}{5} K\{U(n)\} + \frac{2}{5} K\{U(n-1)\} \\
 K\{U_2(n)\} &= \frac{2}{25} K\{U(n)\} - \frac{16}{25} K\{U(n-1)\}
 \end{aligned}$$

The explicit (combinatorial) K formula for $U(n)^2$ is reproduced in CHART I together with the corresponding formulas which were derived for $U_1(n)$ and $U_2(n)$.

Below we give some numerical K values for the classes under consideration. The table includes extrapolated "nominal" K values, which obviously do not correspond to real benzenoids.

n	$K\{U(n)\}$	$K\{U_1(n)\}$	$K\{U_2(n)\}$
0	2	$\frac{1}{2}$	0
1	41	9	2
2	828	182	40
3	16724	3676	808
4	337792	74248	16320
5	6822736	1499664	329632

Conclusion. The present work nearly completes the outlined program¹ as far as the catacondensed systems are concerned. Below we assign the catacondensed all-benzenoids for $h \leq 10$ to different classes. (For $h=11$ the existing all-benzenoids are all pericondensed.) Figure 3 of Ref. 1 should be consulted for a survey of the forms.

$h=1$: Members of several classes degenerate to one hexagon, $L(1)$, for a low parameter ($n=0$ or $n=1$). For example, to take one of the classes of the present study, one has $U_2(1) = L(1)$.

$h=4$: Again several classes contain the appropriate system (triphenylene) as a member. It is the case for $\Psi(1) = \mathbb{K}(1) = U_1(1)$.

$h=7$: The two systems are $\mathbb{O}(2) = U_2(2) = \mathbb{Z}(1)$ with $K=40$, and $\Psi(2) = U(1)$ with $K=41$.

$h=10$: $\mathbb{K}(3)$ with $K=178$; $U_1(2)$ with $K=182$ and an isoarithmic form of the same, say iso- $U_1(2)$; $\Psi(3)$ and iso- $\Psi(3)$ with $K=187$; finally the first system with branched backbone ($K=189$), which is postponed for later considerations as a member of all-benzenoids with trigonal symmetry.

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

References

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