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ENUMERATION AND CLASSIFICATION OF BENZENOID HYDROCARBONS. PART VII: CONCEALED NON-KEKULÉANS WITH HEXAGONAL SYMMETRY

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Abstract: There are 313 concealed non-Kekuléan benzenoids with h (number of hexagons) = 55 and with hexagonal symmetry: 1 belonging to D_{6h} and 312 to C_{6h}. These systems are surveyed in a comprehensive way in terms of a "natural" classification. Complete sets or examples of the benzenoids within different classes are presented in six charts together with detailed results of the enumeration.

Introduction. The search for concealed non-Kekuléan benzenoids has been going on since 1974; see the survey in Part IV [1] of this article series. Part VI [2] contains in an appendix a special treatment of the benzenoids with regular hexagonal (D_{6h} and C_{6h}) symmetry. For the sake of brevity they are referred to as hexagonal benzenoids.

In the below table a survey of the numbers of concealed non-Kekuléans among the hexagonal benzenoids is displayed.

Number of hexagons	Number of concealed non-Kekuléans		Total
	D_{6h}	C_{6h}	$D_{6h} + C_{6h}$
$h \leq 37$	0	0	192
$h = 43$	1	4	540
$h = 49$	0	42	2229
$h = 55$	1	312	9505

The right-hand column includes (in addition to the non-Kekuléans) the Kekuléan systems, both normal and essentially disconnected (there do not exist any obvious non-Kekuléans with hexagonal sym-

metry). These terms are precisely defined in several papers [1, 3-5]. The figures of the above table show how sparsely the non-Kekuléans are distributed among all hexagonal systems. Especially there are very few systems with the D_{6h} symmetry.

In the previous part of this series [2] the 5 concealed hexagonal non-Kekuléans with h=43 and 42 systems with h=49 were depicted. The main subject of the present work is the classification of the 313 systems of concealed non-Kekuléans with h=55. For the sake of brevity we do not show drawings of all these systems, but only some representatives belonging to different classes as defined in the following.

General Description and Definitions. In the h=55 benzenoid systems to be described presently we distinguish between those with a circumcoronene core and those with a coronene core, where the latter category is in great majority. In addition to the core each system possesses six identical arms. An arm in the presence of the circumcoronene core has six hexagons; for the coronene core this number is eight.

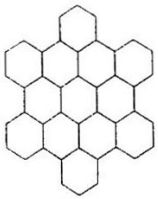
Here we will use the terms fusion and condensation in a strict (and somewhat special) sense as follows. A benzenoid unit is said to be fused to a benzenoid when the two parts share exactly one edge. A unit is condensed to a benzenoid when the two parts share exactly two neighbouring edges.

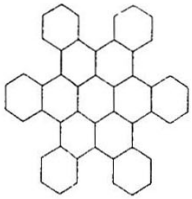
A benzenoid is said to be composite if it consists of at least two fused units. If not composite, the benzenoid is said to be basic.

As a final distinction between benzenoids we define the classes D and F according to the classification of He and He [6, 7]. Benzenoids belonging to F or D have or have not catacondensed appendages, respectively. More precisely these categories are characterized by the absence (D) or presence (F) of at least one hexagon with five free edges. i.e. five edges on the perimeter. All basic benzenoids belong to D, while a composite benzenoid may be either D or F.

For the hexagonal benzenoids of the present study we distinguish between the cases when the arms of the systems are

condensed to the core (A) or fused to the core (B). When the core is coronene, either hexabenzocoronene-A or hexabenzocoronene-B (see below) is a subunit in the two cases A and B, respectively.

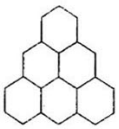




HBC-A Hexabenzocoronene-A; HBC-B Hexabenzocoronene-B

HBC-A is a basic benzenoid, while HBC-B is composite.

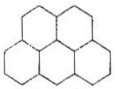
In a more detailed classification different shapes of the arms are distinguished. When the core is circumcoronene the arms consist exclusively of either triangulene (Tr), a basic benzenoid, or two fused phenalenes (Pl:Pl), a composite benzenoid.



Tr Triangulene;

Pl Phenalene

These two units, viz. Tr or Pl, are also the constituents of the arms in most of the systems with the coronene core. In these cases one arm may consist of triangulene with two hexagons fused to it, either separately (as benzenes) or together as naphthalene. It may also consist of fused systems of two phenalenes and two additional hexagons in different conformations. Other systems with the coronene core have an arm as a fused system of (a) naphthanthrene and phenalene or (b) perylene and phenalene.



Naphthanthrene;

Perylene

As far as the benzenoids with the coronene core are concerned we have characterized the systems where the arms are composite. Finally there exist some few systems with the coronene core and two types of basic benzenoids as the arms.

Special Description, and the Enumeration. CHART I shows the totality of 7 concealed non-Kekuléan h=55 benzenoids with hexagonal symmetry possessing the circumcoronene core. The first system is basic, all the other are composite.

CHART I

Circumcoronene core

Arms	A	B
-Tr	1	1
-Pl:Pl	2	3
Total	7	

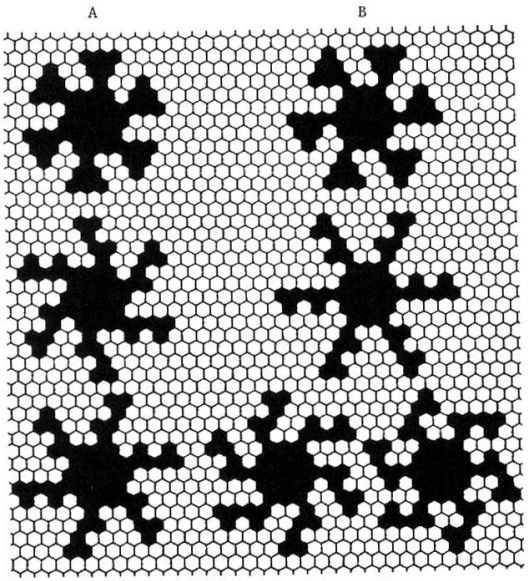
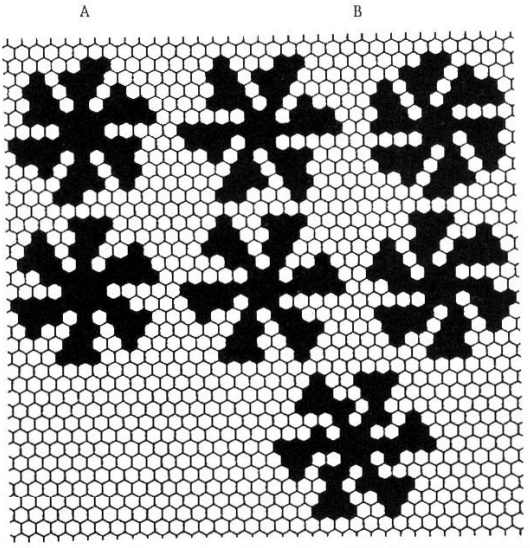


CHART II

Arms basic

A	B
2	4
0	1

Total 7



In CHART I and throughout this paper we use the abbreviations (see also above):

A arms condensed to the core
B arms fused to the core
Tr triangulene
Pl phenalene

The rest of the non-Kekuléan h=55 hexagonal benzenoids possess the coronene core. They are classified into different types in the following.

CHART II shows the totality of 7 systems where the arms are basic benzenoids: in the first six systems the arms are all identical, while the arms in the last system are unique. With regard to the whole systems, those of the A type are basic, and those of the B type composite.

CHART III shows the three existing composite systems where the arms consist of phenalene fused to perylene. For the 5 A-type and 10 B-type systems with phenalene fused to naphthanthrene only one example is depicted for each representative.

This practice of depicting only one example within each enumerated class is followed in the rest of this description.

CHART IV gives the details of the enumeration of the systems with triangulene and phenalene units in the arms and no hexagons with five free edges, i.e. belonging to the class *D*, to which all the benzenoids described above (CHARTS I-III) also belong.

The arms are symbolized in terms of the fused parts, where a colon (:) stands for the edge of fusion. In addition to

CHART III

Arms

perylene:Pl

A	B
0	3

naphthanthrene:Pl

A	B
5	10

Total 18

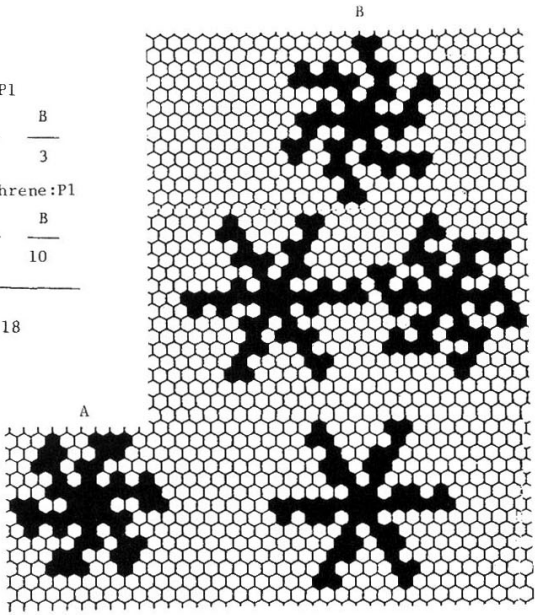


CHART IV
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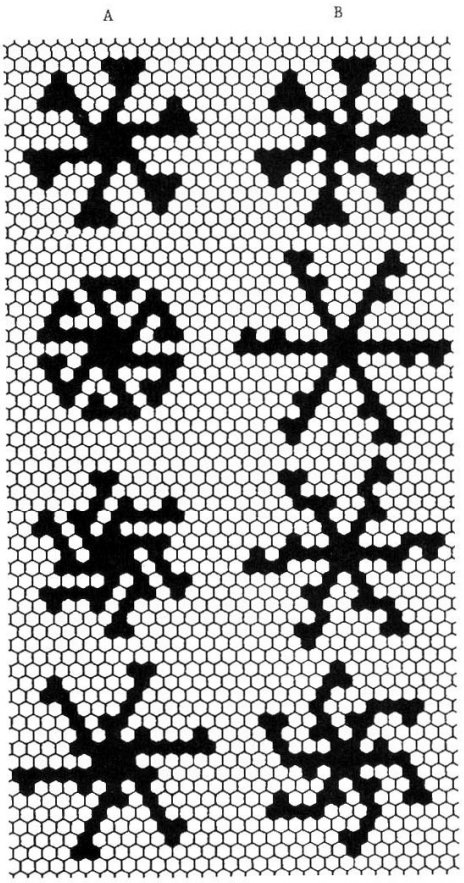
Rest of *D* systems

Arms	A	B
-2:Tr	5	6
-2:Pl:Pl	17	23
-1:Pl:1:Pl	15	15
-Pl:2:Pl	7	18
Total	106	



the symbols Tr and Pl we use the number of hexagons, viz. 1 (benzene) and 2 (naphthalene). The stroke (-) indicates the junction to the core (in which no more hexagons are involved); it may be a condensation (A) or fusion (B).

The two final categories (CHART V and CHART VI) consist of those benzenoids which have hexagons with five free edges,

i.e. belonging to the class *F*. They comprise more than the half of the benzenoids in question.

In CHART V we have collected the systems where the cata-condensed appendages consist of one single hexagon fused to each arm. In the description of the arms (cf. the table in CHART V) we have introduced a frame. It indicates that the additional hexagon (symbolized by :1) may be fused in any allowed position to the unit corresponding to the symbols within the frame. This situation is also referred to as one hexagon annelated to each arm.

CHART V

F systems:
1 annelated hexagon
to each arm

Arms	A	B
-1:Tr:1	7	8
-[1:P1:P1]:1	24	26
-[P1:1:P1]:1	11	32
Total	108	

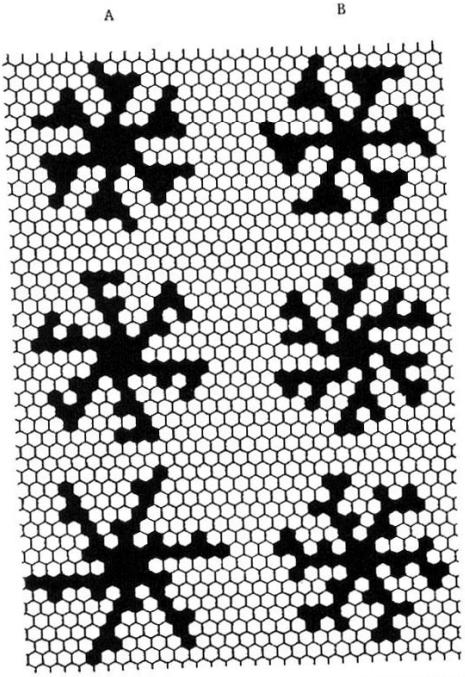


CHART VI
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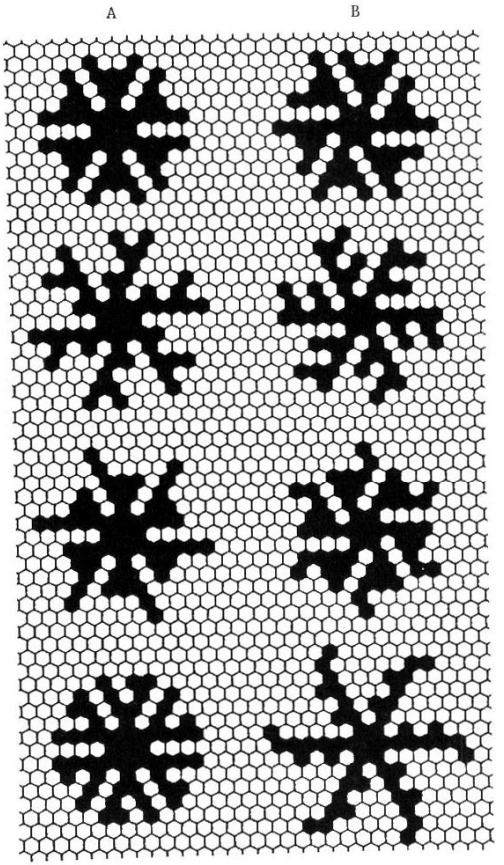
F systems:
2 annelated hexagons
to each arm

Arms	A	B
-[Tr]:1 :1	1	1
-[Pl:Pl]:1 :1	7	13
-Tr:2	3	7
-[Pl:Pl]:2	12	23
Total	67	



The benzenoid systems of CHART VI may be characterized as having two hexagons annelated to each arm. These catacondensed appendages consist of two separated hexagons (benzenes) or one naphthalene. The first system in CHART VI is the unique concealed non-Kekuléan h=55 benzenoid with D_{6h} symmetry.

Summary. CHARTS I-VI give the details of a classification of the 313 (concealed) non-Kekuléan benzenoids with h=55: 1 system belongs to D_{6h} and 312 to C_{6h}. Below we give in summary the total numbers for other coarse classifications of these benzenoid systems.

(i) Cores:	circumcoronene		coronene
	7		306
(ii) Condensed (A) or fused (B) arms to the core	A		B
	119		194
(iii) Without (D) or with (F) a hexagon which has five free edges	D		F
	138		175

(iv) Constituents of arms (basic unit or fused units)

Tr	Pl + Pl	Pl + other	only other
40	248	18	7

Conclusion. In this work we have given a survey of 313 benzenoid systems according to a "natural" (or "chemical") classification, where different subunits of the benzenoids are taken into account. We do not claim that the systems of this investigation (concealed non-Kekuléans of hexagonal symmetry) are particularly important chemically. However, they have great mathematical (graph-theoretical) interest in the studies of topological properties of benzenoid systems. Different theories for concealed non-Kekuléans have been put forward [4, 6, 8-11].

The present work is also supposed to exemplify a natural classification of benzenoids, which may be adapted to other, chemically more important benzenoid systems. Some work in this direction has been performed for benzenoids in general (regardless of symmetry) with h up to 9 [5], and for selected systems beyond this h value [5, 12]. A natural classification of this kind has also been reported for coronoids with h up to 11 [13].

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