



## ALL-BENZENOID SYSTEMS:

## ENUMERATION AND CLASSIFICATION OF BENZENOID HYDROCARBONS. VI

B. N. CYVIN, J. BRUNVOLL and S. J. CYVIN

*Division of Physical Chemistry, The University of Trondheim,  
N-7034 Trondheim-NTH, Norway*

I. GUTMAN

*Faculty of Science, University of Kragujevac, P. O. Box 60,  
YU-34000 Kragujevac, Yugoslavia*

(Received: February 1988)

*Abstract:* All-benzenoid systems have been enumerated by computer aid. Separate numbers for catacondensed (up to  $h=22$ ) and pericondensed (up to  $h=18$ ) systems are reported along with the information about symmetry. Here  $h$  is used to denote the number of hexagons of the system. All the generated systems for  $h \leq 13$  are depicted and their  $K$  numbers given.  $K$  designates the number of Kekulé structures. Fourteen classes of all-benzenoids are summarized; they have been studied previously with respect to the  $K$  numbers. A program is outlined for further studies in this area.

## INTRODUCTION

In the studies of all-benzenoid systems the concept of Clar's sextet [1] is crucial. In the wording of Randić [2]: "For these compounds one can write a valence structure in which a ring is either represented as an isolated sextet or is devoid of conjugation." A precise definition has been given by Polansky and Derflinger [3], followed by a graph-theoretical treatment of Polansky and Rouvray [4]. Later it was commented and supplemented by Polansky and Gutman [5], who also produced a general procedure for determining the number of Kekulé structures for all-benzenoid systems.

An aromatic sextet in a given Kekulé structure is characterized by a hexagon with three double bonds (as in benzene). In an all-benzenoid system it is possible, in a certain number of Kekulé structures, to assign uniquely a pattern of sextets throughout, so that the remaining hexagons do not possess any additional double bonds. The sextets determine the set of full hexagons ( $F$ ), conventionally drawn with inscribed circles, while the others are referred to as empty ( $E$ ). In all-benzenoid systems the classification of

the hexagons into full and empty is unique (see the subsequent article).

Benzene itself and polyphenylenes are trivial examples of all-benzenoid systems without empty hexagons; the polyphenylenes are furthermore disconnected (and therefore not benzenoids in a strict sense). A less trivial example is triphenylene (cf. Fig. 1), an empty hexagon surrounded by three full. As a matter of fact any empty hexagon in an all-benzenoid is always surrounded by three full hexagons in a trigonal configuration as in triphenylene.

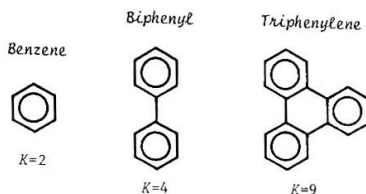


Fig. 1. Simple or trivial examples of all-benzenoid systems.

The present work was inspired by a recent paper of Knop et al. [6] containing extensive computerized enumerations of benzenoids. As a minor part of this paper 18 sextet 2-factorable benzenoids are depicted; the category appears to be synonymous with all-benzenoids. In spite of the relatively small number (eighteen) the reported systems are complete up to  $h=10$ , where  $h$  designates the number of hexagons. We have developed a new, simple algorithm for generating all-benzenoids. It has enabled us to enumerate these systems specifically up to  $h=18$ .

#### GENERATION ALGORITHM

All-benzenoid systems are generated successively by additions of three hexagons, two hexagons or one hexagon to lower members, following certain rules. We refer to these three possibilities as (i)  $h \rightarrow h+3$ , (ii)  $h \rightarrow h+2$  and (iii)  $h \rightarrow h+1$  additions, respectively.

(i)  $h \rightarrow h+3$  (one-contact addition)

A *free edge* is defined as an edge between two vertices of second degree. In an all-benzenoid a free edge can obviously occur only in  $F$ . A new all-benzenoid is produced by adding an  $E$  to the free edge, succeeded by two  $F$ 's added to non-incident free edges of the last added  $E$ . In other words: a phenanthrene is added to a free edge of an  $F$  so that a triphenylene subunit is formed (see Fig. 2).

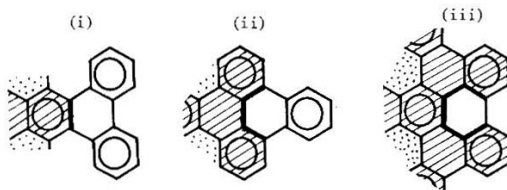


Fig. 2. Three ways of generating an all-benzenoid from an all-benzenoid with less hexagons.

(ii)  $h \rightarrow h+2$  (three-contact addition)

Assume an all-benzenoid with a *bay* region, which by definition is formed by three edges of the perimeter between vertices of second, third, third and second degree in that order. It is evident that a bay region of an all-benzenoid must belong to an  $F-E-F$  configuration. A new all-benzenoid is produced by adding an  $E$  so that three of its edges constitute the bay and annexing an  $F$  to the free edge of this  $E$ . In other words: a naphthalene is imbedded into the bay (see Fig. 2).

(iii)  $h \rightarrow h+1$  (five-contact addition)

A *fjord* may occur in an all-benzenoid and is defined as a configuration of five edges of the perimeter between vertices of second, four times third and second degree in that order. These edges must clearly belong to an  $F-F-F-F-F$  configuration when dealing with all-benzenoids. A new all-benzenoid is produced by adding a hexagon which shares five of its edges with the fjord. In other words: a hexagon (or benzene) is immersed into the fjord (see Fig. 2).

A procedure was added to the previously described computer program [7, 8] to account for the generation of all-benzenoids according to the principles described above.

In a separate run all-benzenoids were generated from benzene by using the  $h \rightarrow h+3$  additions only.

The results of enumeration are collected in Table 1. The numbers for total all-benzenoids reproduce the Knop et al. [6] numbers up to  $h=10$ , which cover 18 systems. Altogether we have generated 13650 systems ( $h \leq 22$  cata-condensed,  $h \leq 18$  total).

Table 1. Numbers of all-benzenoids (*cata* catacondensed; *peri* pericondensed) and their distribution into symmetry groups.

<i>h</i>		$D_{6h}$	$C_{6h}$	$D_{3h}$	$C_{3h}$	$D_{2h}$	$C_{2h}$	$C_{2v}$	$C_s$	Total
1	<i>cata</i>	1	0	0	0	0	0	0	0	1
4	<i>cata</i>	0	0	1	0	0	0	0	0	1
6	<i>peri</i>	0	0	0	0	1	0	0	0	1
7	<i>cata</i>	0	0	0	0	1	0	1	0	2
8	<i>peri</i>	0	0	0	0	0	0	1	0	1
9	<i>peri</i>	0	0	0	0	0	0	1	2	3
10	<i>cata</i>	0	0	1	0	0	0	2	3	9
	<i>peri</i>	0	0	1	0	0	1	1	0	
11	<i>peri</i>	0	0	0	0	2	0	2	6	10
12	<i>peri</i>	0	0	0	0	1	2	5	21	29
13	<i>cata</i>	0	0	1	1	0	3	7	20	57
	<i>peri</i>	1	0	0	0	0	0	3	21	
14	<i>peri</i>	0	0	0	0	1	2	12	87	102
15	<i>peri</i>	0	0	0	0	0	2	14	243	259
16	<i>cata</i>	0	0	0	0	0	0	14	158	526
	<i>peri</i>	0	0	1	1	2	9	18	323	
17	<i>peri</i>	0	0	0	0	2	11	38	1085	1136
18	<i>peri</i>	0	0	0	0	1	22	58	2632	2713
19	<i>cata</i>	0	0	0	2	1	19	41	1076	
22	<i>cata</i>	0	0	0	8	0	0	79	7574	

#### GENERAL CLASSIFICATION

A survey of the enumeration of benzenoids has appeared as a consolidated report by fourteen authors [9]. It may be consulted for definitions of classes of benzenoids.

All-benzenoids are Kekuléan systems and have therefore invariably  $\Delta=0$  (i.e. the same number of black and white vertices). In the frames of the *neo* classification [7, 9] the considered systems are all normal (*n*). A formal demonstration of this fact is given in the subsequent article.

An all-benzenoid may be catacondensed or pericondensed. In the sub-

sequent article it is also shown that catacondensed all-benzenoids occur for every third  $h$  value, viz.  $h = 1, 4, 7, \dots$ , whereas pericondensed all-benzenoids exist for  $h=6$  and all  $h \geq 8$ . The catacondensed systems were generated specifically by taking into account the one-contact additions ( $h \rightarrow h+3$ ) only; see above.

In Table 1 the numbers of catacondensed and pericondensed all-benzenoids are entered separately; the latter ones were obtained by subtraction from total. A special procedure for determining the symmetry was incorporated into the computer program [8]. The numbers within each symmetry group are reported (Table 1).

#### FORMS OF THE SYSTEMS, AND THEIR $K$ NUMBERS

The forms of the generated all-benzenoid systems up to  $h=13$  are displayed in Fig. 3. The first eighteen pictures reproduce exactly those of Knop et al. [6].

A special program, based on a technique proposed by Brown [10], was used to compute the numbers of Kekulé structures ( $K$ ) for the systems. In Fig. 3 the systems are ordered according to increasing  $K$  numbers.

#### SPECIAL CLASSIFICATION

A glance at Fig. 3 shows that several of the benzenoids therein may be grouped into special classes, for which it is of interest to derive the combinatorial  $K$  formulas.

In the monograph [11] results for fourteen classes of all-benzenoids have been collected; one member of each class (for the parameter value equal to 3) is depicted in Fig. 4, which also contains the notation. The mentioned reference [11] gives explicit  $K$  formulas for all these classes but one, viz.  $S(n)$ . Recurrence relations are given for all cases, including  $S(n)$ .

All the benzenoid classes of Fig. 4 may be interpreted as *repeated units* in one way or another with allowance for modifications at the ends. Most of the classes are *fused* repeated units modified at one or both ends. Two benzenoid units are said to be fused when they share exactly one edge.

Several methods for the enumeration of Kekulé structures have been developed, which are applicable to benzenoid systems with repeated units. (i) Studies of the sextet polynomial and its recurrence properties [12-14]. An operator technique has been developed for obtaining efficiently the recurrence relations [15]. (ii) Method of linearly coupled recurrence rela-

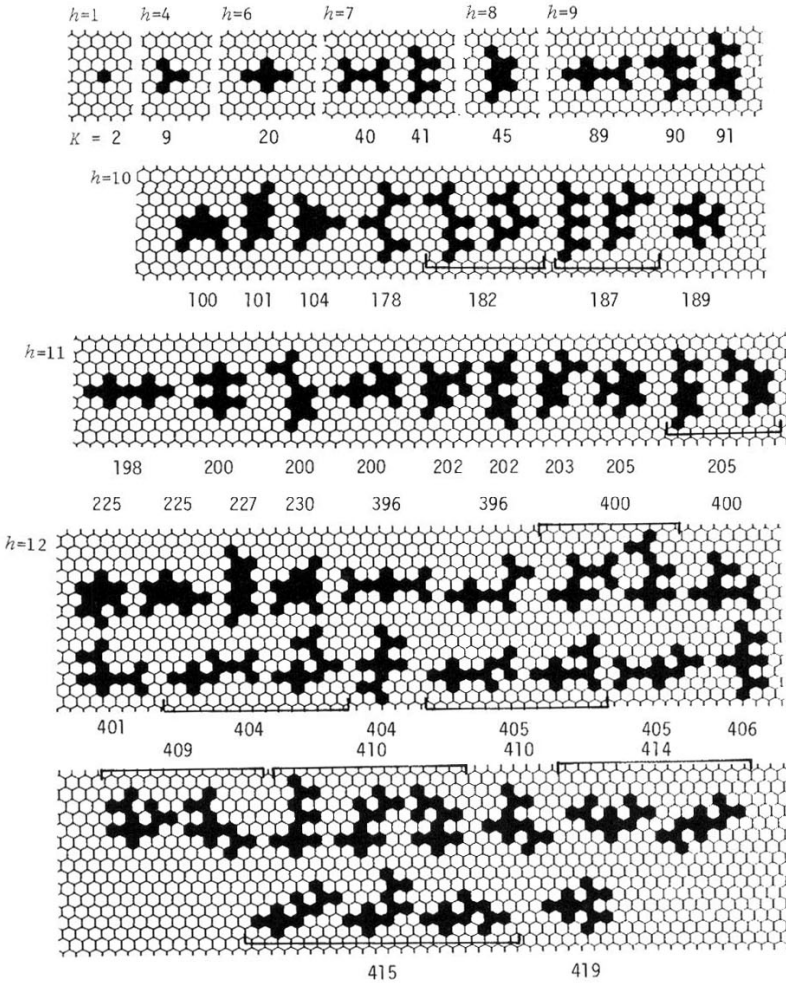


Fig. 3. Listing of all-benzenoids for  $h \leq 13$ .  $K$  numbers are given. Bracketed systems are isoarithmic. (For  $h=13$ , see next page.)



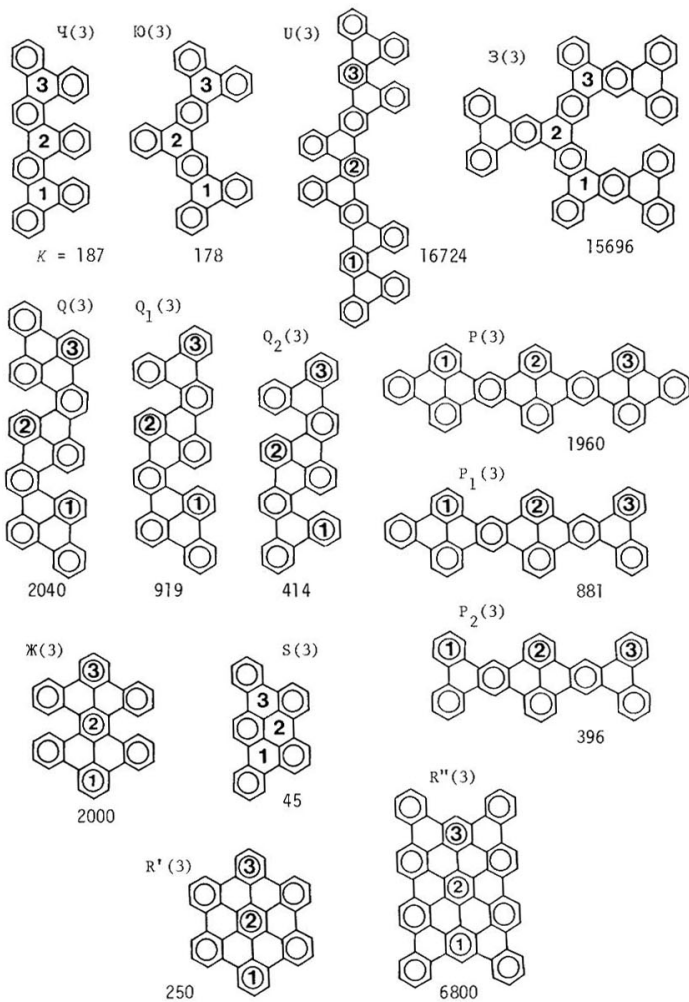


Fig. 4. Members of 14 all-benzenoid classes. The  $K$  numbers are given.



tions [16]. Here several benzenoid classes are considered simultaneously. The method is based on the fragmentation technique due to Randić [17], and has been widely used; see [11] and references cited therein, e.g. [18-22]. A general formulation for fused repeated units is available [23]. (iii) A still more general method for one-dimensional polymers has been worked out [24] and applied to a variety of benzenoid (and non-benzenoid) classes [25]. (iv) Application of the reduced graph model [26]. The technique has been applied to benzenoids with repeated units [27]. (v) A method referred to as the transfer matrix formulation [28] has also been used to enumerate the Kekulé structures of a benzenoid class with repeated units [29].

Figure 5 shows a typical example of an all-benzenoid class, which sometimes is called "pyrenes on a string". Here it is designated by  $P(n)$ . Members of this class have been considered by several authors [2, 5, 6, 11, 14, 22, 23, 30]. The system may be interpreted as  $n$  fused benzof[*e*]pyrenes with one hexagon added at the appropriate end. The recurrence relation for the numbers of Kekulé structures, say  $K\{P(n)\}$ , is implied in the work of Ohkami and Hosoya [14]. It reads

$$K\{P(n)\} = 10K\{P(n-1)\} - K\{P(n-2)\}; \quad n \geq 2$$

The explicit formula was first given by Cyvin, Cyvin and Gutman [22] and reads:

$$K\{P(n)\} = \frac{1}{2\sqrt{6}} \left[ (5 + 2\sqrt{6})^{n+1} - (5 - 2\sqrt{6})^{n+1} \right]$$

The hydrocarbons corresponding to  $P(1)$  and  $P(2)$  are known in organic chemistry according to the recent, useful monograph of Dias [31].

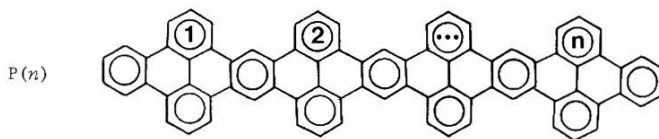


Fig. 5. A class of all-benzenoids: "pyrenes on a string".

#### PROGRAM OF FUTURE WORK

The generated all-benzenoid systems, as displayed in Fig. 3, suggest a number of new classes, which might be interesting to study with respect to their numbers of Kekulé structures. It is planned to give a systematic account of so many new all-benzenoid classes that all the forms for  $h \leq 11$  are covered among their members. In some cases it is expected that known methods will lead to recurrence relations and explicit  $K$  formulas similar to the case of "pyrenes on a string" (see above). But also interesting new features are to be expected.

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

#### REFERENCES

1. E. Clar, *The Aromatic Sextet*, Wiley, London 1972.
2. M. Randić, *Pure & Appl. Chem.* 52, 1587 (1980).
3. O.E. Polansky and G. Derflinger, *Internat. J. Quant. Chem.* 1, 379 (1967).
4. O.E. Polansky and D.H. Rouvray, *Match* 2, 91 (1976).
5. O.E. Polansky and I. Gutman, *Match* 8, 269 (1980).
6. J.V. Knop, W.R. Müller, K. Szymanski and N. Trinajstić, *J. Comput. Chem.* 7, 547 (1986).
7. J. Brunvoll, S.J. Cyvin and B.N. Cyvin, *J. Comput. Chem.* 8, 189 (1987).
8. J. Brunvoll, B.N. Cyvin and S.J. Cyvin, *J. Chem. Inf. Comput. Sci.* 27, 171 (1987).
9. A.T. Balaban, J. Brunvoll, J. Cioslowski, B.N. Cyvin, S.J. Cyvin, I. Gutman, W.C. He, W.J. He, J.V. Knop, M. Kovačević, W.R. Müller, K. Szymanski, R. Tošić and N. Trinajstić, *Z. Naturforsch.* 42a, 863 (1987).
10. R.L. Brown, *J. Comput. Chem.* 4, 556 (1983).
11. S.J. Cyvin and I. Gutman, *Kekulé Structures in Benzenoid Hydrocarbons*, *Lecture Notes in Chemistry*, Springer-Verlag, Berlin (in press).
12. H. Hosoya and T. Yamaguchi, *Tetrahedron Letters*, 4659 (1975).
13. I. Gutman, H. Hosoya, T. Yamaguchi, A. Motoyama and N. Kuboi, *Bull. Soc. Chim. Beograd* 42, 503 (1977).
14. N. Ohkami and H. Hosoya, *Theor. Chim. Acta* 64, 153 (1983).
15. H. Hosoya and N. Ohkami, *J. Comput. Chem.* 4, 585 (1983).
16. I. Gutman, *Match* 17, 3 (1985).
17. M. Randić, *J. Chem. Soc. Faraday Trans. 2* 72, 232 (1976).
18. R.S. Chen, *J. Xinjiang Univ.* 3(2), 13 (1986).
19. F.J. Zhang and R.S. Chen, *J. Xinjiang Univ.* 3(3), 10 (1986).

20. S.J. Cyvin, B.N. Cyvin and J.L. Bergan, *Match* 19, 189 (1986).
21. L.X. Su, *Match* 20, 229 (1986).
22. S.J. Cyvin, B.N. Cyvin and I. Gutman, *Coll. Sci. Papers Fac. Sci. Kragujevac* 7, 5 (1986).
23. S.J. Cyvin, B.N. Cyvin and I. Gutman, *Z. Naturforsch.* 42a, 181 (1987).
24. A. Graovac, D. Babić and M. Strunje, *Chem. Phys. Letters* 123, 433 (1986).
25. D. Babić and A. Graovac, *Croat. Chem. Acta* 59, 731 (1986).
26. B. Džonova-Jerman-Blažič and N. Trinajstić, *Croat. Chem. Acta* 55, 347 (1982).
27. P. Křivka, S. Nikolić and N. Trinajstić, *Croat. Chem. Acta* 59, 659 (1986).
28. D.J. Klein, G.E. Hite, W.A. Seitz and T.G. Schmalz, *Theor. Chim. Acta* 69, 409 (1986).
29. D.J. Klein, G.E. Hite and T.G. Schmalz, *J. Comput. Chem.* 7, 443 (1986).
30. M. Randić, *Internat. J. Quant. Chem.* 17, 549 (1980).
31. J.R. Dias, *Handbook of Polycyclic Hydrocarbons. Part A. Benzenoid Hydrocarbons*, Elsevier, Amsterdam 1987.