



ALL-BENZENOID SYSTEMS WITH TRIGONAL SYMMETRY*

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

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

(received: January 1992)

Abstract: All-benzenoids with trigonal (D_{3h} and C_{3h}) symmetry are enumerated up to h (the number of hexagons) = 37. The Kekulé structure counts (K) of the systems are treated. A number of combinatorial K formulas are derived.

INTRODUCTION

An extensive study on the enumeration of all-benzenoid systems [1] and their Kekulé structures was initiated recently [2]. In the present work the all-benzenoids with trigonal symmetry, viz. D_{3h} or C_{3h} , are treated.

The first enumeration of all-benzenoids is probably due to Dias [3], who was soon followed by Knop et al. [4] and Cyvin et al. [2]. Additional works in this area by Dias [5-7] and by Cyvin et al. [8] are available.

The enumeration of Kekulé structures (or Kekulé structure count) for all-benzenoids is treated in several works [8-13].

* Part XIV of the series "Enumeration and Classification of Benzenoid Hydrocarbons".

Benzenoid systems with trigonal symmetry have been treated in particular, both the enumeration of such systems [14] and their Kekulé structure count [14,15]. Also Dias [7] has treated benzenoids with trigonal symmetry in particular.

TABLE 1
Numbers of all-benzenoids with trigonal symmetry

h	Catacondensed		Pericondensed		D_{3h}	Total	
	D_{3h}	C_{3h}	D_{3h}	C_{3h}		C_{3h}	$D_{3h}+C_{3h}$
4	1	0	0	0	1	0	1
7	0	0	0	0	0	0	0
10	1	0	1	0	2	0	2
13	1	1	0	0	1	1	2
16	0	0	1	1	1	1	2
19	0	2	4	3	4	5	9
22	0	8	1	4	1	12	13
25	0	0	4	18	4	18	22
28	0	11	6	47	6	58	64
31	1	47	6	63	7	110	117
34	0	0	11	229	11	229	240
37	0	68	15	522	15	590	605

ENUMERATION

All-benzenoids with trigonal symmetry and increasing h values (numbers of hexagons) were enumerated specifically by computer aid. The results are collected in Table 1, which also accounts for the catacondensed and pericondensed systems separately. The lowest values (pericondensed for $h \leq 16$, catacondensed for $h \leq 22$) agree with the previously published numbers [2], while the higher numbers are original.

In Fig. 1 the forms of the all-benzenoids with trigonal symmetry up to $h = 22$ are depicted as black silhouettes on the background of a hexagonal lattice. The white circles indicate full hexagons. The Kekulé structure counts (K numbers) are given in the figure. Herein the bracket-type lines embrace isoarithmic systems.

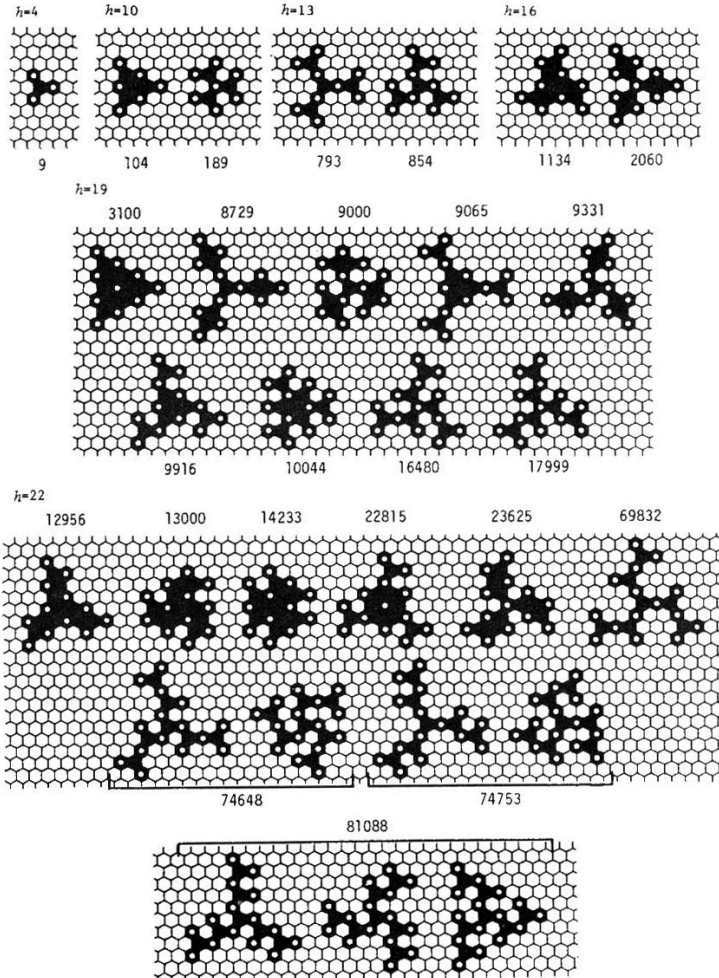


Fig. 1. The all-benzenoids with trigonal symmetry (D_{3h} and C_{3h}) for $h < 25$. K numbers are given.

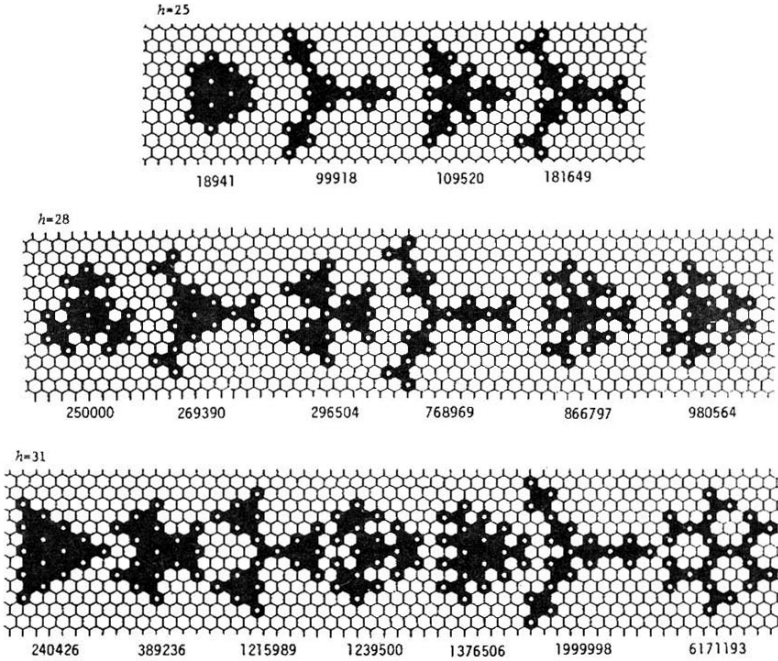


Fig. 2. The all-benzenoids with regular trigonal symmetry (D_{3h}) for $25 \leq h \leq 31$. K numbers are given.

All-benzenoids with regular trigonal (D_{3h}) symmetry in particular are depicted in Fig. 2, in continuation of the systems of this kind already covered by Fig. 1. The two figures together display all the D_{3h} all-benzenoid systems for $h < 34$.

The K numbers of Figs. 1 and 2 were obtained by computer aid.

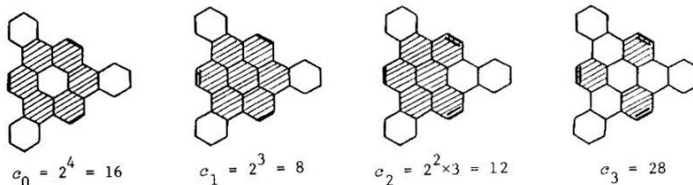
KEKULÉ STRUCTURE COUNTS

Three annelated units

The symmetry-adapted method of fragmentation [15] has been employed in order to derive several combinatorial formulas for Kekulé structure counts (K) of benzenoids with trigonal symmetry [14]. Different classes of benzenoids were considered, in which each member can be interpreted as three identical Kekuléan units annelated to three (symmetrically equivalent) free edges of a core.

The information about the combinatorial K formulas of the previous work is summarized in a compressed form in Table 2, which is augmented by a number of new cores.




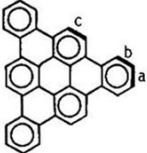

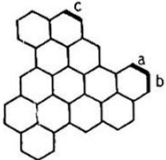
Below we show the derivation of one of the new formulas, where the core (No. 4 in Table 2) is the all-benzenoid tribenzo[a,g,m]coronene. The edge of annelation marked c in Table 2 is considered. The coefficients c_0 , c_1 , c_2 and c_3 emerge as the Kekulé structure counts when the three edges of annelation in the core are assumed to hold zero, one, two and three double bonds, respectively. The actual numbers pertain to the unhatched fragments of the core as is illustrated below.








Now let the Kekulé structure count of the annelated unit be U , while u_d emerges by assuming its edge of annelation to be a double bond. Then the combinatorial K formula in question reads

$$\begin{aligned}
 K &= c_3 U^3 + 3c_2 U^2 u_d + 3c_1 U u_d^2 + c_0 u_d^3 \\
 &= 28U^3 + 36U^2 u_d + 24U u_d^2 + 16u_d^3
 \end{aligned}
 \tag{1}$$

TABLE 2
Listing of coefficients in combinatorial X formulas*

Core	Form	Coefficients for:			
		U^3	$U^2 u_d$	$U u_d^2$	u_d^3
1		1	0	0	1
2		$\left\{ \begin{array}{l} a \ 1 \\ b \ 2 \end{array} \right.$	3	3	2
			3	3	1
3		9	6	3	2
4		$\left\{ \begin{array}{l} a \ 9 \\ b \ 20 \\ c \ 28 \end{array} \right.$	33	42	20
			42	33	9
			36	24	16
5		35	90	90	35
6		$\left\{ \begin{array}{l} a \ 20 \\ b \ 35 \\ c \ 104 \end{array} \right.$	60	75	35
			75	60	20
			66	18	2

(continues)

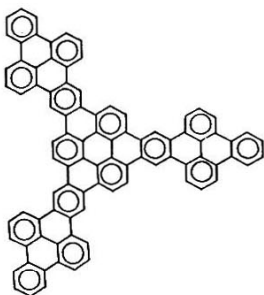
7		250	225	90	20
8		585	285	90	20
9		250	9/5	1290	585
10		585	2040	2415	980
11		3100	11340	14100	6020

* One edge of annelation in each case is heavy.

Notice that for the core itself the Kekulé structure count, say C , is $C = a_0 + 3a_1 + 3a_2 + a_3$. Hence it is obtained simply as the sum of the listed coefficients.

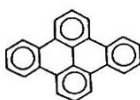
cf. the listing in Table 2.

Table 2 includes cores which are not all-benzenoids. The corresponding K formulas may in fact be very useful in the analyses of all-benzenoids with trigonal symmetry. Let us use the coronene core (No. 3 in Table 2) as example. Then, for instance, the K number of the below system is readily deduced by means of our knowledge to all-benzenoid systems [2].

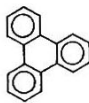


$$K = 99918 \text{ (cf. Fig. 2; } h=25)$$

One only has to use the appropriate coefficients listed in Table 2 together with:



$$U = 20$$

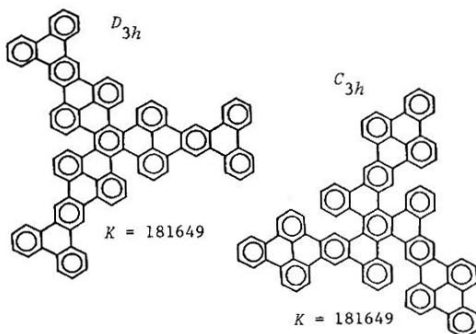


$$u_d = 9$$

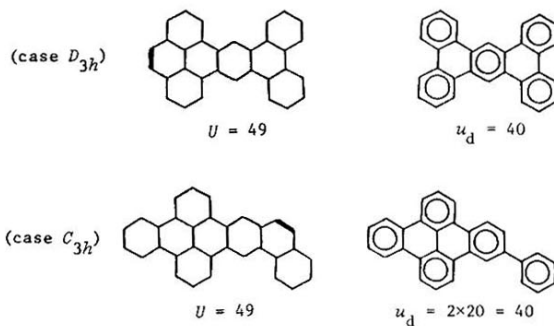
Example of accidental isoarithmicity

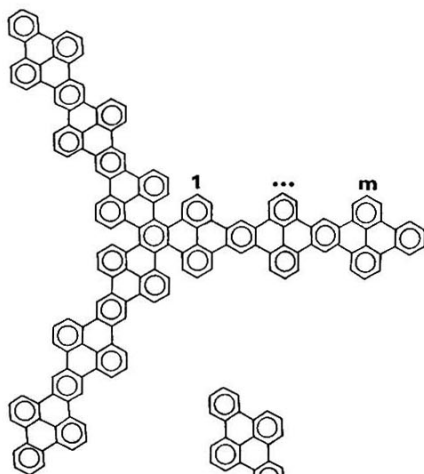
In Fig. 1 some examples of isoarithmicity [10,16] are found; the isoarithmic systems are embraced by a bracket-like line. These systems only differ in the ways the kinks go for angularly annelated catacondensed fragments. They exhibit the same K number, but this is not a sufficient condition for isoarithmicity. Two benzenoids which are not isoarithmic may have the same K number; then one speaks about accidental isoarithmicity.

The last D_{3h} system with $h = 25$ in Fig. 2 appears to have the same K number as an all-benzenoid with C_{3h} symmetry and the same h value:

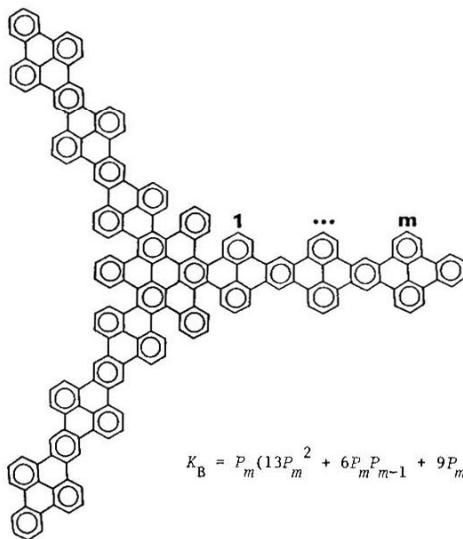


This is clearly a case of accidental isoarithmeticity. The combinatorial K formula for benzene core (No. 1 in Table 2) gives $K = U^3 + u_d^3$, which is applicable to both of the cases above. However, the two fragments (with Kekulé structure counts U and u_d) are completely different, as is shown below (the edge of annelation is heavy).





$$K_A = \frac{1}{4} P_m (P_m^2 + 3P_{m-1}^2)$$



$$K_B = P_m (13P_m^2 + 6P_m P_{m-1} + 9P_{m-1}^2)$$

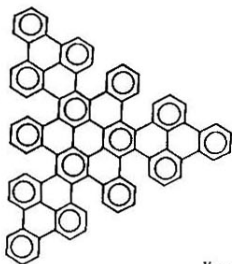
Fig. 3. Combinatorial K formulas containing a parameter ($m > 0$) for two classes of all-benzenoids.

Two combinatorial formulas

There is no limitation for the number of combinatorial K formulas containing a parameter, which can be derived for classes of all-benzenoids with trigonal symmetry. Figure 3 shows two examples, where the formulas are fairly simple. They are expressed in terms of P_m , which designates the Kekulé structure count of "pyrenes on a string" [2], m being the number of pyrene units. The explicit formula for P_m is known [2,10], and numerical P_m values have been listed up to $m = 10$. For the sake of convenience we give some of the first P_m values below.

m	P_m
0	2
1	20
2	198
3	1960
4	19402
5	192060

The formula for K_A in Fig. 3 reproduces $K = 2060$ for $m = 1$ (cf. Fig. 1; $h = 16$) and $K = 1999998$ for $m = 2$ (cf. Fig. 2; $h = 31$). The formula for K_B reproduces $K = 109520$ for $m = 1$:



$K = 109520$ (cf. Fig. 2; $h=25$)

Double annelation to coronene

The consideration of three pairs of annelated units (i.e. a double annelation) to a core in a trigonal arrangement (if possible), is a useful generalization. As an example we shall consider such a double annelation to coronene. Let U and u_d pertain to one triple of the identical units, while V and v_d with the analogous meaning pertain to the other triple. It was arrived at the formula

$$\begin{aligned}
 K = & U^3 V^3 + 3U^2 V v_d (V + v_d) + 3V^3 U u_d (U + u_d) \\
 & + 2(U^3 v_d^3 + V^3 u_d^3) + 3U^2 V^2 u_d v_d
 \end{aligned}
 \tag{2}$$

This formula is applicable to the system depicted above. The pertinent K number (= 109520) is reproduced by inserting: $U = 11$, $u_d = 9$, $V = 2$, $v_d = 1$.

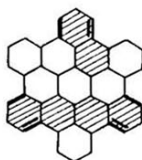
Condensation to tribenzo[bc,hi,no]coronene

Among the all-benzenoids with regular trigonal (D_{3h}) symmetry it is distinguished between those where the two-fold symmetry axes (a) bisect edges or (b) go through vertices and edges. In Figs. 1 and 2 the two types manifest themselves by having (a) a horizontal two-fold symmetry axis or (b) a vertical two-fold symmetry axis, respectively. In our collection (Figs. 1 and 2) there is only one system belonging to the (b) type, viz. the first (smallest K number) D_{3h} all-benzenoid with $h = 28$ (cf. Fig. 2). This system may be interpreted as in the title of this paragraph. In the following we shall derive the K number of the system under consideration, but take into account a wider class of benzenoids.

Assume three identical Kekuléan units condensed into the positions ef , kl and qr of tribenzo[bc,hi,no]coronene. Then the following fragmentation schemes for the core come into operation.



$$k_1 = 35$$

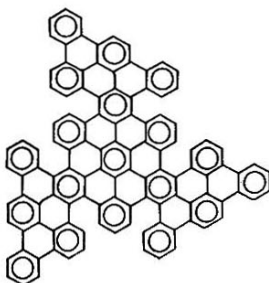


$$k_2 = 2 \times 15 = 30$$

Here the hexagons with one single and one double bond marked by heavy lines belong to the condensed units. Now let u_s and u_d denote the Kekulé structure counts obtained when the edges of condensation of the unit are assigned to single/double or double/single bonds, respectively. It is unimportant to specify which is which because of the symmetry of the problem. Then the total Kekulé structure count is

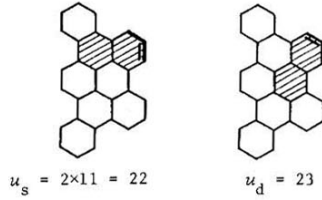
$$K = k_1(u_s^3 + u_d^3) + 3k_2 u_s u_d (u_s + u_d) \quad (3)$$

The above formula applies to C_{3h} cases as well as D_{3h} . Consider, for example, the below system.



$$K = 2847825$$

The appropriate fragments of the unit are:

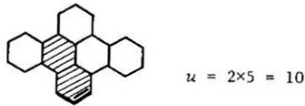


On inserting these u_s and u_d values into (3) together with the numerical coefficients ($k_1 = 35$, $k_2 = 30$) one arrives at the K number given above.

In the cases of D_{3h} symmetry eqn. (3) is simplified by virtue of $u_s = u_d = u$. Hence

$$K = (2k_1 + 6k_2)u^3 \tag{4}$$

which is applicable to the first D_{3h} all-benzenoid with $h = 28$, which was mentioned above. For this particular example one has:



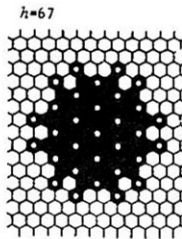
Hence $K = 250 u^3 = 250 \times 10^3$ in consistence with the appropriate value given in Fig. 2.

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

APPENDIX



All-benzenoids with hexagonal (D_{6h} or C_{6h}) symmetry belong to the class of benzenoids called snowflakes and have been referred to as all-flakes. They are treated elsewhere in a paper [17] which is considered as No. 7 in this series of all-benzenoid systems. The depiction for the D_{6h} all-flake with $h = 67$ therein is a wrong figure; it should be:



No. 8 of the present series has appeared as Ref. 18.

REFERENCES

1. O. E. Polansky and G. Derflinger, *Internat. J. Quant. Chem.* **1**, 379 (1967).
2. B. N. Cyvin, J. Brunvoll, S. J. Cyvin and I. Gutman, *Match* **23**, 163 (1988).
3. J. R. Dias, *Nouv. J. Chim.* **9**, 125 (1985).
4. J. V. Knop, W. R. Müller, K. Szymanski and N. Trinajstić, *J. Comput. Chem.* **7**, 547 (1986).
5. J. R. Dias, *Thermochim. Acta* **122**, 313 (1987).
6. J. R. Dias, *Handbook of Polycyclic Hydrocarbons. Part A. Benzenoid Hydrocarbons*, Elsevier, Amsterdam 1987.
7. J. R. Dias, *J. Mol. Struct. (Theochem)* **185**, 57 (1989).
8. S. J. Cyvin, B. N. Cyvin and J. Brunvoll, *J. Mol. Struct.* **198**, 31 (1989).
9. O. E. Polansky and I. Gutman, *Match* **8**, 269 (1980).
10. S. J. Cyvin and I. Gutman, *Kekulé Structures in Benzenoid Hydrocarbons (Lecture Notes in Chemistry 46)*, Springer-Verlag, Berlin 1988.
11. S. J. Cyvin, J. Brunvoll and B. N. Cyvin, *Match* **24**, 59 (1989).
12. B. N. Cyvin, S. J. Cyvin and J. Brunvoll, *Match* **24**, 65 (1989).
13. S. J. Cyvin, B. N. Cyvin and J. Brunvoll, *Match* **25**, 105 (1990).
14. S. J. Cyvin, J. Brunvoll and B. N. Cyvin, *J. Mol. Struct. (Theochem)* **180**, 329 (1988).
15. S. J. Cyvin, B. N. Cyvin and J. Brunvoll, *J. Mol. Struct. (Theochem)* **151**, 271 (1987).
16. A. T. Balaban and I. Tomescu, *Match* **14**, 155 (1983).
17. S. J. Cyvin, B. N. Cyvin and J. Brunvoll, *J. Mol. Struct.* **198**, 31 (1989).
18. J. Brunvoll, B. N. Cyvin and S. J. Cyvin, *Match* **26**, 3 (1991).