Topological Properties of Circumcoronenes

Ivan Gutman, Sven J. Cyvin[a], and Vesna Ivanov-Petrović

Faculty of Science, University of Kragujevac, P. O. Box 60, YU-34000 Kragujevac, Yugoslavia
[a] Department of Physical Chemistry, University of Trondheim, N-7034 Trondheim, Norway

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The regular-hexagon-shaped benzenoid hydrocarbons: B_1 = benzene (C_6H_6), B_2 = coronene ($C_{24}H_{12}$), B_3 = circumcoronene ($C_{54}H_{18}$), B_4 = circumcircumcoronene ($C_{150}H_{30}$), etc. possess unique topological properties. General expressions for the most important of such properties (number of fundamental structural invariants, number of Kekulé and Clar structures, number of aromatic sextets, Wiener and Szeged indices, spectral moments) are given, including a number of results that are communicated here for the first time. Cyclic conjugation in circumcoronenes is analyzed by means of its energy-effect, and found to agree with the predictions of Clar's aromatic sextet theory only in the case of B_1 and B_2.

Key words: Circumcoronenes; Benzenoid Hydrocarbons; Topological Properties (of Benzenoid Hydrocarbons); Kekulé Structures; Clar Theory

Introduction

Recent progress [1]–[5] in the synthesis and isolation of very large benzenoid hydrocarbons (with 20 and more hexagons) renewed interest in their topological properties. Molecular-topology-based theories of benzenoid and other polycyclic conjugated molecules were elaborated in numerous papers and monographs (see [6]–[9] and the references cited therein). Yet, with a few exceptions, they were (tacitly) restricted to moderate-sized systems. Here we focus our attention to a distinguished series of benzenoids, whose members rapidly become enormously large.

In this paper we report general expressions for a variety of topological properties of the regular-hexagon-shaped benzenoid hydrocarbons B_k, $k = 1, 2, \ldots$, possessing a D_{6h} symmetry, the first members of which are benzene ($k = 1$), coronene ($k = 2$), circumcoronene ($k = 3$), circumcircumcoronene ($k = 4$), see Figure 1.

The benzene-coronene-circumcoronene series is a distinguished class of benzenoid systems [6]–[9]. Results concerning the topological properties of these molecules have been communicated on many different places [6], [7], [10]–[21]. The aim of this paper is to collect all these results and to complete them by those which have not yet been reported.

The $(k + 1)$-th member of the benzene-coronene-circumcoronene series is formally obtained by circumscribing hexagons around the k-th member. The general case of such a circumscribing procedure has been outlined elsewhere [15], [17]. Further general formulations ca be found in [16].

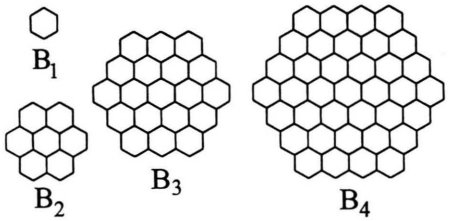

Fig. 1. The first members of the benzene-coronene-circumcoronene series: B_1 = benzene, B_2 = coronene, B_3 = circumcoronene, B_4 = circumcircomcoronene.

Number of Fundamental Structural Invariants

In accordance with the notation used in the book [7], a benzenoid system has n vertices, h hexagons, m edges, n_i internal vertices, n_2 vertices of degreee two, n_3 vertices of degree three, and the size of its perimeter is n_p. For the benzenoid system B_k we have

$$n = 6\,k^2, \tag{1}$$

$$h = 3\,k^2 - 3\,k + 1, \tag{2}$$

$$m = 9\,k^2 - 3\,k, \tag{3}$$

$$n_i = 6(k-1)^2, \tag{4}$$

$$n_2 = 6\,k, \tag{5}$$

Reprint requests to Prof. I. Gutman; Fax: ++381-34-335040.

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$$n_3 = 6\,k(k-1), \tag{6}$$

$$n_p = 6(2\,k-1). \tag{7}$$

The relations (1)–(7) hold for all values of k, $k \geq 1$. Equivalents of (2) and (3) were given in [14].

In order to deduce (1), notice that the vertices of B_k lie on k pairs of horizontal (zig-zag) lines, containing $2\,i+1$ vertices, $i = k,\ k+1,\ \ldots,\ 2\,k-1$. Then (1) follows from

$$2\sum_{i=k}^{2k-1}(2i+1) = 6k^2\,.$$

Equation (4) is an immediate consequence of (1) because the internal vertices of B_k form a system B_{k-1}. Formula (7) is then obtained from $n_i + n_p = n$.

Equation (2) follows from (1) and (4) in view of the relation [7] $n = 4h + 2 - n_i$.

Equation (3) follows from (1) and (2) in view of the relation [7] $m = n + h - 1$.

Formula (6) is obtained from (2) and the relation [7] $n_3 = 2(h-1)$ and then (5) results from $n_2 + n_3 = n$.

According to the expression (1) and (5) the benzenoid hydrocarbon corresponding to B_k has the formula [14] $C_{6k^2}H_{6k}$ or $C_nH_{\sqrt{6n}}$. More general chemical formulas for circumscribed benzenoids are given in [15]–[17].

The circumcoronenes B_k belong to extremal benzenoid systems [22] because they possess minimal numbers of edges for a given number of hexagons [11]. In addition to this, circumcoronenes possess the maximal number of Kekulé structures among all benzenoid systems of the same size [23].

Number of Kekulé Structures

The Kekulé structure count of B_k is given by the beautiful combinatorial expression

$$K(B_k) = \prod_{i=0}^{k-1} \frac{\binom{2k+1}{k}}{\binom{k+1}{k}}, \tag{8}$$

which holds for $k \geq 1$. This formula was first communicated by Gordon and Davison [10], but it was discovered prior to 1952 by Everett. Its first proof was published only in 1988 [13]. (For further details on (8) and its generalizations see p. 104 of [6].)

For the series B_k, $k = 1, 2, \ldots$, the K-values may be calculated recursively by means of the hitherto not reported formula

$$K(B_{k+1}) = \alpha_k K(B_k),$$

where

$$\alpha_k = \frac{(3k+2)!\,k!}{(2k+1)!^2}\prod_{i=1}^{k-1}\frac{(2k+1+i)(2k+2+i)}{(k+1+i)^2}.$$

With increasing k the value of $K(B_k)$ increases very rapidly. Thus we have

$K(B_1) = 2,$
$K(B_2) = 2^2 \cdot 5 = 20,$
$K(B_3) = 2^2 \cdot 5 \cdot 7^2 = 980,$
$K(B_4) = 2^4 \cdot 3^3 \cdot 7^2 \cdot 11 = 232,848,$
$K(B_5) = 2^2 \cdot 3^3 \cdot 11^4 \cdot 13^2 = 267,227,532,$
$K(B_6) = 2^4 \cdot 11^4 \cdot 13^5 \cdot 17 = 1,478,619,421,136$
$\approx 1.4786\ 10^{12},$
$K(B_7) = 2^6 \cdot 5 \cdot 11 \cdot 13^5 \cdot 17^4 \cdot 19^2 \approx 3.9406\ 10^{16},$
$K(B_8) = 2^8 \cdot 5 \cdot 13^2 \cdot 17^7 \cdot 19^5 \cdot 23 \approx 5.0552\ 10^{21},$
$K(B_9) = 2^6 \cdot 5^2 \cdot 17^7 \cdot 19^8 \cdot 23^4 \approx 3.1203\ 10^{27},$
$K(B_{10}) = 2^4 \cdot 3^3 \cdot 5^5 \cdot 7^2 \cdot 17^4 \cdot 19^8 \cdot 23^7 \cdot 29$
$\approx 9.2650\ 10^{33}.$

It has been shown [12] that for large enough k

$$\ln K(B_k) \approx \left(\frac{3}{2}\ln\frac{27}{16}\right)k^2\,. \tag{9}$$

The quality of this estimate can be judged from the ratio of $\ln K(B_k)$ and the right-hand side of (9). For $k = 3, 4, \ldots, 10$ this ratio is equal to 0.975, 0.984, 0.989, 0.9917, 0.9936, 0.9949, 0.9958 and 0.9965, respectively.

Number of Clar Structures

According to a theory put forward by Clar [24], the dominant modes of cyclic conjugation in a benzenoid hydrocarbon are respresented by so-called Clar structural formulas [7], [25]. For odd values of k the system B_k possesses a unique Clar formula. For even values of k, B_k has two symmetry-equivalent Clar formulas. These are illustrated in Fig. 2 for the cases $k = 4$ and $k = 5$.

In order to count the aromatic sextets in the Clar formulas of B_k notice that they are arranged in parallel vertical rows. If k is odd, then these rows contain $(k+1)/2$, $\ldots, k-1, k, k-1, \ldots, (k-1)/2$ aromatic sextets. The sum of these terms is equal to

$$2\sum_{i=(k+1)/2}^{k-1} i + k = \frac{3k^2+1}{4}.$$

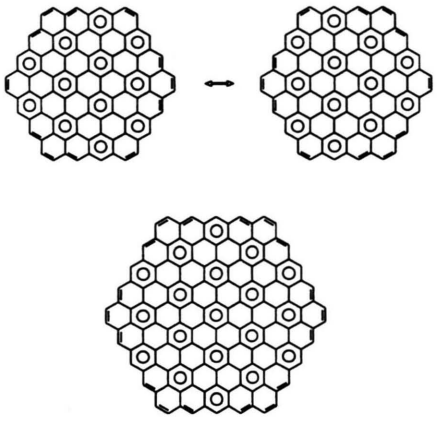

Fig. 2. Examples illustrating the rule that if k is even, then B_k has two Clar structural formulas whereas if k is odd then B_k has a unique Clar formula.

In an analogous manner, for even k the number of aromatic sextets is found to be equal to $3k^2/4$.

In summary, the number of aromatic sextets in a Clar formula of B_k is equal to

$$\left\lceil \frac{3k^2}{4} \right\rceil = \begin{cases} \dfrac{3k^2+1}{4} & \text{if } k = 1,3,5,\ldots, \\ \dfrac{3k^2}{4} & \text{if } k = 2,4,6,\ldots. \end{cases}$$

Wiener and Szeged Indices

Although the Wiener index W of benzenoid molecules has been extensively studied in the last two decades, the calculation of the W-values of B_k proved to be a rather difficult task and has for a long time resisted solution. Quite recently Shiu and Lam [21], by means of a specially designed method, established that

$$W(B_k) = \frac{1}{5}(164k^5 - 30k^3 + k). \qquad (10)$$

Eventually, one of the present authors and Klavžar [19] elaborated a novel method for calculation of Wiener indices of benzenoid molecules, by means of wich (10) could be deduced relatively easily. A similar approach [18], applied to the Szeged index of B_k, yields

$$Sz(B_k) = \frac{3}{2}(36k^6 - k^4 + k^2).$$

Note that, whereas the Wiener index of B_k increases as the fifth power of k, the Szeged index increases as the sixth power. This difference in the asymptotic behavior of $W(B_k)$ and $Sz(B_k)$ was found to be of a certain importance in the theory of benzenoid hydrocarbons [20]. The first few values of $W(B_k)$ and $Sz(B_k)$ are given in Table 1.

Table 1. Wiener and Szeged indices of the first few members of the benzene-coronene-circumcoronene family.

k	$W(B_k)$	$Sz(B_k)$
1	27	54
2	1,002	3,438
3	13,015	39,258
4	33,204	220,824
5	101,751	842,859
6	253,758	2,517,534
7	549,213	6,349,518
8	1,071,720	14,149,728
9	1,932,435	28,688,094
10	3,274,002	53,985,150

Total π-electron Energy and Spectral Moments

Denote the eigenvalues [26] of B_k by $x_i(B_k)$, $i = 1, 2, \ldots, 6k^2$, and assume that they are ordered in a non-decreasing manner. Then the total π-electron energy and the p-th spectral moment of B_k are given by [26]

$$E = E(B_k) = 2\sum_{i=1}^{3k^2} x_i(B_k) = \sum_{i=1}^{6k^2} |x_i(B_k)|$$

and

$$M_p = M_p(B_k) = \sum_{i=1}^{6k^2} [x_i(B_k)]^p,$$

respectively.

No analytical expression is known either for the eigenvalues of B_k or for the respective total π-electron energy. The finding of these expressions remains a challenging task for the future.

In Table 2 are given the total π-electron energies of B_k, $k \leq 8$ together with the corresponding energy-per-electron values E/n. It is noteworthy that with increasing k the ratio E/n only very slowly converges to its limit value (contrary to the previously studied case of linear polyacenes [27]). This implies that the π-electron properties of the circumcoronenes differ significantly from the analogous properties of the infinite graphite lattice. Therefore, even for relatively large values of k, it seems not justified to use B_k as a model for graphite.

The spectral moments of benzenoid hydrocarbons attracted a lot of attention, and their dependence on molec-

Table 2. Total π-electron energies (E) of the first few members of the benzene-corone-circumcoronene family; n = number of vertices, cf. (1).

k	E	E/n
1	8.0000	1.3333
2	34.5718	1.4405
3	79.8560	1.4788
4	143.9166	1.4991
5	226.7940	1.5120
6	328.5150	1.5209
7	449.0972	1.5275
8	588.5524	1.5327

ular structure was studied in due detail (see, for instance, [28], [29] and the references cited therein). Because of the pairing theorem [26], the p-th spectral moment of any benzenoid system is zero whenever p is odd. For even values of p, each spectral moment of the circumcoronene B_k is fully determined by the parameter k. Furthermore, we found that $M_p(B_k)$ is a quadratic polynomial in the variable k. In particular,

$$M_0(B_k) = 6\,k^2, \tag{11}$$

$$M_2(B_k) = 18\,k^2 - 6\,k, \tag{12}$$

$$M_4(B_k) = 90\,k^2 - 54\,k, \tag{13}$$

$$M_6(B_k) = 558\,k^2 - 474\,k + 48, \tag{14}$$

$$M_8(B_k) = 3834\,k^2 - 4086\,k + 720, \tag{15}$$

$$M_{10}(B_k) = 27918\,k^2 - 35106\,k + 8280, \tag{16}$$

$$M_{12}(B_k) = 211050\,k^2 - 302310\,k + 86976, \tag{17}$$

$$M_{14}(B_k) = 1638018\,k^2 - 2613078\,k + 875448. \tag{18}$$

Formulas (11)–(14) hold for all $k \geq 1$, whereas formulas (15)–(18) apply for $k \geq 2$.

On Cyclic Conjugation and its Energy-effects

Cyclic conjugation has a crucial significance for the π-electron properties of polycyclic conjugation molecules, and benzenoid hydrocarbons in particular. Several quantitative and semiquantitative approaches have been proposed for determining the effect of an individual cycle on the overall pattern of conjugation of a polycyclic molecule. Of them, the method based on the partitioning of the total π-electron energy [30] is free of any assumption concerning Kekulé or Clar structures and can thus be used for testing the applicability of the Kekulé and/or Clar picture (for details see [31], [32]).

Table 3. Energy-effects of the symmetry-nonequivalent six-membered rings of the first few members of the benzene-corone-circumcoronene family; the rings are labeled as shown in Fig. 3; according to the Clar model, a six-membered ring may be "full" (F), possessing an aromatic sextet in all Clar formulas, may be "empty" (E), devoid of aromatic sextets in all Clar formulas, or may be full in some and empty in other Clar formulas (FE).

Ring	$k=1$	$k=2$	$k=3$	$k=4$	$k=5$	$k=6$	$k=7$
1,1	0.2726 F	0.0298 E	0.0440 F	0.0352 E	0.0386 F	0.0365 E	0.0375 F
2,1		0.0703 EF	0.0354 E	0.0392 EF	0.0366 E	0.0375 EF	0.0369 E
3,1			0.0516 E	0.0390 EF	0.0371 E	0.0375 EF	0.0370 E
3,2			0.0572 F	0.0350 E	0.0391 F	0.0365 E	0.0375 F
4,1				0,0476 E	0.0399 F	0.0368 E	0.0376 F
4,2				0.0492 EF	0.0365 E	0.0379 EF	0.0369 E
5,1					0.0473 E	0.0393 EF	0.0370 E
5,2					0.0456 F	0.0374 E	0.0373 F
5,3					0.0459 F	0.0369 E	0.0377 F
6,1						0.0476 E	0.0386 E
6,2						0.0445 EF	0.0377 F
6,3						0.0437 EF	0.0374 E
7,1							0.0479 E
7,2							0.0445 E
7,3							0.0429 E
7,4							0.0426 F

In Table 3 are given the energy-effects of all the symmetry-nonequivalent six-membered rings pertaining to B_k, $k \leq 7$. As usual [30]–[32], these energies are expressed in β-units and, therefore, the greater is their value, the greater is the stabilizing effect of the respective ring, and the greater is the extent of cyclic conjugation in this ring. The way in which the symmetry-nonequivalent hexagons of B_k are labeled is shown in Figure 3.

The main conclusion that can be drawn from the data given in Table 3 are the following:

1. The differences between the energy-effects of the hexagons of B_k rapidly attenuate with increasing k, and assume a value near 0.04 β.

2. Peripheral hexagons (i.e., those incident to the boundary of B_k) have somewhat greater energy-effects than the central hexagons.

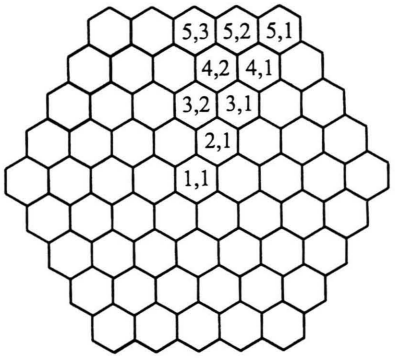

Fig. 3. Labeling of the symmetry-nonequivalent hexagons of B_k.

3. Except for the first few values of k, the energy-effect is only slightly sensitive on the finer details of molecular topology. In particular, in the sense of the Clar model [24], a six-membered ring may be "full" (F), "empty" (E) or "half-empty" (EF), but this has hardly any influence on the magnitude of the respective energy-effect.

An inspection of Table 3 reveals that already at $k = 3$ the Clar picture is violated: the extent of cyclic conjugation in the "empty" hexagon 3,1 of B_3 is found to be much greater than in the "full" hexagon 1,1 of B_3.

It may be argued that violations of the Clar picture are encountered if we compare the energy-effects of peripheral hexagons (having fewer than 6 branching points) with the energy-effects of inner hexagons (which all have 6 branching points). Indeed, if we distinguish between peripheral and inner hexagons, then violations of the Clar picture do not occur until B_5, and violations in the case of inner hexagons do not occur until B_7. However, for k being sufficiently large, the Clar picture seems to be completely inadequate to describe the conjugation models of circumcoronenes, B_k.

Thus the circumcoronenes B_k, $k \geq 3$, provide further examples of benzenoid systems in which the Clar aromatic sextet model is found to be inapplicable. This observation raises doubts whether topological models based (solely) on Clar and/or Kekulé structural formulas are capable of correctly describing the π-electron properties of very large benzenoid hydrocarbons. To resolve this problem, further research is needed, preferably based on methods that are more accurate than the presently existing topological approaches.

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