Number of Benzenoid Hydrocarbons

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The number of benzenoid hydrocarbons with h hexagons can be estimated by means of the formula $B_h = 0.045\, h^{-3/2}\,(5.4)^h$. The analogous estimate for the number of catacondensed benzenoids is $C_h = 0.049\, h^{-5/4}\,(4.27)^h$.

Introduction

The problem of the enumeration of alkanes and related chemical compounds has been solved by Pólya long time ago [1, 2]. Another problem of this kind, namely the enumeration of benzenoid hydrocarbons, seems to be much more difficult and was not satisfactorily solved so far. In spite of serious attempts of a number of mathematicians [3–6], at the present moment we do not know anything better than to construct the benzenoids and then to count them. Several approaches along these lines have been elaborated [7–15], usually based on an extensive use of computers.

In the following we shall be interested in geometrically planar, simply connected benzenoids [16]. The number of such systems, possessing h hexagons will be denoted by B_h. In addition to this, C_h is the number of geometrically planar catacondensed benzenoids [16] with h hexagons. The numbers B_h and C_h are nowadays known for $h \leqq 11$ and are given in Tables 1 and 2.

For small values of h, B_h and C_h can be obtained without difficulty. For h up to 10, B_h and C_h were first reported by Knop et al. [11, 12], whereas B_{11} and C_{11} were recently calculated by Doroslovački and Tošić [15]. The amount of computing, required for the evaluation of B_h for $h \geqq 10$ is enormous and increases very rapidly with the increasing number of hexagons. Therefore, even when quite powerful computing machines have been employed, the enumeration procedure could not exceed $h = 10$ [11, 14] and $h = 11$ [15].

These difficulties motivated us to develop approximate expressions for B_h and C_h which enable the estimation of these numbers for large (greater than eleven) values of h.

Asymptotic expressions for the estimation of the number of combinatorial objects of certain types are often met in the theory of enumeration [17]. Already Pólya [1] deduced such a formula for the number of alkanes. In a great number of cases [17], the asymptotes have the form

$$X_n \sim a\, n^p\, b^n\,; \quad n \to \infty\,, \tag{1}$$

where a and b are some constants and the exponent p is a rational number.

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In particular, Harary and Read [5] showed that for large values of h,

$$H_h \sim \sqrt{\frac{5}{4}}\;\frac{(2h-1)!}{(h-1)!\,(h+2)!}\left(\frac{5}{4}\right)^h, \tag{2}$$

where H_h counts the catacondensed benzenoids (both geometrically planar and non-planar), with h hexagons. Using the Stirling approximation, we can transform (2) into

$$H_h \sim \sqrt{\frac{5}{16\pi}}\; h^{-5/2}\, 5^h\,, \tag{3}$$

which is just a special case of (1).

An Approximate Asymptote for C_h

Bearing in mind the result (3), we considered the formula

$$C_h \sim a\, h^p\, b^h\,, \tag{4}$$

which is expected to hold for sufficiently large values of h. In order to determine the exponent p we have calculated the expression

$$b_h = \left(\frac{h}{h+1}\right)^p \frac{C_{h+1}}{C_h}$$

for the known C_h's (see Table 1). If C_h behaves according to (4), then for a properly chosen p the sequence $b_1, b_2, b_3, \ldots$ will rapidly converge to its limit value b. By varying p we found that the best convergence occurs for $p = -5/4$. (As a matter of fact, the choice $p = -1.25$ is better than $p = -1.24$ or $p = 1.26$.) The last calculated members of the sequence b_h, for $p = -5/4$ are given as

h	b_h
7	4.116
8	4.198
9	4.26887
10	4.26895 ,

from which we conclude that the limiting value of b_h is about 4.27.

It remains to determine the parameter a as the limit of the sequence $a_1, a_2, a_3, \ldots$, where

$$a_h = C_h/(h^p\, b^h)\,.$$

The fact that for $p = -5/4$ and $b = 4.27$,

h	a_h
8	0.0500
9	0.049187
10	0.049174
11	0.049162

implies $a = 0.049$.

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Table 1. Exact and estimated values for the number C_h of geometrically planar catacondensed benzenoid systems with h hexagons.

Table 2. Exact and estimated values for the number B_h of geometrically planar, simply connected benzenoid systems with h hexagons.

Table 1

h	C_h	Estimate (5)
1	1	0
2	1	0
3	2	1
4	5	3
5	12	9
6	36	32
7	118	111
8	411	402
9	1 489	1 483
10	5 572	5 552
11	21 115	21 046
12		80 604
13		311 408
14		1 212 066
15		4 747 884

Table 2

h	B_h	Estimate (6)
1	1	0
2	1	0
3	3	1
4	7	5
5	22	18
6	81	76
7	331	325
8	1 435	1 438
9	6 505	6 507
10	30 086	30 002
11	141 229	140 428
12		665 527
13		3 187 251
14		15 400 439
15		74 986 317

Thus we arrived at the approximate asymptotic expression

$$C_h \sim 0.049\, h^{-5/4}\, (4.27)^h\,, \tag{5}$$

whose quality can be seen from the data given in Table 1. In Table 1 we also presented the predicted (approximate) values of C_{12}, C_{13}, C_{14} and C_{15}.

An Approximate Asymptote for B_h

In the case of B_h, a completely analogous variational procedure gave the optimal value -1.47 for the exponent p, which is satisfactorily close to the adopted value $-3/2$. The choice $p = -3/2$ leads then to the numbers

h	b_h	a_h
7	5.297	
8	5.409	0.0449
9	5.41693	0.044985
10	5.41562	0.045126
11	–	0.045224

which imply

$$B_h \sim 0.045\, h^{-3/2}\, (5.4)^h\,. \tag{6}$$

The exact B_h values as well as those calculated by means of (6) are collected in Table 2, together which the estimates for B_{12}, B_{13}, B_{14} and B_{15}. Formula (6) seems to be somewhat less accurate than (5).

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[14] J. Ciosłowski (Washington, USA), private communication, Spring 1986.
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[16] A benzenoid system is geometrically planar if its non-adjacent (regular) hexagons do not overlap. A benzenoid system is simply connected if it separates the plane into an infinite region and h finite regions, all of which are (regular) hexagons. A benzenoid system is catacondensed if no three of its hexagons are mutually adjacent. More details on benzenoid systems can be found in: I. Gutman and O. E. Polansky, Mathematical Concepts in Organic Chemistry, Springer-Verlag, Berlin 1986, pp. 59–61.
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