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 $h \leq 11$ 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 $h \geq 10$ 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

$$X_n \sim a n^p b^n; \quad n \rightarrow \infty, \quad (1)$$

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

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

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

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

$$H_h \sim \sqrt{\frac{5}{16\pi}} h^{-5/2} 5^h, \quad (3)$$

which is just a special case of (1).

An Approximate Asymptote for C_h

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

$$C_h \sim a h^p b^h, \quad (4)$$

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 $b_1, b_2, b_3, \dots$ 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 $a_1, a_2, a_3, \dots$, 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.

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

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

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

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

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

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

- [1] G. Pólya, Z. Kristal. **93 A**, 415 (1936).
- [2] G. Pólya, Acta Math. **68**, 145 (1937).
- [3] D. A. Klarner, Fibonacci Quart. **3**, 9 (1965).
- [4] D. A. Klarner, Canad. J. Math. **19**, 851 (1967).
- [5] F. Harary and R. C. Read, Proc. Edinburgh Math. Soc. **17**, 1 (1970).
- [6] W. F. Lunnon, in: R. C. Read (Ed.), Graph Theory and Computing, Academic Press, New York 1972, pp. 87–100.
- [7] K. Balasubramanian, J. J. Kaufman, W. S. Koski, and A. T. Balaban, J. Comput. Chem. **1**, 149 (1980).
- [8] J. R. Dias, J. Chem. Inf. Comput. Sci. **22**, 15 (1982).
- [9] J. R. Dias, Match (Mülheim) **14**, 83 (1983).
- [10] J. R. Dias, J. Chem. Inf. Comput. Sci. **24**, 124 (1984).
- [11] J. V. Knop, K. Szymanski, Ž. Jeričević, and N. Trinajstić, J. Comput. Chem. **4**, 23 (1983).
- [12] J. V. Knop, K. Szymanski, Ž. Jeričević, and N. Trinajstić, Match (Mülheim) **16**, 119 (1984).

- [13] S. J. Cyvin and J. Brunvoll (Trondheim, Norway), private communication, Spring 1986.
- [14] J. Ciośłowski (Washington, USA), private communication, Spring 1986.
- [15] R. Doroslovački and R. Tošić (Novi Sad, Yugoslavia), private communication, Spring 1986.
- [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.
- [17] F. Harary and E. P. Palmer, Graphical Enumeration, Academic Press, New York 1973, Chapter 9.