ENUMERATION OF PERIFUSENES WITH ONE INTERNAL VERTEX: A COMPLETE MATHEMATICAL SOLUTION*

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Abstract

Simply connected polyhexes with one internal vertex ($n_i = 1$ perifusenes) are enumerated. Complete mathematical solutions are given in terms of summation formulas and by generating functions. The symmetry is accounted for. The numerical results are used to derive numbers of simply connected helicenic (geometrically nonplanar) polyhexes with $n_i = 1$.

1. Introduction

Complete mathematical solutions in the enumeration of polyhexes are rare. The most famous work in this realm is the derivation of the generating function for catafusenes by Harary and Read [1]. Here, catafusenes (catacondensed fusenes) are defined as the simply connected polyhexes without internal vertices ($n_i = 0$). It is emphasized that the helicenic (geometrically nonplanar) systems are included. The result of Harary and Read [1] enables one to compute the numbers of nonisomorphic catafusenes for any number of hexagons (h) without theoretical limitations. About twenty years later [2], the same problem was solved in terms of summation formulas.

In the present work, we give complete mathematical solutions for the numbers of perifusenes (pericondensed fusenes) with exactly one internal vertex each ($n_i = 1$). The systems form another class of simply connected polyhexes, and helicenes (helicenic fusenes) are again included. First the solution in terms of summations is presented, and then the generating function.

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2. General considerations

A perifusene with $n_i = 1$ is either phenalene ($h = 3$) or phenalene with catacondensed ($n_i = 0$) appendages; cf. fig. 1. One, two or three catafusenes can be appended in nonequivalent positions. This amounts to six possibilities, which are illustrated in fig. 1. Here and throughout, the dualist [3,4] representations are employed.

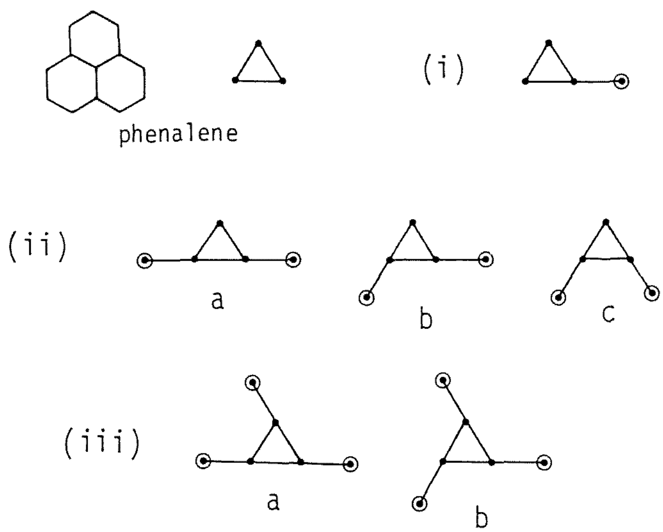


Fig. 1.

The number of nonisomorphic perifusenes with $n_i = 1$ and h hexagons shall presently be identified by the symbol P_h, where

$$h = 3 + a. \tag{1}$$

Hence, a is the number of hexagons in the appended catafusene(s). The number P_h splits according to the number of appendages (cf. fig. 1) as indicated by

$$P_h = P_h(\mathrm{i}) + P_h(\mathrm{ii}) + P_h(\mathrm{iii}). \tag{2}$$

3. Rooted catafusenes

The numbers of catafusenes rooted by an edge and having h hexagons, say U_h, are essential in the present theory. A rooted catafusene is just appended to the phenalene by the root edge in the systems of the present study. The numbers in question are given recursively by [1]

$$U_1 = 1, \quad U_2 = 3U_1,$$
$$U_{h+1} = 3U_h + \sum_{i=1}^{h-1} U_i U_{h-i}; \qquad h = 2, 3, 4, \ldots . \tag{3}$$

Also the generating function for U_i is known [1]:

$$\frac{1}{2}x^{-1}[1 - 3x - (1-x)^{1/2}(1-5x)^{1/2}]$$
$$= \sum_{i=0}^{\infty} U_i x^i = x + 3x^2 + 10x^3 + 36x^4 + 137x^5 + 543x^6 + 2219x^7 + 9285x^8 + 39587x^9 + 171369x^{10} + \ldots . \tag{4}$$

This equation implies $U_0 = 0$.

We shall also make use of the numbers N_i, which are defined by

$$N_0 = 1, \quad N_h = U_h; \quad h > 0. \tag{5}$$

Accordingly, the generating function for N_i is

$$N(x) = 1 + U(x). \tag{6}$$

4. Summation formulas

4.1. ONE APPENDAGE (i)

One clearly has

$$P_{3+a}(\mathrm{i}) = N_a; \qquad a = 0, 1, 2, \ldots . \tag{7}$$

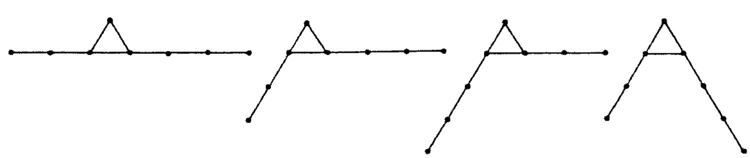
Here, $a = 0$ accounts for the unique system without appendages (viz. phenalene itself).

4.2. TWO APPENDAGES (ii)

The contribution to P_h(ii) from two different sets of rooted catafusenes is

$$4N_iN_{a-i}; \quad i = 1, 2, \ldots, \lfloor a/2 \rfloor \ (i \neq a/2).$$

Example with one representative each from two sets:



For two equal sets of rooted catafusenes ($i = a/2$), the contribution to P_h(ii), say P, splits into M mirror-symmetrical (C_{2v}) and A asymmetrical (C_s) systems:

$$P = M + A, \tag{8}$$

where

$$M = 2N_{a/2}. \tag{9}$$

A "crude total" emerges from $4N_{a/2}^2$ so that the asymmetrical systems are counted twice:

$$4N_{a/2}^2 = M + 2A. \tag{10}$$

Equations (8)–(10) are solved to give

$$P = 2N_{a/2}^2 + N_{a/2}. \tag{11}$$

Consequently,

$$P_{3+a}(\text{ii}) = 4\sum_{i=1}^{(a-1)/2} N_i N_{a-i}; \quad a = 3, 5, 7, 9, \ldots;$$

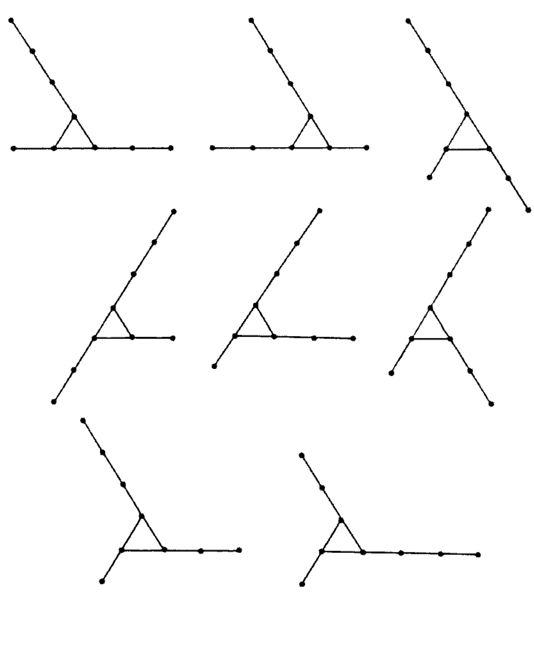
$$P_{3+a}(\text{ii}) = N_{a/2} - 2N_{a/2}^2 + 4\sum_{i=1}^{a/2} N_i N_{a-i}; \quad a = 2, 4, 6, 8, \ldots . \tag{12}$$

4.3. THREE APPENDAGES (iii)

The contribution to P_h(iii) from three sets of rooted catafusenes which all are different is

$$8N_i N_j N_{a-i-j}; \quad i = 1, 2, \ldots, \lfloor a/3 \rfloor, \; j < i \; (2j \neq a - i).$$

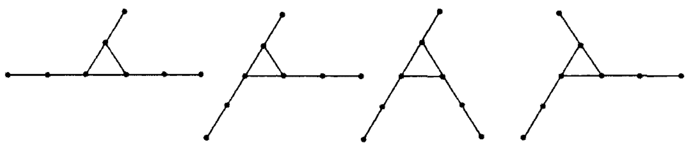
Example with one representative each from three sets:



For two equal sets of rooted catafusenes and one different from them, the contribution of P_h(iii) is

$$4N_i^2 N_{a-2i}; \quad i = 1, 2, \ldots, \lfloor (a-1)/2 \rfloor \quad (i \neq a/3).$$

This feature is explained by the example below.



Finally, assume that the perifusenes have three equal sets of rooted catafusenes ($i = a/3$ in the above case). Then the contribution to P_h(iii), say P, splits into R irregular trigonal (C_{3h}) and A asymmetrical (C_s) systems:

$$P = R + A, \tag{13}$$

where

$$R = N_{a/3}. \tag{14}$$

A crude total is $4N_{a/3}^3$, where the asymmetrical systems are counted three times:

$$4N_{a/3}^3 = R + 3A. \tag{15}$$

Equations (13)–(15) give

$$P = \tfrac{2}{3}\left(2N_{a/3}^3 + N_{a/3}\right). \tag{16}$$

In conclusion, one obtains:

$$P_{3+a}(\text{iii}) = 8\sum_{i=1}^{\lfloor a/3 \rfloor} N_i \sum_{j=i}^{\lfloor (a-i)/2 \rfloor} N_j N_{a-i-j} - 4\sum_{i=1}^{\lfloor (a-1)/2 \rfloor} N_i^2 N_{a-2i}; \quad a = 4,5,7,8,10,11,\ldots \quad (a \neq 3,6,9,12,\ldots);$$

$$P_{3+a}(\text{iii}) = \tfrac{2}{3}\left(N_{a/3} - 4N_{a/3}^3\right) + 8\sum_{i=1}^{a/3} N_i \sum_{j=i}^{\lfloor (a-i)/2 \rfloor} N_j N_{a-i-j} - 4\sum_{i=1}^{\lfloor (a-1)/2 \rfloor} N_i^2 N_{a-2i}; \quad a = 3,6,9,12,\ldots . \tag{17}$$

4.4. FINAL RESULT

The final result for P_h in a compact form is given in the following.

$$P_3 = P_4 = 1, \quad P_5 = 6,$$

$$P_{3+a} = N_a + [1 + (-1)^a]\left[\left(\tfrac{1}{2} N_{a/2} - N_{a/2}^2\right) + \tfrac{2}{3}\left(1 + \lfloor a/3 \rfloor - \lceil a/3 \rceil\right)\left(N_{a/3} - 4N_{a/3}^3\right)\right]$$
$$+ 4 \sum_{i=1}^{\lfloor a/2 \rfloor} N_i N_{a-i} + 8 \sum_{i=1}^{\lfloor a/3 \rfloor} N_i \sum_{j=i}^{\lfloor (a-i)/2 \rfloor} N_j N_{a-i-j}$$
$$- 4 \sum_{i=1}^{\lfloor (a-1)/2 \rfloor} N_i^2 N_{a-2i}; \qquad a = 3,4,5,\ldots \,. \tag{18}$$

One may also introduce, by definition, $P_1 = P_2 = 0$. The numbers N_i are obtainable from eqs. (3) and (5).

5. Generating functions

5.1. DERIVATION

Also in the derivation of the generating function for P_i, viz.

$$P(x) = \sum_{i=1}^{\infty} P_i x^i, \tag{19}$$

the six types of attachments of rooted catafusenes to phenalene (cf. fig. 1) are considered.

For the sake of convenience, define

$$p(x) = x^{-3} P(x). \tag{20}$$

In the case of one appendage (i), the contribution to $p(x)$ is simply $U(x)$. Unity must be added in order to take care of the case with no appendages. So far, we therefore have:

$$1 + U(x).$$

In the cases (iib) and (iiia) with two and three appendages, respectively (cf. fig. 1), the edges of attachments are not in the same orbit of their automorphic groups. The contributions to $p(x)$ are therefore

$$U^2(x) \text{ and } U^3(x),$$

respectively.

For (iia) and (iic), Pólya's theorem [5] can be applied. By taking the configuration group to be S_2 (the symmetric group of degree two), the symmetry under reflection is taken into account, while there is no rotation. Take $U(x)$ to be the figure-counting series and the generating function

$$\frac{1}{2}\left[U^2(x) + U(x^2)\right]$$

emerges. This term contributes twice to $p(x)$.

Finally, for type (iiib) of fig. 1, take the configuration group to be C_3, since in this case one has symmetry under threefold rotation, but no reflection. Using Pólya's theorem again and taking $U(x)$ as the figure-counting series, one obtains the generating function

$$\frac{1}{3}\left[U^3(x) + 2U(x^3)\right]$$

as the last contribution to $p(x)$.

5.2. COMPLETE GENERATING FUNCTION

By adding the contributions to $p(x)$ from the preceding section and multiplying by x^3 in accordance with eq. (20), one obtains:

$$P(x) = x^3\left[1 + U(x) + 2U^2(x) + U(x^2) + \frac{4}{3}U^3(x) + \frac{2}{3}U(x^3)\right]. \tag{21}$$

On inserting $N(x)$ from eq. (6) into eq. (21), one obtains the alternative form:

$$P(x) = x^3\left[N(x) - 1 - 2N^2(x) + N(x^2) + \frac{4}{3}N^3(x) + \frac{2}{3}N(x^3)\right]. \tag{22}$$

5.3. EXPLICIT EXPRESSION

From eqs. (4) and (6), it is obtained that:

$$N(x) = \frac{1}{2}x^{-1}\left[1 - x - (1-x)^{1/2}(1-5x)^{1/2}\right]. \tag{23}$$

Here, $N(x)$ is somewhat more amenable for raising into powers than is the case for $U(x)$ of eq. (4). Hence, we use eq. (22) rather than (21) and insert from eq. (23) together with:

$$N^2(x) = \frac{1}{2}x^{-2}(1-x)\left[1 - 3x - (1-x)^{1/2}(1-5x)^{1/2}\right], \tag{24}$$

$$N^3(x) = \frac{1}{2}x^{-3}(1-x)\left[(1-x)(1-4x) - (1-2x)(1-x)^{1/2}(1-5x)^{1/2}\right]. \tag{25}$$

The net result is the following explicit form of the generating function under consideration.

$$P(x) = \tfrac{1}{2}\left(2 - 9x + 21x^2 - 16x^3\right)$$
$$- \tfrac{1}{6}\left(4 - 18x + 17x^2\right)(1 - x)^{1/2}(1 - 5x)^{1/2}$$
$$- \tfrac{1}{2}\, x\left(1 - x^2\right)^{1/2}\left(1 - 5x^2\right)^{1/2} - \tfrac{1}{3}\left(1 - x^3\right)^{1/2}\left(1 - 5x^3\right)^{1/2}. \quad (26)$$

6. Classification according to symmetry

6.1. INTRODUCTORY REMARKS AND DEFINITIONS

Symmetry considerations had to be made both in the derivation of summation formulas (section 4) and in the derivation of generating functions (section 5). Now it is easy to specify how many of the perifusenes with $n_i = 1$ and a given h belong to the different symmetry groups. Let

$$P_h = T_h + R_h + M_h + A_h, \quad (27)$$

where T, R, M and A refer to D_{3h}, C_{3h}, C_{2v} and C_s, respectively. Correspondingly for the generating function:

$$P(x) = T(x) + R(x) + M(x) + A(x). \quad (28)$$

6.2. REGULAR TRIGONAL SYMMETRY, D_{3h}

Phenalene (fig. 1) is the only perifusene with $n_i = 1$ which belongs to the D_{3h} symmetry. Hence, the trivial result:

$$T_3 = 1, \; T_h = 0; \qquad h \neq 3. \quad (29)$$

$$T(x) = x^3. \quad (30)$$

6.3. IRREGULAR TRIGONAL SYMMETRY, C_{3h}

In accordance with the treatments of sections 4 and 5, one has

$$R_{a+3} = N_{a/3}; \qquad a = 3,6,9,12, \ldots . \quad (31)$$

$$R(x) = x^3 U(x^3) = \tfrac{1}{2}\left[1 - 3x^3 - \left(1 - x^3\right)^{1/2}\left(1 - 5x^3\right)^{1/2}\right]. \quad (32)$$

6.4. MIRROR SYMMETRY, C_{2v}

$$M_{a+3} = 2N_{a/2}; \qquad a = 2,4,6,8, \ldots . \quad (33)$$

$$M(x) = 2x^3 U(x^2) = x\left[1 - 3x^2 - \left(1 - x^2\right)^{1/2}\left(1 - 5x^2\right)^{1/2}\right]. \quad (34)$$

6.5. ASYMMETRICAL SYSTEMS, C_s

The appropriate expression for A_h may of course be found from eqs. (18), (27), (29), (31) and (33). We shall not report this complicated formula here for the sake of brevity. However, the corresponding generating function is not too complex to be reproduced here:

$$A(x) = \tfrac{1}{2}\left(1 - 11x + 21x^2 - 9x^3\right) - \tfrac{1}{6}\left(4 - 18x + 17x^2\right)(1 - x)^{1/2}(1 - 5x)^{1/2}$$

$$+ \tfrac{1}{2}x\left(1 - x^2\right)^{1/2}\left(1 - 5x^2\right)^{1/2} + \tfrac{1}{6}\left(1 - x^3\right)^{1/2}\left(1 - 5x^3\right)^{1/2}. \qquad (35)$$

7. Numerical results: Application to polyhex isomers

An enumeration of polyhexes with a certain value of h and of n_i is virtually an enumeration of polyhexes compatible with a formula C_nH_s. Here, the invariants n and s indicate the numbers of carbon and hydrogen atoms in the corresponding polyhex hydrocarbons. In the present case, when $n_i = 1$, the formulas assume the general form $C_{4h+1}H_{2h+3}$ ($h = 3, 4, 5, \ldots$).

Table 1 shows numerical results from the present work, listed up to $h = 15$. Also included are the numbers of simply connected, geometrically planar polyhexes with $n_i = 1$ (non-Kekuléan peribenzenoids). These numbers, which are known for

Table 1

Numbers of perifusenes with one internal vertex.

h	Formula	Fusenes (benzenoids + helicenes)					Benzenoids total	Helicenes total
		D_{3h}	C_{3v}	C_{2v}	C_s	Total		
3	$C_{13}H_9$	1	0	0	0	1	1	0
4	$C_{17}H_{11}$	0	0	0	1	1	1	0
5	$C_{21}H_{13}$	0	0	2	4	6	6	0
6	$C_{25}H_{15}$	0	1	0	23	24	24	0
7	$C_{29}H_{17}$	0	0	6	103	109	106	3
8	$C_{33}H_{19}$	0	0	0	477	477	453	24
9	$C_{37}H_{21}$	0	3	20	2132	2155	1966	189
10	$C_{41}H_{23}$	0	0	0	9647	9647	8395	1252
11	$C_{45}H_{25}$	0	0	72	43549	43621	35885	7736
12	$C_{49}H_{27}$	0	10	0	197757	197767	152688	45079
13	$C_{53}H_{29}$	0	0	274	901162	901436	648632	252804
14	$C_{57}H_{31}$	0	0	0	4125636	4125636	2749719	1375917
15	$C_{61}H_{33}$	0	36	1086	18962997	18964119	[a]	[a]

[a] Unknown.

$h \leq 14$, have been collected from different sources and are found with proper documentations in a recent review [6]. In consequence, the numbers of helicenes with $n_i = 1$ are accessible up to $h = 14$ by taking differences between the appropriate numbers of table 1. These data are displayed in the last column of the table.

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