Enumeration and Classification of Certain Polygonal Systems Representing Polycyclic Conjugated Hydrocarbons: Annelated Catafusenes

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Catafusenes (catacondensed simply connected polyhexes) annelated to a core are studied. Schemes for handling the enumeration of these systems with four appendages or less are given. In this survey the formalism of combinatorial summations is employed, but the exposition is supported by applications of generating functions. Special cases of interest occur when the core is a q-gon (q-membered polygon). Then the systems are referred to as catacondensed mono-q-fusenes, which are subclasses of the important mono-q-polyhexes.

INTRODUCTION

In a celebrated work, Harary and Read[1] derived a generating function for the numbers of nonisomorphic catafusenes (catacondensed fusenes).[2–4] A catafusene is a simply connected polyhex without internal vertices. It is emphasized that the helicenic (geometrically nonplanar) systems are included. Catafusenes have the chemical counterparts in polycyclic aromatic hydrocarbons, $C_{4h+2}H_{2h+4}$, where h designates the number of six-membered (benzenoid) rings. The work of Harary and Read[1] has been quoted frequently, but it took more than 20 years before their numbers were classified according to the different symmetries of the systems.[5] During the latter work,[5] a new approach was introduced as an alternative to the application of generating functions and may be referred to as combinatorial summation. These techniques were refined by exploitation of symmetry in order to make them practicable. The successful application to annelated pyrenes[6] was a large step forward. In the present work we offer a systematic treatment of the application of combinatorial summations to all cases of catafusenes annelated to a core with four appendages or less. The results are presented so that they should be immediately applicable to special cases with a minimum of computation. Furthermore, the detailed classifications of the numbers according to the numbers of appendages and to symmetries should be accessible. Pólya's theorem[7] is not invoked explicitly, although most of the results are obtainable from it. Generating functions are given parallel with the summation formulas.

The main motivation for this work arised from the recent studies of systems called mono-q-polyhexes.[8] The catacondensed mono-q-fusenes (simply connected mono-q-polyhexes) consist of one q-gon each with a number of catafusenes annelated to it. Hence the enumeration of mono-q-fusenes is a typical problem for the application of the present theory. A solution for monopentafusenes (q = 5) has appeared recently[9] and is relatively simple compared to the case of annelated pyrenes.[6] Also the case of q = 7 can be solved by means of the deductions in the previous work.[6] For q = 8, on the other hand, some supplements to the previous work are needed. They are furnished in the following.

RESULTS AND DISCUSSION

Basic Concepts. Denote by α the number of appendages to the core. The appendages are catafusenes. The total number of hexagons in the appendages is a.[10]

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Table 1. Numbers of Edge-Rooted Catafusenes (N_a) and Some Auxiliary Numbers[a]

a	N_a	M_a	L_a	M_a'	L_a'
0	1				
1	1	1			
2	3	1	1		
3	10	2	2	1	
4	36	2	5	1	1
5	137	5	8	5	2
6	543	5	18	5	8
7	2219	15	28	21	14
8	9285	15	64	21	43
9	39587	51	100	86	72
10	171369	51	237	86	204
11	751236	188	374	355	336
12	3328218	188	917	355	926

[a] This table corrects the erroneous value of $M_9' = M_{10}'$ in Table I of ref 6.

Two quantities are crucial in the present theory: the number N_a of edge-rooted catafusenes and the number M_a of the edge-rooted catafusenes with mirror symmetry.[11] Numerical values are accessible from different sources and are reproduced here for the sake of convenience (Table 1). The reader is referred to our main reference[6] for the relevant summation formulas and explanations. Here we only give the connections[6]

$$N_a = M_{2a+1} - M_{2a}, \quad N_{a/2} = M_{a+1} - M_a \tag{1}$$

Here the symbol $N_{a/2}$ is understood to have nonvanishing values only when a is divisible by 2. The generating functions for N_a and M_a are known. Firstly,[1]

$$U(x) = \sum_{a=1}^{\infty} N_a x^a = {}^1/_2 x^{-1}[1 - 3x - (1-x)^{1/2}(1-5x)^{1/2}] \tag{2}$$

Also the closely related function[9,12]

$$U_0(x) = 1 + U(x) \tag{3}$$

has been employed.[13] One has[12,14]

$$U_0(x) = \sum_{a=0}^{\infty} N_a x^a = {}^1/_2 x^{-1}[1 - x - (1-x)^{1/2}(1-5x)^{1/2}] \tag{4}$$

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Secondly,[9]

$$V(x) = \sum_{a=1}^{\infty} M_a x^a = {}^1/_2 x^{-1}[1 + x - (1-x)^{-1}(1-x^2)^{1/2}(1-5x^2)^{1/2}] \quad (5)$$

For the closely related function[12]

$$V_0(x) = 1 + V(x) \quad (6)$$

one finds

$$V_0(x) = {}^1/_2 x^{-1}[1 + 3x - (1-x)^{-1}(1-x^2)^{1/2}(1-5x^2)^{1/2}] \quad (7)$$

Parallel to eq 1, the following connection between the relevant generating functions exists.[12]

$$V(x) = (1-x)^{-1}x[1 + U(x^2)] = (1-x)^{-1}xU_0(x^2) \quad (8)$$

Auxiliary Numbers. In addition to N_a and M_a, sets of auxiliary numbers, viz., L_a, M_a', L_a', were defined previously[6] in terms of summations. The definitions are not repeated here, but numerical values are included in Table 1. The generating functions which reproduce the above auxiliary numbers are simple in principle. They have been worked out in terms of expressions with $U(x)$ and $U(x^2)$ and finally in explicit forms as follows:

$$L(x) = \sum_{a=2}^{\infty} L_a x^a = V^2(x) = (1-x)^{-1}(1+x)U(x^2)$$

$$= {}^1/_2 x^{-2}(1-x)^{-1}(1+x)[1 - 3x^2 - (1-x^2)^{1/2}(1-5x^2)^{1/2}] \quad (9)$$

$$M'(x) = \sum_{a=3}^{\infty} M_a' x^a = U(x^2)\, V(x) = (1-x)^{-1}[x^{-1}(1-2x^2)U(x^2) - x]$$

$$= {}^1/_2 x^{-3}(1-x)^{-1}[(1-x^2)(1-4x^2) - (1-2x^2)(1-x^2)^{1/2}(1-5x^2)^{1/2}] \quad (10)$$

$$L'(x) = \sum_{a=4}^{\infty} L_a' x^a = U(x^2)\, V^2(x) = (1-x)^{-1}(1+x)[x^{-2}(1-3x^2)U(x^2) - 1]$$

$$= {}^1/_2 x^{-4}(1-x)^{-1}(1+x)[1 - 6x^2 + 7x^4 - (1-3x^2)(1-x^2)^{1/2}(1-5x^2)^{1/2}] \quad (11)$$

Crude Totals. The quantities referred to as crude totals,[6] such as ${}^{\alpha}J_a$, are the numbers of nonisomorphic systems with α appendages if no symmetry is present. They are given in the cited reference[6] for α values up to 4 in terms of summations. Again, the corresponding generating functions are simple in principle. They have been worked out in terms of expressions with $U(x)$ and in explicit forms with the following result for $\alpha = 2, 3, 4$; for $\alpha = 1$, simply ${}^1J(x) = U(x)$.

$${}^2J(x) = U^2(x) = x^{-1}(1-3x)U(x) - 1$$

$$= {}^1/_2 x^{-2}[1 - 6x + 7x^2 - (1-3x)(1-x)^{1/2}(1-5x)^{1/2}] \quad (12)$$

$${}^3J(x) = U^3(x) = x^{-2}(1-2x)(1-4x)U(x) - x^{-1}(1-3x)$$

$$= {}^1/_2 x^{-3}[(1-3x)(1-6x+6x^2) - (1-2x)(1-4x)(1-x)^{1/2}(1-5x)^{1/2}] \quad (13)$$

$${}^4J(x) = U^4(x) = x^{-3}(1-3x)(1-6x+7x^2)U(x) - x^{-2}(1-2x)(1-4x)$$

$$= {}^1/_2 x^{-4}[1 - 12x + 50x^2 - 84x^3 - 47x^4 - (1-3x)(1-6x+7x^2)(1-x)^{1/2}(1-5x)^{1/2}] \quad (14)$$

Comprehensive Survey of Schemes of Annelation. The previous work[6] on annelated pyrenes contains a treatment of all the annelation schemes which occur in these systems. It includes a complete account of the cases of $\alpha = 1$ (one appendage) and $\alpha = 2$ (two appendages). Furthermore, some schemes for $\alpha = 3$ and $\alpha = 4$ are contained therein, but not the complete sets.

An annelation scheme is defined by two pieces of information: (i) α, the number of appendages, and (ii) the highest symmetry group, which is realized for $a = \alpha$ (i.e., one hexagon in each appendage).

In Figure 1 a comprehensive survey of relevant functions in the approach of combinatorial summations is given. The numbers of edge-rooted catafusenes, auxiliary numbers, and crude totals are employed. It is assumed $a \geq \alpha$ throughout. Both $N_{a/t}$ and $M_{a/t}$ are supposed to have nonvanishing values only when a is divisible by t. The corresponding generating functions are

$$\sum_{a=t}^{\infty} N_{a/t} x^a = U(x^t), \quad \sum_{a=t}^{\infty} M_{a/t} x^a = V(x^t) \quad (15)$$

For each α, the schemes are indicated by asterisks in Figure 1 and numbered $j = 0, 1, \ldots$. The j numbers are inscribed in polygons; irregular (3α)-gons are convenient for this purpose. The unsymmetrical (C_s) scheme is always taken as $j = 0$. Here the total number of nonisomorphic systems is ${}^{\alpha}_{0}F = {}^{\alpha}J_a$, the crude total. The numbers for systems of specific symmetries are listed for each scheme using the following symbols.

M, occasionally M^a and M^b: mirror-symmetrical (C_{2v}). The superscripts (a and b) indicate different orientations of the 2-fold symmetry axis. The pertinent axes are indicated by dotted lines in Figure 1.

C	centrosymmetrical (C_{2h})
D	dihedral (D_{2h})
T'	irregular trigonal (C_{3h})
T	regular trigonal (D_{3h})

The numbers of unsymmetrical (C_s) systems are not specified explicitly in Figure 1. Instead, the total numbers, ${}^{\alpha}_{j}F$, are given. Then the numbers of C_s systems, if they are desired, are available by subtraction.

Usually the core itself is counted as one system, which corresponds to $\alpha = 0$ (no appendage). For this case one has

$${}^0F = \lfloor (1+a)^{-1} \rfloor, \quad {}^0F(x) = 1 \quad (16)$$

Examples. Two illustrative examples are offered.

Example 1. Denote by $\boldsymbol{P}$ the number of nonisomorphic systems of catafusenes annelated to phenalene as the core. When assuming $a > 0$, one is faced with the six schemes of annelation,[14] as illustrated in Figure 2. The numbers ${}^{\alpha}\boldsymbol{P}$, into

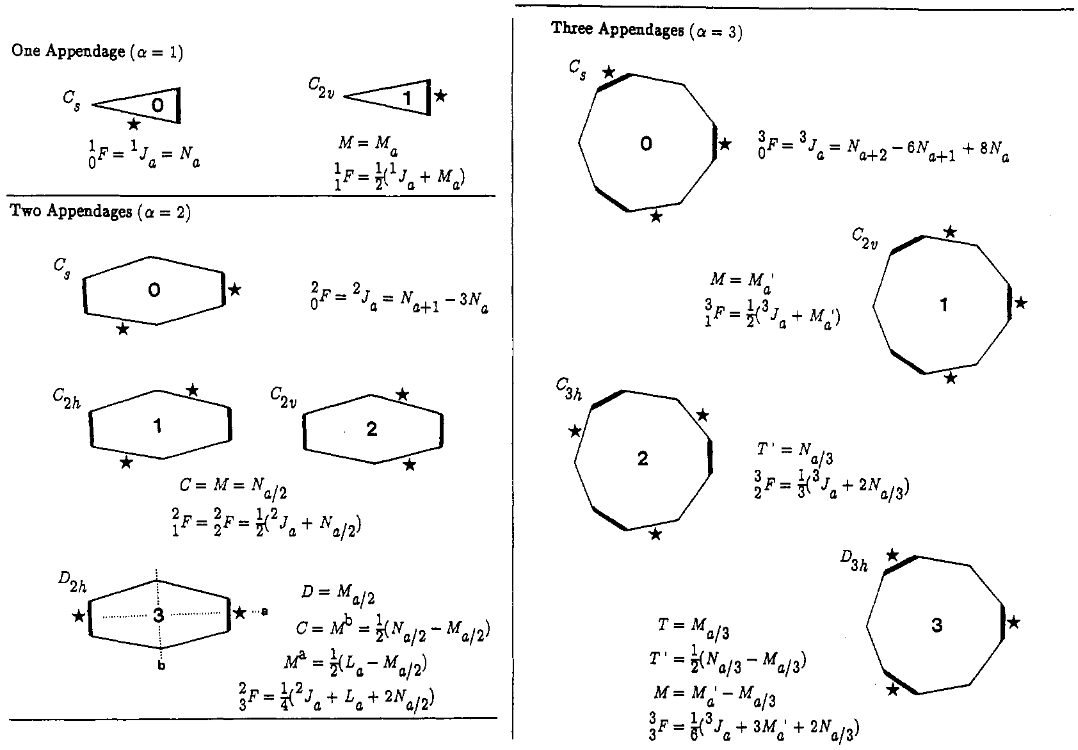


Figure 1. Annelation schemes with one, two, and three appendages. For each α, one set of symmetrically equivalent edges is accentuated by heavy lines. Otherwise, see explanations in the text.

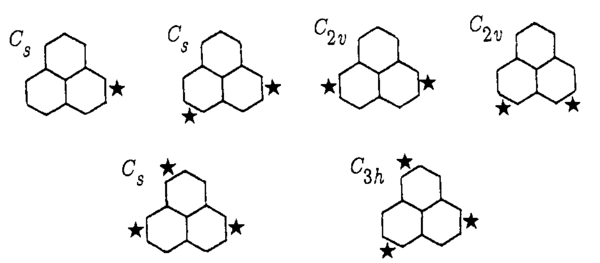


Figure 2. Schemes of annelation to the core phenalene. See example 1.

which P is divided, are found straightforwardly from Figure 1 with the results

$$ {}^1P = {}^1_0F = N_a \tag{17}$$

$$ {}^2P = {}^2_0F + 2({}^2_1F) = 2N_{a+1} - 6N_a + N_{a/2} \tag{18}$$

$$ {}^3P = {}^3_0F + {}^3_2F = {}^1/_3(4N_{a+2} - 24N_{a+1} + 33N_a + 2N_{a/3}) \tag{19}$$

The total is[16]

$$ P = {}^1/_3(4N_{a+2} - 18N_{a+1} + 17N_a + 3N_{a/2} + 2N_{a/3}) \tag{20}$$

The original version of the method of combinatorial summations has led to a substantially more complicated equation.[14] However, it is easy to check the numerical agreement with the previous P values. The generating function for P is[14,17]

$$ P(x) = U(x) + 2U^2(x) + U(x^2) + {}^4/_3U^3(x) + {}^2/_3U(x^3) $$
$$ = {}^1/_2x^{-3}(2 - 3x)(1 - 3x + 6x^2) - {}^1/_6x^{-3}(4 - 18x + 17x^2) \times (1 - x)^{1/2}(1 - 5x)^{1/2} - {}^1/_2x^{-2}(1 - x^2)^{1/2}(1 - 5x^2)^{1/2} - {}^1/_3x^{-3}(1 - x^3)^{1/2}(1 - 5x^3)^{1/2} \tag{21}$$

The exposition of Zhang et al.[12] on catafusenes rooted at a polygon core is rather general but not directly applicable to the above example because the edges of annelation in the core are not isolated. The next example, on the other hand, is virtually identical to one of the examples in Zhang et al.[12]

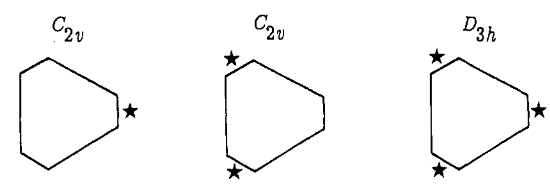


Figure 3. Schemes of annelation in example 2. Only the shorter edges of the core are supposed to be available for annelation.

Example 2. Denote by H the number of nonisomorphic systems of catafusenes annelated to three isolated edges in a regular trigonal configuration; see Figure 3. The three schemes of annelation for $a > 0$ are shown therein. The numbers ${}^\alpha H$ for α = 1, 2, 3 are again obtained straightforwardly from Figure 1:

$$ {}^1H = {}^1_1F = {}^1/_2(N_a + M_a) \tag{22}$$

$$ {}^2H = {}^2_2F = {}^1/_2(N_{a+1} - 3N_a + N_{a/2}) \tag{23}$$

$$ {}^3H = {}^3_3F = {}^1/_6(N_{a+2} - 6N_{a+1} + 8N_a + 3M_a' + 2N_{a/3}) \tag{24}$$

In total,

$$ H = {}^1/_6(N_{a+2} - 3N_{a+1} + 2N_a + 3M_a + 3N_{a/2} + 3M_a' + 2N_{a/3}) \tag{25}$$

Numerical values are given in Table 2. The generating function of H is[12,18]

$$ H(x) = {}^1/_2[U(x) + V(x) + U^2(x) + U(x^2) + U(x^2)\, V(x)] + {}^1/_6U^3(x) + {}^1/_3U(x^3) \tag{26}$$

We shall not give the explicit form of $H(x)$ here for the sake

Table 2. Numbers H from Example 2 (Figure 3) Classified According to the Numbers of Appendages

	α				
a	0	1	2	3	total
0	1	0	0	0	1
1	0	1	0	0	1
2	0	2	1	0	3
3	0	6	3	1	10
4	0	19	16	2	37
5	0	71	66	12	149
6	0	274	300	56	630
7	0	1117	1314	282	2713
8	0	4650	5884	1365	11899
9	0	19819	26304	6666	52789
10	0	85710	118633	32002	236345

Table 3. Numbers H from Example 2 (Figure 3) Classified According to the Symmetry Groups

a	D_{3h}	C_{3h}	C_{2v}	C_s
0	1	0	0	0
1	0	0	1	0
2	0	0	2	1
3	1	0	2	7
4	0	0	6	31
5	0	0	10	139
6	1	1	19	609
7	0	0	36	2677
8	0	0	72	11827
9	2	4	135	52648
10	0	0	274	236071

of brevity. Instead, we show how simply the numbers H are classified according to the symmetry groups from the material of Figure 1. It was readily found

$$T = M_{a/3} \tag{27}$$

$$T' = {}^1/_2(N_{a/3} - M_{a/3}) \tag{28}$$

$$M = M_a + N_{a/2} + M_a' - M_{a/3} \tag{29}$$

for the symmetries D_{3h}, C_{3h}, and C_{2v}, respectively. The numerical values, supplemented with the entry for $a = 0$, are displayed in Table 3, where the numbers under C_s were determined numerically by subtractions from the totals of Table 2.

Overall Crude Totals. The crude totals ${}^{\alpha}J_a$ pertain to the specific schemes of annelation. In the quantity ${}^{\alpha}J$, referred to as the overall crude total, the combinatorial possibilities of symmetrically equivalent annelation schemes must be taken into account:

$${}^{\alpha}J = \sum_{i=0}^{\alpha} \binom{\alpha}{i} {}^{\alpha}J_a \tag{30}$$

One has ${}^0J_a = {}^0F$, given by eq 16, while the quantities ${}^{\alpha}J_a$ for $\alpha > 0$ are specified in Figure 1 (see also eqs 12–14). Consequently, the overall crude totals become ${}^0J = {}^0J_a$ and ${}^1J = N_a$ and as follows for $\alpha = 2, 3, 4$ when $a > 0$ (when $a = 0$, ${}^{\alpha}J = 1$ for all α).

$${}^2J = N_{a+1} - N_a \qquad a > 0 \tag{31}$$

$${}^3J = N_{a+2} - 3N_{a+1} + 2N_a \qquad a > 0 \tag{32}$$

$${}^4J = N_{a+3} - 5N_{a+2} + 7N_{a+1} - 3N_a \qquad a > 0 \tag{33}$$

Numerical values of ${}^{\alpha}J_a$ and ${}^{\alpha}J$ are collected in Table 4. The generating functions for ${}^{\alpha}J$ reduce to an utterly simple form.

Table 4. Crude Totals, ${}^{\alpha}J_a$, and Overall Crude Totals, ${}^{\alpha}J$

a	${}^1J_a$	${}^2J_a$	${}^3J_a$	${}^4J_a$
1	1			
2	3	1		
3	10	6	1	
4	36	29	9	1
5	137	132	57	12
6	543	590	315	94
7	2219	2628	1629	612
8	9285	11732	8127	3605
9	39587	52608	39718	19992
10	171369	237129	191754	106644
a	${}^1J$	${}^2J$	${}^3J$	${}^4J$
0	1	1	1	1
1	1	2	3	4
2	3	7	12	18
3	10	26	49	80
4	36	101	204	355
5	137	406	864	1580
6	543	1676	3714	7066
7	2219	7066	16170	31772
8	9285	30302	71178	143645
9	39587	131782	316303	652860
10	171369	579867	1417248	2981910

In the first place (cf. also eqs 12–14),

$${}^{\alpha}J(x) = \sum_{a=\alpha}^{\infty} ({}^{\alpha}J_a)x^a = U^{\alpha}(x) \tag{34}$$

Consequently,

$${}^{\alpha}J(x) = \sum_{a=0}^{\infty} ({}^{\alpha}J)x^a = \sum_{i=0}^{\alpha} \binom{\alpha}{i} U^{\alpha}(x) = [1 + U(x)]^{\alpha} = U_0{}^{\alpha}(x) \tag{35}$$

An immediate application of the overall crude totals is instructive. Turning back to example 2 (Table 3), it is pointed out that the appropriate overall crude total counts the D_{3h} systems once, the C_{3h} system twice, the C_{2v} system three times, and the C_s systems six times:

$${}^3J_a = T + 2T' + 3M + 6A \tag{36}$$

This relation was checked numerically for $a \le 10$ by means of Tables 3 and 4. In general (for $a > 0$), one finds from eqs 25 and 27–29 for the numbers of unsymmetrical (C_s) systems

$$A = {}^1/_6(N_{a+2} - 3N_{a+1} + 2N_a - 3M_a - 3N_{a/2} - 3M_a' - N_{a/3} + 3M_{a/3}) \tag{37}$$

On inserting from eqs 27–29 and 37 into eq 36, most of the terms cancel, and one indeed arrives at the expression of eq 33.

Four Appendages. Figure 4 shows a survey of the schemes of annelation for $\alpha = 4$ in continuation of Figure 1. The applied symbols are explained above. As a natural extension, also ${}^2J_{a/t}$ and $L_{a/t}$ for integers t (like $N_{a/t}$ and $M_{a/t}$) should have nonvanishing values only when a is divisible by t. A supplement to the symmetry types is needed.

D, occasionally D^a and D^b: dihedral (D_{2h}). The superscript (a and b) indicate different orientations of the twofold symmetry axes (dotted lines in Figure 4).

S' irregular tetragonal (C_{4h})

S regular tetragonal (square; D_{4h})

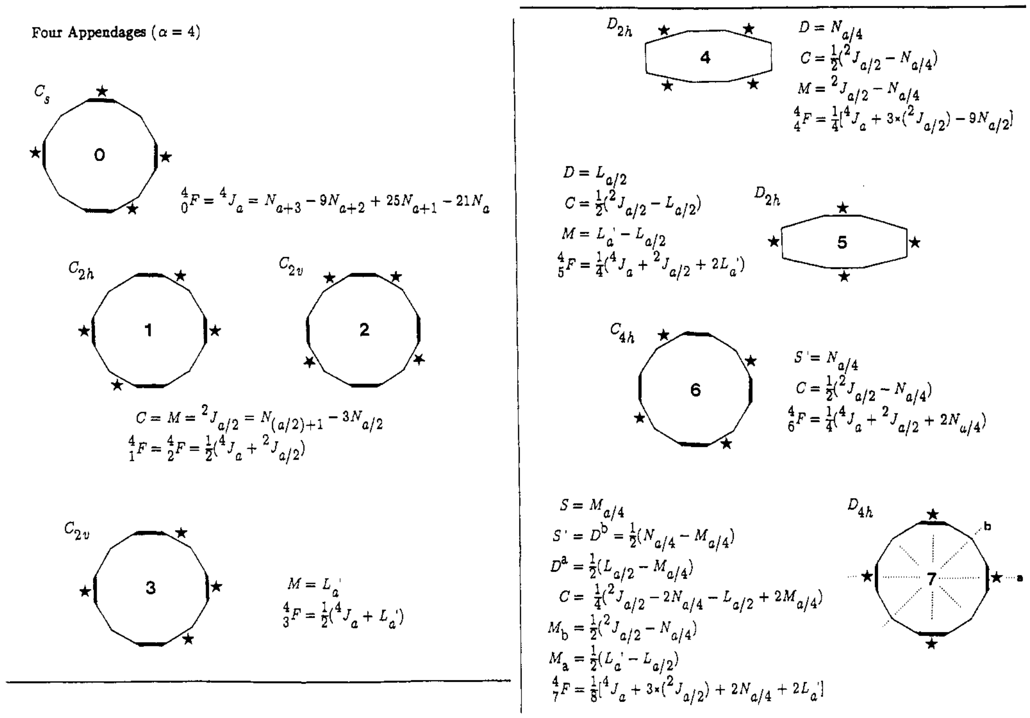
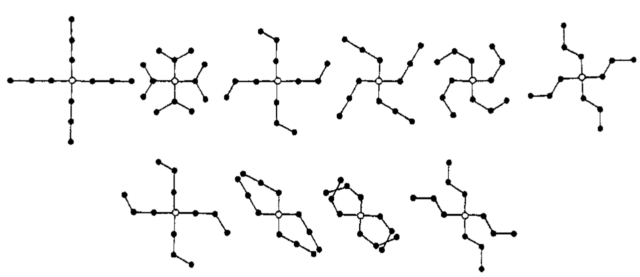


Figure 4. Annelation schemes with four appendages. See legend to Figure 1 and explanations in the text.

Some details in the treatment of the last annelation scheme (No. 7) may be elucidating. The D_{4h}, C_{4h}, and D_{2h}(b) systems have all four appendages equal, and

$$N_{a/4} = S + 2S' = S + 2D^b \quad (38)$$

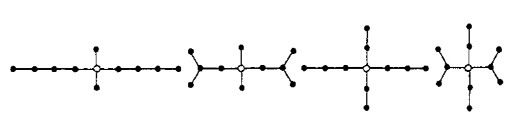
With $S = M_{a/4}$ (see Figure 4) inserted in eq 38 the given expression for $S' = D^b$ emerges. For the sake of clarity the $2D_{4h} + 4C_{4h} + 4D_{2h}$(b) systems at $a = 12$ are shown in the following diagram.



Here and in the following, the dualist representation is employed: each vertex marked as a black dot represents a hexagon, while the white dot represents the core. Similarly

$$L_{a/2} = S + 2D^a \quad (39)$$

gives the expression for D^a. The $4D_{2h}$(a) systems at $a = 10$ are depicted as follows:



The enumeration of the centrosymmetrical (C_{2h}) systems is slightly more complex. One finds

$${}^2J_{a/2} = S + 2S' + 2D^a + 2D^b + 4C \quad (40)$$

from which the appropriate expression for C (see Figure 4)

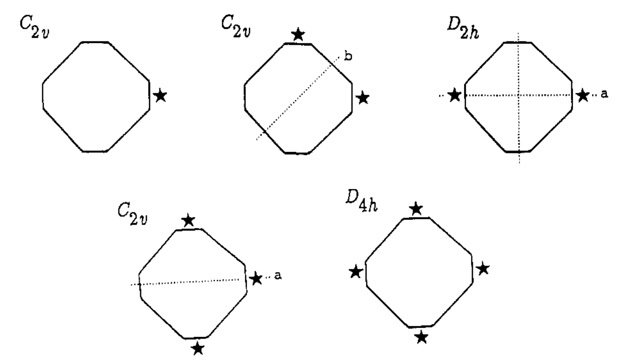
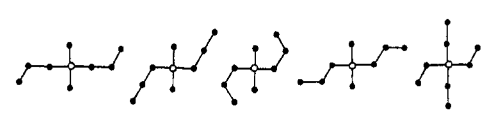


Figure 5. Schemes of annelation in the last example. Only the shorter edges of the core are supposed to be available for annelation.

emerges. The $5C_{2h}$ systems at $a = 8$ are displayed as follows:

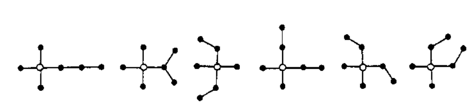


Next the mirror-symmetrical (C_{2v}) systems are enumerated by means of

$${}^2J_{a/2} = S + 2D^b + 2M^b \quad (41)$$

$$L_a' = S + 2D^a + 2M^a \quad (42)$$

There are $19C_{2v}$(a) + $13C_{2v}$(b) of these systems at $a = 8$. For the sake of brevity, only the $3C_{2v}$(a) + $3C_{2v}$(b) systems at $a = 6$ are shown here:



The final step is the determination of the total number ${}^4_7F$ under elimination of the A unsymmetrical (C_s) systems. The crude total counts the D_{4h} systems once, the C_{4h} and D_{2h} systems

Table 5. Numbers O from the Last Example (Figure 5) Classified According to the Numbers of Appendages

	α					
a	0	1	2	3	4	total
0	1	0	0	0	0	1
1	0	1	0	0	0	1
2	0	2	2	0	0	4
3	0	6	5	1	0	12
4	0	19	26	5	1	51
5	0	71	101	31	2	205
6	0	274	457	160	16	907
7	0	1117	1978	825	80	4000
8	0	4650	8851	4074	473	18048
9	0	19819	39481	19902	2517	81719
10	0	85710	178043	95920	13431	373104

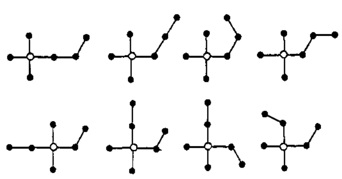
twice, the C_{2h} and C_{2v} systems four times, and finally the C_s systems eight times:

$$^4J_a = S + 2(S' + D^a + D^b) + 4(C + M^a + M^b) + 8A \quad (43)$$

The total is

$$^4_7F = S + S' + D^a + D^b + C + M^a + M^b + A \quad (44)$$

On eliminating A from eqs 43 and 44 and using the expressions derived for all the other numbers but ^4_7F, this quantity is obtained as given in Figure 4. Then, the numbers of the C_s systems (A) are accessible by subtraction. The $8C_s$ systems at $a = 6$ are depicted as follows:



Last Example. Consider the system of Figure 5, which resembles the system of example 2 (Figure 3) but illustrates in a useful way the case of four appendages. Denote by O the number of nonisomorphic systems of the last example (Figure 5). The numbers $^\alpha O$ for $\alpha = 1, 2, 3, 4$ were determined from the information of Figures 1 and 4. For $\alpha = 4$ in particular, $^\alpha O = {}^4_7F$. For the sake of brevity we omit the other details but show the numerical values for $a \leq 10$; see Table 5. In total, it was deduced (for $a > 0$)

$$O = {}^1/_8(N_{a+3} - 5N_{a+2} + 7N_{a+1} - 3N_a + 3N_{(a/2)+1} - N_{a/2}) + {}^1/_4(2M_a + L_a + 2M_a' + N_{a/4} + L_a') \quad (45)$$

The generating function is

$$O(x) = {}^1/_2[U(x) + V(x)] + {}^3/_4U^2(x) + U(x^2) + {}^1/_4V^2(x) + {}^1/_2[U^3(x) + U(x^2)\,V(x)] + {}^1/_8[U^4(x) + 3U^2(x^2)] + {}^1/_4[U(x^4) + U(x^2)\,V^2(x)] \quad (46)$$

The formulas of Zhang et al.[12] are not directly applicable to ^4_7F of Figure 4. Our last example was chosen so that it depends heavily on ^4_7F and can be checked. It is true that Zhang et al.[12] have not elaborated this particular example, but from their general approach[12,19] we have found[20]

$$1 + O(x) = {}^1/_8[U_0{}^4(x) + 3U_0{}^2(x^2) + 2U_0(x^4) + 2U_0(x^2)\,V_0{}^2(x)] \quad (47)$$

Table 6. Numbers O from the Last Example (Figure 5) Classified According to the Symmetry Groups

a	D_{4h}	C_{4h}	D_{2h}(a)	D_{2h}(b)	C	C_{2v}(a)	C_{2v}(b)	C_s
0	1	0	0	0	0	0	0	0
1	0	0	0	0	0	1	0	0
2	0	0	1	0	0	1	1	1
3	0	0	0	0	0	4	0	8
4	1	0	1	0	1	6	3	39
5	0	0	0	0	0	15	0	190
6	0	0	3	0	5	25	13	861
7	0	0	0	0	0	57	0	3943
8	1	1	4	1	22	103	49	17867
9	0	0	0	0	0	223	0	81496
10	0	0	9	0	97	417	203	372378

which is perfectly consistent with eq 46. The following explicit form was deduced.

$$O(x) = {}^1/_{16}x^{-4}[8(1 + x^2 - 6x^3 - x^4) - (1 - 3x) \times (1 - x)^{5/2}(1 - 5x)^{1/2} - (1 - x)^{-1}(5 + 3x - 5x^2 - 7x^3) \times (1 - x^2)^{1/2}(1 - 5x^2)^{1/2} - 2(1 - x^4)^{1/2}(1 - 5x^4)^{1/2}] \quad (48)$$

As in example 2, we give the numbers O classified according to symmetry types:

$$S = M_{a/4} \quad (49)$$

$$S' = D^b = {}^1/_2(N_{a/4} - M_{a/4}) \quad (50)$$

$$D^a = M_{a/2} + {}^1/_2(L_{a/2} - M_{a/4}) \quad (51)$$

$$C = {}^1/_4(N_{(a/2)+1} - N_{a/2} - L_{a/2}) - {}^1/_2(M_{a/2} + N_{a/4} - M_{a/4}) \quad (52)$$

$$M^b = {}^1/_2(N_{(a/2)+1} - N_{a/2} - N_{a/4}) \quad (53)$$

$$M^a = M_a + {}^1/_2(N_{a/2} + L_a - L_{a/2} + L_a') - M_{a/2} + M_a' \quad (54)$$

Table 6 gives the relevant numerical values for $a \leq 10$. Here the A numbers for the unsymmetrical (C_s) systems were obtained by subtraction from the totals in Table 5. The following relation for the appropriate overall crude total was checked numerically with the numbers from Tables 4 and 6. It has the same form as eq 43:

$$^4J = S + 2(S' + D^a + D^b) + 4(C + M^a + M^b) + 8A \quad (55)$$

CONCLUSION

The present work supplies a comprehensive survey of the enumeration method of combinatorial summations, hand in hand with applications of generating functions. All cases of catafusenes annelated to a core with one to four appendages are considered. The schemes which have been elaborated for these cases are supposed to be useful for practical applications. In the first place, it is intended that they be used in enumerations of catacondensed monoheptafusenes and catacondensed monooctafusenes.

In the first applications of the method of combinatorial summations in its refined form,[6] no generating functions were employed. In the following Appendix this omission is remedied. Finally, a unified list of errata to the mentioned work[6] is supplied.

APPENDIX

In the treatment of catafusenes annelated to pyrene,[6] the functions $^\alpha Q_h$ for $\alpha = 1, 2, 3, 4$ designate the numbers of nonisomorphic systems with α appendages. These functions are given algebraically in terms of summations in the cited work.[6] Here we give the corresponding generating functions.

$$^1Q(x) = x^3(1-2x) - {}^1/_4x^3[3(1-x)^{1/2}(1-5x)^{1/2} + (1-x)^{-1}(1-x^2)^{1/2}(1-5x^2)^{1/2}] \quad (A1)$$

$$^2Q(x) = {}^1/_4x^2(1-x)^{-1}(10-48x+74x^2-38x^3) - {}^1/_8x^2[13(1-3x)(1-x)^{1/2}(1-5x)^{1/2} + (1-x)^{-1}(7-5x)(1-x^2)^{1/2}(1-5x^2)^{1/2}] \quad (A2)$$

$$^3Q(x) = x(2-13x+34x^2-29x^3) - {}^3/_2x[(1-2x)\times(1-4x)(1-x)^{1/2}(1-5x)^{1/2} - (1-x)^{-1}(1-2x^2)\times(1-x^2)^{1/2}(1-5x^2)^{1/2}] \quad (A3)$$

$$^4Q(x) = {}^1/_2[(1-x)^{-1}(2-13x+56x^2-134x^3+138x^4-47x^5) - (1-3x)(1-6x+7x^2)(1-x)^{1/2}(1-5x)^{1/2} - (1-x)^{-1}(1-3x^2)(1-x^2)^{1/2}(1-5x^2)^{1/2}] \quad (A4)$$

As a final result, the total number of nonisomorphic annelated pyrenes with catafusenes as appendages, including pyrene itself, is given by

$$Q(x) = x^4 + \sum_{\alpha=1}^{4}{}^{\alpha}Q(x) = {}^1/_2(1-x)^{-1}(2-9x+31x^2-62x^3+45x^4-6x^5) - {}^1/_8[(1-x)(2-3x)(2-7x)\times(1-x)^{1/2}(1-5x)^{1/2} + (1-x)^{-1}(4+4x-5x^2-11x^3)\times(1-x^2)^{1/2}(1-5x^2)^{1/2}] \quad (A5)$$

In other words, this complicated function reproduces the numbers of nonisomorphic normal perifusenes with two internal vertices each.

Errata to ref 6: in eq 3, read $4N_{a+2}$ (instead of N_{a+2}); in Table 1, $M_9' = M_{10}' = 86$ are the correct values (not 50); as a consequence, there are some wrong entries for $h = 13$ and 14 in Tables 2–4. They should be corrected as follows:

h	^3Q_h	C_{2v}(a)	C_s	total	normal helicenes
13	119 240	345	369 330	369 675	97 561
14	575 348	680	1709 087	1710 173	545 976

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(10) The symbol a is adopted from a previous work.[6] We do not use h, the usual symbol for the number of hexagons, because the core also may contain hexagons.

(11) The concept of symmetry, indicated by symmetry groups, is explained in the previous work.[6]

(12) Zhang, F. J.; Guo, X. F.; Cyvin, S. J.; Cyvin, B. N. The Enumeration of Catafusenes Rooted at a Polygon Core. *Chem. Phys. Lett.* **1992**, *190*, 104–108.

(13) The function $U_0(x)$ has also been called[14,15] $N(x)$. The reader should not be confused by the usage of $U(x)$, with proper explanation,[5] as identical to our $U_0(x)$.

(14) Cyvin, S. J.; Zhang, F. J.; Brunvoll, J. Enumeration of Perifusenes with One Internal Vertex: A Complete Mathematical Solution. *J. Math. Chem.* **1992**, *11*, 283–292.

(15) Cyvin, S. J.; Brunvoll, J. Generating Functions for the Harary-Read Numbers Classified According to Symmetry. *J. Math. Chem.* **1992**, *9*, 33–38.

(16) Notice the minor error in eq 3 of ref 6, which is corrected by the present eq 20.

(17) The present eq 22 is compatible with the formation of eq 26 in ref 14, which is $x^3[1 + P(x)]$.

(18) The function given in terms of $U_0(x)$ and $V_0(x)$ under example 6 of ref 12 conforms with our $1 + H(x)$ and has actually a simpler form. The numerical values[12] are reproduced in Table 2.

(19) Cyvin, S. J.; Cyvin, B. N.; Brunvoll, J.; Brendsdal, E.; Zhang, F. J.; Guo, X. F.; Tošić, R. Theory of Polypentagons. *J. Chem. Inf. Comput. Sci.* **1993**, *33*, 466–474.

(20) Use eq A2 of the Appendix in ref 19. Set $n = 4$, $q = 2$, $m_1 = 0$, $m = m_2 = 1$, $k = k_1 = k_2 = 0$, $\varphi(1) = \varphi(2) = 1$, $\varphi(4) = 2$.