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Enumeration of Polyene Hydrocarbons: A Complete Mathematical Solution

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Polyenoid systems (or polyenoids) are trees which can be embedded in a hexagonal lattice and represent C_nH_{n+2} polyene hydrocarbons. Complete mathematical solutions in terms of summations and in terms of a generating function are deduced for the numbers of polyenoids when overlapping edges and/or vertices are allowed. Geometrically planar polyenoids (without overlapping vertices) are enumerated by computer programming. Thus the numbers of geometrically nonplanar polyenoids become accessible. Some of their numbers are confirmed by combinatorial constructions, a pen-and-paper method.

INTRODUCTION

Isomers of conjugated polyene hydrocarbons, C_nH_{n+2}, are of great interest in organic chemistry. The enumeration of their isomers is the topic of the present work. Figure 1 shows the three isomers of C_4H_6 which are taken into account. The molecules of interest are acyclic conjugated hydrocarbons, but also radicals (as e.g., trimethylenemethane) are included.

As chemical graphs,[1] the conjugated polyene hydrocarbons are represented by certain trees, where any two incident edges form an angle of 120°. Their forms up to five vertices (n = 6) are displayed in Figure 2. For the sake of completeness, one vertex alone for n = 1 is included; it represents the CH_3 methyl radical.

The present work was inspired by Kirby,[2] who enumerated conjugated polyene isomers by computer programming based on coding of the structures. The smallest numbers of these isomers are I_n = 1, 1, 1, 3, 4, 12 for n = 1, 2, ..., 6 in consistency with Figure 2. We have achieved a complete mathematical solution for I_n, but only when it is allowed for all structures irrespective of steric hindrances. It is assumed that such structures can be realized chemically by nonplanar molecules. In consequence, we obtain I_7 = 27 versus the 26 isomers for n = 7 reported by Kirby.[2] This feature is explained by our inclusion of the coiled C_7H_9 radical.

The mathematical methods of the present work follow basically Harary and Read[3] in their enumeration of catafusenes. Generating functions are employed extensively, and the Redfield–Pólya theorem[4] is implied, although we do not refer to it explicitly. Parallel with these methods, we have also applied the method of combinatorial summations,[5] which leads to a formula for I_n in closed form.

DEFINITIONS

A polyenoid system (or simply polyenoid) P is one vertex alone or a tree which can be embedded in a planar hexagonal lattice (consisting of congruent regular hexagons). More precisely, P is said to be a geometrically planar polyenoid when defined in this way. A geometrically nonplanar polyenoid P* is defined in the same way, but so that it has at least two overlapping vertices when drawn in a plane. A system P* may be referred to as helicenic in analogy with the helicenic polyhexes.[6]

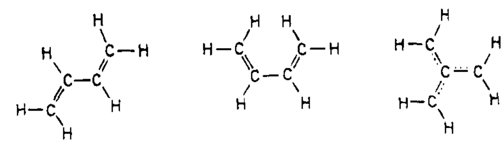

Figure 1. Three isomers of C_4H_6: *trans*- and *cis*-butadiene and the trimethylenemethane radical.

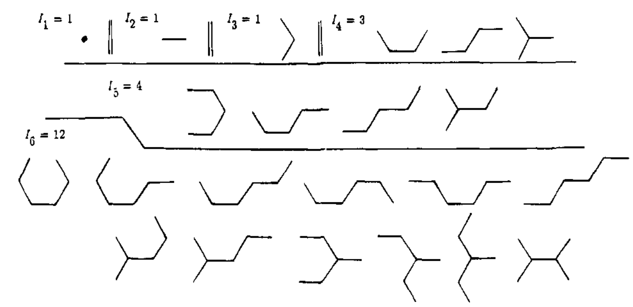

Figure 2. All I_n nonisomorphic polyenoids for $n \leq 6$; they represent C_nH_{n+2} polyene hydrocarbons.

Figure 3. The coiled $C_{10}H_{12}$ polyenoid; in the right-hand drawing the C_{2v} symmetry is accentuated.

A geometrically planar polyenoid (P) can obviously belong to one of the symmetry groups D_{3h}, C_{3h}, D_{2h}, C_{2h}, C_{2v}, or C_s. Then CH_3 and C_2H_4 are attributed to the groups D_{3h} and D_{2h}, respectively. These symmetries are realized if the carbon–hydrogen bonds are included. We shall also assign the same six symmetry groups to the P* systems, disregarding the geometrical nonplanarity. Thus, for instance, all the coiled polyenoids are attributed to C_{2v}. An illustration for $C_{10}H_{12}$ is given in Figure 3.

Two types of C_{2v} systems are distinguished and identified by the symbols C_{2v}(a) and C_{2v}(b). A P or P* system belongs to C_{2v}(a) when its unique twofold symmetry axis (C_2) passes through a vertex; P or P* belongs to C_{2v}(b) when C_2 bisects

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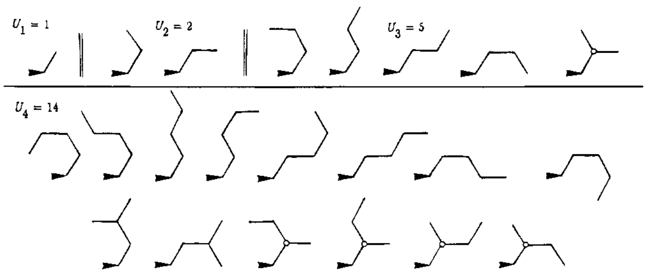

Figure 4. The U_m rooted unsymmetrical polyenoids for $m \leq 4$.

perpendicularly an edge. The coiled system of Figure 3, for instance, is of the type C_{2v}(b), as is any coiled C_nH_{n+2} polyenoid where $n = 4, 6, 8, \ldots$. The coiled C_nH_{n+2} polyenoids for $n = 3, 5, 7, \ldots$ belong to C_{2v}(a).

The number of vertices in a polyenoid is n, while its number of edges will be identified by the symbol m.

ALGEBRAIC SOLUTION

Rooted Unsymmetrical Polyenoids. As an underlying principle, all polyenoids with $m + 1$ edges are generated by adding one edge every time to the polyenoids with m edges. To a free end vertex of an edge (vertex of degree one) a new edge can be added in exactly two directions. A directional walk of this kind has been employed frequently in generation of chemical graphs and their codings.[7-14] This list of references is far from complete.

As a starting point, the U_m numbers of rooted unsymmetrical polyenoids are to be determined. The smallest systems of this category are shown in Figure 4. We distinguish two types: the U_m* systems where the first edge (incident to the root edge) is not incident to a vertex of degree three, and the U_m** systems where the first edge is incident to a vertex of degree three or in other words a branching vertex. These branching vertices are indicated by white dots in Figure 4. Here m does not count the root edge. One has clearly

$$U_m = U_m{}^* + U_m{}^{**} \quad (m > 1), \quad U_1 = 1 \tag{1}$$

Furthermore,

$$U_{m+1}{}^* = 2U_m \quad (m > 0), \quad U_1{}^* = 0 \tag{2}$$

since the U_{m+1}* systems can be obtained from the U_m systems by adding one edge in two directions. It is also clear that

$$U_{m+1}{}^{**} = \sum_{i=1}^{m-1} U_i U_{m-i} (m > 1), \quad U_1{}^{**} = U_2{}^{**} = 0 \tag{3}$$

since these systems may be interpreted as two branches attached to one vertex and having $m - 1$ edges together. On combining eqs 1–3 one arrives at the recurrence relation for U_m

$$U_{m+1} = 2U_m + \sum_{i=1}^{m-1} U_i U_{m-i} \quad (m > 1) \tag{4}$$

The initial conditions are $U_1 = 1$, $U_2 = 2$.

The appropriate generating functions satisfy

$$U(x) = U^*(x) + U^{**}(x) + x \tag{5}$$

where the last x takes care of the $m = 1$ system, which

cf. A002420
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Table 1. Numbers of Some Rooted Unsymmetrical Polyenoids

m	U_m*	U_m**	U_m
0			1
1	0	0	1
2	2	0	2
3	4	1	5
4	10	4	14
5	28	14	42
6	84	48	132
7	264	165	429
8	858	572	1430
9	2860	2002	4862
10	9724	7072	16796

otherwise would not have been counted. Furthermore,

$$U^*(x) = 2x\,U(x), \quad U^{**}(x) = xU^2(x) \tag{6}$$

Hence

$$xU^2(x) + (2x - 1)U(x) + x = 0 \tag{7}$$

from which the following is obtained

$$U(x) = \sum_{m=1}^{\infty} U_m x^m = \frac{1}{2}x^{-1}[1 - 2x - (1 - 4x)^{1/2}] = x + 2x^2 + 5x^3 + 14x^4 + 42x^5 + \ldots \tag{8}$$

Here a plus sign before the square root is extraneous. By definition, we shall put

$$U_0 = 1 \tag{9}$$

and also define the modified generating function

$$U_0(x) = \sum_{m=0}^{\infty} U_m x^m = 1 + U(x) = \frac{1}{2}x^{-1}[1 - (1 - 4x)^{1/2}] = 1 + x + 2x^2 + 5x^3 + 14x^4 + 42x^5 + \ldots \tag{10}$$

Additional numerical values are found in Table 1.

It is interesting to notice that U_m are the Catalan numbers, which keep cropping up in various contexts:[15]

$$U_m = (m + 1)^{-1}\binom{2m}{m} \tag{11}$$

Crude Totals. In the following analysis some "crude totals"[5,6] are needed. The first crude total, presently denoted by ${}^1J_m$, is simply

$${}^1J_m = U_m \quad (m > 0) \tag{12}$$

with the corresponding generating function

$${}^1J(x) = U(x) \tag{13}$$

The next crude total,[5,6] viz. ${}^2J_m$, appears to be identical with U_{m+1}** for $m > 1$; see eq 3. Then, with the aid of eq 4, one obtains

$${}^2J_m = \sum_{i=1}^{m-1} U_i U_{m-i} = U_{m+1} - 2U_m \quad (m > 1) \tag{14}$$

The corresponding generating function is

$${}^2J(x) = U^2(x) = x^{-1}(1 - 2x)U(x) - 1 = \frac{1}{2}x^{-2}[1 - 4x + 2x^2 - (1 - 2x)(1 - 4x)^{1/2}] \tag{15}$$

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Table 2. Crude Totals for Polyenoids

A039598 (table)

m	^1J_m	^2J_m	^3J_m	$^4J^m$
1	1			
2	2	1		
3	5	4	1	
4	14	14	6	1
5	42	48	27	8
6	132	165	110	44
7	429	572	429	208
8	1430	2002	1638	910
9	4862	7072	6188	3808
10	16796	25194	23256	15504
11	58786	90440	87210	62016
12	208012	326876	326876	245157
13	742900	1188640	1225785	961400
14	2674440	4345965	4601610	3749460
15	9694845	15967980	17298645	14567280

Also ^3J_m is needed in the following. It is

$$^3J_m = \sum_{i=1}^{m-2} U_i \sum_{j=1}^{m-i-1} U_j U_{m-i-j} = U_{m+2} - 4U_{m+1} + 3U_m \quad (m > 2) \qquad (16)$$

with the generating function

$$^3J(x) = U^3(x) = x^{-2}(1 - 4x + 3x^2)U(x) - x^{-1}(1 - 2x) = \frac{1}{2}x^{-3}[(1 - 2x)(1 - 4x + x^2) - (1 - 4x + 3x^2)(1 - 4x)^{1/2}] \qquad (17)$$

Finally we shall need the crude totals

$$^4J_m = \sum_{i=1}^{m-3} U_i \sum_{j=1}^{m-i+2} U_j \sum_{k=1}^{m-i-j-1} U_k U_{m-i-j-k} = U_{m+3} - 6U_{m+2} + 10U_{m+1} - 4U_m \quad (m > 3) \qquad (18)$$

The corresponding generating function is

$$^4J(x) = U^4(x) = x^{-3}(1 - 2x)(1 - 4x + 2x^2)U(x) - x^{-2}(1 - 4x + 3x^2) = \frac{1}{2}x^{-4}[1 - 8x + 20x^2 - 16x^3 + 2x^4 - (1 - 2x)(1 - 4x + 2x^2)(1 - 4x)^{1/2}] \qquad (19)$$

Numerical values of the crude totals are collected in Table 2. A peculiar behavior of these numbers is observed. Firstly, $^2J_m < {^1J_m}$ for $m < 4$, $^2J_m > {^1J_m}$ for $m > 4$, while $^2J_4 = {^1J_4} = 14$. Next, $^3J_m < {^2J_m}$ for $m < 12$, $^3J_m > {^2J_m}$ for $m > 12$, while $^3J_{12} = {^2J_{12}} = 326876$. The next "turning point" is (outside the range of Table 2) $^4J_{24} = {^3J_{24}} = 2789279908316$. Presently it will be proven that this behavior is general, and the turning point occurs as

$$^{\alpha+1}J_m = {^\alpha J_m}, \quad m = 2\alpha(\alpha + 1) \qquad (20)$$

First we shall derive the explicit form of $^\alpha J_m$ as

$$^\alpha J_m = \frac{\alpha}{m}\binom{2m}{m+\alpha} \quad (\alpha \geq 1, \quad m \geq \alpha) \qquad (21)$$

in consistency with eq 11 (for $\alpha = 1$). Also for $\alpha = 2$ the formula 21 is verified by means of eq 14. On multiplying eq 7 by $U^\alpha(x)$ one gets

$$xU^{\alpha+2}(x) + (2x - 1)U^{\alpha+1}(x) + xU^\alpha(x) = 0 \qquad (22)$$

and from this it follows that

$$^{\alpha+2}J_m = {^{\alpha+1}J_{m+1}} - 2({^{\alpha+1}J_m}) - {^\alpha J_m} \qquad (23)$$

This relation was used to prove eq 21 by complete induction on α. Equation 21 now yields

$$^{\alpha+1}J_m = \beta({^\alpha J_m}), \quad \beta = \alpha^{-1}(\alpha + 1)(m - \alpha)(m + \alpha + 1)^{-1} \qquad (24)$$

Then eq 20 follows from the fact that $\beta = 1$ if and only if $m = 2\alpha(\alpha + 1)$. Furthermore, $\beta < 1$ if and only if $m < 2\alpha(\alpha + 1)$ and $\beta > 1$ if and only if $m > 2\alpha(\alpha + 1)$, which fully explains the behavior described below eq 19.

It is interesting that our crude totals are exactly the elements in the Catalan triangle of Shapiro.[16] This author has both deduced the explicit form (21) and pointed out the relevance of $U^\alpha(x)$.

Atom-Rooted Polyenoids. A polyenoid emerges by attaching α appendages to a vertex, where α = 1, 2, or 3. Let the numbers of these "atom-rooted" systems with m edges be $^1\mathcal{A}_m$, $^2\mathcal{A}_m$, and $^3\mathcal{A}_m$, respectively. For the sake of completeness, define also

$$^0\mathcal{A} = 1 \quad (m = 0) \qquad (25)$$

which accounts for one vertex alone.

For $\alpha = 1$ (one appendage), assume that there are (for a given m) M systems with mirror symmetry and A without. Then

$$^1J_m = M + 2A, \quad {^1\mathcal{A}_m} = M + A \qquad (26)$$

where

$$M = U_{(m-1)/2} \quad (m > 0) \qquad (27)$$

Here and in the following it is always assumed that U and similar quantities are only defined as nonvanishing numbers for integer subscripts (occasionally including zero). Therefore, in eq 27, m = 1, 3, 5, 7, ... The quantity ^1J_m is the crude total of eq 12. On eliminating A from eq 26 and inserting M from eq 27, the following is obtained

$$^1\mathcal{A}_m = \frac{1}{2}[U_m + U_{(m-1)/2}] \qquad (28)$$

The generating function for M is $x\,U_0(x^2)$; hence

$$^1\mathcal{A}(x) = \sum_{m=1}^{\infty}({^1\mathcal{A}_m})x^m = \frac{1}{2}[U(x) + xU_0(x^2)] = \frac{1}{4}x^{-1}[2(1 - x) - (1 - 4x)^{1/2} - (1 - 4x^2)^{1/2}] = x + x^2 + 3x^3 + 7x^4 + 22x^5 + 66x^6 + ... \qquad (29)$$

For $\alpha = 2$ (two appendages), assume again that there are M mirror-symmetrical (C_{2v}) and A unsymmetrical (C_s) systems. Now

$$^2J_m = M + 2A, \quad {^2\mathcal{A}_m} = M + A \qquad (30)$$

where

$$M = U_{m/2} \quad (m > 1) \qquad (31)$$

D3h (without zeros) = A000108

C3h = A000150 (without zeros)

Hence

$$^{2}\mathcal{A}_m = \frac{1}{2}[^{2}J_m + U_{m/2}] = \frac{1}{2}[U_{m+1} - 2U_m + U_{m/2}] \quad (32)$$

The generating function for M is $U(x^2)$, while $^{2}J(x)$ is found in eq 15. Finally, for the numbers $^{2}\mathcal{A}_m$ the following was arrived at

$$^{2}\mathcal{A}(x) = \sum_{m=2}^{\infty} (^{2}\mathcal{A}_m)x^m = \frac{1}{2}[U^2(x) + U(x^2)] = \frac{1}{2}x^{-1}[(1-2x)U(x) + xU(x^2) - x] = \frac{1}{4}x^{-2}[2(1-2x) - (1-2x)(1-4x)^{1/2} - (1-4x^2)^{1/2}] = x^2 + 2x^3 + 8x^4 + 24x^5 + 85x^6 + ... \quad (33)$$

For $\alpha = 3$ (three appendages), assume that there are T systems of D_{3h}, R of C_{3h}, M of C_{2v}, and A of the C_s symmetry. Then

$$^{3}J_m = T + 2R + 3M + 6A, \quad ^{3}\mathcal{A}_m = T + R + M + A \quad (34)$$

where

$$T = U_{(m-3)/6} \quad (m > 2) \quad (35)$$

T=D3h

with the generating function $x^3U_0(x^6)$. Consequently, the numbers R are obtained as

$$U_{m/3} = T + 2R, \quad R = \frac{1}{2}[U_{m/3} - U_{(m-3)/6}] \quad (36)$$

R=C3h

with the generating function $U(x^3)$ for $U_{m/3}$. For the systems with mirror symmetry it was found

$$\sum_{i=0}^{(m-3)/2} U_iU_{(m-1)/2-i} = U_{(m-1)/2} + {}^{2}J_{(m-1)/2} = T + M$$

$$M = {}^{2}J_{(m-1)/2} + U_{(m-1)/2} - U_{(m-3)/6} = U_{(m+1)/2} - U_{(m-1)/2} - U_{(m-3)/6} \quad (37)$$

C2v = M (here) + M (Eq. (31))

From 34 and the subsequent equations, in addition to eq 16, one finds

$$^{3}\mathcal{A}_m = \frac{1}{6}[^{3}J_m + 5T + 4R + 3M] = \frac{1}{6}[U_{m+2} - 4U_{m+1} + 3U_m + 3U_{(m+1)/2} - 3U_{(m-1)/2} + 2U_{m/3}] \quad (m > 0) \quad (38)$$

For these numbers $^{3}\mathcal{A}_m$ the following generating function was deduced.

$$^{3}\mathcal{A}(x) = \frac{1}{6}[U^3(x) + 3x^{-1}U(x^2) - 3xU_0(x^2) + 2U(x^3)] = \frac{1}{12}x^{-3}[6(1 - x - x^3) - (1 - 4x + 3x^2)(1-4x)^{1/2} - 3(1-x^2)(1-4x^2)^{1/2} - 2(1-4x^3)^{1/2}] = x^3 + x^4 + 6x^5 + 19x^6 + 76x^7 + ... \quad (39)$$

The final result for atom-rooted polyenoids concerns their total numbers $\mathcal{A}_m$, viz. $\mathcal{A}_m = {}^{0}\mathcal{A}_m + {}^{1}\mathcal{A}_m + {}^{2}\mathcal{A}_m + {}^{3}\mathcal{A}_m$. It was found that

$$\mathcal{A}_m = \frac{1}{6}[U_{m+2} - U_{m+1} + 3U_{(m+1)/2} + 3U_{m/2} + 2U_{m/3}] \quad (m > 0) \quad (40)$$

while $\mathcal{A}_0 = 1$. The corresponding generating function was also determined; in explicit form it reads:

$$\mathcal{A}(x) = \sum_{m=0}^{\infty} \mathcal{A}_m x^m = \frac{1}{12}x^{-3}[6(1-x^2) - (1-x)(1-4x)^{1/2} - 3(1+x)(1-4x^2)^{1/2} - 2(1-4x^3)^{1/2}] \quad (41)$$

The numbers to $m = 15$ are given in Table 3, and the smallest forms (for $m \le 4$) are depicted in Figure 5. Information about the symmetry groups is contained in the above material, and the pertinent numbers are included in Table 3.

Table 3. Numbers of Atom-Rooted Polyenoids, Classified According to Symmetry

A063786(?) A000908 A003446

m	D_{3h}	C_{3h}	C_{2v}	C_s	total $\mathcal{A}_m$
0	1	0	0	0	1
1	0	0	1	0	1
2	0	0	1	1	2
3	1	0	1	4	6
4	0	0	2	14	16
5	0	0	5	47	52
6	0	1	5	164	170
7	0	0	14	565	579
8	0	0	14	1982	1996
9	1	2	41	6977	7021
10	0	0	42	24850	24892
11	0	0	132	89082	89214
12	0	7	132	321855	321994
13	0	0	429	1169853	1170282
14	0	0	429	4276923	4277352
15	2	20	1428	15713799	15715249

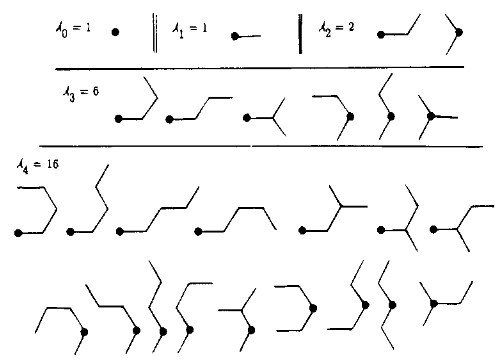


Figure 5. The $\mathcal{A}_m$ atom-rooted polyenoids for $m \le 4$. Root vertices are indicated as black dots.

Bond-Rooted Polyenoids. The "bond-rooted" polyenoid systems emerge by attaching α appendages to the ends of an edge, where $\alpha = 0, 1, 2, 3,$ or 4. The symbol $^{\alpha}\mathcal{B}_m$ will be used to denote the number of bond-rooted polyenoids with m edges and α appendages. One edge alone is represented by

$$^{0}\mathcal{B}_1 = 1 \quad (42)$$

while $^{0}\mathcal{B}_m = 0$ for $m > 1$. The corresponding generating function reads simply

$$^{0}\mathcal{B}(x) = x \quad (43)$$

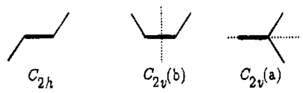
For $\alpha = 1$ all the ${}^1\mathcal{B}_m$ systems are unsymmetrical, and it is found

$$ {}^1\mathcal{B}_m = U_{m-1} \quad (m > 1) \tag{44}$$

with the generating function

$$ {}^1\mathcal{B}(x) = x\,U(x) = x^2 + 2x^3 + 5x^4 + 14x^5 + 42x^6 + \ldots \tag{45}$$

For $\alpha = 2$ three schemes of attachments are distinguished:



The indicated symmetry types, viz. C_{2h}, C_{2v}(b), and C_{2v}(a), occur in addition to C_s. Denote by C, M(b), and M(a) the numbers of C_{2h}, C_{2v}(b) and C_{2v}(a) systems, respectively. Then

$$ {}^2J_{m-1} = C + 2A = M(\mathrm{b}) + 2A = M(\mathrm{a}) + 2A \tag{46}$$

where

$$ C = M(\mathrm{b}) = M(\mathrm{a}) = U_{(m-1)/2} \quad (m > 2) \tag{47}$$

with the generating function $xU(x^2)$. There are also the same number of A unsymmetrical (C_s) systems for each of the schemes of attachments. Hence this case is very similar to the case of $\alpha = 2$ for the atom-rooted polyenoids, and one finds

$$ {}^2\mathcal{B}_m = \frac{3}{2}[{}^2J_{m-1} + U_{(m+1)/2}] = \frac{3}{2}[U_m - 2U_{m-1} + U_{(m-1)/2}] \tag{48}$$

to be compared with eq 32. The pertinent generating function is similar to eq 33, viz.

$$ {}^2\mathcal{B}(x) = \sum_{m=3}^{\infty}({}^2\mathcal{B}_m)x^m = 3x[{}^2\mathcal{A}(x)] = 3x^3 + 6x^4 + 24x^5 + 72x^6 + 255x^7 + \ldots \tag{49}$$

For $\alpha = 3$ all the ${}^3\mathcal{B}_m$ systems are unsymmetrical, and one has simply

$$ {}^3\mathcal{B}_m = {}^3J_{m-1} = U_{m+1} - 4U_m + 3U_{m-1} \quad (m > 3) \tag{50}$$

The pertinent generating function is similar to eq 17, viz.

$$ {}^3\mathcal{B}(x) = x[{}^3J(x)] = x^4 + 6x^5 + 27x^6 + 110x^7 + 429x^8 + \ldots \tag{51}$$

For $\alpha = 4$,

$$ {}^4J_{m-1} = D + 2C + 2M(\mathrm{b}) + 2M(\mathrm{a}) + 4A, \quad {}^4\mathcal{B}_m = D + C + M(\mathrm{b}) + M(\mathrm{a}) + A \tag{52}$$

Here

$$ D = U_{(m-1)/4} \quad (m > 4) \tag{53}$$

with the generating function $xU(x^4)$. These numbers count the dihedral (D_{2h}) systems. The numbers of C_{2h} systems are given by

$$ \sum_{i=1}^{(m-3)/2} U_i U_{(m-1)/2-i} = {}^2J_{(m-1)/2} = D + 2C \quad (m > 4) \tag{54}$$

These numbers (C) are also equal to the numbers of the C_{2v}(b) and the C_{2v}(a) systems. Consequently,

$$ C = M(\mathrm{b}) = M(\mathrm{a}) = \frac{1}{2}[{}^2J_{(m-1)/2} - U_{(m-1)/4}] = \frac{1}{2}[U_{(m+1)/2} - 2U_{(m-1)/2} - U_{(m-1)/4}] \tag{55}$$

with the generating function $\frac{1}{2}[x^{-1}U(x^2) - 2xU(x^2) - xU_0(x^4)]$. From eq 52 and the subsequent equations, one finds

$$ {}^4\mathcal{B}_m = \frac{1}{4}[{}^4J_{m-1} + 3D + 2C + 2M(\mathrm{b}) + 2M(\mathrm{a})] = \frac{1}{4}[U_{m+2} - 6U_{m+1} + 10U_m - 4U_{m-1} + 3U_{(m+1)/2} - 6U_{(m-1)/2}] \quad (m > 1) \tag{56}$$

For these numbers the following generating function was deduced.

$$ {}^4\mathcal{B}(x) = \frac{1}{4}[xU^4(x) + 3x^{-1}(1 - 2x^2)U(x^2) - 3x] = \frac{1}{8}x^{-3}[4(1 - 2x + 2x^2 - 4x^3 + 2x^4) - (1 - 2x)(1 - 4x + 2x^2)(1 - 4x)^{1/2} - 3(1 - 2x^2)(1 - 4x^2)^{1/2}] = x^5 + 2x^6 + 14x^7 + 52x^8 + 238x^9 + \ldots \tag{57}$$

The final result for bond-rooted polyenoids, viz. $\mathcal{B}_m = {}^0\mathcal{B}_m + {}^1\mathcal{B}_m + {}^2\mathcal{B}_m + {}^3\mathcal{B}_m + {}^4\mathcal{B}_m$, reads

$$ \mathcal{B}_m = \frac{1}{4}[U_{m+2} - 2U_{m+1} + 3U_{(m+1)/2}] \quad (m > 2) \tag{58}$$

while $\mathcal{B}_0 = 0$, $\mathcal{B}_1 = \mathcal{B}_2 = 1$. The corresponding generating function in explicit form reads

$$ \mathcal{B}(x) = \sum_{m=1}^{\infty}\mathcal{B}_m x^m = \frac{1}{8}x^{-3}[4(1 - x - x^2) - (1 - 2x)(1 - 4x)^{1/2} - 3(1 - 4x^2)^{1/2}] \tag{59}$$

The numbers to $m = 15$ are given in Table 4, and the smallest forms are depicted in Figure 6. The numbers pertaining to the different symmetry groups are included in Table 4.

Symmetrical Free Polyenoids. The next task is to enumerate the free (unrooted) polyenoids. The numbers of symmetrical systems of this category are obtained relatively easily on the basis of the above results for rooted polyenoids.

The free polyenoids of trigonal symmetries (D_{3h} and C_{3h}) possess one central vertex each. Hence their numbers are identical to those of the atom-rooted polyenoids. For the D_{3h} systems eq 24 is sound and should only be supplemented by $T = 1$ for $m = 0$. Accordingly, the corresponding generating function reads

$$ T(x) = 1 + x^3U_0(x^6) = \frac{1}{2}x^{-3}[1 + 2x^3 - (1 - 4x^6)^{1/2}] = 1 + x^3 + x^9 + 2x^{15} + \ldots \tag{60}$$

A000108 A000150

Table 4. Numbers of Bond-Rooted Polyenoids, Classified According to Symmetry A000912 A000913 A006078

m	D_{2h}	C_{2h}	C_{2v}	C_s	total $\mathscr{B}_m$
1	1	0	0	0	1
2	0	0	0	1	1
3	0	1	2	2	5
4	0	0	0	12	12
5	1	2	4	38	45
6	0	0	0	143	143
7	0	7	14	490	511
8	0	0	0	1768	1768
9	2	20	40	6268	6330
10	0	0	0	22610	22610
11	0	66	132	81620	81818
12	0	0	0	297160	297160
13	5	212	424	1086172	1086813
14	0	0	0	3991995	3991995
15	0	715	1430	14731290	14733435

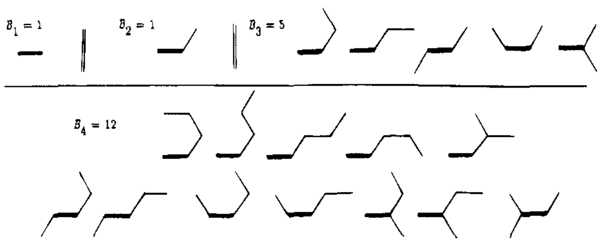


Figure 6. The $\mathscr{B}_m$ bond-rooted polyenoids for $m \leq 4$. Root edges are indicated as heavy lines.

For the C_{3h} systems eq 36 is valid, and

$$R(x) = \frac{1}{2}[U(x^3) - x^3U_0(x^6)] = \frac{1}{4}x^{-3}[(1-4x^6)^{1/2} - (1-4x^3)^{1/2} - 2x^3] = x^6 + 2x^9 + 7x^{12} + 20x^{15} + \ldots \quad (61)$$

The numerical values of the coefficients in eqs 60 and 61 are included in Table 3.

The free dihedral (D_{2h}) and centrosymmetrical (C_{2h}) polyenoids possess one central edge each. Hence their numbers are identical to those of the bond-rooted polyenoids. For the D_{2h} systems eq 53 is valid and should be supplemented by $D = 1$ for $m = 1$. Accordingly, the corresponding generating function is (cf. also Table 4)

$$D(x) = xU_0(x^4) = \frac{1}{2}x^{-3}[1 - (1-4x^4)^{1/2}] = x + x^5 + 2x^9 + 5x^{13} + \ldots \quad (62)$$

For the C_{2h} systems one should add the contributions from ${}^2\mathscr{B}_m$, eq 47, and from ${}^4\mathscr{B}_m$, eq 55. The result, viz.

$$C_m = \frac{1}{2}[U_{(m+1)/2} - U_{(m-1)/4}] \quad (63)$$

could also be obtained more directly from $D_m + 2C_m = U_{(m+1)/2}$, and it leads to

$$C(x) = \frac{1}{2}[x^{-1}U(x^2) - xU_0(x^4)] = \frac{1}{4}x^{-3}[(1-4x^4)^{1/2} - (1-4x^2)^{1/2} - 2x^2] = x^3 + 2x^5 + 7x^7 + 20x^9 + \ldots \quad (64)$$

Additional numerical values for the coefficients are found in Table 4.

The free C_{2v}(b) polyenoids are the same in number as the corresponding C_{2h} systems, viz., C_m. The C_{2v}(a) and D_{3h} systems together are counted by $C_m + U_{m/2}$, where the last term had to be added in order to include the systems with only one central vertex, which occur for $m = 2, 4, 6, \ldots$. In conclusion,

$$M_m + T_m = 2C_m + U_{m/2}$$
$$M_m = U_{(m+1)/2} + U_{m/2} - U_{(m-1)/4} - U_{(m-3)/6} \quad (65)$$

The smallest numbers of the C_{2v} systems are $M_0 = M_1 = 0$, $M_2 = 1$. The M_m systems are distributed into the types C_{2v}(b) and C_{2v}(a) according to C_m and $M_m - C_m$, respectively. The generating function for the numbers M_m was determined as

$$M(x) = x^{-1}(1+x)U(x^2) - xU_0(x^4) - x^3U_0(x^6) = \frac{1}{2}x^{-3}[(1-4x^6)^{1/2} + (1-4x^4)^{1/2} - (1+x)(1-4x^2)^{1/2} - 1 + x - 2x^2 - 2x^3] = x^2 + x^3 + 2x^4 + 4x^5 + 5x^6 + \ldots \quad (66)$$

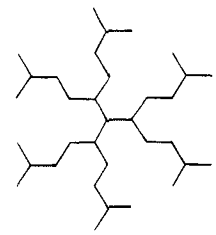


Figure 7. A $C_{34}H_{36}$ polyenoid of D_{3h} symmetry with $n = 34$, $m = 33$; $n^* = 7$, $m^* = 6$.

Total Number of Free Polyenoids. The ultimate goal is to find the $\mathscr{T}_m$ free polyenoids in total. The method of Harary with collaborators,[3,17,18] based on Otter,[19] for passing from rooted to unrooted trees, as was explained and applied by Harary and Read,[3] is also applicable to the present problem.

Firstly, it is ascertained that for a tree

$$n - m = 1 \quad (67)$$

Now we shall compute the number of equivalence classes for vertices and edges, say n^* and m^*, respectively, under the different symmetry types.

For a polyenoid of D_{3h} symmetry (see Figure 7) one finds

$$n^* = \frac{1}{6}(n-4) + 2 = \frac{1}{6}(n+8), \quad m^* = \frac{1}{6}(m-3) + 1 = \frac{1}{6}(m+3), \quad n^* - m^* = \frac{1}{6}(n-m) + \frac{5}{6} = 1 \quad (68)$$

In a similar way, for C_{3h}

$$n^* = \frac{1}{3}(n-1) + 1 = \frac{1}{3}(n+2), \quad m^* = \frac{1}{3}m, \quad n^* - m^* = \frac{1}{3}(n-m) + \frac{2}{3} = 1 \quad (69)$$

The D_{2h} symmetry is especially important in the present context; the count of equivalence classes yields in this case (see Figure 8)

$$n^* = \frac{1}{4}(n-2) + 1 = \frac{1}{4}(n+2), \quad m^* = \frac{1}{4}(m-1) + 1 = \frac{1}{4}(m+3), \quad n^* - m^* = \frac{1}{4}(n-m) - \frac{1}{4} = 0 \quad (70)$$

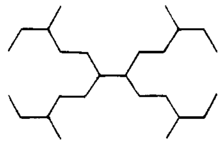


Figure 8. A $C_{26}H_{28}$ polyenoid of D_{2h} symmetry with $n = 26$, $m = 25$; $n^* = 7$, $m^* = 7$.

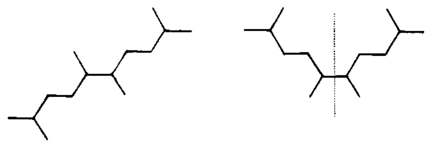


Figure 9. Two isomers (*trans* and *cis*) of $C_{14}H_{16}$ polyenoids, C_{2h} left and C_{2v}(b) right; each of them has $n = 14$, $m = 13$; $n^* = 7$, $m^* = 7$.

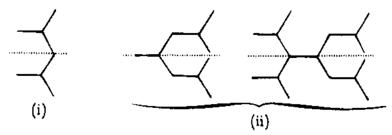


Figure 10. Examples of C_{2v}(a) polyenoids of two types: (i) only one central vertex and (ii) one central edge.

In a similar way, one obtains for C_{2h} and C_{2v}(b); cf. Figure 9

$$n^* = \frac{1}{2}n, \quad m^* = \frac{1}{2}(m-1) + 1 = \frac{1}{2}(m+1), \quad n^* - m^* = \frac{1}{2}(n-m) - \frac{1}{2} = 0 \quad (71)$$

For C_{2v}(a) two types are distinguished as illustrated in Figure 10. In the case of i

$$n^* = \frac{1}{2}(n-1) + 1 = \frac{1}{2}(n+1), \quad m^* = \frac{1}{2}m, \quad n^* - m^* = \frac{1}{2}(n-m) + \frac{1}{2} = 1 \quad (72)$$

and in the case ii

$$n^* = \frac{1}{2}(n-2) + 2 = \frac{1}{2}(n+2), \quad m^* = \frac{1}{2}(m-1) + 1 = \frac{1}{2}(m+1), \quad n^* - m^* = \frac{1}{2}(n-m) + \frac{1}{2} = 1 \quad (73)$$

Finally, for a C_s polyenoid one has simply

$$n^* = n, \quad m^* = m, \quad n^* - m^* = n - m = 1 \quad (74)$$

In conclusion, one finds $n^* - m^* = 1$ in all cases but D_{2h}, C_{2h}, and C_{2v}(b), while $n^* - m^* = 0$ for D_{2h}, C_{2h}, and C_{2v}(b).

Consider a free polyenoid P. It is clear that P is counted n^* times among the $\mathcal{A}_m$ atom-rooted polyenoids and m^* times among the $\mathcal{B}_m$ bond-rooted polyenoids. Hence the difference $\mathcal{A}_m - \mathcal{B}_m$ catches up every free polyenoid once, except those of the symmetry types D_{2h}, C_{2h}, and C_{2v}(b), which are missed. Notice that the number of C_{2h} and C_{2v}(b) systems is the same. Therefore one obtains ultimately

$$\mathcal{I}_m = \mathcal{A}_m - \mathcal{B}_m + D_m + 2C_m = \frac{1}{12}[4U_{m/3} + 6U_{m/2} + 9U_{(m+1)/2} + 4U_{m+1} - U_{m+2}] \quad (m > 0) \quad (75)$$

while $\mathcal{I}_0 = 1$. Equation 75 was obtained from eqs 40, 53, 58, and 63. The corresponding generating function was obtained from eqs 41, 59, 62, and 64 with the result

$$\mathcal{I}(x) = \sum_{m=0}^{\infty} \mathcal{I}_m x^m = \frac{1}{24}x^{-3}[12(1 + x - 2x^2) + (1-4x)^{3/2} - 3(3+2x)(1-4x^2)^{1/2} - 4(1-4x^3)^{1/2}] \quad (76)$$

Numerical values are given in Table 5. In this table, we have passed from m to n as the leading parameter; $I_{m+1} = \mathcal{I}_m$, $I(x) = x\mathcal{I}(x)$. The distribution into symmetry groups is included in Table 5.

Table 5. Numbers of Free Polyenoids, Classified According to Symmetry

n	D_{3h}	C_{3h}	D_{2h}	C_{2h}	C_{2v}	C_s	total I_n
1	1	0	0	0	0	0	1
2	0	0	1	0	0	0	1
3	0	0	0	0	1	0	1
4	1	0	0	1	1	0	3
5	0	0	0	0	2	2	4
6	0	0	1	2	4	5	12
7	0	1	0	0	5	21	27
8	0	0	0	7	14	61	82
9	0	0	0	0	14	214	228
10	1	2	2	20	39	669	733
11	0	0	0	0	42	2240	2282
12	0	0	0	66	132	7330	7528
13	0	7	0	0	132	24695	24834
14	0	0	5	212	424	83257	83898
15	0	0	0	0	429	284928	285357
16	2	20	0	715	1428	981079	983244

Table 6. Numbers of Free Geometrically Planar Polyenoids, Classified According to Symmetry

n	D_{3h}	C_{3h}	D_{2h}	C_{2h}	C_{2v}	C_s	total I_n'
1	1	0	0	0	0	0	1[a]
2	0	0	1	0	0	0	1[a]
3	0	0	0	0	1	0	1[a]
4	1	0	0	1	1	0	3[a]
5	0	0	0	0	2	2	4[a]
6	0	0	1	2	4	5	12[a]
7	0	1	0	0	4	21	26[a]
8	0	0	0	7	12	58	77[a]
9	0	0	0	0	10	194	204[a]
10	1	2	2	20	29	570	624[a]
11	0	0	0	0	27	1790	1817
12	0	0	0	63	88	5434	5585
13	0	7	0	0	76	16924	17007
14	0	0	3	191	247	52362	52803
15	0	0	0	0	217	163784	164001

[a] Kirby (1992).[2]

COMPUTER PROGRAMMING

The systems enumerated by Kirby[2] are the geometrically planar polyenoids to $n = 10$. All the polyenoids through $n = 6$ are geometrically planar, and our I_n ($n \le 6$) numbers (Table 5) indeed reproduce the results of Kirby.[2] For the numbers of geometrically planar polyenoids in general, however, no mathematical solution is available and is not likely to be found. Therefore we resorted to computer programming, like Kirby,[2] in order to produce these numbers, but using quite different methods, which allowed an extension of the data to $h = 15$; see Table 6.

There is a one-to-one correspondence between the geometrically planar polyenoids and the catacondensed benzenoids with equidistant linear segments of a length $l > 2$. An illustration is furnished by Figure 11. This correspondence was exploited in the present computer program-

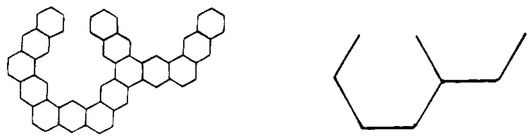


Figure 11. A catacondensed benzenoid with equidistant linear segment of the length $l = 3$ (left) and the corresponding polyenoid system (right).

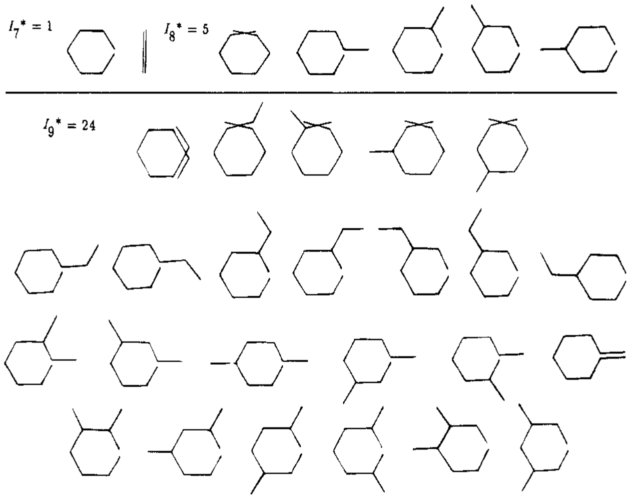


Figure 12. The I_n^* geometrically nonplanar polyenoids for $n \leq 9$.

ming, using $l = 3$ as the segment length. In fact, the unbranched systems of the category in question, referred to as nonhelicenic generalized fibonacenes, have been enumerated before.[6,20] In the present work a new program was designed, in which the branched systems are taken into account. The DAST (dualist angle-restricted spanning tree) code[12,13,21] was employed.

COMBINATORIAL CONSTRUCTIONS

The systems of free polyenoids depicted in Figure 2 were generated by hand (on the pen-and-paper level). These drawings are consistent with the numbers in Table 5, as they, of course, should be. This agreement includes nicely the symmetry distributions. The corresponding systems for the next two or three n values would still be manageable in the same way. However, it is more interesting to consider the pen-and-paper generation of geometrically nonplanar polyenoids.

The smallest geometrically nonplanar polyenoids were generated by the method of combinatorial constructions.[5,22] Figure 12 shows the resulting 1, 5, and 24 systems for $n = 7-9$, respectively, in perfect consistency with the pertinent numbers of Table 7. The 109 geometrically nonplanar polyenoids with $n = 10$ were also constructed: one coiled system and attachments to smaller coiled systems according to the following scheme; see also Figure 13.

Case 1. Coiled $C_{10}H_{12}$.

Case 2. Attachments to coiled C_9H_{11}.

Case 3. Attachments to coiled C_8H_{10}.

The rest of the constructions (Case 4) are attachments to the smallest geometrically nonplanar polyenoid: C_7H_9.

Subcase 4a. The $I_3 = 5$ polyenoids are attached to different sites, taking the mirror symmetry into account.

Subcase 4b. The $I_2 = 2$ polyenoids are attached, one at a time, to C_8H_{10}, viz. a substituted C_7H_9.

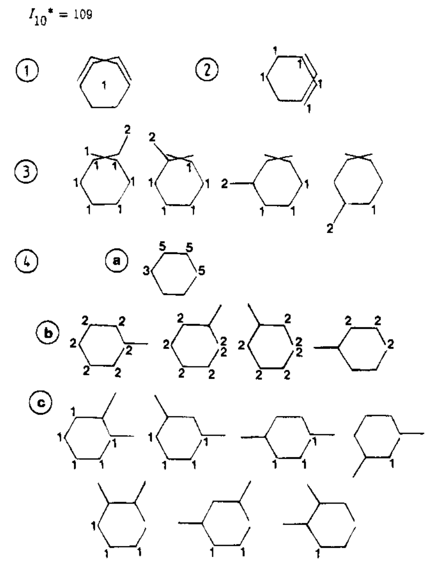


Figure 13. Summary of the combinatorial constructions of the geometrically nonplanar polyenoids for $n = 10$. The number $I_{10}^* = 109$ is obtained on adding the numbers on the drawings. Encircled numerals and characters indicate the cases and subcases as described in the text.

Table 7. Numbers of Free Geometrically Nonplanar (Helicenic) Polyenoids Classified According to Symmetry A000948 A000953 A000947

n	D_{3h}	C_{3h}	D_{2h}	C_{2h}	C_{2v}	C_s	total I_n^*
7	0	0	0	0	1	0	1
8	0	0	0	0	2	3	5
9	0	0	0	0	4	20	24
10	0	0	0	0	10	99	109
11	0	0	0	0	15	450	465
12	0	0	0	3	44	1896	1943
13	0	0	0	0	56	7771	7827
14	0	0	2	21	177	30895	31095
15	0	0	0	0	212	121144	121356

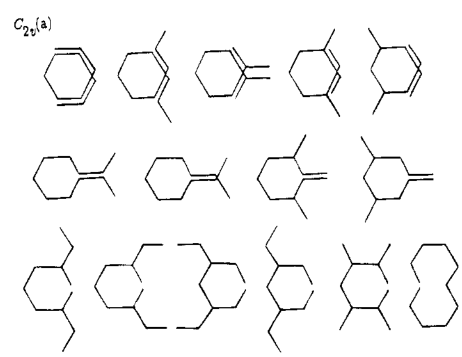


Figure 14. The 15 geometrically nonplanar polyenoids with $n = 11$.

Subcase 4c. The $I_1 = 1$ polyenoid is attached to C_9H_{11}, viz. doubly substituted C_7H_9.

The constructions described above resulted in 1, 2, 4, and 10 geometrically nonplanar polyenoid systems of C_{2v} symmetry with $n = 7$, 8, 9, and 10, respectively, in consistency with the predictions of Table 7. Also the 15 C_{2v} systems depicted in Figure 14 are compatible with Table 7. The smallest ($n = 12$) geometrically nonplanar polyenoids of C_{2h} symmetry are shown in Figure 15. Furthermore, the construction of the 21 such systems with $n = 14$ is indicated by numerals therein, similarly as in Figure 13. Finally, the two D_{2h} geometrically nonplanar polyenoids are included in Figure 15. Geometrically nonplanar polyenoids of the

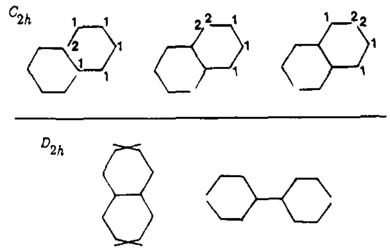


Figure 15. The smallest geometrically nonplanar polyenoids of symmetries C_{2h} and D_{2h}.

symmetries D_{3h} and C_{3h} occur at $n = 16$, just beyond the range of Table 7.

CONCLUSION

The main result of the present work is the mathematical solution for the numbers of free polyenoids, as given in eqs 75 and 76; see also eq 11 for an explicit formula for U_m. Geometrically planar (free) polyenoids were enumerated by computer aid, whereby the numbers of geometrically nonplanar (free) polyenoids became accessible. The smallest such systems were also constructed by hand. Thus the present work demonstrates an example of combined enumerations by mathematical methods, computer programming, and pen-and-paper constructions.

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