Enumeration and Classification of Benzenoid Systems. 32. Normal Perifusenes with Two Internal Vertices

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A normal perifusene with two internal vertices ($n_i = 2$) is said to belong to the class PF2. These systems consist of pyrene and pyrene with annealated catafusenes. A complete mathematical solution for the numbers of the PF2 systems, as a function of the number of hexagons (h), is derived using the so-called method of combinatorial summation. A normal peribenzenoid with $n_i = 2$, belonging to the class PF2′, may be pyrene or pyrene with annealated catabenzenoids. Computerized enumerations of these systems are recalled, and some recent extensions of the data to higher h values are reported. Finally a class PF2* is defined as consisting of normal perihelicenes with $n_i = 2$. The numbers of the PF2* systems for given h values are reported; they were obtained by appropriate subtractions (PF2* = PF2 − PF2′). Some of the lowest of these numbers are reproduced by an analytical method (without computers), referred to as combinatorial enumeration.

INTRODUCTION

A polyhex is a system of regular hexagons. Precise definitions of this and other relevant concepts are given in the next section. Here we wish to recall that polyhexes have obvious counterparts in polycyclic hydrocarbons with exclusively six-membered (benzenoid) rings. Balaban and Artemi[1] have recently stated about these systems: "The enumeration of polycyclic benzenoid hydrocarbons (polyhexes, or benzenoids) continues to be a challenging problem". The present work supports this statement.

Complete mathematical solutions for the numbers of polyhexes within different classes are rare and represent a special challenge. In this realm the most famous achievement is the generating function of Harary and Read[2] for the numbers of catafusenes, viz. the "Harary–Read numbers". The Harary–Read numbers were recently revisited and derived by means of a new method,[3] which presently shall be referred to as the combinatorial summation method. It does not invoke generating functions or an explicit reference to Pólya's theorem.[4] The mentioned work[3] includes a classification of the Harary–Read numbers according to symmetry. Also the generating functions for the symmetry-classified Harary–Read numbers have been produced.[5]

Very recently a complete mathematical solution was found for the numbers of perifusenes with one internal vertex, which correspond to phenalene and annealated phenalenes.[6] The problem was solved both by the combinatorial summation method and in terms of generating functions.

The present work deals mainly with the enumeration of normal perifusenes with two internal vertices, corresponding to pyrene and annealated pyrenes.

Phenalene and annealated phenalenes are non-Kekuléan systems, i.e. they do not possess Kekulé structures.[7] As such they do not exist chemically, at least not as stable compounds. It is a fact, namely, that not a single polyhex hydrocarbon without Kekulé structures has been synthesized so far.[8,9]

Pyrene and annealated pyrenes, on the other hand, are Kekuléan and normal (in contrast to essentially disconnected);[7,9] they possess Kekulé structures without fixed (double and/or single) bonds. These compounds are of great interest in organic chemistry. Pyrene itself, one of the many $C_{16}H_{10}$ isomers, but the unique $C_{16}H_{10}$ benzenoid isomer, is a key compound[10] being the smallest pericondensed benzenoid hydrocarbon which exists chemically. With regard to annealated pyrenes Dias[11] has catalogized 86 such systems as chemical compounds, with a documentation of their chemical interest included. Here we only mention the formulas for Kekulé structure counts of certain classes of annealated pyrenes[7,12] and cite some experimental works of special relevance to these Kekulé structure counts.[13–17]

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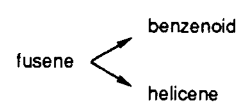
DEFINITIONS

A polyhex is a connected system of congruent regular hexagons, where any two hexagons either share exactly one edge or they are disconnected. A fusene[18] is a simply connected polyhex. This definition implies that coronoids[19] (with holes) are excluded. On the other hand, both the geometrically planar (nonhelicenic) and geometrically nonplanar (helicenic) systems are taken into account. These classes are often referred to as benzenoids[7,9] and helicenes, respectively. For the sake of clarity we show a schematic representation:



Here the term "geometrically planar" is used in accordance with the well-established practice in the theory of polyhex systems.[20] The word "geometrically" is used in order to distinguish the term from planar in the graph-theoretical sense. It is emphasized that the present definition applies to the geometrical constructions (polyhex systems) and does not always reflect the planarity of the real hydrocarbon molecules, which correspond to these constructions. Since the definition of benzenoids is also somewhat controversial[20,21] it is emphasized that a benzenoid (as well as a helicene, or in general a fusene), according to the definition adopted here, is either Kekuléan or non-Kekuléan, i.e. it may or may not possess Kekulé structures.

Another subdivision of the fusenes distinguishes between the catacondensed and pericondensed systems; one speaks about catafusenes and perifusenes,[18] respectively. A catacondensed polyhex has $n_i = 0$, while in a pericondensed poly-

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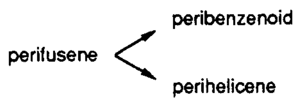
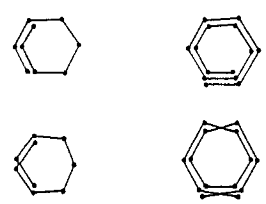
hex $n_i > 0$, where n_i is used to denote the number of internal vertices. In the present work only perifusenes are treated; they are classified into the pericondensed benzenoids and pericondensed helicenes called peribenzenoids and perihelicenes, respectively:



The number of hexagons in a polyhex system is designated by the symbol h.

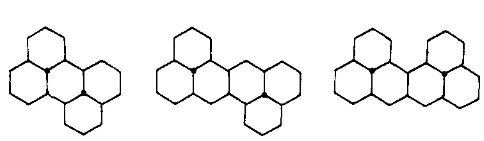
When helicenic polyhexes are classified into symmetry groups the nonplanarity is, according to usual practice, not taken into account. Therefore these symmetries are not compatible with the established or expected symmetries of the corresponding real hydrocarbons. For instance, all the normal [h]helicenes, which are known to be coiled molecules, correspond to polyhex systems of the symmetry C_{2v}. In the diagram below the dualists of [9]helicene and [14]helicene are depicted for illustration. The top row shows the usual representations, while the bottom row is a modification which complies with the symmetry group C_{2v}.



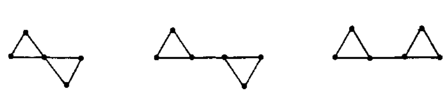
A perifusene with one internal vertex ($n_i = 1$) is either phenalene ($h = 3$) or phenalene with one or more (up to three) simply connected catacondensed appendage(s). In other words, for $h > 3$ these systems have catafusenes annealated to phenalene. By definition, a catafusene annealated to a polyhex P shares exactly one edge with P; the whole system is also called an annealated P. The class of phenalene and annealated phenalenes has been designated PF1.[22]

The main subject of the present work is the enumeration of normal perifusenes with $n_i = 2$. This class shall presently be designated PF2. A normal polyhex is by definition a Kekuléan polyhex which is not essentially disconnected.[7,9,23] An essentially disconnected polyhex has double and/or single fixed bonds in all its Kekulé structures. In the below diagram I (perylene) and II (zethrene) are essentially disconnected. The system III (dibenzo[*de*,*hi*]naphthacene) is non-Kekuléan. All the systems I–III have $n_i = 2$. They are represented by hexagons and as dualists,[1,7,9,18,24] in which a vertex corresponds to a hexagon of the polyhex. The dualist representation is employed throughout the subsequent depictions of this paper.

It appears that a polyhex of the class PF2 is pyrene or annealated pyrene.



I II III



The numbers of catafusenes rooted by an edge[2] are essential in the present theory. The appendages to phenalene or pyrene are just attached by the root edges.

Table I. Numbers of Edge-Rooted Catafusenes (N_a) and Some Auxiliary Numbers

a	N_a eq 1	M_a eq 13	L_a eq 22	M_a' eq 26	L_a' eq 32
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	50	72
10	171369	51	237	50	204
11	751236	188	374	355	336
12	3328218	188	917	355	926

ROOTED CATAFUSENES

Let the number of edge-rooted catafusenes with a hexagons be designated N_a. Then[2]

$$N_1 = 1, N_2 = 3N_1 = 3, N_{a+1} = 3N_a + \sum_{i=1}^{a-1} N_i N_{a-i} \qquad (a = 2, 3, 4, ...) \quad (1)$$

For $a = 0$, as a degenerate case, we adhere to the definition[3]

$$N_0 = 1 \quad (2)$$

Numerical values of N_a, as obtained recursively from eq 1, are found in Table I.

ANNEALATED PHENALENES

The combinatorial summation method, when applied to the title systems, resulted in a somewhat complicated expression for the number of these systems.[6] It appeared to be impracticable to follow the same procedure for annealated pyrenes. However, a new version of the method led to a considerably simplified result for the annealated phenalenes. In fact, all the signs of summation from the final result[6] were eliminated. Furthermore, the new version appeared to be convenient for an extension to the case of annealated pyrenes, which is treated in detail below. In this section we shall only give the final result for the numbers of annealated phenalenes, as obtained by a corresponding treatment.

Let P_h be the number of nonisomorphic annealated phenalenes, viz. perifusenes with $n_i = 1$, $h > 3$. Then

$$P_{3+a} = \frac{1}{3}(N_{a+2} - 18N_{a+1} + 17N_a + 3\epsilon N_{a/2} + 2\delta N_{a/3}) \qquad (a > 0) \quad (3)$$

Here $\epsilon = 1$ when a is even, and $\epsilon = 0$ when a is odd; $\delta = 1$ when a is divisible by three, while $\delta = 0$ otherwise. The solution (3) can of course be supplemented by the trivial number

$$P_3 = 1 \quad (4)$$

which pertains to phenalene itself. In this way eqs 3 and 4 together cover the class PF1.

ANNEALATED PYRENES

Types of Annelation. Figure 1 shows the different types of annealation to pyrene for (i) one, (ii) two, (iii) three, and (iv) four appendages.

Notation. Let Q_h be the number of nonisomorphic polyhexes of the class PF2. As defined above, they consist of pyrene and pyrenes with appended catafusenes, which follow

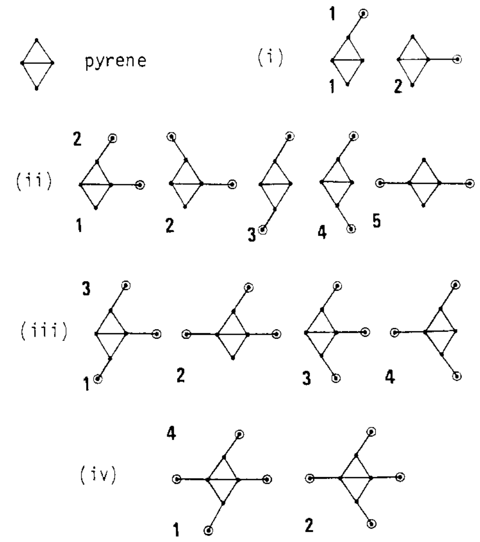


Figure 1. Types of annealation to pyrene.

the scheme of Figure 1. When

$$h = 4 + a \tag{5}$$

then a is obviously the number of hexagons in the appendage(s). Let the numbers of systems within each type of annealation by denoted by ${}^1_1Q$, ${}^1_2Q$, ${}^2_1Q$, ..., ${}^4_2Q$. Furthermore,

$${}^1Q = {}^1_1Q + {}^1_2Q \quad {}^2Q = \sum_{i=1}^{5} {}^2_iQ \quad {}^3Q = \sum_{i=1}^{4} {}^4_iQ$$

$${}^4Q = {}^4_1Q + {}^4_2Q \tag{6}$$

As we shall see below, it is natural to let pyrene itself (a = 0) be included in the symbol ${}^1_1Q$. All the above symbols can also be supplied with subscripts which indicate the number of hexagons in the complete polyhex as ${}^1_1Q_h$, ${}^1_2Q_h$, ..., ${}^1Q_h$, ... When these subscripts are missing, as in eq 6, it is tacitly assumed that all the symbols in the equation pertain to the same h value. Finally, for the total number Q_h one has

$$Q_h = {}^1Q_h + {}^2Q_h + {}^3Q_h + {}^4Q_h \tag{7}$$

One Appendage. Under the first type of annealation of one catafusene to pyrene, with reference to Figure 1 (i), all the systems are unsymmetrical, i.e. they have strictly speaking the symmetry C_s. The number of the systems is simply given by

$${}^1_1Q_{4+a} = N_a \tag{8}$$

where a = 0 takes care of pyrene itself.

In order to derive ${}^1_2Q_h$, symmetry must be taken into account. A system with the annealation scheme under consideration may be mirror-symmetrical of the kind C_{2v}(a), or it may be unsymmetrical (C_s). Here C_{2v}(a) refers to C_{2v} symmetry where the 2-fold symmetry axis, say C_2, bisects edges of the polyhex in question; the C_2 axis is horizontal when the polyhex is oriented as in Figure 1.[9] Let the separate numbers of the mirror-symmetrical and unsymmetrical systems by denoted by ${}^1_2Q^{M(a)}$ and ${}^1_2Q^A$, respectively, so that

$${}^1_2Q = {}^1_2Q^{M(a)} + {}^1_2Q^A \tag{9}$$

Also the two symbols on the right-hand side of eq 9 can be supplied with subscripts indicating the numbers of hexagons.

A mirror-symmetrical system of this category is composed of a linear chain of hexagons of a certain length, to which two identical catafusenes are annealated symmetrically to the end hexagon, i.e. the hexagon mostly remote from the pyrene unit.

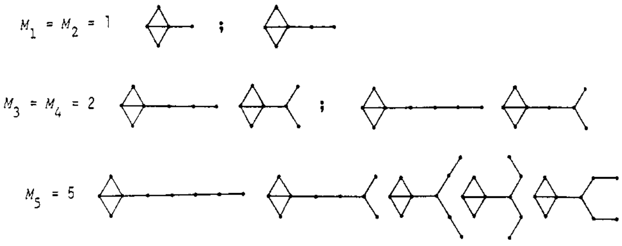


Figure 2. The eleven smallest PF2 polyhexes with one catafusene annealated to pyrene and belonging to the symmetry C_{2v}(a).

The number of the mirror-symmetrical systems, viz. ${}^1_2Q^{M(a)}$, becomes a sum of numbers of edge-rooted catafusenes, where the different terms are associated with the different lengths of the linear chain of hexagons, which are possible. Specifically,

$${}^1_2Q^{M(a)}_{4+a} = \sum_{i=0}^{\lfloor (a-1)/2 \rfloor} N_i \quad (a \geq 1) \tag{10}$$

Here the "floor function" is employed: $\lfloor x \rfloor$ is the largest integer not larger than x.

The number N_a as in eq 8 gives now what could be called a "crude total", where the unsymmetrical systems are counted twice, but the mirror-symmetrical only once. Hence

$$N_a = {}^1_2Q^{M(a)}_{4+a} + 2({}^1_2Q^A_{4+a}) \tag{11}$$

From eqs 9–11 it is obtained

$${}^1_2Q_{4+a} = \frac{1}{2}\left(N_a + \sum_{i=0}^{\lfloor (a-1)/2 \rfloor} N_i\right) \quad (a \geq 1) \tag{12}$$

Auxiliary Numbers (I). We shall find the numbers of eq 10 very useful also in the following. It is expedient to introduce the simple symbol M_a as

$$M_a = \sum_{i=0}^{\lfloor (a-1)/2 \rfloor} N_i \quad (a \geq 1) \tag{13}$$

These numbers are most easily found according to the initial condition and recurrence relation

$$M_1 = 1 \qquad M_{a+1} = M_a + \epsilon N_{a/2} \tag{14}$$

where ϵ is defined after eq 3.[25]

Numerical values of M_a are included in Table I. It should be clear that M_a indicates the number of C_{2v}(a) polyhexes of the class PF2 with one appendage. In Figure 2 some of the smallest of these systems are depicted.

Two Appendages. Under the two first types of annealation of two catafusenes to pyrene, cf. Figure 1 (ii), all the systems are unsymmetrical (C_s), and their numbers are given by

$${}^2_1Q_{4+a} = {}^2_2Q_{4+a} = \sum_{i=1}^{a-1} N_i N_{a-i} \quad (a \geq 2) \tag{15}$$

The next two numbers, viz. ${}^2_3Q$ and ${}^2_4Q$, may contain centrosymmetrical (C_{2h}) or mirror-symmetrical systems of the kind C_{2v}(a), respectively. Let their numbers be ${}^2_3Q^C$ and ${}^2_4Q^{M(a)}$. Here, in the superscripts, C refers to the centrosymmetrical and M to the mirror-symmetrical systems. These numbers are simply given by

$${}^2_3Q^C_{4+a} = {}^2_4Q^{M(a)}_{4+a} = \epsilon N_{a/2} \tag{16}$$

Now the summation of eq 15 gives the crude total, which counts the unsymmetrical (C_s) systems twice, but the centrosymmetrical or mirror-symmetrical systems once. By an

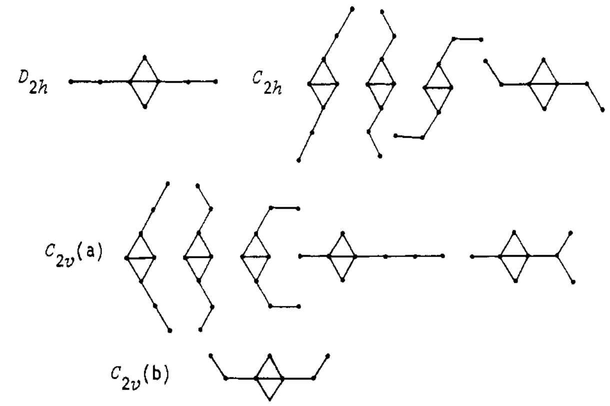


Figure 3. The $h = 8$ PF2 polyhexes with two catafusenes annealated to pyrene and belonging to the indicated symmetries.

analysis in analogy with the derivation of ${}^1_2Q$ (under One Appendage above) it is found

$$ {}^2_3Q_{4+a} = {}^2_4Q_{4+a} = \frac{1}{2}(\epsilon N_{a/2} + \sum_{i=1}^{a-1} N_iN_{a-i}) \quad (a \geq 2) \quad (17) $$

Under the last type of two catafusenes annealated to pyrene, cf. Figure 1 (ii), it must be accounted for dihedral symmetry (D_{2h}), centrosymmetry (C_{2h}), and for the mirror-symmetries of the types C_{2v}(a) and C_{2v}(b). In the systems belonging to C_{2v}(b) the 2-fold symmetry axis (C_2) goes through vertices of the polyhex.[9] When the systems are drawn as in Figure 1, the C_2 axis is vertical. Let the numbers of the polyhexes under consideration which belong to the different symmetries be ${}^2_5Q^D$, ${}^2_5Q^C$, ${}^2_5Q^{M(a)}$, and ${}^2_5Q^{M(b)}$, pertaining to D_{2h}, C_{2h}, C_{2v}(a), and C_{2v}(b), respectively. The following expressions were found for these numbers by simple combinatorial reasonings:

$$ {}^2_5Q^D_{4+a} = \epsilon M_{a/2} \quad (18) $$

$$ {}^2_5Q^C_{4+a} = {}^2_5Q^{M(b)} = \frac{1}{2}\epsilon(N_{a/2} - M_{a/2}) \quad (19) $$

$$ {}^2_5Q^{M(a)}_{4+a} = \sum_{i=1}^{\lfloor (a-1)/2 \rfloor} M_iM_{a-i} + \frac{1}{2}\epsilon M_{a/2}(M_{a/2} - 1) $$

$$ = \frac{1}{2}(\sum_{i=1}^{a-1} M_iM_{a-i} - \epsilon M_{a/2}) \quad (a \geq 2) \quad (20) $$

Figure 3 illustrates the above equations by depictions of the $h = 8$ ($a = 4$) systems which are counted by the numbers in question. The summation of eq (15) gives again a crude total, which now counts the unsymmetrical (C_s) systems four times, the C_{2h}, C_{2v}(a), and C_{2v}(b) systems twice each, and the dihedral (D_{2h}) systems once. An analysis in analogy with some of the above derivations gave the following result:

$$ {}^2_5Q_{4+a} = \frac{1}{2}\epsilon N_{a/2} + \frac{1}{4}\sum_{i=1}^{a-1}(N_iN_{a-i} + M_iM_{a-i}) \quad (a \geq 2) \quad (21) $$

Auxiliary Numbers (II). The above treatment of the systems with two appendages gives rise to another definition of auxiliary numbers, which also will be useful in the subsequent treatments, especially for four appendages. Let L_a be defined as the last summation in eq 20, viz.

$$ L_a = \sum_{i=1}^{a-1} M_iM_{a-i} \quad (a \geq 2) \quad (22) $$

Numerical values of L_a are included in Table I.

Three Appendages. The procedure is analogous with the treatments for one appendage and two appendages described above. Firstly, one has for the two first types of annealation indicated in Figure 1 (iii):

$$ {}^3_1Q_{4+a} = {}^3_2Q_{4+a} = \sum_{i=1}^{a-2} N_i \sum_{j=1}^{a-i-1} N_jN_{a-i-j} \quad (a \geq 3) \quad (23) $$

Under the two last types of annealation, which are associated with the numbers ${}^3_3Q$ and ${}^3_4Q$, mirror-symmetrical systems of C_{2v}(a) occur. Their numbers were found to be

$$ {}^3_3Q^{M(a)}_{4+a} = {}^3_4Q^{M(a)}_{4+a} = \sum_{i=1}^{\lfloor (a-1)/2 \rfloor} N_iM_{a-2i} \quad (a \geq 3) \quad (24) $$

In this case the crude total, given by eq 23, counts the C_s systems twice and the C_{2v}(a) systems once. Following the same procedure as in the analogous cases above, it was arrived at

$$ {}^3_3Q_{4+a} = {}^3_4Q_{4+a} = \frac{1}{2}(\sum_{i=1}^{\lfloor (a-1)/2 \rfloor} N_iM_{a-2i} + \sum_{i=1}^{a-2} N_i \sum_{j=1}^{a-i-1} N_jN_{a-i-j}) \quad (a \geq 3) \quad (25) $$

Auxiliary Numbers (III). A new set of auxiliary numbers are defined here, just by a renaming of the summation in eq 24:

$$ M_a' = \sum_{i=1}^{\lfloor (a-1)/2 \rfloor} N_iM_{a-2i} \quad (a \geq 3) \quad (26) $$

Table I includes numerical values of M_a'. It is clear that these numbers indicate the numbers of C_{2v}(a) systems for pyrenes with three annealated catafusenes under each of the two pertinent types of annealation. These systems for $h = 9$ ($a = 5$) are depicted in Figure 4.

Four Appendages. Under the two last types of annealations, cf. Figure 1 (iv), ${}^4_1Q$ and ${}^4_2Q$ may contain centrosymmetrical (C_{2h}) or mirror-symmetrical systems of the kind C_{2v}(a), respectively. The crude total, which is the summation on the left-hand side of the below equation, counts the unsymmetrical (C_s) systems twice, and the C_{2h} or C_{2v}(a) systems once

$$ \sum_{i=1}^{a-3} N_i \sum_{j=1}^{a-i-2} N_j \sum_{k=1}^{a-i-j-1} N_kN_{a-i-j-k} = {}^4_1Q^C_{4+a} + 2({}^4_1Q^A_{4+a}) = $$

$$ {}^4_2Q^{M(a)}_{4+a} + 2({}^4_2Q^A_{4+a}) \quad (a \geq 4) \quad (27) $$

The following expressions were found for the numbers of the symmetrical systems:

$$ {}^4_1Q^C_{4+a} = \epsilon \sum_{i=1}^{(a/2)-1} N_iN_{(a/2)-i} \quad (a \geq 4) \quad (28) $$

$$ {}^4_2Q^{M(a)}_{4+a} = \sum_{i=1}^{\lfloor (a-2)/2 \rfloor} N_i \sum_{j=1}^{a-2i-1} M_jM_{a-2i-j} $$

$$ = \sum_{i=1}^{\lfloor (a-2)/2 \rfloor} N_iL_{a-2i} \quad (a \geq 4) \quad (29) $$

From these equations, by the same procedure as above, the following were obtained:

$$ {}^4_1Q_{4+a} = \frac{1}{2}(\sum_{i=1}^{a-3} N_i \sum_{j=1}^{a-i-2} N_j \sum_{k=1}^{a-i-j-1} N_kN_{a-i-j-k} + \epsilon \sum_{i=1}^{(a/2)-1} N_iN_{(a/2)-i}) \quad (a \geq 4) \quad (30) $$

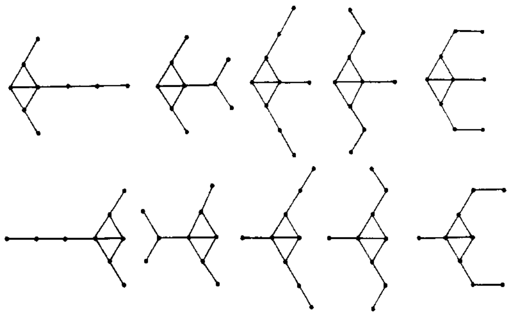


Figure 4. The $h = 9$ PF2 polyhexes with three catafusenes annealated to pyrene and belonging to the symmetry C_{2v}(a).

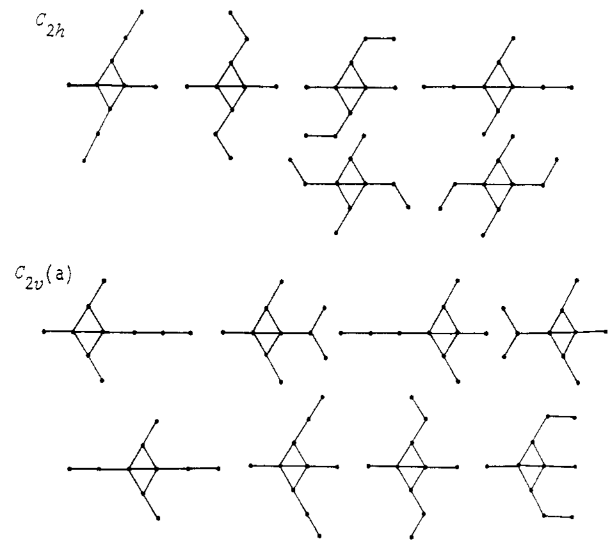


Figure 5. The $h = 10$ PF2 polyhexes with four catafusenes annealated to pyrene and belonging to the indicated symmetries.

and

$$ {}^4_2Q_{4+a} = \frac{1}{2}\left(\sum_{i=1}^{a-3} N_i \sum_{j=1}^{a-i-2} N_j \sum_{k-1}^{a-i-j-1} N_k N_{a-i-j-k} + \sum_{i=1}^{\lfloor (a-2)/2 \rfloor} N_i L_{a-2i}\right) \quad (a \geq 4) \quad (31) $$

Auxiliary Numbers (IV). The last set of auxiliary numbers is defined by the summation of eq 29, viz.

$$ L_a' = \sum_{i=1}^{\lfloor (a-2)/2 \rfloor} N_i L_{a-2i} \quad (a \geq 4) \quad (32) $$

Numerical values of L_a' are included in Table I. It is clear that they represent the numbers of C_{2v}(a) systems for pyrenes with four annealated catafusenes. These systems for $h = 10$ ($a = 6$) are depicted in Figure 5, together with the corresponding C_{2h} systems.

Assembling of Formulas. On adding eqs 8 and 12 one obtains, in accord with eq 6, the total number of nonisomorphic PF2 polyhexes with one appendage, viz.

$$ {}^1Q_{4+a} = \frac{1}{2}(3N_a + M_a) \quad (a \geq 1) \quad (33) $$

where also the notation of eq 13 is employed. Correspondingly, for two appendages one obtains the following from eqs 15, 17, and 21, together with the notation of eq 22:

$$ {}^2Q_{4+a} = \frac{3}{2}\epsilon N_{a/2} + \frac{1}{4}\left(L_a + 13\sum_{i=1}^{a-1} N_i N_{a-i}\right) \quad (a \geq 2) \quad (34) $$

For three appendages, the equations to be used are eqs 23, 25, and 26, from which the following result was obtained:

$$ {}^3Q_{4+a} = M_a' + 3\sum_{i=1}^{a-2} N_i \sum_{j=1}^{a-i-1} N_j N_{a-i-j} \quad (a \geq 3) \quad (35) $$

Finally for four appendages, on adding eqs 30 and 31 and making use of the notation of eq 32, the following result emerges:

$$ {}^4Q_{4+a} = \frac{1}{2}\left(L_a' + \epsilon \sum_{i=1}^{(a/2)-1} N_i N_{(a/2)-i}\right) + \sum_{i=1}^{a-3} N_i \sum_{j=1}^{a-i-2} N_j \sum_{k=1}^{a-i-j-1} N_k N_{a-i-j-k} \quad (a \geq 4) \quad (36) $$

In order to attain at the total number of nonisomorphic PF2 systems, viz. Q_h, one has to add the four equations in this paragraph together, in accord with eq 7. Before executing this step we shall treat the crude totals which appear as summations in eqs 34, 35, and 36. Considerable simplifications of these expressions are achieved.

CRUDE TOTALS

The treatment of this section is quite general, not confined to the classes PF1 and PF2, but applicable to any systems where catafusenes are annealated to a polyhex.

The first simplification concerns the summation in eq 15, which is the crude total for two annealated catafusenes. From eq 1 the following is readily obtained:

$$ \sum_{i=1}^{a-1} N_i N_{a-i} = N_{a+1} - 3N_a \quad (a \geq 2) \quad (37) $$

From eq (37) one has

$$ \sum_{j=1}^{a-i-1} N_j N_{a-i-j} = N_{a-i+1} - 3N_{a-i} \quad (38) $$

which inserted into the summation of eq 23 gives

$$ \sum_{i=1}^{a-2} N_i \sum_{j=1}^{a-i-1} N_j N_{a-i-j} = \sum_{i=1}^{a-2} N_i N_{a-i+1} - 3\sum_{i=1}^{a-2} N_i N_{a-i} \quad (39) $$

The first summation on the right-hand side of eq 39 can be manipulated in the following way so that the sign of summation is eliminated by means of eq 37.

$$ \sum_{i=1}^{a-2} N_i N_{a-i+1} = -N_a N_1 - N_{a-1} N_2 + \sum_{i=1}^{a} N_i N_{a+1-i} = N_{a+2} - 3N_{a+1} - 3N_{a-1} - N_a \quad (40) $$

A corresponding manipulation of the last summation of eq 39 gives

$$ \sum_{i=1}^{a-2} N_i N_{a-i} = -N_{a-1} N_1 + \sum_{i=1}^{a-1} N_i N_{a-i} = N_{a+1} - 3N_a - N_{a-1} \quad (41) $$

On inserting from eqs 40 and 41 into eq 39 one obtains the net result

$$ \sum_{i=1}^{a-2} N_i \sum_{j=1}^{a-i-1} N_j N_{a-i-j} = N_{a+2} - 6N_{a+1} + 8N_a \quad (a \geq 3) \quad (42) $$

This is the crude total for three annealated catafusenes.

The procedure can be extended to larger numbers of annealated catafusenes without limitation, at least theoretically, although the practical computation soon becomes rather

Table II. Numbers of Polyhexes of the Class PF2: One, Two, Three, and Four Catafusenes Annealated to Pyrene

h	${}^1Q_h$	${}^2Q_h$	${}^3Q_h$	${}^4Q_h$
5	2			
6	5	5		
7	16	20	4	
8	55	100	28	2
9	208	431	176	13
10	817	1937	950	101
11	3336	8548	4908	619
12	13935	38199	24402	3641
13	59406	171001	119204	20028
14	257079	770934	575312	106812
15	1126948	3492251	2757460	554352
16	4992421	15905897	13157752	2828660

laborious. For the case of four annealated catafusenes the following result was achieved:

$$\sum_{i=1}^{a-3} N_i \sum_{j=1}^{a-i-2} N_j \sum_{k=1}^{a-i-j-1} N_k N_{a-i-j-k} = N_{a+3} - 9N_{a+2} + 25N_{a+1} - 21N_a \quad (a \geq 4) \quad (43)$$

FINAL RESULTS FOR ANNEALATED PYRENES

Total Numbers. For the numbers of nonisomorphic polyhexes of the class PF2 with one appendage, viz. ${}^1Q_{4+a}$, eq 33 should be consulted. The corresponding formulas for two, three, and four appendages are given by eqs 34–36, respectively. These three equations are now simplified by means of the expressions for the crude totals in eqs 41–43. Furthermore, the summation multiplied by ϵ in eq 36 is reduced to

$$\sum_{i=1}^{(a/2)-1} N_i N_{(a/2)-i} = N_{(a/2)+1} - 3N_{a/2} \quad (44)$$

by virtue of eq 37. Finally also ϵ can be eliminated; eq 14 gives

$$\epsilon N_{a/2} = M_{a+1} - M_a, \; \epsilon N_{(a/2)+1} = M_{a+3} - M_{a+2} \quad (45)$$

With all these modifications also the numbers ${}^2Q$, ${}^3Q$, and ${}^4Q$, as well as ${}^1Q$, are expressed exclusively in terms of the numbers which are listed in Table I. The results are as follows:

$${}^2Q_{4+a} = \frac{13}{4}(N_{a+1} - 3N_a) + \frac{3}{2}(M_{a+1} - M_a) + \frac{1}{4}L_a \quad (a \geq 2) \quad (46)$$

$${}^3Q_{4+a} = 3(N_{a+2} - 6N_{a+1} + 8N_a) + M_a' \quad (a \geq 3) \quad (47)$$

$${}^4Q_{4+a} = N_{a+3} - 9N_{a+2} + 25N_{a+1} - 21N_a + \frac{1}{2}(M_{a+3} - M_{a+2} - 3M_{a+1} + 3M_a + L_a') \quad (a \geq 4) \quad (48)$$

Numerical values for ${}^iQ$ (i = 1, 2, 3, 4) are shown in Table II.[26] The grand total for PF2 polyhexes ($a \geq 4$) is obtained on addition of these numbers. The corresponding mathematical expression reads:

$$Q_{4+a} = N_{a+3} - 6N_{a+2} + \frac{1}{4}(41N_{a+1} - 21N_a) + \frac{1}{2}(M_{a+3} - M_{a+2} + M_a) + \frac{1}{4}L_a + M_a' + \frac{1}{2}L_a' \quad (a \geq 4) \quad (49)$$

This equation is also valid for a = 1, 2, 3 if the meaningless symbols (such as L_1, M_2', etc.) are omitted under its application. The appropriate results, viz. Q_5, Q_6, Q_7, are found under the totals in Table III. In addition, eq 49 should be supplemented

Table III. Numbers of Polyhexes of the Class PF2: Classification According to Symmetry

h	D_{2h}	C_{2h}	C_{2v}(a)	C_{2v}(b)	C_s	total
4	1	0	0	0	0	1
5	0	0	1	0	1	2
6	1	1	2	0	6	10
7	0	0	5	0	35	40
8	1	5	10	1	168	185
9	0	0	21	0	807	828
10	2	20	41	4	3738	3805
11	0	0	85	0	17326	17411
12	2	82	167	17	79909	80177
13	0	0	273	0	369366	369639
14	5	335	608	66	1709123	1710137
15	0	0	1421	0	7929590	7931011
16	5	1402	2823	269	36880231	36884730

with the trivial value (for a = 0)

$$Q_4 = 1 \quad (50)$$

which pertains to pyrene itself.

Distribution into Symmetries. The numbers of PF2 polyhexes with specific symmetries, which are implied in the above developments, were also assembled in order to produce expressions for these numbers in total. The final results are reported below:

$$Q_{4+a}^D = \epsilon M_{a/2} \quad (a > 0) \quad (51)$$

$$Q_{4+a}^C = M_{a+3} - M_{a+2} - \frac{1}{2}(3M_{a+1} - 3M_a + \epsilon M_{a/2}) \quad (a > 0) \quad (52)$$

$$Q_{4+a}^{M(a)} = M_{a+1} + \frac{1}{2}(L_a - \epsilon M_{a/2}) + 2M_a' + L_a' \quad (a \geq 4) \quad (53)$$

$$Q_{4+a}^{M(b)} = \frac{1}{2}(M_{a+1} - M_a - \epsilon M_{a/2}) \quad (a > 0) \quad (54)$$

$$Q_{4+a}^{(A)} + N_{a+3} - 6N_{a+2} + \frac{1}{4}(41N_{a+1} - 21N_a) - \frac{1}{2}(M_{a+3} - M_{a+2} + M_a - \epsilon M_{a/2}) - \frac{1}{4}L_a - M_a' - \frac{1}{2}L_a' \quad (a \geq 4) \quad (55)$$

The superscripts, viz. D, C, etc., indicate as previously the different symmetries. Here the coefficient ϵ occurs before $M_{a/2}$.[27] It is given in mathematical terms by

$$\epsilon = \frac{1}{2}[1 + (-1)^a] \quad (56)$$

Equation 51 should be supplemented by

$$Q_4^D = 1 \quad (57)$$

for pyrene itself. Equations 53 and 55 are also valid for a = 1, 2, 3 if the meaningless symbols (such as L_1, M_2', etc.) again are omitted.

The numbers of the nonisomorphic polyhexes of the class PF2, including their distributions into the different symmetries, are collected in Table III.

Forms. In Figure 6 the smallest annealated pyrenes, in addition to pyrene itself, are shown.

NORMAL BENZENOIDS WITH TWO INTERNAL VERTICES

Preliminaries. The title class of polyhexes is a subclass of PF2. It consists of pyrene and annealated pyrenes, but without helicenes. Let this class be designated PF2′. It is also a subclass of benzenoids, which have been enumerated very

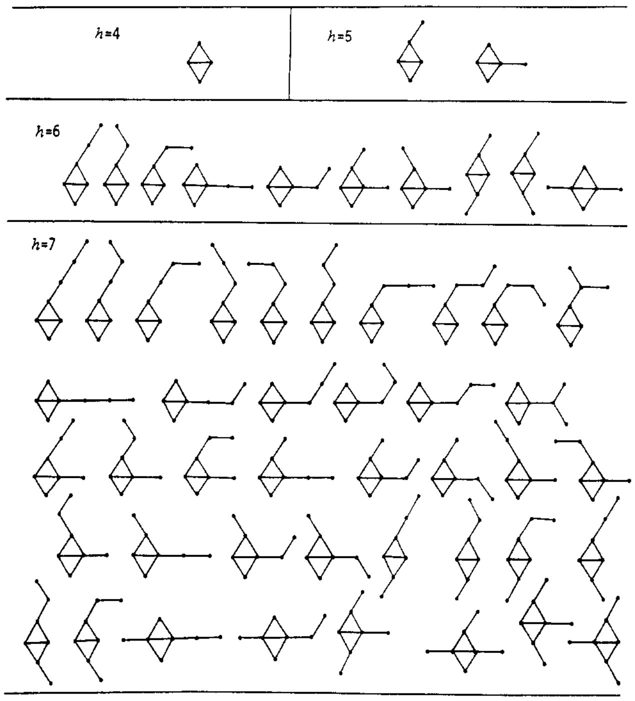


Figure 6. All $h \leq 7$ PF2 polyhexes.

extensively by computers under different points of view.[9,20,21,23,24,28] By subtracting the PF2′ peribenzenoids from the PF2 perifusenes, one is left with the perihelicenes belonging to PF2, a class which presently shall be denoted by PF2*; PF2* = PF2 − PF2′. This subtraction has been done, as is reported in the following. Literature data, which are available for $h \leq 10$,[29] have been employed for this purpose; furthermore, these data were extended to $h = 14$.

Very recently an analytical method (without using computers), referred to as combinatorial enumeration, has been applied to perihelicenes.[30,31] Analyses of this kind, specifically aimed at the PF2* class, provide a useful check of the formulas of the present work, as should be clear from the above considerations.

Annealated Pyrene Benzenoids. In a relatively early computer enumeration of benzenoids[32] the annealated pyrenes up to $h = 9$ were generated. In fact, these systems were also classified according to different types of annealation for $h \leq 8$. The total numbers 2, 10, 40, 180, and 777 were reported for $h = 5, 6, 7, 8$, and 9, respectively. This is nothing else than an enumeration for the class PF2′. The method of computer programming, which was used in the work under consideration,[32] falls under the category specific generation.[33]

Subclass of Benzenoid Isomers. Some of the recent computer enumerations of benzenoids deal with C_nH_s isomers.[29,34–36] The number of benzenoid isomers is defined, in a restricted sense, as the number of nonisomorphic benzenoid systems which are compatible with a given formula C_nH_s. It is recalled that a class of benzenoids (or, more generally, of polyhexes) with a given pair of invariants (h, n_i) also is characterized by a definite formula C_nH_s.[29] For $n_i = 2$ in particular, the formulas follow the pattern $C_{4h}H_{2h+2}$.

In a computer enumeration of benzenoid isomers by Brunvoll and Cyvin[29] all the C_nH_s systems for $h \leq 10$ are classified into Kekuléans and non-Kekuléans, and the Kekuléans are also divided into normal and essentially disconnected systems. Here the normal (Kekuléan) $C_{4h}H_{2h+2}$ isomers represent exactly the members of the class PF2′. The appropriate numbers for $h \leq 8$ are consistent with those derived by specific generations of annealated pyrene benzenoids[32] (see above).

Table IV. Numbers of Polyhexes of the Classes PF2′ and PF2*: Normal (Kekuléan) Peribenzenoids and Perihelicenes, Respectively, with Two Internal Vertices

h	formula	normal benzenoids	normal helicenes
4	$C_{16}H_{10}$	1	0
5	$C_{20}H_{12}$	2[a]	0
6	$C_{24}H_{14}$	10[a]	0
7	$C_{28}H_{16}$	40[a]	0
8	$C_{32}H_{18}$	180[a]	5
9	$C_{36}H_{20}$	777[a]	51
10	$C_{40}H_{22}$	3403[b]	402
11	$C_{44}H_{24}$	14699	2712
12	$C_{48}H_{26}$	63436	16741
13	$C_{52}H_{28}$	272114	97525
14	$C_{56}H_{30}$	1164197	545940

[a] Ref 32. [b] Ref 29.

The numbers of interest were extended to $h = 11, 12, 13$, and 14 by means of a complete computer generation of the benzenoids with these numbers of hexagons. This analysis reproduced the literature numbers of 141 229,[37] 669 584,[38] 3 198 256,[39,40] and 15 367 577 systems,[40] respectively. Detailed classifications were executed within each of these sets, including the enumeration of C_nH_s isomers and the distinction between normal and essentially disconnected (Kekuléan) systems. The essentially disconnected systems were detected by recognition[33] according to a method[41] which implies the computation of Pauling bond orders.

A collection of the numbers of nonisomorphic PF2′ systems is given in Table IV.

NORMAL HELICENES WITH TWO INTERNAL VERTICES

General Considerations. The title systems represent the class PF2*. Their numbers (for $h \leq 14$) were obtained by subtractions of the numbers for benzenoids (class PF2′) in Table IV from the totals (class PF2) in Table III. The resulting numbers are found as the last column in Table IV.

The interest in helicenic hydrocarbons[42] and their enumeration seems to be increasing.[43,44] It is an intriguing aspect of the enumerations that there, in many cases, tend to be more helicenes than benzenoids within corresponding classes of polyhexes for sufficient large h values.[43,45–48] In the case of the present study we find still that there are more benzenoids than helicenes among the PF2 polyhexes for $h \leq 14$, cf. Table IV. However, the relative abundance of helicenes increases with increasing h, and it is to be expected that from a certain h value the numbers of helicenes become larger than the numbers of benzenoids.

It is a useful check of the analysis of the present work that the three smallest nonvanishing numbers of helicenes in Table IV (viz. 5, 51, and 402) are confirmed by the method of combinatorial enumerations. This method[30,31] was used to generate all perihelicenes with $h = 8$ and $h = 9$[30] and all Kekuléan perihelicenes with $h = 10$.[31] These deductions are supported by graph-theoretical proofs. The systems of interest (i.e. belonging to PF2*) are contained among the generated systems by the method of combinatorial enumerations and are easily extracted from them. Here we shall not treat this method in detail, but only report briefly the results of relevance to the present work.

Among the PF2 systems with $h \leq 7$ (see Figure 6) there are no helicenes.

Figure 7 shows the definition of seven catahelicenes C_1, ..., C_7 adopted from previous works;[30,31] most of them are utilized in the below descriptions.

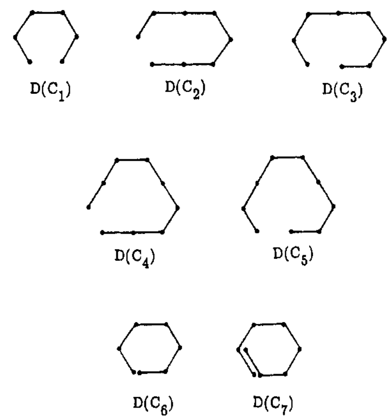


Figure 7. Dualists of seven catahelicenes.

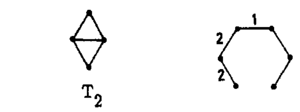


Figure 8. Generation of the $h = 8$ PF2* polyhexes: 5 systems.

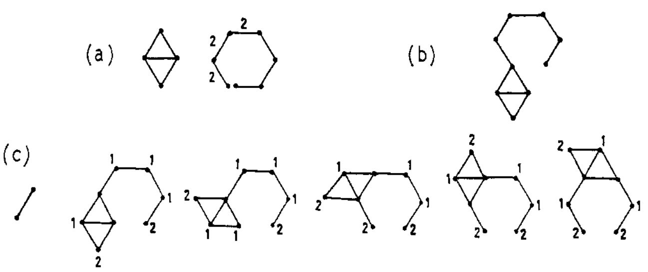


Figure 9. Generation of the $h = 9$ PF2* polyhexes: 51 systems.

Systems with Eight Hexagons. Let the dualist of a helicene H be denoted by $D(\mathrm{H})$, cf. also Figure 7. Here it is assumed that H belongs to the class PF2*. Assume also that $h = 8$ in H. Then, by a reasoning which is described in detail elsewhere,[30] it is perceived that $D(\mathrm{H})$ can only be of one special type, viz. the dualist of pyrene (T_2; see Figure 8) added to the dualist of hexahelicene, $D(C_1)$, so that T_2 shares one edge with $D(C_1)$. A complete set of nonisomorphic systems $D(\mathrm{H})$ are obtained by adding T_2 to three edges (one from each set of symmetrically equivalent edges) in a certain number of ways as is indicated in the right-hand drawing of Figure 8. Symmetry considerations of this type have also been done, without further mentioning in some of the cases in the following paragraphs. The result in the present case is 5 nonisomorphic $D(\mathrm{H})$, and therefore also H systems, in consistency with Table IV. Complete depictions of these five systems (as dualists) are found in the bottom line of Figure 9, where the numerals attached to some of the vertices should be disregarded for this moment.

Systems with Nine Hexagons. Assume that $h = 9$ in H, which still is supposed to designate a polyhex (perihelicene) of the class PF2*. It was found[30] that there are exactly three cases for the generation of $D(\mathrm{H})$: (a) T_2 added to the dualist of heptahelicene, $D(C_6)$, so that T_2 shares one edge with $D(C_6)$. The 6 resulting $D(\mathrm{H})$ systems are indicated in Figure 9. (b) T_2 shares only one vertex with $D(C_1)$: only 1 $D(\mathrm{H})$ system of this kind is possible, cf. Figure 9. (c) Start with the five $h = 8$ systems of PF2* (see the text above and the bottom row of Figure 9). One more edge should be added to selected vertices of these dualists and in so many ways as indicated by the appropriate numerals in Figure 9. The number of nonisomorphic $D(\mathrm{H})$ systems under this case is obtained on adding these numerals, which gives the result 44.

In conclusion, the total number for H with $h = 9$ is $6 + 1 + 44 = 51$. This again is consistent with Table IV.

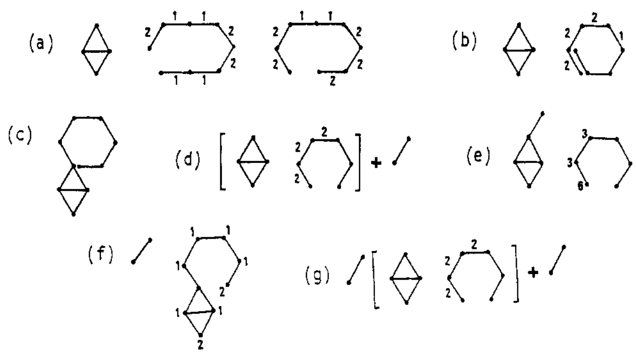


Figure 10. Incomplete account of the generation of the $h = 10$ PF2* polyhexes: 402 systems.

Systems with Ten Hexagons. Assume that $h = 10$ in H. The seven cases[31] are mapped in Figure 10. For the sake of brevity we shall give an incomplete account of the generation of the $D(\mathrm{H})$ systems under consideration. The cited reference[31] may be consulted for further details.[49] (a) T_2 added to $D(C_2)$ or $D(C_3)$ so that T_2 shares one edge with the appropriate catahelicene: 22 $D(\mathrm{H})$ systems. (b) T_2 shares one edge with $D(C_7)$: 7 $D(\mathrm{H})$ systems. (c) T_2 shares only one vertex with $D(C_6)$: 1 $D(\mathrm{H})$ system. (d) Start with T_2 added to $D(C_6)$ as under $h = 9$, Figure 9 (a). Add one more edge to each of the six resulting systems in appropriate positions: 59 $D(\mathrm{H})$ systems. Figure 10 (d) gives an incomplete account of this generation. (e) T_2 shares no vertex with $D(C_1)$: 12 $D(\mathrm{H})$ systems. (f) Start with T_2 which shares only one vertex with $D(C_1)$ as in Figure 9 (b). Add one more edge as indicated in Figure 10 (f): 10 $D(\mathrm{H})$ systems. (g) Start with the 44 $h = 9$ systems as specified in Figure 9 (c). Add one more edge in appropriate positions: 291 $D(\mathrm{H})$ systems. Figure 10 (g) again gives an incomplete account of the generations in question. In conclusion, the total number for H with $h = 10$ is $22 + 7 + 1 + 59 + 12 + 10 + 291 = 402$, the same number as in Table IV.

CONCLUSION

The method of combinatorial summation was applied to the enumeration of catafusenes,[3] about twenty years after the same problem had been solved[2] by generating functions under the exploitation of Pólya's theorem.[4] Both of these methods have also recently been applied to the enumeration of phenalene with annealated catafusenes.[6] In the present work a new version of the combinatorial summation method was developed. By this new procedure a considerable simplification of the result for annealated phenalenes was achieved. Furthermore, it proved to be useful for the enumeration of pyrene with annealated catafusenes. A treatment of this problem, which led to a complete mathematical solution, is described in detail here. So far we have not been able to solve the same problem in terms of generating functions. Furthermore, a preliminary consideration seems to indicate that the current Pólya's theorem[4] is not sufficient in this case. This says something, perhaps, about the virtue of the present method of combinatorial summation in its new version.

The potentiality of the present method is not believed to be exhausted. One may think, for instance, of the annealated coronenes, which have a considerable interest in organic chemistry.[7,16,17,50] The enumeration of coronenes with annealated catafusenes by means of the method of combinatorial summation might be a tractable problem.

ACKNOWLEDGMENT

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(25) Strictly speaking, the symbol $N_{a/2}$ is meaningless when a is odd. But, in this case $\epsilon = 0$, and $\epsilon N_{a/2}$ should be interpreted so that the whole term vanishes.

(26) In order to accomplish these calculations through $a = 12$ ($h = 16$) one also needs: $N_{13} = 14\,878\,455$, $N_{14} = 67\,030\,785$, $N_{15} = 304\,036\,170$, $M_{13} = M_{14} = 731$, and $M_{15} = 2950$.

(27) The above note (25) about $N_{a/2}$ applies also to $M_{a/2}$.

(28) Only a short extract of the voluminous material on benzenoid enumerations can be cited here: Balasubramanian, K.; Kaufman, J. J.; Koski, W.; Balaban, A. T. Graph Theoretical Characterization and Computer Generation of Certain Carcinogenic Benzenoid Hydrocarbons and Identification of Bay Regions. *J. Comput. Chem.* **1980**, *1*, 149–157. Knop, J. V.; Szymanski, K.; Jeričević, Ž.; Trinajstić, N. Computer Enumeration and Generation of Benzenoid Hydrocarbons and Identification of Bay Regions. *J. Comput. Chem.* **1983**, *4*, 23–32. He, W. C.; He, W. J. A Novel Nomenclature of Polycyclic Aromatic Hydrocarbons without Using Graph Centre. *Theor. Chim. Acta* **1985**, *68*, 301–313. Cioslowski, J. Computer Enumeration of Polyhexes Using the Compact Naming Approach. *J. Comput. Chem.* **1987**, *8*, 906–915. Balaban, A. T.; Brunvoll, J.; Cioslowski, J.; Cyvin, B. N.; Cyvin, S. J.; Gutman, I.; He, W. C.; He, W. J.; Knop, J. V.; Kovačević, M.; Müller, W. R.; Szymanski, K.; Tošić, R.; Trinajstić, N. Enumeration of Benzenoid and Coronoid Hydrocarbons. *Z. Naturforsch. A* **1987**, *42*, 863–870. Tošić, R.; Kovačević, M. Generating and Counting Unbranched Catacondensed Benzenoids. *J. Chem. Inf. Comput. Sci.* **1988**, *28*, 29–31. Brunvoll, J.; Cyvin, B. N.; Cyvin, S. J.; Gutman, I. Some Benzenoid Hydrocarbons with Extremal Properties. *Z. Naturforsch. A* **1988**, *43*, 889–894. Müller, W. R.; Szymanski, K.; Knop, J. V.; Nikolić, S.; Trinajstić, N. On the Enumeration and Generation of Polyhex Hydrocarbons. *J. Comput. Chem.* **1990**, *11*, 223–235. However, several additional references, which are of relevance to the topic, are found among the subsequent citations.

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