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Graph-theoretical studies on fluoranthenoids and fluorenoids: enumeration of some catacondensed systems$^{\alpha}$

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Abstract

Precise definitions are given for some classes of molecular graphs with one pentagon and otherwise hexagons: the monopentapolyhexes. The fluoranthenoid and fluorenoid systems belong to monopentapolyhexes. Complete mathematical solutions, using combinatorial summations on the one hand and generating functions on the other hand, are given for the numbers of catacondensed simply connected monopentapolyhexes (catafluorenoids and the corresponding helicenic systems). Generating functions and numerical values are included.

Introduction

Fluoranthenoids (or fluoranthenes) and fluorenoids (or fluorenes) are polycyclic hydrocarbons consisting of one five-membered ring and varying numbers of six-membered rings [1]. These two classes are distinguished by an even or odd number of carbon atoms (and hydrogen atoms), respectively, in the pertinent hydrocarbons. Among the fluorenoids are the important catacondensed hydrocarbons without internal carbon atoms, i.e. in which there is no carbon atom shared by three rings. Catacondensed fluorenoids have the formulae $C_{4r+1}H_{2r+3}$, where r is used to designate the number of rings. These compounds are radicals and as such chemically unstable. However, several of the corresponding $C_{4r+1}H_{2r+4}$ molecules are known, such as cyclopentadiene C_5H_6 corresponding to cyclopentadienyl C_5H_5. Similarly, the molecules corresponding to the following radicals are current in the chemical literature (and laboratories): indenyl C_9H_7, fluorenyl $C_{13}H_9$, benzo[*a*]fluorenyl (chrysofluorenyl) $C_{17}H_{11}$, and two isomers of $C_{21}H_{13}$, i.e. dibenzo[*a, g*]fluorenyl and dibenzo[*b, h*]fluorenyl.

Dias [2] has identified the three isomers of $C_{13}H_9$ fluorenoids, but otherwise the numbers of catacondensed fluorenoid isomers seem not to be known. In the present work we give a complete mathematical solution for the numbers of $C_{4r+1}H_{2r+3}$ fluorenoid isomers augmented by the corresponding helicenic systems.

Fluorenoid (and fluoranthenoid) systems

Fluorenoid systems (or simply fluorenoids), which have their chemical counterparts in fluorenoid hydrocarbons, belong to a class we shall refer to as monopentapolyhexes. This class

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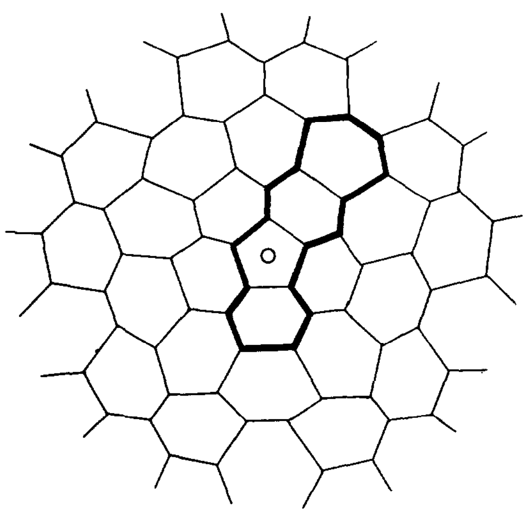

Fig. 1. The monopentahexagonal lattice, where the pentagon is marked by a circle. The perimeter of benzo[*a*]fluorenyl (chrysofluorenyl) is indicated in bold.

is similar to polyhexes, which are represented exclusively by congruent regular hexagons in a plane. The designation "monopentapolyhex" is open for extension to analogical terms like dipentapolyhex, polypentapolyhex, monooctapolyhex, etc.

A monopentahexagonal lattice is similar to the hexagonal lattice used in the definition of polyhexes and benzenoids [3,4] in particular. The monopentahexagonal lattice is a planar array of hexagons built around one regular pentagon. Only each set of hexagons at the same distance from the pentagon are mutually congruent, but none of the hexagons can be regular.

The fluorenoid (and fluoranthenoid) systems are simply connected geometrically planar (nonhelicenic) monopentapolyhexes. As such they are analogous to benzenoids (when the latter class is defined as simply connected geometrically planar polyhexes). A fluorenoid (or fluoranthenoid) is defined by a cycle on the monopentahexagonal lattice and its interior, which should include the pentagon. The cycle represents the boundary of the fluorenoid/fluoranthenoid system in question and is usually called the perimeter. An illustration is provided in Fig. 1.

The subject of the present work are the catacondensed simply connected monopentapolyhex systems, which may be either geometrically planar (nonhelicenic) or geometrically nonplanar (helicenic). These subclasses shall be referred to as catafluorenoids and catahelifluorenes, respectively. A more detailed scheme of classification of the simply connected monopentapolyhexes is proposed in Fig. 2. For the sake of comparison the

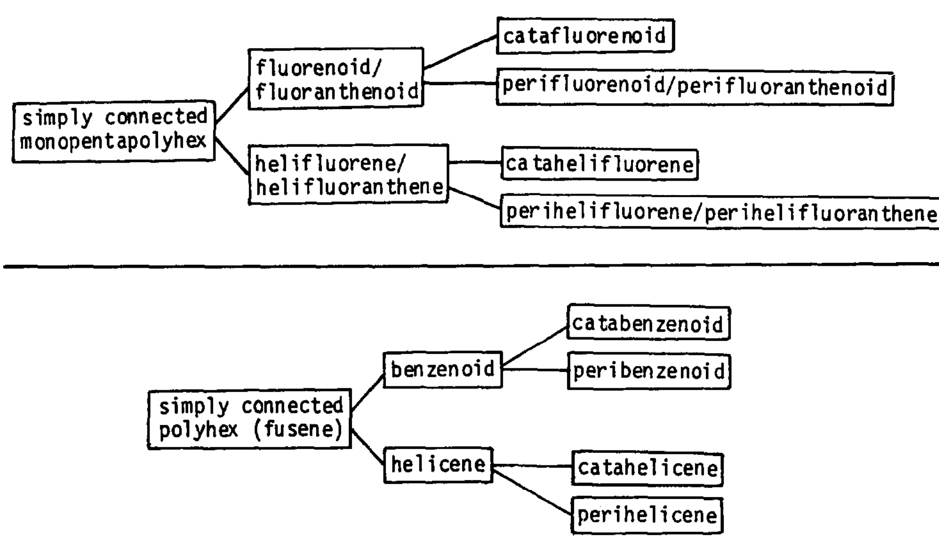

Fig. 2. Classification schemes of simply connected monopentapolyhexes and simply connected polyhexes.

Table 1
Numerical values of some variables defined in the text[a]

h	U_h	V_h	F_{1+h}(i)	F_{1+h}(ii)	F_{1+h}
1	1	1	1	0	1
2	3	1	2	1	3
3	10	2	6	3	9
4	36	2	19	16	35
5	137	5	71	66	137
6	543	5	274	300	574
7	2219	15	1117	1314	2431
8	9285	15	4650	5884	10534
9	39587	51	19819	26304	46123
10	171369	51	85710	118633	204343
11	751236	188	375712	537255	912967
12	3328218	188	1664203	2447172	4111375

[a] See Eqs. (2), (13) and (17)–(19).

corresponding classification scheme for the simply connected polyhexes [5,6] is included in Fig. 2.

Enumeration of the catacondensed simply connected monopentapolyhexes by combinatorial summations

General

Let the title class be designated by F. A general formula has been derived for the numbers of nonisomorphic systems of the class F as a function of h, where

$$r = 1 + h \tag{1}$$

and h is used to designate the number of hexagons, so that r is the total number of polygons (one pentagon and the rest hexagons, if any).

A member of the class F is either one pentagon (cyclopentadienyl), or one pentagon with one or two annelated catacondensed simply connected polyhexes (catafusenes).

The method which is employed here is referred to as combinatorial summations. It has previously been applied to catafusenes with regular trigonal symmetry [7] and to catafusenes in general [8]. The catafusenes rooted by an edge play a crucial role in the method. The catafusenes which are annelated to the pentagon are only annelated by the root edges.

Rooted catafusenes

The number of edge-rooted catafusenes with h hexagons, say U_h, is given recursively by [7–9]

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

By definition,

$$U_0 = 0 \tag{3}$$

Numerical values of U_h for $1 \leqslant h \leqslant 12$ are found in Table 1.

Annelation schemes

A system of the class F may have (i) one catafusene or (ii) two catafusenes annelated to the pentagon, apart from being the pentagon itself. Examples for the schemes (i) and (ii) are found in Fig. 3. In each of these cases only one scheme is possible when isomorphic systems are to be avoided.

Let the numbers of nonisomorphic systems with r polygons each be designated by F_r(i)

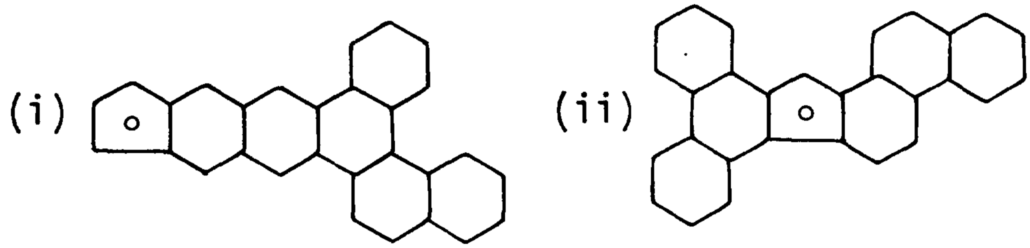

Fig. 3. Examples of the schemes of annelations to a pentagon (marked by a circle): (i) one annelated catafusene; (ii) two annelated catafusenes.

and F_r(ii) under schemes (i) and (ii), respectively (see Fig. 3). Then the total number F_r is

$$F_r = F_r(\mathrm{i}) + F_r(\mathrm{ii}) \qquad (h \geqslant 1) \tag{4}$$

One appendage (scheme (i))

In this treatment, $h \geqslant 1$. The systems under consideration are split into

$$F_r(\mathrm{i}) = F_r^{\mathrm{M}}(\mathrm{i}) + F_r^{\mathrm{A}}(\mathrm{i}) \tag{5}$$

where M and A refer to mirror-symmetrical (C_{2v}) and unsymmetrical (C_s) systems, respectively. Here

$$F_{1+h}^{\mathrm{M}}(\mathrm{i}) = \sum_{i=0}^{\lfloor (h-1)/2 \rfloor} (1 + U_i) \tag{6}$$

where the floor function is employed in the upper index: $\lfloor x \rfloor$ is the largest integer not larger than x. Now U_h will count the unsymmetrical systems twice, but the mirror-symmetrical only once, so that

$$U_h = F_{1+h}^{\mathrm{M}}(\mathrm{i}) + 2F_{1+h}^{\mathrm{A}}(\mathrm{i}) \tag{7}$$

A combination of Eqs. (5)–(7) gives

$$F_{1+h}(\mathrm{i}) = \frac{1}{2}\left[U_h + \sum_{i=0}^{\lfloor (h-1)/2 \rfloor} (1 + U_i)\right] \tag{8}$$

Two appendages (scheme (ii))

Here it is assumed $h \geqslant 2$. We write, by analogy with Eq. (5),

$$F_r(\mathrm{ii}) = F_r^{\mathrm{M}}(\mathrm{ii}) + F_r^{\mathrm{A}}(\mathrm{ii}) \tag{9}$$

where

$$F_{1+h}^{\mathrm{M}}(\mathrm{ii}) = \epsilon U_{h/2} \tag{10}$$

here $\epsilon = 1$ when h is even, and $\epsilon = 0$ when h is odd. In the latter case the symbol $U_{h/2}$ is meaningless, but it is understood that the whole term vanishes. In the present case it is found

$$\sum_{i=1}^{h-1} U_i U_{h-i} = F_{1+h}^{\mathrm{M}}(\mathrm{ii}) + 2F_{1+h}^{\mathrm{A}}(\mathrm{ii}) \tag{11}$$

which gives, together with Eqs. (9) and (10)

$$F_{1+h}(\mathrm{ii}) = \frac{1}{2}\left(\epsilon U_{h/2} + \sum_{i=1}^{h-1} U_i U_{h-i}\right) \tag{12}$$

Simplification of formulae

In the first place, introduce the simplified notation

$$V_h = \sum_{i=0}^{\lfloor (h-1)/2 \rfloor} (1 + U_i) \qquad (h \geqslant 1) \tag{13}$$

for the summation of Eq. (8). The numbers of Eq. (13) are most easily found according to the initial condition and recurrence relation

$$V_1 = 1, V_{h+1} = V_h + \epsilon U_{h/2} \tag{14}$$

where ϵ is defined after Eq. (10). Numerical values of V_h for $1 \leqslant h \leqslant 12$ are included in Table 1.

Now we are ready for the following simplifications. First, the simplified notation of Eq. (13) is introduced in Eq. (8). Next, the two terms in parentheses in Eq. (12) may be substituted by

$$\epsilon U_{h/2} = V_{h+1} - V_h \qquad (h \geqslant 1) \qquad (15)$$

and

$$\sum_{i=1}^{h-1} U_i U_{h-i} = U_{h+1} - 3U_h \qquad (h \geqslant 2) \qquad (16)$$

as obtained from Eqs. (14) and (2), respectively. The results are

$$F_{1+h}(\mathrm{i}) = \tfrac{1}{2}(U_h + V_h) \qquad (17)$$

$$F_{1+h}(\mathrm{ii}) = \tfrac{1}{2}(U_{h+1} + V_{h+1} - 3U_h - V_h) \qquad (18)$$

Both Eqs. (17) and (18) are valid for $h \geqslant 1$. Numerical values of the variables in these equations are again found in Table 1.

Total numbers with distributions into symmetry groups

On inserting the expressions from Eqs. (17) and (18) into Eq. (4) one obtains the final result for the number of nonisomorphic systems of the class F as

$$F_{1+h} = \tfrac{1}{2}(U_{h+1} + V_{h+1}) - U_h \qquad (19)$$

For numerical values of F_{1+h} ($1 \leqslant h \leqslant 12$), see Table 1. The above equation is also valid for $h = 0$, in which case it gives $F_1 = 1$. This accounts for the pentagon alone.

From the above analysis we are also able to give the numbers of nonisomorphic systems of the class F separately for the mirror-symmetrical and unsymmetrical (C_s) systems, say F_r^{M} and F_r^{A}, respectively. They are

$$F_{1+h}^{\mathrm{M}} = V_{h+1} \qquad (20)$$

$$F_{1+h}^{\mathrm{A}} = \tfrac{1}{2}(U_{h+1} - V_{h+1}) - U_h \qquad (21)$$

Here the numbers of Eq. (20) include $F_1^{\mathrm{M}} = 1$ for the pentagon itself. It is the only system of the class F with the regular pentagonal ($D_{5\mathrm{h}}$) symmetry; otherwise the mirror-symmetrical systems of this class all belong to $C_{2\mathrm{v}}$. In Table 2 the numbers of the monopentapolyhexes of the class F are given, including their distributions into the symmetry

Table 2
Numbers of catacondensed simply connected monopentapolyhexes (catafluorenoids + catahelifluorenes); the symmetry distribution is included

r	$D_{5\mathrm{h}}$	$C_{2\mathrm{v}}$	C_{s}	Total (F_r)
1	1	0	0	1
2	0	1	0	1
3	0	2	1	3
4	0	2	7	9
5	0	5	30	35
6	0	5	132	137
7	0	15	559	574
8	0	15	2416	2431
9	0	51	10483	10534
10	0	51	46072	46123
11	0	188	204155	204343
12	0	188	912779	912967
13	0	731	4110644	4111375
14	0	731	18636572	18637303
15	0	2950	84985825	84988775
16	0	2950	389586145	389589095
17	0	12235	1794268460	1794280695
18	0	12235	8298524480	8298536715
19	0	51822	38527095859	38527147681
20	0	51822	179487051589	179487103411

groups of interest, i.e. D_{5h}, C_{2v} and C_s. The totals (F_r) in Table 2 are found to be consistent with those of Table 1 (F_{1+h}).

Enumeration of the catacondensed simply connected monopentapolyhexes by generating functions

Generating functions provide an elegant way to represent different sets of numbers. Such functions were also derived for the main numbers of the present study (including F_r).

In the celebrated work of Harary and Read [9], the enumeration problem for the catacondensed simply connected polyhexes (catafusenes) was solved in terms of generating functions. The same procedure can easily be adapted to the class F of the present study, for which the enumeration problem is in fact substantially simpler. Therefore, it should not be necessary to treat this procedure in detail here. We shall only quite briefly translate some of the relations already given above into the language of generating functions.

The generating function for the numbers of edge-rooted catafusenes (U_h) is known [8,9] and reads

$$U(x) = \sum_{i=1}^{\infty} U_i x^i = \tfrac{1}{2}x^{-1}[1 - 3x - (1-x)^{1/2} \times (1-5x)^{1/2}] \qquad (22)$$

From Eq. (15) we find

$$1 + U(x^2) = x^{-1}V(x) - V(x) \qquad (23)$$

where $V(x)$ is the generating function for V_h. It follows that

$$V(x) = x(1-x)^{-1}[1 + U(x^2)] \qquad (24)$$

and consequently

$$V(x) = \sum_{i=1}^{\infty} V_i x^i = \tfrac{1}{2}x^{-1}[1 + x - (1-x)^{-1} \times (1-x^2)^{1/2}(1-5x^2)^{1/2}] \qquad (25)$$

The main result, i.e. Eq. (19), is transferred to a relation between generating functions like

$$x^{-1}F(x) = \tfrac{1}{2}x^{-1}[U(x) + V(x)] - U(x) \qquad (26)$$

Hence

$$F(x) = \tfrac{1}{2}[(1-2x)U(x) + V(x)] \qquad (27)$$

On inserting the functions from Eqs. (22) and (25) it was obtained as

$$F(x) = \sum_{i=1}^{\infty} F_i x^i = \tfrac{1}{2}x^{-1}[1 - 2x + 3x^2 - \tfrac{1}{2} \times (1-2x)(1-x)^{1/2}(1-5x)^{1/2} - \tfrac{1}{2}(1-x)^{-1}(1-x^2)^{1/2}(1-5x^2)^{1/2}] \qquad (28)$$

Introduce also the generating functions for the separate numbers which pertain to the different symmetries, say $F^{M}(x)$ and $F^{A}(x)$, which pertain to F_r^{M} and F_r^{A}, respectively. Then the following relations, which are consistent with Eqs. (20) and (21), are valid.

$$F^{M}(x) = V(x) \qquad (29)$$

where $V(x)$ is given by Eq. (25), and

$$F^{A}(x) = \tfrac{1}{2}[(1-2x)U(x) - V(x)] \qquad (30)$$

which again could be given explicitly by inserting from Eqs. (22) and (25).

Conclusion

In the present work a complete mathematical solution was achieved for the numbers of monopentapolyhexes of the class F: catacondensed simply connected monopentapolyhexes (catafluorenoids + catahelifluorenes). The method of combinatorial summations was employed, but the solution is also given in terms of generating functions. It was checked numerically that the two representations, e.g. Eqs. (19) and (28), are consistent. In fact, Table 1 was produced entirely from the combinatorial summations, without use of computers. The same is the case for the numbers at $r \leqslant 13$ in Table 2. Next, a simple computer program was implemented for the generating functions. This resulted in data which were completely consistent (as they should be) with the $r \leqslant 13$ numbers of Table 2 and made an extension of Table 2 practicable.

Whereas an immense body of literature has accumulated on the graph-theoretical studies of polyhexes, very little has previously been done for monopentapolyhexes in this area. The proposed terms like dipentapolyhexes, polypentapolyhexes, monooctapolyhexes, etc. suggest that many related nonbenzenoid systems, possibly with generalizations, could be treated according to the present approach.

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