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A Class of Polygonal Systems Representing Polycyclic Conjugated Hydrocarbons: Catacondensed Monoheptafusenes

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Summary. Catacondensed monoheptafusenes consist of catafusenes annelated to a heptagon. Complete mathematical solutions are reported for the numbers of these systems. Two methods were applied: combinatorial summations and application of generating functions. Catacondensed monoheptabenzenoids (geometrically planar catacondensed monoheptafusenes) were enumerated by computer programming, and the numbers of catacondensed monoheptahelicenes (the corresponding geometrically nonplanar systems) were obtained as differences. Some of the forms of these helicenes are depicted.

Keywords. Polycyclic hydrocarbon; Monoheptapolyhex; Enumeration.

Eine polycyclische konjugierte Kohlenwasserstoffe darstellende Klasse polygonaler Kohlenwasserstoffe: katakondensierte Monoheptafusene.

Zusammenfassung. Katakondensierte Monoheptafusene bestehen aus Katafusenen, welche zu einem Heptagon verknüpft sind. Für die Zahlen der möglichen derartigen Verknüpfungen werden geschlossene mathematische Ausdrücke abgeleitet. Zwei Methoden wurden angewendet: (1) das direkte Aufsummieren der kombinatorischen Ausdrücke und (2) Summenbildung mit Hilfe von erzeugenden Funktionen. Katakondensierte Monoheptabenzenoide, darunter versteht man katakondensierte Monoheptafusene mit planarer Geometrie, wurden mittels Computersimulation abgezählt und die Zahl der katakondensierten Monoheptahelicene – dies sind die nicht planaren katakondensierten Monoheptafusene – wurden durch Differenzbildung erhalten. Einige ausgewählte Geometrien von Helicenen werden gezeigt und diskutiert.

Introduction

In a previous work [1] some classes of polycyclic conjugated hydrocarbons with six-membered and seven-membered rings are treated. As chemical graphs [2] they are represented by polygonal systems consisting of hexagons and heptagons. In particular, a monoheptapolyhex [1], which is a mono-q-polyhex [3, 4] with $q = 7$, consists of exactly one heptagon and otherwise hexagons (if any). Also the classes of monoheptabenzenoids and monoheptahelicenes, which together form the class of monoheptafusenes, are defined in the previous work [1] (but see also below).

A catafusene [5–7] is a catacondensed fusene [8], *viz.* a catacondensed simply connected polyhex [9]. In a paper by *Harary* and *Read* [10], the catafusenes were successfully enumerated according to their numbers of hexagons. A complete mathematical solution was achieved and expressed in terms of a complicated generating function. The catafusenes are divided into catabenzenoids and catahelicenes according to:

$$\text{fusene}\begin{cases}\text{benzenoid}\\ \text{helicene}\end{cases}$$

Extensive enumeration works on catabenzenoids (catacondensed benzenoids) started some time ago [11–13]. Later works in this area are reviewed elsewhere [9]. Also the numbers of catahelicenes (catacondensed helicenes) have been considered separately [9, 13].

The present work on catacondensed monoheptafusenes is parallel to the above description for catafusenes with respect to the main lines. However, a classification of the deduced numbers according to symmetry is undertaken. The corresponding classification for catafusenes [14–16] was not achieved before twenty years after the appearance of the pioneering paper by *Harary* and *Read* [10]. In addition, the present work takes advantage of the method of combinatorial summations [14, 15, 17], which is an alternative to the application of generating functions, but the generating functions are also employed. In particular, a complicated expression of the *Harary–Read* type [10] is deduced for the total numbers of catacondensed monoheptafusenes.

Results and Discussion

Basic Concepts

In a polygonal system, any two polygons should either share exactly one edge or be disjointed. A simply connected polygonal system has no holes (like *e.g.* the coronoids [18]). An internal vertex of a polygonal system is a vertex shared by three polygons. Catacondensed systems have no internal vertices. After these preparations, a monoheptafusene is characterized precisely as a simply connected monoheptapolyhex (see above). One has the classification:

$$\text{monoheptafusene}\begin{cases}\text{monoheptabenzenoid}\\ \text{monoheptahelicene}\end{cases}$$

A monoheptabenzenoid (like a benzenoid [9]) should be geometrically planar (non-helicenic), *i.e.* there should be no overlapping edges when the system is embedded in a monoheptahexagonal lattice [3] (analoguously to the hexagonal lattice of benzenoids). A monoheptahelicene (like a helicene [9]) is geometrically nonplanar (helicenic).

When helicenic systems are classified into symmetry groups, the nonplanarity is not taken into account. For instance, all the normal (*h*) helicenes [19] correspond to systems of the symmetry C_{2v} (see Fig. 1, where the dualists [5, 6, 20] are employed as a convenient representation; in a dualist, each vertex represents a polygon).

Denote a catacondensed monoheptafusene by F_7. It may be the heptagon alone. Otherwise F_7 consists of α appendages which are catafusenes and annelated to the

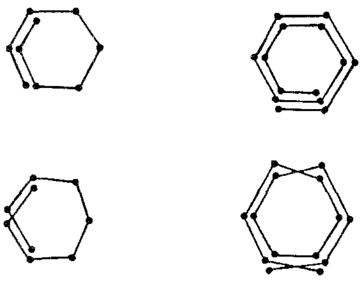

Fig. 1. The dualists of (9)helicene and (14)helicene. The top row shows the usual representation, while the bottom row is a modification which complies with the symmetry group C_{2v}

heptagon. Here $\alpha = 1$, 2 or 3. The h number of hexagons of F_7 are distributed over the appendages. Apart from the case of $h = 0$ (the heptagon itself), associated with the symmetry D_{7h}, only two symmetry groups are possible, *viz.* C_{2v} and C_s.

Two quantities are crucial in the present theory. Firstly, the numbers N_h of edge-rooted catafusenes with h hexagons are obtained by a recursive algorithm [1], which can be expressed in the compact form [14, 15, 17].

$$N_1 = 1, \quad N_2 = 3N_1 = 3, \quad N_{h+1} = 3N_h + \sum_{i=1}^{h-1} N_i N_{h-i} \, (h > 1) \tag{1}$$

Secondly, the numbers M_h of the edge-rooted catafusenes with mirror symmetry [17] are

$$M_1 = 1, \quad M_h = \sum_{i=0}^{\lfloor (h-1)/2 \rfloor} N_i (h > 1) \tag{2}$$

The generating functions for N_h and M_h are known. Firstly [10],

$$\begin{aligned} U(x) = \sum_{h=1}^{\infty} N_h x^h &= \frac{1}{2} x^{-1} [1 - 3x - (1-x)^{1/2} (1-5x)^{1/2}] \\ &= x + 3x^2 + 10x^3 + 36x^4 + 137x^5 + 543x^6 \\ &\quad + 2219x^7 + 9285x^8 + 39587x^9 + 171369x^{10} + \dots \end{aligned} \tag{3}$$

Secondly [21],

$$\begin{aligned} V(x) = \sum_{h=1}^{\infty} M_h x^h &= x(1-x)^{-1} [1 + U(x^2)] \\ &= \frac{1}{2} x^{-1} [1 + x - (1-x)^{-1} (1-x^2)^{1/2} (1-5x^2)^{1/2}] \\ &= x + x^2 + 2x^3 + 2x^4 + 5x^5 + 5x^6 + 15x^7 + 15x^8 + 51x^9 + 51x^{10} + \dots \end{aligned} \tag{4}$$

In addition, we shall need the numbers [17]

$$M'_h = \sum_{i=1}^{\lfloor (h-1)/2 \rfloor} N_i M_{h-2i} (h > 2) \tag{5}$$

The corresponding generating function is

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

$$= \frac{1}{2} x^{-3}[(1+x)(1-4x^2) - (1-x)^{-1}(1-2x^2)(1-x^2)^{1/2}(1-5x^2)^{1/2}]$$
$$= x^3 + x^4 + 5x^5 + 5x^6 + 21x^7 + 21x^8 + 86x^9 + 86x^{10} + \dots \qquad 6$$

Catacondensed Monoheptafusenes

In the following, complete mathematical solutions are reported for the enumeration of the title systems.

Annelation Schemes

Four schemes of annelation for the F_7 systems are illustrated in Fig. 2. The number of nonisomorphic systems under a given scheme is ${}^{\alpha}F$. These numbers are functions of h. Notice that there are two schemes with $\alpha = 2$, which are associated with the same function (${}^{2}F$). The total number of nonisomorphic F_7 systems is

$$F_7 = {}^{1}F + 2 \times ({}^{2}F) + {}^{3}F \; (h > 0) \qquad 7$$

In addition,

$$F_7 = 1 \quad \text{for } h = 0, \qquad 8$$

which accounts for the hexagon alone.

Crude Totals

The quantities referred to as crude totals [17], say ${}^{\alpha}J_h$, are the numbers of nonisomorphic systems for a scheme with α appendages if no symmetry is present. It has been found [17] (for $h > 0$):

$$ {}^{1}J_h = N_h \qquad 9$$
$$ {}^{2}J_h = N_{h+1} - 3N_h \qquad 10$$
$$ {}^{3}J_h = N_{h+2} - 6N_{h+1} + 8N_h \qquad 11$$

The generating functions for ${}^{\alpha}J_h$ are simple:

$$ {}^{\alpha}J(x) = \sum_{h=1}^{\infty} ({}^{\alpha}J_h)x^h = U^{\alpha}(x) \qquad 12$$

The following explicit expressions and numerical values were found for $\alpha = 2$ and 3:

$$ {}^{2}J(x) = \frac{1}{2} x^{-2}[1 - 6x + 7x^2 - (1-3x)(1-x)^{1/2}(1-5x)^{1/2}]$$
$$= x^2 + 6x^3 + 29x^4 + 132x^5 + 590x^6 + 2628x^7$$
$$+ 11732x^8 + 52608x^9 + 237129x^{10} + \dots \qquad 13$$

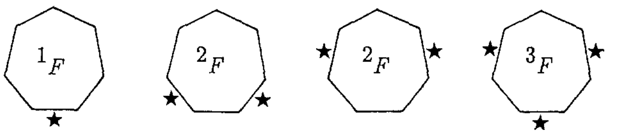

Fig. 2. Schemes of annelation for catacondensed monoheptafusenes (F_7). The asterisks indicate the sites of annelation

$$^{3}J(x) = \frac{1}{2}x^{-3}[(1-3x)(1-6x+6x^{2}) - (1-2x)(1-4x)(1-x)^{1/2}(1-5x)^{1/2}]$$
$$= x^{3} + 9x^{4} + 57x^{5} + 315x^{6} + 1629x^{7} + 8127x^{8} + 39718x^{9} + 191754x^{10} + \ldots \quad 14$$

One Appendage

The crude total $^{1}J_{h}$ (for $\alpha = 1$) counts the M mirror-symmetrical (C_{2v}) systems once and the A unsymmetrical (C_{s}) systems twice:

$$^{1}J_{h} = M + 2A \quad 15$$

where

$$M = M_{h} \quad 16$$

as given in Eq. 2. The ^{1}F number of F_{7} systems is

$$^{1}F = M + A \quad 17$$

On eliminating A from 15 and 17, one finds

$$^{1}F = \frac{1}{2}(^{1}J_{h} + M) \quad 18$$

and consequently

$$^{1}F = \frac{1}{2}(N_{h} + M_{h})\ (h > 0) \quad 19$$

Two Appendages

In a similar way as above, one has for $\alpha = 2$:

$$^{2}J_{h} = M + 2A \quad 20$$

where, for the sake of simplicity, the same symbols M and A are applied as in Eq. 15 although they are different functions of h. In the present case,

$$M = N_{h/2} \quad 21$$

where $N_{h/2}$ is supposed to have nonvanishing values only when h is divisible by two. Furthermore,

$$^{2}F = M + A \quad 22$$

whereupon one finds the final expression

$$^{2}F = \frac{1}{2}(N_{h+1} - 3N_{h} + N_{h/2})\ (h > 0) \quad 23$$

Three Appendages

Finally, for $\alpha = 3$ one has

$$^{3}J_{h} = M + 2A \quad 24$$

where

$$M = M'_h \tag{25}$$

As before,

$$^3F = M + A \tag{26}$$

and finally:

$$^3F = \frac{1}{2}(N_{h+2} - 6N_{h+1} + 8N_h + M'_h)\ (h > 0) \tag{27}$$

Total Numbers and Symmetry

The quantities ^1F, $2 \times (^2F)$, and ^3F are given numerically in Table 1 together with their sums which, in consistency with Eq. 7, yields the total numbers of F_7 systems. The algebraic expression for this total was found to be

$$F_7 = \frac{1}{2}(N_{h+2} - 4N_{h+1} + 3N_h + M_h + 2N_{h/2} + M'_h)\ (h > 0) \tag{28}$$

The data for $1 \leqslant h \leqslant 10$ are completed by the relevant entries for $h = 0$ ($\alpha = 0$) in Table 1.

The above expressions give the numbers of mirror-symmetrical $(C_{2v})F_7$ systems as

$$M_7 = M_h + 2N_{h/2} + M'_h\ (h > 0) \tag{29}$$

The generating function for $M_h + M'_h$, say $W(x)$, is obtained from Eqs. 3, 4 and 6 as

$$\begin{aligned} W(x) &= V(x) + U(x^2)V(x) = x^{-1}(1+x)U(x^2) \\ &= \frac{1}{2}x^{-3}(1+x)[1 - 3x^2 - (1-x^2)^{1/2}(1-5x^2)^{1/2}] \end{aligned} \tag{30}$$

Table 1. Numbers of nonisomorphic catacondensed monoheptafusenes classified according to the numbers of appendages

	α				
h	0	1	2	3	Total
0	1	0	0	0	1
1	0	1	0	0	1
2	0	2	2	0	4
3	0	6	6	1	13
4	0	19	32	5	56
5	0	71	132	31	234
6	0	274	600	160	1034
7	0	1117	2628	825	4570
8	0	4650	11768	4074	20492
9	0	19819	52608	19902	92329
10	0	85710	237266	95920	418896

If we write

$$W(x) = (1 + x^{-1})U(x^2), \tag{31}$$

it becomes apparent that

$$M_h + M'_h = N_{\lceil h/2 \rceil}\ (h > 0) \tag{32}$$

which yields a simplification of 29 as:

$$M_7 = N_{\lceil h/2 \rceil} + 2N_{h/2}\ (h > 0) \tag{33}$$

Herefrom, the generating function for M_7 is readily obtained:

$$M_7(x) = W(x) + 2U(x^2) = x^{-1}(1 + 3x)U(x^2)$$
$$= \frac{1}{2}x^{-3}(1 + 3x)[1 - 3x^2 - (1 - x^2)^{1/2}(1 - 5x^2)^{1/2}] \tag{34}$$

The numerical values of M_7 are entered in the column under C_{2v} in Table 2. In the above deductions, no expressions were derived explicitly for the unsymmetrical (C_s) systems. However, the numerical values (see Table 2) are readily obtained by subtractions from the totals (Table 1). Table 2 is supplemented by the appropriate entries which pertain to the heptagon alone ($h = 0$).

A good check on the numbers of Table 2 is an overall crude total:

$$J_7 = {}^1J_h + 2 \times ({}^2J_h) + {}^3J_h = N_{h+2} - 4N_{h+1} + 3N_h\ (h > 0) \tag{35}$$

This quantity counts the C_{2v} systems once and the C_s systems twice.

Finally, the generating function for the F_7 numbers of nonisomorphic F_7 systems in total is reported:

$$F_7(x) = 1 + \frac{1}{2}[U(x) + V(x)] + U^2(x) + U(x^2) + \frac{1}{2}[U^3(x) + U(x^2)V(x)]$$

Table 2. Numbers of nonisomorphic catacondensed monoheptafusenes classified according to symmetry

h	D_{7h}	C_{2v}	C_s	Total*
0	1	0	0	1
1	0	1	0	1
2	0	3	1	4
3	0	3	10	13
4	0	9	47	56
5	0	10	224	234
6	0	30	1004	1034
7	0	36	4534	4570
8	0	108	20384	20492
9	0	137	92192	92329
10	0	411	418485	418896

* see also Table 1

$$= \frac{1}{4} x^{-3} [2(1 - 2x + 5x^2 - 6x^3) - (1 - x)(1 - 3x)(1 - x)^{1/2}(1 - 5x)^{1/2}$$
$$- (1 + 3x)(1 - x^2)^{1/2}(1 - 5x^2)^{1/2}] \qquad 36$$

The unity was added in order to account for the heptagon alone.

Catacondensed Monoheptabenzenoids

No mathematical solution is expected to be found for the enumeration of the title systems. As in the case of (catacondensed) benzenoids, it was resorted to numerical solutions by computer programming. The previous work on monoheptabenzenoids [1] contains the enumeration results for the catacondensed systems up to $h = 7$. In Table 3 this material is extended to $h = 8$.

Catacondensed Monoheptahelicenes

The numbers of monoheptahelicenes which are displayed in Table 4 were obtained on subtracting the numbers of Table 3 from the corresponding ones of Table 2. This step implies subtractions between large numbers, and therefore it is essential that these numbers are exact. The correctness of the present analysis can be corroborated by an independent generation of some of the monoheptahelicenes.

Table 3. Numbers of nonisomorphic catacondensed monoheptabenzenoids classified according to symmetry

h	D_{7h}	C_{2v}	C_s	Total
0	1	0	0	1
1	0	1	0	1
2	0	3	1	4
3	0	3	10	13
4	0	9	47	56
5	0	10	221	231
6	0	29	970	999
7	0	35	4241	4276
8	0	99	18294	18393

Table 4. Numbers of nonisomorphic catacondensed monoheptahelicenes classified according to symmetry

h	C_{2v}	C_s	Total
5	0	3	3
6	1	34	35
7	1	293	294
8	9	2090	2099

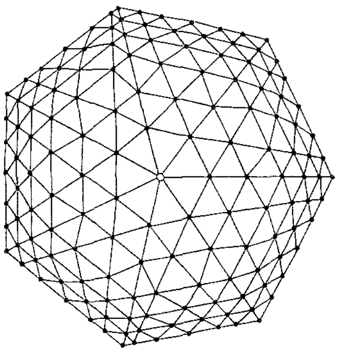

Fig. 3. Distorted trigonal lattice for representations of monoheptafusenes as dualists

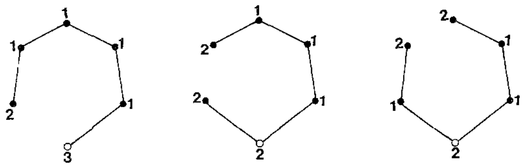

Fig. 4. The $3C_s$ catacondensed monoheptahelicenes with $h = 5$. The numerials indicate annelations of hexagons

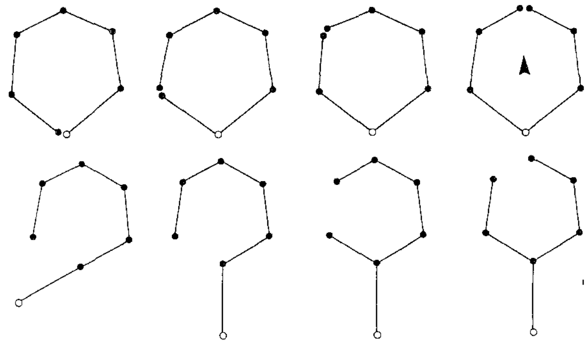

Fig. 5. The unique C_{2v} catacondensed monoheptahelicene with $h = 6$ and 7 of the relevant C_s systems (out of 34)

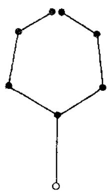

Fig. 6. The unique C_{2v} catacondensed monoheptahelicene with $h = 7$

Catafusenes and especially catahelicenes are conveniently represented by dualists as in Fig. 1. These constructions can be embedded in a regular trigonal lattice. This representation was adopted to monoheptafusenes by introducing a distorted trigonal lattice ("spider web"; Fig. 3).

A systematic method for generations of helicenes was developed by *Guo et al.* [22]. Their approach was adapted to catacondensed monoheptahelicenes with the results depicted in Figs. 4–7. Herein the black dots indicate hexagons, while the heptagon in each system is identified by a white dot. Fig. 4, where the numerals

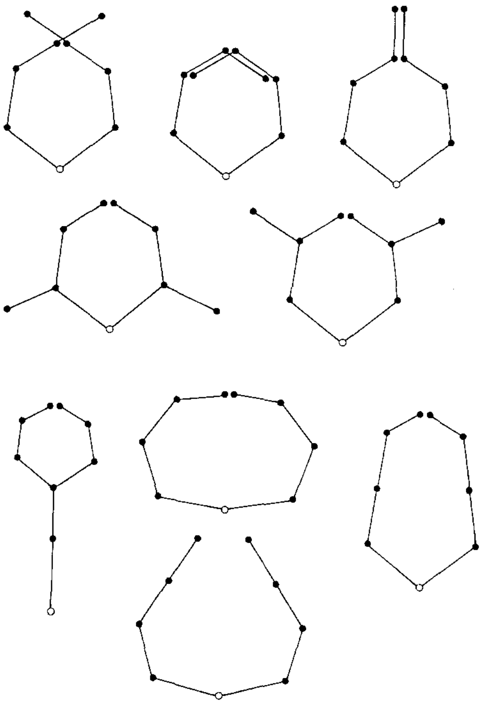

Fig. 7. The $9C_{2v}$ catacondensed monoheptahelicenes with $h = 8$

should be disregarded for a moment, shows the smallest ($h = 5$) $3C_s$ nonisomorphic catacondensed monoheptahelicenes. In Fig. 5, $1C_{2v}$ (marked by an arrow head) and $7C_s$ systems with $h = 6$ and of the category under consideration are depicted. Additional $27C_s$ systems are obtained on annelating one hexagon at a time to the systems of Fig. 4 according to the numerals therein. For the larger catacondensed monoheptahelicenes we were content with the generation of some of the smallest symmetrical (C_{2v}) systems only: $1C_{2v}$ for $h = 7$ (Fig. 6) and $9C_{2v}$ for $h = 8$ (Fig. 7). All these findings are in perfect agreement with the numbers of Table 4.

Acknowledgement

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