Enumeration of Unbranched Catacondensed Polygonal Systems: General Solution for Two Kinds of Polygons

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An α-*p*-catapoly-*q*-gon is a catacondensed polygonal system with α *p*-gons and $r-\alpha$ *q*-gons, which represents a polycyclic conjugated hydrocarbon. Here *r* is the total number of polygons or rings. A complete mathematical solution for the numbers of nonisomorphic unbranched α-*p*-catapoly-*q*-gons is reported. It is expressed by complicated explicit formulas in *r*, α, *p*, and *q*, and it represents a generalization of several special cases studied previously. The solution was achieved by means of certain generalized triangular matrices with interesting mathematical properties.

INTRODUCTION

Since the classical work on unbranched catafusenes by Balaban and Harary,[1] the catacondensed polygonal systems have attached much interest. A catafusene[1−4] is a simply connected catacondensed polygonal system consisting of exclusively hexagons. It has a chemical counterpart in a polycyclic conjugated hydrocarbon with six-membered (benzenoid) rings. The catafusenes consist of the geometrically planar catabenzenoids and geometrically nonplanar catahelicenes.[5,6] In the current studies of chemical graphs,[7] the importance of polygons others than hexagons was recognized early.[8]

A catapoly-*q*-gon is a catacondensed polygonal system consisting of exclusively *q*-gons. The algebraic solution for the numbers of nonisomorphic unbranched catapolypentagons ($q = 5$) has been given[9,10] in the same style as the classical solution for unbranched catafusenes ($q = 6$).[1] A natural extension of these results was the enumeration of catacondensed polygonal systems with two types of polygons. For the sake of brevity, we omit references to the numerous works in this area. With regard to the unbranched systems of the category in question, which are especially relevant to the present work, an algebraic solution was found for the numbers of di-4-catafusenes (2 tetragons, $r-2$ hexagons).[11] In that work, an interesting triangular matrix was introduced, and the mathematical approach in terms of different triangular matrices was later found to be convenient for generalizations. Firstly, the enumerations of unbranched di-4-catafusenes were generalized to unbranched α-4-catafusenes (α tetragons, $r-\alpha$ hexagons).[12] Secondly, the corresponding problem was solved for unbranched α-5-catafusenes (α pentagons, $r-\alpha$ hexagons).[13]

In Conclusion of the latter work,[13] several possibilities for further applications of the triangular matrices and extensions of the enumerations are suggested: “The name of the possibilities are legion, only restricted by lack of imagination. In fact, one of the main problems seems to be to select systems which promise the most interesting properties, unless one can achieve still higher degrees of generalization”. But this is exactly what we have achieved in the present work; a complete mathematical solution was derived for the numbers of unbranched catacondensed polygonal systems with two kinds of polygons of arbitrary sizes. This is a generalization of which several special cases (including those with one kind of polygons) have been studied by different investigators.[1,5,8−19] The problem turned out to be surprisingly complicated; nevertheless, it was solved in terms of explicit formulas. Presumably, the present work represents the highest degree of generalization which practically can be achieved in closed form. It should not be suppressed, however, that Balaban[8] has considered the most general case with arbitrary ring sizes, but he has not aimed at explicit formulas, rather being content with algorithmic solutions.

In the present work, the concept of conjugated hydrocarbon is used in a broad sense which includes the pertinent (open-shell) radicals. Firstly, every polycyclic conjugated hydrocarbon with an odd-numbered carbon content is known to belong to this category. But also otherwise, as pointed out by Balaban,[20] certain chemical structures which obey the Hückel rule may be unstable due to quantum-mechanical properties which make them electronically different from usual benzenoids. The unstable radicals are counted here, in addition to the stable (closed-shell) molecules. In fact, the systems with hexagons and heptagons were chosen as the main examples in order to illustrate the new methods. Many of these structures correspond to radicals, and, in particular, every mono-7-catafusene corresponds to a conjugated hydrocarbon with an odd number of carbons. Of course, the examples were not chosen because of chemical significance, but because they are simple and yet instructive for illustrations of the different features. The main formulas of the present work are applicable to much more than these examples and are also supposed to have considerable chemical interest, as is documented in the following.

Many theoretical studies on catacondensed polygonal systems have been conducted. A complete survey of the literature is too voluminous to be included here, so we concentrate upon the systems with tetragons and hexagons, viz. α-4-catafusenes in the present nomenclature. Randić[21,22] investigated the conjugated circuits for more than 20 such structures, which include five unbranched mono-4-catafusenes with five polygons each. It may be useful to know that this set is a selection of exactly 23 such systems, which could be identified and used in a more extensive study of conjugated circuits. In addition to the conjugated circuits and resonance energies, many other properties of catacon-

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densed polygonal systems including those with tetragons and hexagons have been investigated, e.g., Kekulé and algebraic structure counts, bond orders, local aromaticity, total π-electron energy, and cyclic conjugation;[23-35] additional relevant references are found elsewhere.[11] Some of the cited works[33-35] are devoted to [n]phenylenes, which are represented by systems with alternating tetragons and hexagons; references to additional theoretical works are again found elsewhere.[11] The class of [n]phenylenes has attracted considerable interest in organic chemistry. The angular form of [3]phenylene[36,37] was first synthesized relatively early and linear [3]phenylene[38-40] somewhat later, while the syntheses of angular [4]phenylene and [5]phenylene were achieved quite recently.[41]

THE SYSTEMS

The considered simply connected, catacondensed polygonal systems are termed unbranched α-p-catapoly-q-gons. A member of this class contains α p-gons and $r - \alpha$ q-gons, where r is used to denote the total number of polygons. Throughout in the following it is assumed $r > 1$. Furthermore, one should have $p < q$ by convention; this does not represent any limitation. The range of α goes from zero to r inclusive. In particular, the cases $\alpha = 0$ and $\alpha = r$ are associated with exclusively q-gons and exclusively p-gons, respectively.

MATHEMATICAL TOOLS

Triangular Matrices. Define the matrix elements $a(x,y)_{ij}$, where x and y are integers, in terms of the following recurrence relation and initial conditions:

$$a(x,y)_{11} = 1, \quad a(x,y)_{(i+1)j} = xa(x,y)_{ij} + ya(x,y)_{i(j-1)} \tag{1}$$

while $a(x,y)_{i0} = 0$, $a(x,y)_{ij} = 0$ when $j > i$. The matrix itself is triangular and is denoted $\mathbf{A}(x,y)$. Then the matrices $\mathbf{A}$ and $\overline{\mathbf{A}}$, which were introduced in a previous paper,[13] are the special cases $\mathbf{A}(2,1)$ and $\mathbf{A}(1,2)$, respectively. Furthermore, $\mathbf{A}(1,1)$ is the Pascal triangle

$$\mathbf{A}(1,1) = \begin{bmatrix} 1 & & & & \\ 1 & 1 & & & \\ 1 & 2 & 1 & & \\ 1 & 3 & 3 & 1 & \\ . & . & . & . & \end{bmatrix} \tag{2}$$

Another example is

$$\mathbf{A}(1,3) = \begin{bmatrix} 1 & & & \\ 1 & 3 & & \\ 1 & 6 & 9 & \\ 1 & 9 & 27 & 27 \\ . & . & . & . \end{bmatrix} \tag{3}$$

Notice that the first row of nonvanishing elements in an $\mathbf{A}(x,y)$ matrix is always [1], while the second row is [x y].

The explicit expression for the matrix elements in question reads

$$a(x,y)_{ij} = \binom{i-1}{j-1} x^{i-j} y^{j-1} \tag{4}$$

A useful multiplication rule for two matrices of the considered class is given below.

$$\mathbf{A}(x_1,y_1)\mathbf{A}(x_2,y_2) = \mathbf{A}(x_1 + x_2 y_1,\, y_1 y_2) \tag{5}$$

The following special case is of particular interest:

$$\mathbf{A}(x,y)\mathbf{A}(1,1) = \mathbf{A}(x+y,\, y) \tag{6}$$

Herefrom one obtains with the aid of eq 4

$$\sum_{j=1}^{i} a(x,y)_{ij} a(1,1)_{jk} = \sum_{j=1}^{i} \binom{j-1}{k-1} a(x,y)_{ij} = \sum_{j=1}^{i} \binom{i-1}{j-1}\binom{j-1}{k-1} x^{i-j} y^{j-1} = \binom{i-1}{k-1} (x+y)^{i-k} y^{k-1} \tag{7}$$

where the last two terms on the right-hand side represent a nontrivial mathematical identity involving binomial coefficients.

Trapezoidal Matrices. The Pascal triangle (eq 2) may be truncated into trapezoidal matrices by deleting some of the top rows:

$$\mathbf{A}'(1,1) = \begin{bmatrix} 1 & 1 & & & \\ 1 & 2 & 1 & & \\ 1 & 3 & 3 & 1 & \\ 1 & 4 & 6 & 4 & 1 \\ . & . & . & . & . \end{bmatrix} \tag{8}$$

$$\mathbf{A}''(1,1) = \begin{bmatrix} 1 & 2 & 1 & & & \\ 1 & 3 & 3 & 1 & & \\ 1 & 4 & 6 & 4 & 1 & \\ 1 & 5 & 10 & 10 & 5 & 1 \\ . & . & . & . & & \end{bmatrix} \tag{9}$$

The generalizations to $\mathbf{A}'''(1,1)$, $\mathbf{A}^{(4)}(1,1)$, etc., are obvious. These trapezoidal matrices are generalized to $\mathbf{A}'(x,y)$, $\mathbf{A}''(x,y)$, etc., but they are not obtained simply by deleting rows of $\mathbf{A}(x,y)$. Instead, start with the top row [1 1] or [1 2 1] in order to generate $\mathbf{A}'(x,y)$ or $\mathbf{A}''(x,y)$, respectively; apply the same recurrence relation as in eq 1, while $a'(x,y)_{i0} = a''(x,y)_{i0} = 0$, and $a'(x,y)_{ij} = 0$ when $j > i + 1$; $a''(x,y)_{ij} = 0$ when $j > i + 2$. Example: for $x = 1$, $y = 3$ (as in eq 3) one has

$$\mathbf{A}'(1,3) = \begin{bmatrix} 1 & 1 & & & \\ 1 & 4 & 3 & & \\ 1 & 7 & 15 & 9 & \\ 1 & 10 & 36 & 54 & 27 \\ . & . & . & . & \end{bmatrix} \tag{10}$$

$$\mathbf{A}''(1,3) = \begin{bmatrix} 1 & 2 & 1 & & & \\ 1 & 5 & 7 & 3 & & \\ 1 & 8 & 22 & 24 & 9 & \\ 1 & 11 & 46 & 90 & 81 & 27 \\ . & . & . & . & & \end{bmatrix} \tag{11}$$

In analogy with eq 6, one finds that

$$\mathbf{A}(x,y)\,\mathbf{A}'(1,1) = \mathbf{A}'(x+y,\, y) \tag{12}$$

It is of interest to deduce the explicit formula for the elements of the matrix at the right-hand side of eq 12. One obtains by means of eq 7

$$\sum_{j=1}^{i} \binom{j}{k-1} a(x,y)_{ij} = \sum_{j=1}^{i} \left[\binom{j-1}{k-2} + \binom{j-1}{k-1}\right] a(x,y)_{ij} = \binom{i-1}{k-2}(x+y)^{i-k+1} y^{k-2} + \binom{i-1}{k-1}(x+y)^{i-k} y^{k-1} \tag{13}$$

and finally

$$a'(x+y,\, y)_{ik} = \left[\binom{i-1}{k-2}(x+y) + \binom{i-1}{k-1}y\right](x+y)^{i-k}y^{k-2} \tag{14}$$

Next, the following matrix product is expanded:

$$\mathbf{A}(x,y)\mathbf{A}''(1,1) = \mathbf{A}''(x+y,\, y) \tag{15}$$

In analogy with eq 13, one has

$$\sum_{j=1}^{i}\binom{j+1}{k-1}a(x,y)_{ij} = \sum_{j=1}^{i}\left[\binom{j-1}{k-3} + 2\binom{j-1}{k-2} + \binom{j-1}{k-1}\right]a(x,y)_{ij} \tag{16}$$

which finally yields

$$a''(x+y,\, y)_{ik} = \left[\binom{i-1}{k-3}(x+y)^2 + 2\binom{i-1}{k-2}(x+y)y + \binom{i-1}{k-1}y^2\right](x+y)^{i-k}y^{k-3} \tag{17}$$

DERIVATION OF FORMULAS

General Remarks. For the sake of brevity, we shall not go into detail of the combinatorial reasonings behind the deductions. Instead, the reader is referred to previous treatments of different special cases.[11−13] In addition, the present deductions are supported by numerical examples. For this purpose, the unbranched α-6-catapolyheptagons ($p = 6$, $q = 7$) were selected. From the chemical point of view, the systems with hexagons and one other kind of polygons are especially important. Those systems where these other kind of polygons are tetragons or pentagons have been treated previously,[11−13] but heptagons are also of great interest chemically.[42−45]

Basic Principle. The unbranched α-*p*-catapoly-*q*-gons under consideration ($r > 1$) are distributed under the symmetry groups D_{2h}, C_{2h}, C_{2v}, and C_s. As has been explained previously,[11−13] the $I_{r\alpha}$ total number of isomers is given by

$$I_{r\alpha} = \frac{1}{4}(J_{r\alpha} + 3D_{r\alpha} + 2L_{r\alpha} + 4C_{r\alpha} + 2K_{r\alpha}) \tag{18}$$

where $J_{r\alpha}$ are the crude totals, while the numbers of D_{2h} and C_{2h} systems are denoted by $D_{r\alpha}$ and $C_{r\alpha}$, respectively. The C_{2v} systems are divided into the three subclasses: (i) $L_{r\alpha}$ linear; (ii) the $C_{r\alpha}$ systems in one-to-one correspondence with those of C_{2h} as *cis*/*trans* isomers; (iii) the $K_{r\alpha}$ remaining C_{2v} systems, which each consists of one central polygon with two equivalent branches annelated angularly to it.

Crude Total. For unbranched α-*p*-catapoly-*q*-gons, the crude totals in matrix form read

$$\mathbf{J} = \mathbf{A}(q\text{-}p,\, p\text{-}3)\,\mathbf{A}''(1,1) = \mathbf{A}''(q\text{-}3,\, p\text{-}3) \tag{19}$$

Hence the explicit formula for the **J** matrix elements, viz. $J_{ik} = a''(q\text{-}3, p\text{-}3)_{ik}$ (i, k = 1, 2, 3, ...) is obtained from eq 17. Since $J_{r\alpha} = J_{r-1(\alpha+1)}$ (r = 2, 3, 4, ...; α = 0, 1, 2, ...), one obtains finally the formula for $J_{r\alpha}$ as given in Chart 1.

For the unbranched α-6-catapolyheptagons ($p = 6$, $q = 7$), one has

$$\mathbf{J} = \mathbf{A}(1,3)\mathbf{A}''(1,1) = \mathbf{A}''(4,3) \tag{20}$$

Chart 1. Crucial Formulas (Crude Totals) in the Enumerations of Unbranched α-*p*-Catapoly-*q*-gons

$$J_{r\alpha} = \left[\binom{r-2}{\alpha-2}(q-3)^2 + 2\binom{r-2}{\alpha-1}(q-3)(p-3) + \binom{r-2}{\alpha}(p-3)^2\right] \times (q-3)^{r-\alpha-2}(p-3)^{\alpha-2}$$

$$H_{\lfloor r/2\rfloor\lfloor\alpha/2\rfloor} = \left[\binom{\lfloor r/2\rfloor-1}{\lfloor\alpha/2\rfloor-1}(q-3) + \binom{\lfloor r/2\rfloor-1}{\lfloor\alpha/2\rfloor}(p-3)\right] \times (q-3)^{\lfloor r/2\rfloor-\lfloor\alpha/2\rfloor-1}(p-3)^{\lfloor\alpha/2\rfloor-1}$$

Table 1

	α					
r	0	1	2	3	4	5
						($J_{r\alpha}$)
2	1	2	1			
3	4	11	10	3		
4	16	56	73	42	9	
5	64	272	460	387	162	27

Table 2

	⌊α/2⌋			
⌊r/2⌋	0	1	2	3
1	1	1		
2	4	7	3	
3	16	40	33	9

where **A**(1,3) and **A**″(1,1) are given in eqs 3 and 11, respectively. Consequently, the $J_{r\alpha}$ crude totals, which are contained as the elements in $\mathbf{J} = \mathbf{A}''(4,3)$, may be worked out according to the appropriate recurrence relation; this appears to be easier than a direct application of eq 20. The resulting numbers are found in Table 1.

Another Kind of Crude Totals. Strictly speaking, the $J_{r\alpha}$ numbers should be referred to as the overall crude totals. Another kind of crude totals are needed when the numbers $C_{r\alpha}$ and $K_{r\alpha}$ are to be determined. These new crude totals are contained in a matrix, say **H**, which in analogy with eq 19 reads

$$\mathbf{H} = \mathbf{A}(q\text{-}p,\, p\text{-}3)\mathbf{A}'(1,1) = \mathbf{A}'(q\text{-}3,\, p\text{-}3) \tag{21}$$

Hence the explicit formula for the **H** matrix elements, viz. H_{ik}, are obtained from eq 14. The crude totals under consideration are denoted $H_{\lfloor r/2\rfloor\lfloor\alpha/2\rfloor}$ since they are functions of ⌊r/2⌋ and ⌊α/2⌋. This is explained by the fact that the pertinent C_{2h} and C_{2v} systems are determined by specifying one of the two symmetrical arms in each system, occasionally along with a central polygon and the sites of annelation to it. The connection with H_{ik} is given by $i = \lfloor r/2\rfloor$, $k = \lfloor\alpha/2\rfloor + 1$. In conclusion, the explicit formula for $H_{\lfloor r/2\rfloor\lfloor\alpha/2\rfloor}$ as given in Chart 1 was derived.

In our example of unbranched α-6-catapolyheptagons, one has in analogy with eq 20

$$\mathbf{H} = \mathbf{A}(1,3)\mathbf{A}'(1,1) = \mathbf{A}'(4,3) \tag{22}$$

The $H_{\lfloor r/2\rfloor\lfloor\alpha/2\rfloor}$ numbers in this example are found in Table 2.

Linear Systems. In a linear unbranched catacondensed polygonal system, the centers of all polygons, when drawn as regular polygons, form a straight line. Such a system (for $r > 1$) belongs to the symmetry group D_{2h} or C_{2v}. In unbranched α-*p*-catapoly-*q*-gons, the $D_{r\alpha}$ numbers of D_{2h} systems and $L_{r\alpha}$ numbers of linear C_{2v} systems depend only on the parities of p and q. Four cases are distinguished: p and q both odd; p even and q odd; p odd and q even; and both p and q even. In the first three cases, the numbers for a given (r, α) obey (a) $D_{r\alpha} = 1$, $L_{r\alpha} = 0$, (b) $D_{r\alpha} = 0$, $L_{r\alpha} =$

Chart 2. Numbers of (Linear) Unbranched α-*p*-Catapoly-*q*-gons with D_{2h} Symmetry: $D_{r\alpha}$

	α				p & q odd	
r	0	1	2	3	4	5
2	1	0	1			
3	0	0	0	0		
4	0	0	0	0	0	
5	0	0	0	0	0	0

	α				p even, q odd	
r	0	1	2	3	4	5
2	1	0	1			
3	0	1	0	1		
4	0	0	1	0	1	
5	0	0	0	1	0	1

	α				p odd, q even	
r	0	1	2	3	4	5
2	1	0	1			
3	1	0	1	0		
4	1	0	1	0	0	
5	1	0	1	0	0	0

	α				p & q even	
r	0	1	2	3	4	5
2	1	0	1			
3	1	1	1	1		
4	1	0	2	0	1	
5	1	1	2	2	1	1

$$D_{r\alpha} = \tfrac{1}{4}[1-(-1)^p]\left\{[1-(-1)^q]\binom{2}{r} + 1 + (-1)^q\right\}\left[2\binom{0}{\alpha} - 2\binom{1}{\alpha} + \binom{2}{\alpha}\right] + \tfrac{1}{4}[1+(-1)^p]\left\{[1-(-1)^q]\left[2\binom{0}{r-\alpha} - 2\binom{1}{r-\alpha} + \binom{2}{r-\alpha}\right] + \tfrac{1}{4}[1+(-1)^q][3+(-1)^{r+\alpha}+(-1)^\alpha-(-1)^r]\binom{\lfloor r/2\rfloor}{\lfloor \alpha/2\rfloor}\right\}$$

Chart 3. Numbers of Linear Unbranched α-*p*-Catapoly-*q*-gons with C_{2v} Symmetry: $L_{r\alpha}$

	α				p & q odd	
r	0	1	2	3	4	5
2	0	1	0			
3	0	0	0	0		
4	0	0	0	0	0	
5	0	0	0	0	0	0

	α				p even, q odd	
r	0	1	2	3	4	5
2	0	1	0			
3	0	0	1	0		
4	0	0	0	1	0	
5	0	0	0	0	1	0

	α				p odd, q even	
r	0	1	2	3	4	5
2	0	1	0			
3	0	1	0	0		
4	0	1	0	0	0	
5	0	1	0	0	0	0

	α				p & q even	
r	0	1	2	3	4	5
2	0	1	0			
3	0	1	1	0		
4	0	2	2	2	0	
5	0	2	4	4	2	0

$$L_{r\alpha} = \tfrac{1}{4}[1-(-1)^p]\left\{[1-(-1)^q]\binom{2}{r} + 1 + (-1)^q\right\}\left[\binom{1}{\alpha} - \binom{0}{\alpha}\right] + \tfrac{1}{4}[1+(-1)^p]\left\{[1-(-1)^q]\left[\binom{1}{r-\alpha} - \binom{0}{r-\alpha}\right] + \tfrac{1}{2}[1+(-1)^q]\left[\binom{r}{\alpha} - \tfrac{1}{4}[3+(-1)^{r+\alpha}+(-1)^\alpha-(-1)^r]\binom{\lfloor r/2\rfloor}{\lfloor \alpha/2\rfloor}\right]\right\}$$

1, or (c) $D_{r\alpha} = L_{r\alpha} = 0$. Only in the last case when p and q are both even, do the derivations of $D_{r\alpha}$ and $L_{r\alpha}$ need some easy combinatorics. The details (in all the four cases) are summarized in Chart 2 for $D_{r\alpha}$ and Chart 3 for $L_{r\alpha}$. The general algebraic formulas are included therein.

Centrosymmetrical Systems. Starting with our example ($p = 6$, $q = 7$), we tabulate certain numbers called $X_{r\alpha}$, which are composed of the **H** matrix elements from eq 22 when r and α have the same parity, but $X_{r\alpha} = 0$ when r and α have

Table 3

	α					
r	0	1	2	3	4	5
						($X_{r\alpha}$)
2	1	0	1			
3	0	1	0	1		
4	4	0	7	0	3	
5	0	4	0	7	0	3

Table 4

	α					
r	0	1	2	3	4	5
						($C_{r\alpha}$)
2	0	0	0			
3	0	0	0	0		
4	2	0	3	0	1	
5	0	2	0	3	0	1

different parities. Table 3 emerges. The schemes for nonvanishing $X_{r\alpha}$ numbers are different, depending on the parities of p and q. One finds the following: (a) when p and q are both odd, r and α must both be even; (b) when p is even and q odd, r and α must have the same parity (as in the above example); (c) when p is odd and q even, α must be even; (d) when both p and q are even, either r is odd, or r is even while also α is even. These features are expressed mathematically in the following.

$$X_{r\alpha} = \frac{1}{4}[1+(-1)^\alpha][1+(-1)^r]H_{\lfloor r/2\rfloor\lfloor\alpha/2\rfloor};\quad p \text{ and } q \text{ odd} \tag{23}$$

$$X_{r\alpha} = \frac{1}{2}[1+(-1)^{r+\alpha}]H_{\lfloor r/2\rfloor\lfloor\alpha/2\rfloor};\quad p \text{ even, } q \text{ odd} \tag{24}$$

$$X_{r\alpha} = \frac{1}{2}[1+(-1)^\alpha]H_{\lfloor r/2\rfloor\lfloor\alpha/2\rfloor};\quad p \text{ odd, } q \text{ even} \tag{25}$$

$$X_{r\alpha} = \frac{1}{2}\left\{[1-(-1)^r] + \frac{1}{2}[1+(-1)^r][1+(-1)^{r+\alpha}]\right\}H_{\lfloor r/2\rfloor\lfloor\alpha/2\rfloor};\quad p \text{ and } q \text{ even} \tag{26}$$

In general,

$$X_{r\alpha} = \frac{1}{16}\{[1-(-1)^p][1+(-1)^\alpha][3-(-1)^{r+q} + (-1)^r + (-1)^q] + [1+(-1)^p][5-(-1)^{r+\alpha+q} + 3(-1)^{r+\alpha} + (-1)^{\alpha+q} - (-1)^{r+q} - (-1)^r + (-1)^\alpha + (-1)^q]\}H_{\lfloor r/2\rfloor\lfloor\alpha/2\rfloor} \tag{27}$$

In all cases (for any combination of the parities of p and q), one has for the $C_{r\alpha}$ numbers of centrosymmetrical (C_{2h}) unbranched α-*p*-catapoly-*q*-gons

$$C_{r\alpha} = \frac{1}{2}(X_{r\alpha} - D_{r\alpha}) \tag{28}$$

where the $D_{r\alpha}$ numbers are given in Chart 2. In our example of unbranched α-6-catapolyheptagons see Table 4.

Mirror-Symmetrical Systems. The $M_{r\alpha}$ numbers of mirror-symmetrical (C_{2v}) unbranched α-*p*-catapoly-*q*-gons are

$$M_{r\alpha} = L_{r\alpha} + C_{r\alpha} + K_{r\alpha} \tag{29}$$

Table 5

	α					
r	0	1	2	3	4	5
						($Y_{r\alpha}$)
2	0	0	0			
3	1	1	1	1		
4	0	0	0	0	0	
5	4	4	7	7	3	3

Table 6

	α					
r	0	1	2	3	4	5
						($K_{r\alpha}$)
2	0	0	0			
3	2	1	2	1		
4	0	0	0	0	0	
5	8	4	14	7	6	3

Chart 4. Total Numbers of Unbranched α-*p*-Catapoly-*q*-gons, $I_{r\alpha}$

$$\begin{aligned}I_{r\alpha} = {} & \tfrac{1}{4}\left[\binom{r-2}{\alpha-2}(q-3)^2 + 2\binom{r-2}{\alpha-1}(q-3)(p-3) + \binom{r-2}{\alpha}(p-3)^2\right] \times \\ & \qquad (q-3)^{r-\alpha-2}(p-3)^{\alpha-2} + \\ & \tfrac{1}{16}\left[1-(-1)^p\right]\left\{\left[1-(-1)^q\right]\binom{2}{r} + 1 + (-1)^q\right\}\binom{2}{\alpha} + \\ & \tfrac{1}{16}\left[1+(-1)^p\right]\left\{\left[1-(-1)^q\right]\binom{2}{r-\alpha} + \left[1+(-1)^q\right]\binom{r}{\alpha}\right\} + \\ & \tfrac{1}{8}\left\{\tfrac{1}{4}\left[1-(-1)^p\right]\left[1+(-1)^\alpha\right]\left[3-(-1)^{r+q}+(-1)^r+(-1)^q\right] + \right. \\ & \tfrac{1}{4}\left[1+(-1)^p\right]\left[5-(-1)^{r+\alpha+q}+3(-1)^{r+\alpha}+(-1)^{\alpha+q} - \right. \\ & \left.(-1)^{r+q}-(-1)^r+(-1)^\alpha+(-1)^q\right] + \\ & \left[1-(-1)^{r+\alpha}-(-1)^r+(-1)^\alpha\right]\left\lfloor\tfrac{q-3}{2}\right\rfloor + \\ & \left.\left[1+(-1)^{r+\alpha}-(-1)^r-(-1)^\alpha\right]\left\lfloor\tfrac{p-3}{2}\right\rfloor\right\} \times \\ & \left[\binom{\lfloor r/2\rfloor-1}{\lfloor\alpha/2\rfloor-1}(q-3) + \binom{\lfloor r/2\rfloor-1}{\lfloor\alpha/2\rfloor}(p-3)\right](q-3)^{\lfloor r/2\rfloor-\lfloor\alpha/2\rfloor-1}(p-3)^{\lfloor\alpha/2\rfloor-1}\end{aligned}$$

where $L_{r\alpha}$ is given in Chart 3, and $C_{r\alpha}$ is the same as in eq 28. It remains to determine the $K_{r\alpha}$ numbers. The corresponding systems occur obviously only when r is odd. Therefore we introduce the numbers $Y_{r\alpha}$ as

$$Y_{r\alpha} = \frac{1}{2}[1-(-1)^r]H_{\lfloor r/2\rfloor\lfloor\alpha/2\rfloor} \qquad (30)$$

For the unbranched α-6-catapolyheptagons see Table 5. Now, if α is even, the pertinent systems have a central q-gon; if α is odd, they have a central p-gon. In consequence,

$$K_{r\alpha} = \frac{1}{2}\{[1+(-1)^\alpha]\lfloor(q-3)/2\rfloor + [1-(-1)^\alpha]\lfloor(p-3)/2\rfloor\}Y_{r\alpha} \qquad (31)$$

In our example ($p = 6$, $q = 7$) (see Table 6).

Total Numbers of Isomers. The total numbers of nonisomorphic unbranched α-*p*-catapoly-*q*-gons is denoted by $I_{r\alpha}$. By virtue of eq 18, the above analysis makes it feasible to express $I_{r\alpha}$ explicitly. This expression is given in Chart 4 as a complicated function of r and α with the parameters p and q included. It was assumed $p < q$, thereby avoiding **A** matrices with negative parameters in eqs 19 and 21. However, the final formula of Chart 4 is valid for $p > q$ as well as $p < q$.

NUMERICAL VALUES

Table 7 shows the numerical values of $I_{r\alpha}$ to $r = 5$ from the present analysis for the unbranched α-6-catapolyheptagons. In the special case of $\alpha = 1$, viz. mono-6-catapolyheptagons, the pertinent isomer numbers are found in Table 8, where the distributions into symmetry groups are included. The case of $\alpha = r - 1$ is the subject for Table 9.

Table 7. Numbers of Unbranched α-6-Catapolyheptagons ($p = 6$, $q = 7$)

	α					
r	0	1	2	3	4	5
2	1	1	1			
3	2	4	4	2		
4	6	14	22	11	4	
5	20	72	122	104	44	10

Table 8. Numbers of Unbranched Mono-6-Catapolyheptagons (1 Hexagon, $r - 1$ Heptagons)

r	D_{2h}	C_{2h}	C_{2v}	C_s	total
2	0	0	1	0	1
3	1	0	1	2	4
4	0	0	0	14	14
5	0	2	6	64	72

Table 9. Numbers of Unbranched Mono-7-Catafusenes (1 Heptagon, $r - 1$ Hexagons)

r	C_{2v}	C_s	total
2	1	0	1
3	3	1	4
4	1	10	11
5	7	37	44

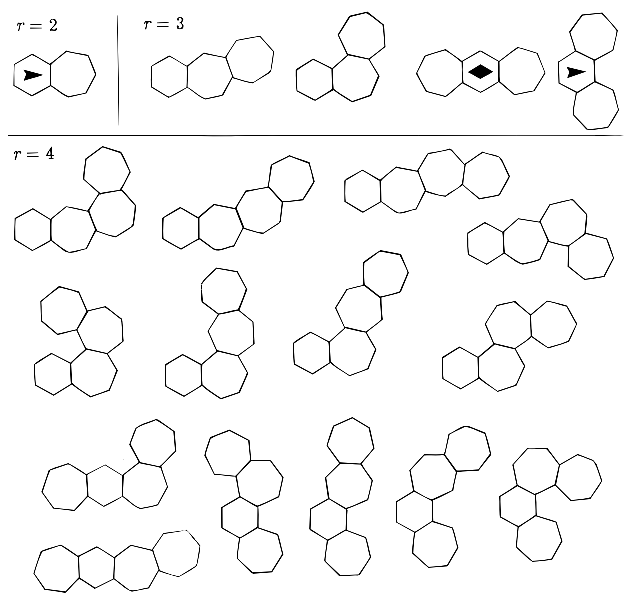

Figure 1. The mono-6-catapolyheptagons with $2 \le r \le 4$. Rhomb: D_{2h} symmetry; arrowhead: C_{2v} symmetry.

The systems of the latter case (Table 9), which may be referred to as unbranched mono-7-catafusenes, are associated with a class of special interest. They contain mono-*q*-polyhexes,[46−49] which are systems containing exactly one *q*-gon each and otherwise only hexagons. Works on different systems of this category have been reported several times in this journal[42,48,50−53] and elsewhere;[43−45,47] the reader is also referred to the bibliography in one of the cited papers.[53]

DEPICTIONS

Figure 1 shows the 1, 4, and 14 unbranched mono-6-catapolyheptagons with $r = 2$, 3, and 4, respectively (cf. Table 8). The eight symmetrical systems of this category are depicted in Figure 2.

Finally, also the forms of some of the smallest unbranched mono-7-catafusenes (cf. Table 9) are shown; see Figure 3.

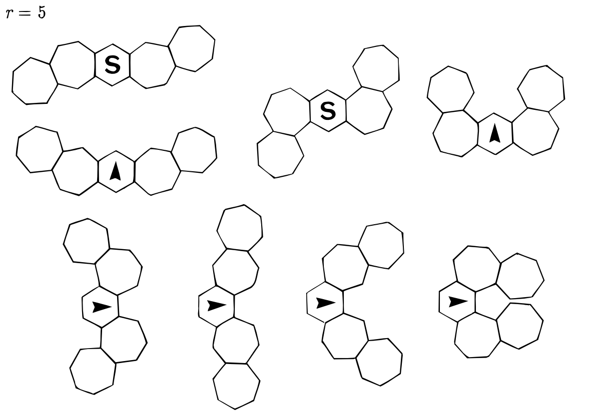

Figure 2. The symmetrical mono-6-catapolyheptagons with $r = 5$. Arrowhead: C_{2v} symmetry; **S**: C_{2h} symmetry.

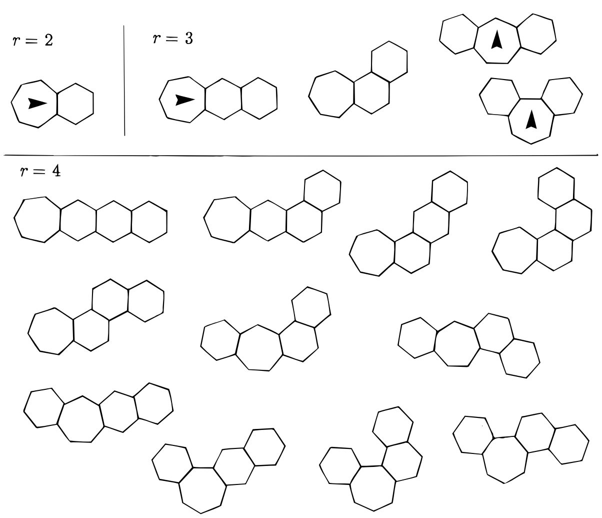

Figure 3. The mono-7-catafusenes with $2 \leq r \leq 4$. Arrowhead: C_{2v} symmetry.

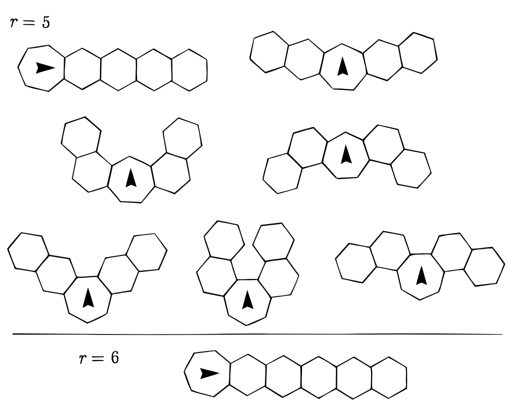

Figure 4. The mono-7-catafusenes with $r = 5$, 6, and C_{2v} symmetry.

The symmetrical (C_{2v}) systems with $r = 5$ and $r = 6$ are found in Figure 4.

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