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Unbranched Catacondensed Polygonal Systems Containing Hexagons and Tetragons

Sven J. Cyvin, Björg N. Cyvin, and Jon Brunvoll

Department of Physical Chemistry, The University of Trondheim, N-7034 Trondheim-NTH, Norway

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An algebraic solution for the isomer numbers of unbranched α-4-catafusenes is presented. An α-4-catafusene is a catacondensed polygonal system consisting of exactly α tetragons each and otherwise only hexagons. This analysis, which makes use of certain triangular matrices including the Pascal triangle, is a continuation of a previous work on di-4-catafusenes. By serendipity, the problem was reversed in the sence that the systems were considered as possessing η hexagons each and otherwise only tetragons. Under this viewpoint the enumeration problem could be solved more directly and led to explicit formulas. Finally, the results are applied to catafusenes as a special case.

INTRODUCTION

In a recent paper[1] on the isomer enumeration of di-4-catafusenes, a complete mathematical solution for the numbers of the unbranched systems of the category in question is reported. A di-4-catafusene is a catacondensed polygonal system consisting of exactly two tetragons and otherwise only hexagons (if any). The cited paper[1] should be consulted for some general references and special references to theoretical investigations on polygonal systems having di-4-catafusenes among them. Furthermore, some relevant works in organic chemistry are cited therein.[1] The scope of the present work is extended to unbranched α-4-catafusenes.

Definition: An α-4-catafusene is a catacondensed polygonal system consisting of exactly α tetragons and otherwise only hexagons (if any).

The number of polygons (or rings) in an α-4-catafusene is identified by the symbol r. Hence the number of hexagons is $r - \alpha$.

In the previous work,[1] a triangular matrix $\boldsymbol{A}$ with elements a_{ij} was introduced. Then the I_r numbers of isomers of the di-4-catafusenes were deduced (a) in terms of summations containing a_{ij}, and (b) by an explicit formula in r.

Then representation in terms of the a_{ij} elements on the one hand, can be generalized to unbranched α-4-catafusenes without too much trouble. On the other hand, the deduction of an explicit formula for the numbers of unbranched α-4-catafusenes is considerably more difficult. In the present work, this goal was achieved by reversing the problem, in a sense, considering the unbranched systems of a class called η-6-catapolytetragons.

Definition: An η-6-catapolytetragon is a catacondensed polygonal system consisting of exactly η hexagons and otherwise only tetragons (if any).

It is clear that, for a given r, the α-4-catafusenes and η-6-catapolytetragons are exactly the same systems. The expressions for the pertinent numbers of isomers are interconnected by the simple relation

$$\eta = r - \alpha \ . \tag{1}$$

It is tempting to attribute this seemingly trivial change of view ($\alpha \rightarrow \eta$) to a serendipity. To wit, there is a very special reason why the treatment of unbranched η-6-catapolytetragons becomes particularly simple. Namely, for a given r, the starting point is a unique catapolytetragon, simply consisting of a linear chain of r tetragons. Subsequently, an unbranched η-6-polytetragon is generated by expanding η tetragons to hexagons. Hereby it must be observed that a polygon can be attached to a hexagon at the end of a chain in three directions. Admittedly, this is a complicating feature in relation to the contraction of hexagons to tetragons in catafusenes, which was the principle used for generating α-4-catafusenes.[1] Nevertheless, it seems fair to say that the gain is larger than the loss. Thus the consideration of η-6-catapolytetragons made it feasible, in a relatively direct way, to deduce the $I_{r\eta}$ numbers of isomers as an explicit formula in r and η, as is demonstrated in the following.

Finally in this work, a fresh approach to the isomer enumertion of unbranched catafusenes is reported.

CHEMICAL FORMULAS

The systems of the present work correspond to polycyclic conjugated hydrocarbons.

A catafusene[2,3] with r rings (all six-membered) is known to have the chemical formula $C_{4r+2}H_{2r+4}$. On contracting α hexagons in a catafusene to tetragons, the formula becomes $C_{4r-2\alpha+2}H_{2r-2\alpha+4}$, which is associated with an α-4-catafusene having r polygons.

A catapolytetragon with r rings (all four-membered) has the formula $C_{2r+2}H_4$. On expanding η tetragons to hexagons, the formula becomes $C_{2r+2\eta+2}H_{2\eta+4}$, which is associated with an η-6-catapolytetragon. The same formula is obtained on substituting α by $r - \eta$ in the α-4-catafusene formula.

BASIC PRINCIPLES AND TRIANGULAR MATRICES

Symmetry

Throughout this work it is assumed $r > 1$. In other words, the trivial cases of one hexagon alone (benzene) and one tetragon alone (cyclobutadiene) are disregarded. Then the unbranched α-4-catafusenes or unbranched η-6-catapolytetragons are distributed among the four symmetry groups D_{2h}, C_{2h}, C_{2v} and C_s.

The numbers of isomers under the specific symmetry groups are identified by the symbols *D, C, M* and *A* in the same order as the groups are mentioned above. In the subsequent sections, these symbols are supplied with the subscripts $r\alpha$ or $r\eta$ when appropriate.

Stupid Sheep Counting

The useful enumeration method which has been called »stupid sheep counting«, is described in the previous paper,[1] where also some of the background of this method is included. In a nutshell, a »crude total« J is determined so that

$$J = D + 2C + 2M + 4A \ , \tag{2}$$

whereupon the I total number of isomers reads

$$I = \frac{1}{4}(J + 3D + 2C + 2M) \ , \tag{3}$$

where A has been eliminated.

Triangular Matrices

In the previous work,[1] a triangular matrix (called $\boldsymbol{A}$) was introduced. Here it is called $\boldsymbol{A}_2$ for reasons which will become apparent presently. In consequence,

$$\boldsymbol{A}_2 = \begin{bmatrix} 1 & & & & \\ 2 & 1 & & & \\ 4 & 4 & 1 & & \\ 8 & 12 & 6 & 1 & \\ 16 & 32 & 24 & 8 & 1 \\ \cdots\cdots & & & & \end{bmatrix} . \tag{4}$$

The Pascal triangle, which often is written as a triangular matrix,[4,5] is here denoted by $\boldsymbol{A}_1$,

$$\boldsymbol{A}_1 = \begin{bmatrix} 1 & & & & \\ 1 & 1 & & & \\ 1 & 2 & 1 & & \\ 1 & 3 & 3 & 1 & \\ 1 & 4 & 6 & 4 & 1 \\ \cdots\cdots & & & & \end{bmatrix} . \tag{5}$$

It has been proved that $\boldsymbol{A}_2 = \boldsymbol{A}_1 \boldsymbol{A}_1$. Now let a generalized triangular matrix $\boldsymbol{A}_\gamma$ be defined by

$$\boldsymbol{A}_\gamma = \boldsymbol{A}_1{}^\gamma . \tag{6}$$

Then the elements of $\boldsymbol{A}_\gamma$, *viz.* $a(\gamma)_{ij}$, where $i, j = 1, 2, 3, \ldots$, are accessible from the following recurrence relation together with its initial conditions:

$$a(\gamma)_{11} = 1 , \quad a(\gamma)_{(i+1)j} = \gamma\, a(\gamma)_{ij} + a(\gamma)_{i(j-1)} , \tag{7}$$

while $a(\gamma)_{i0} = 0$, $a(\gamma)_{ij} = 0$ when $j > i$. Also the explicit expression for the elements under consideration has been found:

$$a(\gamma)_{ij} = \binom{i-1}{j-1} \gamma^{i-j} \,. \tag{8}$$

In the following treatment, also the matrix for a truncated Pascal triangle is invoked; here the top unity is deleted:

$$\boldsymbol{A}_1' = \begin{bmatrix} 1 & 1 & & & & \\ 1 & 2 & 1 & & & \\ 1 & 3 & 3 & 1 & & \\ 1 & 4 & 6 & 4 & 1 & \\ 1 & 5 & 10 & 10 & 5 & 1 \\ \cdots\cdots & & & & & \end{bmatrix} . \tag{9}$$

Similarly, the doubly truncated Pascal triangle emerges by deleting the two top rows; we define:

$$\boldsymbol{A}_1'' = \begin{bmatrix} 1 & 2 & 1 & & & \\ 1 & 3 & 3 & 1 & & \\ 1 & 4 & 6 & 4 & 1 & \\ 1 & 5 & 10 & 10 & 5 & 1 \\ \cdots\cdots & & & & & \end{bmatrix} . \tag{10}$$

When the $\boldsymbol{A}_\gamma$ matrices are called triangular, the matrices $\boldsymbol{A}_1'$ and $\boldsymbol{A}_1''$ may appropriately be called trapezoidal.

It is useful to define the reversing of a matrix as an operation on the triangular and trapezoidal matrices treated above. Then the elements of each row should be reversed; thus, for the triangular matrices,

$$\overline{a}(\gamma)_{ij} = a(\gamma)_{i(i-j+1)} \,, \tag{11}$$

where $\overline{a}(\gamma)_{ij}$ are the elements of the reversed $\boldsymbol{A}_\gamma$, to be denoted by $\overline{\boldsymbol{A}}_\gamma$. One has clearly

$$\overline{\boldsymbol{A}}_1 = \boldsymbol{A}_1 \,, \qquad \overline{\boldsymbol{A}}_1' = \boldsymbol{A}_1' \,, \qquad \overline{\boldsymbol{A}}_1'' = \boldsymbol{A}_1'' \,, \tag{12}$$

but $\overline{\boldsymbol{A}}_2$ different from $\boldsymbol{A}_2$; *cf.* Eq. (4) and:

$$\overline{\boldsymbol{A}}_2 = \begin{bmatrix} 1 & & & & \\ 1 & 2 & & & \\ 1 & 4 & 4 & & \\ 1 & 6 & 12 & 8 & \\ 1 & 8 & 24 & 32 & 16 \\ \cdots\cdots & & & & \end{bmatrix} . \qquad (13)$$

THE UNBRANCHED α-4-CATAFUSENES

General Solution

The solution for the numbers of isomers of the unbranched di-4-catafusenes in terms of $\boldsymbol{A}_2$ matrix elements is treated in details elsewhere.[1] For the sake of brevity, the arguments shall not be repeated here in the generalized

$$J_{r\alpha} = \sum_{j=1}^{r-1} \binom{j+1}{\alpha} a(2)_{(r-1)j}$$

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

$$L_{r\alpha} = \frac{1}{2}\binom{r}{\alpha} - \frac{1}{8}\left[3 + (-1)^{r+\alpha} + (-1)^{\alpha} - (-1)^{r}\right]\binom{\lfloor r/2 \rfloor}{\lfloor \alpha/2 \rfloor}$$

$$C_{r\alpha} = \frac{1}{8}\left[3 + (-1)^{r+\alpha} + (-1)^{\alpha} - (-1)^{r}\right] \sum_{j=1}^{\lfloor r/2 \rfloor - 1} \binom{j}{\lfloor \alpha/2 \rfloor} a(2)_{\lfloor r/2 \rfloor j}$$

$$K_{r\alpha} = \frac{1}{4}\left[1 - (-1)^{r+\alpha} + (-1)^{\alpha} - (-1)^{r}\right] \sum_{j=1}^{\lfloor r/2 \rfloor} \binom{j}{\lfloor \alpha/2 \rfloor} a(2)_{\lfloor r/2 \rfloor j}$$

$$I_{r\alpha} = \frac{1}{4}\left\{\binom{r}{\alpha} + \sum_{j=1}^{r-1}\binom{j+1}{\alpha} a(2)_{(r-1)j} + \left[2 + (-1)^{\alpha} - (-1)^{r}\right] \sum_{j=1}^{\lfloor r/2 \rfloor} \binom{j}{\lfloor \alpha/2 \rfloor} a(2)_{\lfloor r/2 \rfloor j}\right\}$$

Chart 1. Numbers for unbranched α-4-catafusenes, most of them in terms of $\boldsymbol{A}_2$ matrix elements, $a(2)_{ij}$.

TABLE I

Numbers of unbranched α-4-catafusenes of D_{2h} symmetry, $D_{r\alpha}$

r / α	0	1	2	3	4	5	6	7	8	9	10
2	1	0	1								
3	1	1	1	1							
4	1	0	2	0	1						
5	1	1	2	2	1	1					
6	1	0	3	0	3	0	1				
7	1	1	3	3	3	3	1	1			
8	1	0	4	0	6	0	4	0	1		
9	1	1	4	4	6	6	4	4	1	1	
10	1	0	5	0	10	0	10	0	5	0	1

form for the unbranched α-4-catafusenes. It is only mentioned that it is advantageous to treat the cases when α is even or odd separately. Then the separate solutions were merged into expressions valid for both even and odd α values. The deduced formulas are collected in Chart 1.

Here L pertains to the linear systems of C_{2v} symmetry, while K pertains to the C_{2v} systems with a hexagon in the centre and the twofold symmetry axis intersecting two (parallel) edges of this hexagon. In addition, there are C_{2v} systems in a one-to-one correspondence with the C_{2h} systems as *cis*/*trans* isomers. In total, the M number of mirror-symmetrical (C_{2v}) systems is

$$M = L + K + C \ . \tag{14}$$

Matrix Formulation

In Chart 1, $D_{r\alpha}$ and $L_{r\alpha}$ represent the linear systems. The numerical values to $r = 10$ are listed in Tables I and II, respectively. Notice that the numbers of these tables may be interpreted as elements of trapezoidal matrices, say $\boldsymbol{D}$ and $\boldsymbol{L}$, respectively. These matrices are unchanged on reversing:

$$\overline{\boldsymbol{D}} = \boldsymbol{D} \ , \qquad \overline{\boldsymbol{L}} = \boldsymbol{L} \ . \tag{15}$$

The nonvanishing $\boldsymbol{D}$ matrix element (Table I) are exclusively numbers from the Pascal triangle. Specifically, the numbers $D_{2p(2q)}$, where $p = 1, 2, 3, \ldots$; $q = 0, 1, 2, \ldots$, form the $\boldsymbol{A}_1{}'$ matrix of Eq. (9). The same is the case for $D_{2p+1(2q)}$ and $D_{2p+1(2q+1)}$. Furthermore, the $\boldsymbol{L}$ matrix is also accessible from the Pascal triangle since

$$L = \frac{1}{2}(A_1'' - D) , \tag{16}$$

where A_1'' is given by Eq. (10).

TABLE II

Numbers of linear unbranched α-4-catafusenes of C_{2v} symmetry, $L_{r\alpha}$

r / α	0	1	2	3	4	5	6	7	8	9	10
2	0	1	0								
3	0	1	1	0							
4	0	2	2	2	0						
5	0	2	4	4	2	0					
6	0	3	6	10	6	3	0				
7	0	3	9	16	16	9	3	0			
8	0	4	12	28	32	28	12	4	0		
9	0	4	16	40	60	60	40	16	4	0	
10	0	5	20	60	100	126	100	60	20	5	0

This exploitation of the Pascal triangle can be carried further, actually through all the terms of Chart 1. Firstly, the $\boldsymbol{J}$ matrix for the crude totals $J_{r\alpha}$ is given by

$$\boldsymbol{J} = \boldsymbol{A}_2 \boldsymbol{A}_1'' = \boldsymbol{A}_1^2 \boldsymbol{A}_1'' . \tag{17}$$

A portion of this matrix is given below.

$$\boldsymbol{J} = \begin{bmatrix} 1 & 2 & 1 & & & \\ 3 & 7 & 5 & 1 & & \\ 9 & 24 & 22 & 8 & 1 & \\ 27 & 81 & 90 & 46 & 11 & 1 \\ \cdots\cdots & & & & & \end{bmatrix} . \tag{18}$$

This matrix can easily be extended by means of a recurrence relation, which has been found and is given below together with the initial conditions. If the $\boldsymbol{J}$ matrix elements are labeled $\mathscr{J}_{ik} = \mathscr{J}_{r-1(\alpha+1)}$, then

$$\mathscr{J}_{11} = 1 , \quad \mathscr{J}_{12} = 2 , \quad \mathscr{J}_{13} = 1 , \quad \mathscr{J}_{(i+1)k} = 3\mathscr{J}_{ik} + \mathscr{J}_{i(k-1)} , \tag{19}$$

while $\mathscr{J}_{i0} = 0$, $\mathscr{J}_{ik} = 0$ when $k > i + 2$.

A clue to the numbers $C_{r\alpha}$ and $K_{r\alpha}$ of Chart 1 is a trapezoidal matrix with the elements

$$\mathscr{H}_{ik} = \sum_{j=1}^{i} \binom{j}{k-1} a(2)_{ij} \,. \tag{20}$$

In matrix form it is similar to $\boldsymbol{J}$ in Eq. (17), *viz.*

$$\boldsymbol{H} = \boldsymbol{A}_2\,\boldsymbol{A}_1' = \boldsymbol{A}_1^2\,\boldsymbol{A}_1' \,. \tag{21}$$

A portion of the $\boldsymbol{H}$ matrix is given below.

$$\boldsymbol{H} = \begin{bmatrix} 1 & 1 & & & & \\ 3 & 4 & 1 & & & \\ 9 & 15 & 7 & 1 & & \\ 27 & 54 & 36 & 10 & 1 & \\ 81 & 189 & 162 & 66 & 13 & 1 \\ \cdots\cdots & & & & & \end{bmatrix} \tag{22}$$

It has been ascertained that the elements of $\boldsymbol{H}$ obey the same recurrence relation as the elements of $\boldsymbol{J}$; see Eq. (19). However, the initial conditions are slightly different:

$$\mathscr{H}_{11} = \mathscr{H}_{12} = 1 \,, \qquad \mathscr{H}_{(i+1)k} = 3\mathscr{H}_{ik} + \mathscr{H}_{i(k-1)} \,, \tag{23}$$

while $\mathscr{H}_{i0} = 0$, $\mathscr{H}_{ik} = 0$ when $k > i + 1$.

THE UNBRANCHED η-6-CATAPOLYTETRAGONS

Crude Totals

Start from a polytetragon with a given r, *viz.* the linear chain of r tetragons. Expand η of these tetragons to hexagons in all combinatorial ways. To each hexagon which is not at any of the two ends of the chain, a polygon (tetragon or hexagon) can be attached in three directions. Figures 1 and 2 illustrate the cases for $r = 3$ and 4, respectively, while $\eta = 2$ in both cases. In general, the following formula was deduced for the crude totals:

$$J_{r\eta} = \binom{r-2}{\eta} 3^{\eta} + 2\binom{r-2}{\eta-1} 3^{\eta-1} + \binom{r-2}{\eta-2} 3^{\eta-2} . \tag{24}$$

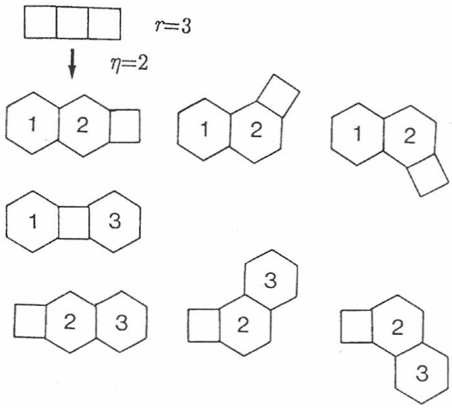

Figure 1. Generation of the $J_{32} = 7$ di-6-catapolytetragons with $r = 3$. The hexagons are numbered according to the sites in the initial polytetragon.

Here the three terms on the right-hand side account for the cases (from the left): no terminal hexagon, one terminal hexagon and two terminal hexagons. An alternative algebraic form of $J_{r\eta}$ is shown in Chart 2. The numeri-

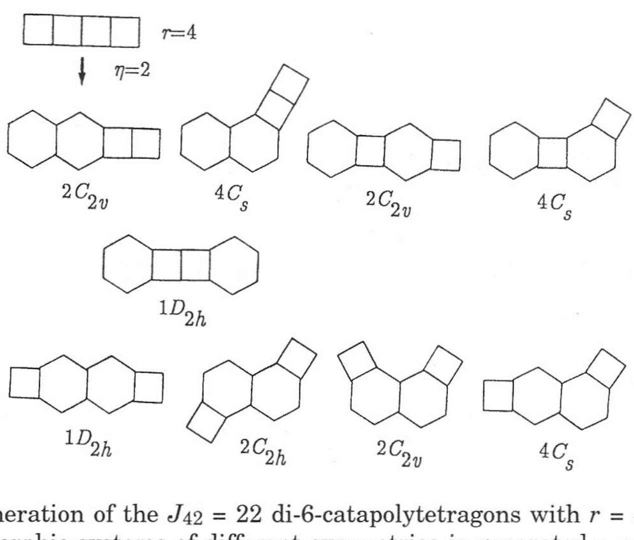

Figure 2. Generation of the $J_{42} = 22$ di-6-catapolytetragons with $r = 4$. Each of the nine nonisomorphic systems of different symmetries is generated a certain number of times as indicated.

$$J_{r\eta} = \frac{(r-2)!}{\eta!(r-\eta)!}\left[9r(r-1) - 4\eta(3r-\eta-2)\right]3^{\eta-2}$$

$$D_{r\eta} = \frac{1}{4}\left[3 + (-1)^{r+\eta} + (-1)^{\eta} + (-1)^{r}\right]\binom{\lfloor r/2 \rfloor}{\lfloor \eta/2 \rfloor}$$

$$L_{r\eta} = \frac{1}{2}\binom{r}{\eta} - \frac{1}{8}\left[3 + (-1)^{r+\eta} + (-1)^{\eta} + (-1)^{r}\right]\binom{\lfloor r/2 \rfloor}{\lfloor \eta/2 \rfloor}$$

$$H_{r\eta} = \frac{(r-1)!}{\eta!(r-\eta)!}(3r-2\eta)\,3^{\eta-1}$$

$$C_{r\eta} = \frac{1}{8}\left[3 + (-1)^{r+\eta} + (-1)^{\eta} - (-1)^{r}\right]\left[H_{\lfloor r/2 \rfloor \lfloor \eta/2 \rfloor} - \binom{\lfloor r/2 \rfloor}{\lfloor \eta/2 \rfloor}\right]$$

$$K_{r\eta} = \frac{1}{4}\left[1 + (-1)^{r+\eta} - (-1)^{\eta} - (-1)^{r}\right]H_{\lfloor r/2 \rfloor \lfloor \eta/2 \rfloor}$$

$$I_{r\eta} = \frac{1}{4}\left\{\binom{r}{\eta} + J_{r\eta} + \left[2 + (-1)^{r+\eta} - (-1)^{r}\right]H_{\lfloor r/2 \rfloor \lfloor \eta/2 \rfloor}\right\},$$

where $J_{r\eta}$ is given above, and

$$H_{\lfloor r/2 \rfloor \lfloor \eta/2 \rfloor} = \frac{(\lfloor r/2 \rfloor - 1)!}{\lfloor \eta/2 \rfloor!\,(\lfloor r/2 \rfloor - \lfloor \eta/2 \rfloor)!}(3\lfloor r/2 \rfloor - 2\lfloor \eta/2 \rfloor)\,3^{\lfloor \eta/2 \rfloor - 1}$$

Chart 2. Numbers for unbranched η-6-catapolytetragons: explicit formulas in η and r.

cal values to $r = 10$ are displayed in Table III. These numbers may be interpreted as a trapezoidal matrix which, by virtue of Eq. (1), is the reversed ***J***, *viz.* ***J***; *cf.* Eq. (18).

TABLE III

Crude totals ($J_{r\eta}$) of unbranched η-6-catapolytetragons

r / η	0	1	2	3	4	5	6	7	8	9	10
2	1	2	1								
3	1	5	7	3							
4	1	8	22	24	9						
5	1	11	46	90	81	27					
6	1	14	79	228	351	270	81				
7	1	17	121	465	1035	1323	891	243			
8	1	20	172	828	2430	4428	4860	2916	729		
9	1	23	232	1344	4914	11718	18144	17496	9477	2187	
10	1	26	301	2040	8946	26460	53298	71928	61965	30618	6561

Linear Systems

The expressions for the $D_{r\eta}$ and $L_{r\eta}$ linear systems of symmetries D_{2h} and C_{2v}, respectively, which are included in Chart 2, are identical to the expressions for $D_{r\alpha}$ and $L_{r\alpha}$ on replacing η by α. This is a consequence of the relations (15). Therefore Tables I and II are also valid for $D_{r\eta}$ and $L_{r\eta}$, respectively, on replacing α by η.

Centrosymmetrical Systems

The $C_{r\eta}$ numbers of unbranched η-6-catapolytetragons can be generated by constructing roughly halves of the systems, or precisely the branches with $\lfloor r/2 \rfloor$ polygons each. In this connection the crude totals $H_{r\eta}$ are defined. These numbers count the D_{2h} systems once and the C_{2h} systems twice like $J_{r\eta,}$ but they are nevertheless different from $J_{r\eta}$. It must be taken into account that the branches are attached either to each other (for even r referring to the whole system) or to a central polygon (for odd r) at one of their ends. Hence the expression for $H_{r\eta}$ contains two terms versus the three terms in $J_{r\eta}$ of Eq. (24):

$$H_{r\eta} = \binom{r-1}{\eta} 3^{\eta} + \binom{r-1}{\eta-1} 3^{\eta-1} \,. \tag{25}$$

These two terms account for no terminal hexagon or one terminal hexagon. The expression (25) was rendered into the form which is included in Chart 2. Numerical values are given in Table IV. As a matter of fact, these numbers

TABLE IV

Crude totals ($H_{r\eta}$) for generating the centrosymmetrical unbranched η-6-catapolytetragons

r / η	0	1	2	3	4	5
1	1	1				
2	1	4	3			
3	1	7	15	9		
4	1	10	36	54	27	
5	1	13	66	162	189	81

are the same as the elements of the $\boldsymbol{H}$ matrix as given in Eq. (32), but with reversed order in each row. In other words, Table IV represents the $\overline{\boldsymbol{H}}$ matrix. Figure 3 illustrates the generation considered here for r = 3 and η = 2.

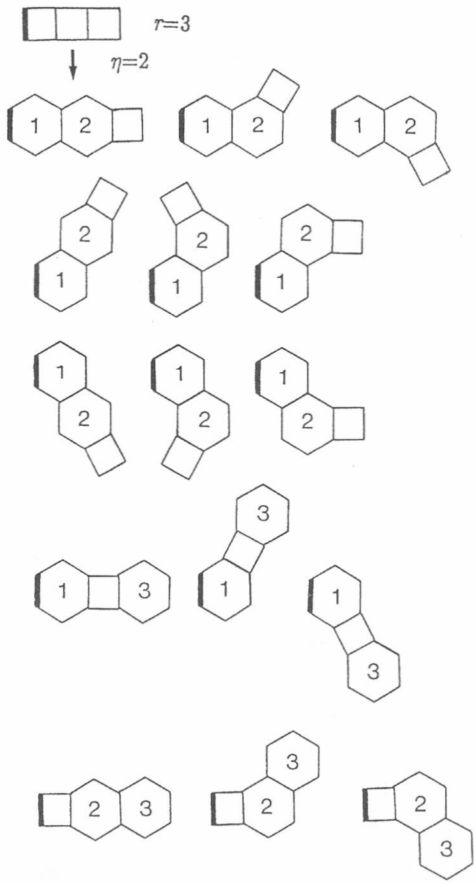

Figure 3. Generation of the H_{32} = 15 di-6-catapolytetragons with r = 3. The hexagons are numbered as in Figure 1. The edge of attachment when forming a centrosymmetrical system is indicated by a heavy stroke.

Now it is a simple matter of an application of stupid sheep counting (see above) to derive the $C_{r\eta}$ numbers. They are

$$C_{r\eta} = \frac{1}{2}\left(H_{\lfloor r/2 \rfloor \lfloor \eta/2 \rfloor} - D_{r\eta}\right) \tag{26}$$

when r and η are both even or when r is odd (arbitrary η). Only when r is even and η is odd the formula (26) is not valid, since $C_{r\eta}$ is obviously zero in these cases. The expression for $C_{r\eta}$ which is entered in Chart 2, is supplied with a factor which makes it valid in general. Numerical values are given in Table V.

TABLE V

Numbers of unbranched η-6-catapolytetragons of C_{2h} symmetry, $C_{r\eta}$

r / η	0	1	2	3	4	5	6	7	8	9	10
2	0	0	0								
3	0	0	0	0							
4	0	0	1	0	1						
5	0	0	1	1	1	1					
6	0	0	2	0	6	0	4				
7	0	0	2	2	6	6	4	4			
8	0	0	3	0	15	0	25	0	13		
9	0	0	3	3	15	15	25	25	13	13	
10	0	0	4	0	28	0	76	0	92	0	40

Mirror-Symmetrical Systems

For every r and η, the mirror-symmetrical unbranched η-6-catapolytetragons (symmetry C_{2v}) are divided into three classes according to Eq. (14):

(i) the $C_{r\eta}$ systems in a one-to-one correspondence with those of C_{2h} as *cis/trans* isomers;

(ii) the $L_{r\eta}$ linear systems;

(iii) the $K_{r\eta}$ systems which constitute the class of the remaining C_{2v} systems to be treated in the following.

The systems under (iii) possess one central hexagon with the twofold symmetry axis intersecting edges of this hexagon as explained under the above treatment of unbranched α-4-catafusenes. It is clear that nonvanishing numbers of $K_{r\eta}$ are only obtained when both r and η are odd numbers, and in these cases

$$K_{r\eta} = H_{\lfloor r/2 \rfloor \lfloor \eta/2 \rfloor} \, . \tag{27}$$

The formula for $K_{r\eta}$ which is valid in general, is entered in Chart 2. The numerical values are those of Table IV, properly spread among zeros.

Total Numbers

The $I_{r\eta}$ total numbers of isomers of unbranched η-6-catapolytetragons are now obtained from a combination of Eqs. (3) and (14):

$$I = \frac{1}{4}\,(J + 3D + 2L + 2K + 4C) \, . \tag{28}$$

TABLE VI

Total numbers ($I_{r\eta}$) of unbranched η-6-catapolytetragon

r / η	0	1	2	3	4	5	6	7	8	9	10
2	1	1	1								
3	1	3	3	2							
4	1	3	9	7	4						
5	1	5	16	29	23	10					
6	1	5	27	62	99	69	25				
7	1	7	39	132	275	351	229	70			
8	1	7	55	221	643	1121	1249	731	196		
9	1	9	72	367	1278	2997	4584	4437	2385	574	
10	1	9	93	540	2322	6678	13458	18012	15597	7657	1681

The resulting algebraic solution is found in Chart 2, and numerical values are exhibited in Table VI.

The above analysis of unbranched η-6-catapolytetragons gives simultaneously the solution for unbranched α-4-catafusenes, as is apparent from Introduction. An explicit formula for $I_{r\alpha}$ is obtained from the expression of Chart 2 by the elementary substitution according to Eq. (1). It was arrived at the following result:

$$I_{r\alpha} = \frac{1}{4}\left\{\binom{r}{\alpha} + (r-2)!\left[\alpha!(r-\alpha)!\right]^{-1}\left[r(r-1) + 4\alpha(r+\alpha-2)\right]3^{r-\alpha-2} + \right.$$

$$+\left[2 + (-1)^{\alpha} - (-1)^{r}\right](\lfloor r/2\rfloor - 1)!\left[\lfloor\alpha/2\rfloor!\,(\lfloor r/2\rfloor - \lfloor\alpha/2\rfloor)!\right]^{-1} \times \tag{29}$$

$$\left. \times (\lfloor r/2\rfloor + 2\lfloor\alpha/2\rfloor)\, 3^{\lfloor r/2\rfloor + 2\lfloor\alpha/2\rfloor - 1}\right\} .$$

MATHEMATICAL IMPLICATIONS

The above analysis implies explicit expressions for the summations of Chart 1. In fact, these expressions are easily deduced from a crucial identity, *viz.*:

$$\sum_{j=1}^{i}\binom{j-1}{k-1} a(\gamma)_{ij} = \sum_{j=1}^{i}\binom{i-1}{j-1}\binom{j-1}{k-1}\gamma^{i-j} = \binom{i-1}{k-1}(\gamma+1)^{i-k} , \tag{30}$$

where Eq. (8) has been applied. Many identities between binomial coefficients similar to (30) are known,[4,6] although this particular one has not been located elsewhere. It has been proved in a direct way without invoking enumerations of chemical graphs, but this is not the place for a report on this pure mathematical piece of the present investigations. Here the special case of (30) for $\gamma = 2$ is of interest:

$$\sum_{j=1}^{i} \binom{i-1}{j-1}\binom{j-1}{k-1} 2^{i-j} = \binom{i-1}{k-1} 3^{i-k} . \tag{31}$$

Herefrom the numbers $\mathscr{H}_{ik}$ of Eq. (20) are readily obtained by a few simple manipulations:

$$\begin{aligned}\mathscr{H}_{ik} &= \sum_{j=1}^{i} \binom{i-1}{j-1}\binom{j}{k-1} 2^{i-j} = \sum_{j=1}^{i} \binom{i-1}{j-1}\left[\binom{j-1}{k-2} + \binom{j-1}{k-1}\right] 2^{i-j} = \\ &= \binom{i-1}{k-2} 3^{i-k+1} + \binom{i-1}{k-1} 3^{i-k} .\end{aligned} \tag{32}$$

The result (32) is consistent with the expression (25) for $H_{r\eta} = \mathscr{H}_{r(r-\eta+1)}$. In other words, Eq. (25) is rederived from (32) on inserting $i = r$, $k = r - \eta + 1$.

Similarly,

$$\begin{aligned}\mathscr{J}_{ik} &= \sum_{j=1}^{i} \binom{j+1}{k-1} a(2)_{ij} = \sum_{j=1}^{i} \binom{i-1}{j-1}\binom{j+1}{k-1} 2^{i-j} = \sum_{j=1}^{i} \binom{i-1}{j-1}\left[\binom{j}{k-2} + \binom{j}{k-1}\right] 2^{i-j} = \\ &= \binom{i-1}{k-3} 3^{i-k+2} + 2\binom{i-1}{k-2} 3^{i-k+1} + \binom{i-1}{k-1} 3^{i-k} .\end{aligned} \tag{33}$$

Herefrom one obtains the expression (24) for $J_{r\eta} = \mathscr{J}_{r-1(r-\eta+1)}$.

UNBRANCHED CATAFUSENES

The enumeration problem for unbranched catafusenes has been solved a long time ago,[2] revisited more recently,[7,8] and finally included in a review.[9]

The unbranched catafusenes with exclusively r hexagons ($r > 1$) are considered. It is clear that these systems emerge as special cases of the unbranched α-4-catafusenes for $\alpha = 0$, and also as special cases of the unbranched η-6-catapolytetragons for $\eta = r$. In the framework of the present

$$J_r = \sum_{j=1}^{r-1} a(2)_{(r-1)j} = 3^{r-2}$$

$$D_r = 1, \quad L_r = 0$$

$$C_r = \frac{1}{2} \sum_{j=1}^{\lfloor r/2 \rfloor - 1} a(2)_{\lfloor r/2 \rfloor j} = \frac{1}{2} \left(3^{\lfloor r/2 \rfloor} - 1\right)$$

$$K_r = \frac{1}{2}\left[1-(-1)^r\right] \sum_{j=1}^{\lfloor r/2 \rfloor} a(2)_{\lfloor r/2 \rfloor j} = \frac{1}{2}\left[1-(-1)^r\right] 3^{\lfloor r/2 \rfloor - 1}$$

$$I_r = \frac{1}{4}\left\{1 + 3^{r-2} + \left[3-(-1)^r\right] 3^{\lfloor r/2 \rfloor - 1}\right\}$$

Chart 3. Numbers for unbranched catafusenes.

formalism, the expressions of Chart 3 are obtained immediately. The expression for the total numbers (I_r) therein, is the simplest and most compact form which has been found for these numbers.

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SAŽETAK

Nerazgranani katakondenzirani poligonski sustavi sa šesterokutima i četverokutima

Sven J. Cyvin, Björg N. Cyvin i Jon Brunvoll

Prikazano je algebarsko rješenje za brojeve izomera nerazgrananih α-4-katafuzena. α-4-katafuzen je katakondenzirani poligonski sustav koji sadrži šesterokute i točno α četverokuta. Ova analiza, u kojoj se rabe određene trokutaste matrice, uključujući Pascalov trokut, nastavak je prethodnog rada na di-4-katafuzenima. Sretnom slučajnošću, problem je obrnut tako da su sustavi razmatrani kao da sadrže četverokute i točno η šesterokuta. Ovako postavljen, problem prebrojavanja može se izravnije riješiti i vodi do posebnih formula. Konačno, rezultati su primijenjeni na katafuzene, kao na posebni slučaj.