Di-4-Catafusenes: A New Class of Polygonal Systems Representing Polycyclic Conjugated Hydrocarbons*

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Di-4-catafusenes are defined as catacondensed polygonal systems consisting of two tetragons each and otherwise only hexagons. Di-4-catafusenes are enumerated by combinatorial constructions and by computer programming. For the unbranched systems (nonhelicenic + helicenic), as the main result of the present work, a complete mathematical solution is reported. A new algebraic approach has been employed, which involves a triangular matrix with some interesting mathematical properties.

INTRODUCTION

Polygonal systems\textsuperscript{2,3} are chemical graphs\textsuperscript{4} which represent condensed polycyclic conjugated hydrocarbons. In precise terms, a polygonal system is a system consisting of simply connected polygons, where any two polygons either share exactly one edge or are disjoint. Many subclasses of polygonal systems have been defined. For instance, biphenylenoids\textsuperscript{5} consist of exactly one tetragon each and otherwise only hexagons. A similar subclass of polygonal systems is introduced in the present work. Only catacondensed systems, \textit{viz.} those without internal vertices, are considered here.

\textit{Definition:} A di-4-catafusene is a catacondensed polygonal system consisting of exactly two tetragons and otherwise only hexagons (if any).

A prototype of di-4-catafusenes is \( C_{18}H_{10} \) [3]phenylene or terphenylene, which has been synthesized both in the angular\textsuperscript{6,7} and in the linear form\textsuperscript{8-11}.

\* Dedicated to Professor Nenad 13-ic\textsuperscript{1}, on the occasion of his appointment to the position of Editor-in-Chief of this Journal.
Many theoretical investigations have been conducted on different polygonal systems with di-4-catafusenes among them.\textsuperscript{2,12–30} These works deal with conjugated circuits, Kekulé and algebraic structure counts, local aromaticity, total $\pi$-electron energy, cyclic conjugation, etc. Some of them are devoted to [h]phenylenes, but none of them treat exclusively the systems defined here as di-4-catafusenes.

In the present work, the di-4-catafusenes were generated, enumerated and classified. Different methods were employed: combinatorial constructions, computer programming, and algebraic deductions. In particular, a complete mathematical solution was achieved for the unbranched systems by means of a new approach, which led to a special triangular matrix. The useful formulation in terms of generating functions\textsuperscript{3,31} is applied to some extent.

The number of polygons (or rings) in a di-4-catafusene is identified by the symbol $r$. Then, the chemical formula reads $C_{4r-2}H_{2r}$.

**COMBINATORIAL CONSTRUCTIONS**

The smallest di-4-catafusenes (see Figure 1) were constructed by systematic drawings. Hereby the different positions of the two tetragons in relation to each other were considered. One might speak about "stratum" in analogy with the generation of double coronoids.\textsuperscript{32}

**COMPUTER PROGRAMMING**

The method of combinatorial constructions described above is not particularly convenient for computerization. Instead, a computer algorithm was based on the generation of catacondensed benzenoids or catabenzenoids (consisting of hexagons only), followed by a conversion of two hexagons in each system to tetragons. A more detailed description of the procedure follows.

In a catabenzenoid, mark the $L_1$ and $L_2$ mode hexagons,\textsuperscript{33,34} viz. the terminal and linearly annelated ones. Convert two of these hexagons to tetragons in all possible ways, assuring that isomorphic systems are avoided if the catabenzenoid has a symmetry higher than $C_s$, viz. $D_{2h}$, $C_{2v}$, or $C_{2v}$. Hereby the $A_2$ mode (angularly annelated) hexagons are neglected, since a conversion to tetragon will straighten out the system so that it becomes isomorphic with one already generated from conversion of $L_2$. Finally, an $A_3$ mode (branching) hexagon cannot be converted to a tetragon at all.

The described algorithm is illustrated in Figure 2. Symmetrically nonequivalent $L_1$ and $L_2$ mode hexagons are indicated by asterisks, the rest of them by dots. The numerals indicate how many nonisomorphic di-4-catafusenes are generated from each of the catabenzenoids.
<table>
<thead>
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<th>$r = 2$</th>
<th>$r = 3$</th>
<th>$r = 4$</th>
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<td>$C_{18}H_{10}$</td>
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![Diagram of di-4-catafusenes with $r = 2$, 3, 4, and 5](image)

Figure 1. The 1, 3, 10 and 36 di-4-catafusenes with $r = 2$, 3, 4 and 5, respectively. Branching hexagons are marked with asterisks.
Figure 2. Generation of the 10 di-4-catafusenes with \( r = 4 \) by conversion of hexagons to tetragons in catabenzenoids.

### TABLE I

Numbers of nonhelicenic unbranched di-4-catafusenes

<table>
<thead>
<tr>
<th>( r )</th>
<th>( D_{2h} )</th>
<th>( C_{2h} )</th>
<th>( C_{2v} )</th>
<th>( C_s )</th>
<th>Total</th>
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### TABLE II

Numbers of nonhelicenic branched di-4-catafusenes

<table>
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<tr>
<th>( r )</th>
<th>( D_{2h} )</th>
<th>( C_{2h} )</th>
<th>( C_{2v} )</th>
<th>( C_s )</th>
<th>Total</th>
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</table>
The numerical results are collected in Tables I and II for the unbranched and branched di-4-catafusenes, respectively. It is emphasized that the numbers pertain to geometrically planar or nonhelicenic\textsuperscript{35} systems only. Nonhelicenic di-4-catafusenes are systems that can be generated from nonhelicenic catabenzenoids. On the other hand, helicenic di-4-catafusenes can be generated in the same way (by conversion of hexagons to tetragons) from cata-condensed helicenes (helicenic catafusenes).\textsuperscript{35}

**ALGEBRAIC SOLUTION FOR UNBRANCHIED SYSTEMS**

*Outline of the Method*

A complete mathematical solution was deduced for the numbers of unbranched di-4-catafusenes, nonhelicenic and helicenic systems taken together. Basically, the same principles were used as on the classical enumeration of unbranched catafusenes by Balaban and Harary,\textsuperscript{36} which has been revisited elsewhere.\textsuperscript{35,37} The method\textsuperscript{38} has been described under the name "stupid sheep counting« (where "stupid« refers to the counting not to the sheep).\textsuperscript{3,39} The term "crude total« belongs to this description. The main line of the stupid sheep counting applied to the unbranched di-4-catafusenes is specified in the following.

For a given number of polygons \((r)\), the crude total, \(J_r\), counts the \(D_{2h}\) systems once, the \(C_{2h}\) and \(C_{2v}\) systems twice, and the \(C_s\) systems four times. Hence,

\[
J_r = D_r + 2C_r + 2M_r + 4A_r
\]  

(1)

where \(D_r\), \(C_r\), \(M_r\) and \(A_r\) pertain to the symmetry groups in the same order as specified above. The total number of systems, say \(I_r\), is simply

\[
I_r = D_r + C_r + M_r + A_r
\]  

(2)

On eliminating \(A_r\) from Eqs. (1) and (2), the following is obtained:

\[
I_r = \frac{1}{4}(J_r + 3D_r + 2C_r + 2M_r)
\]  

(3)

Hence, in order to solve the problem, one has to enumerate specifically the symmetrical \((D_{2h}, C_{2h}\) and \(C_{2v}\) systems, in addition to finding the crude totals.

The generating functions for the numbers of Eq. (3) are defined by:
\[ I(x) = \sum_{r=2}^{\infty} I_r x^r, \quad J(x) = \sum_{r=2}^{\infty} J_r x^r, \quad D(x) = \sum_{r=2}^{\infty} D_r x^r, \]

\[ C(x) = \sum_{r=4}^{\infty} C_r x^r, \quad M(x) = \sum_{r=3}^{\infty} M_r x^r. \]

(4)

**Triangular Matrices**

Define the numbers:

\[ a_{11} = 1, \quad a_{i+1,j} = 2a_{ij} + a_{i,j-1} \]

while \( a_{i0} = 0, \) \( a_{ij} = 0 \) when \( j > i \). Collect these numbers into a triangular \( A \) matrix as:

\[
\begin{array}{cccccc}
  i/j & 1 & 2 & 3 & 4 & 5 & 6 \\
 1 & 1 & & & & & \\
 2 & 2 & 1 & & & & \\
 3 & 4 & 4 & 1 & & & \\
 4 & 8 & 12 & 6 & 1 & & \\
 5 & 16 & 32 & 24 & 8 & 1 & \\
 6 & 32 & 80 & 80 & 40 & 10 & 1 \\
\end{array}
\]

Additional sets of numbers are defined similarly by:

\[ b_{11} = 1, \quad b_{i+1,j} = 2b_{ij} + b_{i,j-1} + \delta_{i+1,j} \]

while \( b_{i0} = 0, \) \( b_{ij} = 0 \) when \( j > i \). Here, \( \delta_{uv} \) is the Kronecker delta: \( \delta_{uv} = 0 \) when \( u \neq v, \delta_{uu} = 1 \). Another triangular matrix \( B \) is constructed:

\[
\begin{array}{cccccc}
  i/j & 1 & 2 & 3 & 4 & 5 & 6 \\
 1 & 1 & & & & & \\
 2 & 2 & 2 & & & & \\
 3 & 4 & 6 & 3 & & & \\
 4 & 8 & 16 & 12 & 4 & & \\
 5 & 16 & 40 & 40 & 20 & 5 & \\
 6 & 32 & 96 & 120 & 80 & 30 & 6 \\
\end{array}
\]

\[
\text{.........}
\]
The $A$ and $B$ matrices are closely related; it was proved that:

$$b_{ij} = \frac{1}{2} a_{(i+1)j} .$$  \hspace{1cm} (7)

**Crude Total**

Elements of the $A$ matrix are chosen so that the sum along a row gives the crude total for unbranched catafusenes\(^{35}\) with $i+1$ hexagons;

$$\sum_{j=1}^{i} a_{ij} = 3^{i-1} .$$  \hspace{1cm} (8)

In matrix notation:

$$A \{ 1, 1, 1, 1, \ldots \} = \{ 1, 3, 9, 27, \ldots \} .$$  \hspace{1cm} (9)

Furthermore, the individual $a_{ij}$ elements count the systems where $r = i + 1$ and $j + 1$ is the number of the $L_1$ and $L_2$ mode hexagons taken together. Therefore,

$$J_{i+1} = \sum_{j=1}^{i} \binom{j+1}{2} a_{ij} .$$  \hspace{1cm} (10)

holds for the crude totals of unbranched di-4-catafusenes; in matrix notation:

$$A' \{ \binom{2}{2}, \binom{3}{2}, \binom{4}{2}, \binom{5}{2}, \ldots \} = \{ 1, 5, 22, 90, \ldots \} .$$  \hspace{1cm} (11)

The pertinent generating function in expanded form is

$$J(x) = x^2 + 5x^3 + 22x^4 + 90x^5 + 351x^6 + 1323x^7 + \ldots$$  \hspace{1cm} (12)

where any number of the coefficients is accessible from the above relations.

**Dihedral and Linear Mirror-Symmetrical Systems**

The dihedral ($D_{2h}$) systems under consideration are linear, and their numbers are

$$D_r = \left\lfloor \frac{r}{2} \right\rfloor$$  \hspace{1cm} (13)
when $|X|$ (the floor of $X$) is the largest integer not larger than $X$. The corresponding generating function is:

$$D(x) = x^2(1 - x)^{-1}(1 - x^2)^{-1} = x^2 + x^3 + 2x^4 + 2x^5 + 3x^6 + 3x^7 + \ldots \quad (14)$$

Let $L_r$ be the number of linear mirror-symmetrical systems; they form a subclass of the $M_r$ systems, which belong to $C_{2v}$. Then, by a little bit of combinatorics, where the stupid sheep counting can be evoked again, the following is found:

$$L_r = \frac{1}{2} \left( \binom{r}{2} - \left\lfloor \frac{r}{2} \right\rfloor \right) \quad (15)$$

and the associated generating function

$$L(x) = x^3(1-x)^{-2}(1-x^2)^{-1} = x^3 + 2x^4 + 4x^5 + 6x^6 + 9x^7 + 12x^8 + \ldots \quad (16)$$

**Centrosymmetrical Systems**

In the enumeration of the $C_r$ centrosymmetrical ($C_{2h}$) systems, the $B$ matrix comes into operation. The sum along a row of $B$ gives the numbers of unbranched $C_{2h}$ catafusenes with $2i + 2$ and with $2i + 3$ hexagons:

$$\sum_{j=1}^{i} b_{ij} = \frac{1}{2}(3^i - 1). \quad (17)$$

In matrix notation:

$$B \{1, 1, 1, 1, \ldots\} = \{1, 4, 13, 40, \ldots\} \quad (18)$$

Now, it is found for the di-4-catafusenes under consideration that

$$C_{2i+2} = C_{2i+3} = \sum_{j=1}^{i} jb_{ij} = \frac{1}{2} \sum_{j=1}^{i} ja_{i+1j}. \quad (19)$$

In matrix notation:

$$B \{1, 2, 3, 4, \ldots\} = \{1, 6, 25, 92, \ldots\} \quad (20)$$

or
\( \frac{1}{2}(A - I)\{1, 2, 3, 4, 5, \ldots\} = \{0, 1, 6, 25, 92, \ldots\} \) \hspace{1cm} (21)

where \( I \) is the identity matrix.

With regard to the formalism of generating functions, it is expedient to introduce \( c_i \) as expression (19), and

\[
c(x) = \sum_{i=1}^{\infty} c_i x^i = x + 6x^2 + 25x^3 + 92x^4 + 321x^5 + 1090x^6 + \ldots
\] \hspace{1cm} (22)

In terms of this function, one finds that

\[
C(x) = x^2(1 + x)c(x^2) = x^4 + x^5 + 6x^6 + 6x^7 + 25x^8 + 25x^9 + \ldots
\] \hspace{1cm} (23)

**Mirror-Symmetrical Systems**

The mirror-symmetrical \((C_{2i})\) unbranched di-4-catafusenes with numbers \( M_k \) are divided into three subclasses according to

\[
M_k = L_k + C_k + K_k .
\] \hspace{1cm} (24)

The numbers \( L_k \) pertain to the linear systems, which are treated above. The \( C_k \) systems stand in a one-to-one correspondence to the centrosymmetrical systems as *cis/trans* isomers.

There remains a class of \( K_k \) systems, which comes up for odd \( r \) values only. In a similar way as in the case of \( C_r \), the following was found:

\[
K_{2i+1} = \sum_{j=1}^{i} ja_{ij} \] \hspace{1cm} (25)

\[
A\{1, 2, 3, 4, \ldots\} = \{1, 4, 15, 54, \ldots\} . \] \hspace{1cm} (26)

In the formalism of generating functions, introduce \( k_i \) as expression (25). Consequently,

\[
k(x) = \sum_{i=1}^{\infty} k_i x^i = x + 4x^2 + 15x^3 + 54x^4 + \ldots
\] \hspace{1cm} (27)

and
\[ K(x) = \sum_{r=3}^{\infty} K_r x^r = xk(x^2) = x^3 + 4x^5 + 15x^7 + 54x^9 + 189x^{11} + \ldots \tag{28} \]

**Further Developments**

The expressions in Eqs. (19) and (25) were obtained in explicit forms by a lengthy derivation, which will not be included here; the result is:

\[ C_{2i+2} = C_{2i+3} = \frac{1}{2}[(i+3)3^{i-1} - (i+1)] \tag{29} \]

\[ K_{2i+1} = (i+2)3^{i-2}. \tag{30} \]

In consequence, functions \( c(x) \) and \( k(x) \) of Eqs. (22) and (27), respectively, are obtainable in explicit forms. The following results were deduced:

\[ c(x) = x(1 - 2x - x^2)(1-x)^{-2}(1-3x)^{-2} \tag{31} \]

\[ k(x) = x(1 - 2x)(1 - 3x)^{-2}. \tag{32} \]

Also, the crude total Eq. (10) was deduced in explicit form by tedious combinatorial considerations. Here, we only give the result:

\[ J_{i+1} = \frac{1}{2}(i+1)(i+8)3^{i-3}. \tag{33} \]

The corresponding generating function (12) is

\[ J(x) = x^2 \left(1 - 4x + 4x^2\right)(1 - 3x)^{-3}. \tag{34} \]

**Complete Solution**

The above analysis made it possible to express the \( I_r \) numbers of unbranched di-4-catapusenes by finite summation in terms of the \( a_{ij} \) elements, which are accessible through Eq. (5). The result is:

\[ I_r = \frac{1}{4} \sum_{j=1}^{r-1} \binom{j+1}{2} a_{(r-1)j} + \binom{r}{2} + \frac{1}{2} \sum_{j=1}^{[r/2]} ja_{r/2,j} + \sum_{j=1}^{(r-1)/2} ja_{(r-1)/2,j}. \tag{35} \]

It is understood that \( a_{ij} \) is equal to zero if \( t \) is not an integer; therefore, the last summation in Eq. (29) is effective only for \( r = 3, 5, 7, \ldots \). The sum-
TABLE III

Numbers of unbranched di-4-catafusenes
(nonhelicenic + helicenic)

<table>
<thead>
<tr>
<th>r</th>
<th>(D_{2h})</th>
<th>(C_{2h})</th>
<th>(C_{2v})</th>
<th>(C_{s})</th>
<th>Total</th>
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</table>

mations can be substituted by virtue of relations (29), (30), and (33), yielding the following result:

\[
I_r = \frac{1}{4} \left[ \frac{1}{2} r(r + 7)3^{r-4} + \left(\frac{r}{2}\right) \right] + 2 \left[ \frac{r/2 + 2}{3} \right] 3^{r/2 - 2} \left[ \frac{r/2 - 1}{2} \right] (r + 3)3^{(r-5)/2} \right].
\] (36)

This formula is explicit in \(r\). Finally, we give the corresponding generation function:

\[
I(x) = \frac{1}{4} x^2 (1 - 4x + 4x^2)(1 - 3x)^{-3} + (3 - x)(1 - x)^{-2}(1 - x^2)^{-1} +
\]

\[
+ 4x^2(1 - 2x^2 - x^4)(1 - x)^{-1}(1 - x^2)^{-1}(1 - 3x^2)^{-2} + 2x(1 - 2x^2)(1 - 3x^2)^{-2} \right].
\] (37)

Numerical values of \(I_r\), including the distributions of these numbers into different symmetry groups, are collected in Table III.

BACK TO COMBINATORIAL CONSTRUCTIONS

The totals in Tables I – III display the rapidly increasing series of integers when \(r\) increases. Very soon, these numbers seem to exceed all imaginable needs in organic chemistry. Nevertheless, the integer series of this
TABLE IV
Numbers of helicenic unbranched di-4-catafuse-nes

<table>
<thead>
<tr>
<th>$r$</th>
<th>$C_{2h}$</th>
<th>$C_{2v}$</th>
<th>$C_s$</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>7</td>
<td>0</td>
<td>1</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>8</td>
<td>0</td>
<td>4</td>
<td>35</td>
<td>39</td>
</tr>
<tr>
<td>9</td>
<td>0</td>
<td>9</td>
<td>208</td>
<td>217</td>
</tr>
<tr>
<td>10</td>
<td>1</td>
<td>22</td>
<td>1098</td>
<td>1121</td>
</tr>
<tr>
<td>11</td>
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<td>46</td>
<td>5169</td>
<td>5216</td>
</tr>
<tr>
<td>12</td>
<td>7</td>
<td>89</td>
<td>22860</td>
<td>22956</td>
</tr>
<tr>
<td>13</td>
<td>9</td>
<td>209</td>
<td>95852</td>
<td>96070</td>
</tr>
<tr>
<td>14</td>
<td>47</td>
<td>356</td>
<td>386990</td>
<td>387393</td>
</tr>
<tr>
<td>15</td>
<td>55</td>
<td>862</td>
<td>1513880</td>
<td>1514797</td>
</tr>
</tbody>
</table>

kind have considerable interest in mathematical chemistry and in pure mathematics. In order to be really useful, it is important that the deduced numbers are exact, no matter how large. This feature is important for several reasons. Firstly, subclasses of different systems are often enumerated in one way and may include small numbers even of chemical interest, but they may add up to large totals enumerated in a different way. Then, a check of the first calculations would be meaningless if one could not trust the large numbers to be exact. Secondly, enumerations may involve relatively small differences between large numbers. Examples of this case are treated in the following.

It is observed that the computer-generated numbers in Table I and the numbers from algebraic solutions in Table III are identical up to $r = 5$. This is as it should be and already a good check, since the smallest helicenic catafusene is known to occur at $r = 6$. In general, the numbers of the helicenic systems under consideration are obtained by subtracting the numbers of Table I from those of Table III. The results are entered in Table IV. Here, for instance, the totals 39 and 217 ($r = 8, 9$) emerge from the differences 1249 – 1210 and 4437 – 4220, respectively.

![Figure 3. Generation of the 5 helicenic unbranched di-4-catafuse-nes with $r = 7$ by conversion of hexagons to tetragons in catafusene.](image-url)
The method of combinatorial constructions (see above) was used to generate all the helicenic unbranched di-4-catafusenes for \( r \leq 9 \). This was a relatively easy task since the forms of the corresponding catafusenes are available.\textsuperscript{35} As a pleasing fact, the relevant numbers of Table IV were indeed reproduced. The procedure is exemplified for \( r = 7 \) in Figure 3. It should be compared with Figure 2 with regard to the marking of hexagons and indicated numbers. However, representation in terms of dualists\textsuperscript{4,35,36,41} is employed in Figure 3.

REFERENCES


**SAŽETAK**

Di-4-katafuzeni: nova klasa poligonskih sustava koji predstavljaju policikličke konjugirane ugljikovodike

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Di-4-katafuzeni definirani su kao katakondenzirani poligonski sustavi koji se sastoje od šesterokuta i točno dva četverokuta. Di-4-katafuzeni prebrojani su kombinatornim i računalnim postupcima. Kao glavni rezultat u radu, prikazano je cjelovito matematičko rješenje za nerazgranate sustave (helicinske i nehelicinske, zajedno). Pri tome je upotrijebljen nov algebarski pristup koji uključuje trokutastu matricu zaminljivih matematičkih svojstava.