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Enumeration of Poly-5-catafusenes Representing a Class of Catacondensed Polycyclic Conjugated Hydrocarbons

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Abstract

This work deals with isomer enumerations of α-5-catafusenes. An α-5-catafusene is a catacondensed polygonal system consisting of α pentagons and otherwise only hexagons (if any). The numbers of isomers of mono-5-catafusenes and tri-5-catafusenes from computer programming are reported. For the I_r numbers of unbranched α-5-catafusenes, where r is the number of polygons, a complete mathematical solution is described. A new approach is employed, which involves a triangular matrix with interesting mathematical properties. The ultimate result is an explicit formula for I_r in r and α.

Introduction

In polycyclic conjugated hydrocarbons the six-membered (benzenoid) rings are by far the most abundant ones, but also other kinds are important, especially the five-membered rings. The corresponding chemical graphs[1] consist of hexagons and pentagons, where any two polygons either share exactly one edge or are disjointed. Several classes of such graphs have been studied with great interest: fluoranthenoids/fluorenoids[2-5] contain exactly one pentagon each and otherwise only hexagons, indacenoids[6,7] contain two pentagons each, while the polypentagons[8] consist of pentagons exclusively.

In the present work the poly-5-catafusenes, or more precisely α-5-catafusenes, are studied with regard to enumerations of their isomers. An α-5-catafusene consists of α pentagons and otherwise only hexagons (if any). These systems are catacondensed in the sense that they do not possess any internal vertices; no vertex is common to three polygons.

Certain subclasses of the α-5-catafusenes are enumerated by computer programming. Furthermore, a complete mathematical solution for the numbers of nonisomorphic unbranched α-5-catafusenes is reported. In the mathematical analysis a new approach is employed, which involves certain original triangular and trapezoidal matrices with interesting properties. The definitions of the different matrix elements resemble the definition of Stirling numbers of the second kind,[9,10] but they are not identical.

Basic Principles

Definitions. A catafusene[11] is a simply connected catacondensed polyhex.[12] It may be a catabenzenoid or a catahelicene, depending on whether it is nonhelicenic or helicenic, respectively. A helicenic polyhex possesses overlapping edges when drawn in a plane (with congruent regular hexagons).

Any α-5-catafusene can be obtained from a catafusene on contracting α of its hexagons to pentagons.

The α-5-catafusenes are divided into α-5-catabenzenoids and α-5-catahelicenes. By definition,

History

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these subclasses are generated from contractions of hexagons to pentagons in catabenzoids or catahelicenes, respectively. A catahelicene possesses at least one overlapping edge when drawn with regular hexagons. Notice that the present definition of α-5-catahelicenes is based on this overlapping in catahelicenes but does not say anything about overlapping after the contractions.

The total number of polygons (or rings) in an α-5-catafusene or catafusene (which corresponds to $\alpha = 0$) is presently identified by the symbol r. Throughout in the following, the trivial cases of $r = 1$ are disregarded.

Contraction. The contraction of rings or polygons is frequently encountered, both in preparative organic chemistry and in theoretical works.[13,14]

A hexagon of a catafusene (with more than one hexagon) is in a mode[15,16] L_1, L_2, A_2, or A_3 (see Figure 1). These modes are described as L_1 terminal; L_2 linearly annelated; A_2 angularly annelated; and A_3 branched. A catafusene is branched or unbranched when it possesses or does not possess an A_3-mode hexagon, respectively.

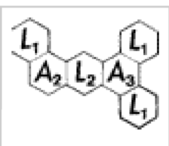

Figure 1 Modes of hexagons in a catafusene.

In a catafusene, the L_1, L_2, and A_2 (but not A_3) mode hexagons can be contracted to pentagons. The A_2 and L_2 modes are known to be associated with a kinked and a linear configuration, respectively. When an A_2-hexagon is contracted, the resulting configuration is again kinked. When an L_2-hexagon is contracted, the configuration transforms from linear to kinked. Consider, for instance $L_1L_2L_1$ (anthracene) and $L_1A_2L_1$ (phenanthrene). On contracting the central hexagons to pentagons in these two nonisomorphic systems (one linear and one kinked), two isomorphic (kinked) systems emerge. Here the terms “linear” and “kinked” are based on regular polygons.

In Figure 2, different contractions of one hexagon to pentagon in the five catafusenes with four hexagons are illustrated. Only L_1 and A_2 mode hexagons are contracted, and only one hexagon is contracted out of sets of symmetrically equivalent hexagons. In this way a complete set of nonisomorphic mono-5-catafusenes with four polygons was generated. These principles of generating nonisomorphic systems are straightforwardly extended to α-5-catafusenes.

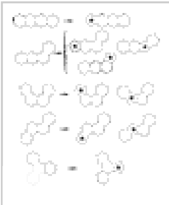

Figure 2 Generation of the nine nonisomorphic mono-5-catafusenes by contractions of hexagons in catafusenes. Pentagons are marked by asterisks.

Symmetry. The symmetry of an α-5-catafusene is defined with respect to regular pentagons (as well as regular hexagons). The possible symmetry groups for unbranched α-5-catafusenes are D_{2h}, C_{2h}, C_{2v}, and C_s. For the branched systems, in addition to these four symmetry groups also D_{3h} and C_{3h} occur.

Stupid Sheep Counting. The enumeration method called “stupid sheep counting” [17] is very useful[18,19] and has been exploited in the present treatment of unbranched α-5-catafusenes.[20] In this case, the “crude total”,[17,21,22] an important concept in stupid sheep countings, counts the D_{2h} systems exactly once, the C_{2h} and C_{2v} systems twice each, and the C_s systems four times. For a given number of polygons (r), the numbers of the systems with the different symmetries are denoted by D_r, C_r, M_r and A_r, pertaining to the symmetry groups in the same order as mentioned above. Then for the total number of isomers, I_r, one obtains

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

where J_r is the crude total, and A_r has been eliminated.

Special Classes

Unbranched Catafusenes. The enumeration problem for unbranched catafusenes has been solved a long time ago,[11] revisited more recently, [23-25] and finally included in a comprehensive review.[12] The solution is

$$J_r = 3^{r-2},\ D_r = 1,\ C_r = \frac{1}{2}\left(3^{\lfloor r/2 \rfloor - 1} - 1\right),$$

$$M_r = C_r + \frac{1}{2}\left[1 - (-1)^r\right] 3^{(r-3)/2} \tag{2}$$

which, after inserting into eq 1, yields

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

Mono-5-catafusenes. The unbranched mono-5-catafusene systems consist of unbranched catafusenes attached to a pentagon. The enumeration problem of catafusenes rooted at a polygon core has been treated in general terms,[26,27] and several treatments of special cases are available.[5,21,22,28] In addition, a work involving unbranched catafusenes[29] is especially relevant.

Consider first the ${}^1I_r$ isomers with one appendage. A piece of combinatorics, where the stupid sheep counting may be invoked, gives

$${}^1I_r = \frac{1}{2}\left(3^{r-2} + L_r\right),\ L_r = 1 \tag{4}$$

Here the first term in the parentheses is the crude total of interest, while L_r represents the unique (linear) system of C_{2v} symmetry for a given r.

For the ${}^2I_r$ isomers with two appendages the analysis is slightly more complicated. The appropriate crude total is

$${}^2J_r = \sum_{i=1}^{r-2} 3^{i-1} e^{r-2-i} = (r-2)\, 3^{r-3} \tag{5}$$

The systems in question are distributed among the symmetry groups C_{2v} and C_s only. Then

$${}^2I_r = \frac{1}{2}\left({}^2J_r + K_r\right),\ K_r = \frac{1}{2}\left[1 - (-1)^r\right] 3^{(r-3)/2} \tag{6}$$

where K_r pertains to the C_{2v} systems.

For the total number of isomers, $I_r = {}^1I_r + {}^2I_r$, it follows

$$I_r = \frac{1}{2}\left\{1 + (r+1)3^{r-3} + \frac{1}{2}[1-(-1)^r]3^{(r-3)/2}\right\} \qquad (7)$$

A computer program was developed for the enumeration of mono-5-catabenzenoids (without helicenic systems). The results to r = 10 are shown in Tables 1 and 2 for the unbranched and branched systems, respectively. In Table 1 the numbers for mono-5-catahelicenes are included (in parentheses), as obtained on subtractions from the catafusene numbers of the algebraic analysis described above.

Table 1. Numbers of Unbranched Mono-5-catabenzenoids (Unbranched Mono-5-catahelicenes in Parentheses)

r	C_{2v}	C_s	total
2	1	0	1
3	2	1	3
4	1	7	8
5	4	25	29
6	1	91 (3)	92 (3)
7	9 (1)	303 (16)	312 (17)
8	1	1004 (89)	1005 (89)
9	24 (4)	3240 (391)	3264 (395)
10	1	10365 (1663)	10366 (1663)

Table 2. Numbers of Branched Mono-5-catabenzenoids

r	C_{2v}	C_s	total
4	1	0	1
5	1	5	6
6	4	38	42
7	5	228	233
8	13	1196	1209
9	20	5832	5852
10	42	27191	27233

Some of the smallest numbers of the unbranched mono-5-catahelicenes can easily be checked directly by systematic drawings. The forms of the 3 and 17 helicenic systems for $r = 6$ and 7, respectively (cf. Table 1), are indicated in Figure 3. Also included are the four C_{2v} systems with $r = 9$. In this figure, the dualists[1,11,12] are employed.

Triangular Matrices

The algebraic methods for deducing the numbers of isomers of unbranched mono-5-catafusenes (eq 7), which is described above, is not convenient for a generalization to α-5-catafusenes. Instead, a new approach was devised, which involves the triangular matrices **A** and $\overline{\mathbf{A}}$ defined in the following.

Figure 4 shows the successive generation of the 1, 3, 9, ..., 3^{i-1}, ... unbranched catafusenes of the crude total for $r = i + 1$. In each system, the hexagons of $L_1 + L_2$ modes or $L_1 + A_2$ modes are counted. The numbers a_{ij} are defined as the numbers of unbranched catafusenes of the crude total which have $i + 1$ hexagons and $j + 1$ L_1- and L_2-mode hexagons taken together ($L_1 + L_2$). Similarly, $\overline{a}_{ij}$ should count the unbranched catafusenes with $i + 1$ hexagons in total and $j + 1$ hexagons of $L_1 + A_2$.

The above definition leads to the following recurrence relation and initial conditions for a_{ij}, the elements of **A**.

$$a_{11} = 1, \ a_{(i+1)j} = 2a_{ij} + a_{i(j-1)} \tag{8}$$

while $a_{i0} = 0$, $a_{ij} = 0$ when $j > i$. A portion of the **A** matrix is shown below. Similarly, the $\overline{a}_{ij}$ elements of $\overline{\mathbf{A}}$ are determined by

$$\overline{a}_{11} = 1, \ \overline{a}_{(i+1)j} = \overline{a}_{ij} + 2\overline{a}_{i(j-1)} \tag{9}$$

while $\overline{a}_{i0} = 0$, $\overline{a}_{ij} = 0$ when $j > i$. A portion of $\overline{\mathbf{A}}$ is shown below The $\overline{\mathbf{A}}$ matrix is clearly obtained from **A** by reversing each of the rows. In mathematical terms

$$\overline{a}_{ij} = a_{i(i-j+1)} \tag{10}$$

	j					
i	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
...						

	j					
i	1	2	3	4	5	6
1	1					
2	1	2				
3	1	4	4			
4	1	6	12	8		
5	1	8	24	32	16	
6	1	10	40	80	80	32
...						

The **A** matrix has been employed in the enumeration of di-4-catafusenes,[30] which consist of two tetragons each and otherwise only hexagons. In the present studies of α-5-catafusenes, the $\bar{\mathbf{A}}$ matrix is of prime interest.

Figure 3 The unbranched mono-5-catahelicenes with *r* = 6, 7, and the C_{2v} such systems with *r* = 9. The large black dots indicate pentagons, one in each system. The numbers of mono-5-catahelicenes generated from each catahelicene are indicated by inscribed numerals.

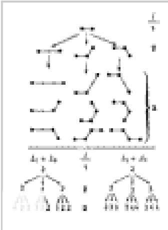

Figure 4 Generation of the crude total unbranched catafusenes in the dualist representation. In each system the hexagons of $L_1 + L_2$ modes or $L_1 + A_2$ modes are counted. The members of the latter set ($L_1 + A_2$) are indicated by larger black dots.

The explicit formula for the $\overline{\mathbf{A}}$ matrix elements reads

$$\bar{a}_{ij} = \binom{i-1}{j-1} 2^{j-1} \quad (11)$$

Here from it is found that

$$\bar{a}_{i1} = 1, \; \bar{a}_{i(j+1)} = 2j^{-1}(i-j)\,\bar{a}_{ij} \quad (12)$$

and

$$\bar{a}_{ii} = 2^{i-1}, \; \bar{a}_{(i+1)j} = i\,(i-j+1)^{-1}\,\bar{a}_{ij} \quad (13)$$

Another triangular matrix is needed, say $\overline{\mathbf{B}}$ with the elements $\bar{b}_{ij}$. Here the numbers $\bar{b}_{ij}$ should count the centrosymmetrical (C_{2h}) unbranched catafusenes with $2(i+1)$ hexagons in total and $2(j+1)$ hexagons of modes L_1 and L_2 taken together; see Figure 5. At the same time, $\bar{b}_{ij}$ counts the C_{2h} unbranched catafusenes with $2i + 3$ hexagons in total and $2(j+1)$ hexagons of $L_1 + A_2$. Accordingly, the $\overline{\mathbf{B}}$ matrix elements are given by

$$\bar{b}_{11} = 1, \; \bar{b}_{(i+1)j} = \delta_{1j} + \bar{b}_{ij} + 2\bar{b}_{i(j-1)} \quad (14)$$

while $\bar{b}_{i0} = 0$, $\bar{b}_{ij} = 0$ when $j > i$. Here δ_{1j} is the Kroneckerdelta; $\delta_{1j} = 0$ for $j \neq 1$, $\delta_{11} = 1$. A portion of the $\overline{\mathbf{B}}$ matrix is On comparing with the $\overline{\mathbf{A}}$ matrix it is observed that

$$\bar{b}_{ij} = \frac{1}{2}\bar{a}_{(i+1)(j+1)} \quad (15)$$

A general proof of this relation has been conducted but is omitted here for the sake of brevity.

Figure 5 Generation of unbranched centrosymmetrical catafusenes with even numbers of hexagons in the dualist representation. Symmetrically nonequivalent $L_1 + A_2$ modes are counted.

	j					
i	1	2	3	4	5	6
1	1					
2	2	2				
3	3	6	4			
4	4	12	16	8		
5	5	20	40	40	16	
6	6	30	80	120	96	32
...						

Finally in this section an alternative interpretation of the $\overline{\mathbf{A}}$ matrix is given. Consider the generation of the mirror-symmetrical (C_{2v}) unbranched catafusenes where the twofold symmetry axis (C_2) intersect hexagon edges; see Figure 6. In this figure, the C_2 axes are horizontal. Now $\overline{a}_{ij}$ is the number of the systems under consideration with 2*i* + 1 hexagons in total and *j* + 1 hexagons of modes $L_1 + A_2$.

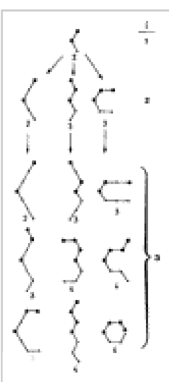

Figure 6 Generation of unbranched mirror-symmetrical catafusenes with twofold axes intersecting hexagon edges. The dualist representation is employed. Symmetrically nonequivalent $L_1 + A_2$ modes are counted.

Sample Analysis

Disposition. In this section, the triangular matrices $\overline{\mathbf{A}}$ and $\overline{\mathbf{B}}$ are applied in enumerations for the unbranched tri-5-catafusenes, systems with three pentagons each and otherwise only hexagons. A complete mathematical solution in terms of explicit formulas is presented. The treatment is convenient for generalization to unbranched α-5-catafusenes.

Computerized enumerations of the isomers of tri-5-catabenzenoids (without helicenic systems) are reported, both for the unbranched and branched systems. Then the numbers of unbranched tri-5-catahelicenes are available by subtractions.

Tri-5-catafusenes. First an algebraic solution for the unbranched tri-5-catafusenes is reported. The crude total for these systems with $r = i + 1$, viz. $J_r = J_{i+1}$, is obtained by contractions of three of the $j + 1$ hexagons of the $L_1 + A_2$ modes in each of the pertinent $\bar{a}_{ij}$ unbranched catafusenes. Hence

$$J_{i+1} = \sum_{j=1}^{i} \binom{j+1}{3}_{ij} \qquad (16)$$

or in matrix notation

$$\{J_{i+1}\} = \overline{\mathbf{A}}\left\{\binom{2}{3}, \binom{3}{3}, \binom{4}{3}, \binom{5}{3}, ...\right\} = \{0, 2, 20, 134, ...\} \qquad (17)$$

The next step is to deduce the numbers of the symmetrical systems. As a matter of fact, only the C_{2v} symmetry group is possible besides C_s in the case of unbranched tri-5-catafusenes. By the same kind of reasoning as above one obtains for the $K_r = K_{2i+1}$ numbers of the C_{2v} systems in question

$$K_{2i+1} = \sum_{j=1}^{i} j\bar{a}_{ij} \qquad (18)$$

or in matrix notation

$$\{K_{2i+1}\} = \overline{\mathbf{A}}\{1, 2, 3, 4, ...\} = \{1, 5, 21, 81, ...\} \qquad (19)$$

The next result for the I_r total numbers of isomers of unbranched tri-5-catafusenes was found with the following result after the proper transformations from *i* to *r* and using eq 1

$$I_r = \frac{1}{4}\left\{\sum_{j=1}^{r-1}\binom{j+1}{3}{}_{(r-1)j} + [1-(-1)^r]\sum_{j=1}^{(r-1)/2} j_{\,(r-1)/2(j)}\right\} \tag{20}$$

The computer program which has been used for mono-5-benzenoids (see above), was adapted to tri-5-benzenoids. The computational results to r = 10 are shown in Tables 3 and 4 for the unbranched and branched systems, respectively. The forms of the 1, 5, and 41 of these systems with r = 3, 4, and 5, respectively, are displayed in Figure 7. These drawings were produced systematically by considering the different constellations of pentagons or hexagons, which are possible. It is an approach which resembles the systematic constructions of double coronoids.[31]

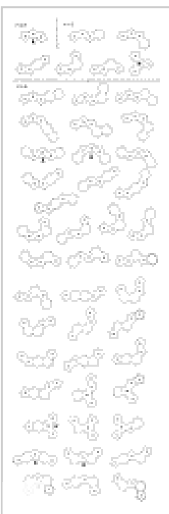

Figure 7 The tri-5-catafusenes with r = 3, 4, 5. The pentagons are marked by asterisks, while the branching hexagons are marked with dots in the C_s systems and a triangle in the D_{3h} system. Arrowheads indicate the C_{2v} systems.

Table 3. Numbers of Unbranched Tri-5-catabenzoids (Unbranched Tri-5-catahelicenes in Parentheses)

r	C_{2v}	C_s	total
3	1	0	1
4	0	5	5

5	5	31	36
6	0	176 (10)	176 (10)
7	18 (3)	841 (71)	859 (74)
8	0	3755 (484)	3755 (484)
9	67 (14)	15756 (2631)	15823 (2645)
10	0	63308 (13480)	63308 (13480)

Table 4. Numbers of Branched Tri-5-catabenzenoids

r	D_{3h}	C_{3h}	C_{2v}	C_s	total
4	1	0	0	0	1
5	0	0	1	4	5
6	0	0	6	55	61
7	1	2	7	494	504
8	0	0	26	3592	3618
9	0	0	44	23031	23075
10	1	11	106	136323	136441

In Table 3 the numbers for unbranched tri-5-catahelicenes are included (in parentheses); they were obtained on subtractions from the catafusene numbers of the algebraic analysis described above. The smallest of these numbers were checked by systematic drawings as in the case of unbranched mono-5-catahelicenes (cf. Figure 3). The 10 C_s systems for r = 6 and three C_{2v} systems for r = 7 were readily obtained from hexahelicene and heptahelicene, respectively; for the sake of brevity we omit the details. More interesting are the 14 C_{2v} systems at r = 9; they are displayed in Figure 8.

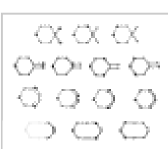

Figure 8 The unbranched C_{2v} tri-5-catahelicenes with r = 9. The asterisks indicate pentagons.

General Algebraic Solution for Unbranched Systems

The above analysis for unbranched tri-5-catafusenes was extended to the general case of unbranched α-5-catafusenes.

The crude totals for the systems under consideration are given by a straightforward generalization of eq 16, viz.

$$J_{i+1} = \sum_{j=1}^{i} \binom{j+1}{\alpha} \, {}_{ij}, \;\; J_r = \sum_{j=1}^{r-1} \binom{j+1}{\alpha} \, {}_{(r-1)j} \tag{21}$$

Linear α-5-catafusenes is a new feature, which was not encountered in the above treatment of tri-5-catafusenes. Firstly, there is exactly one D_{2h} unbranched catafusene and one D_{2h} unbranched di-5-catafusene for every *r*. The latter category is generated by contracting both terminal hexagons of a linear acene to pentagons. In conclusion

$$D_r = \lfloor 3\,(1+\alpha)^{-1} \rfloor - \lfloor 2\,(1+\alpha)^{-1} \rfloor \tag{22}$$

which is a sophisticated way to write $D_r = 1$ for α = 0, 2; otherwise $D_r = 0$. Secondly, there is exactly one linear C_{2v} mono-5-catafusene obtained by contracting one of the terminal hexagons of a linear acene. We write

$$L_r = \lfloor 2\,(1+\alpha)^{-1} \rfloor - 2\lfloor (1+\alpha)^{-1} \rfloor \tag{23}$$

which is equivalent for $L_r = 1$ for α = 1; otherwise $L_r = 0$.

Furthermore, α-5-catafusenes of C_{2h} symmetry must have a hexagon as a central polygon. Therefore such systems can only occur when α is even (including zero). Having in mind the definition of the $\overline{\mathbf{B}}$ matrix, one arrives at

$$C_{2i+2} = C_{2i+3} = \sum_{j=1}^{i} \binom{j+1}{\alpha/2} \bar{b}_{ij} \tag{24}$$

or in matrix notation

$$\{C_{2i+2}\} = \{C_{2i+3}\} = \overline{\mathbf{B}} \left\{ \binom{2}{\alpha/2}, \binom{3}{\alpha/2}, \binom{4}{\alpha/2}, \ldots \right\} \tag{25}$$

Inserting $\bar{b}_{ij}$ from eq 15 into 24 and making the appropriate transformations from *i* to *r* yields

$$C_{2i+2} = C_{2i+3} = \frac{1}{2}\sum_{j=1}^{i}\binom{j+1}{\alpha/2}_{(i+1)(j+1)}$$

$$C_r = \frac{1}{4}[1 + (-1)^{\alpha}]\sum_{j=1}^{\lfloor r/2\rfloor-1}\binom{j+1}{\alpha/2}_{\lfloor r/2\rfloor(j+1)} \tag{26}$$

The K_r systems of C_{2v} symmetry of the same kind as those associated with the same symbol among tri-5-catafusenes (cf. eq 18) are given by the generalized expressions

$$K_{2i+1} = \sum_{j=1}^{i}\binom{j}{\lfloor\alpha/2\rfloor}_{ij}$$

$$K_r = \frac{1}{2}[1 - (-1)^{r}]\sum_{j=1}^{(r-1)/2}\binom{j}{\lfloor\alpha/2\rfloor}_{(r-1)/2(j)} \tag{27}$$

Another kind of unbranched C_{2v} α-5-catafusenes occur for even-numbered α. These systems stand in a one-to-one correspondence with those of the C_{2h} symmetry as *cis*/*trans* isomers, and the twofold symmetry axis passes through two vertices of the central hexagon. In total, the number of C_{2v} systems is $M_r = C_r + L_r + K_r$ (28)

On assembling the information from eqs 24−27 and inserting into 1, a general formula for the I_r numbers of isomers of α-5-catafusenes is obtained as

$$I_r = \frac{1}{4}\Bigg\{3\lfloor 3(1+\alpha)^{-1}\rfloor - \lfloor 2(1+\alpha)^{-1}\rfloor - 4\lfloor(1+\alpha)^{-1}\rfloor + \sum_{j=1}^{r-1}\binom{j+1}{\alpha}_{(r-1)j} + [1 + (-1)^{\alpha}]\sum_{j=1}^{\lfloor r/2\rfloor-1}\binom{j+1}{\alpha/2}_{\lfloor r/2\rfloor(j+} \tag{29}$$

Equation 20 is clearly the special case of 29 for α = 3. In eq 29, the last two summations can be compressed because (for even-numbered α)

$$\sum_{j=1}^{\lfloor r/2\rfloor-1}\binom{j+1}{\lfloor\alpha/2\rfloor}_{\lfloor r/2\rfloor(j+1)} = \sum_{j=1}^{\lfloor r/2\rfloor}\binom{j}{\alpha/2}_{\lfloor r/2\rfloor(j)} - \binom{1}{\alpha/2} \tag{30}$$

while (for arbitrary α)

$$[1 + (-1)^{\alpha}]\binom{1}{\alpha/2} = 2\lfloor 3(1+\alpha)^{-1}\rfloor - 2\lfloor 2(1+\alpha)^{-1}\rfloor \tag{31}$$

The net result was rendered into the form

$$I_r = \frac{1}{4}\left\{\lfloor 3(1+\alpha)^{-1}\rfloor + \lfloor 2(1+\alpha)^{-1}\rfloor - 4\lfloor (1+\alpha)^{-1}\rfloor + \sum_{j=1}^{r-1}\binom{j+1}{\alpha}\ {}_{(r-1)j} + [2 + (-1)^{\alpha} - (-1)^{r}]\sum_{j=1}^{\lfloor r/2\rfloor}\binom{j}{\lfloor \alpha/2\rfloor}\bar{a}_{\lfloor r/2\rfloor(j)}\right\} \qquad (32)$$

Further Developments

Introductory Remarks. It was achieved, as an ultimate goal, to express I_r of eq 32 as an explicit formula in r and α. During these developments some mathematical identities involving the $\bar{a}_{ij}$ numbers had to be deduced; they pertain to eqs 21 and 27. By virtue of eq 11, these identities are equivalent to relations where binomial coefficients are the main entries. Specifically, the following summations are deduced in closed form.

$$T_{i(\beta+1)} = \sum_{j=1}^{i}\binom{i-1}{j-1}\binom{j}{\beta}2^{j-1} \qquad (33)$$

and

$$S_{i(\alpha+1)} = \sum_{j=1}^{i}\binom{i-1}{j-1}\binom{j+1}{\alpha}2^{j-1} \qquad (34)$$

Mathematical Identity. The crucial expression, which needs to be developed, is

$$\sum_{j=1}^{i}\binom{j}{\beta}\ {}_{ij} = T_{i(\beta+1)},\ T_{ik} = \sum_{j=1}^{i}\binom{j}{k-1}\ {}_{ij} \qquad (35)$$

where β = 0, 1, 2, ...; k = 1, 2, 3, ...; cf. eqs 27 and 33.

From eq 9 it follows that

$$\sum_{j=1}^{i+1}\binom{j}{\beta}\ {}_{(i+1)j} = \sum_{j=1}^{i}\binom{j}{\beta}\ {}_{ij} + 2\sum_{j=1}^{i+1}\binom{j}{\beta}\ {}_{i(j-1)} \qquad (36)$$

By some elementary manipulations the following was arrived at

$$\sum_{j=1}^{i+1}\binom{j}{\beta}\ {}_{(i+1)j} = 3\sum_{j=1}^{i}\binom{j}{\beta}\ {}_{ij} + 2\sum_{j=1}^{i}\binom{j}{\beta-1}\ {}_{ij} \qquad (37)$$

This relation is equivalent to a recurrence relation for T_{ik} as given below together with its initial conditions

$$T_{11} = T_{12} = 1,\ T_{(i+1)k} = 3T_{ik} + 2T_{i(k-1)} \tag{38}$$

while T_{i0} = 0, T_{ik} = 0 when $k > i + 1$. The **T** matrix, which is defined by its elements T_{ik}, is trapezoidal in a sense which should be apparent from the following table. This table can easily be enlarged by means of eq 36, and this was the easiest way which was found for generating the numerical values of the quantities of interest (eq 35). The correctness of the generated numbers can be checked by taking the sum along a row, which was proved to be

$$\sum_{k=1}^{i+1} T_{ik} = 2 \times 5^{i-1} \tag{39}$$

	j					
i	1	2	3	4	5	6
1	1	1				
2	3	5	2			
3	9	21	16	4		
4	27	81	90	44	8	
5	81	297	432	312	112	16
...						

Still we do not have an explicit formula for the quantities of eq 35. This task was accomplished by means of the relation 13, which gives

$$(i - j + 1)\sum_{j=1}^{i+1} \binom{j}{\beta} \ _{(i+1)j} = i\sum_{j=1}^{i} \binom{j}{\beta} \ _{ij} \tag{40}$$

After some tedious, but elementary manipulations, where eq 37 was exploited, the following recurrence relation was arrived at

$$3(\beta+1)\sum_{j=1}^{i}\binom{j}{\beta+1}\ {}_{ij} = (2i-5\beta+1)\sum_{j=1}^{i}\binom{j}{\beta}\ {}_{ij} + 2(i-\beta+1)\sum_{j=1}^{i}\binom{j}{\beta-1}\ {}_{ij} \qquad (41)$$

Also the initial conditions were determined, viz.

$$\sum_{j=1}^{i}\overline{a}_{ij} = 3^{i-1} \qquad (42)$$

and

$$\sum_{j=1}^{i} j\ {}_{ij} = (2i+1)\,3^{i-2} \qquad (43)$$

for $\beta = 0$ and 1, respectively.

The deduced relations 41−43 were used to set up the $T_{i(\beta+1)}$ expressions for further β values, actually to $\beta = 6$, which was sufficient to recognize the regularities. A general expression was established as given below and proved by complete induction.

$$T_{i(\beta+1)} = \sum_{j=1}^{i}\binom{j}{\beta}\ {}_{ij} = 2^{\beta-1}(i-1)!\,[\beta!\,(i-\beta)!]^{-1}(2i+\beta)\,3^{i-\beta-1} = 2^{\beta-1}\left[2\binom{i}{\beta}+\binom{i-1}{\beta-1}\right]3^{i-\beta-1} \qquad (44)$$

Crude Totals. In analogy with eq 35, set

$$\sum_{j=1}^{i}\binom{j+1}{\alpha}\ {}_{ij} = S_{i(\alpha+1)},\ \ S_{ik} = \sum_{j=1}^{i}\binom{j+1}{k-1}\ {}_{ij} \qquad (45)$$

cf. also eqs 21 and 34. These quantities are the crude totals, which enter into eq 32. With the knowledge of the identity 44, one obtains readily

$$\sum_{j=1}^{i}\binom{j+1}{\alpha}\ {}_{ij} = \sum_{j=1}^{i}\binom{j}{\alpha}\ {}_{ij} + \sum_{j=1}^{i}\binom{j}{\alpha-1}\ {}_{ij} =$$

$$2^{\alpha-1}\left[2\binom{i}{\alpha} + \binom{i-1}{\alpha-1}\right]3^{i-\alpha-1} +$$

$$2^{\alpha-2}\left[2\binom{i}{\alpha-1} + \binom{i-1}{\alpha-2}\right]3^{i-\alpha} = 2^{\alpha-1}\left[4\binom{i}{\alpha} +\right.$$

$$\left.8\binom{i}{\alpha-1} + \binom{i-1}{\alpha-2}\right]3^{i-\alpha-1} =$$

$$2^{\alpha-2}(i-1)!\,[\alpha!\,(i-\alpha+1)!]^{-1}\left[4i^2 + 4(\alpha+1)i +\right.$$

$$\left.\alpha(\alpha-1)\right]3^{i-\alpha-1} \tag{46}$$

For α = 0, this relation reduces to (42). For α = 1, one obtains

$$\sum_{j=1}^{i}(j+1)\ {}_{ij} = 2(i+1)\,3^{i-2} \tag{47}$$

in consistency with relations 42 and 43.

The trapezoidal **S** matrix with the elements S_{ik} has clearly the same recurrence relation for its elements as the **T** matrix (cf. eq 38), but the initial conditions are different:

$$S_{11} = 1,\ S_{12} = 2,\ S_{13} = 1$$

$$S_{(i+1)k} = 3S_{ik} + 2S_{i(k-1)} \tag{48}$$

while $S_{i0} = 0$, $S_{ik} = 0$ when $k > i + 2$. A portion of the **S** matrix is given below and indicates, in conjunction with eq 48, the easiest way which was found for generating the numerical crude totals. As a check of the correctness of these numbers, the following relation is useful

$$\sum_{k=1}^{i+2} S_{ik} = 4 \times 5^{i-1} \tag{49}$$

---

	k						
i	1	2	3	4	5	6	7

1	1	2	1				
2	3	8	7	2			
3	9	30	37	20	4		
4	27	108	171	134	52	8	
5	81	378	729	744	424	128	16
...							

Ultimate Solution. By means of the identities 44 and 46, we are now in the position to be able to write up the following master formula as the ultimate result of I_r (eq 32) for unbranched α-5-catafusenes.

$$I_r = \frac{1}{4}\Big\{\lfloor 3(1+\alpha)^{-1}\rfloor + \lfloor 2(1+\alpha)^{-1}\rfloor - 4\lfloor(1+\alpha)^{-1}\rfloor + 2^{\alpha-2}(r-2)![\alpha!(r-\alpha)!]^{-1}[4r^2 + 4(\alpha-1)r + \alpha(\alpha-5)]3^{r-\alpha-2} + [2 + (-1)^{\alpha} - (-1)^{r}]2^{\lfloor\alpha/2\rfloor-1}(\lfloor r/2\rfloor - 1)![\lfloor\alpha/2\rfloor!(\lfloor r/2\rfloor - \lfloor\alpha/2\rfloor!]^{-1}(2\lfloor r/2\rfloor + \lfloor\alpha/2\rfloor)3^{\lfloor r/2\rfloor-\lfloor\alpha/2\rfloor-1}\Big\} \qquad (50)$$

The formulas 3 and 7 are special cases of 50 for α = 0 and 1, respectively.

Numerical Values for Unbranched Systems

The equivalent formulas 32 and 50 were used to compute the numercial I_r values of Table 5. The entries for α = 1 and α = 3 are consistent with the totals of Tables 1 and 3, respectively. Also the known values for unbranched catafusenes[11,12,23-25] were reproduced (for α = 0) but are not repeated here. Finally, the values of Table 5 are perfectly consistent with the corresponding values by Dobrynin [32] from computer programming.

Further Applications

The numbers along a diagonal at the extreme right of Table 5 (viz. 1, 1, 2, 3, 6, ...) pertain to the catacondensed polypentagons (r = α), which inevitably are unbranched. Their numbers of isomers[8] are reproduced correctly here. Moreover, on inserting p = r = α in eq 50, it was arrived at

$$I_p = \frac{1}{4}\left(\lfloor 2/p \rfloor + 2^{p-2} + 2^{\lfloor p/2 \rfloor}\right) \qquad (51)$$

where also

$$\lfloor 3\,(1+p)^{-1} \rfloor + \lfloor 2\,(1+p)^{-1} \rfloor - 4\lfloor (1+p)^{-1} \rfloor = \lfloor 2/p \rfloor \qquad (52)$$

has been inserted. The formula 51 applies to the isomers of catacondensed (unbranched) polypentagons with p pentagons. It gives I_2 = 1 and is equivalent to the simple formula for p > 2 deduced previously.[8]

Table 5. Numbers of Unbranched α-5-Catafusenes

	α					
r	1	2	3	4	5	6
2	1	1				
3	3	3	1			
4	8	12	5	2		
5	29	48	36	15	3	
6	95	193	186	114	32	6
7	329	757	933	706	316	80
8	1094	2896	4239	3960	2304	866
9	3659	10834	18468	20313	14787	7184
10	12029	39697	76788	97740	84672	51060
11	39407	142999	309609	446580	449280	322368
12	127940	507364	1213785	1958310	2239488	1865196
	α					
r	7	8	9	10	11	12
7	10					
8	176	20				
9	2238	408	36			

10	20928	5688	896	72		
11	164748	58864	14008	2000	136	
12	1137888	505920	159360	33992	4352	272

The problem of enumerating unbranched α-5-catafusenes can be reversed completely by asking the following question: how many isomers are there of unbranched catacondensed systems with η hexagons and otherwise (r−η) pentagons? Such systems may appropriately be termed η-6-catapolypentagons. The answer to this question is actually contained in eq 50 and can be elaborated explicitly by inserting $\alpha = r - \eta$. We shall not go into details with regard to this general problem but consider only the unbranched mono-6-catapolypentagons, which is the special case of η = 1.

On inserting $\alpha = r - 1$ in eq 50, the following result was achieved

$$I_r = \frac{1}{4}\{\lfloor 3/r\rfloor + \lfloor 2/r\rfloor + (3r-2)\,2^{r-3} + [1-(-1)^r]\,2^{(r-1)/2}\} \quad (53)$$

This formula reproduces the numbers along a diagonal in Table 5 near the extreme right edge, viz. 1, 3, 5, 15, 32, ... In Figure 9 the forms of the smallest of these systems are depicted. The pertinent systems may be interpreted as one hexagon with one or two catacondensed polypentagons rooted to it. On this basis eq 53 could be deduced more directly by the methods applied in the above treatment of mono-5-catafusenes and elsewhere.[8] We shall not pursue this reasoning here.

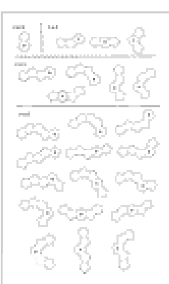

Figure 9 The mono-*6*-catapolypentagons with r = 2, 3, 4, 5. The hexagons are marked with dots.

Conclusion

The main result of the present work is a mathematical solution for the I_r numbers of isomers of unbranched α-5-catafusenes. A new method involving a triangular matrix $\overline{\mathbf{A}}$ was employed. Ultimately, an explicit formula in *r* and α was achieved for I_r.

The preceding section suggest some related works which could be performed in continuation of the present studies, illustrated by mono-6-catapolypentagons as an example.

However, a further application of the triangular **A** matrix seems to be more interesting. It was mentioned that **A** has been used in the enumeration of di-4-catafusenes,[30] but a generalization to α-4-catafusenes is undoubtedly feasible. An α-4-catafusene consists of α tetragons and otherwise only hexagons (if any).

Furthermore, a study of the isomers of catacondensed systems with exclusively pentagons and tetragons might reveal interesting mathematical properties. And still we have not mentioned heptagons, octagons, etc. 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.

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