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ISOMER ENUMERATION OF UNBRANCHED CATACONDENSED POLYGONAL SYSTEMS WITH PENTAGONS AND HEPTAGONS

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Abstract

The α-*5*-catapolyheptagons are catacondensed polygonal systems with α pentagons each and otherwise only heptagons. The isomer enumeration problem for the unbranched systems of this category is solved mathematically in terms of explicit formulas. The method implies certain triangular matrices with interesting mathematical properties. Numerical results are also reported.

Introduction

Azulenoids [1] are polygonal systems consisting of exactly one pentagon each and otherwise heptagons (if any). They have chemical counterparts in certain polycyclic (nonbenzenoid) conjugated hydrocarbons, of which $C_{10}H_8$ azulene (an isomer of naphthalene) is the prototype. An α–*5*–catapolyheptagon contains α pentagons and $r-\alpha$ heptagons, where r is used to denote the total number of polygons or rings. The subclass for $\alpha = 1$, which consists of mono-*5*-catapolyheptagons contains azulenoids among its members. In the following it is assumed $r > 1$ while the case of $r = 1$ (one single pentagon) is trivial.

In the present work, an algebraic formula for the numbers of nonisomorphic unbranched α-*5*-catapolyheptagons was derived. For the sake of brevity, we shall report the different steps in the derivation without going into details on the combinatorial reasoning behind them. However, the reader is referred to previous descriptions of similar derivations [2-5], where certain triangular matrices are employed. The main purpose of this paper is to demonstrate another application of the same approach, but the concept of triangular matrices had to be generalized in order to accomplish the task. Furthermore, the procedure has been systematized and is presented in a new way along with new mathematical properties of the triangular matrices.

The systems under consideration that have an odd number of vertices correspond to radicals, which are chemically unstable. Otherwise, certain chemical compounds of the category in question may be unstable due to quantum–mechanical properties which make them electronically different from usual benzenoids [6].

The present work may be considered as a continuation of the classical enumeration of catafusenes by Balaban and Harary [7] and some later enumerations of a similar kind [8,9]; these works are reviewed elsewhere [10]. However, the present problem is considerably more complex and calls for new mathematical techniques.

Mathematical tools

A triangular matrix $\mathbf{A}(x,y)$ with the elements $a(x,y)_{ij}$, where x and y are integer parameters, is defined in terms of the following recurrence relation and initial conditions.

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

while $a(x,y)_{i0} = 0$, $a(x,y)_{ij} = 0$ when $j > i$. Then the matrices $\mathbf{A}$ and $\bar{\mathbf{A}}$ which were introduced previously [2-5], are the special cases $\mathbf{A}$(2,1) and $\mathbf{A}$(1,2), respectively. Furthermore, $\mathbf{A}$(1,1) is the Pascal triangle, which often is written in a matrix form [11,12]:

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

Another example:

$$\mathbf{A}(4,2) = \begin{bmatrix} 1 & & & \\ 4 & 2 & & \\ 16 & 16 & 4 & \\ 64 & 96 & 48 & 8 \\ . & . & . & . \end{bmatrix} \tag{3}$$

The explicit expression for the matrix elements in question reads:

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

A useful multiplication rule for two matrices of the considered type 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 two special cases are of particular interest.

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

$$\mathbf{A}(1,1)\mathbf{A}(x,y) = \mathbf{A}(x+1,y) \tag{7}$$

From the former relation (6) one obtains with the aid of (4):

$$\begin{aligned} \sum_{j=1}^{i} a(x,y)_{ij} a(1,1)_{jk} &= \sum_{j=1}^{i} \binom{j-1}{k-1} a(x,y)_{ij} = \sum_{j=1}^{i} \binom{i-1}{j-1} \binom{j-1}{k-1} x^{i-j} y^{j-1} \\ &= \binom{i-1}{k-1} (x+y)^{i-k} y^{k-1} \end{aligned} \tag{8}$$

where the last two terms on the right-hand side represent a nontrivial mathematical identity involving binomial coefficients. From the latter relation (7) it is ascertained that any $\mathbf{A}(x,y)$ matrix can be produced from the Pascal triangle. One has namely

$$\mathbf{A}(x,y) = \mathbf{A}(1,1)\mathbf{A}(x-1,y) = \mathbf{A}(1{,}1)^2\mathbf{A}(x-2,y) = ... \quad (9)$$

etc., until

$$\mathbf{A}(x,y) = \mathbf{A}(1,1)^{x-1}\mathbf{A}(1,y) \quad (10)$$

Herefrom $y = 1$ gives:

$$\mathbf{A}(x,1) = \mathbf{A}(1,1)^x \quad (11)$$

In general (for an arbitrary y), eqn. (10) may be carried one step further to yield

$$\mathbf{A}(x,y) = \mathbf{A}(1,1)^x\mathbf{A}(0,y) \quad (12)$$

where $\mathbf{A}(0,y)$ is a diagonal matrix; specifically:

$$\mathbf{A}(x,y) = \mathbf{A}(1,1)^x \mathrm{diag}(1,y,y^2,y^3,....) \quad (13)$$

We shall also find it useful to define truncated Pascal triangles as the "trapezoidal" matrices given below.

$$\mathbf{A}'(1,1) = \begin{bmatrix} 1 & 1 & & & \\ 1 & 2 & 1 & & \\ 1 & 3 & 3 & 1 & \\ 1 & 4 & 6 & 4 & 1 \\ . & . & . & . & . \end{bmatrix} \quad (14)$$

$$\mathbf{A}''(1,1) = \begin{bmatrix} 1 & 2 & 1 & & & \\ 1 & 3 & 3 & 1 & & \\ 1 & 4 & 6 & 4 & 1 & \\ 1 & 5 & 10 & 10 & 5 & 1 \\ . & . & . & . & . & . \end{bmatrix} \quad (15)$$

By definition,

$$\mathbf{A}(x,y)\mathbf{A}'(1,1) = \mathbf{A}'(x+y,y) \quad (16)$$

$$\mathbf{A}(x,y)\mathbf{A}''(1,1) = \mathbf{A}''(x+y,y) \tag{17}$$

which is to be compared with eqn. (6).

The definition (1) is not restricted to positive integers x and y; it works equally well when these parameters are zero or negative. Then obviously $\mathbf{A}(0,1)$ is the unity matrix:

$$\mathbf{A}(0,1) = \mathbf{E} = \begin{bmatrix} 1 & & & \\ 0 & 1 & & \\ 0 & 0 & 1 & \\ 0 & 0 & 0 & 1 \\ . & . & . & . \end{bmatrix} \tag{18}$$

Based on eqn. (5), it is inferred that any $\mathbf{A}(x,y)$ when $y \neq 0$ has an inverse, and specifically that:

$$\mathbf{A}(x,y)\mathbf{A}\left(-\frac{x}{y},\frac{1}{y}\right) = \mathbf{A}\left(-\frac{x}{y},\frac{1}{y}\right)\mathbf{A}(x,y) = \mathbf{E} \tag{19}$$

Basic principle

The unbranched α-*5*-catapolyheptagons under consideration ($r > 1$) are distributed under the symmetry groups D_{2h}, C_{2h}, C_{2v} and C_s. As has been explained previously [2,5], the total number of isomers, $I_{r\alpha}$, is given by

$$I_{r\alpha} = \frac{1}{4}(J_{r\alpha} + 3D_{r\alpha} + 2L_{r\alpha} + 4C_{r\alpha} + 2K_{r\alpha}) \tag{20}$$

Here $J_{r\alpha}$ 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 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 consist of one central heptagon with two equivalent branches annelated to it.

Crude totals

The crude totals $J_{r\alpha}$ appear as elements in the trapezoidal matrix

$$\mathbf{J} = \mathbf{A}(2,2)\mathbf{A}''(1,1) = \mathbf{A}''(4,2) \tag{21}$$

The matrix multiplication herein is consistent with (17). Notice that $\mathbf{A}''$ is not a simple truncation of $\mathbf{A}$(4,2) by deleting its two top rows; cf. eqn. (3). However, $\mathbf{A}$(4,2) and $\mathbf{A}''$(4,2) obey the same recurrence relation, viz. eqn. (1) with $x = 4$, $y = 2$; only the initial conditions are different. Numerical values of $J_{r\alpha}$ are shown in Table 1. From eqn. (21), it was achieved, by means of relation (8), to deduce an explicit expression for $J_{r\alpha}$ as:

$$\begin{aligned} J_{r\alpha} &= \left[16\binom{r-2}{\alpha-2} + 16\binom{r-2}{\alpha-1} + 4\binom{r-2}{\alpha}\right] 4^{r-\alpha-2}2^{\alpha-2} \\ &= \frac{1}{4}\left[\binom{r-1}{\alpha-1} + \frac{1}{4}\binom{r-2}{\alpha}\right] 2^{2r-\alpha} \end{aligned} \tag{22}$$

Strictly speaking, the $J_{r\alpha}$ numbers should be referred to as the over-all 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 $\mathbf{H}$, which in analogy with eqn. (21) reads

$$\mathbf{H} = \mathbf{A}(2,2)\mathbf{A}'(1,1) = \mathbf{A}'(4,2) \tag{23}$$

The elements of $\mathbf{A}'$(4,2) are designated $H_{\lfloor r/2\rfloor\lfloor\alpha/2\rfloor}$ since they are functions of $\lfloor r/2\rfloor$ and $\lfloor\alpha/2\rfloor$. 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 the sites of annelation to the central part. In numerical form, a portion of the $\mathbf{A}'$(4,2) matrix is specified below.

	$\lfloor\alpha/2\rfloor$					
$\lfloor r/2\rfloor$	0	1	2	3	4	5
1	1	1				
2	4	6	2			
3	16	32	20	4		
4	64	160	144	56	8	
5	256	768	896	512	144	16

Table 1. Crude totals ($J_{r\alpha}$) for unbranched α-5-catapolyheptagons.

	α										
r	0	1	2	3	4	5	6	7	8	9	10
2	1	2	1								
3	4	10	8	2							
4	16	48	52	24	4						
5	64	224	304	200	64	8					
6	256	1024	1664	1408	656	160	16				
7	1024	4608	8704	8960	5440	1952	384	32			
8	4096	20480	44032	53248	39680	18688	5440	896	64		
9	16384	90112	217088	301056	265216	154112	59136	14464	2048	128	
10	65536	393216	1048576	1638400	1662976	1146880	544768	176128	37120	4608	256

The elements of $\mathbf{A}'(4,2)$, as well as those of $\mathbf{A}(4,2)$ and $\mathbf{A}''(4,2)$, obey the recurrence relation (1) with $x = 4$, $y = 2$. Similarly to eqn. (22), also an explicit expression for $H_{\lfloor r/2 \rfloor \lfloor \alpha/2 \rfloor}$ was achieved:

$$\begin{aligned} H_{\lfloor r/2 \rfloor \lfloor \alpha/2 \rfloor} &= \left[4 \binom{\lfloor r/2 \rfloor - 1}{\lfloor \alpha/2 \rfloor - 1} + 2 \binom{\lfloor r/2 \rfloor - 1}{\lfloor \alpha/2 \rfloor} \right] 4^{\lfloor r/2 \rfloor - \lfloor \alpha/2 \rfloor - 1} 2^{\lfloor \alpha/2 \rfloor - 1} \\ &= \frac{1}{4} \left[\binom{\lfloor r/2 \rfloor - 1}{\lfloor \alpha/2 \rfloor - 1} + \binom{\lfloor r/2 \rfloor}{\lfloor \alpha/2 \rfloor} \right] 2^{2\lfloor r/2 \rfloor - \lfloor \alpha/2 \rfloor} \end{aligned} \tag{24}$$

Linear systems

In the case of unbranched α-*5*-catapolyheptagons there are only three systems, all of them with $r = 2$, which appropriately are referred to as linear and must be taken into account especially. Two of these systems belong to the D_{2h} symmetry and are represented by two pentagons or two heptagons (pentalene and heptalene, respectively). In addition, there is a C_{2v} system consisting of one pentagon and one heptagon (azulene). In other words, $D_{20} = D_{22} = 1$ and $D_{r\alpha} = 0$ otherwise; $L_{21} = 1$, $L_{r\alpha} = 0$ otherwise. These properties are expressed mathematically in the following sophisticated way:

$$D_{r\alpha} = \binom{2}{r} \left[2\binom{0}{\alpha} - 2\binom{1}{\alpha} + \binom{2}{\alpha} \right] \tag{25}$$

$$L_{r\alpha} = \binom{2}{r} \left[\binom{1}{\alpha} - \binom{0}{\alpha} \right] \tag{26}$$

Centrosymmetrical systems

Centrosymmetrical (C_{2h}) unbranched α-*5*-catapolyheptagons occur only when both r and α are even numbers (or zero for α). Their numbers for $r > 2$ are given by $\frac{1}{2} X_{r\alpha}$, where

$$X_{r\alpha} = \frac{1}{4} \left[1 + (-1)^{\alpha} \right] \left[1 + (-1)^{r} \right] H_{\lfloor r/2 \rfloor \lfloor \alpha/2 \rfloor} \tag{27}$$

For $r = 2$, the presence of the D_{2h} (linear) systems must be taken into account. In effect,

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

Numerical values of $C_{r\alpha}$ are found in Table 2.

Mirror-symmetrical systems

The $K_{r\alpha}$ mirror-symmetrical (C_{2v}) unbranched α-5-catapolyheptagons occur when r is odd. Introduce

$$Y_{r\alpha} = \frac{1}{2}\left[1 - (-1)^r\right] H_{\lfloor r/2 \rfloor \lfloor \alpha/2 \rfloor} \tag{29}$$

Table 2. Numbers of centrosymmetrical (C_{2h}) unbranched α-5-catapolyheptagons: $C_{r\alpha}$.

	α										
r	0	1	2	3	4	5	6	7	8	9	10
2	0	0	0								
3	0	0	0	0							
4	2	0	3	0	1						
5	0	0	0	0	0	0					
6	8	0	16	0	10	0	2				
7	0	0	0	0	0	0	0	0			
8	32	0	80	0	72	0	28	0	4		
9	0	0	0	0	0	0	0	0	0	0	
10	128	0	384	0	448	0	256	0	72	0	8

When α is even, a system of the category in question has a central heptagon, which has two nonequivalent pairs of sites for annelation of the two (equivalent) branches, and the number of systems is $2Y_{r\alpha}$. When α is odd, on the other hand, the central polygon is a pentagon with only one pair of sites, and the number is $Y_{r\alpha}$. In conclusion,

$$K_{r\alpha} = \frac{1}{2}\left\{2\left[1 + (-1)^\alpha\right] + 1 - (-1)^\alpha\right\} Y_{r\alpha} = \frac{1}{2}\left[3 + (-1)^\alpha\right] Y_{r\alpha} \tag{30}$$

Table 3 shows the numerical values of $K_{r\alpha}$ to $r = 10$.

Table 3. Numbers of nonlinear mirror-symmetrical (C_{2v}) unbranched α-5-catapolyheptagons when r is odd: $K_{r\alpha}$.

	α										
r	0	1	2	3	4	5	6	7	8	9	10
2	0	0	0								
3	2	1	2	1							
4	0	0	0	0	0						
5	8	4	12	6	4	2					
6	0	0	0	0	0	0	0				
7	32	16	64	32	40	20	8	4			
8	0	0	0	0	0	0	0	0	0		
9	128	64	320	160	288	144	112	56	16	8	
10	0	0	0	0	0	0	0	0	0	0	0

Total numbers of isomers

Now all the quantities on the right-hand side of eqn. (20) have been analyzed so that they can be expressed explicitly in terms of r and α. The net result for the total numbers $I_{r\alpha}$ of unbranched α-5-catapolyheptagons reads

$$\begin{aligned} I_{r\alpha} &= \frac{1}{4}\left\{J_{r\alpha} + 3D_{r\alpha} + 2L_{r\alpha} + 2\left(X_{r\alpha} - D_{r\alpha}\right) + \left[3 + (-1)^{\alpha}\right] Y_{r\alpha}\right\} \\ &= \frac{1}{4}\left\{J_{r\alpha} + \binom{2}{r}\binom{2}{\alpha} + \left[1 - (-1)^{r}\right]\left[2 + (-1)^{\alpha}\right] H_{\lfloor r/2\rfloor \lfloor \alpha/2\rfloor}\right\} \end{aligned} \tag{31}$$

and finally:

$$\begin{aligned} I_{r\alpha} = \frac{1}{16}\Big\{ &\left[\binom{r-1}{\alpha-1} + \frac{1}{4}\binom{r-2}{\alpha}\right] 2^{2r-\alpha} + 4\binom{2}{r}\binom{2}{\alpha} + \left[2 - (-1)^{r} + (-1)^{\alpha}\right] \\ &\times \left[\binom{\lfloor r/2\rfloor - 1}{\lfloor \alpha/2\rfloor - 1} + \binom{\lfloor r/2\rfloor}{\lfloor \alpha/2\rfloor}\right] 2^{2\lfloor r/2\rfloor - \lfloor \alpha/2\rfloor}\Big\} \end{aligned} \tag{32}$$

Numerical values are given in Table 4.

Table 4. Total numbers of unbranched α-5-catapolyheptagons (α pentagons, $r-\alpha$ heptagons): $I_{r\alpha}$.

	α										
r	0	1	2	3	4	5	6	7	8	9	10
2	1	1	1								
3	2	3	3	1							
4	6	12	16	6	2						
5	20	58	82	53	18	3					
6	72	256	432	352	174	40	6				
7	272	1160	2208	2256	1380	498	100	10			
8	1056	5120	11088	13312	9992	4672	1388	224	20		
9	4160	22560	54432	75344	66448	38600	14840	3644	520	36	
10	16512	98304	262528	409600	416192	286720	136448	44032	9352	1152	72

Table 5. Numbers of unbranched mono-5-catapolyheptagons (including unbranched catacondensed azulenoids).

r	Formula	C_{2v}	C_s	Total
2	$C_{10}H_8$	1	0	1
3	$C_{15}H_{11}$	1	2	3
4	$C_{20}H_{14}$	0	12	12
5	$C_{25}H_{17}$	4	54	58
6	$C_{30}H_{20}$	0	256	256
7	$C_{35}H_{23}$	16	1144	1160
8	$C_{40}H_{26}$	0	5120	5120
9	$C_{45}H_{29}$	64	22496	22560
10	$C_{50}H_{32}$	0	98304	98304

Unbranched mono-5-catapolyheptagons The title systems consist of the unbranched catacondensed azulenoids and the corresponding helicenic systems. Their numbers of isomers are shown in Table 5, where the distributions into symmetry groups are included. Only C_{2v} and C_s are possible. The catacondensed (nonhelicenic) azulenoids, both unbranched and branched, have been enumerated previously to $r = 7$ [1]. In supplement, the total number of 17436 for $r = 8$ was determined; these systems are classified into 5094 C_s unbranched and $19C_{2v}+$ $12323C_s$ branched. From the previous data [1] and the present supplements, along with Table 5, the numbers of helicenic unbranched mono-*5*-catapolyheptagons up to $r = 8$ are available by subtractions. The result is $1C_{2v} + 3C_s$ systems at $r = 7$, which are the smallest helicenic systems of the category under consideration, and $26C_s$ systems at $r = 8$. These numbers and symmetries of helicenic systems were corroborated by combinatorial constructions.

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