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Di–5–Catafusenes: A Subclass of Indacenoids

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Abstract

Indacenoids are chemical graphs consisting of two pentagons each and otherwise only hexagons. Catacondensed indacenoids without helicenic systems are enumerated by computer programming. For the numbers of the unbranched catacondensed indacenoids (with helicenic systems included) a complete mathematical solution was achieved. A new algebraic method was applied, which involves certain triangular matrices.

Introduction

Indacenoids are polygonal systems [1] which consist of two pentagons each and otherwise only hexagons. These systems represent a class of polycyclic conjugated hydrocarbons of considerable interest in organic, physical and mathematical chemistry. The first systematic study of indacenoids is due to Dias [2], who detected constant–isomer series of C_nH_s formulae for these systems. Indacenoids were recently revisited [3], and they are also included in the recent general formulations for di–q–polyhexes [4].

Very little has been done in the enumeration of indacenoid isomers. Dias [2] has reported some rudimentary results by Zahradnik and Pancir [5] and has himself supplied the numbers for twelve constant–isomer series [2]. In addition, Dias [3] has enumerated the $C_{15}H_9$, $C_{20}H_{10}$, $C_{25}H_{11}$ and $C_{30}H_{12}$ indacenoid isomers. The members of constant–isomer series are extremal in the sense that $n_i = (n_i)_{max}$ for a given r, where n_i is the number of internal vertices and r the number of polygons. In the case of the four C_nH_s formulas given above, $n_i = (n_i)_{max} - 1$. In the present work we have attacked the enumeration problem from the other extreme, viz. $n_i = 0$.

In other words, the catacondensed indacenoids are considered. These systems have the chemical formulae $C_{4r}H_{2r+2}$. To our best knowledge, already the thirteen $C_{16}H_{10}$ indacenoid isomers (see Fig. 1) represent a new result. For the unbranched catacondensed indacenoids, a complete mathematical solution is reported, but helicenic systems must be tolerated. By definition, the systems are helicenic when created from helicenic catafusenes. The present algebraic solution is based on the classical enumeration of catafusenes by Balaban and Harary [6], but it is considerably more complex. In fact, an unbranched catacondensed indacenoid (nonhelicenic or helicenic) is generated from any catafusene by converting two of its hexagons to pentagons. This feature gives rise to the designation "di–*5*–catafusenes".

The algebraic approach of the present work led to some triangular matrices with interesting mathematical properties. Their application represents a new approach to chemical combinatorics.

Chemical formulas

Table 1 shows all the possible C_nH_s formulas for indacenoids with $r \leq 10$. This table is consistemt with Dias [2] and with the general mathematical formulations communicated recently [7]. In Table 1, the formulas below the stippled (staircase–like) boundary are possible for fluoranthenoids/fluorenoids [8–10], viz. polygonal systems with one pentagon each and otherwise only hexagons. The formulas below the full–drawn boundary in Table 1 are benzenoid formulas, while those above this boundary are

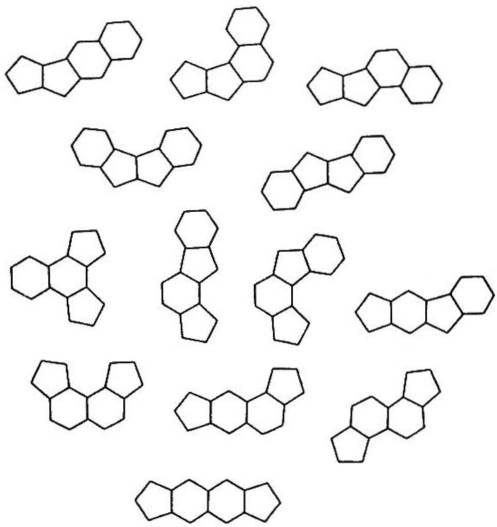

Fig. 1. The thirteen (twelve unbranched, one branched) $C_{16}H_{10}$ indacenoid isomers (r=4).

ultrabenzenoid [7].

The (catacondensed) systems of the present study possess the formulas in the extreme left–hand column of Table 1.

Computer programming

A computer program was designed for the enumeration of di–5–catafusenes without helicenic systems. The results are entered in Tables 2 and 3 for the unbranched and branched catacondensed systems, respectively.

Table 1

Chemical formulas for indacenoids

r \ n_i	0	1	2	3	4	5	6	7	8	9	10	11
2	C_8H_6											
3	$C_{12}H_8$	$C_{11}H_7$										
4	$C_{16}H_{10}$	$C_{15}H_9$	$C_{14}H_8$									
5	$C_{20}H_{12}$	$C_{19}H_{11}$	$C_{18}H_{10}$	$C_{17}H_9$								
6	$C_{24}H_{14}$	$C_{23}H_{13}$	$C_{22}H_{12}$	$C_{21}H_{11}$	$C_{20}H_{10}$	$C_{19}H_9$						
7	$C_{28}H_{16}$	$C_{27}H_{15}$	$C_{26}H_{14}$	$C_{25}H_{13}$	$C_{24}H_{12}$	$C_{23}H_{11}$	$C_{22}H_{10}$					
8	$C_{32}H_{18}$	$C_{31}H_{17}$	$C_{30}H_{16}$	$C_{29}H_{15}$	$C_{28}H_{14}$	$C_{27}H_{13}$	$C_{26}H_{12}$	$C_{25}H_{11}$	$C_{24}H_{10}$			
9	$C_{36}H_{20}$	$C_{35}H_{19}$	$C_{34}H_{18}$	$C_{33}H_{17}$	$C_{32}H_{16}$	$C_{31}H_{15}$	$C_{30}H_{14}$	$C_{29}H_{13}$	$C_{28}H_{12}$	$C_{27}H_{11}$		
10	$C_{40}H_{22}$	$C_{39}H_{21}$	$C_{38}H_{20}$	$C_{37}H_{19}$	$C_{36}H_{18}$	$C_{35}H_{17}$	$C_{34}H_{16}$	$C_{33}H_{15}$	$C_{32}H_{14}$	$C_{31}H_{13}$	$C_{30}H_{12}$	$C_{29}H_{12}$

Table 2

Numbers of nonhelicenic unbranched di–5–catafusenes

r	D_{2h}	C_{2h}	C_{2v}	C_s	Total
2	1	0	0	0	1
3	1	0	1	1	3
4	1	2	2	7	12
5	1	2	7	38	48
6	1	10	7	166	184
7	1	10	28	670	709
8	1	40	29	2545	2615
9	1	40	100	9345	9486
10	1	143	98	33258	33500

Table 3

Numbers of nonhelicenic branched di–5–catafusenes

r	C_{2h}	C_{2v}	C_s	Total
4	0	1	0	1
5	0	1	7	8
6	1	8	64	73
7	1	10	462	473
8	12	41	2788	2841
9	12	65	15426	15503
10	87	198	80173	80458

Algebraic solution for unbranched systems

Triangular matrices

In a recent enumeration of unbranched di–4–catafusenes [11] (systems with two tetragons and otherwise hexagons), the triangular matrix **A** was defined by its elements as:

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

while $a_{i0} = 0$, $a_{ij} = 0$ when $j > i$.

In the following we shall need a modified **A**, say $\bar{\mathbf{A}}$, of which the elements are given by $\bar{a}_{ij} = a_{i(i-j+1)}$. Independently of a_{ij}, the $\bar{a}_{ij}$ elements are accessible by a recurrence relation similar to (1):

$$\bar{a}_{11} = 1 \ , \ \bar{a}_{(i+1)j} = \bar{a}_{ij} + 2\bar{a}_{i(j-1)} \ , \qquad (2)$$

while $\bar{a}_{i0} = 0$, $\bar{a}_{ij} = 0$ when $j > i$. A portion of the (infinite) $\bar{\mathbf{A}}$ is specified below.

i	j: 1	2	3	4	5
1	1				
2	1	2			
3	1	4	4		
4	1	6	12	8	
5	1	8	24	32	16
....					

The following property of $\bar{\mathbf{A}}$ has been proved:

$$\sum_{j=1}^{i} \bar{a}_{ij} = 3^{i-1} \quad , \tag{3}$$

which we write in matrix notation as

$$\bar{\mathbf{A}}\,\{1\} = \{3^{i-1}\} \quad . \tag{4}$$

Another triangular matrix, $\bar{\mathbf{B}}$, is similar to $\bar{\mathbf{A}}$ and defined by:

$$\bar{b}_{11} = 1,\ \bar{b}_{(i+1)j} = \delta_{1j} + \bar{b}_{ij} + 2\ \bar{b}_{i(j-1)} \quad , \tag{5}$$

while $\bar{b}_{i0} = 0$, $\bar{b}_{ij} = 0$ when $j > i$. Here δ_{1j} is the Kronecker delta: $\delta_{1j} = 0$ for $j \neq 1$, $\delta_{11} = 1$. A portion of the $\bar{\mathbf{B}}$ matrix is:

i	j: 1	2	3	4	5
1	1				
2	2	2			
3	3	6	4		
4	4	12	16	8	
5	5	20	40	40	16
....					

It has been proved that:

$$\bar{b}_{ij} = \frac{1}{2}\,\bar{a}_{(i+1)(j+1)}. \tag{6}$$

What have the $\bar{a}_{ij}$ and $\bar{b}_{ij}$ numbers to do with the enumeration of di–5–catafusenes? This question is answered in the subsequent section.

Outline of the method

The present method, where the symmetry of the systems is exploited, has been described as "stupid sheep counting" [12]. 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

$$I_r = D_r + C_r + M_r + A_r = \tfrac{1}{4}(J_r + 3D_r + 2C_r + 2\,M_r) \ , \tag{7}$$

where I_r is the total number of isomers, while D_r , C_r , M_r and A_r are the numbers pertaining to the symmetry groups in the same order as they are specified above. Notice that A_r has been eliminated from the last expression in (7).

As a basic principle, the catacondensed unbranched indacenoids are generated by converting two hexagons in unbranched catafusenes by contraction to pentagons in all combinatorial ways, but so that isomorphic systems are avoided. In a catafusene, the hexagons may occur in three modes [13,14], viz. terminal (L_1), linearly annelated (L_2) and angularly annelated (A_2), out of which L_1 always is present. The contraction of an L_2–mode hexagon to pentagon introduces a kink so that one passes from a linear to an angular annelation. On the other hand, the corresponding contraction of A_2 preserves the angular annelation. Herefrom it is inferred that isomorphic systems are avoided if only the A_2 in addition to L_1–mode hexagons are contracted, but also the symmetry must be taken into account. From the well known generation of unbranched catafusenes [6,15] it was deduced that the a_{ij} numbers count the unbranched catafusene systems in the crude total such that $r = i + 1$, and $j + 1$ is the number of L_1 and L_2 hexagons taken together [11]. Similarly, the $\bar{a}_{ij}$ numbers count the systems where $i + 1$, and $j + 1$ is the number of L_1 and A_2 hexagons. This latter information links the $\bar{\mathbf{A}}$ matrix to the enumeration of unbranched di–*5*–catafusenes. In a similar way, the $\bar{\mathbf{B}}$ matrix is linked to the enumeration of symmetrical unbranched di–*5*–catafusenes. For the sake of brevity, we omit further details of these reasonings. A more detailed report with illustrations is in preparation.

The algebraic results

The different steps of the mathematical analysis are reported very briefly in the following.

The crude totals in matrix notation are:

$$\{J_{i+1}\} = \bar{\mathbf{A}}\,\{\tbinom{j+1}{2}\} = \{1, 7, 37, 171, 729, \dots\} \tag{8}$$

There is exactly one D_{2h} system for each r;

$$D_r = 1\ . \tag{9}$$

The numbers of the C_{2h} systems are somewhat more complicated:

$$\{C_{2i+2}\} = \{C_{2i+3}\} = \bar{\mathbf{B}}\,\{j+1\}\ , \tag{10}$$

which is equivalent to the following in terms of a finite summation.

$$C_{2i+2} = C_{2i+3} = \frac{1}{2}\sum_{j=1}^{i} (j+1)\,\bar{a}_{(i+1)(j+1)}\ . \tag{11}$$

Furthermore, the numbers of the C_{2v} systems are

$$M_k = C_k + K_k \ , \tag{12}$$

where K_k is given by

$$\{K_{2i+1}\} = \bar{\mathrm{A}}\ \{j\} = \{1, 5, 21, 81, 297, \dots\} \ . \tag{13}$$

On assembling the above relations, the following was arrived at in terms of finite summations with the $\bar{a}_{ij}$ elements:

$$I_r = \tfrac{1}{4}\{\ 1 + \sum_{j=1}^{r-1} \binom{j+1}{2} \bar{a}_{(r-1)j} + [3-(-1)^r] \sum_{j=1}^{\lfloor r/2 \rfloor} j\, \bar{a}_{\lfloor r/2 \rfloor j} \} \ . \tag{14}$$

Based on an explicit expression for $\bar{a}_{ij}$, which was found, and certain nontrivial mathematical identities involving binomial coefficients, it was achieved to render the formula (14) into an explicit expression in r. This is not the place to expand this derivation; we only give the final result:

$$I_r = \tfrac{1}{4}\{1 + (2r^2 + 2r - 3)\ 3^{r-4} + [3-(-1)^r](2\lfloor r/2 \rfloor + 1)\ 3^{\lfloor r/2 \rfloor - 2}\} \ . \tag{15}$$

Numerical values of the above analysis are collected in Table 4. It is noteworthy that these numbers are perfectly consistent with those from a computer analysis by Dobrynin [16], who based his algorithm on principles entirely different from ours.

Table 4
Numbers of unbranched di–5–catafusenes (nonhelicenic + helicenic)

r	D_{2h}	C_{2h}	C_{2v}	C_s	Total
2	1	0	0	0	1
3	1	0	1	1	3
4	1	2	2	7	12
5	1	2	7	38	48
6	1	10	10	172	193
7	1	10	31	715	757
8	1	40	40	2815	2896
9	1	40	121	10672	10834
10	1	148	148	39400	39697

Discussion and conclusion

The numbers in Tables 2 and 4 are identical up to $r \leq 5$ as they should be because the smallest helicenic catafusene has six hexagons. It is also a good check that the numbers for $r = 4$ are consistent with Fig. 1. From hexahelicene, $3C_{2v} + 6C_3$ indacenoids are created in consistency with the tables. In general, the number of helicenic unbranched catacondensed indacenoids are obtained on subtracting the numbers of Table 4 from those of Table 2.

The present work is a significant contribution to the enumeration of isomers of the indacenoid hydrocarbons [2–4], which have attracted renewed interest after the recent synthesis of $C_{30}H_{12}$ semibuckminsterfullerene [17]. Even more important, however, is the presentation of a new method of chemical enumerations, which so far has been applied to only one more case [11] simultaneously with the present work. This method, where certain triangular matrices are employed, is supposed to be applicable to several additional cases because the contraction of rings in organic chemistry, such as the conversion of hexagons to pentagons in the present work, is a frequently encountered process.

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