Enumeration of Chemical Isomers of Polycyclic Conjugated Hydrocarbons with Different Ring Sizes

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Polygonal systems, corresponding to completely condensed polycyclic conjugated hydrocarbons with arbitrary ring sizes, are studied. For all the cases up to four rings inclusive, the numbers of C_nH_s isomers are reported, as well as for some classes of the systems with five rings. Explicit combinatorial expressions and the solutions in terms of generating functions are given in some cases. These solutions were corroborated and extended by computer programming. Chemical applications are reported with references to hydrocarbons which are known in organic chemistry.

Introduction

The enumeration of isomers is a well-established branch of chemistry, especially in the organic chemistry. In the present work a certain class of polycyclic conjugated hydrocarbons is considered. With reference to chemical graphs [1] the structures of interest are represented by polygonal systems (see below for precise definitions). Mathematicians have been engaged in the enumeration problems of such systems for a long time [2–4]. Some works of Harary with collaborators [5, 6] and one of Read [7] are especially relevant to the present work, but not directly applicable.

The polycyclic conjugated hydrocarbons which are considered here, should be completely condensed in the sense that every carbon atom should belong to at least one ring. All possible ring sizes are taken into account. Only secondary and tertiary carbon atoms are allowed, and the secondary carbons (to which the hydrogen atoms are attached) should all be found at the outer boundary of the hydrocarbon. This specification excludes molecules with holes [8] as, e.g. kekulene [9].

In the present work the C_nH_s isomers for some subclasses of the polycyclic conjugated hydrocarbons are enumerated by analytical methods. Similar enumerations have been performed for catafusenes [5, 10, 11], which consist of six-membered rings only, and also for special forms of perifusenes [12, 13]. Papers in preparation deal with corresponding enumerations for mono-q-polyhexes [14], viz. polygonal systems with a

unique q-gon and otherwise hexagons. The cases for $q = 3$, 4 and 5 have been considered. In all these cases the sizes of the polygons are severely restricted. It seems that very little work in the same direction has been done for polygonal systems with arbitrary ring sizes. Dias [15] has emphasized the chemical interest of such studies and focused his attention on the polycyclic conjugated C_nH_s isomers where C_nH_s represents a benzenoid formula. He generated relevant isomers only for a few C_nH_s formulas and restricted the ring sizes (q) to $3 \leq q \leq 9$. Our approach is substantially more general.

Definitions and Notation

A polycyclic conjugated hydrocarbon of the kind which is considered here, is by definition represented by a system P of simply connected polygons, a polygonal system. Any two polygons should either share exactly one edge or they should be disjoint. In consequence, only vertices of degrees two and three will be present, corresponding to the secondary and tertiary carbon atoms, respectively. In some of the works which are mentioned in the above introduction [6, 7] allowance is made for vertices of degree four. Figure 1 exemplifies a polygonal system P and corresponds to a polycyclic conjugated hydrocarbon, $C_{26}H_{14}$, which is chemically known [15].

Let the number of q-gons in P be denoted by r_q, viz. $r_3, r_4, r_5, \ldots$, while r shall be used to identify the total number of polygons (or rings). In general, $q \geq 3$, but not otherwise restricted. In a given system P, however, there is clearly a polygon with the largest size, say $q = q(\text{max})$, in terms of the number of polygon edges.

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Then

$$r = r_3 + r_4 + r_5 + \ldots + r_{q(\max)} \ . \qquad (1)$$

Another important invariant (in addition to r) is n_i, indicating the number of internal vertices. In the system of Fig. 1, for instance, $r = 7$, $n_i = 4$. A (chemical) formula $C_n H_s$ is associated with a polygonal system P, as well as with the corresponding hydrocarbon. Then the number of carbon atoms (n) corresponds to the total number of vertices in P, while the number of hydrogens (s), corresponds to the number of vertices of degree two. The symbol $P(n; s)$ indicates that P has the formula $C_n H_s$.

The number of (chemical) $C_n H_s$ isomers among the polycyclic conjugated hydrocarbons is defined as the number of nonisomorphic polygonal systems (P) compatible with the given formula ($C_n H_s$). Two polygonal systems are nonisomorphic when they cannot be brought into each other by a rotation or a reflection, or a combination of these two operations, occasionally accompanied by deformations of the polygons.

Symmetry considerations are crucial in the present treatment. The symmetry group of a polygonal system P shall presently refer to the highest possible symmetry of P, where the geometrical planarity of P is preserved in particular. This symmetry conforms often, but not always, to the observed or expected symmetry of the corresponding hydrocarbon.

Finally in this section we shall define the polygon-edge sum, denoted by Σq. It is the sum of the edges for all the polygons taken individually, viz.

$$\Sigma q = 3r_3 + 4r_4 + 5r_5 + \ldots + q(\max) r_{q(\max)} \ . \quad (2)$$

For naphthalene, for instance, $\Sigma q = 12$.

Basic Principles

First Principle

Two polygonal systems with the same formula $C_n H_s$, viz. $P_1(n; s)$ and $P_2(n; s)$, have the same number of polygons (r).

In fact, r is determined by the pair of invariants (n, s). Specifically, one has

$$r = \tfrac{1}{2}(n - s) + 1 \ . \qquad (3)$$

Second Principle

Two polygonal systems $P_1(n; s)$ and $P_2(n; s)$ with the same number of internal vertices (n_i), have the same polygon-edge sum (Σq).

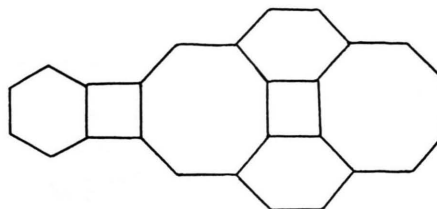

Fig. 1. A polygonal system corresponding to a polycyclic conjugated hydrocarbon $C_{26}H_{14}$.

This principle emerges from the following relation, which is easily found and has been given implicitly by Dias [15].

$$\Sigma q = n + 2r + n_i - 2 = 2n - s + n_i \ . \qquad (4)$$

The Method of Stupid Sheep Counting

Symmetry has been exploited many times in the enumerations of different classes of polygonal systems [4, 5, 13, 16, 17]. In this connection it is relevant to quote Redelmeier [18] in his work on counting polyominoes: "There is a well known way to count cattle in a herd: count the number of legs and divide by four." Although this "method" is referred to jokingly it is instructive to pursue the analogy with cattle counting in order to explain an essential part of the present methods. Assume that the legs of unknown numbers of sheep and shepherds were counted with the result J altogether. Next, assume that the number of shepherds was determined to be M when counted by heads. These two pieces of information are sufficient to give us the number of sheep (say U) and number of shepherds (M) separately, since we know that each sheep has four legs and a shepherd two. Hence the sum $I = M + U$ is determined, actually as $I = \tfrac{1}{4}(J + 2M)$. Because of this analogy we shall refer to our approach in the enumeration of polygonal systems as the method of "stupid sheep counting". Here "stupid" refers to the counting, not to the sheep.

Generating Functions

Generating functions represent a powerful tool in different enumeration problems [5–7, 11, 12, 19, 20], and they are often employed in connection with symmetry considerations. Also in the present work we have found it convenient to express the main results in terms of generating functions.

Mathematical Solutions of Numbers of Nonisomorphic Polygonal Systems

Classification of the Systems

A polygonal system P with r polygons may have a number of internal vertices up to a certain maximum: $n_i = 0, 1, 2, \ldots, (n_i)_{max}$. For $r = 1$ and $r = 2$, only $n_i = 0$ is possible; for $r = 3$, $n_i = 0$ or 1 (cf. Fig. 2, **I–IV**). For $r = 4$, the values $n_i = 0, 1, 2$ or 3 were found (**V–IX**). The case of $r = 4$, $n_i = 0$ splits into branched and unbranched (catacondensed) systems, identified in Fig. 2 as **VIII** and **IX**, respectively. Finally, Fig. 2 specifies fourteen classes (**X–XXIII**) for $r = 5$, where the n_i values are 0, 1, 2, 3, 4, 5.

Figure 2 includes the adopted coding for the different classes of polygonal systems; i, j, k, l, and m indicate the sizes (q) of the polygons. The codes are sometimes, but not always sufficient for identifying all the nonisomorphic isomers in question.

General Remarks

The goal is to find the number of nonisomorphic polygonal systems as a function of the polygon-edge sum (Σq) for as many as possible of the classes **I, II, III, ...** according to the above specifications (cf. especially Figure 2). Let this number be denoted by $\#I$. This is a reasonable notation since it represents the number of C_nH_s isomers for the relevant class of polycyclic conjugated hydrocarbons. The coefficients of the formula C_nH_s are determined by (r, n_i, Σq). Specifically, the relations (3) and (4) yield:

$$n = \Sigma q - 2r - n_i + 2, \tag{5}$$

$$s = n - 2r + 2 = \Sigma q - 4r - n_i - 4. \tag{6}$$

In the following we give the complete mathematical solutions of $\#I(\Sigma q)$ for the cases **I, II, III, IV, V, VI** and **XI**.

One Polygon

The trivial case of $r = 1$ (**I**) is included here for the sake of completeness. Then obviously $\#I = 1$ for each $\Sigma q = q = 3, 4, 5, \ldots$. The symmetry group is D_{qh}, viz. $D_{3h}, D_{4h}, D_{5h}, \ldots$. The appropriate generating function, viz. $I(x) = x^3 + x^4 + x^5 + \ldots$, is found in Table 1.

Two Polygons

Also the case of $r = 2$ (**II**) is easily solved. One finds the total numbers of isomers, $\#I = 1, 1, 2, 2, 3, 3, \ldots$

for $\Sigma q = 6, 7, 8, 9, 10, 11, \ldots$. Out of these there is exactly one isomer with the symmetry D_{2h} if and only if Σq is even. A mathematical expression for this number, viz. $\#I(D_{2h})$, is found in Table 1. All the other $\#I(C_{2v})$ isomers belong to C_{2v}. Table 1 includes a mathematical expression for the total number of isomers ($\#I$), and also the generating functions $D(x)$, $M(x)$ and $I(x)$, which reproduce the numbers $\#I(D_{2h})$, $\#I(C_{2v})$ and $\#I$, respectively. Notice that $M(x) = xI(x)$.

Three Polygons with One Internal Vertex

It seems worth while to treat the case of $r = 3$, $n_i = 1$ (**III**) in some detail; it is still quite simple, but lends itself to illustrate the applied methods.

Start with the pure combinatorial exercise to determine all permutations of the integers $a, b, c = 1, 2, 3, \ldots, N$ under the constraint $a + b + c = N + 2$. Example:

$$N = 4; \quad 114,$$
$$123, \ 213,$$
$$132, \ 222, \ 312,$$
$$141, \ 231, \ 321, \ 411.$$

The total number of permutations is

$$J = 1 + 2 + 3 + \ldots + N = \tfrac{1}{2} N(N+1) = \binom{N+1}{2}. \tag{7}$$

Now we must eliminate the equivalent permutations, e.g., by adopting the convention $a \le b \le c$ in (abc). Then (abc) represents (i) six permutations if $a < b < c$, (ii) three permutations if $a = b < c$ or $a < b = c$, and (iii) one permutation if $a = b = c$. Let the numbers of (abc) triples be U, M and T in the cases (i), (ii) and (iii), respectively. Then

$$J = T + 3M + 6U. \tag{8}$$

In the above example ($N = 4$, $J = 10$), one has $T = M = U = 1$. Introduce the total number of nonequivalent permutations as

$$I = T + M + U. \tag{9}$$

On eliminating U from (8) and (9) it is obtained

$$I = \tfrac{1}{6}(J + 5T + 3M). \tag{10}$$

Two more pieces of information are needed in order to determine I. Firstly, $T = 1$ if $N \equiv 1 \pmod 3$, otherwise $T = 0$; in other words: $T = 1, 0, 0, 1, 0, 0, \ldots$ for $N = 1$,
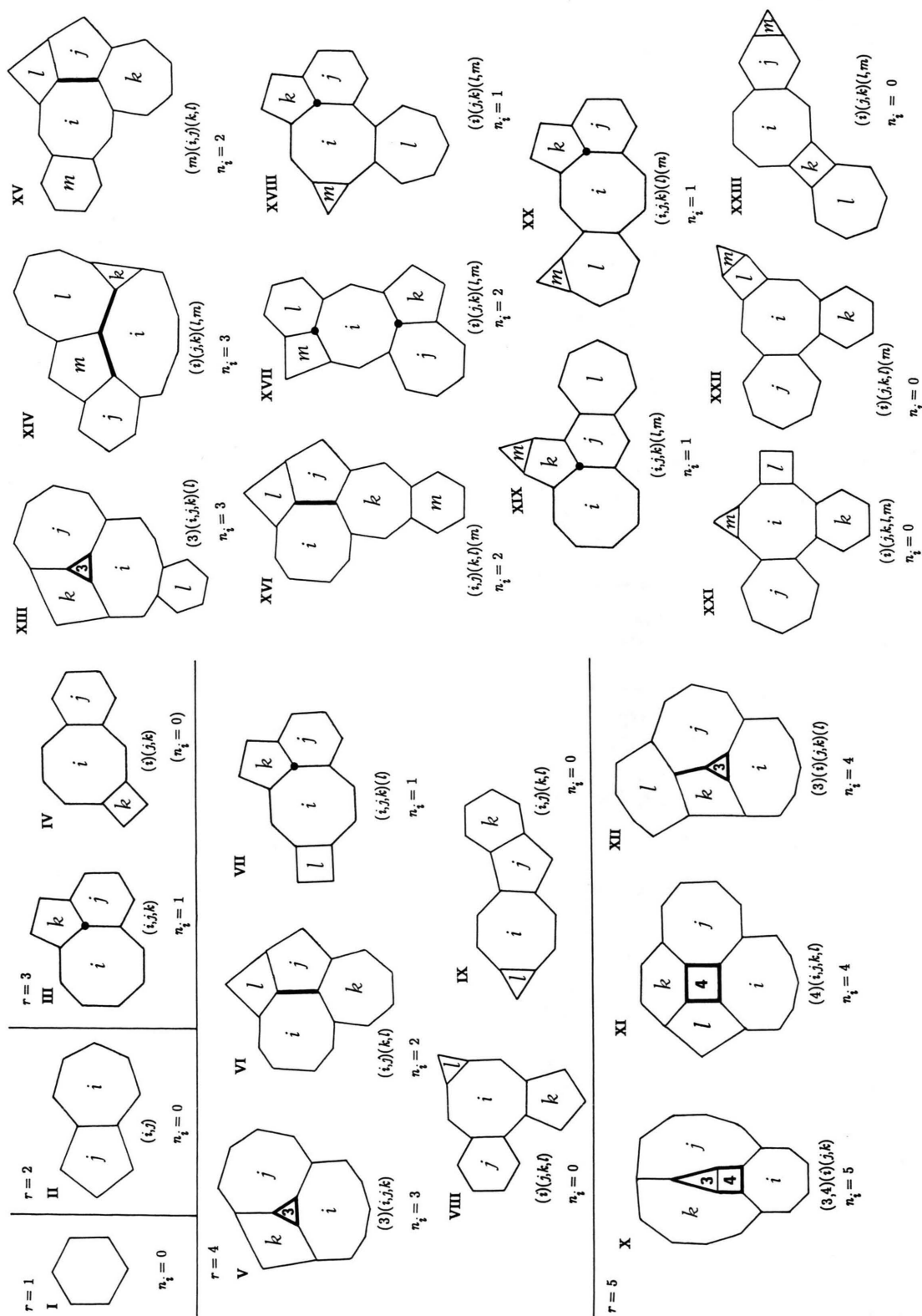
Fig. 2. Classes of polygonal systems with the number of polygons $r \leq 5$. Internal vertices are indicated by black dots or connected by heavy lines.

Table 1. Numbers of isomers within classes of polygonal systems or polycyclic conjugated hydrocarbons.

Class		Explicit expressions	Generating functions
I	$r=1$ $(n_i=0)$	$\#I = \#I(\mathrm{D}_{qh}) = 1$	$I(x) = x^3(1-x)^{-1}$
II	$r=2$ $(n_i=0)$	$\#I(\mathrm{D}_{2h}) = 1 - \lceil \frac{1}{2}\Sigma q \rceil + \lfloor \frac{1}{2}\Sigma q \rfloor$ $\#I = \lfloor \frac{1}{2}\Sigma q \rfloor - 2$	$D(x) = x^6(1-x^2)^{-1}$ $M(x) = x^7(1-x)^{-1}(1-x^2)^{-1}$ $I(x) = x^6(1-x)^{-1}(1-x^2)^{-1}$
III	$r=3$ $(n_i=1)$	$\#I(\mathrm{D}_{3h}) = 1 - \lceil \frac{1}{3}\Sigma q \rceil + \lfloor \frac{1}{3}\Sigma q \rfloor$ $\#I(\mathrm{D}_{3h}) + \#I(\mathrm{C}_{2v}) = \lceil \frac{1}{2}\Sigma q \rceil - 4$ $\#I = \frac{1}{12}(\Sigma q - 7)(\Sigma q - 8) + \frac{1}{2}\lceil \frac{1}{2}\Sigma q \rceil$ $\quad - \frac{1}{3}(\lceil \frac{1}{3}\Sigma q \rceil - \lfloor \frac{1}{3}\Sigma q \rfloor) - \frac{5}{3}$	$T(x) = x^9(1-x^3)^{-1}$ $M(x) = x^{10}(1+2x)(1-x^2)^{-1}(1-x^3)^{-1}$ $U(x) = x^{12}(1-x)^{-1}(1-x^2)^{-1}(1-x^3)^{-1}$ $I(x) = x^9(1-x)^{-1}(1-x^2)^{-1}(1-x^3)^{-1}$
IV	$r=3$ $(n_i=0)$	$\#I(\mathrm{D}_{2h}) = (1 - \lceil \frac{1}{2}\Sigma q \rceil + \lfloor \frac{1}{2}\Sigma q \rfloor)(\frac{1}{2}\Sigma q - 4)$ $\#I(\mathrm{C}_{2v}) = \lceil \frac{1}{2}\Sigma q - 4 \rceil \times \lceil \frac{1}{2}\Sigma q - 5 \rceil$ $\#I = \frac{1}{6}\lceil \frac{1}{2}\Sigma q - 3 \rceil (\Sigma q - 7)\lfloor \frac{1}{2}\Sigma q - 4 \rfloor$	$D(x) = x^{10}(1-x^2)^{-2}$ $M(x) = 2x^{11}(1+x)(1-x^2)^{-3}$ $U(x) = x^{12}(1-x)^{-2}(1-x^2)^{-2}$ $I(x) = x^{10}(1-x)^{-2}(1-x^2)^{-2}$
V	$r=4$ $(n_i=3)$	$\#I(\mathrm{D}_{3h}) = 1 - \lceil \frac{1}{3}\Sigma q \rceil + \lfloor \frac{1}{3}\Sigma q \rfloor$ $\#I(\mathrm{D}_{3h}) + \#I(\mathrm{C}_{2v}) = \lceil \frac{1}{2}\Sigma q \rceil - 7$ $\#I = \frac{1}{12}(\Sigma q - 13)(\Sigma q - 14) + \frac{1}{2}\lceil \frac{1}{2}\Sigma q \rceil$ $\quad - \frac{1}{3}(\lceil \frac{1}{3}\Sigma q \rceil - \lfloor \frac{1}{3}\Sigma q \rfloor) - \frac{19}{6}$	$T(x) = x^{15}(1-x^3)^{-1}$ $M(x) = x^{16}(1+2x)(1-x^2)^{-1}(1-x^3)^{-1}$ $U(x) = x^{18}(1-x)^{-1}(1-x^2)^{-1}(1-x^3)^{-1}$ $I(x) = x^{15}(1-x)^{-1}(1-x^2)^{-1}(1-x^3)^{-1}$
VI	$r=4$ $(n_i=2)$	$\#I(\mathrm{D}_{2h}) = (1 - \lceil \frac{1}{2}\Sigma q \rceil + \lfloor \frac{1}{2}\Sigma q \rfloor)(\frac{1}{2}\Sigma q - 6)$ $\#I(\mathrm{C}_{2v}) = \lceil \frac{1}{2}\Sigma q - 6 \rceil \times \lceil \frac{1}{2}\Sigma q - 7 \rceil$ $\#I = \frac{1}{6}\lceil \frac{1}{2}\Sigma q - 5 \rceil (\Sigma q - 11)\lfloor \frac{1}{2}\Sigma q - 6 \rfloor$	$D(x) = x^{14}(1-x^2)^{-2}$ $M(x) = 2x^{15}(1+x)(1-x^2)^{-3}$ $U(x) = x^{16}(1-x)^{-2}(1-x^2)^{-2}$ $I(x) = x^{14}(1-x)^{-2}(1-x^2)^{-2}$

2, 3, 4, 5, 6,.... In explicit form:

$$T = 1 - \lceil \tfrac{1}{3}(N-1) \rceil + \lfloor \tfrac{1}{3}(N-1) \rfloor . \tag{11}$$

Secondly, $T + M = N/2$ if $N \equiv 0 \pmod 2$ and $T + M = \frac{1}{2}(N+1)$ if $N \equiv 1 \pmod 2$. In explicit form:

$$T + M = \lceil N/2 \rceil . \tag{12}$$

Now the number I for every N is obtainable from the relations (7) and (10)–(12). In the above analysis the method of stupid sheep counting is clearly recognized.

The generating function which corresponds to J is an elementary result with reference to the expression (7); one has:

$$J(x) = \sum_{N=1}^{\infty} \binom{N+1}{2} x^N = x(1-x)^{-3} . \tag{13}$$

Also the generating functions which are associated with (11) and (12), are readily determined, viz.

$$T(x) = x(1-x^3)^{-1} \tag{14}$$

and

$$T(x) + M(x) = x(1-x)^{-1}(1-x^2)^{-1}, \tag{15}$$

which yields

$$M(x) = x^2(1+2x)(1-x^2)^{-1}(1-x^3)^{-1} . \tag{16}$$

Consequently, one obtains the generating function for the numbers I, viz. $I(x)$, from the relation for generating functions of the same form as (10). Consequently,

$$I(x) = x(1-x)^{-1}(1-x^2)^{-1}(1-x^3)^{-1} . \tag{17}$$

Also the generating function $U(x)$ for the numbers U is now accessible from (9); the interesting relation $U(x) = x^3 I(x)$ was deduced.

The above analysis is readily applicable to the class **III** of polygonal systems. Convert (a, b, c) to (i, j, k) by $i = a+2, j = b+2, k = c+2$. This is consistent with the transformation $\Sigma q = i+j+k = a+b+c+6 = N+8$. In consequence I reproduces exactly the numbers of isomers, $\#I$, when N is identified with $\Sigma q - 8$. The

same transformation converts also U, M, and T to $\#I(C_s)$, $\#I(C_{2v})$ and $\#I(D_{3h})$, respectively, since the symmetry groups of the isomers conform with the conditions: (i) unsymmetrical (C_s) isomers when $i < j < k$; (ii) mirror-symmetrical (C_{2v}) isomers when $i = j < k$ or $i < j = k$; (iii) regular trigonal (D_{3h}) isomers when $i = j = k$. The explicit expressions for $\#I(D_{3h})$, $\#I(D_{3h}) + \#I(C_{2v})$ and $\#I$ in terms of Σq are found in Table 1. Let now $T(x)$, $M(x)$, $U(x)$ and $I(x)$ be used to identify the generating functions for the numbers $\#I(D_{3h})$, $\#I(C_{2v})$, $\#I(C_s)$ and $\#I$, respectively, when related to Σq. The appropriate transformation $\Sigma q = N + 8$ yields simply $T(x) = x^8 T(x)$, $M(x) = x^8 M(x)$, etc. The resulting four functions are included in Table 1.

Three Polygons without Any Internal Vertex

In the coding $(i)(j, k)$ for the case $r = 3$, $n_i = 0$ (**IV**), the ring size i refers to the middle ring, to which the rings of the sizes j and k are annelated. The possible values of i, j and k are given by $a, b, c = 1, 2, 3, \ldots, N$ when $i = a + 3$, $j = b + 2$ and $k = c + 2$. Then $\Sigma q = N + 9$. An i-membered ring has $i - 3 = a$ sites of annelation for two other rings. For each a or i there are $N - a + 1 = \Sigma q - i - 5$ permutations of b and c or j and k. Hence for the "crude total" of the number of the isomers one has

$$J = \sum_{a=1}^{N} (N - a + 1) \, a = \tfrac{1}{6} N(N+1)(N+2) \quad (18)$$

and the corresponding generating function:

$$J(x) = \sum_{N=1}^{\infty} \binom{N+2}{3} x^N = x(1-x)^{-4}. \quad (19)$$

This crude total counts the D_{2h}, C_{2v} and C_s isomers once, twice and four times, respectively;

$$J = D + 2M + 4U. \quad (20)$$

Hence for the number of nonisomorphic isomers (I) one has:

$$I = D + M + U = \tfrac{1}{4}(J + 3D + 2M). \quad (21)$$

It was found: $\#I(D_{2h}) = \varepsilon(\tfrac{1}{2}\Sigma q - 4)$, where $\varepsilon = 1$ when Σq is even, and $\varepsilon = 0$ when Σq is odd. Furthermore, $\#I(C_{2v}) = \tfrac{1}{4}(\Sigma q - 8)(\Sigma q - 10)$ when Σq is even, and $\#I(C_{2v}) = \tfrac{1}{4}(\Sigma q - 7)(\Sigma q - 9)$ when Σq is odd. These findings are consistent with the pertinent explicit expressions in Table 1, which also includes the explicit result for $\#I$. The relevant generating func-

tions, $D(x) = x^9 D(x)$, $M(x) = x^9 M(x)$, etc., are also given (Table 1). Notice that $U(x) = x^2 I(x)$.

The C_{2v} isomers were found to be equally partitioned into two types, say C_{2v}^a and C_{2v}^b, where the two-fold symmetry axis passes between the two outer polygons or goes through them, respectively.

Four Polygons with Three Internal Vertices

In the case of $r = 4$, $n_i = 3$ (**V**) the central polygon is invariably a triangle. The minimum value of i, j and k is 4, while Σq starts at 15. This case is clearly isomorphous with the one of $r = 3$, $n_i = 1$ (**III**). One only has to substitute Σq in the expressions under **III** by $\Sigma q - 6$ and multiply the generating functions by x^6.

Four Polygons with Two Internal Vertices

In the coding $(i, j)(k, l)$ for the case $r = 4$, $n_i = 2$ (**VI**), the first pair, (i, j), refers to the polygons which share the middle edge, while the polygons of the second pair, (k, l), are disjoint. The minimum value of i and j is 4, while it is 3 for k and l. The Σq value starts at 14. It was found that this case is isomorphous with the one of $r = 3$, $n_i = 0$. One only has to substitute Σq in the expressions under **IV** by $\Sigma q - 4$ and multiply the generating functions by x^4.

The isomorphism with the case **IV** implies an equipartition of the C_{2v} systems. The two types C_{2v}^a and C_{2v}^b are recognized in the present case (**VI**) as those with $i \neq j$ & $k = l$ or $i = j$ & $k \neq l$, respectively.

Five Polygons with Four Internal Vertices in a Cycle

Start with the permutations of $a, b, c, d = 1, 2, 3, \ldots, N$ under the constraint $a + b + c + d = N + 3$. The expressions for the total number of permutations (crude total) and the corresponding generating function are identical with the appropriate expressions of case **IV** and given by (19). In the present case,

$$J = S + 2D + 4M + 8U \quad (22)$$

and

$$I = S + D + M + U = \tfrac{1}{8}(J + 7S + 6D + 4M), \,(23)$$

where S, D, M, and U pertain to the symmetry groups D_{4h}, D_{2h}, C_{2v}, and C_s, respectively. If $N \equiv 1 \pmod 4$, then $S = 1$, else $S = 0$. Furthermore, if $N \equiv 1 \pmod 2$, then $S + D = \lceil \tfrac{1}{4}(N+1) \rceil$, else $S + D = 0$. Finally, if $N \equiv 0 \pmod 2$, then $S + 2M = 2 + 4 + 6 + \ldots + N = \tfrac{1}{4}N(N+2)$; if $N \equiv 1 \pmod 2$, then $S + 2M = 1 + 3 + 5 + \ldots + N =$

$\frac{1}{4}(N+1)^2$. The expressions of S, D, and M are converted to $\#I(D_{4h})$, $\#I(D_{2h})$ and $\#I(C_{2v})$, respectively, by means of the substitution $N=\Sigma q-19$. Hence:

$$\#I(D_{4h}) = 1-\lceil\tfrac{1}{4}\Sigma q\rceil+\lfloor\tfrac{1}{4}\Sigma q\rfloor, \tag{24}$$

$$\#I(D_{4h}) + \#I(D_{2h})$$
$$= (1-\lceil\tfrac{1}{2}\Sigma q\rceil+\lfloor\tfrac{1}{2}\Sigma q\rfloor)(\lfloor\tfrac{1}{4}\Sigma q\rfloor-4), \tag{25}$$

$$\#I(D_{4h}) + 2\,[\#I(C_{2v})]$$
$$= (\lceil\tfrac{1}{2}\Sigma q\rceil-9)(\lfloor\tfrac{1}{2}\Sigma q\rfloor-9). \tag{26}$$

Furthermore, for the number of nonisomorphic isomers, one has

$$\#I = \tfrac{1}{48}(\Sigma q-18)\,[(\Sigma q-17)(\Sigma q-19)+3\,(\Sigma q-15)]$$
$$+\tfrac{1}{4}(1-\lceil\tfrac{1}{4}\Sigma q\rceil+\lfloor\tfrac{1}{4}\Sigma q\rfloor) \tag{27}$$

when Σq is even, and

$$\#I = \tfrac{1}{48}(\Sigma q-15)(\Sigma q-17)(\Sigma q-19) \tag{28}$$

when Σq is odd. Also the relevant generating functions, viz. $S(x)$, $D(x)$, etc., were worked out and transformed to $\boldsymbol{S}(x)=x^{19}S(x)$, $\boldsymbol{D}(x)=x^{19}D(x)$, etc. The results are

$$\boldsymbol{S}(x) = x^{20}(1-x^4)^{-1}, \tag{29}$$

$$\boldsymbol{D}(x) = x^{22}(1-x^2)^{-1}(1-x^4)^{-1}, \tag{30}$$

$$\boldsymbol{M}(x)= x^{21}(1-x)^{-2}(1-x^4)^{-1}, \tag{31}$$

$$\boldsymbol{U}(x) = x^{23}(1-x)^{-2}(1-x^2)^{-1}(1-x^4)^{-1}, \tag{32}$$

$$\boldsymbol{I}(x) = x^{20}(1-x+x^2)(1-x)^{-2}(1-x^2)^{-1}(1-x^4)^{-1}. \tag{33}$$

The C_{2v} isomers of the category under consideration split into the two types C_{2v}^a and C_{2v}^d, where the two-fold symmetry axis intersects two edges of the central quadrangle or passes through two vertices of it, respectively. Then, for the pertinent numbers of isomers, $\#I(C_{2v}^d) = \#I(D_{2h})$ and $\#I(C_{2v}^a)= \#I(C_{2v}) - \#I(D_{2h})$. For the corresponding generating functions, one finds $\boldsymbol{M}^d(x) = \boldsymbol{D}(x)$ and

$$\boldsymbol{M}^a(x) = x^{21}(1-x)^{-1}(1-x^2)^{-2}. \tag{34}$$

Numerical Solutions for Numbers of Nonisomorphic Polygonal Systems

Computerized enumerations of C_nH_s isomers for most of the classes of polygonal systems which are specified in Fig. 2, were performed parallel with the mathematical analyses of the preceding section. The computer programs for this purpose were based on straightforward combinatorics. In this way all the above analytical results, which are summarized in Table 1 and Eqs. (24)–(34), were checked numerically. In addition, numerical results were achieved for several classes for which no analytical solution is available. In fact, the numbers of C_nH_s isomers were found for all the classes I–XIII with computer aid. For the sake of brevity we shall not reproduce the voluminous data, which were generated, in the present paper. However, several of these numbers are employed in the subsequent applications.

Chemical Applications

General

The numbers of C_nH_s isomers for benzenoids, the polygonal systems possessing exclusively hexagons, are known to a large extent [21]. Some works in the same direction have recently been done on fluorenoids/fluoranthenoids [22–24], each of these systems consisting of exactly one pentagon and otherwise hexagons. Similar studies of biphenylenoids [25] have been initiated. A biphenylenoid consists of exactly one

Table 2. Numbers of C_nH_s isomers for polygonal systems or polycyclic conjugated hydrocarbons.

r	Formula	n_i	Benz- enoids[a]	Fluor- anth- enoids	Biphenyl- enoids	Others	Total
1	C_4H_4	0	0	0	1 [b]	0	1
	C_6H_6	0	1	0	0	0	1
2	C_8H_6	0	0	0	1 [b]	2	3
	$C_{10}H_8$	0	1	0	0	3	4 [c]
	$C_{12}H_{10}$	0	0	0	0	5	5
3	$C_{12}H_8$	0	0	0	3	27	30
		1	0	1 [d]	0	9	10
	$C_{14}H_{10}$	0	2	0	0	53	55
		1	0	0	0	14	14
4	$C_{14}H_8$	2	0	0	2 [b]	53	55
	$C_{16}H_{10}$	0	0	0	8 [e]	487	495
		1	0	4 [e]	0	361	365
		2	1	0	0	90	91
		3	0	0	0	14	14
5	$C_{16}H_8$	4	0	0	1	123	124
	$C_{18}H_{10}$	3	0	3 [d]	0	873	876
		4	0	0	0	208	208

[a] Brunvoll and Cyvin [21] with references cited therein.
[b] Cyvin et al. [25]. – [c] Dias (1984) [27]. – [d] Dias (1991) [22].
[e] Dias (1988) [15].

tetragon and otherwise hexagons. Finally, some results on isomer enumeration for indacenoids [26], each consisting of two pentagons and otherwise hexagons, are available.

We are now able to give the numbers of C_nH_s isomers for the smallest polygonal systems with arbitrary polygon sizes. Such data for selected even-carbon C_nH_s formulas of chemical importance are collected in Table 2. Numbers for the subclasses of polygonal systems which represent benzenoids, fluoranthenoids and biphenylenoids are given separately therein.
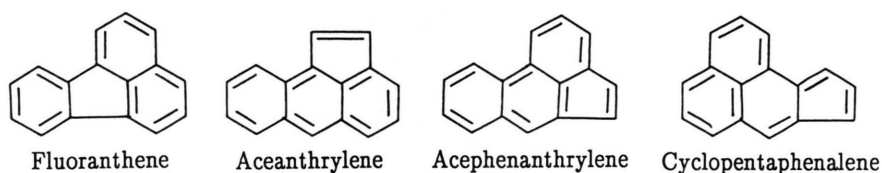
Two Polygons

Among the 3 isomers of C_8H_6 is the unique indacenoid isomer [26] with this formula, viz. pentalene, coded **II**(5, 5) with reference to Figure 2. In Table 2, $C_{10}H_8$ is the formula of naphthalene, viz. **II**(6, 6), azulene, **II**(7, 5), **II**(8, 4) and **II**(9, 3) [15, 27]. Heptalene, **II**(7, 7) is an isomer of $C_{12}H_{10}$.

Benzo[*a*]azulene   Benzo[*e*]azulene   Benzo[*f*]azulene
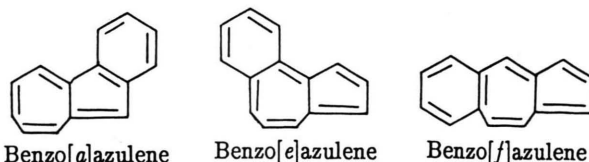
At least two $C_{14}H_{10}$ isomers within the class $r = 3$, $n_i = 1$ are chemically known [15]: aceheptylene, **III**(7, 7, 5); cyclohepta[*de*]naphthalene, **III**(7, 6, 6).

Four Polygons

Among the $C_{14}H_8$ isomers with $n_i = 2$, apart from the two biphenylenoids [25], one finds the three indacenoids [26], out of which pyracylene, coded **VI**(6, 6)(5, 5), is known in organic chemistry. The pyrene ($C_{16}H_{10}$) isomers are especially of interest [15]. A few $n_i = 0$ polycyclic conjugated hydrocarbons with this formula are known [15], both biphenylenoids and indacenoids. As to the $n_i = 1$ isomers of $C_{16}H_{10}$ one finds fluoranthene among them:

Fluoranthene   Aceanthrylene   Acephenanthrylene   Cyclopentaphenalene

Three Polygons

The first formula for $r = 3$ in Table 2, viz. $C_{12}H_8$, represents biphenylene, **IV**(4)(6, 6), and within the same class ($n_i = 0$) the three existing indacenoid isomers [27] with this formula: **IV**(6)(5, 5) indacenes; **IV**(5)(6, 6) benzopentalene. Structural formulas:

s–Indacene   *as*–Indacene   Benzopentalene
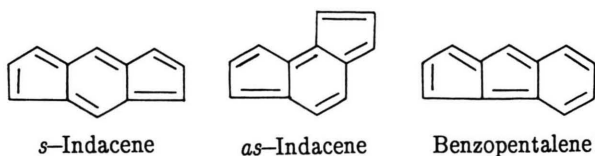
In the class of $r = 3$, $n_i = 1$, the unique $C_{12}H_8$ fluoranthenoid [22, 23] is acenaphthylene, **III**(6, 6, 5). The important anthracene/phenanthrene isomers have the formula $C_{14}H_{10}$. In the class with $n_i = 0$, apart from the two mentioned benzenoids, three isomers of benzoazulenes are chemically known:

Here the three **VII**(6, 6, 5)(6) isomers are chemically known [15], while **VII**(6, 6, 6)(5) seems to be unknown. The formula $C_{18}H_{12}$ (not included in Table 2) represents the 5 catacondensed benzenoids and the total of 1154 polygonal systems with $r = 4$, $n_i = 0$. The corresponding numbers for $n_i = 1$, 2, and 3 were found to be 693, 140, and 19, respectively. There are no fluoranthenoids or biphenylenoids with this formula.

Five Polygons

A unique biphenylenoid with the formula $C_{16}H_8$, viz. **XI**(4)(6, 6, 6, 6), can be constructed. There are three fluoranthenoids with the formula $C_{18}H_{10}$ [22, 23]; they belong to the class **XIV**. Our final example is one of the 72 $C_{20}H_{12}$ isomers, viz. the D_{2h} system of **XI**(4)(8, 8, 6, 6), which has been listed as chemically known [15]; it is the core of the system depicted in Figure 1.

Conclusion

The present work sheds light into the enumeration of C_nH_s isomers of polycyclic conjugated hydrocarbons of an unprecedented generality, but only the structures with five rings or less are treated ($r \leq 5$). Complete solutions for the numbers of isomers were achieved for $r \leq 4$, but incomplete for $r = 5$. On the other hand, the C_nH_s formulas which are accounted for, contain many chemically important formulas. An extension of this work, first of all to the remaining classes with $r = 5$ (**XIV**−**XXIII** of Fig. 2), would certainly be of interest in organic chemistry.

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