

NUMBER AND FORMS OF TETRACYCLIC POLYGONAL PYRENE ISOMERS

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Abstract: Polygonal systems (P) correspond to polycyclic conjugated hydrocarbons. The (cyclic polygonal) pyrene isomers ($C_{16}H_{10}$) belonging to the class P are enumerated. The resulting 965 isomers are specified in terms of polygon sizes within the five subclasses: $n_i = 0$ (branched and unbranched), $n_i = 1, 2, 3$. Here n_i is used to denote the number of internal vertices.

Enumerations of chemical graphs corresponding to different classes of molecules are of current interest in mathematical chemistry. Some time ago an enumeration of $C_{16}H_{10}$ (pyrene) tetracyclic polygonal isomers among completely condensed polycyclic conjugated hydrocarbons was reported in this journal [1]. That work included depictions of the relevant forms, but several of them must have been inadvertently omitted, as has been documented recently in an article entitled "The number of pyrene isomers is still unknown" [2]. This statement is no longer true. In a series of works [3] the enumeration problem was solved completely, not only for pyrene isomers, but for all structures of the class of interest with numbers of rings $r \leq 5$ (pyrene has $r = 4$).

In some of the cited works [3] generating functions are employed, a useful tool in different kinds of enumerations [4]. In the present work the generating functions which pertain to the pyrene problem are quoted and used to deduce the total number of isomers. Furthermore, all the forms of these pyrene isomers are specified for the first time.

Classes of hydrocarbons. The completely condensed polycyclic conjugated hydrocarbons are represented by polygonal systems, P. A system P is defined as a geometrical arrangement of simply connected polygons, where any two polygons either share exactly one edge or are disjoint. Four polygons ($r = 4$) may be arranged into P systems so that the n_i number of vertices is 0, 1, 2 or 3; the last possibility has been overlooked in some of the earlier works [1, 2]. In the case of $n_i = 0$, the subclasses of branched and unbranched (catacondensed) systems are distinguished.

The five subclasses to be taken into account are exemplified in Fig. 1.

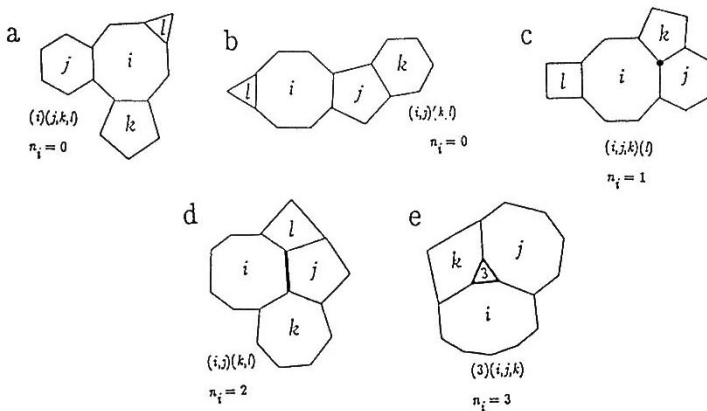


Figure 1. The five subclasses of polygonal systems (P) with four polygons each ($r = 4$). Codings of the forms in terms of polygon sizes (i, j, k, l) are indicated.

The polygons represent q -membered rings, where $q \geq 3$. The sizes (q) of the four rings are symbolized by i, j, k and l .

A chemical formula $C_n H_s$ is associated with any P system. Given a formula, the r number of polygons is determined. The relations

$$s = \Sigma q - 4r - n_i + 4, \quad n = s + 2r - 2 \quad (1)$$

are generally valid for P. Here Σq is the polygon-edge sum. For $r = 4$, the case of interest in the present work, one has $\Sigma q = i + j + k + l$, and consequently:

$$s = i + j + k + l - n_i - 12, \quad n = s + 6 \quad (2)$$

Numbers of isomers. The subclasses of P isomers ($r = 4$) with different values of n_i are considered separately. In each case, the generating function [3] is specified in the following as

$$\alpha I(x) = \sum_{s=s_{\min}}^{\infty} (\alpha I_s) x^s \quad (3)$$

where αI_s identifies the numbers of $C_n H_s$ isomers for the subclass $\alpha = a, b, c, d$ or e (cf. Fig. 1).

a: Branched catacondensed ($n_i = 0$) P systems.

$$\begin{aligned} a I(x) &= \sum_{s=3}^{\infty} (a I_s) x^s = x^3 (1+x^2+2x^3+x^4+x^6)(1-x)^{-2} (1-x^2)^{-2} (1-x^3)^{-2} \\ &= x^3 + 2x^4 + 6x^5 + 14x^6 + 28x^7 + 52x^8 + 93x^9 + 152x^{10} + 242x^{11} + 370x^{12} + \dots \end{aligned} \quad (4)$$

Here the coefficient for x^{10} (underlined) indicates the 152 $C_{16}H_{10}$ isomers belonging to the subclass a.

b: Unbranched catacondensed ($n_i = 0$) P systems.

$$\begin{aligned} {}^bI(x) &= \sum_{s=2}^{\infty} ({}^bI_s)x^s = x^2(1-x+2x^2)(1-x)^{-3}(1-x^2)^{-3} \\ &= x^2+2x^3+8x^4+16x^5+38x^6+68x^7+128x^8+208x^9+\underline{343}x^{10}+518x^{11}+784x^{12}+ \dots \end{aligned} \quad (5)$$

c: P systems with one internal vertex ($n_i = 1$).

$$\begin{aligned} {}^cI(x) &= \sum_{s=1}^{\infty} ({}^cI_s)x^s = x(1+x^2)(1-x)^{-3}(1-x^2)^{-2} \\ &= x+3x^2+9x^3+19x^4+38x^5+66x^6+110x^7+170x^8+255x^9 \\ &\quad +\underline{365}x^{10}+511x^{11}+693x^{12}+ \dots \end{aligned} \quad (6)$$

d: P systems with two internal vertices ($n_i = 2$), which are connected.

$$\begin{aligned} {}^dI(x) &= \sum_{s=0}^{\infty} ({}^dI_s)x^s = (1-x)^{-2}(1-x^2)^{-2} \\ &= 1+2x+5x^2+8x^3+14x^4+20x^5+30x^6+40x^7+55x^8+70x^9 \\ &\quad +\underline{91}x^{10}+112x^{12}+140x^{12}+ \dots \end{aligned} \quad (7)$$

Among the 91 $C_{16}H_{10}$ isomers of this subclass one finds pyrene (for $i = j = k = l = 6$).

e: P systems with three internal vertices ($n_i = 3$).

$$e_I(x) = \sum_{s=0}^{\infty} (e_{I_s}) x^s = (1-x)^{-1} (1-x^2)^{-1} (1-x^3)^{-1}$$

$$= 1+x+2x^2+3x^3+4x^4+5x^5+7x^6+8x^7+10x^8+12x^9+\underline{14}x^{10}+16x^{11}+19x^{12}+ \dots \quad (8)$$

The total number of $C_{16}H_{10}$ isomers among the polycyclic conjugated hydrocarbons represented by P is - cf. eqns. (4)-(8) - $152+343+365+91+14 = \underline{965}$.

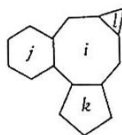
Forms of isomers. Codings for the forms of the isomers within the five subclasses under consideration, are indicated in Fig. 1. All the isomers are listed by these codes in Charts A - E for the subclasses a - e, respectively. In the cases A and B, the codes in terms of polygon sizes (i, j, k, l) are usually not sufficient to specify all the individual isomers because there may be different combinatorial possibilities for annelations of polygons. Therefore a parameter a is added (after a colon) to the code in these cases, indicating the number of possible annelations.

In the present analysis it is allowed for polygon sizes $q \geq 3$ with no upper limit. Nevertheless, q has a maximum value for the different subclasses, viz. 13, 12, 14, 14 and 14 for a - e, respectively. In the work of Reference [1] only the polygon sizes $3 \leq q \leq 9$ were considered. The isomers which comply with this restriction, are marked with asterisks in Charts A - E.

a: Branched catacondensed ($n_i = 0$) P systems. The pertinent codes and a values (numbers of annelation schemes) are specified in Chart A. The example in Fig. 1 has the code (8)(6,5,3), for which $a = 6$. The corresponding six schemes of annelation are easily deduced and shown in Fig. 2. Similarly, it is assumed that the different annelation schemes are easily obtained by a piece of combinatorial reasoning, so that the detailed specifications are not needed here.

Chart A

Branched catacondensed



(i) (j,k,l):a

(13) (3,3,3):8	(9) (6,4,3):10*	(7) (9,3,3):2*	(6) (9,4,3):1*
(12) (4,3,3):16	(9) (5,5,3):6*	(7) (8,4,3):3*	(6) (8,5,3):1*
(11) (5,3,3):12	(9) (5,4,4):6*	(7) (7,5,3):3*	(6) (8,4,4):1*
(11) (4,4,3):12	(8) (8,3,3):4*	(7) (7,4,4):2*	(6) (7,6,3):1*
(10) (6,3,3):9	(8) (7,4,3):6*	(7) (6,6,3):2*	(6) (7,5,4):1*
(10) (5,4,3):15	(8) (6,5,3):6*	(7) (6,5,4):3*	(6) (6,6,4):1*
(10) (4,4,4):4	(8) (6,4,4):4*	(7) (5,5,5):1*	(6) (6,5,5):1*
(9) (7,3,3):6*	(8) (5,5,4):4*	(6) (10,3,3):1	

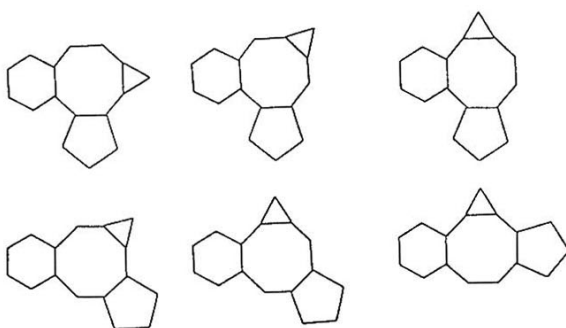
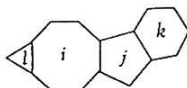


Figure 2. The six isomers coded (8)(6,5,3) in Subclass a.

b: Unbranched catacondensed (n_i) P systems; see Chart B. The example in Fig. 1 is (8,5)(6,3), for which $a = 10$. The corresponding ten schemes of annelation are depicted in Fig. 3.

Chart B

Unbranched catacondensed



$(i,j)(k,l):a$

(12,4)(3,3):5	(8,7)(4,3):20*	(7,5)(5,5):4*	(5,5)(9,3):2*
(11,5)(3,3):8	(8,6)(5,3):16*	(7,4)(8,3):4*	(5,5)(8,4):2*
(11,4)(4,3):8	(8,6)(4,4):8*	(7,4)(7,4):4*	(5,5)(7,5):2*
(10,6)(3,3):11	(8,5)(6,3):10*	(7,4)(6,5):4*	(5,5)(6,6):2*
(10,5)(4,3):14	(8,5)(5,4):10*	(6,6)(7,3):5*	(5,4)(10,3):2
(10,4)(5,3):8	(8,4)(7,3):6*	(6,6)(6,4):5*	(5,4)(9,4):2*
(10,4)(4,4):4	(8,4)(6,4):6*	(6,6)(5,5):4*	(5,4)(8,5):2*
(9,7)(3,3):12*	(8,4)(5,5):3*	(6,5)(8,3):6*	(5,4)(7,6):2*
(9,6)(4,3):18*	(7,7)(5,3):8*	(6,5)(7,4):6*	(4,4)(11,3):1
(9,5)(4,4):6*	(7,7)(4,4):6*	(6,5)(6,5):6*	(4,4)(10,4):1
(9,5)(5,3):12*	(7,6)(6,3):12*	(6,4)(9,3):4*	(4,4)(9,5):1*
(9,4)(6,3):6*	(7,6)(5,4):12*	(6,4)(8,4):4*	(4,4)(8,6):1*
(9,4)(5,4):6*	(7,5)(7,3):8*	(6,4)(7,5):4*	(4,4)(7,7):1*
(8,8)(3,3):9*	(7,5)(6,4):8*	(6,4)(6,6):2*	

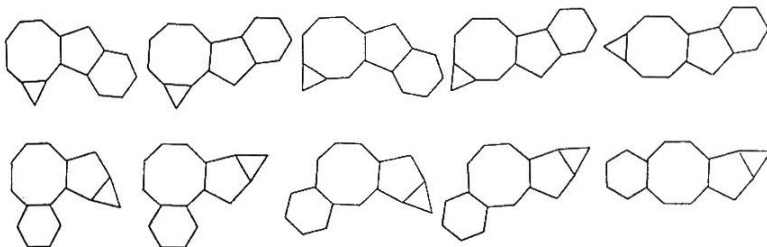
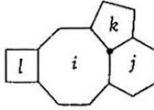


Figure 3. The ten isomers coded (8,5)(6,3) in Subclass b.

c: P systems with one internal vertex ($n_i = 1$); see Chart C. The example in Fig 1 is $(8,6,5)(4)$. The three polygons which share the internal vertex, are found to have seven free edges which all are distinct (symmetrically nonequivalent) and available for annelation. Hence $a = 7$ in this case, in consistency with Chart C.

Chart C

One internal vertex



$(i,j,k)(l):a$

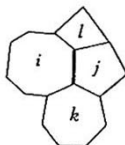
$(14,3,3) (3):5$	$(9,7,3) (4):8^*$	$(7,6,5) (5):6^*$	$(9,3,3) (8):3^*$
$(13,4,3) (3):9$	$(8,8,3) (4):4^*$	$(6,6,6) (5):1^*$	$(8,4,3) (8):4^*$
$(12,5,3) (3):9$	$(11,4,4) (4):4$	$(11,3,3) (6):4$	$(7,5,3) (8):4^*$
$(11,6,3) (3):9$	$(10,5,4) (4):7$	$(10,4,3) (6):6$	$(6,6,3) (8):2^*$
$(10,7,3) (3):9$	$(9,6,4) (4):7^*$	$(9,5,3) (6):6^*$	$(7,4,4) (8):2^*$
$(9,8,3) (3):9^*$	$(8,7,4) (4):7^*$	$(8,6,3) (6):6^*$	$(6,5,4) (8):3^*$
$(12,4,4) (3):4$	$(9,5,5) (4):4^*$	$(7,7,3) (6):3^*$	$(5,5,5) (8):1^*$
$(11,5,4) (3):8$	$(8,6,5) (4):7^*$	$(9,4,4) (6):3^*$	$(8,3,3) (9):2^*$
$(10,6,4) (3):8$	$(7,7,5) (4):4^*$	$(8,5,4) (6):5^*$	$(7,4,3) (9):3^*$
$(9,7,4) (3):8^*$	$(7,6,6) (4):4^*$	$(7,6,4) (6):5^*$	$(6,5,3) (9):3^*$
$(8,8,4) (3):4^*$	$(12,3,3) (5):4$	$(7,5,5) (6):3^*$	$(6,4,4) (9):1^*$
$(10,5,5) (3):4$	$(11,4,3) (5):7$	$(6,6,5) (6):3^*$	$(5,5,4) (9):1^*$
$(9,6,5) (3):8^*$	$(10,5,3) (5):7$	$(10,3,3) (7):3$	$(7,3,3) (10):2$
$(8,7,5) (3):8^*$	$(9,6,3) (5):7^*$	$(9,4,3) (7):5^*$	$(6,4,3) (10):2$
$(8,6,6) (3):4^*$	$(8,7,3) (5):7^*$	$(8,5,3) (7):5^*$	$(5,5,3) (10):1$
$(7,7,6) (3):4^*$	$(10,4,4) (5):3$	$(7,6,3) (7):5^*$	$(5,4,4) (10):1$
$(13,3,3) (4):5$	$(9,5,4) (5):6^*$	$(8,4,4) (7):2^*$	$(6,3,3) (11):1$
$(12,4,3) (4):8$	$(8,6,4) (5):6^*$	$(7,5,4) (7):4^*$	$(5,4,3) (11):1$
$(11,5,3) (4):8$	$(7,7,4) (5):3^*$	$(6,6,4) (7):2^*$	$(5,3,3) (12):1$
$(10,6,3) (4):8$	$(8,5,5) (5):3^*$	$(6,5,5) (7):2^*$	

d: P systems with two internal vertices ($n_i = 2$); see Chart D.

e: P systems with three internal vertices ($n_i = 3$); see Chart E. One of the polygons is fixed to be a triangle, as manifested by $l = 3$.

Chart D

Two internal vertices

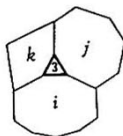


$(i,j) (k,l)$

(14,4)	(3,3)	(9,8)	(4,3)*	(8,4)	(7,5)*	(6,5)	(7,6)*
(13,5)	(3,3)	(9,7)	(5,3)*	(8,4)	(6,6)*	(6,4)	(11,3)
(13,4)	(4,3)	(9,7)	(4,4)*	(7,7)	(7,3)*	(6,4)	(10,4)
(12,6)	(3,3)	(9,6)	(6,3)*	(7,7)	(6,4)*	(6,4)	(9,5)*
(12,5)	(4,3)	(9,6)	(5,4)*	(7,7)	(5,5)*	(6,4)	(8,6)*
(12,4)	(5,3)	(9,5)	(7,3)*	(7,6)	(8,3)*	(6,4)	(7,7)*
(12,4)	(4,4)	(9,5)	(6,4)*	(7,6)	(7,4)*	(5,5)	(11,3)
(11,7)	(3,3)	(9,5)	(5,5)*	(7,6)	(6,5)*	(5,5)	(10,4)
(11,6)	(4,3)	(9,4)	(8,3)*	(7,5)	(9,3)*	(5,5)	(9,5)*
(11,5)	(5,3)	(9,4)	(7,4)*	(7,5)	(8,4)*	(5,5)	(8,6)*
(11,5)	(4,4)	(9,4)	(6,5)*	(7,5)	(7,5)*	(5,5)	(7,7)*
(11,4)	(6,3)	(8,8)	(5,3)*	(7,5)	(6,6)*	(5,4)	(12,3)
(11,4)	(5,4)	(8,8)	(4,4)*	(7,4)	(10,3)	(5,4)	(11,4)
(10,8)	(3,3)	(8,7)	(6,3)*	(7,4)	(9,4)*	(5,4)	(10,5)
(10,7)	(4,3)	(8,7)	(5,4)*	(7,4)	(8,5)*	(5,4)	(9,6)*
(10,6)	(5,3)	(8,6)	(7,3)*	(7,4)	(7,6)*	(5,4)	(8,7)*
(10,6)	(4,4)	(8,6)	(6,4)*	(6,6)	(9,3)*	(4,4)	(13,3)
(10,5)	(6,3)	(8,6)	(5,5)*	(6,6)	(8,4)*	(4,4)	(12,4)
(10,5)	(5,4)	(8,5)	(8,3)*	(6,6)	(7,5)*	(4,4)	(11,5)
(10,4)	(7,3)	(8,5)	(7,4)*	(6,6)	(6,6)*	(4,4)	(10,6)
(10,4)	(6,4)	(8,5)	(6,5)*	(6,5)	(10,3)	(4,4)	(9,7)*
(10,4)	(5,5)	(8,4)	(9,3)*	(6,5)	(9,4)*	(4,4)	(8,8)*
(9,9)	(3,3)*	(8,4)	(8,4)*	(6,5)	(8,5)*		

Chart E

Three internal vertices



$(3) (i,j,k)$

(3) (14,4,4)	(3) (11,7,4)	(3) (10,6,6)	(3) (8,8,6)*
(3) (13,5,4)	(3) (11,6,5)	(3) (9,9,4)*	(3) (8,7,7)*
(3) (12,6,4)	(3) (10,8,4)	(3) (9,8,5)*	
(3) (12,5,5)	(3) (10,7,5)	(3) (9,7,6)*	

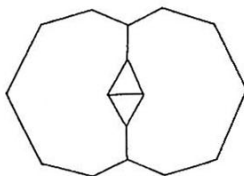


Figure 4. A system coded $(3,3)(10,10)$, not included in the class of P systems.

Not included systems. Figure 4 shows a system of polygons, which has $n_i = 4$ and $\Sigma q = i + j + k + l = 26$. Thus it obeys eqns. (1), (2), and it does correspond to a tetracyclic polygonal conjugated hydrocarbon; the depicted example (Fig. 4) has the pyrene formula $C_{16}H_{10}$. Nevertheless, this structure is not counted among the pyrene isomers because the system violates our definition of P; a pair of polygons share two edges.

The system of Fig. 4 belongs to a class with four internal edges ($n_i = 4$) and two polygons fixed as triangles ($k = l = 3$). It is reasonable to adopt the code $(3,3)(i,j)$ for these systems. Then all the six $C_{16}H_{10}$ isomers belonging to the subclass in question are given by: $(3,3)(15,5)$, $(3,3)(14,6)$, $(3,3)(13,7)$, $(3,3)(12,8)$, $(3,3)(11,9)$, $(3,3)(10,10)$.

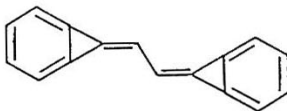
The generating function for the f_{I_s} numbers of C_nH_s isomers of the kind as in Fig. 4 was found to be:

$$f_I(x) = \sum_{s=0}^{\infty} (f_{I_s}) x^s = (1-x)^{-1} (1-x^2)^{-1}$$

$$= 1 + x + 2x^2 + 2x^3 + 3x^4 + 3x^5 + 4x^6 + 4x^7 + 5x^8 + 5x^9 + 6x^{10} + 6x^{11} + 7x^{12} + \dots \quad (9)$$

This counting starts with a carbon cluster C_6 .

Many other tetracyclic conjugated $C_{16}H_{10}$ systems do not belong to the class P and are not included in the present analysis, e.g.:



In addition, many $C_{16}H_{10}$ hydrocarbons are not tetracyclic, e.g. ethynyltolanes, diethynylbiphenyls, diphenylbutadiyne.

Concluding remark. Among the 965 P systems of $C_{16}H_{10}$ isomers, the subclass with polygon sizes $3 \leq q \leq 9$ (marked with an asterisk in Charts A–E) may be of interest. From the present analysis their number is found to be 634 and not 420, as has been claimed previously [1].

Acknowledgements. The authors are grateful to the Referees for helpful comments: one of them expanded the chemical context, while the other checked the calculations and pointed out an error in the original eqn. (9).

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