

Structure/formula informatics of isomeric sets of fluorantheneoid/fluoreneoid and indaceneoid hydrocarbons

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Abstract The systematics of fluorantheneoid/fluoreneoid and indaceneoid hydrocarbons is studied. Successive circumscribing a set of isomeric structures that result in a constant number of isomers at each circumscribing step gives what is called a constant-isomer series. Constant-isomer series have a repetitive isomer number pattern in which those series with the same isomer number have a one-to-one matching in topology among their membership. The general formulas of the matching constant-isomer sets of indaceneoids are reproduced by $C_{4p^2+1}H_{4p+1}$ and $C_{4p^2+4p+3}H_{4p+3}$, respectively, by successively inputting $p = 1, 2, 3, \dots$, and the general formula for the unique indaceneoid constant-isomers is reproduced by $C_{p^2+3p+4}H_{2p+4}$. Similar general formulas for the fluorantheneoid/fluoreneoid hydrocarbon constant-isomer series are also presented.

Keywords Fluorantheneoid/fluoreneoid and indaceneoid hydrocarbons · Successive circumscribing · Constant-isomer series · Formula/structure informatics · Topological characteristics · Formula periodic tables · Systematic organization

1 Introduction

Fluorantheneoid/fluoreneoid and indaceneoid hydrocarbons are ubiquitous pyrolytic pollutants that are formed on the pathway enroute to fullerene carbons [1, 2]. Many known representatives of these compounds that are isomeric to benzenoid hydrocarbons are listed in the Part B book of Dias [3]. The first enumerations of fluorantheneoid/fluoreneoid and indaceneoid hydrocarbons isomers were reported by Dias [4–8] and subsequently pursued by the research group of Cyvin [9–13]. Since these works, numerous

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new representatives have been synthesized, including the smallest indacenoid, pentalene (C_8H_6), [14] principally by flash vacuum pyrolysis [15–18]. The purpose of this paper is to study the formula/structure informatics of these important classes of polycyclic aromatic hydrocarbons. We will start by examining and supplementing some of the subsequent work by the Cyvin group [9–13] based on the Harary and Harborth paper [19].

2 Results and discussion

2.1 Definitions

Fluoranthenoid (even carbon systems)/fluorenoïd (odd carbon systems) and indacenoid hydrocarbons have molecular graphs with one and two pentagonal rings among otherwise hexagonal rings (Fig. 1), respectively [4–8]. Here we regard molecular graphs as polypent/polyhex depictions of fluoranthenoid/fluorenoïd and indacenoid hydrocarbons where only the carbon–carbon bonds are shown as lines (edges) connecting (carbon) vertices. In the molecular graph, the number of degree-2 vertices (s) correspond to the number of C–H hydrogens (N_H), the number of peripheral degree-3 vertices (n_p) correspond to the number of tertiary carbons at the juncture of two rings (N_{pc}) which occur on the perimeter, the number of internal degree-3 vertices (n_i) correspond to the number of tertiary carbons at the juncture of three rings (N_{ic}), the total number of vertices (n) correspond to the total number of carbons (N_C), and the number of edges (q) correspond to the number of (conjugated) C–C and C=C bonds. Herein, only systems with polygons (specifically polypent/polyhex systems) that are simply connected (fused systems without holes) are treated.

Series of polycyclic conjugated hydrocarbons that are generated by successive circumscribing of base (first generation) structures which result in a constant number of isomers at each circumscribing step are called constant-isomer series. A 2-dimensional array of formulas having a least element and has a metric compliant to the triad principle that establishes a hierarchical ordering is called a periodic table. Herein, the systematics of constant-isomer series and periodic tables for fluoranthenoid/fluorenoïd and indacenoid hydrocarbons will be discussed.

2.2 Preliminaries

The values of the invariants of n, q, r, s , and n_3 are identical for the molecular graphs of any set of polycyclic conjugated hydrocarbon isomers composed of only fused (condensed) rings [3–8]. The interrelationships among these invariants are $q = r + n - 1 = \frac{1}{2}(3n - s)$, $r = \frac{1}{2}(n - s + 2)$ and $n_3 = n - s = 2(r - 1)$ which means that for isomers with any combination of ring sizes, the number of vertices (n), edges (q), degree-2 vertices (s), and degree-3 vertices (n_3) are fixed. Within an isomer set, the invariants of d_s, n_i, n_p, q_I , and q_p depend on the ring sizes and their number. Table 1 list a number of relationships as functions of (n, s) and (r, n_i) . Only the invariants of r, n_i , and q_I have consecutive positive integer values (1, 2, 3, ...) including zero for n_i . To illustrate application of some of these equa-

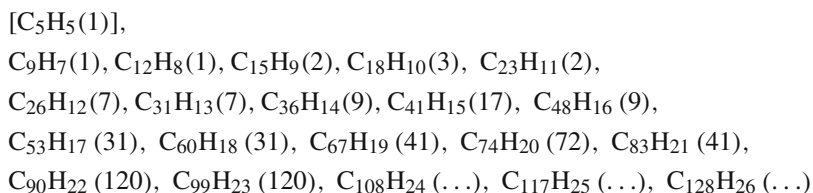
Table 1 Molecular graph invariants for fluorantheneoid/fluoreneoid ($r_5 = 1$) and indaceneoid ($r_5 = 2$) hydrocarbons

Invariant	Function of (n, s)	Function of (r, n_i)
R	$1/2(n - s + 2)$	r
$n = N_c$	n	$4r - n_i + 2 - r_5$
Q	$1/2(3n - s)$	$5r - n_i + 1 - r_5$
$n_i = N_{Ic}$	$n - 2s + 6 - r_5$	n_i
$n_e = q_p$	$2s - 6 + r_5$	$4r - 2n_i + 2 - r_5$
$s = N_H$	s	$2r - n_i + 4 - r_5$
$n_{p3} = N_{pc}$	$s - 6 + r_5$	$2r - n_i - 2$
n_3	$n - s$	$2r - 2$
q_1	$1/2(3n - 5s) + 6 - r_5$	$r + n_i - 1$
d_s	$1/2(3s - n) - 7 + r_5$	$r - n_i - 2$

tions, let us consider the Schlegel of C60 buckminsterfullerene with a hexagonal outer rim. Per $r = 1/2(n - s + 2) = r = 1/2(60 - 0 + 2) = 31$; this equation only counts rings. For the 3-dimensional C60 buckminsterfullerene cluster, Euler's equation counts faces which would be 32. Reorganizing the 4th relation in Table 1 gives $4r = n + n_i - 2 + r_5 = 60 + 54 - 2 + 12 = 124$ or $r = 31$ for the C60 Schlegel. For $q = 1/2(3n - s) = 5r - n_i + 1 - r_5$ from the 5th and 6th relations of Table 1, we get $q = 1/2(3 \times 60 - 0) = 5 \times 31 - 54 + 1 - 12 = 90$; note that the Schlegel of C60 buckminsterfullerene with a hexagonal outer rim has $q_p = 6$, $q_1 = 84$, and $n_i = 54$.

2.3 Formula periodic table for fluorantheneoid/fluoreneoid hydrocarbons [Table PAH5,6(F/F)]

Table 2 denoted by the generic as Table PAH5,6(F/F) presents the formula periodic table for fluorantheneoid/fluoreneoid hydrocarbons [4–8]. The left-hand staircase boundary edge is of prime importance because these formulas correspond to the most condensed fluorantheneoid/fluoreneoid hydrocarbon structures and is where the constant-isomer fluorantheneoid/fluoreneoid series reside. Constant-isomer fluorantheneoid/fluoreneoid series are generated by successive circumscribing and have successive formulas per the operator of $P(C_n H_s) \rightarrow C(C_{n+2s+5} H_{s+5})$. The first generation formulas of the constant-isomer fluorantheneoid/fluoreneoid series are listed below (the corresponding number of isomers are in parentheses). Note the a, a, b, c, b, ... repetitive isomer number pattern.



The formulas in Table PAH5,6(F/F) increase by C_3H as one goes down any column and by C_4H_2 as one goes from left to right. All the fluorantheneoid/fluoreneoid hydrocarbon structures in the same column have the same d_s values (net disconnections/connections among the internal edges) and in the same row have the same N_{IC} values. The formulas below and to the right of the dashed staircase line also correspond to benzenoid structures but the ones above and to the left of the dashed staircase line can only correspond to fluorantheneoid/fluoreneoid hydrocarbon structures; there are no fluorantheneoids/fluoreneoids with benzenoid catacondensed formulas. Each step on the left-hand staircase boundary of Table PAH5,6(F/F) consists of a protrusive ledge at the top and a juncture at the bottom going from one step to another. For example C_9H_7 , $C_{20}H_{10}$, $C_{28}H_{12}$, $C_{33}H_{13}$, etc. are located on the protrusive ledge and $C_{21}H_{11}$, $C_{29}H_{13}$, $C_{34}H_{14}$, $C_{39}H_{15}$, $C_{44}H_{16}$, $C_{46}H_{16}$, $C_{51}H_{17}$, $C_{56}H_{18}$, $C_{58}H_{18}$, $C_{63}H_{19}$, etc. are formulas located on the step juncture. The formulas in Table PAH5,6(F/F) can be reproduced from Harary/Harborth-like [19] expressions and alternative formulas developed by the author that will be discussed.

2.4 Maximum and minimum values of the invariants which defines the left-hand staircase boundary of Table PAH5,6(F/F)

Extremal fluorantheneoid/fluoreneoid hydrocarbons are the most condensed systems and have formulas on the left-hand staircase boundary of Table PAH5,6(F/F). Members of the constant-isomer series are extremal fluorantheneoid/fluoreneoid hydrocarbons but not all extremal fluorantheneoid/fluoreneoid hydrocarbons are members of constant-isomer series. An extremal fluorantheneoid/fluoreneoid hydrocarbon can be defined as possessing the maximum number of internal vertices $[(n_i)_{\max}]$ for a given number of rings (r). Thus, molecular graphs with C/H formulas located at the bottom juncture of each step are not extremal fluorantheneoid/fluoreneoid hydrocarbons and $C_{48}H_{16}$ is an example of an extremal fluorantheneoid hydrocarbon that is not member of constant-isomer series.

Our original algorithm [4–8] for constructing Table PAH5,6(F/F) started with successive circumscribing of the three one-isomer series to define the initial part of the left-hand staircase boundary, i.e., starting with C_5H_5 , C_9H_7 , and $C_{12}H_8$ and using the recursion of $N_c' = N_c + 2N_H + 5$ and $N_H' = N_H + 5$ one gets the respective series of $C_{20}H_{10}$, $C_{45}H_{15}$, ..., $C_{28}H_{12}$, $C_{57}H_{17}$, ..., and $C_{33}H_{13}$, $C_{64}H_{18}$, ... all which are located on the upper part of the staircase protrusive ledge of Table PAH5,6(F/F). This table possesses a hierarchical ordering according to the invariants of d_s and N_{IC} .

2.5 Derivation of some mathematical relationships for fluorantheneoid/fluoreneoid hydrocarbons

Cyvin et al. [9–13] presented Harary/Harborth-like equations for fluorantheneoid/fluoreneoid hydrocarbon molecular graphs that we now exploit. Fluorantheneoid/fluoreneoid hydrocarbon molecular graphs exist if and only if n (number of vertices), and r (number of rings) are integers within the ranges of

$$2r + 1 + \lceil 1/2(40r - 15)^{1/2} - 1/2 \rceil \leq n \leq 4r + 1 \quad (1)$$

$$\lceil 1/4(n - 1) \rceil \leq r \leq n + 1 - \lceil 1/2(n + 5^{1/2}n^{1/2}) \rceil \quad (2)$$

where $\lceil x \rceil$ is the ceiling function (round decimal up) and corresponds to the smallest integer not smaller than x . The two sides of these equations define the extreme values (upper and lower bounds) for n and r for polyhexes having one pentagonal ring. In general, a given property p will have the following maximum/minimum characteristics: $p(\min) \leq p \leq p(\max)$ and $p(\max) \geq p \geq p(\min)$. The right-hand of Eq. (1) corresponds to the catacondensed fluorenoids [$n(\max)$] located on the right-hand horizontal edge of Table PAH5,6(F/F), and the left-hand side of Eq. (1) corresponds to fluoranthenoids/fluorenoids [$n(\min)$] having formulas on the extreme left-hand staircase boundary edge of Table PAH5,6(F/F). Except for some smaller fluoranthenoid/fluorenoide molecular graphs, specific values for n , s , and r occur for several systems, though not at the same time, whereas specific q values only occur for one system. For example, acenaphthylene ($C_{12}H_8$) and benzo[*b*]indenylyl ($C_{13}H_9$) and its two other fluorenoide isomers all have $r = 3$, but the former has $q = 14$ and the latter has $q = 15$; no other fluoranthenoids/fluorenoids have $q = 14$ or 15. Using Eq. (1) and $r = q + 1 - n$, we get

$$3r + \lceil 1/2(40r - 15)^{1/2} - 1/2 \rceil \leq q \leq 5r \quad (3)$$

where the right-hand of Eq. (3) corresponds to the molecular graphs of catacondensed fluorenoids ($n_i = 0$) and the left-hand side corresponds to fluoranthenoid/fluorenoide hydrocarbons having formulas on the extreme left-hand staircase edge of Table PAH5,6(F/F). Except for some smaller fluoranthenoid/fluorenoide hydrocarbon molecular graphs, specific values for n , s , and r occur for several systems, though not at the same time, whereas specific q values only occur for one system. From $q + q_I + 1 = 6r$, $q = q_I + q_p$, and Eq. (3), we get for a given r the range of q_I and q_p with the following inequalities

$$3r - 1 - \lceil 1/2(40r - 15)^{1/2} - 1/2 \rceil \geq q_I \geq r - 1 \quad (4)$$

$$2\lceil 1/2(40r - 15)^{1/2} - 1/2 \rceil + 1 \leq q_p \leq 4r + 1 \quad (5)$$

where the right-hand side of these equations correspond to catacondensed fluorenoids; note the minimum/maximum switch in Eq. (4) is the result of the negative sign in $q = 6r - q_I - 1$.

From Eq. (1), the minimum number of carbons n and maximum number of internal degree-3 carbon vertices n_i for a given number of rings r is derived as

$$n(\min) = 2r + 1 + \lceil 1/2(40r - 15)^{1/2} - 1/2 \rceil \quad (6)$$

$$n_i(\max) = 2r - \lceil 1/2(40r - 15)^{1/2} - 1/2 \rceil \quad (7)$$

where the latter evolves from $n_i = 4r + 1 - n$; note that the minimum/maximum switch is the result of the negative sign. Both $n(\min)$ and $n_i(\max)$ occur for the formulas on the extreme left-hand staircase edge of Table 2; fluoranthenoid/fluorenoide

where $n_p + s = q_p = q - q_I = 2s - 5$ (s = number of degree-2 vertices and n_p = number of peripheral degree-3 vertices) corresponds to the size of the periphery of a fluoranthenoid/fluorenoïd. This Eq. (9) can be reduced to the following inequality

$$\lceil 1/2(40r - 15)^{1/2} - 1/2 \rceil + 3 \leq s \leq 2r + 3 \quad (10)$$

In order for n_i to be a maximum, s has to be a minimum for a constant number of rings. Inserting $r = 2 - 13$, we get $[(n_i)_{\max}, s_{\min}] = [2r - \lceil 1/2(40r - 15)^{1/2} - 1/2 \rceil, \lceil 1/2(40r - 15)^{1/2} - 1/2 \rceil + 3] = [0, 7], [1, 8], [2, 9], [3, 10], [5, 10], [6, 11], [7, 12], [9, 12], [10, 13], [12, 13], [13, 14],$ and $[15, 14]$ which corresponds to C_9H_7 , $C_{12}H_8$, $C_{15}H_9$, $C_{18}H_{10}$, $C_{20}H_{10}$, $C_{23}H_{11}$, $C_{26}H_{12}$, $C_{28}H_{12}$, $C_{31}H_{13}$, $C_{33}H_{13}$, $C_{36}H_{14}$, and $C_{38}H_{14}$, respectively, on the left-hand staircase boundary edge of Table PAH5,6(F/F). With this latter expression for the left-hand staircase boundary and the general formula of $C_{4r+1}H_{2r+3}$ for the right-hand horizontal boundary which lists the formulas for the catacondensed fluorenoïds, Table PAH5,6(F/F) can easily be constructed. In general, for a given $r : n(\max), q(\max), q_I(\min), q_p(\max)$ and $s(\max)$ pertain to the catacondensed fluoranthenoids/fluorenoïds (given by the right-hand side of the inequalities Eqs. (1), (3), (4), (5), and (10), respectively), while $n(\min), q(\min), q_I(\max), q_p(\min)$ and $s(\min)$ pertain to extremal fluoranthenoids/fluorenoïds.

These extremal relationships are deemed more convenient if they can be recast in terms of the chemical formulas C_nH_s , namely in terms of n and s exclusively. For that purpose the following relationships will be useful: $q = 1/2(3N_c - N_H)$, $r = q + 1 - N_c = 1/2(N_c - N_H + 2)$, $N_{pc} = N_H - 5$, $N_c = N_{Ic} + N_{pc} + N_H$, and $N_c + N_{Ic} = 4r + 1$; note that for the catacondensed fluorenoïds $N_c = 4r + 1$ for which $N_{Ic} = 0$. Reversing the order of Eq. (2) gives

$$n + 1 - \lceil 1/2(n + 5^{1/2}n^{1/2}) \rceil \geq r \geq \lceil 1/4(n - 1) \rceil$$

Using $r = 1/2(n - s + 2)$ and multiplying throughout by 2 gives

$$2n + 2 - 2\lceil 1/2(n + 5^{1/2}n^{1/2}) \rceil \geq n - s + 2 \geq 2\lceil 1/4(n - 1) \rceil$$

Subtracting $n + 2$ throughout this inequality gives

$$n - 2\lceil 1/2(n + 5^{1/2}n^{1/2}) \rceil \geq -s \geq -n - 2 + 2\lceil 1/4(n - 1) \rceil$$

Multiplying this inequality by minus throughout reverses the inequality signs to give

$$2\lceil 1/2(n + 5^{1/2}n^{1/2}) \rceil - n \leq s \leq n + 2 - 2\lceil 1/4(n - 1) \rceil \quad (11)$$

Equation (11) gives the range for the number of hydrogens (s) for a given number of carbons (n) found in fluoranthenoids/fluorenoïd molecular graphs. For example, consider $n = 45$. Application of Eq. (11) gives $2\lceil 1/2(45 + 5^{1/2}45^{1/2}) \rceil - 45 \leq s \leq 45 + 2 - 2\lceil 1/4(45 - 1) \rceil$ or $15 \leq s \leq 25$, i.e., $C_{45}H_{15}$ to $C_{45}H_{25}$ where $C_{45}H_{15}$ is the 3rd generation member, circumcorannulene (or dicircumcyclopentadienyl), of the D_{5h}

one-isomer series and $C_{45}H_{25}$ corresponds to the 39,407 unbranched catacondensed fluorenoic isomers (both helicenic and nonhelicenic) [20,21].

It now remains to determine the first generation formula for any given constant-isomer series. This was done by exploiting the behavior and properties of the three one-isomer and two two-isomer fluorantheneoic d/fluorenoic series (first generation members are shown in Fig. 1) on the staircase edge of Table PAH5,6(F/F) and our aufbau principle. These constant isomer fluorantheneoic/fluorenoic series have the largest number of rings for a given perimeter length ($q_p = 2s - 5$ or s value). Using this property and Eq. (10), we get the following successive equations

$$\begin{aligned}
 s &= \lceil 1/2(40r - 15)^{1/2} - 1/2 \rceil + 3 \\
 s &\geq 1/2(40r - 15)^{1/2} - 1/2 + 3 \\
 (2s - 5)^2 &\geq 40r - 15 \\
 4s^2 - 20s + 25 &\geq 40r - 15 \\
 s^2 - 5s + 10 &\geq 10r \\
 r &\leq 1/10(s^2 - 5s + 10) \\
 r(\max) &= \lfloor 1/10(s^2 - 5s + 10) \rfloor = 1/2(n + 2 - s) \\
 n &= 2\lfloor 1/10(s^2 - 5s) \rfloor + s
 \end{aligned} \tag{12}$$

where $\lfloor x \rfloor$ is the floor function and corresponds to the largest integer not larger than x (round the decimal down). Since these five fluorantheneoic/fluorenoic series have formulas that pass through all possible numbers of hydrogen ($s = 5$ and $s \geq 7$), starting with pentadienyl Eq. (12) gives all the formulas belonging to the members of these constant-isomer fluorantheneoic/fluorenoic series. To use Eq. (12) just simply input successively the number of fluorantheneoic/fluorenoic hydrogens possible ($s = 5, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, \dots$). For example, these 12 values for s give $C_5H_5, C_9H_7, C_{12}H_8, C_{15}H_9, C_{20}H_{10}, C_{23}H_{11}, C_{28}H_{12}, C_{33}H_{13}, C_{38}H_{14}, C_{45}H_{15}, C_{50}H_{16}, C_{57}H_{17}, \dots$, respectively. After the first step, the second and successive higher generation members to these five fluorantheneoic/fluorenoic constant-isomer series occur on a the protrusive ledge location of the staircase edge of Table PAH5,6(F/F) (Table 1). Immediately beneath these protrusive constant isomer formulas of subscript coefficients (n', s'), one finds the formulas of subscript coefficients (n, s) for the first-generation members of the constant-isomer series with higher numbers of isomers. Using the elementary aufbau of C_3H on these five protrusive fluorantheneoic/fluorenoic constant-isomer formulas, we can get the formula for all the first-generation fluorantheneoic/fluorenoic constant-isomer series. Performing a retro-aufbau operation $(n - 3, s - 1) = (n', s')$ on the first-generation formula of a higher constant-isomer, transforms Eq. (13) to

$$n - 3 = 2\lfloor 1/10[(s - 1)^2 - 5(s - 1)] \rfloor + (s - 1)$$

where n and s now correspond to the formula of the higher first generation fluorantheneoic/fluorenoic constant-isomers occurring immediately beneath a one-isomer or two-isomer formula (n', s'). Simplification of this latter equation gives

$$n = s + 2\lfloor^{1/10}(s^2 - 7s + 16)\rfloor \quad (13)$$

where $\lfloor x \rfloor$ is the floor function and corresponds to the largest integer not larger than x . Equation (13) determines the first generation formula for any given fluoranthenoid/fluorenoide constant-isomer series. To use Eq. (13) successively input the number of fluoranthenoid/fluorenoide hydrogens possible ($s = 5, 7, 8, 9, 10, 11, 12, \dots$). For example, $s = 11$ gives $n = 11 + 2\lfloor 6 \rfloor = 23$ which gives $C_{23}H_{11}$ as the first generation formula for one of the two two-isomer fluoranthenoid/fluorenoide series. The second, third, fourth, etc. generation formulas are given by the recursion relationships of $N_{c'} = N_c + 2N_H + 5$ and $N_{H'} = N_H + 5$ giving $C_{50}H_{16}$, $C_{87}H_{21}$, $C_{134}H_{26}$, etc. As other examples, $s = 14$ & 16 give $n = 14 + 2\lfloor 11.4 \rfloor = 14 + 2 \times 11 = 36$ & $n = 16 + 2\lfloor 16 \rfloor = 48$ which give $C_{36}H_{14}$ & $C_{48}H_{16}$, respectively, as the first generation formulas for the matching pair of 9-isomer series. In this way Eq. (13) generates all 18 formulas (C_5H_5 , C_9H_7 , $C_{12}H_8$, $C_{15}H_9$, $C_{18}H_{10}$, $C_{23}H_{11}$, $C_{26}H_{12}$, $C_{31}H_{13}$, $C_{36}H_{14}$, $C_{41}H_{15}$, $C_{48}H_{16}$, \dots , $C_{99}H_{23}$, \dots) in reference 3.

While the above Harary/Harborth-like equations relate extremal properties of fluoranthenoid/fluorenoide molecular graphs, they convey nothing about the matching topological properties of the constant isomer series. Constant-isomer fluoranthenoid/fluorenoide series have a repetitive isomer number pattern of a, a, b, c, b, \dots in which those series with the same isomer number have a one-to-one matching in topology among their membership. We now give an alternative way to obtain the formulas of constant-isomer fluoranthenoid/fluorenoide series which at the same time distinguishes between the a, a, b, b, and c isomer types. The formulas of the matching two a-types of constant-isomers [i.e., $C_9H_7(1)$, $C_{26}H_{12}(7)$, $C_{53}H_{17}(31)$, $C_{90}H_{22}(120)$, \dots and $C_{12}H_8(1)$, $C_{31}H_{13}(7)$, $C_{60}H_{18}(31)$, $C_{99}H_{23}(120)$, \dots] are reproduced by $C_{5p^2+2p+2}H_{5p+2}$ and $C_{5p^2+4p+3}H_{5p+3}$, respectively, by successively inputting $p = 1, 2, 3, \dots$; the number of matching isomers are given in parentheses. For example, inputting $p = 3$ into both these general formulas gives $C_{53}H_{17}$ and $C_{60}H_{18}$, respectively, as the first generation formulas to the constant-isomer fluoranthenoid/fluorenoide hydrocarbons having 31 isomers with a one-to-one matching in topology between their membership. The formulas of the matching two b-types of constant-isomers [i.e., $C_{15}H_9(2)$, $C_{36}H_{14}(9)$, $C_{67}H_{19}(41)$, \dots and $C_{23}H_{11}(2)$, $C_{48}H_{16}(9)$, $C_{83}H_{21}(41)$, \dots] are reproduced by $C_{5p^2+6p+4}H_{5p+4}$ and $C_{5p^2+10p+8}H_{5p+6}$, respectively, by successively inputting $p = 1, 2, 3, \dots$; the number of matching isomers are given in parentheses. The formula of the unique c-type of constant-isomers [i.e., $C_5H_5(1)$, $C_{18}H_{10}(3)$, $C_{41}H_{15}(17)$, $C_{74}H_{20}(72)$, \dots] are reproduced by $C_{5p^2-2p+2}H_{5p}$ by successively inputting $p = 1, 2, 3, \dots$; the number of isomers is given in parentheses. Using these general formulas and our above recursion equations, one can easily construct Table PAH5,6(F/F).

2.6 Formula periodic table for indacenoide hydrocarbons [Table PAH5,6(I)].

Table 3 denoted by the generic as Table PAH5,6(I). presents the formula periodic table for indacenoide hydrocarbons [4–8]. The left-hand staircase boundary edge

reproduced from Harary/Harborth-like [19] expressions and alternative formulas developed by the author that will be discussed.

2.7 Maximum and minimum values of the invariants which defines the left-hand staircase boundary of Table PAH5,6(I)

Extremal indacenoid hydrocarbons are the most condensed systems and have formulas on the left-hand staircase boundary of Table PAH5,6(I). Members of the constant-isomer series are extremal indacenoid hydrocarbons but not all extremal indacenoid hydrocarbons are members of constant-isomer series. An extremal indacenoid hydrocarbon can be defined as possessing the maximum number of internal vertices $[(n_i)_{\max}]$ for a given number of rings (r). Thus, molecular graphs with C/H formulas located at the bottom juncture of each step are not extremal indacenoid hydrocarbons and $C_{49}H_{15}$ is an example of an extremal indacenoid hydrocarbon that is not member of constant-isomer series.

Our original algorithm [4–8] for constructing Table PAH5,6(I) started with successive circumscribing of the three one-isomer series to define the initial part of the left-hand staircase boundary, i.e., starting with $(C_5H_5)C_{19}H_9$, C_8H_6 , and $C_{11}H_7$ and using the recursion of $N_c' = N_c + 2N_H + 4$ and $N_H' = N_H + 4$ one gets the respective series of $C_{19}H_9$, $C_{41}H_{13}$, ..., $C_{24}H_{10}$, $C_{48}H_{14}$, ..., and $C_{29}H_{11}$, $C_{55}H_{15}$, ... all which are located on the upper part of the staircase protrusive ledge of Table PAH5,6(I). This table possesses a hierarchical ordering according to the invariants of d_s and N_{IC} .

2.8 Derivation of some mathematical relationships for indacenoid hydrocarbons

We now exploit Harary/Harborth-like equations for indacenoid hydrocarbons derived in part from relationships given by Cyvin and coworkers [22–24]. Molecular graphs of indacenoid hydrocarbons exist if and only if n (number of vertices), and r (number of rings) are integers within the ranges of

$$2r + \lceil (8r)^{1/2} \rceil \leq n \leq 4r \quad (14)$$

$$\lceil 1/4(n) \rceil \leq r \leq n + 2 - \lceil 1/2(n) + (n + 1)^{1/2} \rceil \quad (15)$$

where $\lceil x \rceil$ is the ceiling function (round the decimal up) and corresponds to the smallest integer not smaller than x . The two sides of these equations define the extreme values (upper and lower bounds) for n and r for polyhexes having two pentagonal rings. The right-hand of Eq. (14) corresponds to the catacondensed indacenoids $[n(\max)]$ located on the right-hand horizontal edge of Table PAH5,6(I), and the left-hand side of Eq. (14) corresponds to indacenoids $[n(\min)]$ having formulas on the extreme left-hand staircase boundary edge of Table PAH5,6(I). Except for some smaller indacenoid molecular graphs, specific values for n , s , and r occur for several systems, though not at the same time, whereas specific q values only occur for one system. For example, pyracylene ($C_{14}H_8$) and its two other indacenoid isomers (Fig. 1) and indeno[2,1-*a*]indenene ($C_{16}H_{10}$) and its five other isomers all have $r = 4$ but the former has $q = 17$

and the latter gas $q = 19$; no other indacenoids have $q = 17$ or 19 . Using Eq. (14) and $r = q + 1 - n$, we get

$$3r - 1 + \lceil (8r)^{1/2} \rceil \leq q \leq 5r - 1 \quad (16)$$

where the right-hand of Eq. (16) corresponds to the catacondensed indacenoids and the left-hand side corresponds to indacenoids having formulas on the extreme left-hand staircase edge of Table PAH5,6(I). From $q + q_I + 2 = 6r$, $q = q_I + q_p$, and Eq. (16), we get for a given r the range of q_I and q_p with the following inequalities

$$3r - 1 - \lceil (8r)^{1/2} \rceil \geq q_I \geq r - 1 \quad (17)$$

$$2\lceil (8r)^{1/2} \rceil \leq q_p \leq 4r \quad (18)$$

where the right-hand side of these equations correspond to catacondensed indacenoids; note the minimum/maximum switch in Eq. (17) is the result of the negative sign in $q = 6r - q_I - 2$.

From Eq. (14), the minimum number of carbons n and maximum number of internal degree-3 carbon vertices n_i for a given number of rings r is derived as

$$n(\min) = 2r + \lceil (8r)^{1/2} \rceil \quad (19)$$

$$n_i(\max) = 2r - \lceil (8r)^{1/2} \rceil \quad (20)$$

where the latter evolves from $n_i = 4r - n$; note that the minimum/maximum switch is the result of the negative sign. Both $n(\min)$ and $n_i(\max)$ occur for the formulas on the extreme left-hand staircase edge of Table PAH5,6(F/F); indacenoid hydrocarbons having $n_i(\max)$, i.e., those having a maximum number of internal (third degree) vertices for a given number of rings, are called extremal indacenoid hydrocarbons. Thus, for a given r the range of n_i is given by the following inequality

$$0 \leq n_i \leq 2r - \lceil (8r)^{1/2} \rceil \quad (21)$$

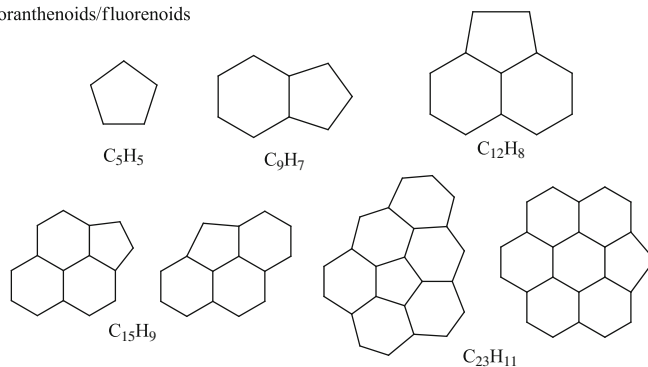
where $n_i(\min) = 0$ pertains to the catacondensed and $n_i(\max)$ to the extremal indacenoids. To illustrate application of Eq. (21), consider $r = 18$. This inequality gives $0 \leq n_i \leq 2 \times 18 - \lceil 12 \rceil$ or $0 \leq n_i \leq 24$, i.e., from the catacondensed indacenoids ($C_{72}H_{28}$, $n_i = 0$) to the 3rd generation member to the D_{2h} one-isomer series ($C_{48}H_{14}$, $n_i = 24$). Using Eqs. (14) and (21), from $N_c - N_{Ic} = N_{pc} + N_H$, we get

$$2\lceil (8r)^{1/2} \rceil \leq n - n_i = n_p + s = 2s - 4 \leq 4r \quad (22)$$

where $n_p + s = q_p = q - q_I$ ($2s - 4$ ($s =$ number of degree-2 vertices and $n_p =$ number of peripheral degree-3 vertices) corresponds to the size of the periphery of a indacenoid. This Eq. (22) can be reduced to the following inequality

$$\lceil (8r)^{1/2} \rceil + 2 \leq s \leq 2r + 2 \quad (23)$$

fluoranthenoids/fluorenooids



indacenoids

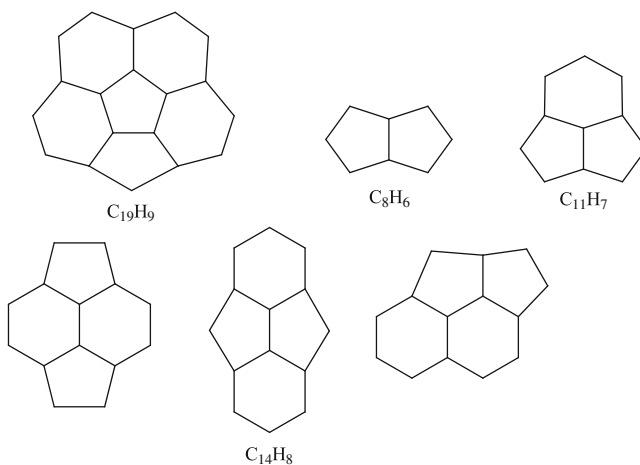


Fig. 1 Smallest fluoranthenoid/fluorenooid and indacenoid hydrocarbon molecular graphs that are first generation members of constant-isomer series

In general, for a given r : $n(\max)$, $q(\max)$, $q_I(\min)$, $q_p(\max)$ and $s(\max)$ pertain to the catacondensed indacenoids (given by the right-hand side of the inequalities Eqs. (1), (3), (4), (5), and (10), respectively), while $n(\min)$, $q(\min)$, $q_I(\max)$, $q_p(\min)$ and $s(\min)$ pertain to extremal indacenoids.

These extremal relationships are deemed more convenient if they can be recast in terms of n and s exclusively. For that purpose the following relationships will be useful: $q = 1/2(3N_c - N_H)$, $r = q + 1 - N_c = 1/2(N_c - N_H + 2)$, $N_{pc} = N_H - 4$, $N_c = N_{Ic} + N_{pc} + N_H$, and $N_c + N_{Ic} = 4r$; note that for the catacondensed indacenoids $N_c = 4r$ for which $N_{Ic} = 0$. Reversing the order of Eq. (15) gives

$$n + 2 - \lceil 1/2(n) + (n + 1)^{1/2} \rceil \geq r \geq \lceil 1/4(n) \rceil$$

Using $r = 1/2(n - s + 2)$ and multiplying throughout by 2 gives

$$2n + 4 - 2\lceil 1/2(n) + (n + 1)^{1/2} \rceil \geq n - s + 2 \geq 2\lceil 1/4(n) \rceil$$

Subtracting $n + 2$ throughout this inequality gives

$$n + 2 - 2\lceil 1/2(n) + (n + 1)^{1/2} \rceil \geq -s \geq -n - 2 + 2\lceil 1/4(n) \rceil$$

Multiplying this inequality by minus throughout reverses the inequality signs to give

$$2\lceil 1/2(n) + (n + 1)^{1/2} \rceil - n - 2 \leq s \leq n + 2 - 2\lceil 1/4(n) \rceil \quad (24)$$

Equation (24) gives the range for the number of hydrogens (s) for a given number of carbons (n) found in indacenoids. For example, consider $n = 48$. Application of Eq. (24) gives $2\lceil 1/2(48 + 5^{1/2}48^{1/2}) \rceil - 48 - 2 \leq s \leq 48 + 2 - 2\lceil 1/4(48) \rceil$ or $14 \leq s \leq 26$, i.e., $C_{48}H_{14}$ to $C_{48}H_{26}$ where $C_{48}H_{14}$ is the 3rd generation member of the D_{2h} one-isomer series and $C_{48}H_{26}$ corresponds to 507364 unbranched catacondensed indacenoid isomers (both helicenic and nonhelicenic) [20,21].

It now remains to determine the first generation formula for any given constant-isomer series. This was done by exploiting the behavior and properties of the three one-isomer and one three-isomer indacenoids series (first generation members are shown in Fig. 1) on the staircase edge of Table PAH5,6(I) and our aufbau principle. These constant isomer indacenoids series have the largest number of rings for a given perimeter length ($q_p = 2s - 4$ or s value). Using this property and Eq. (23), we get the following successive equations

$$\begin{aligned} s &= \lceil (8r)^{1/2} \rceil + 2 \\ s &\geq (8r)^{1/2} + 2 \\ (s - 2)^2 &\geq 8r \\ s^2 - 4s + 4 &\geq 8r \\ r &\leq 1/8(s^2 - 4s + 4) = 1/8(s - 2)^2 \\ r(\max) &= \lfloor 1/8(s^2 - 4s + 4) \rfloor = \lfloor 1/8(s - 2)^2 \rfloor = 1/2(n + 2 - s) \\ n &= 2\lfloor 1/8(s^2 - 4s - 4) \rfloor + s = 2\lfloor 1/8(s - 2)^2 \rfloor + s - 2 \end{aligned} \quad (25)$$

where $\lfloor x \rfloor$ is the floor function and corresponds to the largest integer not larger than x (round the decimal down). Since these four indacenoid series have formulas that pass through all possible numbers of hydrogen ($s \geq 5$), starting with pentadienyl Eq. (25) gives all the formulas belonging to the members of these constant-isomer indacenoid series. To use Eq. (25) just simply input successively the number of indacenoid hydrogens possible ($s = 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, \dots$). For example, these 12 values for s give $C_5H_5, C_8H_6, C_{11}H_7, C_{14}H_8, C_{19}H_9, C_{24}H_{10}, C_{29}H_{11}, C_{34}H_{12}, C_{41}H_{13}, C_{48}H_{14}, C_{55}H_{15}, C_{62}H_{16}, \dots$, respectively. After the first step, the second and successive higher generation members to these five indacenoid constant-isomer series occur on a the protrusive ledge location of the staircase edge of Table PAH5,6(I). Immediately beneath these protrusive constant isomer formulas of subscript coefficients (n', s'), one finds the formulas of subscript coefficients (n, s) for the first-generation members of the constant-isomer series with higher numbers of isomers. Using the elementary aufbau of C_3H on these four protrusive indacenoid constant-isomer formulas, we can get the formula for all the first-generation indacenoid constant-isomer

series. Performing a retro-aufbau operation $(n - 3, s - 1) = (n', s')$ on the first-generation formula of a higher first generation constant-isomer, transforms Eq. (26) to

$$n - 3 = 2\lfloor \frac{1}{8}[(s - 1)^2 - 4(s - 1) - 4] \rfloor + (s - 1)$$

where n and s now correspond to the formula of the higher indacenoid constant-isomers occurring immediately beneath a one-isomer or three-isomer formula (n', s') . Simplification of this latter equation gives

$$n = s - 4 + 2\lfloor \frac{1}{8}(s^2 - 6s + 25) \rfloor = s + 2\lfloor \frac{1}{8}(s - 3)^2 \rfloor \quad (26)$$

where $\lfloor x \rfloor$ is the floor function and corresponds to the largest integer not larger than x . Equation (26) determines the first generation formula for any given indacenoid constant-isomer series. To use Eq. (26) successively input the number of indacenoid hydrogens possible ($s = 5, 6, 7, 8, 9, 10, 11, 12, \dots$). For example, $s = 11$ gives $n = 11 - 4 + 2\lfloor 10 \rfloor = 27$ which gives $C_{27}H_{11}$ as the first generation formula for one of the two six-isomer indacenoid series. The second, third, fourth, etc. generation formulas are given by the recursion relationships of $N_c' = N_c + 2N_H + 4$ and $N_H' = N_H + 4$ giving $C_{53}H_{15}$, $C_{87}H_{19}$, $C_{129}H_{23}$, etc. As other examples, $s = 14$ & 16 give $n = 14 - 4 + 2\lfloor 17.1 \rfloor = 14 - 4 + 2 \times 17 = 44$ & $n = 16 - 4 + 2\lfloor 23.1 \rfloor = 58$ which give $C_{44}H_{14}$ & $C_{58}H_{16}$, respectively, as the first generation formulas for 26-isomer & 51-isomer series, respectively. In this way Eq. (26) reproduces all 12 formulas (C_5H_5 , C_8H_6 , $C_{11}H_7$, $C_{14}H_8$, $C_{17}H_9$, $C_{22}H_{10}$, $C_{27}H_{11}$, $C_{32}H_{12}$, $C_{37}H_{13}$, $C_{44}H_{14}$, $C_{51}H_{15}$, $C_{58}H_{16}$) in reference 3.

While the above Harary/Harborth-like equations relate extremal properties of indacenoid molecular graphs, they convey nothing about the matching topological properties of the constant isomer series. Constant-isomer indacenoid series have a repetitive isomer number pattern of a, b, a, c, \dots in which those series with the same isomer number have a one-to-one matching in topology among their membership. We now give an alternative way to obtain the formulas of constant-isomer indacenoid series which at the same time distinguishes between the a, a and b, c isomer types. The formulas of the two matching a -types of constant-isomers [i.e., C_5H_5 ($C_{19}H_9$ (1), $C_{17}H_9$ (6), $C_{37}H_{13}$ (28), $C_{65}H_{17}$ (unknown), ... and $C_{11}H_7$ (1), $C_{27}H_{11}$ (6), $C_{51}H_{15}$ (28), $C_{83}H_{19}$ (unknown), ...] are reproduced by $C_{4p^2+1}H_{4p+1}$ and $C_{4p^2+4p+3}H_{4p+3}$, respectively, by successively inputting $p = 1, 2, 3, \dots$; the number of matching isomers are given in parentheses. For example, inputting $p = 3$ into both these general formulas gives $C_{37}H_{13}$ and $C_{51}H_{15}$, respectively, as the first generation formulas to the constant-isomer indacenoid hydrocarbons having 28 isomers with a one-to-one matching in topology between their membership. The formula of the unique b -type of constant-isomers [i.e., C_8H_6 (1), $C_{14}H_8$ (3), $C_{22}H_{10}$ (7), $C_{32}H_{12}$ (12), $C_{44}H_{14}$ (26), $C_{58}H_{16}$ (51)...] are reproduced by $C_{p^2+3p+4}H_{2p+4}$ by successively inputting $p = 1, 2, 3, \dots$; the number of isomers is given in parentheses. Using these general formulas and our above recursion equations, one can easily reproduce Table PAH5.6(I).

3 Summary

For the first time, general formulas for fluoranthenoid/fluorenoïd and indacenoïd constant-isomer series have been presented which distinguish between both matching isomeric sets and the unique isomeric sets. Successive circumscribing can lead to nanocones which have been generated by several methods and observed via scanning tunneling microscopy and scanning electron microscopy [25–27]. The simplest nanoconic series is the result of successive circumscribing of corannulene ($C_{20}H_{10}$, circum-pentadienyl) which is the D_{5h} one-isomer fluoranthenoid/fluorenoïd series ($C_5H_5 \rightarrow C_{20}H_{10} \rightarrow C_{45}H_{15} \rightarrow C_{80}H_{20} \rightarrow \dots$). Among others, several nanocones having equivalence to the smallest constant-isomer series belonging to the first generation members in Fig. 1 have been discussed by Klein and Balaban [28,29]. Thus, this work is a contribution with relevance to the growth of nanocones and related pyrolytic systems.

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