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More about extremal animals*

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The analysis of extremal hexanimals by Harary and Harborth (HH) is set in focus. The spiral walk used in this analysis is treated in some detail. Furthermore, the HH analysis is coupled with the phenomenon of circumscribing. The following theorem is proved: every hexanimal becomes extremal by sufficiently many circumscribings, if they can be executed.

1. Introduction

This work could not have been accomplished without the fundamental analysis of extremeal animals by Harary and Harborth [1], in the following abbreviated to HH. In the present paper, only *hexagonal animals* (polyhexes, benzenoids, fusenes, etc.) are treated; they consist of hexagonal *cells* (or hexagons). Such a hexagonal animal or *hexanimal* is characterized by a pair of invariants, eg. (h, n_i), where h is the number of cells and n_i the number of *internal vertices*. Many other invariants of the hexanimal can be expressed in terms of the mentioned pair. Thus, another pair of independent invariants is given by [2]

$$(n; s) = (4h - n_i + 2; 2h - n_i + 4). \tag{1}$$

Here, n is used to denote the (total) number of vertices, while s is the number of vertices of degree two. This pair of invariants is especially significant inasmuch n and s also give the number of carbon atoms and hydrogens, respectively, in the polycyclic hydrocarbon which corresponds to the hexanimal in question. Accordingly, we shall identify the chemical formula C_nH_s with the symbol $(n; s)$.

An *extremal* hexanimal is defined by

$$n_i = (n_i)_{max} = 2h + 1 - \left\lceil (12h-3)^{1/2} \right\rceil. \tag{2}$$

In other words, it is a hexanimal with the maximum number of internal vertices for a given number of cells. The above relation [3] is a straightforward deduction from the very useful relations of the HH analysis [1]. Several other deductions of this

*Dedicated to Professor Frank Harary on his 70th anniversary.

type have been published [3–7], and especially in connection with the studies of C_nH_s isomers [8–14], where the HH analysis has been exploited to a great extent.

The main result of the present work is a theorem about hexanimals deduced from eq. (2). It has far-reaching consequences in the studies of the C_nH_s hexanimal isomers, as is demonstrated by some examples. The phenomenon of circumscribing (see below) is crucial in parts of these studies, and is here coupled with the studies of extremal hexanimals.

2. Spiral walk

2.1. GENERAL

The foundation of the analysis of HH [1] is the generation of extremal animals by adding cells in a spiral fashion, here referred to as the *spiral walk*. For hexanimals, it is illustrated in fig. 1. The spiral walk generates, obviously, one

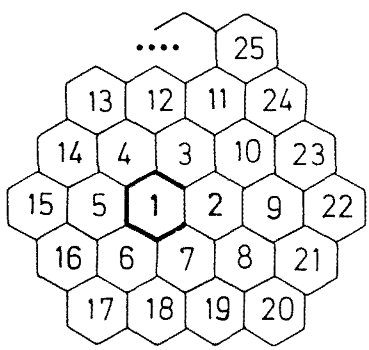

Fig. 1. Illustration of the spiral walk; the cell growth propagates according to the inscribed numerals.

extremal hexanimal for each h value. Many species are missed by this procedure, since it is a fact that there exist numerous nonisomorphic hexanimals with $n_i = (n_i)_{max}$ for given h values [4,9,11,13–16]. However, also unique species exist for selected h values; they are the topic of the next section.

2.2. CIRCULAR HEXANIMALS

During the spiral walk, the addition of the cell No. 2 (cf. fig. 1) does not increase the number of internal vertices (n_i). This is an edge effect which never happens again. In all the subsequent additions, n_i increases either by one unit or two units. If the addition No. $h + 1$ increase n_i by one or zero, then the preceding extremal animal is a unique such system with h cells. It is called a *circular* hexanimal. The condition about zero includes benzene ($h = 1$) among the circular hexanimals. Loosely speaking, a circular hexanimal is produced whenever a whole round is completed during the spiral walk. In precise terms, this happens for

$$h = \left\lfloor \frac{1}{12} (t^2 + 6t + 12) \right\rfloor; \quad t = 1, 2, 3, 4, \ldots . \tag{3}$$

This equation for the number of cells in circular hexanimals is based on the HH analysis [1] and easily obtained with the aid of a previous deduction [5]. A circular hexanimal may also be defined as the (unique) extremal hexanimal with the number of cells given by eq. (3).

Another definition of a circular hexanimal, perhaps the most instructive one: a circular hexanimal is defined by having the maximum number of cells ($h = h_{max}$) for a given circumference (*perimeter* length) [14]. The circular hexanimals manifest themselves in six characteristic shapes. The significance of these shapes was at least known already by Balaban [17] in his studies of annulenes; this topic was recently revisited [6]. The same shapes re-appear among special coronoids called hollow hexagons [6,7,18,19]. Furthermore, each circular hexanimal is identified by its formula C_nH_s, which belongs to a so-called one-isomer series. Also in this connection, the six characteristic shapes have been displayed [11,20,21]. The circular hexanimals form a subclass of the generalized hexagon-shaped hexanimals [22].

2.3. MODIFIED SPIRAL WALK

Some extremal hexanimals, which are not generated by the ordinary spiral walk (fig. 1), are easily obtained by a simple modification. When a circular hexanimal with h cells is produced, add the cell No. $h + 1$ in a place which is not prescribed by the ordinary spiral walk, but also adds one internal vertex to the hexanimal. Example: to the circular hexanimal with $(h, n_i) = (5, 3)$, the sixth cell may be added in three ways so as to generate all the nonisomorphic extremal hexanimals characterized by (6, 4); see fig. 2. In the same way, the four existing nonisomorphic (9, 8) hexanimals are obtained (fig. 2), and the same for the two species of (11, 11). The method fails to produce all the nonisomorphic hexanimals when we come to the addition of one cell to the circular hexanimal with $(h, n_i) = (12, 13)$. Then the spiral walk and its modification give the two species in the top row of fig. 3, while those in the bottom row are missed. In order to go deeper into this problem, we turn to another principle of generating hexanimals, different from the spiral walk with modifications.

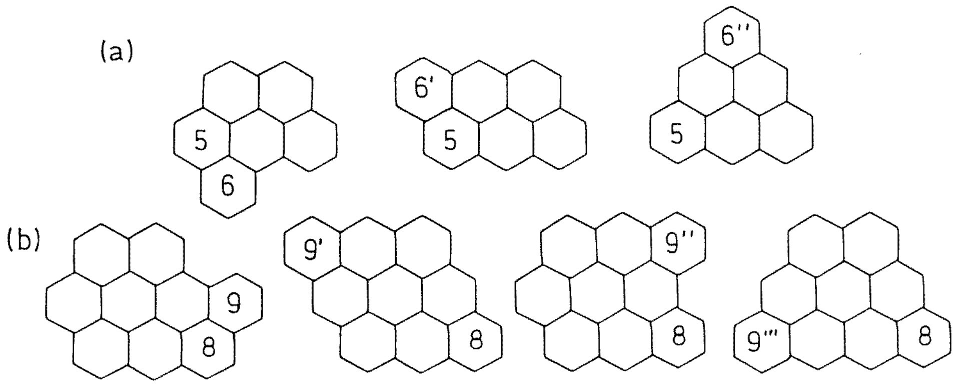

Fig. 2. Generation of all nonisomorphic extremal hexanimals with (a) $h = 6$ and (b) $h = 9$ by the ordinary spiral walk (fig. 1) for the species at the extreme left and the modified spiral walk for the others.

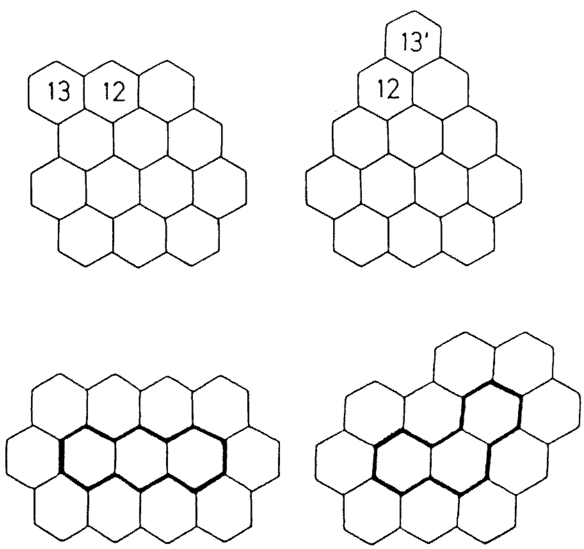

Fig. 3. The four nonisomorphic extremal hexanimals with $h = 13$, $n_i = 14$.

3. Circumscribing

3.1. GENERAL

A hexanimal is said to be *circumscribed* when cells are added to all edges of the perimeter so that they form a closed (*corona-condensed* [23,24]) single chain. In other words, the *dualist* [7,22,23,25] of the added cells is a cycle. The importance of circumscribing was realized at an early stage in the studies of C_nH_s isomers by Dias [26,27].

An analytical result for circumscribing reads: if $(n; s)$ is the formula for a hexanimal A, which can be circumscribed, then the formula for the circumscribed species, circum-A, becomes $(n + 2s + 6; s + 6)$ [11]. Here, we need a result which is a little more advanced. Let a hexanimal A, which can be circumscribed k times, be characterized by (h, n_i). Then the number of cells (h_k) and of internal vertices $(n_i)_k$, for the k-times circumscribed species, viz. k-circum-A, become

$$h_k = 3k^2 + k(2h - n_i + 1) + h, \tag{4}$$

$$(n_i)_k = 6k^2 + 2k(2h - n_i - 2) + n_i. \tag{5}$$

Here, also $k < 0$ makes sense. Then $|k|$ indicates the number of *excisings*. An excising is by definition the opposite process of circumscribing.

3.2. CATACONDENSED HEXANIMALS

As an introduction to the theorems in the next section, consider again fig. 3 with the two hexanimals (bottom row) which are not accessible by the spiral walk, with or without modification. They are the two circumscribed $h = 3$ *catacondensed* $(n_i = 0)$ hexanimals.

Now it is inferred: if C is a catacondensed hexanimal with h cells and which can be circumscribed k times, then k-circum-C is an extremal animal for

$$k > \frac{1}{12}(4h^2 - 12h + 3). \tag{6}$$

Example: $h = 4$, $k > 1$; fig. 4 shows two extremal hexanimals out of 39 [11] with $h = 34$, obtained by double circumscribing of selected catacondensed $h = 4$ hexanimals.

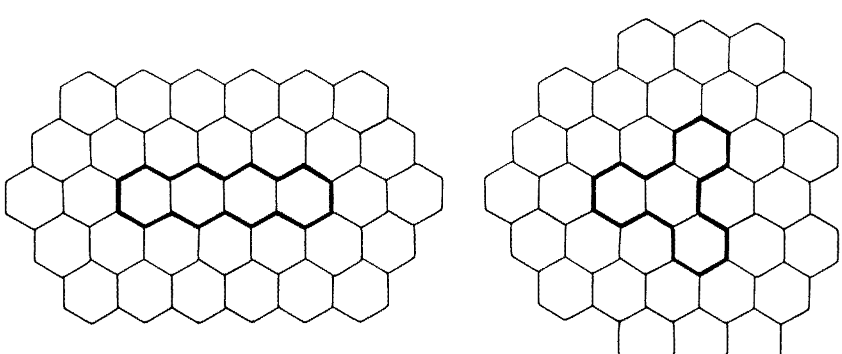

Fig. 4. Two extremal hexanimals with $h = 34$, $n_i = 48$.

4. Two theorems

4.1. INTRODUCTION

It is known that not every hexanimal can be circumscribed [14]. Figure 5 shows five out of the ten unbranched catacondensed hexanimals [22,23]. Those in the top row (a) can be circumscribed k times without limitation; the species in the middle (b) is interesting inasmuch it can be circumscribed once, but not twice; finally, the two bottom species (c) cannot be circumscribed even once. The theorem in the next section is no contradiction to these properties.

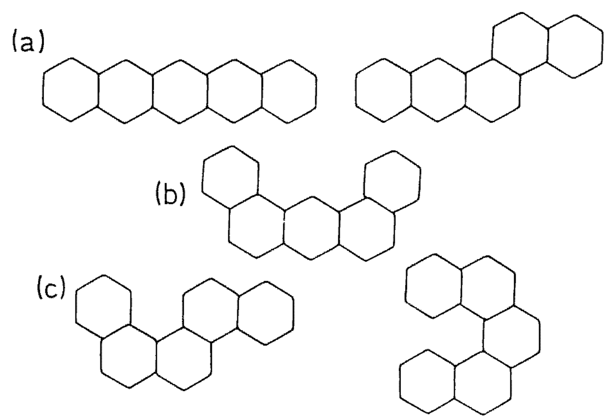

Fig. 5. Hexanimals which can be circumscribed (a) arbitrarily many times, (b) once, but not twice, and (c) which cannot be circumscribed at all.

4.2. THEOREM 1

Among the hexanimals characterized by a pair of invariants (h, n_i) with arbitrary values (within the permitted limits [1]), there exists (at least) one species which can be circumscribed arbitrarily many times.

4.3. PROOF OF THEOREM 1

Construct a selected set of hexanimals, one for each pair (h, n_i) by the following principles. (i) Spiral walk (section 2); (ii) spiral walk up to a point where an added cell would increase n_i by two units, then add a cell which increases n_i by one unit instead; (iii) annelate (i.e. add to a free edge) a catacondensed fragment of $l = 1, 2, 3, 4, \ldots$ cells to all the species (for $h > 1$) constructed under (i) and (ii).

Here, the principles (i) and (ii) produce a hexanimal with the minimum of cells ($h = h_{min}$) for each $n_i = 0, 1, 2, 3, \ldots$. The principle (iii) produces hexanimals with increasing number of cells, $h + l$, without affecting n_i, thus filling out the rest for all the permitted (h, n_i) combinations.

The principle (i) produces invariably hexanimals which can be circumscribed arbitrarily many times. By taking proper precautions, this can always be accomplished also in the cases of (ii) and (iii), for instance in the following way. (ii) When adding the last cell, go one step backwards in relation to the direction of the spiral walk; (iii) choose a linear chain of l cells and annelate it to the free edge (or one of the free edges) as far as possible (reckoned along the perimeter) from the last added cell.

Figure 6 illustrates the above principles. In the examples (a) and (c) therein, (i) + (iii) comes into operation; in (b), it is (ii) + (iii). The values of (h_{min}, n_i) are (11, 11), (12, 12) and (12, 13) in the three cases (a), (b) and (c), respectively.

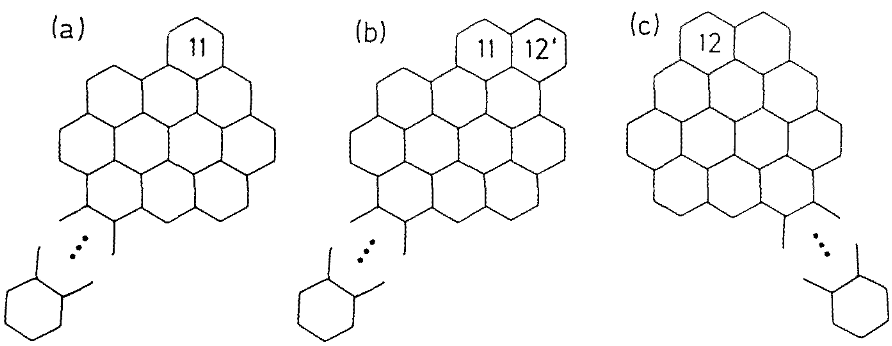

Fig. 6. Construction of hexanimals which can be circumscribed arbitrarily many times: (a) $n_i = 11$, $h = 11 + l$; (b) $n_i = 12$, $h = 12 + l$; (c) $n_i = 13$, $h = 12 + l$. Here, l is the number of cells in a single linear chain.

4.4. THEOREM 2

Any hexanimal A characterized by (h, n_i) becomes an extremal hexanimal when circumscribed sufficiently many times (if possible).

This is our main theorem. Together with theorem 1 it is assured that it is always possible to choose A for an arbitrary pair (h, n_i) so that k-circum-A is extremal. It should be understood that there exists a critical minimum value, say $x = k_{min}$, for which x-circum-A is extremal, and all subsequent circumscribings $(k > x)$ continue to generate extremal hexanimals.

4.5. PROOF OF THEOREM 2

Theorem 2 is proved by an analytical derivation of k and x in general. One simply has to substitute h and n_i in eq. (2) by h_k from (4) and $(n_i)_k$ from (5), respectively. These substitutions yield

$$6k + 2h - n_i + 1 = \left\lceil 3^{1/2}[12k^2 + 4k(2h - n_i + 1) + 4h - 1]^{1/2} \right\rceil. \tag{7}$$

After some manipulation, we obtained

$$k > \frac{1}{12}\,[(2h - n_i)^2 - 12h + 3]. \tag{8}$$

Finally, one obtains the critical value of $x = k_{\min}$ as

$$x = \left\lfloor \frac{1}{12}[(2h - n_i)^2 - 12h + 15] \right\rfloor. \tag{9}$$

It may happen that $x < 0$. Then $|x|$ according to eq. (9) is meaningful as well and indicates the number of excisings ("negative circumscribings").

5. Application of the main theorem

5.1. CATACONDENSED HEXANIMALS

It is seen that eq. (6) of section 3.2 is the special case of (8) for $n_i = 0$.

5.2. HEXANIMALS WITH ONE INTERNAL VERTEX

A hexanimal with $n_i = 1$ is either phenalene ($h = 3$) or phenalene with one, two or three catacondesed fragment(s) annelated to it. Figure 7 shows some such hexanimals; in all these examples, the species can be circumscribed arbitrarily

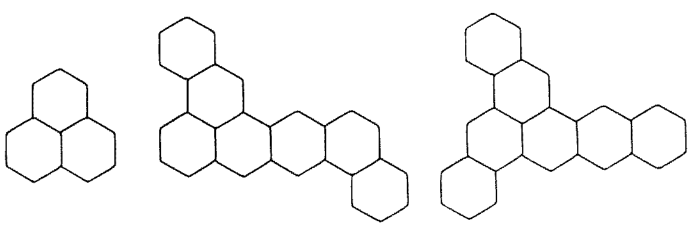

Fig. 7. Hexanimals with one internal vertex each.

many times. Equations (8) and (9) assume particularly simple forms in this case; the latter one becomes

$$x = \left\lfloor \tfrac{1}{3}(h - 2)^2 \right\rfloor. \tag{10}$$

5.3. TRIANGULENE HOMOLOGUES

The triangulene homologues T (see fig. 8) consist of the trivial case C_6H_6 benzene, $C_{13}H_9$ phenalene, $C_{22}H_{12}$ triangulene, $C_{33}H_{15}$, $C_{46}H_{18}$, ... These hexanimals have the Δ values 0, 1, 2, 3, 4, . . . , as was pointed out by Gutman [28]. Here, Δ (the color excess [9]) is the absolute magnitude of the difference between the

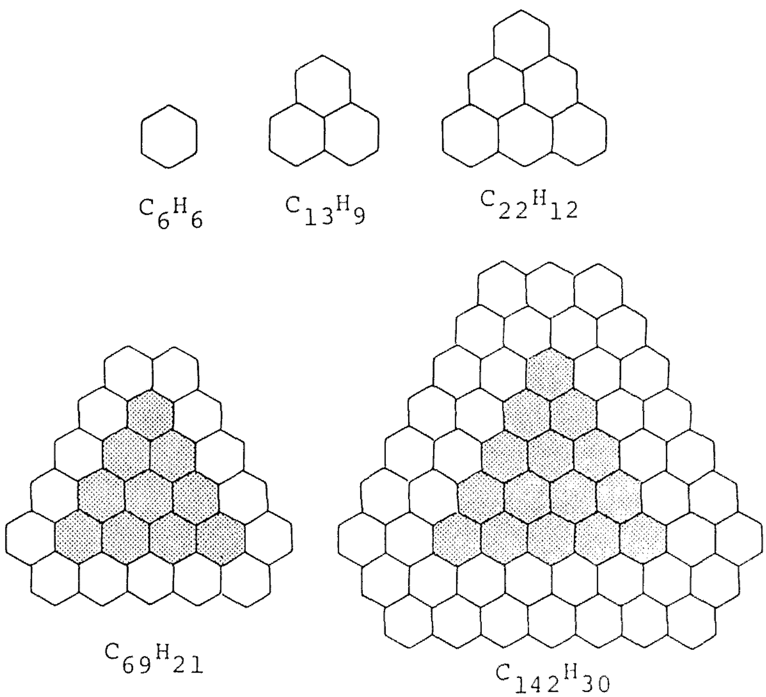

Fig. 8. The smallest extremal hexanimals for $\Delta = 0, 1, 2, 3$ and 4. They have $h = 1, 3, 6, 25$ and 57, respectively.

numbers of black and white (or starred and unstarred) vertices. It is reasonable to believe, with support from previous findings [29], that the smallest hexanimal with a given Δ is T (for $\Delta \leq 2$) or x-circum-T (for $\Delta > 2$). Although this property is not rigorously proved, it is of interest to determine the x values (minimum number of circumscribings) for the series of homologues under consideration.

For a k-times circumscribed triangulene homologue, viz. k-circum-T, it was found that

$$h_k = 3k(k + \Delta + 1) + \tfrac{1}{2}(\Delta + 1)(\Delta + 2), \tag{11}$$

$$(n_i)_k = 6k(k + \Delta) + \Delta^2. \tag{12}$$

Herefrom, the (h, n_i) pair is readily obtained by inserting $k = 0$. The two parameters were inserted into eq. (9), with the result:

$$x = \left\lfloor \frac{1}{12}(3\Delta^2 - 6\Delta + 7) \right\rfloor. \tag{13}$$

Figure 8 includes the examples for $\Delta = 3$ and $\Delta = 4$. According to (13), the extremal hexanimals are obtained by circumscribing the triangulene homologues (shaded areas in the figure) once ($x = 1$) and twice ($x = 2$), respectively.

This problem was considered (from a slightly different point of view) in a paper by Dias [30], which contains many interesting aspects on constant-isomer series of hexanimals. Four of the formulas for constant-isomer series, which he has reported, viz. $C_{69}H_{21}$, $C_{142}H_{30}$, $C_{325}H_{45}$ and $C_{706}H_{66}$, should conform to the cases $\Delta = 3, 4, 5$ and 6, respectively, in our analysis. To be precise, the formulas, say $(n_x; s_x)$, should pertain to x-circum-T for the given Δ values. It was found that

$$(n_x; s_x) = (\Delta^2 + 6(x+1)(x+1+\Delta);\ 6(x+1) + 3\Delta), \tag{14}$$

where x might be inserted from (13). Equation (14) confirms the first three of the Dias [30] formulas, but we believe that the last one is in error; we find it should be $C_{582}H_{60}$.

Acknowledgement

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