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GENERATION AND ENUMERATION OF PLANAR POLYCYCLIC AROMATIC HYDROCARBONS

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Abstract - In this paper, we propose a method of the computer generation of all planar polyhexes and display the results of the numbers of polyhexes with up to 9 hexagons.

Introduction

This paper is the continuation of our work[1] on non-numerical computations. The hydrogen-deleted graphs of condensed benzenoid hydrocarbons(polycyclic aromatic hydrocarbons or PAH's) are portions of the graphite(honeycomb) lattice, i.e. polyhexes.

Our discussions are limited to the planar polyhex graphs. In other words, we don't consider any kind of helicenes (since they have non-planar structures).Note that the term "planar" is used here without regard to the possible molecular twist caused by the internal interaction.

The problem of generation and enumeration of polyhexes is a well-known cell-growth problem with hexagonal animals.[2-4] Although this problem has been investigated by many authors,[2-20] the method of generation and enumeration of all planar polyhexes is still an unsolved problem. In the references[8,13], the number of polyhexes included the number of helicenes which are non-planar, and in another reference[11],the coronene with 7 benzene rings was considered as the circulene with 6 benzene rings. Therefore the enumeration of PAH's was confused.

In this paper, we propose a method which can be used for generating all planar polyhexes including all kinds of corona-fused polyhexes or circulenes, and present the results of classification and enumeration of planar polyhexes with up to 9 hexagons.

Characteristic graph of a PAH molecule, He-matrix of characteristic graph, and nomenclature of a PAH molecule(or a polyhex)

The so called PAH characteristic (or dualist) graph $G(V,E)$[21-23]is a graph in which the vertex set V consists of all central points of benzene rings of the PAH molecule and the edge set E consists of all lines connecting the central points of the adjacent condensed benzene rings (see[14,21-23]). For example, a PAH molecule (or a polyhex) having hexagons written with some edges in vertical position, together

with its corresponding characteristic graph is shown in Fig.1, in which the ordinal numbers of vertices are given by sweeping from the left to the right and from top to bottom.

An He-matrix[1] of G(V,E) is an NxN matrix(a_{ij}), where N is the total number of vertices in the characteristic graph G(V,E), and V_i (i=1,2,...,N) represents the i-th vertex of G(V,E).

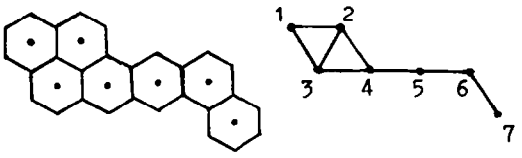


Fig.1 Characteristic graph

$$a_{ij}=\begin{cases}0 \text{ (if } i=j, \text{ or } V_i \text{ isn't adjacent to } V_j)\\ 1 \text{ (if } V_i \text{ is adjacent to } V_j, \text{ and the angle between } \overline{ij} \text{ and the positive horizontal direction is } k\pi) \quad i\text{—}j\\ 2 \text{ (if } V_i \text{ is adjacent to } V_j, \text{ and the angle stated above is } k\pi+\pi/3) \quad \begin{matrix}&j\\ i\diagup&\end{matrix}\\ 3 \text{ (if } V_i \text{ is adjacent to } V_j, \text{ and the angle stated above is } k\pi+2\pi/3) \quad \begin{matrix}j\diagdown&\\ &i\end{matrix}\end{cases}$$

(Note: the positive horizontal direction is from the left to the right.)

Thus, the He-matrix of the characteristic graph in Fig.1 is as follows.

$$(a_{ij})=\begin{pmatrix}0&1&3&0&0&0&0\\1&0&2&3&0&0&0\\3&2&0&1&0&0&0\\0&3&1&0&1&0&0\\0&0&0&1&0&1&0\\0&0&0&0&1&0&3\\0&0&0&0&0&3&0\end{pmatrix} \qquad (1)$$

According to Fig.1(or its He-matrix), we can write down one nomenclature series (or name)[1] of the polyhex, i.e.

2;4/6,7;5;2,4;1,3

The nomenclature series is divided into two sections by symbol "/". The numbers in section 1 represent the number of vertices in every layer(transverse row) from top to bottom except the lowest layer, whereas the arrangement of vertices in section 2 represents the order of the initial ordinal numbers of vertices in every transverse row (i.e. between two adjacent semicolons) after we turn the polyhex graph through an angle 60° counterclockwise.

By rotation and reflection[1], we can obtain 12 He-matrix and 12 nomenclature series corresponding to the 12 different orientations of the polyhex, respectively. Choose the minimum in lexicographic order from those having the minimum layers in the first section of nomenclature series as the standard name. To go into detail, see Ref.1.

Computer generation of polyhexes

For generating characteristic graphs with N+1 vertices (simply, (N+1)-graphs) from N-graphs, the steps are as follows.

Step 1. From a vertex V_i ($i=1,2,\ldots,N$) of an oriented characteristic graph, generate a new vertex which is adjacent to V_i, and is to the right of V_i. (If the new generated vertex is coincident with any vertex of the N-graph, i.e. for the N-graph, $a_{i,i+1}=1$, then such a generation should be excluded.)

Denote the new generated vertex by V_{i+1}. Then change the ordinal numbers of vertices $i+1,i+2,\ldots,N$ into $i+2,i+3,\ldots,N+1$, respectively.

Step 2. Find the nomenclature of the new generated (N+1)-graph:

If in the N-graph, V_i belongs to the m-th layer of section 1, and the p-th layer of section 2, then in the new generated (N+1)-graph, V_{i+1} will belong to the m-th layer of section 1 (and so the total number of vertices in the layer will be changed into A_m+1 from A_m.), and to the (p-1)-th layer of section 2. Because of the increasing arrangement of numbers in every layer of section 2, we can easily insert the number i+1 into the (p-1)-th layer ($p=2,3,\ldots$) at a suitable place. If p=1, then V_{i+1} will precede the initial first layer of section 2 and become the new first layer of section 2.

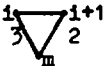
Step 3. Find the He-matrix corresponding to the new generated (N+1)-graph. The He-matrix $(\bar{a}_{kj})$ is a (N+1)×(N+1) matrix. Its elements are as follows.

1)
$$\bar{a}_{kj}=\begin{cases} a_{kj} & (k\not\leftarrow j\not\leftarrow i) \\ a_{k-1,j-1} & (i+2\not\leftarrow k\not\leftarrow j) \\ a_{k,j-1} & (k+2\not\leftarrow i+2\not\leftarrow j) \end{cases}$$

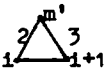
where a_{kj} and $\bar{a}_{kj}$ are the elements of the He-matrix of the N-graph and the elements of the new generated He-matrix, respectively.

2) $\bar{a}_{i,i+1}=1$, $\quad i\longleftarrow i+1$

3) $\bar{a}_{i+1,m}=2$ (if $\bar{a}_{im}=3$ and $m\not\rightarrow i+1$),



4) $\bar{a}_{m',i+1}=3$ (if $\bar{a}_{m',i}=2$ and $m'\not< i$),



5) $\bar{a}_{i+1,i+2}=1$ $\qquad i+1\longleftarrow i+2$

(if V_{i+2} belongs to the same layer as V_{i+1} in section 1 of the new generated nomenclature, and to one layer upper than V_{i+1} in section 2),

6) $\bar{a}_{j,i+1}=2$

(if V_j, where $j\not< i+1$, belongs to one layer upper than V_{i+1} in either section),

7) $\bar{a}_{i+1,j}=3$

(if V_j, where $j\not> i+1$, belongs to one layer lower than V_{i+1} in section 1, and to the

same layer as V_{i+1} in section 2),

8) $\bar{a}_{k,i+1}=\bar{a}_{i+1,j}=0$ $(k\leqslant i+1\leqslant j)$ for the other cases,

9) $\bar{a}_{rs}=\bar{a}_{sr}$ $(r>s)$.

Step 4. According to the method in Ref.1, find the standard name of the generated (N+1)-graph.

Step 5. For every vertex, from i=1 to N, of the oriented characteristic graph with N vertices, proceed with step 1 to step 4. If a new generated (N+1)-graph is coincident with one of the preceding generated (N+1)-graphs, then this new graph should be deleted.

Step 6. According to the method in Ref.1, proceed with classification and enumeration of the generated graphs.

Step 7. For the other five rotation orientations of the N-graph, proceed with step 1 to step 6.

Step 8. For every other N-graph, proceed with step 1 to step 7.

Thus, we can obtain all characteristic graphs with N+1 vertices and their standard nomenclature series.

It must be prevented that for only one generation step, more than one vertex be generated, For example, in Fig.2a, while V_{i+1} is generated, the central point is also generated; and in Fig.2f, for only one generation step, four new vertices are simultaneously generated.

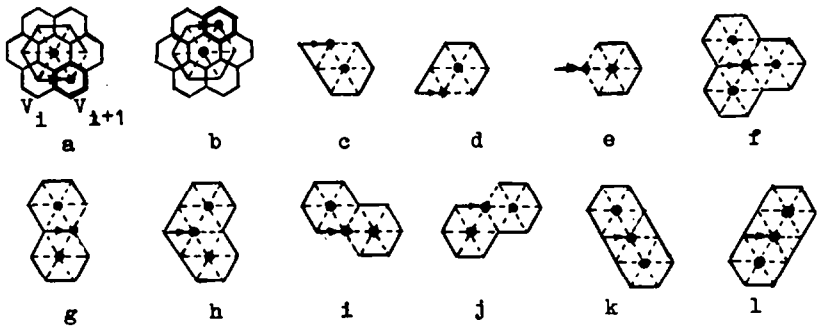


Fig.2 Generation of more than one vertex

In order to prevent the enumeration errors caused by such cases, we use the following method.

At first, we restrict the generation only in the case $\bar{a}_{i+1,f}=0(f>i+1)$. In other words, the generation for $\bar{a}_{i+1,f}\neq 0(f>i+1)$ is excluded. This restriction is reasonable, because it can't decrease the enumeration of polyhexes, but can considerably simplify the non-numerical computation.

In addition to this restriction, we only need to exclude the case in Fig.2a (the other cases in Fig.2 have been excluded by the restriction stated above). In other words, for the generating graph(a fragment of characteristic graph) shown in Fig.3,

the generation of the new vertex V_{i+1} from V_i must be excluded. Using the elements of He-matrix (a_{ij}), we can easily know whether such a fragment of Fig.3 exists. Thus, we prevent the generation of more than one vertex for only one generation step.

The process of generation, nomenclature[1], classification and enumeration of polyhexes can be easily performed. Since the algorithm belongs to the polynomial algorithms(p-algorithms), it is still efficient for rather large N(the number of hexagons of a polyhex), provided the storage capacity of the computer is large enough. The programme in detail is available from the authors upon request. The flow chart of the generation procedure from N-graphs to (N+1)-graphs is given as follows.

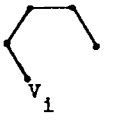


Fig.3 Exclusion of generation

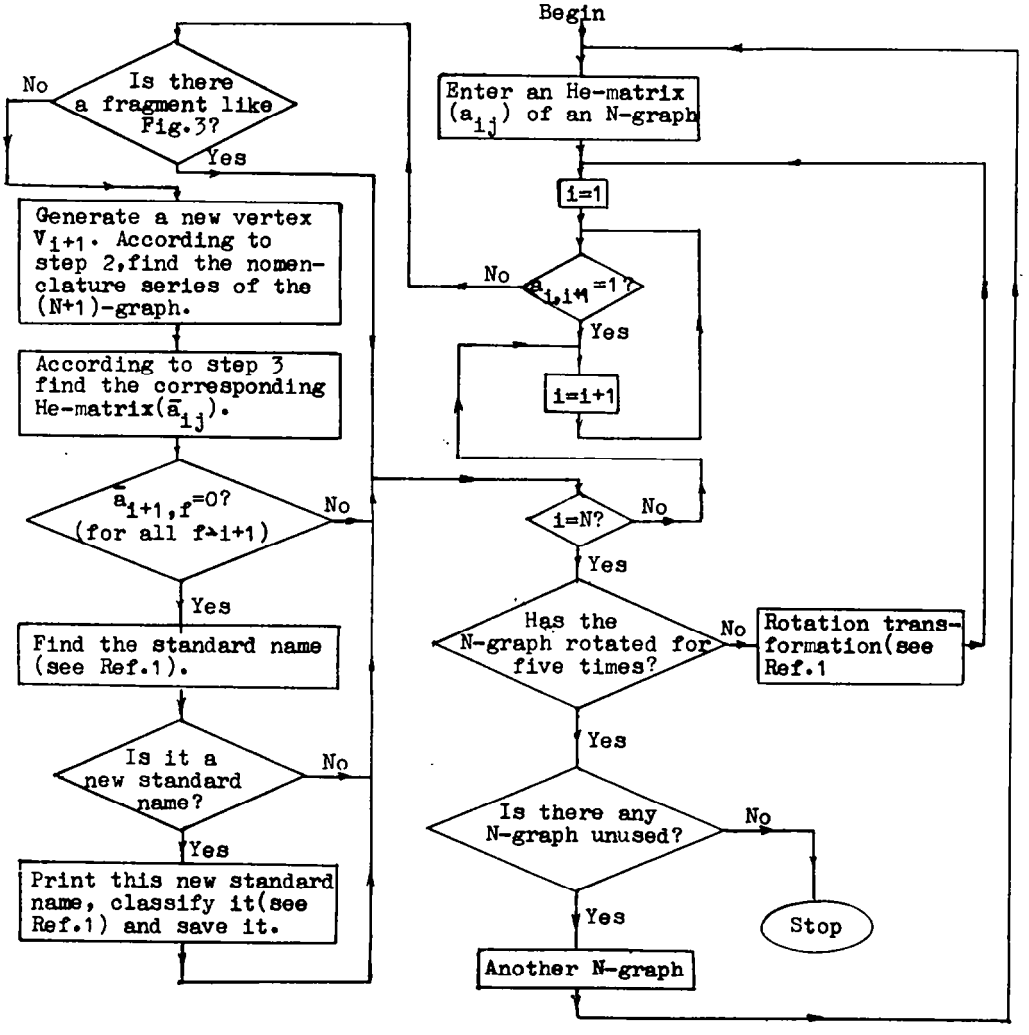


Fig.4 Flow chart of the generation procedure

Enumeration of planar PAH's

Only using a personal computer, we obtain the nomenclature, the classification and the enumeration of planar PAH systems with up to 9 benzene rings. The results except the nomenclature series, which are too numerous, are shown in Table 1. With regard to the computer classification method of PAH's, including the method partitioning PAH's into those having or not having Kekulé structures, see Ref.1.

In Table 1, k is the number of Kekulé patterns of a PAH molecule. B represents a cata-condensed molecule without branches. C represents a cata-condensed molecule with branches.

Table 1. Classification and enumeration of PAH's

	k≠0						k=0			
N	B	C	D	F	E	Total	D	F	Total	Total
1	1	0	0	0	0	1	0	0	0	1
2	1	0	0	0	0	1	0	0	0	1
3	2	0	0	0	0	2	1	0	1	3
4	4	1	1	0	0	6	0	1	1	7
5	10	2	1	2	0	15	1	6	7	22
6	24	12	3	12	0	51	3	27	30	81
7	67	51	6	66	0	190	9	132	141	331
8	182	229	22	331	1	765	27	644	671	1436
9	520	969	58	1678	1	3226	119	3165	3284	6510

D represents a peri-condensed or cyclic peri-condensed molecule, E represents a corona-condensed molecule and F represents a derived condensed molecule from D and E.

Our results are different from the data in the literatures[5,6,8-11,13,17,20].

1) Since our results include the case of corona-condensed polyhexes or circulenes, whereas the results of DZG(the Düsseldorf-Zagreb Group)[5] don't, for N=1 to 7, both are identical, but for N≥8 difference appears.(See Table 2) The missing graphs (characteristic graphs) by DZG boundary code method are shown in Fig.5.

Table 2. Difference between DZG numbers and ours

N	DZG numbers	Our numbers
8	1435	1436
9	6505	6510

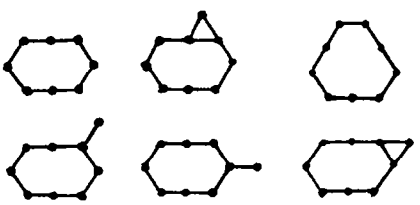


Fig.5 Illustration of Table 2

2) Balaban-Harary numbers[8,13] didn't include peri-condensed systems and corona--condensed systems, but included helicenes. So far as the number of cata-condensed systems is concerned, for N≥6 Balaban-Harary numbers are different from ours.(See Table 3) The excess of Balaban-Harary numbers over ours are the numbers of helicenes(see Fig.6). The graphs of helicenes with 9 benzene rings are too numernous to be shown.

3) Lunnon numbers[11] included planar mono-circulenes. In his work, the coronene fragment with 7 benzene rings was treated as the circulene fragment with 6 benzene rings. The difference between his results and ours is shown in Table 4 and Fig.7.

Table 3. Numbers of cata-condensed systems

N	Balaban-Harary numbers	Our numbers (B+C)
1	1	1
2	1	1
3	2	2
4	5	5
5	12	12
6	37	36
7	123	118
8	446	411
9	1689	1489

Table 4. Difference between Lunnon numbers and ours

N	Lunnon numbers of mono-circulenes	ours (See Fig.5)
1	0	0
2	0	0
3	0	0
4	0	0
5	0	0
6	1	0
7	2	0
8	13	1
9	67	5

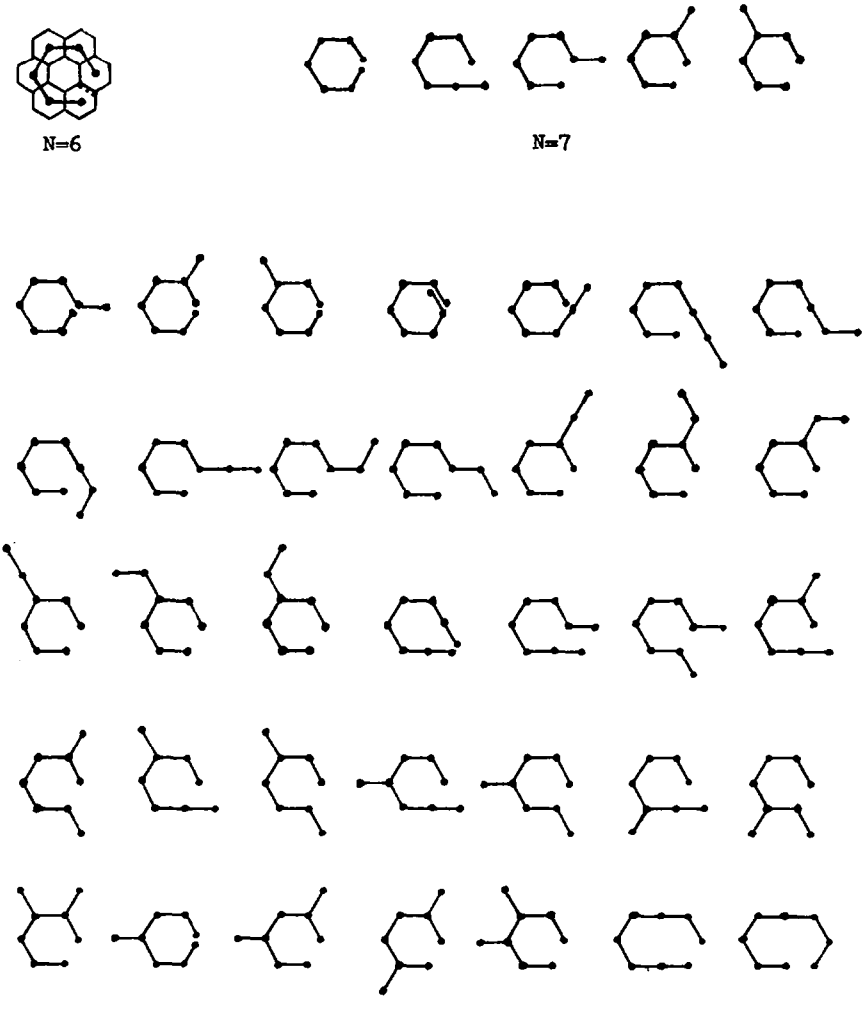


Fig.6 Helicenes

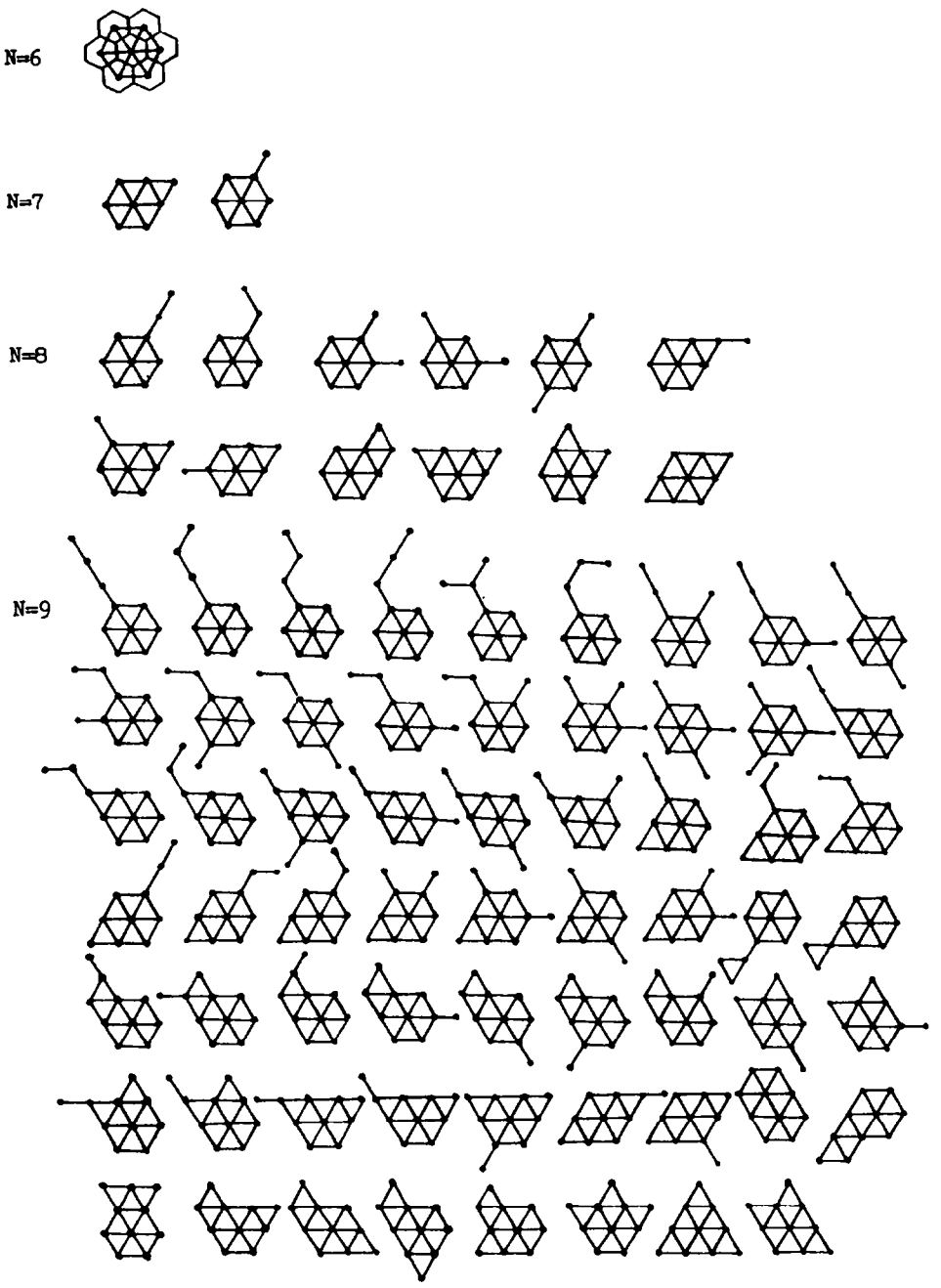


Fig.7 Illustration of Table 4

4) Dias numbers[6] also differ from ours. His values for cata-condensed benzenoid systems including cata-condensed helicenes are identical with Balaban-Harary values(See Table 3). For non-cata-condensed systems, in Dias' work[6], only closed--shell structures(i.e. non-radical structures, whose number of Kekulé patterns k≠0) were considered. However, he missed some non-radical structures.[5]

Discussions

(1) In a similar way to the method suggested in this paper, we can carry out the generation and the enumeration of planar connected systems composed of triangles or squares.

(2) If in the preceding step 3, all the elements in the (i+1)-th row and in the (i+1)-th column $\bar{a}_{k,i+1}=\bar{a}_{i+1,j}=0(k\leq i+1\leq j)$ except the cases 2)-4), then we can obtain the generation and enumeration of cata-condensed and peri-condensed polyhexes(including helicenes). The obtained numbers of cata-condensed polyhexes including cata-condensed helicenes are identical with Balaban-Harary values.

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