CROATICA CHEMICA ACTA CCACAA **67** (4) 481–492 (1994)

ISSN 0011–1643
CCA–2201

Original Scientific Paper

The Enumeration of Polyhexes with Caterpillar Shape*

Frank Harary

Department of Computer Science, New Mexico State University, Las Cruces, NM 88003, USA

and

Ronald C. Read

Department of Combinatorics and Optimization, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

Received November 3, 1993; revised July 7, 1994; accepted July 10, 1994

We consider the special case of treelike polyhexes for which the consecutive removal of endhexagons results in a path, or complete disappearance. We derive a generating function for counting the isomorphism classes of these »polycats« up to reflection and rotation.

INTRODUCTION

The study of the various ways in which six-membered rings of carbon atoms can be combined to form more complicated chemical structures (as for example in Figures 1 and 2) is one of considerable importance for organic chemists. It corresponds to the geometrical problem of combining, in the plane, regular hexagons of equal size, by the process of bringing hexagons together at common edges. It is natural to ask whether a formula can be found that gives the number of different ways of combining a given number n of hexagons. This problem has all appearances of being completely intractable, for two main reasons.

First, such a configuration could be »peri-condensed«, meaning that there is at least one point which is common to three hexagons (as in Figure 1 with the hexagons marked A, B and C). If peri-condensation is allowed, our problem becomes a variant of the cell-growth problem[4,6] for which no counting formula has yet been found.

Secondly, even if we restrict our attention to »cata-condensed« structures, that is, those that are not peri-condensed, following the now standard terminology intro-

* Dedicated to Paul Mezey on his 50th birthday

duced,[1] there is still the possibility of the hexagons forming a closed ring, as in Figure 2. If this is allowed, the enumeration problem is still intractable. Since peri-condensed compounds and compounds containing rings of hexagons are of importance in chemistry, it is unfortunate that their enumeration appears to be out of reach.

Figure 1.

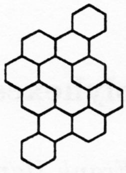

Figure 2.

Figure 3.

In order to arrive at a more restricted, but tractable problem, Balaban and Harary introduced the structures called »polyhexes«. A »treelike polyhex«[7] can be defined in various ways; perhaps the simplest is to define it as any structure in the plane which can be built up, starting with a single hexagon, by adding new hexagons, one at a time, subject to the rule that a new hexagon is joined only at a single edge on the boundary of the existing structure. Since, to achieve a peri-condensed structure, or one containing a ring of hexagons, it would be necessary, at some stage, to join a new hexagon at two or more edges, these two sources of difficulty are excluded. The enumeration of treelike polyhexes proved to be tractable, and was carried out by us in Ref. 7.

One further rule is required for the proper definition of a treelike polyhex, namely that we must not attach two hexagons to a third at adjacent edges, as shown in Figure 3. Fortunately, this restriction is a reasonable one from a chemical point of view. It follows that a hexagon can have 1, 2 or 3 neighbours (as shown by A, B and C respectively in Figure 4) but no more. For the number of neighbours we shall use the graph-theoretical term 'degree'. There are essentially two different kinds of hexagon of degree 2, according as its neighbours abut on opposite edges or not (D and E in Figure 4). A hexagon of degree three will be called a 'branch hexagon'; there is only one kind.

One further comment is necessary. In the course of assembling a treelike polyhex it may happen that the hexagons will assume positions where, if the construction were literally in the plane, a ring would have to be formed (Figure 5). In that case we may think of the hexagons as »overlapping« (Figure 5 again). It is immaterial which part of the structure is regarded as being on top and which beneath.

Our purpose is to enumerate a special subset of treelike polyhexes. The nature of this subset is best explained by reference to the »dual« of a polyhex. This is not

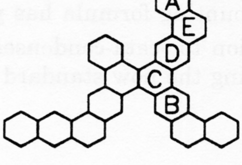

Figure 4.

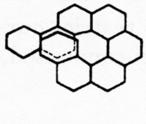

Figure 5.

strictly a dual operation, since performing it twice does not give back the original structure. This concept was introduced in Ref. 2 where it was called the »weak dual« or »inner dual«. This is the graph obtained by placing a node at the centre of each hexagon and joining two nodes if and only if their hexagons abut (Figure 6). It follows from the definition of a treelike polyhex that the resulting graph is a tree (for graph theoretical terminology see Ref. 5). We now define an operation called *path reduction*. Every node of degree 1 (endnode) defines a unique path, starting at that node and continuing through nodes of degree 2 (if any) until a node of degree not 2 is reached. To »path-reduce« a tree we note all endnodes and the paths that they define, and then simultaneously delete all the nodes of degree 1 and 2 on these paths. The treelike polyhex that remains (if it does not vanish altogether) is the *path-reduction* of the original.

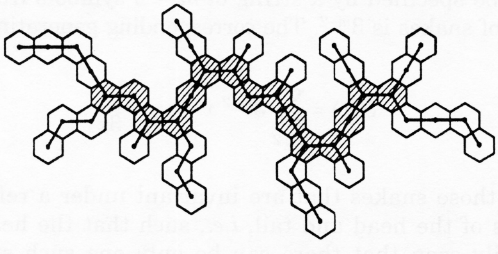

Figure 6.

The treelike polyhexes that we shall enumerate are those whose path-reduction is a path, including (for completeness) those whose path-reductions are empty. This is a generalization of an existing graph-theoretical concept. A tree which reduces to a path when just the endnodes are deleted has been called a »caterpillar«.[8,9] Our new polyhexes could be described as being »super-caterpillars« or »long-legged caterpillars«; but we need a more concise term. We shall call them *polycats*, where the 'cat' part of the name serves the dual purpose of reminding us that we are dealing with catacondensed structures, and that these are, in a sense, caterpillar-like. It will be convenient to refer to the path to which a polycat reduces as the »spine« of the polycat.

The methods that we shall use are quite standard, being variations on those used in Ref. 7. We shall say that two polyhexes are equivalent if one can be obtained from the other by a rotation or reflection of the plane. An important tool for problems of this type is Burnside's lemma. This is described in Ref. 6 but a rough précis of it is the following. In order to determine the number of inequivalent configurations under the action of a group (such as the rotations and reflections just mentioned) it suffices to compute, for each group element, the number of configurations that are invariant under that group element, and then take the average of the numbers so obtained.

It will be convenient to treat separately three types of polycats, as follows:

Type I: those having no branch cells (these are therefore paths to start with).

Type II: those having exactly one branch cell (from which, therefore, three paths will arise).

Type III: those having two or more branch cells.

POLYCATS OF TYPE I – NO BRANCH HEXAGONS

These polycats consist of a sequence of hexagons. There are two »end hexagons«, and every other hexagon is adjacent only to its predecessor and its successor in the sequence (Figure 7). We first consider polycats of this type that are fixed in the plane. The two end hexagons are therefore distinguished from each other, and it will assist our exposition to call these hexagons the »head« and »tail«, and to refer to the fixed polycat as a »snake«.

The enumeration of snakes is very easy. If we traverse the length of the snake, say from tail to head, then at every »inner« hexagon, *i.e.* other then the head and tail, there can be a change of direction, to the left (call it »type 0«) or to the right (»type 2«), or a continuation of the previous direction (»type 1«). Note that each hexagon is drawn with two vertical edges, as in the figures. If the snake contains m hexagons in all, it can be specified by a string of $m - 2$ symbols from the set $\{0,1,2\}$ and hence the number of snakes is 3^{m-2}. The corresponding generating function is therefore

$$S(x) = \sum_{m \geq 2} 3^{m-2}\, x^m = \frac{x^2}{1 - 3x}\,. \tag{1}$$

Consider now those snakes that are invariant under a reflection about the line joining the centres of the head and tail, *i.e.*, such that the head and tail remain in position. It is easily seen that there can be only one such snake on m hexagons, namely the »straight« snake shown in Figure 8.

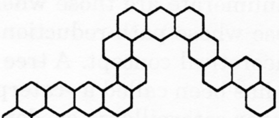

Figure 7.

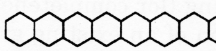

Figure 8.

Consider those snakes that are invariant about a line perpendicular to the previous line of reflection. If such a snake has an even number, $m = 2k$, of hexagons (Figure 9), then it is fully determined by its first $k + 1$ hexagons, and consists of a snake on $k + 1$ hexagons, minus its head, joined to its mirror image, its reflection in the dotted line of Figure 9. (The reason for including the $(k + 1)$'st hexagon is to determine how these two portions are joined together). Hence the number of such snakes is 3^{k-1}. If the snake has an odd number, $m = 2k + 1$, of hexagons (Figure 10), it can be constructed by joining each of the two »headless« snakes to a central hexagon, an operation which is possible in three ways according to whether the edges of attachement are opposite each other or not. Figure 10 shows one of the two cases when they are not, and uses the same »half-snake« as for Figure 9. Hence in this case the number is 3^k.

Finally we consider those snakes having the remaining kind of symmetry, that of a rotation through 180° which interchanges the head and tail. For snakes on $2k$ hexagons the situation is the same as before, except that the »half-snake« is joined,

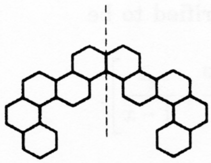

Figure 9.

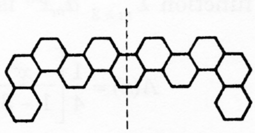

Figure 10.

not to its mirror image, but to a 180° rotation of itself (Figure 11). The number of such snakes is therefore again 3^{k-1}. However, if the number of hexagons is $2k + 1$ (Figure 12), the situation is different, since the symmetry requires that the central three hexagons be in a straight line.

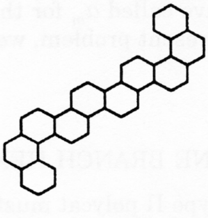

Figure 11.

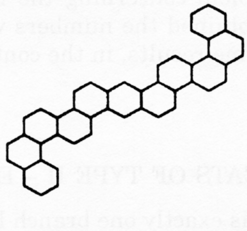

Figure 12.

Thus, whereas for the case of reflection we had three ways of attaching the two half-snakes to the central hexagon, we now have only one. Hence the number is 3^{k-1}.

These numbers are summarized in Table I. Note that the heading »All snakes« is consistent with the others since it can be paraphrased as »Invariant under the identity operation of the group«.

TABLE I

	$m = 2k$	$m = 2k + 1$
All snakes	3^{m-2}	3^{m-2}
Invariant under reflection (1)	1	1
Invariant under reflection (2)	3^{k-1}	3^{k-1}
Invariant under 180° rotation	3^{k}	3^{k-1}

Burnside's lemma now gives us the numbers of inequivalent snakes, that is, the number of polycats of type I. We have

$$a_m = \frac{1}{4}\,(3^{m-2} + 2.3^{k-1} + 1) \ \text{if} \ m = 2k$$

$$\text{and} \quad a_m = \frac{1}{4}\,(3^{m-2} + 3^{k-1} + 3^{k-2} + 1) \ \text{if} \ m = 2k + 1 \tag{2}$$

The generating function $\Sigma_{m \geq 2}\ a_m x^m$ is readily verified to be

$$A(x) = \frac{1}{4}\left[\frac{x^2}{1-3x} + \frac{2x^2+4x^3}{1-3x^2} + \frac{x^2}{1-x}\right]. \tag{3}$$

This can also be written as a single rational function, namely

$$\frac{x^2(1-2x-4x^2+6x^3)}{(1-x)(1-2x)(1-3x^2)}. \tag{4}$$

The first few values for a_m are given in Table II.

The results just obtained are not new. Foster[3] considered a different (but equivalnet) problem concerning the number of ways of bending a piece of wire in the plane. He obtained the numbers which we have called a_m for the solution to his problem. The same results, in the context of the present problem, were also obtained in Ref. 1.

POLYCATS OF TYPE II – EXACTLY ONE BRANCH HEXAGON

Since there is exactly one branch hexagon, a type II polycat must consist of three headless snakes attached at alternate edges of the branch hexagon (Figure 4). If this hexagon, and the edges at which the snakes are attached, is fixed then the three choices for the snakes are independent. Hence the generating function for fixed polycats of type II is

$$x\,[x^{-1}\,S(x)]^3\,,$$

where the x^{-1} allows for the removal of the head of each snake. This generating function is therefore

$$\frac{x^4}{(1-3x)^3}. \tag{5}$$

We now consider the possible symmetries of these polycats. First, there are two symmetries of rotation, namely by 120° and 240° about the centre of the branch hexagon. For invariance under such a rotation, the three attached snakes must be identical (Figure 13). Since each choice of a hexagon in one snake determines two others (so that the hexagons occur in triads) the generating function for these polycats is

$$x\,[x^{-3}\,S(x^3)] = \frac{x^4}{1-3x^3} \tag{6}$$

for each of the two rotations.

There are also the reflectional symmetries about an axis of symmetry of the central hexagon (Figure 14). Clearly the snake that is attached along the axis of symmetry must be the straight snake. The other two are mirror inages of each other.

Hence the required generating function is

$$\frac{x^2}{1-x}\,[x^{-2}S(x^2)] = \frac{x^4}{(1-x)\,(1-3x^2)}\,. \tag{7}$$

This holds for each of the three symmetries of this type.

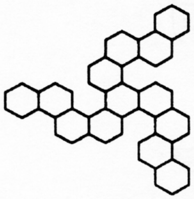

Figure 13.

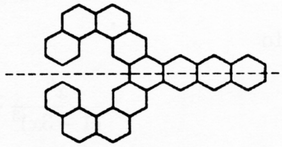

Figure 14.

We now apply Burnside's lemma and take the average of the six generating functions just obtained. The result is the generating function

$$\frac{1}{6}\left[\frac{x^4}{(1-3x)^3} + \frac{3x^4}{(1-x)\,(1-3x^2)} + \frac{2x^4}{1-3x^3}\right] \tag{8}$$

which can also be written as

$$\frac{x^4\,(1-8x+24x^2-23x^3-13x^4+15x^5+12x^6)}{(1-x)\,(1-3x)^3\,(1-3x^2)\,(1-3x^3)}\,. \tag{9}$$

POLYCATS OF TYPE III

For these polycats it is clear that the path to which each reduces must have a branching hexagon at each end, and that any other branching hexagon must belong to the spine. We therefore start by enumerating snakes on m hexagons in which exactly b inner hexagons are marked as future branch hexagons.

Given a snake on m hexagons we first choose the b marked hexagons. These hexagons must be of type 0 or 2. The remaining $m-2-b$ inner hexagons can be of any type. Hence for given b, the required number of snakes is

$$\binom{m-2}{b}\,2^b\,3^{m-2-b}\,.$$

For each such snake as spine, we attach headless snakes at each of the marked hexagons and two headless snakes at each end. Since the generating function for headless snakes is $x(1-3x)^{-1}$, we obtain the generating function

$$x^m\binom{m-2}{b}\,2^b\,3^{m-2-b}\left(\frac{x}{1-3x}\right)^{b+4}$$

for fixed polycats of type III with given m and b.

Summing over b we obtain

$$\frac{x^{m+4}}{(1-3x)^4}\left(\frac{2x}{1-3x}+3\right)^{m-2}.$$

Summing over m we obtain

$$\frac{x^4}{(1-3x)^4}\sum_{m\geq 2} x^m\left(\frac{3-7x}{1-3x}\right)^{m-2}$$

which reduces to

$$\frac{x^6}{(1-3x)^3}\cdot\frac{1}{1-6x+7x^2}. \tag{10}$$

We now consider the number of type III polycats with the various allowable symmetries.

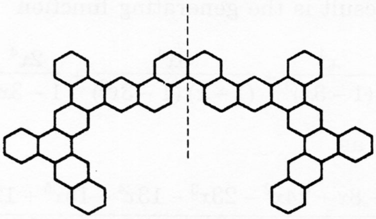

Figure 15.

If $m = 2k$ and the polycat is symmetrical about the common edge of the two centre hexagons of the spine (Figure 15), then the whole polycat is determined by the first k hexagons of the spine plus the attached paths. This collection of hexagons forms a configuration, H, which is similar to a type III polycat except that it is missing the hexagon and the two attached paths at one end. By the methods just used for the fixed type III polycats we find the generating function for configurations like H to be

$$\frac{x^3}{1-3x}\cdot\frac{1}{1-6x+7x^2}. \tag{11}$$

Since every hexagon of H is duplicated to form the full polycat, the generating function for these polycats is seen to be

$$\frac{x^6}{1-3x^2}\cdot\frac{1}{1-6x^2+7x^4}. \tag{12}$$

To enumerate polycats with this same type of symmetry and an odd number of hexagons we construct them from those with an even number of hexagons by inserting an extra cell in the middle. For each polycat with an even number of cells this can be done in exactly three ways, as illustrated in Figure 16 which shows the three polycats obtainable from the one in Figure 15.

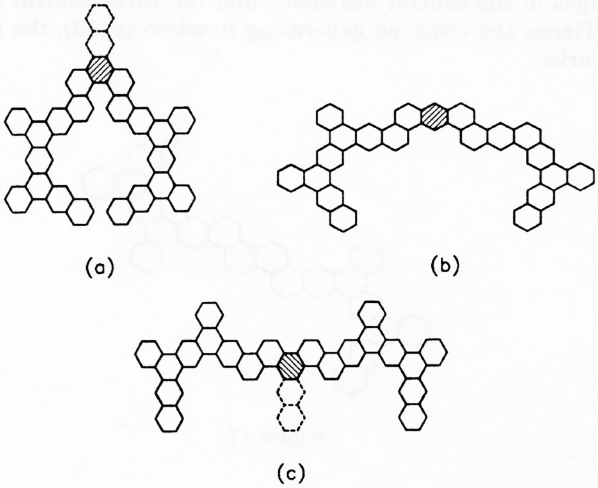

Figure 16.

If the three central cells are in a line (Figure 16b) we obtain at once the generating function

$$\frac{x^7}{1-3x^2}\cdot\frac{1}{1-6x^2+7x^4}\,. \tag{13}$$

However, in the other two cases (Figure 16a and c) it is possible to attach an extra headless snake at the central hexagon. Because of the symmetry this snake must be a straight one, for which the generating function is $(1-x)^{-1}$. Hence for these two cases together we have the generating function

$$\frac{2x^7}{(1-3x^2)(1-x)}\cdot\frac{1}{1-6x^2+7x^4}\,. \tag{14}$$

Hence for all the polycats with this kind of symmetry (which interchanges the two end of the spine) the generating function is

$$\frac{1}{(1-3x^2)(1-6x^2+7x^4)}\left[x^6+x^7+\frac{2x^7}{1-x}\right]=\frac{x^6(1+2x-x^2)}{(1-x)(1-3x^2)(1-6x^2+7x^4)}\,. \tag{15}$$

We now consider those polycats that are equivalent under a rotation through 180° which interchanges the centres of the two end hexagons of the spine. For those with $2k$ hexagons (Figure 17) the situation is almost as before, except that in constructing the polycat we attach the second half the other way around, that is, with-out reflecting it (compare Figures 15 and 17). The number of polycats obtained is the same as before, and so is the generating function, which is (12).

For those with $2k + 1$ hexagons the situation is again similar, but, as in Section 2, the restrictions of this symmetry require that the two »half-polycats« be attached at opposite edges of the central hexagons, and the three central hexagons are in a straight line. Hence the required generating function is (13); the case to which (14) refers cannot arise.

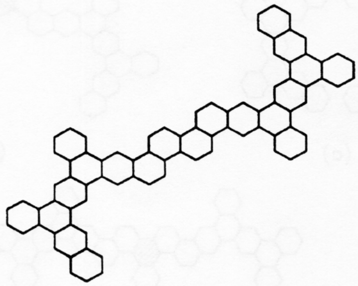

Figure 17.

Finally, we look at the remaining type of symmetry that a type III polycat can have, namely, symmetry about a line joining the centres of the end hexagons of the spine. It is easily seen that the spine itself must be straight and that headless snakes may be attached only to the end hexagons of the spine. Moreover, the two headless snakes at one end of the spine must be mirror images, and similarly for the other end. For each such pair the generating function is $x^2(1 - 3x^2)^{-1}$, while that for the spine is $x^2(1 - x)^{-1}$. Hence the required generating function is

$$\frac{x^2}{1-x}\left(\frac{x^2}{1-3x^2}\right)^2 = \frac{x^6}{(1-x)\,(1-3x^2)^2}\,. \tag{16}$$

The results will be combined, using Burnside's lemma, in the next section.

THE MAIN RESULT

In the preceding section we showed that the generating function for all fixed polycats of type III was given by Eq. (10); that those with one kind of reflectional symmetry were enumerated by the generating function (15); that those with rotational symmetry were enumerated by the sum of (12) and (13), namely

$$\frac{x^6}{1-3x^2}\cdot\frac{1}{1-6x^2+7x^4}+\frac{x^2}{1-3x^2}\cdot\frac{1}{1-6x^2+7x^4}=\frac{x^6\,(1+x)}{(1-3x^2)\,(1-6x^2+7x^4)} \tag{17}$$

and that those with the other kind of reflectional symmetry are enumerated by (16).

Some numerical values for the coefficients in these four generating functions are given in Table II below, in columns (a), (b), (c) and (d).

Adding these results and dividing by 4 we obtain the generating function for the numbers of equivalence classes of type III polycats. Expressed as a single rational function it is

$$\frac{x^6(1-11x+52x^2-91x^3-132x^4+722x^5-683x^6-660x^7+1440x^8-630x^9)}{(1-x)(1-3x)^3(1-3x^2)^2(1-6x+7x^2)(1-6x^2+7x^4)}. \qquad (18)$$

Table II also gives some numerical values for the results in sections 2 and 3, and the total numbers of polycats of all types for n from 1 to 21.

TABLE II

n	Type I	Type II	Type III (a)	(b)	(c)	(d)	Total type III	All
1	1							1
2	1							1
3	2							2
4	4	1						5
5	10	2						12
6	25	11	1	1	1	1	1	37
7	70	48	15	3	1	1	5	123
8	196	209	137	11	9	7	41	446
9	574	857	987	29	9	7	258	1689
10	1681	3425	6178	76	56	34	1586	6692
11	5002	13142	35262	188	56	34	8885	27029
12	14884	49268	188738	432	300	142	47403	111555
13	44530	180497	964326	1032	300	142	241450	466477
14	133225	649721	4760035	2221	1489	547	1191073	1974019
15	399310	2303093	22892493	5199	1489	547	5724932	8427335
16	1196836	8060762	107931947	10787	7077	2005	26987954	36245552
17	358944	27901199	501161697	24941	7077	2005	125298930	156789543
18	10764961	95661020	2299807684	50632	32768	7108	514974568	681400529
19	32291602	325243613	10458118140	116168	32768	7108	2614568546	2972103761
20	96864964	1097696306	47224011332	232656	149256	24604	11806104462	13000665732
21	29058505	3680499566	212088692364	531168	149256	24604	53022349348	56993433964

Acknowledgement. – We are grateful to the referee for his various suggestions regarding the presentation of the generating functions.

REFERENCES

1. A. T. Balaban and F. Harary, *Tetrahedron* **24** (1968) 2505–2516..
2. H. J. Fleischner, D. P. Geller, and F. Harary, *J. Indian Math. Soc.* **38** (1974) 215.
3. R. M. Foster, *Amer. Math. Monthly* **44** (1937) 50–51.
4. F. Harary in: H. Sachs (Ed.) *Beitrage zur Graphentheorie,* Teubner, Leipzig, 1968, 49–60.
5. F. Harary, *Graph Theory*, Addison-Wesley, Reading, Mass. 1969.
6. F. Harary and E. M. Palmer, *Graphical Enumeration*, Academic Press, New York, 1973.
7. F. Harary and R. C. Read, *Proc. Edinburgh. Math. Soc.* **17** (1970) 1–13.
8. F. Harary and A. J. Schwenk, *Mathematika* **18** (1971) 138–140.
9. F. Harary and A. J. Schwenk, *Discrete Math.* **6** (1973) 359–365.

SAŽETAK

Prebrojavanje poliheksa gusjeničnog oblika

Frank Harary i Ronald C. Read

Razmatrani su poliheksi nalik na stabla kod kojih se uzastopnim uklanjanjem krajnjih šesterokuta dobiva staza ili oni potpuno izčezavaju. Izvedena je generirajuća funkcija za prebrojavanje izomorfnih klasa ovih naročitih poliheksa do refleksije i rotacije.