Enumeration of tree-like octagonal systems

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Tree-like octagonal systems (O) are catacondensed systems of octagons, which represent a class of polycyclic conjugated hydrocarbons. Their numbers of isomers are determined and expressed in terms of generating functions.

1. Introduction

In a pioneering work from 1970, Harary and Read [9] demonstrated an excellent application of modern methods in discrete mathematics to an enumeration of chemical isomers. The resulting "Harary–Read numbers", a term coined by Knop et al. [11], count the nonisomorphic tree-like hexagonal systems or catafusenes [1]. More than twenty years later a new theoretical contribution to the Harary–Read numbers was published [2,4]: a complete classification into symmetry groups. Harary et al. [7] have extended the scope of the original work [9] to arbitrary polygons, but they have actually not provided a natural extension of the Harary–Read numbers. That would be an enumeration of tree-like polygonal systems with polygons other than hexagons. Recently we have solved this problem for heptagons and arrived at the following generating function:

$$\begin{aligned}&\frac{1}{54x^2}\Big[5+12x-27x^2+16x^3+3x^4+\frac{1}{4}\big(1-8x+4x^2\big)^{3/2}\\&\qquad-\frac{3}{4}\big(7+12x+2x^2\big)\big(1-8x^2+4x^4\big)^{1/2}\Big]\\&\quad=x+x^2+2x^3+7x^4+26x^5+126x^6+640x^7+3559x^8+\cdots. \qquad (1)\end{aligned}$$

The same problem for octagons, which is the subject of the present work, turns out to be considerably more complicated. It introduces a "new dimension" through the possibility of attaching four branches to one polygon. The problem was solved completely, but an explicit form of the generating function as in (1) was abandoned due to the very complicated form of the solution to a cubic equation.

It seems to be of interest in mathematical chemistry that the present problem with the "new dimension" included could be solved successfully, especially in continuation of other publications in this journal [2,4]. However, it is admitted that a direct connection to organic chemistry through the pertinent chemical graphs is weak, e.g., because of the antiaromatic nature of conjugated eight-membered rings. Therefore the following exposition is kept as brief as possible, especially where relevant references to previous applications of parts of the method could be cited.

2. Definitions and statement of the problem

The polygonal systems under consideration are referred to as "tree-like" because their dualists [1,12] are trees in the graph-theoretical sense, or strictly speaking angle-restricted trees. The systems are catacondensed [1] in the sense that no internal vertices are present.

The goal is to determine the number I_r of nonisomorphic free (unrooted) tree-like octagonal systems as a function of r, the number of octagons. In order to reach this goal, different kinds of rooted tree-like octagonal systems had to be enumerated. The methods which were employed, are basically the same as in Harary and Read [9], but with some significant modifications [3].

For the sake of brevity, the tree-like octagonal systems are in the following identified by the symbol O.

3. Edge-rooted systems

The edge-rooted O systems are counted by

$$U(x) = U^*(x) + U^{**}(x) + U^{***}(x) + x, \tag{2}$$

where the terms on the right-hand side pertain to systems with one, two or three branches attached to the octagon with the root edge, respectively, and finally this octagon alone. There are five edges available for attachments, six ways to attach two branches, and one way to attach three branches. Hence

$$U^*(x) = 5xU(x), \qquad U^{**}(x) = 6xU^2(x), \qquad U^{***}(x) = xU^3(x), \tag{3}$$

$$U(x) = x\left[1 + 5U(x) + 6U^2(x) + U^3(x)\right] = x + 5x^2 + 31x^3 + 216x^4 + 1617x^5 + 12705x^6 + 103358x^7 + 863161x^8 + \cdots . \tag{4}$$

Here $U(x)$ is not given explicitly, but any number of the coefficients of its expansion can nevertheless be determined recursively [5,14]. The systems under consideration correspond to "rooted unsymmetrical systems" in the terminology employed previously [3]. Hence, for instance, for two octagons the five systems correspond to the five possible sites of attachment to an octagon with a root edge, and no symmetry considerations are appropriate.

Mirror symmetry is possible with respect to the plane perpendicular to the root edge and bisecting this edge. This symmetry is taken into account by the generating function $V(x)$; it counts the mirror-symmetrical edge-rooted O systems; specifically,

$$V(x) = x\left[1 + U\left(x^2\right)\right]\left[1 + V(x)\right] + xU\left(x^2\right), \tag{5}$$

$$\begin{aligned} V(x) &= \left[x + 2xU\left(x^2\right)\right]\left[1 - x - xU\left(x^2\right)\right]^{-1} \\ &= x + x^2 + 3x^3 + 4x^4 + 15x^5 + 23x^6 + 94x^7 + 155x^8 + \cdots . \end{aligned} \tag{6}$$

4. Polygon-rooted systems

The enumeration of catafusenes rooted at a polygon core is well understood [16,17]. In the present case the core is an octagon, and the appendages are not catafusenes, but O systems. Nevertheless, one of the results in the previous work [17] is immediately applicable with a small modification in order to include the root octagon itself. The following generating function applies to the polygon-rooted O systems:

$$\begin{aligned} P(x) = x\Bigg[&1 + \frac{1}{2}U(x) + \frac{5}{4}U^2(x) + U^3(x) + \frac{1}{8}U^4(x) \\ &+ \frac{1}{2}V(x) + \frac{1}{4}V^2(x) + \frac{3}{2}U\left(x^2\right) + \frac{3}{8}U^2\left(x^2\right) \\ &+ V(x)U\left(x^2\right) + \frac{1}{4}V^2(x)U\left(x^2\right) + \frac{1}{4}U\left(x^4\right)\Bigg]. \end{aligned} \tag{7}$$

5. Systems rooted at a polygon pair

The next task is to enumerate the O systems rooted at a pair of adjacent octagons. This is most easily done by interpreting each of these systems as a pair of edge-rooted O systems where the two root edges coalesce [3,5,9,14]. Then the following generating function for the O systems rooted at a polygon pair emerges:

$$Q(x) = \frac{1}{4}\left[U^2(x) + V^2(x)\right] + \frac{1}{2}U\left(x^2\right). \tag{8}$$

6. Free systems

The passing from rooted to unrooted (free) systems represents a nontrivial enumeration problem. In this connection, the following passage from Read [14] is instructive: “The early researchers in this field (Cayley, Blair and Henze, and even Pólya) had a great difficulty with this problem, … . More recent developments have provided a powerful tool by which the enumeration of unrooted trees can be performed with comparative ease.” This powerful tool [6,8,13] has been applied with success at several occasions in chemical contexts [3,5,9,10,14,15]. In the present case, $P(x) - Q(x)$

counts all the free O systems exactly once, except: (i) those of D_{2h} symmetry; (ii) C_{2h}; (iii) the subset belonging to C_{2v} where the systems are in a one-to-one correspondence with the C_{2h} systems as *cis/trans* isomers. Let $D(x)$ and $C(x)$ refer to the generating functions for the pertinent D_{2h} and C_{2h} systems, respectively. Then

$$I(x) = P(x) - Q(x) + D(x) + 2C(x), \tag{9}$$

$$D(x) = V(x^2), \qquad 2C(x) = U(x^2) - D(x). \tag{10}$$

On inserting into (9) from (7), (8) and (10) one obtains a rather awkward expression, but it can be simplified by elementary manipulations using (4) and (5). The final form which was arrived at, reads:

$$\begin{aligned} I(x) = \sum_{r=1}^{\infty} I_r x^r &= \frac{1}{8}\Big[2x + (2-7x)U(x) - (1+7x)U^2(x) + 2(2-x)V(x) \\ &\quad + 4(1+x)U\big(x^2\big) + 3xU^2\big(x^2\big) + 2xU\big(x^4\big)\Big] \\ &= x + x^2 + 3x^3 + 11x^4 + 56x^5 + 341x^6 + 2351x^7 + 17329x^8 + \cdots . \end{aligned} \tag{11}$$

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