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# ENUMERATION OF UNBRANCHED CATACONDENSED SYSTEMS OF CONGRUENT POLYGONS

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## Introduction

In a classical work, Balaban and Harary [1] published the algebraic formulas for the isomer numbers of unbranched catafusenes, a class of chemical graphs. The systems in question represent certain polycyclic conjugated hydrocarbons with exclusively six-membered rings. They consist of congruent regular hexagons and are catacondensed in the sense that there is no vertex shared by three hexagons in such a system. The enumeration of unbranched catafusenes has been revisited or reviewed many times [2-10]. Corresponding systems with other polygons than hexagons are also of interest in chemistry, and especially those with pentagons or five-membered rings. Algebraic formulas for the isomer numbers of unbranched catapolypentagons, which consist of pentagons exclusively, are also known [10-13].

The $P_r$ numbers of nonisomorphic unbranched catapolypentagons and $H_r$ numbers of unbranched catafusenes are given by

$$P_r = \frac{1}{4}\binom{2}{r} + 2^{r-4} + 2^{\lfloor r/2 \rfloor - 2}, \qquad r > 1, \tag{1}$$

and

$$H_r = \frac{1}{4}\{1 + 3^{r-2} + [3-(-1)^r]3^{\lfloor r/2\rfloor-1}\}, \quad r > 1, \qquad (2)$$

respectively, as expressed in a most compact way. Here and throughout in the following, r is used to denote the number of polygons (or rings). In addition to the works cited above [2-12], Balaban [14] has given an equivalent expression to (1) for even-numbered r. His formula emerged from an algorithmic treatment of a rather general class of systems, viz. unbranched catacondensed systems consisting of polygons with arbitrary sizes. However, he did not aim at the derivation of explicit formulas in more general cases. Another algorithm for the numbers of unbranched catapolypentagons is available [15].

In the present work, we have achieved the general formula for the numbers of nonisomorphic unbranched catapoly-q-gons, a class whose members consist exclusively of q-gons (or q-membered rings). Equations (1) and (2) are the special cases for q = 5 and q = 6, respectively.

## 1. The systems

An unbranched catapoly-q-gon is a simply connected system of r q-gons (where q is fixed) which (for r > 1) possesses exactly two terminal q-gons attached to one neighbouring q-gon each, and all the other q-gons (for r > 2) possess exactly two neighbours each. The systems are simply connected in the sense that they do not have any holes like coronoids [16,17].

When a catapoly-q-gon is drawn in a plane and only congruent regular q-gons are applied, it may happen that a part of the system overlaps itself. It should be emphasized that such "helicenic" systems are included among the classes considered here. Among polyhexes (which consist of hexagons exclusively), the helicenic systems are well known [8,9,18]. The helicenic catafusenes in particular, have been referred to as catahelicenes, and among the unbranched catahelicenes one finds the familiar normal helicenes (hexahelicene, heptahelicene, etc.), of which many of the chemical counterparts have been synthesized. These compounds, as well as others which represent helicenic systems, are known to be distorted from planarity in a "helical" fashion. Accordingly, the helicenic systems are also referred to as geometrically nonplanar, but they are planar in the graph-theoretical sense, i.e. they correspond to planar graphs.

As an alternative to the above descriptions, the unbranched catapoly-q-gons may be defined precisely in terms of the way they may be generated: For any q, there exists a unique catapoly-q-gon with $r = 1$ (the degenerate system of one q-gon alone) and likewise a unique system with $r = 2$. All unbranched catapoly-q-gons with a given $r > 2$ are generated by attaching a q-gon to one of the terminal q-gons in all the nonisomorphic systems of the considered category with r-1 q-gons in all possible ways (but one at a time). The added q-gon should be attached to a "free" edge of the pertinent terminal q-gon. Here a free edge is defined as an edge between two vertices which each possess the degree two.

## 2. Symmetry

The degenerate catapoly-q-gon ($r = 1$), when represented by a regular q-gon, belongs to the symmetry group $D_{qh}$. With regard to the nondegenerate systems ($r > 1$), all the unbranched catapoly-q-gons (for arbitrary q) are distributed among the four symmetry groups $D_{2h}$, $C_{2h}$, $C_{2v}$ and $C_s$. These considerations are based on systems drawn in a plane using congruent regular q-gons. Accordingly, the geometrical nonplanarity is not taken into account. Thus, for instance, all the normal helicenes are attributed to the symmetry $C_{2v}$.

## 3. Derivation of formulas

In the present derivation of the numbers of nonisomorphic unbranched catapoly-q-gons, the symmetry is exploited. Let these total numbers of isomers be denoted by $I_r$, which is a function of r and q. We write

$$I_r = D_r + C_r + M_r + A_r, \tag{3}$$

where the symbols on the right-hand side designate the appropriate numbers for systems of symmetries $D_{2h}$, $C_{2h}$, $C_{2v}$ and $C_s$, respectively (from the left). Here and throughout in the following it is assumed $r > 1$. A total which does not take symmetry into account, viz.

$$J_r = (q-3)^{r-2} \tag{4}$$

counts the $D_{2h}$ systems once, the $C_{2h}$ and $C_{2v}$ systems twice each and the $C_s$ systems four times:

$$J_r = D_r + 2C_r + 2M_r + 4A_r. \tag{5}$$

On eliminating $A_r$ from (3) and (5) and inserting from (4) one obtains

$$I_r = \frac{1}{4}[(q-3)^{r-2} + 3D_r + 2C_r + 2M_r]. \tag{6}$$

In consequence, it is needed to derive the numbers of the symmetrical systems.

For every r, $D_r = 1$ when q is even. On the other hand, $D_2 = 1$, $D_r = 0$ $(r > 2)$ when q is odd. In summary,

$$D_r = \frac{1}{2}[1+(-1)^q] + \frac{1}{2}[1-(-1)^q]\binom{2}{r}. \tag{7}$$

It is recalled that $\binom{a}{b} = 0$ when $b > a$.

In counting the $C_{2h}$ systems, the crucial quantity, to be compared with (2), is

$$H_{\lfloor r/2 \rfloor} = (q-3)^{\lfloor r/2 \rfloor - 1}. \qquad (8)$$

In the cases when $C_r \neq 0$, $H_{\lfloor r/2 \rfloor}$ counts the $D_{2h}$ systems once and the $C_{2h}$ systems twice each. If both q and r are odd numbers, then $C_r = 0$. In general, one finds

$$\frac{1}{2}\{1 + (-1)^q + \frac{1}{2}[1-(-1)^q][1 + (-1)^r]\}H_{\lfloor r/2 \rfloor} = D_r + 2C_r. \qquad (9)$$

Herefrom $C_r$ is available (as a function of q and r) by means of (7) and (8). Fig.1 shows some simple examples of unbranched catapoly-q-gons of $C_{2h}$ symmetry.

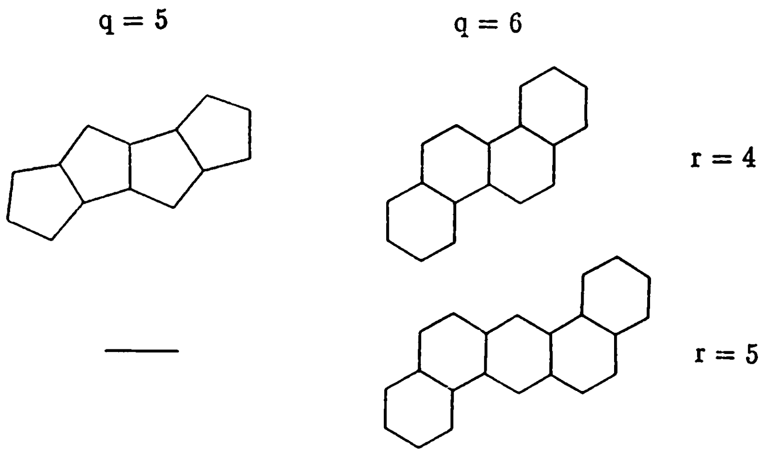


Fig. 1

With regard to $C_{2v}$ symmetry, one has firstly the $C_r$ systems which correspond to those of the $C_{2h}$ symmetry as cis/trans isomers. Secondly, one has the remaining systems, which only occur for odd r; such a system consists of two branches attached to

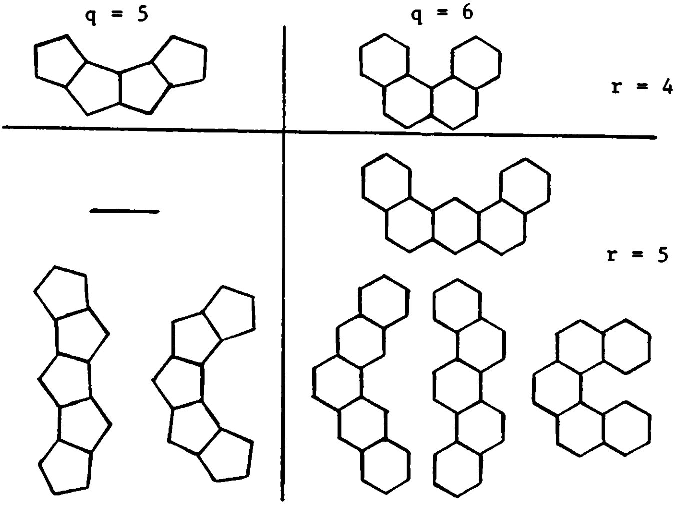


Fig. 2

a central polygon. Some simple examples are furnished by Fig. 2. Let the numbers of the latter category be identified by the symbol $K_r$ so that

$$M_r = C_r + K_r. \tag{10}$$

It is found that

$$K_r = \frac{1}{2}[1 - (-1)^r] \lfloor (q-3)/2 \rfloor H_{\lfloor r/2 \rfloor}. \tag{11}$$

Here the factor $\lfloor (q-3)/2 \rfloor$ indicates the number of nonequivalent sites for attaching the two branches to the central q-gon. Furthemore, $H_{\lfloor r/2 \rfloor}$ is found in (8).

On combining the formulas (6)-(11), one obtains the final result for the numbers of nonisomorphic unbranched catapoly-q-gons in the compact form:

$$I_r = \frac{1}{4}(q-3)^{r-2} + \frac{1}{8}[1 + (-1)^q] + \frac{1}{8}[1 - (-1)^q]\binom{2}{r} + \\ + \frac{1}{4}\{1 + (-1)^q + \frac{1}{2}[1-(-1)^q][1 + (-1)^r] + \\ + [1-(-1)^r]\lfloor (q-3)/2 \rfloor\}(q-3)^{\lfloor r/2 \rfloor - 1}, \quad r > 1. \qquad (12)$$

## 4. Numerical results

Numerical results of $I_r$ for $5 \leq q \leq 10$ are listed in Table. They are consistent with the previous data from literature [1-15] as far as they are known, and a substantial extension of

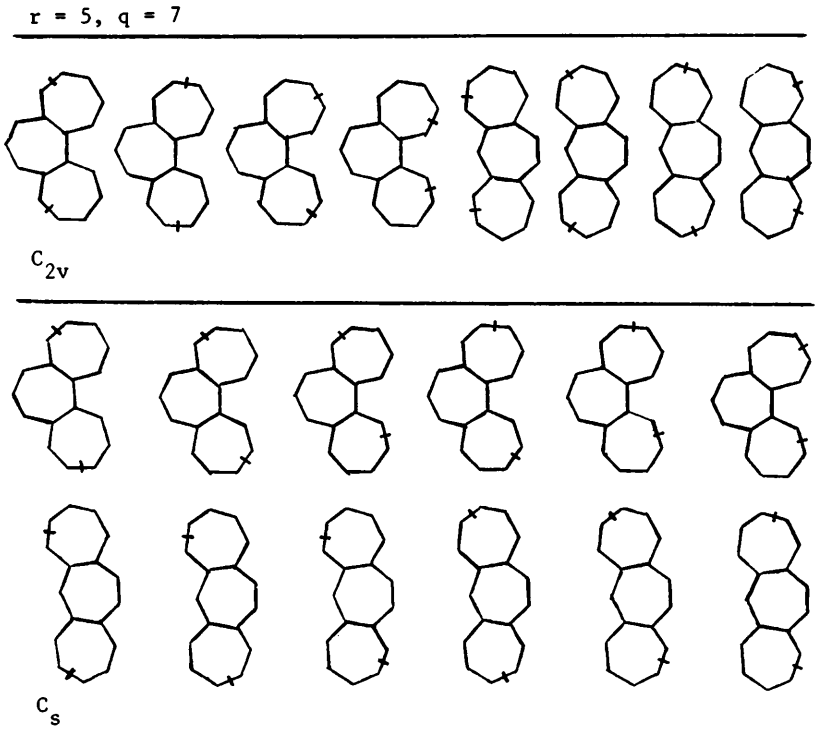


Fig.3. The 20 nonisomorphis unbranched catapentaheptagons

T a b l e

Number of unbranched catapoly-q-gons

| r | q | | |
|---|---|---|---|
| | 5 | 6 | 7 |
| 2 | 1[a] | 1[d] | 1 |
| 3 | 1[a] | 2[d] | 2 |
| 4 | 2[b] | 4[d] | 6[b] |
| 5 | 3[a] | 10[d] | 20 |
| 6 | 6[b] | 25[d] | 72[b] |
| 7 | 10[a] | 70[d] | 272 |
| 8 | 20[b] | 196[d] | 1056[b] |
| 9 | 36[c] | 574[d] | 4160 |
| 10 | 72[c] | 1681[d] | 16512 |

| r | q | | |
|---|---|---|---|
| | 8 | 9 | 10 |
| 2 | 1 | 1 | 1 |
| 3 | 3 | 3 | 4 |
| 4 | 9 | 12 | 16 |
| 5 | 39 | 63 | 100 |
| 6 | 169 | 342 | 625 |
| 7 | 819 | 1998 | 4300 |
| 8 | 3969 | 11772 | 29584 |
| 9 | 19719 | 70308 | 206572 |
| 10 | 97969 | 420552 | 1442401 |

[a] Elk(1987) [15].

[b] Balaban (1970) [14].

[c] Dobrynin (1991) [12] .

[d] Balaban and Harary (1968) [ 1 ] .

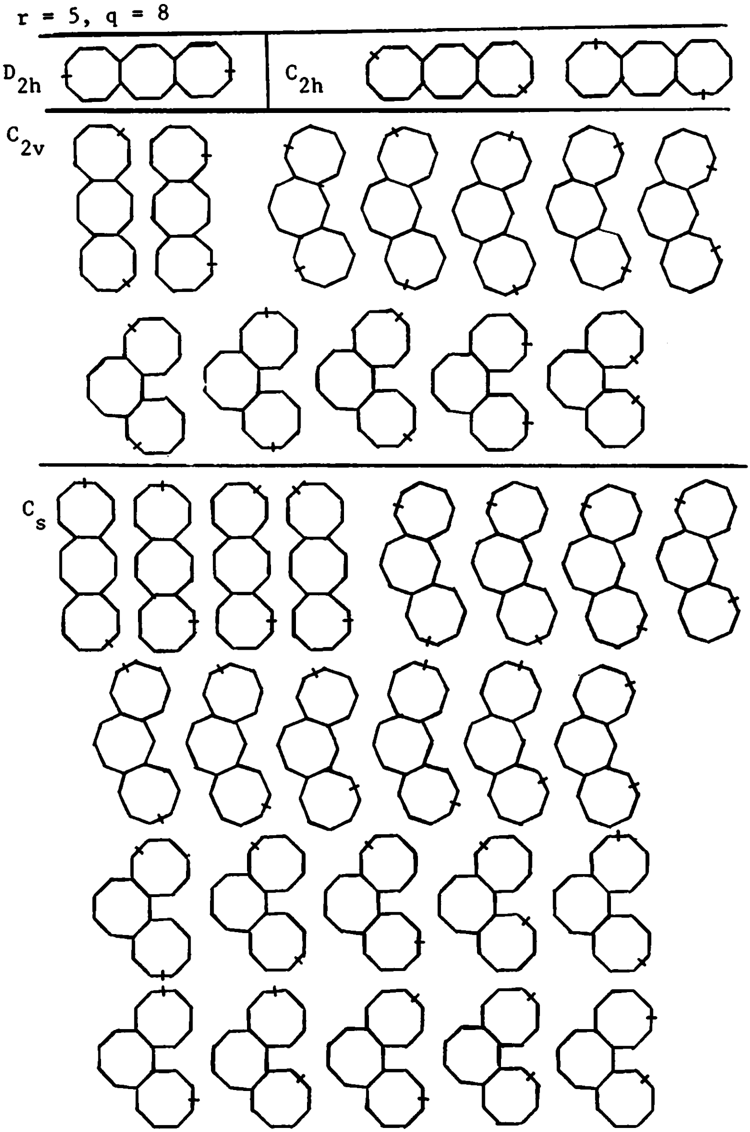


Fig.4. The 39 nonisomorphic unbranched catapentaoctagons

these data is presented here. The data of Table can of course be extended further by equation (12).

For $q = 4$ in particular, one has obviously $I_r = 1$ for all r. This (trivial) result is also consistent with (12). Furthermore, for $q = 3$ one has $I_2 = 1$, $I_r = 0$ when $r > 2$; in other words $I_r = \binom{2}{r}$. It is interesting that (12) also is compatible with this answer, provided that $0^0$ is identified with 1.

## 5. Illustrations

It is supposed to be instructive to illustrate some of the numbers of Table by depictions of the actual forms.The unbranched catapenta-q-gons (r=5) with q=7 and q=8 were selected for this purpose. The 20 unbranched catapentaheptagons (q=7) are specified in Fig.3; these systems are distributed into the symmetry groups according to $8C_{2v} + 12C_s$. Similarly, the 39 unbranched catapentaoctagons (q=8), distributed according to $1D_{2h} + 2C_{2h} + 12C_{2v} + 24C_s$, are found in Fig.4. For the sake of convenience, the terminal polygons are indicated by heavy strokes in both of these figures.

## L i t e r a t u r e

1. BALABAN A.T., HARARY F. Chemical graphs.V. Enumeration and proposed nomenclature of benzenoid cata-condensed polycy - clic aromatic hydrocarbons //Tetrahedron. - 1968. - Vol. 24. - P. 2505-2516.

2. BALABAN A.T. Chemical graphs. VII. Proposed nomencla - ture of branched cata-condensed benzenoid polycyclic hydrocarbons //Tetrahedron. - 1969. - Vol.25. - P. 2949-2956.

3. BALABAN A.T. Enumeration of catafusenes, diamondoid hydrocarbons, and staggered alkane C-rotamers //Commun. Math. Chem. - 1976. - N2. -P. 51-61.

4. BALABAN A.T. Chemical graphs. XXVII. Enumeration and codification of staggered conformations of alkanes //Rev. Roumaine Chim. - 1976. - Vol. 21. - P. 1049-1071.

5. BALABAN A.T., BRUNVOLL J., CYVIN B.N., CYVIN S.J. Enumeration of branched catacondensed benzenoid hydrocarbons and their numbers of Kekulé structures //Tetrahedron. - 1988. - Vol. 44. - P. 221-228.

6. ДОБРЫНИН А.А. Эффективный алгоритм генерации графов неразветвленных гексагональных систем //Математические вопросы химической информатики. - Новосибирск, 1989. - Вып. 130: Вычислительные системы. - С. 3-38.

7. BRUNVOLL J., TOŠIĆ R., KOVAČEVIĆ M., BALABAN A.T., GUTMAN I., CYVIN S.J. Enumeration of catacondensed benzenoid hydrocarbons and their numbers of Kekulé structures //Rev.Roumaine Chim. - 1990. - Vol. 35. - P. 85-96.

8. ДОБРЫНИН А.А. Распределения значений дистанции графов неразветвленных гексагональных систем// Математические исследования в химической информатике. - Новосибирск, 1990. - Вып. 136: Вычислительные системы. - С. 61-140.

9. CYVIN B.N., BRUNVOLL J., CYVIN S.J. Enumeration of benzenoid systems and other polyhexes //Top. Current Chem. - 1992. - Vol. 162. - P. 65-180.

10. DOBRYNIN A.A. Generation of graphs of unbranched pentahexagonal catacondensed systems //Croat. Chem. Acta. - 1993. - Vol. 66. -P. 91-100.

11. ELK S.B. Enumeration of the set of saturated compounds that, in theory, could be formed by the linear fusion of regular pentagonal modules, including the logical extrapolation to "helicanes" //J.Mol.Struct. (Theochem). - 1989. - Vol. 201. - P. 75-86.

12. ДОБРЫНИН А.А. Генерация графов неразветвленных пентагональных и пентагексагональных систем//Математические методы в химической информатике. - Новосибирск, 1991. - Вып. 140: Вычислительные системы. - С. 143-206.

13. CYVIN S.J., CYVIN B.N., BRUNVOLL J., BRENDSDAL E., ZHANG F.J., GUO X.F., TOŠIĆ R. Theory of polypentagons//J.Chem. Inf.Comput. Sci. - 1993. - Vol. 33. - P. 466-474.

14. BALABAN A.T. Chemical graphs. XI. (Aromaticity. IX). Isomerism and topology of non-branched cata-condensed polycyclic conjugated non-benzenoid hydrocarbons //Rev.Roumaine Chim. - 1970. - Vol. 15. - P. 1251-1262.

15. ELK S.B. An algorithm to identify and count coplanar isomeric molecules formed by the linear fusion of cyclopentane modules //J.Chem. Inf. Comput. Sci. - 1987. -Vol.27. - P.67-69.

16. BRUNVOLL J., CYVIN B.N., CYVIN S.J. Enumeration and classification of coronoid hydrocarbons //J.Chem.Inf. Comput. Sci. - 1987. - Vol. 27. - P. 14-21.

17. ДОБРЫНИН А.А. Перечисление некоторых подклассов графов неразветвленных гексагональных систем // Математические исследования в химической информатике. - Новосибирск, 1990. - Вып. 136: Вычислительные системы. - С. 16-34.

18. CYVIN S.J., ZHANG F.J., CYVIN B.N., GUO X.F. Theory of helicenic hydrocarbons. Part 1. Invariants and symmetry // Struct. Chem. - 1993. - Vol. 4. - P. 149-160.

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