Theory of Polypentagons

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Polypentagons are systems consisting of pentagons exclusively. Some of their topological properties are studied, including the relations between certain invariants. Complete mathematical solutions are reported for the numbers of polypentagons within certain classes: catacondensed systems (without internal vertices) and systems with one internal vertex and with two connected internal vertices. A complete account on proper polypentagons is given. These systems can, by definition, be embedded on a regular dodecahedron. It is found that exactly 39 such systems exist. Their chemical formulas (C_nH_s), forms, and symmetries are specified.

INTRODUCTION

Very much work has been done on the theory of polyhex systems,[1] which consist of exclusively hexagons and correspond to polycyclic conjugated hydrocarbons with six-membered (benzenoid) rings. In comparison with this large volume of literature the available works on chemical graphs with polygons other than hexagons are very sparse. Recently the systems with one pentagon each and otherwise hexagons have been treated to some extent.[2,3] On the other extreme, one has the chemical graphs consisting of exclusively pentagons. They are mentioned by Dias in one of the works cited above,[2] but treated very briefly, in continuation of a previous work by the same author.[4] These systems, referred to as polypentagons, are treated in a more complete way in the present work.

BASIC DEFINITIONS

A *polypentagon* is a connected system consisting of pentagons, where any two pentagons either share exactly one edge, or they are disjointed. In this way any vertex has either the degree 2 or the degree 3.

The polypentagon systems (polypentagons) represent chemical graphs of conjugated hydrocarbons; i.e. vertices of the hydrogen-depleted graph symbolize carbons. The systems are similar to the polyhexes. However, we do not have a geometrically planar lattice of regular polygons at our disposal in the case of polypentagons, in contrast to the situation for polyhexes. Instead, eleven (out of the twelve) faces of the regular (pentagonal) dodecahedron may be employed to some extent in connection with the definition of polypentagons, as explained below. But first it should be mentioned that the present theory is restricted to simply connected polypentagons, in other words systems without holes. For the sake of brevity it is tacitly assumed throughout this paper that the term "polypentagon" refers to a simply connected polypentagon.

Another approach to the definition of a polypentagon, in analogy with a simply connected polyhex, makes use of the generating (or building-up) of these systems: All polypentagons with $p + 1$ pentagons are generated (or built up) by additions of pentagons, one at a time, to all the polypentagons with p pentagons each.

In this building-up process the pentagons should be added to the boundary of the system, usually called the perimeter. There are four types of these additions, as illustrated in Figure 1: (i) one-, (ii) two-, (iii) three-, and (iv) four-contact additions.

Some additional concepts are defined in connection with the four types of additions (Figure 1). Firstly, the formations of the perimeter which come in contact with the added pentagon in each of the four cases and are paths of one to four edges are referred to as (i) *free edge*, (ii) *fissure*, (iii) *bay*, and (iv) *fjord*, respectively.[5] Secondly, the eight *modes of pentagons* are defined, out of which there are four addition modes (of pentagons).[6] The addition modes of pentagons are identified by the symbols L_1, P_2, L_3, and L_4, which pertain to the added pentagons in cases i, ii, iii, and iv, respectively. For the sake of completeness we must also define the remaining four modes (see Figure 1): L_0 is unique for one single pentagon; a pentagon is said to be in the mode A_2 when it shares one edge with each of two disjoint pentagons; a pentagon in the mode P_3 shares two incident and one isolated edge with three neighboring pentagons; finally, an L_5-mode pentagon is completely surrounded by five other pentagons.

In accord with the above descriptions, all polypentagons are successively generated by starting with one pentagon and executing the appropriate additions. Assume that all the pentagons are embedded on the surface of a regular dodecahedron. Then the additions of pentagons must inevitably, sooner or later, lead to overlapping edges. Polypentagons with overlapping edges in this sense are referred to as *helicenic polypentagons* (in analogy with helicenic polyhexes). Polypentagons which are not helicenic shall presently be referred to as *proper polypentagons*.

A *pentagonal lattice* is defined as the system obtained from the dodecahedron graph (which is planar in the graph-theoretical sense) by removing one pentagon (without removing any vertices or edges). Then a proper polypentagon may be defined in terms of a cycle on the pentagonal lattice and its interior. By definition, the interior is the part which does not contain the "missing" pentagon. A proper polypentagon can obviously not have more than eleven pentagons. In precise terms, one has for the number of pentagons (p) of a proper

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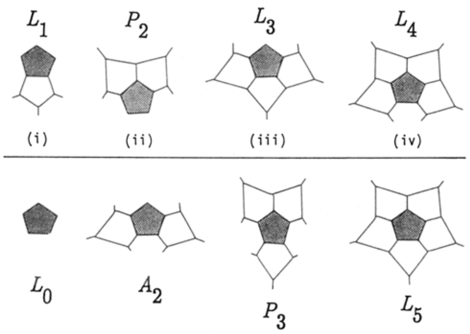


Figure 1. (Top row) The four types of addition in the building-up process of polypentagons. The added pentagons are grey. (Both rows) The eight modes of pentagons. The pendent lines symbolize pentagons which may, but need not exist.

polypentagon

$$1 \leq p \leq 11 \tag{1}$$

In the following, when it is referred to a symmetry group of a polypentagon, the geometrical nonplanarity of the pentagonal lattice is not taken into account. In other words, the symmetries pertain to geometrically planar systems. Then, altogether, a polypentagon may belong to the symmetry D_{5h}, D_{3h}, C_{3h}, D_{2h}, C_{2h}, C_{2v}, or C_s.

INVARIANTS

Definitions. A set of invariants for polypentagons is listed in the following:

p = no. of pentagons

n = no. of vertices

m = no. of edges

n_i = no. of internal vertices

n_e = no. of external vertices

s = no. of vertices of degree two ($\equiv n_2$)

t = no. of external vertices of degree three

n_3 = no. of vertices of degree three

m_i = no. of internal edges

An internal vertex is by definition shared by three pentagons. Polypentagons without internal vertices ($n_i = 0$) are called *catacondensed*, while polypentagons with at least one internal vertex ($n_i > 0$) are called *pericondensed*. External vertices are the vertices which are not internal; they are found on the boundary of the polypentagon, usually called the perimeter. Their number, viz., n_e, is also the number of the edges along the perimeter and referred to as the perimeter length. All vertices of degree 2 are situated on the perimeter. An internal edge is an edge which does not belong to the perimeter.

Relations. Any two of the invariants listed above are independent with the exception of p and n_3. A pair of independent invariants can be used to express any of the others as a linear combination. The number of pentagons and number of internal vertices, in the present case (p, n_i), are currently used for this purpose. Another important pair of independent invariants is (n, s), since their values indicate the number of carbon atoms and hydrogens, respectively, in the chemical formula (C_nH_s) which corresponds to a polypentagon. The relations for all the invariants under consideration were rederived as functions of (p, n_i) and (n, s) in an elementary way. They are consistent with previously published relations of this kind.[7] For the sake of convenience they are collected in a comprehensive way in Table I.

Table I. Invariants of Polypentagons as Functions of (p,n_i) and (n,s)

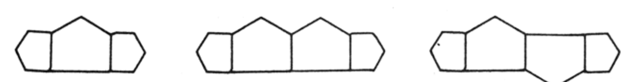
invariant	function of (p,n_i)	function of (n,s)
p	p	$p = {}^1/_2(n - s) + 1$
n	$3p - n_i + 2$	n
m	$4p - n_i + 1$	${}^1/_2(3n - s)$
n_i	n_i	${}^1/_2(n - 3s) + 5$
n_e	$3p - 2n_i + 2$	${}^1/_2(n + 3s) - 5$
$s \equiv n_2$	$p - n_i + 4$	s
t	$2p - n_i - 2$	${}^1/_2(n + s) - 5$
n_3	$2p - 2$	$n - s$
m_i	$p + n_i - 1$	$n - 2s + 5$

ENUMERATION OF CATACONDENSED POLYPENTAGONS

Previous Work. Explicit formulas for the numbers of isomers of catacondensed polypentagons were derived, probably for the first time, by Balaban[8] in a work on unbranched catacondensed polygonal systems with arbitrary polygon sizes. In the case of pentagons, he assumed p (our notation) to be even, since he only considered Kekuléan systems. In a more recent paper, Elk[9] described the catacondensed polypentagons in detail without any restriction on the parity of p.[10] In a subsequent paper, Elk[11] derived an explicit formula for the numbers of isomers, using a largely different approach from the one of Balaban.[8] Our derivation in the subsequent sections follows closely the approach of Balaban.[8] It is also similar to an enumeration of caterpillar trees,[12] and still more to a recent enumeration of fibonacenes.[13]

Basic Properties and Coding. All the catacondensed polypentagons are unbranched systems. The unique such systems for p = 1, 2, and 3 have the symmetries D_{5h}, D_{2h}, and C_{2v}, respectively. For $p \geq 3$ the possible symmetries are C_{2h}, C_{2v}, and C_s.

A catacondensed polypentagon may be represented by a row of pentagons, where some of the nonterminal pentagons point upward (+) or downward (−) as shown in the following.



o + o (m) o + + o (m) o + − o (c)

By convention, the second pentagon from the left is here always taken to point upward (+). In the adopted coding (see the above diagram) the terminal pentagons are indicated by o. The parenthesized symbols (m) and (c) indicate the mirror-symmetry (C_{2v}) and centrosymmetry (C_{2h}), respectively. An unsymmetrical (C_s) catacondensed polypentagon, indicated by (u), occurs for the first time at p = 5 and is found among the combinatorial possibilities specified below in terms of the adopted coding.

o + + + o(m) {o + + − o(u)
o + − + o(m) o + − − o(u)}

Here the two (u) systems are isomorphic. It is a general feature that the unsymmetrical systems are counted twice by the 2^{p-3} ($p > 2$) combinations, while the symmetrical systems, viz., (m) and (c), are counted once each. Another example (for p = 6) is shown as follows, where the two pairs of isomorphic systems are embraced in curled parentheses.

o + + + + o(m) {o + + + − o(u)
o + − − + o(m) o + − − − o(u)}

o + + − − o(c) {o + + − + o(u)
o + − + − o(c) o + − + + o(u)}

Table II. Numbers of Catacondensed Polypentagons

p	D_{5h}	D_{2h}	$C_{2h}(c)$	$C_{2v}(m)$	$C_s(u)$	total C
1	1	0	0	0	0	1
2	0	1	0	0	0	1
3	0	0	0	1	0	1
4	0	0	1	1	0	2
5	0	0	0	2	1	3
6	0	0	2	2	2	6
7	0	0	0	4	6	10
8	0	0	4	4	12	20
9	0	0	0	8	28	36
10	0	0	8	8	56	72
11	0	0	0	16	120	136
12	0	0	16	16	240	272
13	0	0	0	32	496	528
14	0	0	32	32	992	1056
15	0	0	0	64	2016	2080
16	0	0	64	64	4032	4160
17	0	0	0	128	8128	8256
18	0	0	128	128	16256	16512
19	0	0	0	256	32640	32896
20	0	0	256	256	65280	65792

Explicit Formulas. c, m, and u are used to denote the numbers of nonisomorphic catacondensed polypentagons belonging to the symmetry groups C_{2h}, C_{2v}, and C_s, respectively. It should be clear that the symbols are used as functions of p. Furthermore, C denotes the total number. Then (for a given p)

$$C = c + m + u \tag{2}$$

$$2^{p-3} = c + m + 2u; \quad p = 3, 4, 5, 6, \ldots \tag{3}$$

The number of centrosymmetrical systems are found to be

$$c = 0; \quad p = 3, 5, 7, \ldots \tag{4a}$$

$$c = 2^{(p-4)/2}; \quad p = 4, 6, 8, \ldots \tag{4b}$$

Similarly, for the mirror-symmetrical systems

$$m = 2^{(p-3)/2}; \quad p = 3, 5, 7, \ldots \tag{5a}$$

$$m = 2^{(p-4)/2}; \quad p = 4, 6, 8, \ldots \tag{5b}$$

or in compressed form

$$m = 2^{\lfloor (p-3)/2 \rfloor}; \quad p = 3, 4, 5, 6, \ldots \tag{5}$$

Equations 3–5, when solved for u, yield

$$u = 2^{p-4} - 2^{\lfloor (p-4)/2 \rfloor}; \quad p = 3, 4, 5, 6, \ldots \tag{6}$$

Finally, for the total number of catacondensed polypentagons, one obtains from eq 2

$$C = 2^{p-4} + 2^{\lfloor (p-4)/2 \rfloor}; \quad p = 3, 4, 5, 6, \ldots \tag{7}$$

Numerical values are displayed in Table II. It is noted that helicenic polypentagons are included in these counts.

Generating Functions. Many enumeration problems can be solved in an elegant way in terms of generating functions. On the basis of the well-known expansion

$$(1 - 2x)^{-1} = 1 + 2x + 4x^2 + 8x^3 + \ldots + 2^i x^i + \ldots \tag{8}$$

the following generating functions were found for the numbers c, m, and u, which pertain to the different symmetries as specified above.

$$c(x) = x^4(1 - 2x^2)^{-1} \tag{9}$$

$$m(x) = x^3(1 + x)(1 - 2x^2)^{-1} \tag{10}$$

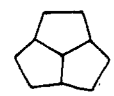
$$u(x) = x^5(1 - 2x)^{-1}(1 - 2x^2)^{-1} \tag{11}$$

Finally, for the total number of nonisomorphic catacondensed polypentagons

$$C(x) = x(1 + x) + c(x) + m(x) + u(x)$$
$$= x(1 - x)(1 - 3x^2 - x^3)(1 - 2x)^{-1}(1 - 2x^2)^{-1} \tag{12}$$

ENUMERATION OF POLYPENTAGONS WITH ONE INTERNAL VERTEX

General. The title systems consist of the core $C_{10}H_6$ with zero (accounting for the core itself), one-, two-, or three-catacondensed appendages annelated to it. Here $C_{10}H_6$ represents the unique pericondensed polypentagon with p = 3:



$C_{10}H_6$

This core has three free edges, to which the catacondensed fragments can be attached.

The numbers of nonisomorphic systems of the category under consideration are denoted by ${}^0P_p$, ${}^1P_p$, ${}^2P_p$, and ${}^3P_p$, pertaining to zero-, one-, two-, and three-attachments, respectively. Here p indicates the total number of pentagons. If a is used to denote the number of pentagons in the appendages, then

$$p = 3 + a \tag{13}$$

No Appendage. For the core alone (without appendages) one has simply

$${}^0P_3 = 1 \qquad a = 0 \tag{14}$$

This unique system (when assumed to be geometrically planar) belongs to the symmetry group D_{3h}.

One Appendage. For a = 1, viz., one pentagon attached to $C_{10}H_6$, there is a unique system of symmetry C_{2v}. For larger appendages ($a > 1$) all the systems under consideration belong to C_s. One has, from a combinatorial reasoning similar to the one of the previous section,

$${}^1P_4 = 1 \qquad a = 1 \tag{15a}$$

$${}^1P_{3+a} = 2^{a-2}; \quad a > 1 \tag{15b}$$

In compact form, for $a \geq 1$

$${}^1P_{3+a} = {}^1/_2(2^{a-1} + \lfloor 1/a \rfloor) \tag{15}$$

Two Appendages. The systems with two catacondensed fragments attached to $C_{10}H_6$ are either mirror-symmetrical (C_{2v}) or unsymmetrical (C_s). Their numbers (as functions of a) are identified by M and A, respectively. Then, for $a \geq 1$

$${}^2P_{3+a} = M + A \tag{16}$$

$$S_2(a) = M + 2A \tag{17}$$

where

$$S_2(a) = \sum_{i=1}^{a-1} 2^{i-1} 2^{a-i-1} = (a-1)2^{a-2} \qquad (18)$$

Here S represents the number of combinations without taking symmetry into account. One has

$$M = \epsilon \times 2^{(a-2)/2} \qquad (19)$$

where $\epsilon = 0$ when a is odd and $\epsilon = 1$ when a is even. Consequently,

$$A = {}^1/_2[(a-1)2^{a-2} - \epsilon \times 2^{(a-2)/2}] \qquad (20)$$

$${}^2P_{3+a} = {}^1/_2[(a-1)2^{a-2} + \epsilon \times 2^{(a-2)/2}] \quad a \geq 1 \qquad (21)$$

Three Appendages. For $a = 3$, viz., three pentagons attached to each of the three free edges of $C_{10}H_6$, one obtains a unique system of symmetry D_{3h}. Otherwise the systems with three appendages belong to either C_{3h}, C_{2v}, or C_s. Their numbers are designated R, M, and A, respectively. Then, for $a > 3$,

$${}^3P_{3+a} = R + M + A \qquad (22)$$

$$S_3(a) = 2R + 3M + 6A \qquad (23)$$

where

$$S_3(a) = \sum_{i=1}^{a-2} 2^{i-1} \sum_{j=1}^{a-i-1} 2^{j-1} 2^{a-i-j-1} = {}^1/_2(a-1)(a-2)2^{a-3} \qquad (24)$$

It is found

$$R = \delta \times 2^{(a-6)/3} \qquad (25)$$

where $\delta = 0$ when a is not divisible by 3, while $\delta = 1$ when a is divisible by 3. Furthermore,

$$M = 2\epsilon' \times 2^{(a-5)/2} = \epsilon' \times 2^{(a-3)/2} \qquad (26)$$

where

$$\epsilon' = {}^1/_2(1 - \epsilon) \qquad (27)$$

In other words, $\epsilon' = 1$ when a is odd, and $\epsilon' = 0$ when a is even. From eqs 22 to 26, it is obtained

$$A = {}^1/_3(a-1)(a-2)2^{a-5} - \epsilon' \times 2^{(a-5)/2} - {}^1/_3\delta \times 2^{(a-6)/3} \quad a > 3 \qquad (28)$$

$${}^3P_{3+a} = {}^1/_3(a-1)(a-2)2^{a-5} + \epsilon' \times 2^{(a-5)/2} + {}^1/_3\delta \times 2^{(a-3)/3} \quad a \geq 3 \qquad (29)$$

Notice that the value ${}^3P_6 = 1$ ($a = 3$) is incorporated in eq 29.

Total Numbers. In summary, the total numbers of polypentagons with one internal vertex each, say P_p, are given by

$$P_p = \sum_{i=0}^{3} ({}^iP_p) \qquad (30)$$

By means of eqs 14, 15, 21, and 29, it was found

$$P_3 = P_4 = 1 \quad a = 0, 1 \qquad (31a)$$

$$P_{3+a} = {}^1/_3(a+2)(a+7)2^{a-5} + 2^{\lfloor (a-4)/2 \rfloor} + {}^1/_3\delta \times 2^{(a-3)/2}; \quad a \geq 2 \qquad (31b)$$

Table III. Numbers of Polypentagons with One Internal Vertex

p	D_{3h}	C_{3h}	C_{2v}	C_s	total P_p
3	1	0	0	0	1
4	0	0	1	0	1
5	0	0	1	1	2
6	1	0	0	4	5
7	0	0	2	10	12
8	0	0	2	27	29
9	0	1	4	67	72
10	0	0	4	166	170
11	0	0	8	396	404
12	0	2	8	934	944
13	0	0	16	2168	2184
14	0	0	16	4984	5000
15	0	4	32	11332	11368
16	0	0	32	25584	25616
17	0	0	64	57312	57376
18	0	8	64	127624	127696
19	0	0	128	282560	282688
20	0	0	128	622528	622656

Numerical values of $P_{3+a} = P_p$ are found in Table III. The distribution into symmetry groups is included therein.

Generating Function. The enumeration of systems with catacondensed appendages rooted at a polygon core has been studied by Zhang et al.[14] Especially for a core of D_{3h} symmetry with three disjoint free edges they gave the generating function

$$P(x) = {}^1/_6[U_0{}^3(x) + 2U_0(x^3) + 3U_0(x^2)\, V_0(x)] \qquad (32)$$

where $U_0(x)$ and $V_0(x)$ are certain functions, which the authors specified for the case of catacondensed appendages with hexagons only (catafusenes). The same expression (32) is applicable to the present case with catacondensed polypentagons as appendages if the $U_0(x)$ and $V_0(x)$ functions are changed appropriately. Now $U_0(x)$ is the generating function for edge-rooted catacondensed (unbranched) polypentagons, and $V_0(x)$ is the generating function for edge-rooted catacondensed polypentagons with a 2-fold symmetry axis bisecting perpendicularly the root edge; in both cases the empty graph is included. It was found that these functions read

$$U_0(x) = 1 + x(1 - 2x)^{-1} \qquad (33)$$

$$V_0(x) = 1 + x \qquad (34)$$

Then eq 32 generates the number P_p according to

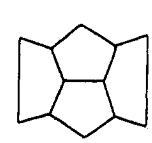
$$P(x) = \sum_{a=0}^{\infty} P_{3+a} x^a \qquad (35)$$

The explicit form of $P(x)$ was determined to be

$$P(x) = {}^1/_6(1-x)^3(1-2x)^{-3} + {}^1/_2(1-x^2)(1+x) \times (1-2x^2)^{-1} + {}^1/_3(1-x^3)(1-2x^3)^{-1} \qquad (36)$$

ENUMERATION OF POLYPENTAGONS WITH TWO CONNECTED INTERNAL VERTICES

General. The title systems consist of the core $C_{12}H_6$ with zero-, one-, or two-catacondensed appendages annelated to it. Here $C_{12}H_6$ represents the unique polypentagon with $p = 4$ and $n_i = 2$:



$C_{12}H_6$

This core has two free edges, which are available for annelation.

${}^0Q_p$, ${}^1Q_p$, and ${}^2Q_p$ are used to denote the numbers of nonisomorphic systems with zero-, one-, and two-attachments, respectively. If a again is used to denote the number of pentagons in the appendages, then

$$p = 4 + a \qquad (37)$$

No Appendage. For the core alone one has

$${}^0Q_4 = 1 \qquad a = 0 \qquad (38)$$

This unique system (when assumed to be geometrically planar) has the symmetry D_{2h}.

One Appendage. In the case of one catacondensed fragment attached to $C_{12}H_6$ the solution is analogous to eqs 15a and 15b

$${}^1Q_5 = 1 \qquad a = 1 \qquad (39a)$$

$${}^1Q_{4+a} = 2^{a-2} \qquad a > 1 \qquad (39b)$$

Here the $a = 1$ system belongs to C_{2v}, while all of those with $a > 1$ belong to C_s.

Two Appendages. For $a = 2$, viz., two pentagons attached to each of the two free edges of $C_{12}H_6$, one obtains a unique system of symmetry D_{2h}

$${}^2Q_6 = 1 \qquad a = 2 \qquad (40)$$

For $a > 2$ the systems with two catacondensed fragments attached to $C_{12}H_6$ are either centrosymmetrical (C_{2h}), mirror-symmetrical (C_{2v}), or unsymmetrical (C_s). Their numbers are identified by C, M, and A, respectively. Then

$${}^2Q_{4+a} = C + M + A \qquad (41)$$

$$S_2(a) = 2C + 2M + 4A \qquad (42)$$

where $S_2(a)$ is given explicitly in eq 18. One has

$$C = M = \epsilon \times 2^{(a-4)/2} \qquad a > 2 \qquad (43)$$

It follows

$$A = (a-1)2^{a-4} - \epsilon \times 2^{(a-4)/2} \qquad (44)$$

$${}^2Q_{4+a} = (a-1)2^{a-4} + \epsilon \times 2^{(a-4)/2} \qquad a > 2 \qquad (45)$$

Total Numbers. In summary, the total numbers of polypentagons with two connected internal vertices each, Q_p, are given by

$$Q_p = {}^0Q_p + {}^1Q_p + {}^2Q_p \qquad (46)$$

From the above analysis the following final result was obtained.

$$Q_4 = Q_5 = 1 \qquad a = 0, 1 \qquad (47a)$$

$$Q_6 = 2 \qquad a = 2 \qquad (47b)$$

$$Q_{4+a} = (a+3)2^{a-4} + \epsilon \times 2^{(a-4)/2}; \quad a > 2 \qquad (47c)$$

Numerical values of $Q_{4+a} = Q_p$ are shown in Table IV, where also the distribution into symmetry groups is accounted for.

Generating Function. Zhang et al.[14] have also considered cores of D_{2h} symmetry in their enumeration studies for catacondensed annelations. From that work we have deduced

Table IV. Numbers of Polypentagons with Two Connected Internal Vertices

p	D_{2h}	C_{2h}	C_{2v}	C_s	total Q_p
4	1	0	0	0	1
5	0	0	1	0	1
6	1	0	0	1	2
7	0	0	0	3	3
8	0	1	1	6	8
9	0	0	0	16	16
10	0	2	2	34	38
11	0	0	0	80	80
12	0	4	4	172	180
13	0	0	0	384	384
14	0	8	8	824	840
15	0	0	0	1792	1792
16	0	16	16	3824	3856
17	0	0	0	8192	8192
18	0	32	32	17376	17440
19	0	0	0	36864	36864
20	0	64	64	77760	77888

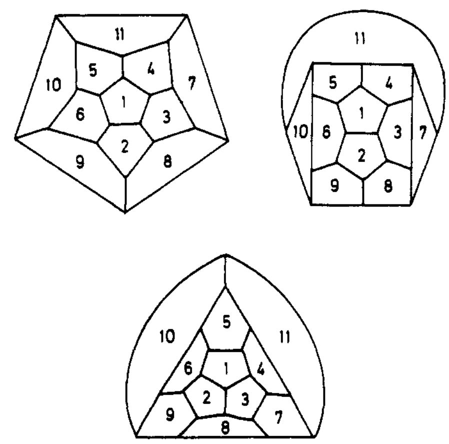


Figure 2. Pentagonal lattice with numbered pentagons in three representations, which are equivalent graphs.

the generating function

$$Q(x) = {}^1/_4[U_0^2(x) + 2U_0(x^2) + V_0^2(x)] \qquad (48)$$

where, in the present case, $U_0(x)$ and $V_0(x)$ should again be inserted from eq 33 and eq 34, respectively. Then

$$Q(x) = \sum_{a=0}^{\infty} Q_{4+a}x^a \qquad (49)$$

in analogy with eq 35. The explicit form of $Q(x)$ reads

$$Q(x) = {}^1/_4(1-x)^2(1-2x)^{-2} + {}^1/_2(1-x^2)(1-2x^2)^{-1} + {}^1/_4(1+x)^2 \qquad (50)$$

EXTREMAL POLYPENTAGONS AND CIRCUMSCRIBING

Extremal Polypentagon. An *extremal polypentagon* is defined by possessing the maximum number of internal vertices for a given number of pentagons: $n_i = (n_i)_{\max}(p)$.

The extremal polypentagons up to $p = 11$ are generated by a spiral walk on the pentagonal lattice as indicated in Figure 2. The pentagons are supposed to be added in the sequence of the numerals inscribed in the pentagons. The numbering of pentagons was chosen so that no. 1 is opposite to the missing pentagon no. 12, and in general so that nos. a and $(13 - a)$ are opposite to each other. Here "opposite" refers to the inversion through the center of the dodecahedron. In consequence, there is a jump in the spiral walk when pentagon no. 7 is added, and change of direction after this pentagon.

Table V. Increments of Selected Invariants by the Different Types of Pentagon Additions

addition type[a]	Δn_i	$(\Delta n;\Delta s)$	addition type[a]	Δn_i	$(\Delta n;\Delta s)$
i	0	(3;1)	iii	2	(1;–1)
ii	1	(2;0)	iv	3	(0;–2)

[a] See Figure 1.

Table VI. Values of $(n_i)_{max}$ for $p \le 11$ and the Corresponding Formulas

p	$(n_i)_{max}$	formula	p	$(n_i)_{max}$	formula
1	0	C_5H_5	11	15	$C_{20}H_0$
2	0	C_8H_6	10	12	$C_{20}H_2$
3	1	$C_{10}H_6$	9	10	$C_{19}H_3$
4	2	$C_{12}H_6$	8	8	$C_{18}H_4$
5	3	$C_{14}H_6$	7	6	$C_{17}H_5$
6	5	$C_{15}H_5$	6	5	$C_{15}H_5$

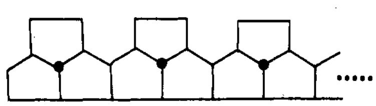
The spiral walk starts with a one-contact addition, followed by three two-contact additions. The addition of pentagon no. 6 is a three-contact addition and of no. 7 again a two-contact addition. Three three-contact additions follow, while the last addition (no. 11) is a four-contact addition. Table V shows the effect on some invariants by the different types of addition. The C_nH_s formula shift may be described in terms of an attachment of C_3H_1 or C_2H_0 in the cases of the one- (i) and two-contact (ii) additions, respectively. The three-contact addition (iii) is accompanied by a gain in one C atom and a loss of an H atom, symbolized by C_1H_{-1}. Finally, in this notation, the four-contact addition (iv) should be symbolized by C_0H_{-2}. The resulting values of $(n_i)_{max}$ for $p \le 11$ are shown in Table VI.

In summary, the extremal polypentagons for $1 \le p \le 11$ have the formulas which are specified in Table VI. Only one polypentagon isomer exists for each of these formulas, and it is a proper polypentagon.[15]

One should not be misled into believing that a polypentagon in general cannot have more than fifteen internal vertices. This is of course true for proper polypentagons; in this case one has, in addition to eq 1,

$$0 \le n_i \le 15 \tag{51}$$

When it is allowed for helicenic systems, then n_i has no upper bound. That is easily seen, for instance, by the following example of polypentagons with $p = 3N$; they have $n_i = N$, where N is arbitrarily large.



Presently we shall not consider $(n_i)_{max}$ for $p > 11$.

Circumscribing. A *circumscribed polypentagon* P, viz., circum-P, is defined in analogy with a circumscribed benzenoid. Suppose that s pentagons can be added around the perimeter of a polypentagon P with p hexagons, n_i internal vertices, and the formula C_nH_s so that it forms a circular single chain of pentagons (in analogy with a primitive coronoid among polyhexes).

p', n_i', n', and s' are used to denote the appropriate invariants of circum-P. Then

$$p' = p + s = 2p - n_i + 4 \tag{52}$$

$$n_i' = n = 3p - n_i + 2 \tag{53}$$

Furthermore, the formula for circum-P is given by

$$n' = {}^1/_2(3s + n) + 5 \tag{54}$$

$$s' = 5 - {}^1/_2(n - s) \tag{55}$$

The process of circumscribing has a very limited application for polypentagons, in sharp contrast to the situation for benzenoids. It is observed, for instance, that a polypentagon with a bay (or a fjord) cannot be circumscribed. As a matter of fact, only five polypentagons can be circumscribed! All of them are extremal proper polypentagons, and the circumscribed systems belong to the same category. Specifically: circum-C_5H_5 = $C_{15}H_5$, circum-C_8H_6 = $C_{18}H_4$, circum-$C_{10}H_6$ = $C_{19}H_3$, circum-$C_{12}H_6$ = $C_{20}H_2$, and circum-$C_{15}H_5$ = $C_{20}H_0$.

PROPER POLYPENTAGONS

Introductory Remarks. In this section we shall expand the following result: There are exactly 39 nonisomorphic proper polypentagons. Therefore it is a conceivable task to tabulate all the formulas (C_nH_s) for these systems, depict their forms, and indicate their symmetries.

It is recalled that a proper polypentagon can be embedded on a dodecahedron and is defined by a cycle on the dodecahedron surface (see above). If the missing pentagon, which is a part of the definition of the pentagonal lattice, is not fixed, then the cycle may be taken to define two proper polypentagons, which share the perimeter. This leads to the concept of reciprocity, which has proved to be very useful in the studies of proper polypentagons, and more important than circumscribing. There is no analogous concept to reciprocity for benzenoids or polyhexes.

Reciprocity. The *reciprocal polypentagon* to a proper polypentagon P, denoted recip-P, consists of exactly the pentagons of the dodecahedron which are not contained in P. Thus recip-P is also a proper polyhexagon, and in a one-to-one correspondence with P. One has clearly recip-(recip-P) = P.

The invariants p, n_i, n_e, n, and s are associated with P, and identify the corresponding invariants of recip-P by the symbols p^*, n_i^*, n_e^*, n^*, and s^*, respectively. Then

$$p^* = 12 - p \tag{56}$$

$$n_i^* = 20 - n = n_i - 3p + 18 \tag{57}$$

Notice also

$$n_e^* = n_e \tag{58}$$

It is especially useful to determine the formula of recip-P in terms of the invariants of the formula of P (C_nH_s). The following relations were found.

$$n^* = 15 + {}^1/_2(3s - n) \tag{59}$$

$$s^* = {}^1/_2(n + s) - 5 \tag{60}$$

Formulas. All the possible formulas for proper polypentagons are collected in Table VII. A pair of P and recip-P is found symmetrically around the middle row (in boldface). Notice that the formulas are "self-reciprocal" for $p = 6$ (i.e. $n^* = n$, $s^* = s$). Furthermore, it is found that recip-P is an extremal polypentagon if and only if P is extremal. Table VI is arranged so that each row pertains to two extremal polypentagons which are reciprocal to each other.

Table VII. All Formulas for Proper Polypentagons

p	formulas					
1	C_5H_5					
2	C_8H_6					
3	$C_{11}H_7$	$C_{10}H_6$				
4	$C_{14}H_8$	$C_{13}H_7$	$C_{12}H_6$			
5	$C_{17}H_9$	$C_{16}H_8$	$C_{15}H_7$	$C_{14}H_6$		
6	$\mathbf{C_{20}H_{10}}$	$\mathbf{C_{19}H_9}$	$\mathbf{C_{18}H_8}$	$\mathbf{C_{17}H_7}$	$\mathbf{C_{16}H_6}$	$\mathbf{C_{15}H_5}$
7	$C_{20}H_8$	$C_{19}H_7$	$C_{18}H_6$	$C_{17}H_5$		
8	$C_{20}H_6$	$C_{19}H_5$	$C_{18}H_4$			
9	$C_{20}H_4$	$C_{19}H_3$				
10	$C_{20}H_2$					
11	$C_{20}H_0$					

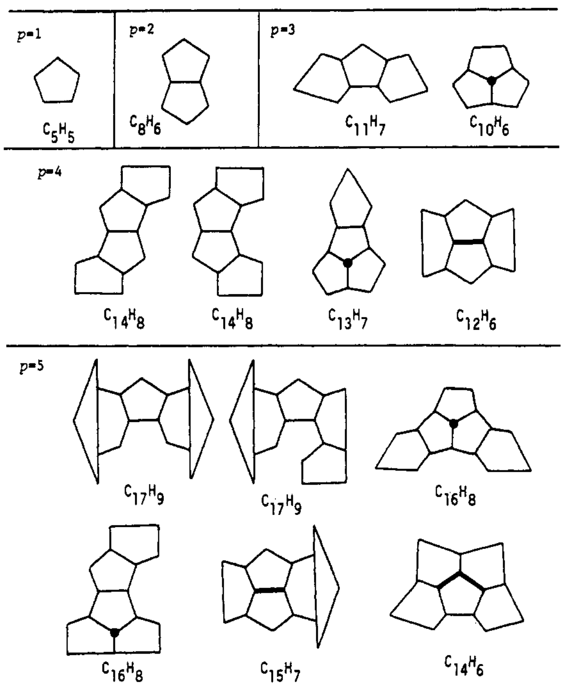


Figure 3. All proper polypentagons with $p < 6$.

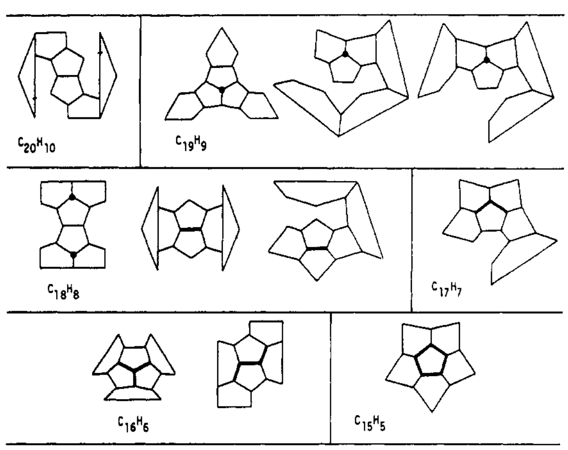


Figure 4. All proper polypentagons with $p = 6$.

Enumeration and Forms. The proper polypentagons with $p < 6$ (Figure 3) and $p = 6$ (Figure 4) were generated by systematic additions of pentagons, assuring that isomorphic and helicenic systems were eliminated. All the systems with $p = 6$ are reciprocal to themselves one by one. However, all the nonisomorphic proper polypentagons with $p > 6$ (Figure 5) can be constructed systematically by taking the reciprocal polypentagons to those with $p < 6$. In this way the forms of Figure 5 were derived, one by one, from those of Figure 3. In Figures 3–5 the internal vertices are either marked by black dots or connected by heavy lines.

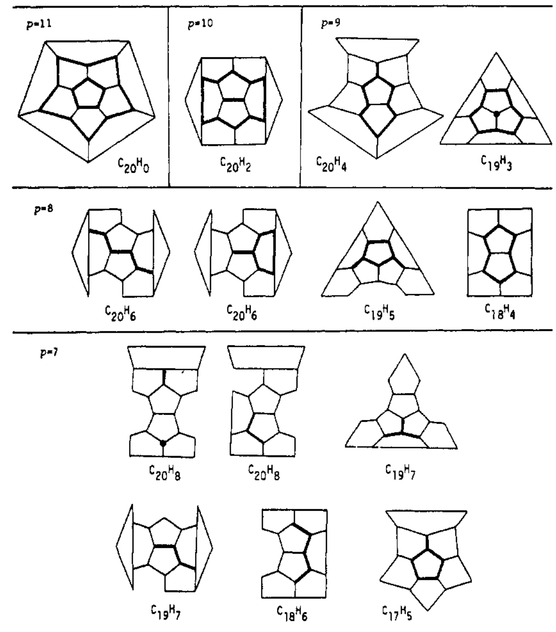


Figure 5. All proper polypentagons with $p > 6$.

Table VIII. Numbers and Symmetries of All Isomers of Proper Polypentagons[a]

	formulas	no. of isomers	symmetry of isomers
X	C_5H_5, $C_{15}H_5$, $C_{20}H_0$	1	D_{5h}
X	C_8H_6, $C_{12}H_6$, $C_{18}H_4$, $C_{20}H_2$	1	D_{2h}
	$C_{11}H_7$, $C_{20}H_4$	1	C_{2v}
X	$C_{10}H_6$, $C_{19}H_3$	1	D_{3h}
	$C_{14}H_8$, $C_{20}H_6$	2	$C_{2h} + C_{2v}$
	$C_{13}H_7$, $C_{19}H_5$	1	C_{2v}
	$C_{17}H_9$, $C_{20}H_8$	2	$C_{2v} + C_s$
	$C_{16}H_8$, $C_{19}H_7$	2	$C_{2v} + C_s$
	$C_{15}H_7$, $C_{18}H_6$	1	C_{2v}
X	$C_{14}H_6$, $C_{17}H_5$	1	C_{2v}
	$C_{20}H_{10}$	1	C_{2h}
	$C_{19}H_9$	3	$D_{3h} + 2C_s$
	$C_{18}H_8$	3	$2D_{2h} + C_s$
	$C_{17}H_7$	1	C_s
	$C_{16}H_6$	2	$D_{3h} + C_{2h}$

[a] X: extremal systems.

It should be clear that there is an equivalence between the numbers of isomers for two formulas which pertain to P and recip-P. The same is also true for P and circum-P (when P can be circumscribed). The equivalence is not limited to the number of isomers, but applies also to the symmetries of the individual forms in a one-to-one correspondence. Table VIII summarizes the enumeration results for the proper polypentagons. The symmetry groups, to which they belong, are indicated.[16] In this table the formulas for P, recip-P and circum-P (when they exist) are taken together. In particular, it is noted that recip-$C_{10}H_6$ = circum-$C_{10}H_6$ = $C_{19}H_3$.

CONCLUSION

The present theory of polypentagons is supposed to be rather complete with respect to some topological properties, in particular those which involve the invariants, and the enumeration of the systems. This enumeration is related to the chemical formulas (C_nH_s). In the chemical context, C_8H_6 pentalene has been considered[17] as an annulenoannulene.[18] The polypentagon $C_{20}H_0$ is chemically indistinguishable from a C_{20} carbon cluster with the structure of a regular dodecahedron (with no missing pentagon specified). Several studies

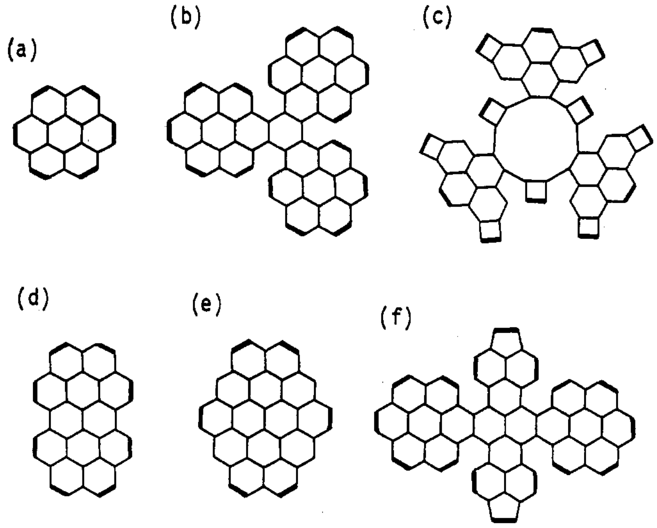


Figure 6. Examples of R* cores with symmetries: (a) D_{6h}; (b and c) D_{3h}; (d, e, and f) D_{2h}. Free edges are indicated by heavy lines.

of this structure (considered as a chemical graph) have been done.[19-22] The C_{20} cluster may be the smallest fullerene.[23]

The generating functions $P(x)$ and $Q(x)$ in eq 32 and eq 48, respectively, were derived as special cases of more general formulas from Zhang et al.[14] for enumeration of catafusenes rooted at a polygon core. However, the treatment therein for a core of symmetry D_{nh}, $n \geq 3$, is not general. Therefore we give a general treatment, which covers all cases of D_{nh}, $n \geq 2$ in the following Appendix.

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APPENDIX

Here the same notation is used as in Zhang et al.[14] Consider the case when a core R* belongs to the symmetry group D_{nh} ($n \geq 2$). A catacondensed fragment can be appended to an edge of R* between two vertices of degree 2. Such edges are referred to as free (or available[14]) edges. In the case under consideration the free edges of R* can be divided in n subsets so that the free edges in one subset are transformed to the free edges in another subset under the operation of rotation of D_{nh}. Furthermore, R^* can be divided in $2n$ parts of which n parts are identical, and so are the other n parts. Each of the $2n$ parts is mirror-symmetrical; see Figure 6c,e,f. Sometimes n identical parts are empty or, in other words, R* can be divided in n identical parts, as is exemplified in Figure 6a,b,d. In the general case, m_1 and m_2 designate the number of free edges which are intersected by a mirror plane of R* in two different parts, while k_1 and k_2 indicate the numbers of the other edges. Accordingly, the total number of free edges is $n(2k + m)$, where $k = k_1 + k_2$, and $m = m_1 + m_2$. Obviously m_1, m_2 = 0 or 1; hence m = 0, 1, or 2. Examples with reference to Figure 6

$$\text{(a) } k = 0, \quad m = 1$$
$$\text{(b) } k = 2, \quad m = 1$$
$$\text{(c) } k_1 = 1, \quad k_2 = 0, \quad m_1 = m_2 = 1$$
$$\text{(d) } k = 2, \quad m = 0$$
$$\text{(e) } k_1 = 1, \quad k_2 = 0, \quad m_1 = 0, \quad m_2 = 1$$
$$\text{(f) } k_1 = 1, \quad k_2 = 2, \quad m_1 = m_2 = 1$$

By the methods of the cited work[14] we find the generating function for $\Pi(R^*)$ as

$$\frac{1}{2}[Z(C_{nh},U_0^{2k+m}(x)) + U_0^{p(2k+m)+k}(x^2)\, V_0^{m}(x)] = \frac{1}{2n}[\sum_{j|n}\varphi(j)\, U_0^{n(2k+m)/j}(x^j) + nU_0^{p(2k+m)+k}(x^2)\, V_0^{m}(x)] \quad \text{(A1)}$$

when $n = 2p + 1$ (p = 1, 2, 3, ...), and

$$\frac{1}{2}\Big[Z(C_{nh},U_0^{2k+m}(x)) + \frac{1}{2}U_0^{q(2k+m)-m_1}(x^2)\, V_0^{2m_1}(x) + \frac{1}{2}U_0^{q(2k+m)-m_2}(x^2)\, V_0^{2m_2}(x)\Big] = \frac{1}{2n}\Big[\sum_{j|n}\varphi(j)\, U_0^{n(2k+m)/j}(x^j) + \frac{1}{2}nU_0^{q(2k+m)-m_1}(x^2)\, V_0^{2m_1}(x) + \frac{1}{2}nU_0^{q(2k+m)-m_2}(x^2)\, V_0^{2m_2}(x)\Big] \quad \text{(A2)}$$

when $n = 2q$ (q = 1, 2, 3, ...). In (A1) and (A2), $\varphi(j)$ is the Euler φ-function, viz., the number of positive integers $\leq j$ that are relatively prime to j (for $j \geq 1$). The summations are taken for all $j \geq 1$ when n is divisible by j.

The generating functions for $\Pi(R^*)$ in all the examples of Figure 6 except (c) are worked out elsewhere.[14] Here we show the application of eq A1 to the case of Figure 6c. Then $n = 3$, $p = 1$, and j = 1, 3. Furthermore, $\varphi(1) = 1$ and $\varphi(3) = 2$, while $k = 1$, $m = 2$ (see above). In consequence

$$^1/_6[U_0^{12}(x) + 2U_0^{4}(x^3) + 3U_0^{5}(x^2)\, V_0^{2}(x)] = 1 + 3x + 21x^2 + 132x^3 + 828x^4 + 4987x^5 + 29155x^6 + 165219x^7 + 915201x^8 + 4973580x^9 + ... \quad \text{(A3)}$$

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(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**, *201*, 75–86.
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