New Picture for Constant-Isomer Series of Benzenoids and Related Systems

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The C_nH_s formulas of ground forms of constant-isomer benzenoid series are studied. The derivation of an expression for these formulas in a "new picture" as a generating function amounts to the solution of the following purely mathematical problem: $n(s) - 6x^6 = \sum_{s=8}^{\infty}(s + 2\lfloor {}^1/_{12}(s^2 - 8s + 19)\rfloor)x^s$. Here the coefficients (n_s) on the right-hand side are given in the "Harary–Harborth picture". Another expression for n_s is quoted and said to be in the "Balaban picture". The function $n(s)$ is given explicitly. It is also generalized to mono-q-polyhexes for $2 \leq q \leq 6$. A mono-q-polyhex is a polygonal system consisting of exactly one q-gon and otherwise hexagons. The smallest ground forms of the C_nH_s isomers of constant-isomer series for mono-4-, mono-3-, and mono-2-polyhexes are depicted. Finally some new data in the C_nH_s isomer enumeration are reported.

INTRODUCTION

A constant-isomer benzenoid series[1-3] is a sequence of $C_nH_s \equiv (n; s)$ formulas for benzenoids, viz., $(n_0; s_0)$, $(n_1; s_1)$, $(n_2; s_2)$, ..., where the same number of isomers is associated with each formula, and all the $(n_k; s_k)$ benzenoids are obtained by k-fold circumscribings of those pertaining to $(n_0; s_0)$. Here the benzenoid isomers of $(n_0; s_0)$ are referred to as the ground forms of the constant-isomer series in question. It is of interest to identify the $(n_0; s_0)$ formulas for all the values $s_0 = 6, 8, 9, 10, 11, ...$, which are possible for benzenoids. Here and in the following, the term "benzenoid" is used in the sense of a benzenoid system according to well-established definitions.[4-6]

Two forms of general expressions for the C_nH_s formulas of benzenoid ground forms, viz., $(n_0; s_0)$, have been given.[7] These two expressions were referred to as belonging to the (a) Harary–Harborth and (b) Balaban schemes, later designated as the (a) Harary–Harborth and (b) Balaban "pictures", respectively.[8,9] These designations are appropriate because the pertinent expressions have relevance to (a) the analysis of extremal benzenoids by Harary and Harborth[10] on one hand and (b) an analysis of annulenes by Balaban[11] on the other. Recently Dias[12] has published a "floating function" for $(n_0; s_0)$, derived from an interesting algorithm, which was based on differences between the formula coefficients n_0. It appears that this floating function is equivalent to the corresponding expression in the Balaban picture published previously.[3,7,13] This fact corroborates the validity of the Dias algorithm for benzenoids.

In the present work we have used the differences in n_0 (see above) to deduce a general formulation for $(n_0; s_0)$ in a new "picture", making use of generating functions. These functions are known to represent a powerful tool in different enumeration problems.[14-17] Here we give for the first time a generating function for chemical formulas (C_nH_s).

The present considerations are extended to mono-q-polyhexes,[18] viz., systems which each contain one q-gon and otherwise hexagons. The cases with q = 2, 3, 4, and 5 are considered, while q = 6 accounts for the benzenoids. The q = 2 systems in question are degenerate polygonal systems including a "2-gon".

RESULTS AND DISCUSSION

General Remarks. $C_nH_s \equiv (n; s)$ denotes a formula for benzenoid ground forms (or a single form in the case of one-isomer series). The first ten of these formulas, according to increasing s values, read as follows: C_6H_6, $C_{10}H_8$, $C_{13}H_9$, $C_{16}H_{10}$, $C_{19}H_{11}$, $C_{22}H_{12}$, $C_{27}H_{13}$, $C_{30}H_{14}$, $C_{35}H_{15}$, and $C_{40}H_{16}$. Presently we shall use the notation n_s so that $n_6 = 6$, $n_8 = 10$, $n_9 = 13$, etc.

In the Harary–Harborth picture for $(n; s)$, the "floor" function, $\lfloor a\rfloor$, is an essential part of the expression for n; $\lfloor a\rfloor$ is the largest integer not larger than a. In the Balaban picture, two parameters are employed, viz., j and δ. Accordingly, an $(n; s)$ formula for a ground form benzenoid can be identified alternatively by $\{j, \delta\}$.[8] In the new picture, a generating function, $n(x)$, is to be deduced so that

$$n(x) = 6x^6 + \sum_{s=8}^{\infty} n_s x^s \qquad (1)$$

Harary–Harborth Picture. The following general expression for $(n; s)$ is known.[7-9,19]

$$(n; s) = (s + 2\lfloor {}^1/_{12}(s^2 - 8s + 19)\rfloor; s) \qquad (2)$$

Here $s = 6$ or $s \geq 8$.

Balaban Picture. For $(n; s) \equiv \{j, \delta\}$ one has[3,7,8]

$$(n; s) = (6j^2 + 12j + (2j + 3)\delta + 7 + 2\lfloor \delta/6\rfloor; 6j + \delta + 7) \qquad (3)$$

Here j = 0, 1, 2, ..., and δ = 1, 2, 3, 4, 5, 6. As such eq 3 does not cover the formula C_6H_6, which corresponds to $\{-1,5\}$.[20]

Brief Discussion of the Harary–Harborth and Balaban Pictures. The formula in the Harary–Harborth picture (eq 2) has the obvious virtue that n is expressed as an explicit function of s. This was achieved through an advanced application of the floor function. Here the coefficients s are related straightforwardly to the appropriate expression from the Balaban picture (eq 3), viz., $6j + \delta + 7$. The two parameters, j and δ, which occur in this picture, are very useful for certain purposes because of their significant interpretations: the δ parameters originate from the six characteristic forms of circular benzenoids (which are related to the ground forms of the constant-isomer series), while j comes from the number of circumscribings.[8]

New Picture. The differences in the n coefficients of $(n; s)$ are defined by $\Delta_6 = 3$ (s = 6) and $\Delta_s = n_{s+1} - n_s$ for $s \geq 8$. Then eq 3 gives readily $\Delta_s = 2j + 3$ for δ = 1, 2, 3, 4, and 6, and $\Delta_s = 2j + 5$ for $\delta = 5$. For the sake of clarity we give a table of Δ_s as follows:

Δ_s	s					
3	6	8	9	10	11	13
5	12	14	15	16	17	19
7	18	20	21	22	23	25
⋮	...					

The first task is to deduce the generating function for the odd numbers Δ_s, viz.,

$$p(x) = 3 + 5x^2 + 7x^3 + ... \qquad (4)$$

One has the well-known geometrical series

$$(1-x)^{-1} = 1 + x + x^2 + ... \qquad (5)$$

and similarly

$$(1-x)^{-2} = 1 + 2x + 3x^2 + ... \qquad (6)$$

Hence for even numbers

$$2(1-x)^{-2} = 2 + 4x + 6x^2 + ... \qquad (7)$$

Then obviously

$$(1-x)^{-1} + 2(1-x)^{-2} = 3 + 5x + 7x^2 + ... \qquad (8)$$

which yields

$$p(x) = (3-x)(1-x)^{-2} = \sum_{p=0}^{\infty}(2p+3)x^p \qquad (9)$$

Here x is only the variable in functions equated to each other. The expansions of eq 5–9 and those in the following converge for $|x| < 1$; otherwise the specific values of x are of no interest.

The next step is

$$x^6p(x^6) = \sum_{p=0}^{\infty}(2p+3)\,x^{6p+6} = 3x^6 + 5x^{12} + 7x^{18} + ... \qquad (10)$$

Now the Δ_s numbers for the first column of s values of the above table are reproduced. All the Δ_s numbers are clearly given by

$$\Delta(x) = 3x^6 + \sum_{s=8}^{\infty}\Delta_s x^s = (1 + x^2 + x^3 + x^4 + x^5 + x^7)\,x^6p(x^6) \qquad (11)$$

Herefrom, the generating function for the n_s values is deduced by

$$n(x) = x(1-x)^{-1}[\Delta(x) + 7x^7] + 6x^6 - 3x^7 \qquad (12)$$

where the two last terms were added in order to get $n_6 = 6$ and $n_7 = 0$, which takes care of the irregular start of the sequence of n values. The explicit form of the generating function for n_s reads

$$n(x) = x^6(1-x)^{-1}[6 - 9x + 10x^2 + x(1 + x^2 + x^3 + x^4 + x^5 + x^7)(3 - x^6)(1 - x^6)^{-2}] \qquad (13)$$

Extension to Related Systems. The mono-q-polyhexes[18] are defined as polygonal systems consisting of exactly one q-gon each and otherwise hexagons. The cases of $q = 6$, 5, and 4 are represented by benzenoids, fluorenoids/fluoranthenoids,[21] and biphenylenoids,[22] respectively. The mono-3-polyhexes and mono-2-polyhexes are also of interest. All these systems exhibit constant-isomer series.[1-3,21,22]

Table I. Coefficients of C_nH_s Formulas of Ground Forms of Mono-q-polyhexes

	n				
s	$q = 6$	$q = 5$	$q = 4$	$q = 3$	$q = 2$
2					2
3				3	–
4			4	–	6
5		5	–	7	11
6	6	–	8	10	14
7	–	9	11	15	21
8	10	12	14	18	26
9	13	15	19	23	35
10	16	18	22	30	42
11	19	23	27	35	53
12	22	26	32	42	62
13	27	31	39	51	75
14	30	36	44	58	86
15	35	41	51	67	101
16	40	48	58	78	114
17	45	53	67	87	131
18	50	60	74	98	146
19	57	67	83	111	165
20	62	74	92	122	182
21	69	83	103	135	203
22	76	90	112	150	222
23	83	99	123	163	245
24	90	108	134	178	266
25	99	117	147	195	291
26	106	128	158	210	314
27	115	137	171	227	341
28	124	148	184	246	366
29	133	159	199	263	395
30	142	170	212	282	422

It appears as a tractable problem to generalize the above treatment of n_s in terms of the new picture to mono-q-polyhexes for $q = 2, 3, 4, 5, 6$. Then the differences in n should be defined by $\Delta_q = 3$ ($s = q$) and $\Delta_s = n_{s+1} - n_s$ for $s \geq q + 2$. The generalization of eq 11 reads

$$\Delta(q,x) = 3x^q + \sum_{s=q+2}^{\infty}\Delta_s x^s = \left(\sum_{i=0}^{q+1}x^i - x - x^q\right)x^q p(x^q) \qquad (14)$$

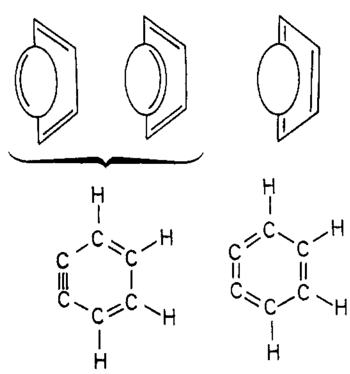
and the final result is

$$n(q,x) = \frac{x^q}{1-x}\left[q - (q+3)x + (q+4)x^2 + x\left(\sum_{i=0}^{q+1}x^i - x - x^q\right)\frac{3-x^q}{(1-x^q)^2}\right] \qquad (15)$$

A simple computer program was implemented in order to expand the generating function (eq 15) for $q = 2, 3, 4, 5, 6$. The results up to $s = 30$ are collected in Table I. The first three columns of n values (for $q = 6, 5, 4$) reproduced the previously known data,[1,2,21,22] while the numbers in the two last columns (for $q = 3, 2$) are new.

Ground Forms of Constant-Isomer Series. The forms of the C_nH_s isomers of benzenoids are known to a great extent,[8,23,24] including many of those for constant-isomer series. Several corresponding depictions are also available for fluorenoids and fluoranthenoids.[21] In supplement of this material we show the smallest ground forms of mono-4-polyhexes (representing biphenylenoids[22]) and of mono-3-polyhexes in Figures 1 and 2, respectively. It is observed in particular that, for instance, $C_{12}H_8$ biphenylene and its biphenylenoid isomers are not members of constant-isomer series, but $C_{32}H_{12}$ circumbiphenylene is a ground form.

The mono-2-polyhexes are somewhat special. They are degenerate polygonal systems, in a sense, but have nevertheless chemical counterparts, inasmuch as the 2-gon can be related to acetylene[25] or cumulated carbon–carbon double bonds. For example, one 2-gon and one hexagon combine to the following system with three Kekulé structures.



This system is associated with the formula C_6H_4 and corresponds to benzyne, a well-known intermediate in organic chemistry. Its two valence structures are indicated in the above diagram. Hydrocarbons with triple and cumulated double bonds as in the above benzyne structures are conveniently handled by the two-dimensional Hückel molecular orbital theory.[26] Another special feature of mono-2-polyhexes is worth mentioning. In a configuration with two hexagons which both are in contact with the 2-gon, these two hexagons share two edges. A corresponding topological property is not found in any other mono-q-polyhex; in all other cases (including benzenoids) any two polygons either share exactly one edge or they are disjoint. The smallest ground forms of mono-2-polyhexes are displayed in Figure 3.

In Figures 1–3 the internal vertices of the depicted polygonal systems are indicated by black dots or (more frequently) connected by heavy lines.[27]

Numbers of Isomers for Constant-Isomer Series. The numbers of C_nH_s isomers of benzenoids are well-known,[8,24] including those for the constant-isomer series. Corresponding data are also available for fluorenoids/fluoranthenoids,[21] especially for the pertinent constant-isomer series. For the biphenylenoids, corresponding enumerations have just been initiated.[22] The systems mentioned above fall under the mono-q-polyhexes with q = 6, 5, and 4, respectively. Numbers of C_nH_s isomers for the constant-isomer series of these systems are quoted in Table II. Only the C_nH_s formulas for the ground forms are specified therein.

Special computer programs were designed for the isomer enumeration of different mono-q-polyhexes, and in particular for q = 3 and q = 2. In this way it was feasible to supplement the data which are referred to above, by the new numbers for mono-3-polyhexes and mono-2-polyhexes; see Table II.

CONCLUSION

The generating function (eq 13) for the C_nH_s formulas of ground forms of constant-isomer benzenoid series represents a new picture, in addition to the previously published expressions in the Harary–Harborth picture (eq 2) and in the Balaban picture (eq 3). It is admitted that the generating function is somewhat complicated and therefore not so convenient for practical use as the expressions in the two other pictures. Dias[12] has given the expressions which correspond to the Balaban picture for constant-isomer series of mono-5-polyhexes (fluoranthenoids/fluorenoids). The more general expressions for mono-q-polyhexes ($2 \le q \le 6$) have been worked out by us, both in the Balaban picture (unpublished) and the Harary–Harborth picture.[22] Finally, Dias[12] has included a formulation corresponding to the Balaban picture for di-5-polyhexes (indacenoids).

The present work tends to demonstrate the virtue and flexibility of generating functions in enumeration problems. It was demonstrated for the first time that a generating function

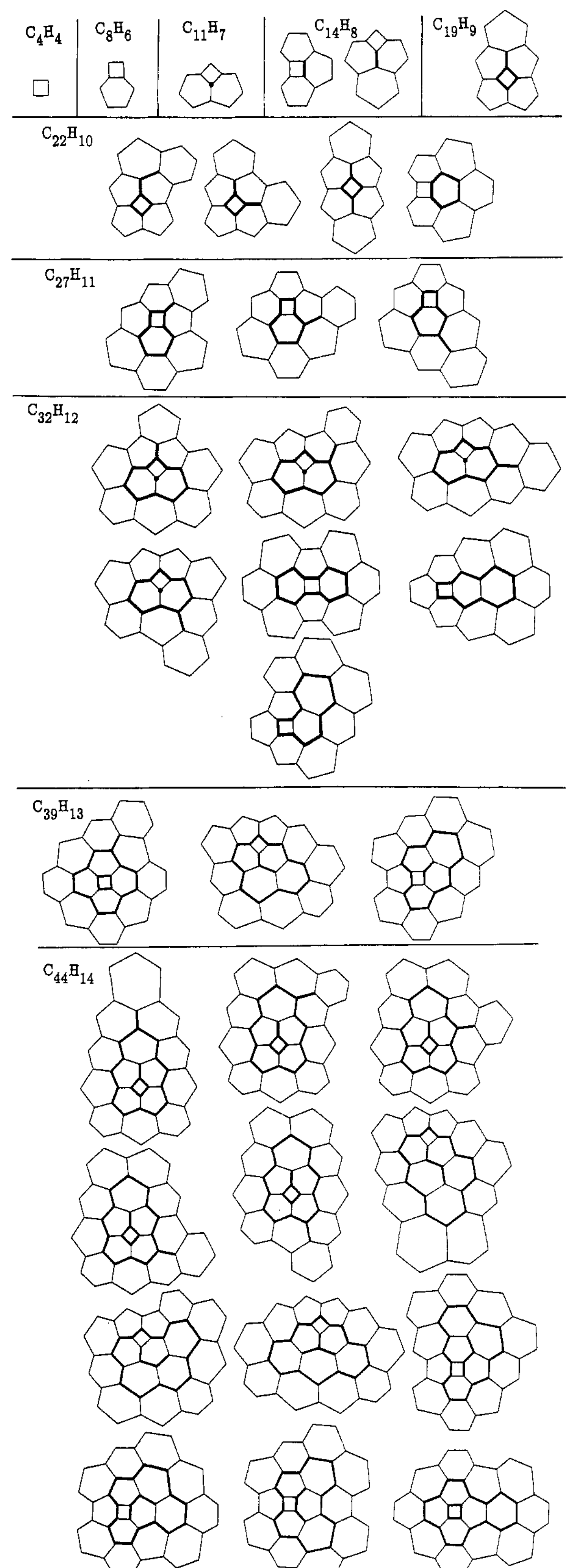


Figure 1. Ground forms of constant-isomer series for the smallest mono-4-polyhexes: $s \le 14$.

Table II. Numbers of C_nH_s Isomers for Constant-Isomer Series of Mono-q-polyhexes[a]

$q = 6$[b]		$q = 5$[c]		$q = 4$[d]		$q = 3$		$q = 2$	
C_6H_6	1	C_5H_5	1	C_4H_4	1	C_3H_3	1	C_2H_2	1
$C_{10}H_8$	1	C_9H_7	1	C_8H_6	1	C_7H_5	1	C_6H_4	1
$C_{13}H_9$	1	$C_{12}H_8$	1	$C_{11}H_7$	1	$C_{10}H_6$	1	$C_{11}H_5$	1
$C_{16}H_{10}$	1	$C_{15}H_9$	2	$C_{14}H_8$	2	$C_{15}H_7$	1	$C_{14}H_6$	2
$C_{19}H_{11}$	1	$C_{18}H_{10}$	3	$C_{19}H_9$	1	$C_{18}H_8$	2	$C_{21}H_7$	1
$C_{22}H_{12}$	3	$C_{23}H_{11}$	2	$C_{22}H_{10}$	4	$C_{23}H_9$	3	$C_{26}H_8$	4
$C_{27}H_{13}$	1	$C_{26}H_{12}$	7	$C_{27}H_{11}$	3	$C_{30}H_{10}$	2	$C_{35}H_9$	3
$C_{30}H_{14}$	4	$C_{31}H_{13}$	7	$C_{32}H_{12}$	7	$C_{35}H_{11}$	6	$C_{42}H_{10}$	8
$C_{35}H_{15}$	2	$C_{36}H_{14}$	9	$C_{39}H_{13}$	3	$C_{42}H_{12}$	8	$C_{53}H_{11}$	5
$C_{40}H_{16}$	4	$C_{41}H_{15}$	17	$C_{44}H_{14}$	12	$C_{51}H_{13}$	6	$C_{62}H_{12}$	13
$C_{45}H_{17}$	4	$C_{48}H_{16}$	9	$C_{51}H_{15}$	13	$C_{58}H_{14}$	14	$C_{75}H_{13}$	11
$C_{50}H_{18}$	9	$C_{53}H_{17}$	31	$C_{58}H_{16}$	21	$C_{67}H_{15}$	19	$C_{86}H_{14}$	24
$C_{57}H_{19}$	4	$C_{60}H_{18}$	31	$C_{67}H_{17}$	13	$C_{78}H_{16}$	14	$C_{101}H_{15}$	18
$C_{62}H_{20}$	16	$C_{67}H_{19}$	41	$C_{74}H_{18}$	†	$C_{87}H_{17}$	†	$C_{114}H_{16}$	†
$C_{69}H_{21}$	13	$C_{74}H_{20}$	72	$C_{83}H_{19}$	†	$C_{98}H_{18}$	†	$C_{131}H_{17}$	†
$C_{76}H_{22}$	16	$C_{83}H_{21}$	41	$C_{92}H_{20}$	†	$C_{111}H_{19}$	†	$C_{146}H_{18}$	†
$C_{83}H_{23}$	20	$C_{90}H_{22}$	120	$C_{103}H_{21}$	†	$C_{122}H_{20}$	†	$C_{165}H_{19}$	†
$C_{90}H_{24}$	39	$C_{99}H_{23}$	120	$C_{112}H_{22}$	†	$C_{135}H_{21}$	†	$C_{182}H_{20}$	†

[a] † = unknown. [b] Reference 8 with documentation to the original sources therein. [c] Reference 21. [d] Reference 22.

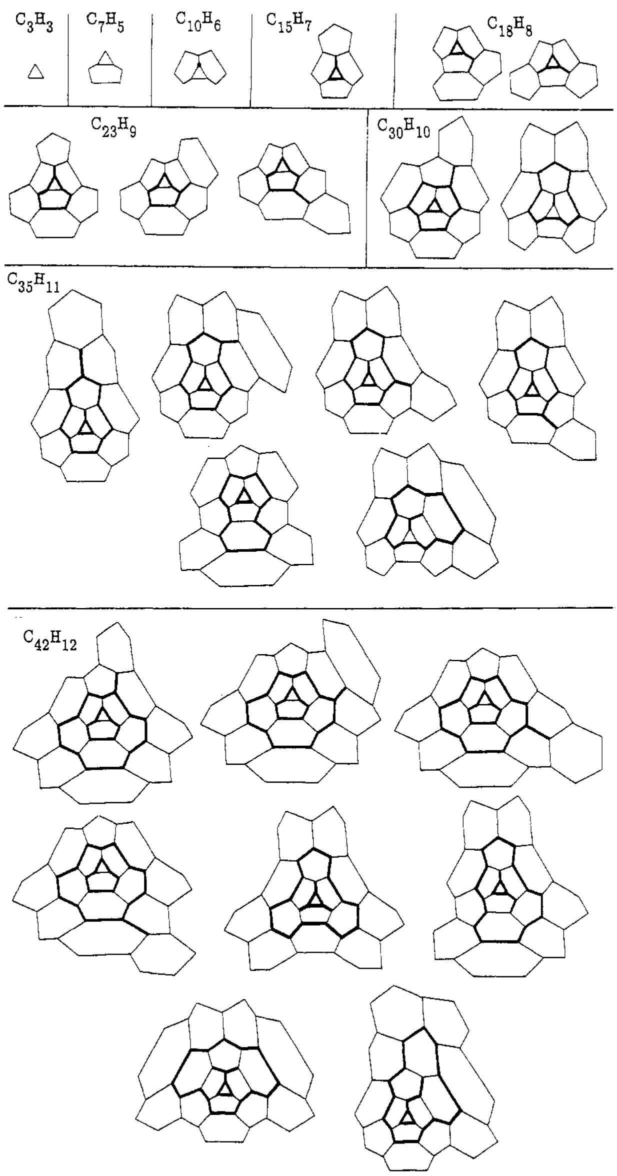


Figure 2. Ground forms of constant-isomer series for the smallest mono-3-polyhexes: $s \leq 12$.

can reproduce a sequence of chemical formulas of a special class. Furthermore, the generating function for benzenoids could be generalized to mono-q-polyhexes for all $2 \leq q \leq 6$.

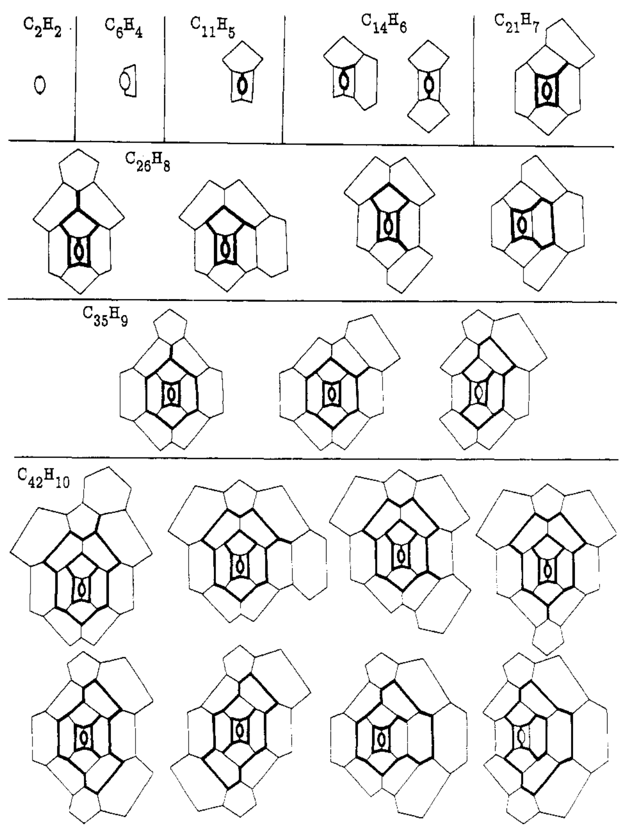


Figure 3. Ground forms of constant-isomer series for the smallest mono-2-polyhexes: $s \leq 10$.

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