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Isomers of Polyenes Attached to Benzene

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A polyene graph is a tree that can be embedded in a hexagonal lattice. Systems of polyene graphs attached to one hexagon are considered. Overlapping edges and/or vertices (geometrically nonplanar systems) are allowed. A complete mathematical solution is presented in terms of a generating function for the numbers of isomers of the systems in question. The corresponding geometrically planar systems, referred to as styrenoids, are enumerated by computer programming. Finally, in the Appendix, the generating function is given for the numbers of free polyene graphs.

INTRODUCTION

The C_nH_{n+2} polyenes are represented by polyene graphs. A (free) polyene graph is defined as one vertex alone or a tree that can be embedded in a hexagonal lattice. Kirby[1] has recently enumerated the geometrical isomers of these systems by computer programming. A complete mathematical solution for these numbers has been achieved (see Appendix) when it is allowed for overlapping edges and/or vertices on the hexagonal lattice. Such geometrically nonplanar systems were excluded in Kirby's[1] enumerations.

The main topic of the present work are the systems of polyene subgraphs attached to one hexagon. These systems represent important conjugated hydrocarbons, of which the smallest systems of the category in question are displayed in Figure 1.

POLYENE SUBGRAPHS ATTACHED TO ONE HEXAGON

Definitions and Introductory Remarks

The $C_{a+6}H_{a+6}$ isomers of the title systems were enumerated by means of generating functions.[2–5] Symbol a is used to designate the number of edges in the appendages. For the sake of clarity, it is repeated that the overlapping edges and/or vertices are allowed, both between the appendages and with the hexagon. The famous paper by Harary and Read,[2] who enumerated catafusenes[6] (a class of polyhexes) was found to be especially instructive. Also, a more recent work by Zhang *et al.*[7] is highly relevant to the present work.

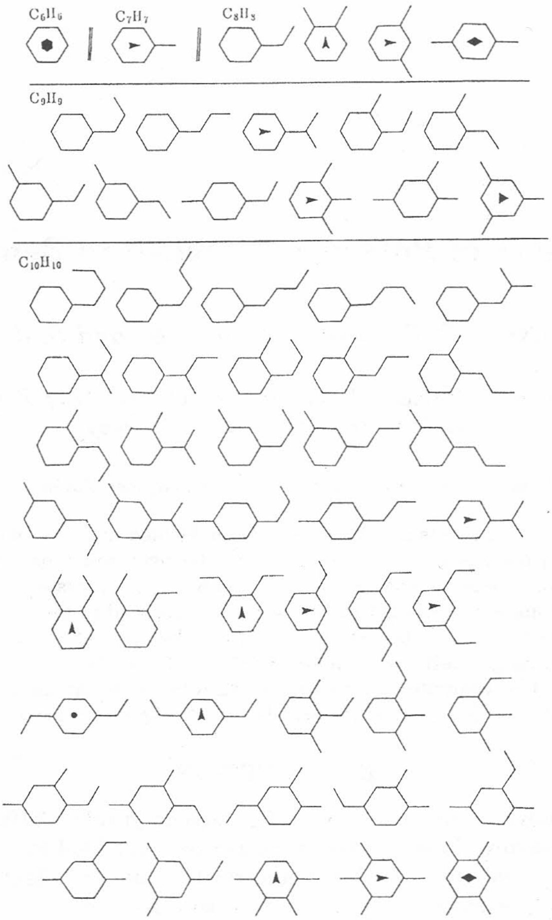

Figure 1. The smallest $C_{a+6}H_{a+6}$ ($0 \le a \le 4$) chemical graphs representing polyenes attached to benzene. Symmetry types are indicated by: hexagon D_{6h}; triangle D_{3h}; rhomb D_{2h}; dot C_{2h}; vertical arrowhead C_{2v}(b); horizontal arrowhead C_{2v}(a).

Auxiliary Functions

The basic function $U_0(x)$ is the generating function which counts the U_a rooted unsymmetrical polyene graphs. These numbers are given by the recurrence relation

$$U_{a+1} = 2U_a + \sum_{i=1}^{a-1} U_i U_{a-i} \; (a>1) \tag{1}$$

with the initial conditions $U_1 = 1$, $U_2 = 2$. The relation (1) was derived in the same way as the corresponding relation for catafusenes.[2,8] By definition, set $U_0 = 1$ (for $a = 0$), corresponding to the empty graph. The generating function for U_a was deduced as:

$$U_0(x) = \sum_{a=0}^{\infty} U_a x^a = \frac{1}{2} x^{-1} \left[1 - (1 - 4x)^{\frac{1}{2}} \right] = 1 + x + 2x^2 + 5x^3 + 14x^4 + 42x^5 + \ldots \quad (2)$$

A similar function, $V_0(x)$, counts the rooted mirror-symmetrical polyene graphs supplemented by the empty graph ($V_0 = 1$). It was found:

$$V_0(x) = 1 + xU_0(x^2) = 1 + x + x^3 + 2x^5 + 5x^7 + 14x^9 + 42x^{11} + \ldots. \quad (3)$$

Functions $U_0(x)$ and $V_0(x)$ are analogous to those for catafusene appendages, which were designated by the same symbols.

Additional auxiliary functions of the form $U_0^{\alpha}(x^{\mu})\, V_0^{\beta}(x^{\nu})$ are of interest. Firstly, some powers of $U_0(x)$ and $V_0(x)$ are needed; then, $\beta = 0$ or $\alpha = 0$, respectively. Specifically,

$$U_0^2(x) = x^{-1}\,[U_0(x) - 1] \quad (4)$$

$$U_0^3(x) = x^{-2}[(1 - x)\, U_0(x) - 1] \quad (5)$$

$$U_0^6(x) = x^{-5}[(1 - 4x + 3x^2)\, U_0(x) - (1 - 3x + x^2)] \quad (6)$$

and

$$V_0^2\,(x) = (1 + 2x)\, U_0\,(x^2)\,. \quad (7)$$

Secondly, three useful mixed functions were worked out as:

$$U_0\,(x^2)\, V(x) = x^{-1}\left[(1 + x)\, U_0\,(x^2) - 1\right] \quad (8)$$

$$U_0\,(x^2)\, V_0^2(x) = x^{-2}\,(1 + 2x)\left[U\,(x^2) - 1\right] \quad (9)$$

$$U_0^2\,(x^2)\, V_0^2\,(x) = x^{-4}\,(1 + 2x)\left[(1 - x^2)\, U_0\,(x^2) - 1\right]. \quad (10)$$

Preliminary Symmetry Considerations

The systems of polyene subgraphs attached to one hexagon are distributed among eight symmetry groups, which are specified in the following together with the symbols used for the corresponding generating functions. The nonplanarity for geometrically nonplanar systems is not taken into acount.

Regular hexagonal (D_{6h}) : $H(x)$
Nonregular hexagonal (C_{6h}) : $X\,(x)$
Regular trigonal (D_{3h}) : $T\,(x) = T_{\mathrm{b}}\,(x) + T_{\mathrm{a}}\,(x)$
Nonregular trigonal (C_{3h}) : $R\,(x)$
Dihedral (D_{2h}) : $D\,(x)$

Centrosymmetrical $(C_{2h}) : C(x)$
Mirror-symmetrical $(C_{2v}) : M(x) = M_b(x) + M_a(x)$
Unsymmetrical $(C_s) : A(x)$

Functions $M_b(x)$ and $M_a(x)$ pertain to the two types of mirror-symmetrical systems, *viz.* C_{2v}(b) and C_{2v}(a), respectively. In a C_{2v}(b) system, the unique twofold symmetry axis (C_2) bisects perpendicularly a central edge, while in C_{2v}(a) the C_2 axis goes through a central vertex. Also, two types, *viz.* D_{3h}(b) and D_{3h}(a) are distinguished among the regular trigonal systems; these types correspond to $T_b(x)$ and $T_a(x)$, respectively. In a D_{3h}(b) system, the three C_2 axes bisect edges of the central hexagon, while in D_{3h}(a) the C_2 axes pass through the hexagon vertices.

The generating function $U_0^6(x)$ counts the systems belonging to different symmetry groups a certain number of times according to the relation

$$U_0^6(x) = H(x) + 2X(x) + 2T(x) + 4R(x) + 3D(x) + 6C(x) + 6M(x) + 12A(x)\,. \tag{11}$$

Hence, for the total number of isomers, the generating function $I(x)$ reads

$$\begin{aligned} I(x) &= H(x) + X(x) + T(x) + R(x) + D(x) + C(x) + M(x) + A(x) = \\ &= \frac{1}{12}\left[U_0^6(x) + 11H(x) + 10X(x) + 10T(x) + 8R(x) + 9D(x) + 6C(x) + 6M(x)\right] \end{aligned} \tag{12}$$

where $A(x)$ is eliminated from the last expression.

Numbers of Symmetrical Isomers

In order to deduce the total numbers of isomers, as given by $I(x)$, it is necessary to enumerate the isomers for all the pertinent symmetry groups except C_s; *cf.* Eq. (12). In general, certain functions of the type $U_0^\alpha(x^\mu)\, V_0^\beta(x^\nu)$ are employed. Such a function pertains to α μ-tuple unsymmetrical polyene subgraphs and β ν-tuple mirror- symmetrical polyene subgraphs as appendages. The total number of appendages, which are of interest in the case at hand, is

$$\alpha\mu + \beta\nu = 6 \tag{13}$$

but the empty graph is counted among the μ or ν appendages by virtue of the definition $U_0 = V_0 = 1$ (see above). The application of the composite generating functions $U_0^\alpha(x^\mu)\, V_0^\beta(x^\nu)$ will be explained by numerous examples in the following. Symmetry D_{6h} is realized by one sextet of identical mirror-symmetrical polyene subgraphs, *i.e.* $\beta = 1$, $\nu = 6$. Hence,

$$H(x) = V_0(x^6) = 1 + x^6\, U_0(x^{12}) \tag{14}$$

where Eq. (3) has been employed. The hexagonal systems (D_{6h} and C_{6h}) are realized by sextets of identical unsymmetrical polyene subgraphs ($\alpha = 1$, $\mu = 6$). However, function $U_0(x^6)$ counts each C_{6h} system twice and each D_{6h} system once. Moreover, there is a one-to-one correspondence between the C_{6h} and D_{3h}(b) systems. Hence,

$$U_0(x^6) = H(x) + 2X(x)\,, \quad X(x) = T_\mathrm{b}(x) = \frac{1}{2}\Big[U_0(x^6) - V_0(x^6)\Big]. \tag{15}$$

The systems of the type D_{3h}(a) are realized by two triplets of mirror-symmetrical polyene subgraphs, *i.e.* $\beta = 2$, $\nu = 3$, but the appropriate function, *viz.* $V_0^2(x^3)$, counts the D_{3h}(a) systems twice and includes the D_{6h} systems once. Hence,

$$V_0^2(x^3) = (1 + 2x^3)\, U_0(x^6) = H(x) + 2T(x)\,, \quad T_\mathrm{a}(x) = \frac{1}{2}\Big[V_0^2(x^3) - V_0(x^6)\Big] \tag{16}$$

where Eqs. (7) and (14) have been employed. In order to find the numbers of C_{3h} systems, one should invoke two triplets of unsymmetrical polyene subgraphs ($\alpha = 2$, $\mu = 3$); in this case, $U_0^2(x^3)$ counts each C_{3h} system four times, together with the systems of higher symmetries according to the scheme below.

$$U_0^2(x^3) = x^{-3}\Big[U_0(x^3) - 1\Big] = H(x) + 2X(x) + 2T_\mathrm{b}(x) + 2T_\mathrm{a}(x) + 4R(x)\,,$$

$$R(x) = \frac{1}{4}\Big[U_0^2(x^3) - V_0^2(x^3) - 2U_0(x^6) + 2V_0(x^6)\Big] \tag{17}$$

Symmetry D_{2h} is realized by one quartet of unsymmetrical polyene subgraphs combined with a pair of mirror- symmetrical polyene subgraphs. The pertinent systems are counted precisely by $U_0(x^4)\, V_0(x^2)$, but together with the D_{6h} systems. Hence,

$$U_0(x^4)\, V_0(x^2) = x^{-2}\Big[(1 + x^2)\, U_0(x^4) - 1\Big] = H(x) + D(x)\,, \quad D(x) = U_0(x^4)\, V_0(x^2) - V_0(x^6) \tag{18}$$

where Eq. (8) has been employed, as well as Eq. (14) again.

In order to enumerate the C_{2h} systems, consider three pairs of unsymmetrical polyene subgraphs, giving rise to function $U_0^3(x^2)$. It counts systems of several symmetries various numbers of times according to:

$$U_0^3(x^2) = x^{-4}\Big[(1 - x^2)\, U_0(x^2) - 1\Big] = H(x) + 2X(x) + 3D(x) + 6C(x)\,,$$

$$C(x) = \frac{1}{6}\Big[U_0^3(x^2) - 3U_0(x^4)\, V_0(x^2) - U_0(x^6) + 3V_0(x^6)\Big]. \tag{19}$$

Function $U_0^3(x^2)$ counts also the C_{2v}(b) systems; it has been found:

$$U_0^3(x^2) = H(x) + 2T_b(x) + D(x) + 2M_b(x) ,$$

$$M_b(x) = \frac{1}{2}\left[U_0^3(x^2) - U_0(x^4)\, V_0(x^2) - U_0(x^6) + V_0(x^6)\right]. \tag{20}$$

Finally, the C_{2v}(a) systems should be considered. They are realized by two pairs of unsymmetrical polyene subgraphs and two single mirror-symmetrical polyene subgraphs. Hence, function $U_0^2(x^2)\, V_0^2(x)$ from Eq. (10) is to be used. It was found, similarly to Eq. (20),

$$U_0^2(x^2)\, V_0^2(x) = H(x) + 2T_a(x) + D(x) + 2M_a(x) ,$$

$$M_a(x) = \frac{1}{2}\left[U_0^2(x^2)\, V_0^2(x) - V_0^2(x^3) - U_0(x^4)\, V_0(x^2) + V_0(x^6)\right]. \tag{21}$$

It is evident that the C_{2v}(b) systems, like those of C_{2h} and D_{2h}, occur only when a is even-numbered, while the C_{2v}(a) systems occur for all $a > 0$. However, for an even-numbered a, one has the same number of C_{2v}(a) and C_{2v}(b) systems.

Total Number of Isomers

The expressions from Eqs. (14) – (21) were inserted into (12). Then, the following equation emerged for the total number of isomers:

$$I(x) = \frac{1}{12}\left[U_0^6(x) + 4U_0^3(x^2) + 3U_0^2(x^2)\, V_0^2(x) + 2U_0^2(x^3) + 2U_0(x^6)\right] \tag{22}$$

which is compatible with Example 4 of Zhang *et al.*[7] A further elaboration of Eq. (22), inserting the expressions in terms of $U_0(x^{\mu})$ for every term, yields:

$$I(x) = \frac{1}{12}\, x^{-5}\, [(1 - 4x + 3x^2)\, U_0(x) + x(7 + 6x)(1 - x^2)\, U_0(x^2)$$

$$+ 2x^2\, U_0(x^3) + 2x^5\, U_0(x^6) - (1 + 4x + 9x^2)] . \tag{23}$$

Ultimately, we give function $I(x)$ in its explicit form, as derived from Eq. (23) by means of (2).

$$I(x) = \frac{1}{24}\, x^{-6}\, [12(1 - x^2 - 2x^3) - (1 - 4x + 3x^2)(1 - 4x)^{1/2} - (7 + 6x)(1 - x^2)(1 - 4x^2)^{1/2}$$

$$- 2(1 - 4x^3)^{1/2} - 2(1 - 4x^6)^{1/2}] \tag{24}$$

The total numbers of isomers from the above analysis are given in Table I to $a = 12$. The distribution into symmetry groups is included.

TABLE I

Numbers of $C_{a+6}H_{a+6}$ isomers representing polyenes attached to benzene

a	D_{6h}	C_{6h}	D_{3h}	C_{3h}	D_{2h}	C_{2h}	C_{2v}	C_s	Total
0	1	0	0	0	0	0	0	0	1
1	0	0	0	0	0	0	1	0	1
2	0	0	0	0	1	0	2	1	4
3	0	0	1	0	0	0	2	8	11
4	0	0	0	0	1	1	8	31	41
5	0	0	0	0	0	0	9	132	141
6	1	0	0	1	1	4	26	500	533
7	0	0	0	0	0	0	28	1924	1952
8	0	0	0	0	2	14	88	7216	7320
9	0	0	1	3	0	0	89	27194	27287
10	0	0	0	0	5	47	292	101978	102322
11	0	0	0	0	0	0	297	383319	383616
12	0	1	2	9	5	164	994	1440970	1442145

STYRENOIDS

The algebraic solution (24) and the corresponding numbers (Table I) allow for systems with overlapping vertices. We shall refer to the pertinent systems without overlapping vertices as geometrically planar. It is also reasonable to use the term *styrenoids* for the geometrically planar systems consisting of polyene subgraphs attached to a hexagon. The benzene graph is reckoned among the styrenoids as a trivial system of this kind. Styrene (C_8H_8) represents a nontrivial styrenoid as a prototype of great interest in organic chemistry. It has been subjected to many studies during a long period of time, and a modern structural investigation of this molecule has appeared very recently.[9]

TABLE II

Numbers of $C_{a+6}H_{a+6}$ geometrically planar isomers representing polyenes attached to benzene (styrenoids)

a	D_{6h}	D_{3h}	C_{3h}	D_{2h}	C_{2h}	C_{2v}	C_s	Total
0	1	0	0	0	0	0	0	1
1	0	0	0	0	0	1	0	1
2	0	0	0	1	0	2	1	4
3	0	1	0	0	0	2	8	11
4	0	0	0	1	1	8	31	41
5	0	0	0	0	0	9	129	138
6	1	0	1	1	4	25	470	502
7	0	0	0	0	0	27	1720	1747
8	0	0	0	2	14	80	6069	6165
9	0	1	3	0	0	77	21339	21420

A computer program was implemented in order to generate and enumerate the styrenoids. The results that were obtained to $a = 9$, are entered in Table II. The distribution into symmetry groups is included therein; it was determined by a special algorithm in the same way as in the case of benzenoids.[10]

GEOMETRICALLY NONPLANAR SYSTEMS

The numbers in Table III were obtained by subtracting the numbers of (geometrically planar) styrenoids in Table II from the totals of Table I. Thus, the numbers in Table III count the pertinent geometrically nonplanar systems, *viz.* those which contain at least one pair of overlapping vertices when drawn on the background of the hexagonal lattice.

TABLE III

Numbers of $C_{a+6}H_{a+6}$ geometrically nonplanar isomers representing polyenes attached to benzene

a	C_{2v}	C_s	Total
5	0	3	3
6	1	30	31
7	1	204	205
8	8	1147	1155
9	12	5855	5867

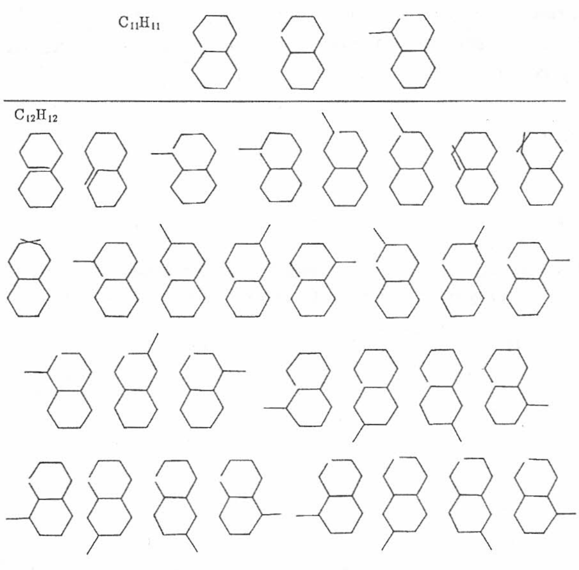

Figure 2. The smallest geometrically nonplanar systems of polyene subgraphs attached to one hexagon.

Several of the numbers in Table III can be checked by systematic generations on the pen-and-paper level. Firstly, one finds the 3 and 31 systems for $a = 5$ ($C_{11}H_{11}$) and $a = 6$ ($C_{12}H_{12}$) respectively, as shown in Figure 2. Secondly, the generation of C_{2v} systems was continued through $a = 9$, with the results displayed in Figure 3. The smallest C_{2h} systems of the category under consideration occur for $a = 10$, as shown in Figure 4. This figure includes the smallest of such systems belonging to the D_{2h} symmetry; it has $a = 12$. The a value must be increased further in order to produce the geometrically nonplanar systems with higher symmetries (trigonal and hexagonal), but it is not difficult to draw the smallest of such systems. We omit the details.

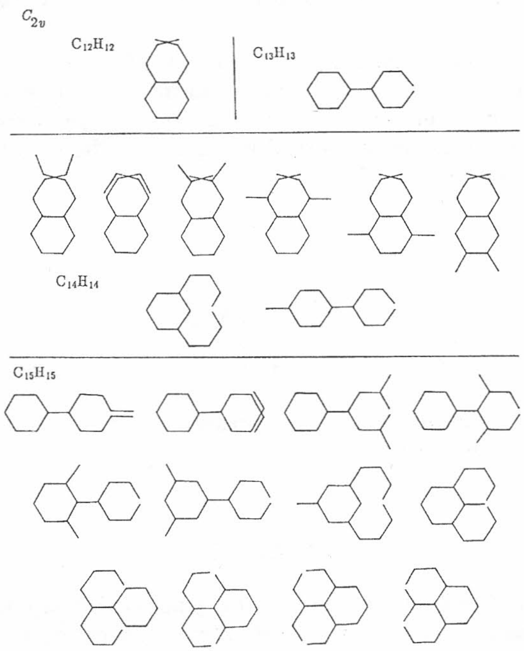

Figure 3. The smallest C_{2v} geometrically nonplanar systems of polyene subgraphs attached to one hexagon.

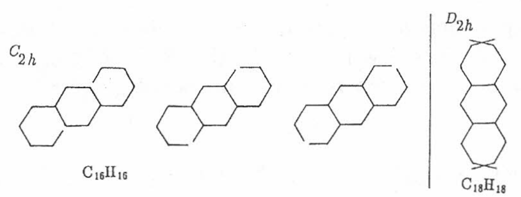

Figure 4. The smallest C_{2h} and D_{2h} geometrically nonplanar system of polyene subgraphs attached to one hexagon.

VALENCE STRUCTURES OF STYRENOIDS

The existence or non-existence of valence structures for the styrenoids is of prime interest in chemistry. Therefore, the generated styrenoids (*cf.* Table II) were classified according to the valence structures. There are three possibilities specified in the following.

K = 0: no valence structure, corresponding to a radical;

K = 1: one valence structure with all double and single bonds fixed;

K = 2: two valence structures, which arise from an aromatic sextet for the benzene ring.

These three cases were recognized by an extra algorithm on the basis of the determinant of the adjacency matrix, which is K^2; hence, it may assume the value of 0, 1 or 4.

All styrenoids with odd-carbon formulas, *viz.* C_nH_n where n is odd, have obviously K = 0. A styrenoid with an even-carbon formula (C_nH_n where n is even), on the other hand, may have either K = 0, 1 or 2. The C_8H_8 systems (a = 2) furnish elucidating examples, which are displayed in Figure 5. The results of the classified enumeration are shown in Table IV.

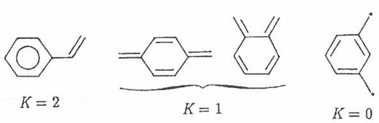

Figure 5. The four C_8H_8 styrenoid isomers, which represent: styrene with K = 2; two molecules with K = 1; one radical with K = 0.

APPENDIX

The J_m numbers of isomers of free polyene graphs with m edges (including the geometrically nonplanar systems) are counted by a generating function as:

$$J(x) = \sum_{m=0}^{\infty} J_m x^m = 1 + x + x^2 + 3x^3 + 4x^4 + 12x^5 + 27x^6 + \dots \quad (25)$$

The following expression for function (25) was deduced, following basically the methods of Harary and Read,[2] which imply the Redfield-Pólya theorem[4] and the method of Otter[11] for passing from rooted to unrooted graphs.

$$J(x) = \frac{1}{24} x^{-3} \left[12(1 + x - 2x^2) + (1 - 4x)^{3/2} - 3(3 + 2x)(1 - 4x^2)^{1/2} - 4(1 - 4x^3)^{1/2}\right] \quad (26)$$

A report on the details of the derivation of Eq. (26) is under preparation.

TABLE IV

Numbers of styrenoid isomers classified according to valence structures

a	Formula	*K*	D_{6h}	D_{3h}	C_{3h}	D_{2h}	C_{2h}	C_{2v}	C_s	Total
0	C_6H_6	2	1	0	0	0	0	0	0	1
1	C_7H_7	0	0	0	0	0	0	1	0	1
2	C_8H_8	0	0	0	0	0	0	1	0	1
		1	0	0	0	1	0	1	0	2
		2	0	0	0	0	0	0	1	1
3	C_9H_9	0	0	1	0	0	0	2	8	11
4	$C_{10}H_{10}$	0	0	0	0	1	0	2	11	14
		1	0	0	0	0	0	1	12	13
		2	0	0	0	0	1	5	8	14
5	$C_{11}H_{11}$	0	0	0	0	0	0	9	129	138
6	$C_{12}H_{12}$	0	0	0	0	1	0	10	211	222
		1	1	0	0	0	4	15	146	166
		2	0	0	1	0	0	0	113	114
7	$C_{13}H_{13}$	0	0	0	0	0	0	27	1720	1747
8	$C_{14}H_{14}$	0	0	0	0	0	7	39	3220	3266
		1	0	0	0	0	0	9	1731	1740
		2	0	0	0	2	7	32	1118	1159
9	$C_{15}H_{15}$	0	0	1	3	0	0	77	21339	21420

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SAŽETAK

Izomeri poliena vezanih na benzen

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Polienski graf jest stablo koje se dade smjestiti na šesterokutnu mrežu. Razmatraju se polienski grafovi vezani na jedan šesterokut, pri čemu se dopušta prekrivanje grana i/ili čvorova (*geometrijski* neplanarnih sustava). Nađeno je potpuno matematičko rješenje (u obliku generirajućih funkcija) za broj izomera takovih grafova. Za pripadne, geometrijski planarne sustave – sterinoide – broj izomera nađen je računalom. U dodatku je dana generirajuća funkcija za broj izomera slobodnih polienskih grafova.