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Enumeration of the Isomers of Phenylenes

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Summary. The [h]phenylene $C_{6h}H_{2h+4}$ isomers are enumerated up to $h = 12$. The numbers are compared with old and new data for C_nH_s isomers of benzenoids, fluoranthenoids and biphenylenoids.

Keywords. Phenylene; Isomer enumeration.

Anzahl möglicher Isomerer von Phenylenen

Zusammenfassung. Die Anzahl der [h]Phenylen-Isomeren $C_{6h}H_{2h+4}$ wurde bis $h = 12$ ausgewertet. Die Zahlen wurden mit alten und neuen Daten für C_nH_s-Isomere von Benzenoiden, Fluoranthenoiden und Biphenyloiden verglichen.

Introduction

Phenylenes are non-benzenoid polycyclic conjugated hydrocarbons, which are currently studied with great interest. The smallest member of these compounds, viz. [2]phenylene or biphenylene, is long known [1]; for details of its chemistry see the recent review [2]. A number of higher members of the phenylene series have also been synthesized (either as the parent hydrocarbons or their derivatives) [3–9]. The synthesis of a certain phenylene may represent a route to a synthesis of antikekulene [5, 9, 10], a macrocyclic conjugated hydrocarbon, that can be viewed as a circular [6]phenylene. This synthesis has so far not been achieved. A large number of theoretical considerations of the π-electron structure and geometry of both phenylenes [11–17] and antikekulene [11, 14, 18, 19] have recently been offered.

In the present work the isomers of phenylenes are treated. Their numbers up to twelve hexagons have been computed.

Definitions and Some Topological Properties

The carbon-atom skeleton of a phenylene molecule is represented by means of a simply connected, geometrically planar construction, which we call a "phenylene system". A phenylene system consists of congruent regular hexagons. Two such hexagons are either joined to each other through a square, or are not connected at all. A phenylene containing h hexagons is referred to as an [h]phenylene. The aim

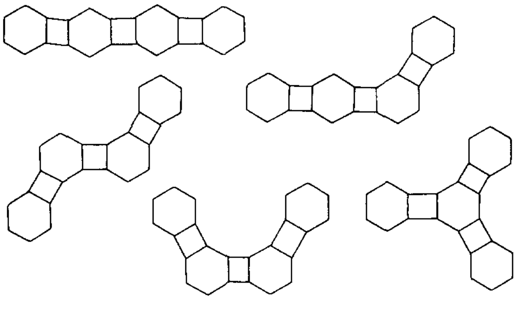

Fig. 1. The five isomers of phenylenes (nonisomorphic systems) with h (number of hexagons) = 4

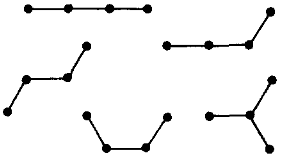

Fig. 2. Five dualists which represent the nonisomorphic phenylenes with $h = 4$ (Fig. 1) and at the same time the five isomers of catabenzenoids with $h = 4$

of this work is to establish the number of distinct [h]phenylene isomers. We accomplished this task for $h = 2, 3, \ldots, 12$.

The phenylene systems have no internal vertices, a property which they share with the catacondensed polyhexes. In fact, each [h]phenylene is associated with a unique h-cyclic catafusene [20]. Here a catafusene is defined as a simply connected catacondensed polyhex. It is implied that this polyhex may be helicenic. A catafusene which is not helicenic (and therefore geometrically planar) is a catabenzenoid. For precise definitions in the classification of polyhexes, the reader may consult a recent review [21]. Also a theoretical study of helicenic polyhexes (helicenes), which has been initiated [22], is of relevance to the present work.

The catafusene which is associated with a given phenylene, has been referred to as the hexagonal squeeze [17] of the phenylene is question. Figure 1 shows the five nonisomorphic [4]phenylenes. The hexagonal squeeze of each of these systems, viz. the five nonisomorphic catafusenes with $h = 4$ (which also are catabenzenoids), have been depicted many times [21] and shall not be reproduced here. Instead we show the corresponding dualists (Fig. 2), where each vertex (black dot) represents a hexagon. A dualist of a phenylene represents at the same time its squeeze. In these dualists the angles between incident edges can only be 180° or 120°.

The correspondence between phenylenes and catafusenes does not go the other way; there does not exist a phenylene for every catafusene. More precisely, one finds a unique [h]phenylene for every catabenzenoid with $h \geqslant 2$ and for some, but not for all catahelicenes. In the latter case one would have to allow for helicenic (geometrically nonplanar) systems, which fall outside the strict definition of phenylenes (see above). In this connection we shall distinguish between "soft" and "hard" helicenes. Let a soft helicene be defined as a simply connected polyhex where at least two edges overlap when drawn in a plane, but no hexagons overlap. In a hard helicene at least two hexagons overlap when drawn in a plane. Now the correlations with helicenes are simple: every soft catahelicene corresponds to a unique phenylene, but there is no phenylene counterpart to a hard helicene.

In summary, the phenylenes are associated in a one-to-one correspondence with the h-cyclic catabenzenoids and soft catahelicenes. Consequently, the number of

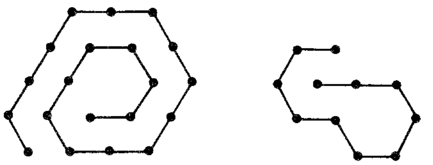

Fig. 3. Two dualists for soft catahelicenes

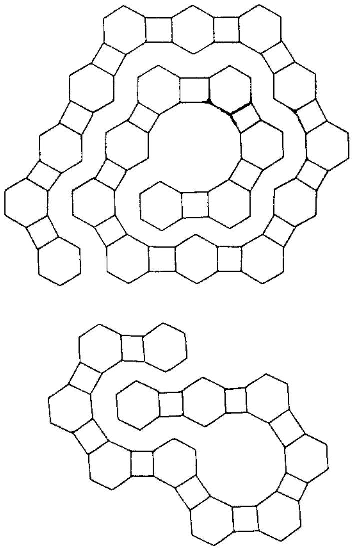

Fig. 4. The phenylenes which are represented by the dualists of Fig. 3

[h]phenylenes is equal to the number of h-cyclic catabenzenoids plus the number of h-cyclic soft catahelicenes.

It is noted that any number of edges of a hexagon in a soft helicene may overlap with edges of other hexagons. The left-hand part of Fig. 3 shows a dualist of a soft catahelicene, where one hexagon is completely surrounded by other hexagons so that all its edges overlap. This situation was achieved after a kind of spiral generation of the system up to $h = 20$. The same feature can be achieved for a smaller system with only $h = 11$ as shown in the right-hand part of Fig. 3. The phenylenes which are represented by the dualists of Fig. 3, are displayed in Fig. 4.

Results and Discussion

Enumeration of Catafusenes and Phenylenes

Catafusenes

According to the above discussion the enumeration of phenylenes is closely connected with the enumeration of catafusenes. A complete mathematical solution is available for the numbers of catafusenes (including all catahelicenes). It was first given by Harary and Read [21, 23] in terms of a generating function. The explicit expressions of Balaban and Harary [21, 24] for the numbers of unbranched catafusenes include the distributions into symmetry groups. A classification of the total numbers of catafusenes into symmetries was achieved later [25, 26].

The numbers of catabenzenoids up to $h = 15$ were produced by computer programming during several years of current research; the recent review [21] should be consulted for references to the original works. These numbers are also classified into symmetry groups and given for the branched and unbranched systems separately.

On subtracting the numbers of catafusenes from those of catabenzenoids one obtains the numbers of catahelicenes, but without the distinction between the soft and hard helicenes. This piece of information is needed in order to deduce the numbers of phenylenes.

Soft Catahelicenes and Phenylenes

A computer program based on a code called DAST (dualist angle-restricted directional information) [27] has been used previously for generating and enu-

Table 1. Numbers of unbranched [*h*]phenylenes

h	D_{2h}	C_{2h}	C_{2v}	C_s	Total unbranched
2	1	0	0	0	1
3	1	0	1	0	2
4	1	1	1	1	4
5	1	1	4	4	10
6	1	4	4	16	25
7	1	4	12	52	69
8	1	13	11	167	192
9	1	13	35	506	555
10	1	40	33	1529	1603
11	1	40	99	4537	4677
12	1	120	92	13428	13641

Table 2. Numbers of branched [*h*]phenylenes

h	D_{3h}	C_{3h}	D_{2h}	C_{2h}	C_{2v}	C_s	Total branched
4	1	0	0	0	0	0	1
5	0	0	0	0	1	1	2
6	0	0	1	0	4	7	12
7	1	1	1	0	4	46	53
8	0	0	1	4	20	222	247
9	0	0	1	4	27	1054	1086
10	2	4	4	26	77	4671	4784
11	0	0	4	26	121	20370	20521
12	0	0	4	146	326	87044	87520

merating catabenzenoids [21, 28]. This program was modified in order to include the soft catahelicenes. Since the numbers of catabenzenoids are known up to large h values ($h = 15$) these systems were sifted out from those generated by the modified program. In this way the elimination of duplicated systems could be simplified substantially. In conclusion, the soft catahelicenes were generated and enumerated up to $h = 12$, including the symmetry distributions and distinction between branched and unbranched systems. The corresponding known numbers of catabenzenoids [21] were added in order to produce the total numbers of phenylenes. These latter results are shown in Tables 1 and 2 for the unbranched and branched systems, respectively.

Hard Catahelicenes and Phenylenes

An alternative route to the enumeration of phenylenes is outlined in the following. Take the numbers of catafusenes and subtract the corresponding numbers of hard catahelicenes. All the information on catafusenes which is needed for this purpose, viz. their numbers including classifications, is known [21, 29]. Some of the smallest hard catahelicenes were generated by hand, viz. those for $h \leqslant 9$; see Fig. 5. These depictions are consistent with the appropriate numbers in Tables 3 and 4, which pertain to the unbranched- and branched hard catahelicenes, respectively. Now the numbers of unbranched catafusenes may simply be retrieved on adding the appropriate numbers from Tables 1 and 3. Similarly for the branched catafusenes from Tables 2 and 4.

Table 3. Numbers of unbranched hard catahelicenes

h	C_{2h}	C_{2v}	C_s	Total unbranched
7	0	1	0	1
8	0	2	2	4
9	0	5	14	19
10	0	7	71	78
11	0	22	303	325
12	1	29	1213	1243

Table 4. Numbers of branched hard catahelicenes

h	C_{2h}	C_{2v}	C_s	Total branched
8	0	1	2	3
9	0	3	26	29
10	0	13	215	228
11	0	27	1484	1511
12	2	91	9133	9226

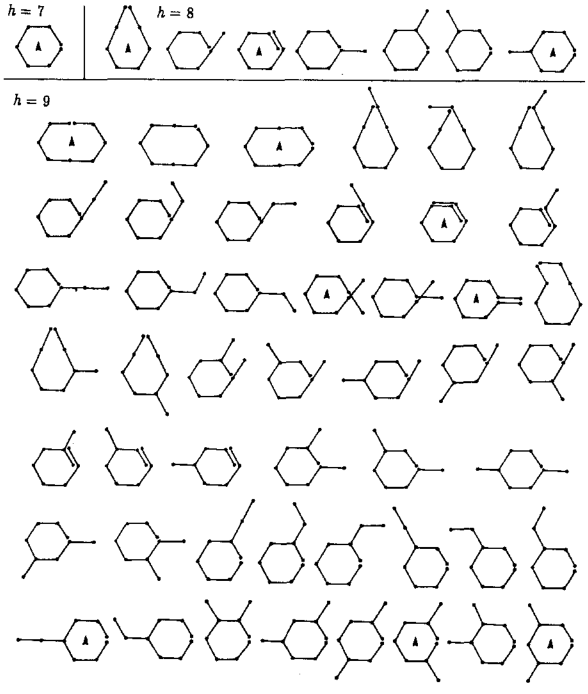

Fig. 5. All nonisomorphic hard cata-helicenes with $h \leqslant 9$. The C_{2v} systems are marked with arrow heads

Enumeration of Other Classes of Chemical Isomers

An [h]phenylene corresponds to a hydrocarbon with the formula $C_{6h}H_{2h+4}$. The present work is therefore an enumeration of the chemical (C_nH_s) isomers for these systems. The eleven C_nH_s formulas in question, together with the total numbers of phenylene isomers, are listed in Table 5. It is of interest to compare these numbers with other data of C_nH_s isomers

The benzenoids [36] (simply connected, geometrically planar polyhexes) represent an important class of polygonal systems, which correspond to polycyclic

Table 5. Numbers of C_nH_s isomers of phenylenes, benzenoids, fluoranthenoids and biphenylenoids

Formula	Phenylenes	Benzenoids	Fluoranthenoids	Biphenylenoids
$C_{12}H_8$	1	0	1[a]	3
$C_{18}H_{10}$	2	0	3[a]	8
$C_{24}H_{12}$	5	1[b]	17[c]	44
$C_{30}H_{14}$	12	4[b]	111	310
$C_{36}H_{16}$	37	26[d]	924	2293
$C_{42}H_{18}$	122	187[d]	†	†
$C_{48}H_{20}$	439	1570[d]	†	†
$C_{54}H_{22}$	1641	13286[d]	†	†
$C_{60}H_{24}$	6387	116648[d]	†	†
$C_{66}H_{26}$	25198	1029521[d]	†	†
$C_{72}H_{28}$	101161	†	†	†

[a] Ref. 33; [b] Ref. 31; [c] Ref. 37; [d] Ref. 32; † Unknown

conjugated hydrocarbons. The first two of the phenylene C_nH_s formulas, viz. $C_{12}H_8$ and $C_{18}H_{10}$ (cf. Table 5), are not benzenoid formulas. However, this is the case for the other ($s > 10$) formulas. The numbers of the relevant benzenoid isomers are known up to $s = 26$ [21, 31, 32] and are entered in Table 5. It is interesting to observe that for $s \leqslant 16$ there are more C_nH_s isomers of phenylenes than those of benzenoids. However, for $s > 16$ the situation is reversed. These benzenoids are pericondensed; for instance, $C_{24}H_{12}$ pertains to coronene, which is the unique benzenoid with this formula. In general, $C_{6h}H_{2h+4}$ ($h > 3$) pertains to benzenoid isomers with n_i (the number of internal vertices) $= 2h - 2$.

Other classes of polygonal systems, which are of interest, are for instance the fluoranthenoids [33, 34] and biphenylenoids [35]. Together with the benzenoids these classes are special cases of simply connected, geometrically planar mono-q-polyhexes [36]. A mono-q-polyhex consists of exactly one q-gon and otherwise hexagons. Benzenoids, fluoranthenoids and biphenylenoids correspond to $q = 6$, 5 and 4, respectively. Hence biphenylene is a member of biphenylenoids (mono-4-polyhexes), but none of the higher phenylenes belong to this class. All the phenylene formulas, viz. $C_{6h}H_{2h+4}$ ($h \geqslant 2$), are also fluoranthenoid- and biphenylenoid formulas. A mono-q-polyhex with the formula $C_{6h}H_{2h+4}$ has $n_i = 2h + q - 8$.

The numbers of fluoranthenoid isomers for the first three C_nH_s formulas of Table 5($s = 8$, 10, 12) have been given previously [33, 37]. They are quoted in Table 5 together with two supplementary numbers. The five entries for biphenylenoids are new.

Concluding Remarks

In the present work the C_nH_s isomers of a new class of polygonal systems, namely [h]phenylenes, were enumerated, $n = 6h$, $s = 2h + 4$. The results are compared with the numbers of isomers for other classes of polygonal systems (cf Table 5). The open places in this table suggest that there is more work to be done in this area. Additional classes of polygonal systems, not included in the table, may also be of interest.

Systematic studies on all kinds of polygonal systems, which represent completely condensed polycyclic conjugated hydrocarbons, have recently been initiated [38, 39]. Here a polygonal system is defined as a geometrical construction of polygons of any sizes, where any two polygons either share exactly one edge, or they are disconnected. For this rather general class of systems there were found to be [40] 40 $C_{12}H_8$ isomers and 13197 $C_{18}H_{10}$ isomers. For these two formulas, Table 5 accounts for only 4 and 13 isomers, respectively.

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