

Benzenoids with Dihedral Symmetry. Survey and First Enumeration of Isomers

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A brief introduction is given to the theory of benzenoids, with an emphasis on those systems with D_{2h} (dihedral) symmetry. The corresponding chemically known benzenoid hydrocarbons are surveyed. The C_nH_m formulae for D_{2h} benzenoids are treated, and results of an isomer enumeration of these formulae are reported. It is found statistically that, in a sense, the dihedral benzenoid hydrocarbons are over-represented among synthesized benzenoid hydrocarbons.

A benzenoid hydrocarbon is a polycyclic aromatic hydrocarbon (PAH) with exclusively six-membered (benzenoid) rings. PAH compounds are ubiquitous both in nature and the laboratory. They are of great interest in organic and industrial chemistry, not least in the oil industry. PAHs have also been studied extensively in physical and theoretical chemistry. Only a few of the available handbooks or monographs on PAHs can be cited here.^{1–4} The importance of PAHs in environmental chemistry is also clearly documented in these books; benzenoid hydrocarbons, in particular, are known to be serious pollutants. Also, the carcinogenic nature of these compounds is well known. Finally we may mention the astrophysical interest in PAHs: there is strong evidence for the occurrence of these compounds in interstellar space.⁵

The enumeration of isomers is a well established branch of chemistry, especially in organic chemistry and now also in computational chemistry. From the above discussion it should be clear that the enumeration of isomers of benzenoid hydrocarbons is of prime interest. Nevertheless, while the studies of alkane isomers, for instance, started more than hundred years ago,⁶ systematic enumeration of benzenoid hydrocarbons are relatively recent.^{7–9}

The present work is a contribution to the enumeration of certain classes of benzenoid systems.⁴ These geometrical objects have been defined stringently in mathematical chemistry (see below) and have chemical counterparts in the benzenoid hydrocarbons. The classification of benzenoid systems into symmetry groups is very useful.¹⁰ Here systems with D_{2h} (dihedral) symmetry are treated. Surprisingly many benzenoid hydrocarbons are known which correspond to these benzenoid systems, and several important key molecules are among them, e.g. naphthalene, anthracene, pyrene, perylene and ovalene.

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Theoretical introduction

Definition of a benzenoid system. A benzenoid system **B**, or simply a benzenoid, is defined (among several alternatives)⁴ as a cycle on a hexagonal lattice and the interior of this cycle; cf. Fig. 1. The hexagonal lattice emerges by tiling the plane with congruent regular hexagons. In consequence, **B** consists of congruent regular hexagons which are connected. The cycle on the hexagonal lattice is referred to as the perimeter (or boundary) of **B**.

Invariants. A benzenoid system can be interpreted as a set of vertices and edges; each hexagon possesses six vertices and six edges. As such the benzenoid represents a graph. It is among the molecular graphs which have been introduced in mathematical chemistry. In fact, graph theory has become an important tool in this relatively new branch of science.^{11,12}

A benzenoid **B** possesses a number of characteristic quantities called invariants. The number of vertices (n) and number of edges (m) are among them. Another important invariant is the number of hexagons, h . The internal vertices of **B** constitute a subset of the vertices. By definition, an internal vertex is shared by three hexagons (cf. Fig. 1). Vertices of **B** which are not internal are called external; they are found on the perimeter of **B**. The numbers of internal and external vertices of **B** are identified by the symbols n_i and n_e , respectively ($n_i + n_e = n$). Here n_e also indicates the number of edges of the perimeter and is sometimes called the perimeter length. Another subdivision of the vertices of **B** is based on the degree of a vertex. It is the number of edges which meet at the vertex in question. In any benzenoid a vertex can only have a degree of either two or three. Obviously an internal vertex always has degree three. An external vertex may be of both kinds. The number of vertices of degree two (on the perimeter of **B**), another important invariant, is often denoted by s .

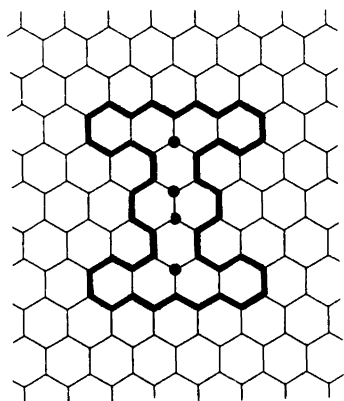


Fig. 1. A benzenoid defined by its perimeter (boundary) on the hexagonal lattice. Internal vertices are marked with black dots.

The following important connections between different invariants of a benzenoid exist. First one has eqn. (1), and conversely eqn. (2). For the number of edges one has eqn. (3), and finally, one has for the perimeter length eqn. (4).

$$n = 4h - n_i + 2, \quad s = 2h - n_i + 4 \quad (1)$$

$$h = \frac{1}{2}(n - s) + 1, \quad n_i = n - 2s + 6 \quad (2)$$

$$m = 5h - n_i + 1 = \frac{1}{2}(3n - s) \quad (3)$$

$$n_e = 4h - 2n_i + 2 = 2s - 6 \quad (4)$$

Example. The benzenoid B of Fig. 1 has $n = 46$, $m = 57$, $h = 12$, $n_i = 4$, $n_e = 42$, $s = 24$.

Connection between benzenoid systems and benzenoid hydrocarbons. A benzenoid system B is defined so that a benzenoid hydrocarbon, chemically known or unknown, always corresponds to B. The carbon atoms correspond to the vertices of B, while the carbon-carbon bonds correspond to the edges. The vertices of degree two and three have their counterparts in the secondary and tertiary carbon atoms, respectively.

A benzenoid hydrocarbon which corresponds to a benzenoid system B has clearly n carbon atoms in total and s secondary carbon atoms (hence the symbol s). This number (s) is also the number of hydrogens. Consequently, a formula C_nH_s may be associated with any B. Example: The benzenoid B of Fig. 1 has the formula $C_{46}H_{24}$, but so far no benzenoid hydrocarbon with this formula is known chemically. Because of the close connection between benzenoid systems and benzenoid hydrocarbons it is also usual to attach the chemical names (naphthalene, pyrene, etc.) to the appropriate benzenoid systems.

Survey of dihedral benzenoid hydrocarbons

Introductory remarks. A benzenoid system may belong to one of the eight symmetry groups:⁴ D_{6h} , C_{6h} , D_{3h} , C_{3h} ,

D_{2h} , C_{2h} , C_{2v} , C_s . In the present work the benzenoids of symmetry D_{2h} are treated. Here we give a survey of the corresponding benzenoid hydrocarbons which are known in organic chemistry. When they are referred to as 'dihedral benzenoid hydrocarbons' it should be emphasized that the dihedral (D_{2h}) symmetry refers to the benzenoid systems, while it does not always apply to the actual structures of the molecules in question. Nevertheless, most of the known dihedral benzenoid hydrocarbons do exhibit D_{2h} symmetry, although the benzenoid rings are usually distorted from regular hexagons. There are exceptions when the hydrocarbon is distorted from planarity, a condition which automatically forbids the D_{2h} symmetry.

The present listing of chemically known dihedral benzenoid hydrocarbons is based on the compilations of Dias.^{3,13}

Catacondensed benzenoids. A benzenoid system is said to be catacondensed when it does not possess any internal vertex ($n_i = 0$). Correspondingly, one speaks about catacondensed benzenoid hydrocarbons. A catacondensed benzenoid with h hexagons has the general formula $C_{4h+2}H_{2h+4}$. Catacondensed benzenoids of D_{2h} symmetry consist of the class of linear polyacenes ($h > 1$) and of linear polyacenes with additions at their terminal hexagons.¹⁴ These two classes represent unbranched and branched catacondensed benzenoids, respectively.

The linear polyacenes are known up to $h = 7$: naphthalene, anthracene, naphthacene, pentacene, hexacene, heptacene. As to the branched systems under consideration, four homologs of the series defined in Fig. 2 are known. They pertain to $j = 2, 3, 4, 5$: $C_{26}H_{16}$ dibenzo- $[g,p]$ chrysene, $C_{30}H_{18}$ tetrabenzo- $[a,c,h,j]$ anthracene, $C_{34}H_{20}$ tetrabenzo- $[a,c,j,l]$ naphthacene, $C_{38}H_{22}$ tetrabenzo- $[a,c,l,n]$ pentacene. The general formula in terms of j is included in Fig. 2.

Pyrene, perylene, and these two benzenoids with additions. A benzenoid system or hydrocarbon which is not catacondensed ($n_i > 0$), is said to be pericondensed. Benzenoids with two internal vertices each ($n_i = 2$) and symmetry D_{2h} can only consist of $C_{16}H_{10}$ pyrene (1), $C_{20}H_{12}$ perylene (5), or one of these systems with catacondensed appendages (Fig. 3). A benzenoid B with catacondensed appendage(s) is sometimes referred to as an annelated B. In the classes considered here an annelated pyrene must have two appendages, while an annelated perylene must have four.

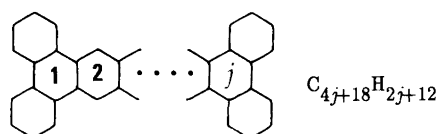


Fig. 2. A homologous series of branched catacondensed benzenoids.

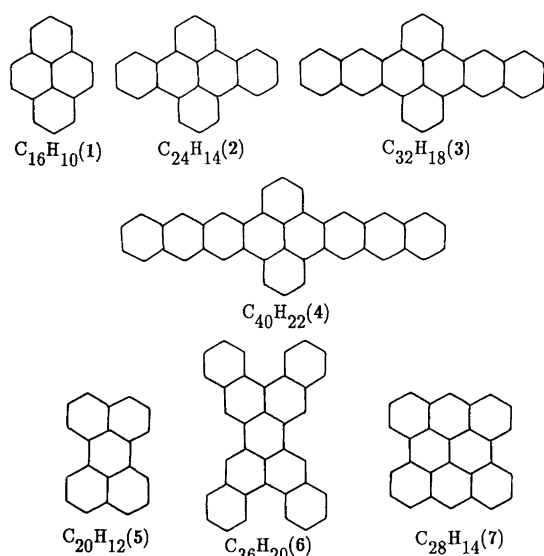


Fig. 3. Pyrene (1), perylene (5) and some of their derivatives.

Pyrene and perylene are well known and important chemical substances. The three known annelated pyrenes among dihedral benzenoid hydrocarbons are: $C_{24}H_{14}$ dibenzo[*fg,op*]naphthacene (2), $C_{32}H_{18}$ dibenzo[*hi,uv*]-hexacene (3) and $C_{40}H_{22}$ dibenzo[*jk,a'b'*]octacene (4) (Fig. 3). They are members of a homologous series with the general formula $C_{8j+16}H_{4j+10}$ for $j=1, 2, 3$ ($j=0$ represents pyrene itself). The only known annelated perylene, which is depicted in Fig. 3, corresponds to the hydrocarbon $C_{36}H_{20}$ dinaphtho[1,2,3'-*fg*:1'2'3-*qr*]-pentacene (6).

Bisanthene. $C_{28}H_{14}$, dibenzo[*fg,op*]anthanthrene or bisanthene (7), is an interesting chemical compound (Fig. 3). This benzenoid can be interpreted as four hexagons condensed with pyrene. Here a condensation is defined as an addition which increases the number of internal vertices. Accordingly, bisanthene can be called a condensed pyrene.

Benzenoids with two pyrene units. The benzenoid systems depicted in Fig. 4 correspond to the following known

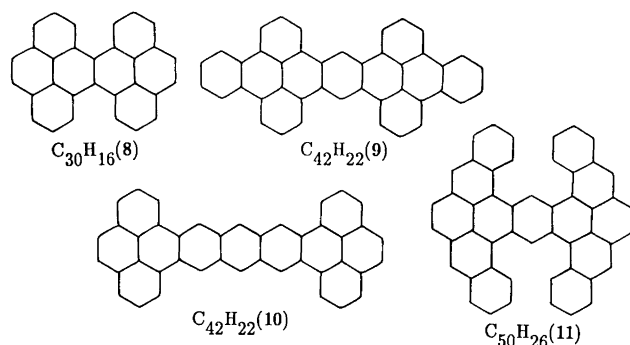


Fig. 4. Four benzenoid hydrocarbons with two pyrene units each.

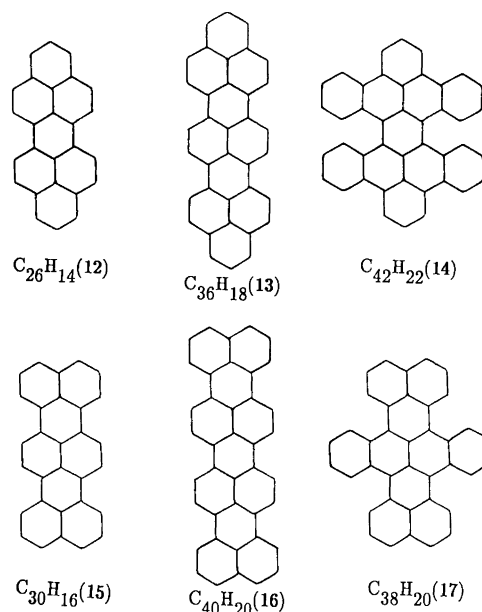


Fig. 5. Peropyrene (12), terrylene (15) and some of their derivatives.

hydrocarbons: $C_{30}H_{16}$ tetrabenzo[*de,hi,mn,qr*]naphthacene or pyreno[4,5-*e*]pyrene (8), $C_{42}H_{22}$ tetrabenzo[*fg,lm,uv,a'b'*]heptacene (9), $C_{42}H_{22}$ tetrabenzo[*de,no,st,c',d'*]heptacene (10), $C_{50}H_{26}$ tetranaphtho[3,2,1-*de*:1',2',3'-*jk*:3'',2'',1''-*op*:1''',2''',3'''-*uv*]pentacene (11).

Peropyrene and terrylene with homologs and additions. $C_{26}H_{14}$ peropyrene (12) may be interpreted as a benzenoid with two compressed pyrenes (Fig. 5). This system is a member of a homologous series governed by the general formula $C_{10j+16}H_{4j+10}$, where peropyrene corresponds to $j=1$ (and pyrene itself to $j=0$). The next member (for $j=2$) is also known (Fig. 5): $C_{36}H_{18}$ teropyrene (13). In addition, one has: $C_{42}H_{22}$ tetrabenzo[*a,h,l,s*]peropyrene (14). A quite different homologous

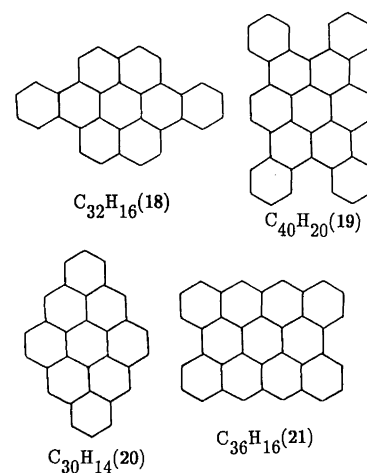


Fig. 6. Four derivatives of coronene.

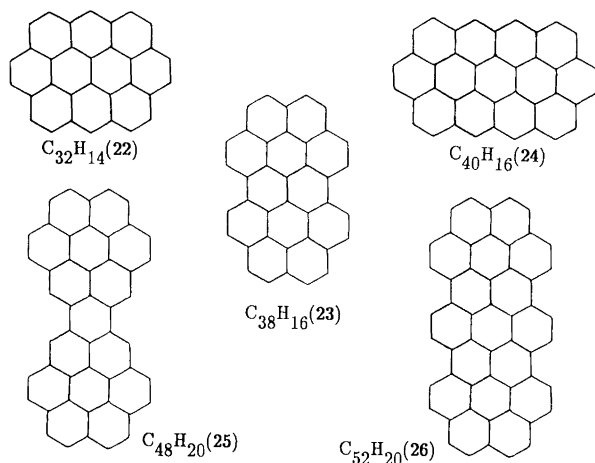


Fig. 7. Five large benzenoid hydrocarbons.

series contains $C_{30}H_{16}$ tribenzo[*de,kl,rst*]pentaphene or terrylene (15) (Fig. 5). The homologs of this series have formulae of the form $C_{10j+20}H_{4j+12}$, where $j=1$ pertains to terrylene (and $j=0$ to perylene). Here again the member for $j=2$ is known: $C_{40}H_{20}$ quaterrylene (16) (Fig. 5). In addition, one has: $C_{38}H_{20}$ dibenzo[*j,w*]terrylene (17).

Annelated and condensed coronene. $C_{24}H_{12}$ coronene is a well known benzenoid of regular hexagonal symmetry (D_{6h}). Two annelated coronenes correspond to known dihedral benzenoid hydrocarbons (Fig. 6): $C_{32}H_{16}$ dibenzo[*a,j*]coronene (18) and $C_{40}H_{20}$ tetrabenzo[*a,d,j,m*]coronene (19). In addition, one has the condensed coronenes: $C_{30}H_{14}$ dibenzo[*bc,kl*]coronene (20) and $C_{36}H_{16}$ tetrabenzo[*bc,ef,kl,no*]coronene (21).

The last five benzenoids. The last D_{2h} benzenoid systems of this listing (Fig. 7) correspond to certain large dihedral benzenoid hydrocarbons, which include the largest ($h=17$) benzenoid hydrocarbon which has yet been synthesized. The five hydrocarbons in question are: $C_{32}H_{14}$ ovalene (22), $C_{38}H_{16}$ circumbiphenyl (23), $C_{40}H_{16}$ circumanthracene (24), $C_{48}H_{20}$ dicoronene (25) and $C_{52}H_{20}$ circumparaterphenyl (26).

Which formulae are possible for benzenoids?

Even-carbon formulae and odd-carbon formulae. In a benzenoid formula C_nH_s the coefficients (n,s) have the same parity, i.e. either both n and s are even integers, or both of them are odd. Accordingly, one distinguishes between even-carbon and odd-carbon formulae, respectively. Out of these, the even-carbon formulae have the far greatest interest in chemistry. Namely, any benzenoid with an odd-carbon formula is non-Kekuléan, i.e. it does not possess any Kekulé (valence) structure, and not a single benzenoid hydrocarbon of this kind has been synthesized so far. On the other hand, a benzenoid with an even-carbon formula may be either Kekuléan (possessing Kekulé structures) or non-Kekuléan. Non-Kekuléan benzenoid hydrocarbons have a radicalic nature and are not expected to exist as stable compounds.

Tabulation. It is obviously of interest to investigate the theoretical possibilities of benzenoid C_nH_s formulae and not only to list those for actually synthesized benzenoid hydrocarbons. A great deal of work has been done in this area; cf. a recent review¹⁵ and references cited therein.

In Scheme 1 all the first ($h \leq 17$) theoretical even-

h	n_i										
	0	2	4	6	8	10	12	14	16	18	20
1	C_6H_6										
2	$C_{10}H_8$										
3	$C_{14}H_{10}$										
4	$C_{18}H_{12}$	$C_{16}H_{10}$									
5	$C_{22}H_{14}$	$C_{20}H_{12}$									
6	$C_{26}H_{16}$	$C_{24}H_{14}$	$C_{22}H_{12}$								
7	$C_{30}H_{18}$	$C_{28}H_{16}$	$C_{26}H_{14}$	$C_{24}H_{12}$							
8	$C_{34}H_{20}$	$C_{32}H_{18}$	$C_{30}H_{16}$	$C_{28}H_{14}$							
9	$C_{38}H_{22}$	$C_{36}H_{20}$	$C_{34}H_{18}$	$C_{32}H_{16}$	$C_{30}H_{14}$						
10	$C_{42}H_{24}$	$C_{40}H_{22}$	$C_{38}H_{20}$	$C_{36}H_{18}$	$C_{34}H_{16}$	$C_{32}H_{14}$					
11	$C_{46}H_{26}$	$C_{44}H_{24}$	$C_{42}H_{22}$	$C_{40}H_{20}$	$C_{38}H_{18}$	$C_{36}H_{16}$					
12	$C_{50}H_{28}$	$C_{48}H_{26}$	$C_{46}H_{24}$	$C_{44}H_{22}$	$C_{42}H_{20}$	$C_{40}H_{18}$	$C_{38}H_{16}$				
13	$C_{54}H_{30}$	$C_{52}H_{28}$	$C_{50}H_{26}$	$C_{48}H_{24}$	$C_{46}H_{22}$	$C_{44}H_{20}$	$C_{42}H_{18}$	$C_{40}H_{16}$			
14	$C_{58}H_{32}$	$C_{56}H_{30}$	$C_{54}H_{28}$	$C_{52}H_{26}$	$C_{50}H_{24}$	$C_{48}H_{22}$	$C_{46}H_{20}$	$C_{44}H_{18}$	$C_{42}H_{16}$		
15	$C_{62}H_{34}$	$C_{60}H_{32}$	$C_{58}H_{30}$	$C_{56}H_{28}$	$C_{54}H_{26}$	$C_{52}H_{24}$	$C_{50}H_{22}$	$C_{48}H_{20}$	$C_{46}H_{18}$		
16	$C_{66}H_{36}$	$C_{64}H_{34}$	$C_{62}H_{32}$	$C_{60}H_{30}$	$C_{58}H_{28}$	$C_{56}H_{26}$	$C_{54}H_{24}$	$C_{52}H_{22}$	$C_{50}H_{20}$	$C_{48}H_{18}$	
17	$C_{70}H_{38}$	$C_{68}H_{36}$	$C_{66}H_{34}$	$C_{64}H_{32}$	$C_{62}H_{30}$	$C_{60}H_{28}$	$C_{58}H_{26}$	$C_{56}H_{24}$	$C_{54}H_{22}$	$C_{52}H_{20}$	$C_{50}H_{18}$

Scheme 1. Tabulation of benzenoid formulae (for details, see the text).

carbon benzenoid formulae are tabulated. All of them but those in frames are compatible with benzenoids of D_{2h} (dihedral) symmetry. The heavy-type formulae indicate the chemically known dihedral benzenoid hydrocarbons according to the above survey.

General formulations. It appears that any benzenoid with D_{2h} symmetry has an even-carbon formula. For the formulae of catacondensed benzenoids (viz. the first column of formulae in Scheme 1) there are certainly representatives with D_{2h} symmetry (for $h \geq 2$), at least the linear polyacenes, but also branched systems when $h \geq 6$. It is also relatively easy to explain the lack of D_{2h} benzenoids for $C_{28}H_{16}$, $C_{44}H_{24}$ and $C_{60}H_{32}$ (cf. the second column of Scheme 1). A benzenoid of D_{2h} symmetry with two internal vertices ($n_i = 2$) can only be pyrene, perylene or one of these two systems with catacondensed appendages (Fig. 3). Pyrene and pyrene with catacondensed additions take care of $h = 4 + 2j$ ($j = 0, 1, 2, \dots$). Similarly for perylene: $h = 5 + 4j$. Hence we are left with $h = 7 + 4j$, for which the formulae, viz. $C_{16j+28}H_{8j+16}$, are not compatible with D_{2h} benzenoids. Scheme 1 includes the framed formulae for $j = 0, 1, 2$, but the pattern continues infinitely through the second column of the scheme. Apart from this full account for the two first columns ($n_i = 0, 2$) of Scheme 1 we have not been able to deduce any general rules for the formulae which are not realized in benzenoids with D_{2h} symmetry. There are four additional of such formulae in Scheme 1, viz. $C_{22}H_{12}$, $C_{24}H_{12}$, $C_{34}H_{16}$ and $C_{52}H_{22}$. Furthermore, it was verified by computer search that there is not a single formula for $n_i > 2$ which would qualify to be framed in a continuation of Scheme 1 when $17 < h \leq 50$.

For benzenoids in general (i.e. for all symmetries), an account of the possible C_nH_s formulae has been evaluated.¹⁵ In addition, the staircase-like boundary at the right-hand side of Scheme 1 (drawn with heavy lines) was determined on the basis of an analysis by Harary and Harborth,¹⁶ with the result given by expression (5). Here

$$0 \leq n_i \leq 2h - 2\lceil \frac{1}{2} \rceil (12h - 3)^{1/2} \rceil - \frac{1}{2} \rceil \quad (5)$$

the 'ceiling' function is employed: $\lceil x \rceil$ indicates the smallest integer larger than or equal to x .

Also the following question is of prime interest: When n is given, which C_nH_s formulae are possible for benzenoids? Similarly: When s is given, which C_nH_s formulae are possible? The answers to these questions are implied in inequalities (6) and (7).¹⁵ Here expression (7) corrects

$$2\lceil \frac{1}{2} (n + 6^{1/2}n^{1/2}) \rceil - n \leq s \leq n + 2 - 2\lceil \frac{1}{4} (n - 2) \rceil \quad (6)$$

$$s - 6 + 2\lceil s/2 \rceil \leq n \leq s + 2\lfloor \frac{1}{12} (s^2 - 6s) \rfloor \quad (7)$$

a misprint.¹⁵ In addition to the ceiling function, the 'floor' function is employed in expression (7): $\lfloor x \rfloor$ is the largest integer smaller than or equal to x . Examples of the application of (a) expression (6) and (b) expression (7) are given in the following. (a) For $n = 40$, the possible

benzenoid formulae are $C_{40}H_{16}$, $C_{40}H_{18}$, $C_{40}H_{20}$ and $C_{40}H_{22}$. Representative hydrocarbons have been synthesized for all these formulae but $C_{40}H_{18}$ (cf. Scheme 1). (b) For $s = 16$, the possible benzenoid formulae are $C_{26}H_{16}$, $C_{28}H_{16}$, $C_{30}H_{16}$, $C_{32}H_{16}$, $C_{34}H_{16}$, $C_{36}H_{16}$, $C_{38}H_{16}$, $C_{40}H_{16}$ and $C_{42}H_{16}$. Out of these formulae $C_{28}H_{16}$ and $C_{34}H_{16}$ are not possible for dihedral benzenoid hydrocarbons, while $C_{42}H_{16}$ has one chemically unknown isomer, viz. circumpylene of D_{2h} symmetry; for the other H_{16} formulae, chemical representatives of dihedral hydrocarbons are known; cf. Scheme 1.

Enumeration of benzenoid isomers

Definitions. The number of benzenoid C_nH_s isomers is the number of nonisomorphic benzenoid systems compatible with the given formula ($n; s$). Two benzenoids are said to be isomorphic if they can be brought into each other by a rotation, reflection or a combination of these two operations. Here we are particularly interested in the numbers of dihedral benzenoid isomers, viz. the numbers of nonisomorphic benzenoid systems of symmetry D_{2h} with given formulae ($n; s$).

Results of enumeration. Numbers of dihedral benzenoid isomers were produced by a computer program according

Table 1. Numbers of benzenoid isomers.^a

h	n_i	Formula	D_{2h}	Total Kekuléan
2	0	$C_{10}H_8$	1(1)	1(1)
3	0	$C_{14}H_{10}$	1(1)	2(2)
4	0	$C_{18}H_{12}$	1(1)	5(5)
	2	$C_{16}H_{10}$	1(1)	1(1)
5	0	$C_{22}H_{14}$	1(1)	12(12)
	2	$C_{20}H_{12}$	1(1)	3(3)
6	0	$C_{26}H_{16}$	2(2)	36(36)
	2	$C_{24}H_{14}$	1(1)	13(13)
7	0	$C_{30}H_{18}$	2(2)	118(35)
	4	$C_{26}H_{14}$	1(1)	9(9)
8	0	$C_{34}H_{20}$	2(1)	411(10)
	2	$C_{32}H_{18}$	1(1)	287(22)
	4	$C_{30}H_{16}$	2(2)	58(58)
	6	$C_{28}H_{14}$	1(1)	8(8)
9	0	$C_{38}H_{22}$	2(1)	1489(4)
	2	$C_{36}H_{20}$	2(1)	1352(16)
	6	$C_{32}H_{16}$	1(1)	46(46)
	8	$C_{30}H_{14}$	1(1)	3(3)
10	2	$C_{40}H_{22}$	2(1)	6256(2)
	4	$C_{38}H_{20}$	3(1)	1907(9)
	6	$C_{36}H_{18}$	1(1)	337(12)
	10	$C_{32}H_{14}$	1(1)	1(1)
11	4	$C_{42}H_{22}$	3(3)	10552(9)
	6	$C_{40}H_{20}$	3(2)	2191(6)
	10	$C_{36}H_{16}$	1(1)	20(20)
12	12	$C_{38}H_{16}$	1(1)	10(10)
13	4	$C_{50}H_{26}$	5(1)	300833(1)
	14	$C_{40}H_{16}$	1(1)	3(1)
15	14	$C_{48}H_{20}$	3(1)	1124(1)
17	18	$C_{52}H_{20}$	3(1)	525(1)

^aNumbers in parentheses refer to the chemically known hydrocarbons.

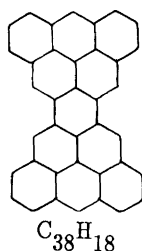


Fig. 8. The Clar goblet.

to an unpublished algorithm. A description of this algorithm is in preparation, along with an extensive report on the enumeration results from the program. Here we only give the (small) numbers which were computed for the C_nH_s formulae of particular chemical interest, viz. those for which there exist dihedral benzenoid hydrocarbons chemically according to the above survey. These results are found in Table 1, together with the corresponding numbers of chemically known isomers in parentheses.

For the sake of comparison some total numbers of benzenoid isomers, which take into account all symmetries, are included in Table 1. The numbers of Kekuléan benzenoid isomers are given therein for the same C_nH_s formulae as in the case of the D_{2h} systems. These data are found in the recent review,¹⁵ which includes documentations of the original sources. Again, the corresponding numbers of chemically known benzenoid isomers are included in parentheses (Table 1), as extracted from the compilations of Dias.^{3,13}

Discussion. All the dihedral benzenoid isomers which are listed in Table 1 are Kekuléan. Therefore it is reasonable to compare their numbers with the total numbers of the Kekuléan benzenoids only. This does not mean, however, that non-Kekuléan benzenoids of symmetry D_{2h} cannot be constructed at all. The smallest such system is the celebrated 'Clar goblet'^{17,18} (Fig. 8). It has eleven hexagons ($h = 11$), eight internal vertices ($n_i = 8$) and the formula $C_{38}H_{18}$. No dihedral benzenoid isomer with this formula has been synthesized, although we have found that there is one theoretically possible Kekuléan hydrocarbon of this category. Also for $C_{34}H_{18}$ ($h = 9$, $n_i = 4$) exactly one dihedral benzenoid is possible, but has not been synthesized; cf. Scheme 1.

As a whole, the observed dihedral benzenoid hydrocar-

bons which have been synthesized are over-represented in a sense. For the formulae listed in Table 1, according to the numbers therein, about 70% of the theoretically possible D_{2h} benzenoids have been synthesized, while the corresponding fraction for Kekuléan benzenoids of all symmetries is only 0.1%. In the most extreme case, 300833 Kekuléan benzenoid isomers of $C_{50}H_{26}$ can be constructed (Table 1). Only one of the corresponding benzenoid hydrocarbons has been synthesized, and represents a dihedral system (out of five such possibilities).

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