

Figure 1. Boiling points, observed versus predicted, derived from the PDDSA(D) index values of the alkanes listed in Table I, methane excluded.

matrices justified the conclusion that the data did not constitute monotonic series and hence were useless as topological indices. However, the sums of the dexter diagonal products (SDDP) and the products of the dexter diagonal sums of the upper (lower) triangle (PDDSA) of the distance matrices, even though variant and representing canonically numbered graphs, were easily calculated index values and also appeared to be unique and single-sum, and constituted a monotonic series of values. The permanent, PRS, SDDP, and PDDSA indices can be utilized as topological indices for quantitative-structural property relationship comparisons. Additionally, the row sums of the distance matrices were demonstrated to have potential utility for establishing priority sequences of graph vertices.

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Notes on Fully Benzenoid Hydrocarbons and Their Constant-Isomer Series

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All-benzenoids (corresponding to fully benzenoid or total resonant sextet hydrocarbons) are treated. The possible values of n and s in an all-benzenoid formula C_nH_s are specified in general terms. Many other general formulations are reported, such as the general expressions of C_nH_s formulas for protrusive all-benzenoids, circular all-benzenoids, and extremal all-benzenoids. All these classes are precisely defined. The latter class (extremal all-benzenoids) contains exactly (if biphenyl is added) the members of constant-isomer series of all-benzenoids, the main subject of this work. Associated all-benzenoids give the link of these members to the members of the (ordinary) constant-isomer series of benzenoids. Supercircumscribing, a kind of an augmented circumscribing, is a crucial concept in these studies. Finally, the previously known numerical data for constant-isomer all-benzenoid series are supplemented.

INTRODUCTION

The fully benzenoid hydrocarbons are known to be of great importance in organic chemistry.¹⁻³ A necessary and sufficient condition, which defines a fully benzenoid hydrocarbon, is the existence of Kekulé structures where all the double bonds belong to aromatic sextets.³ Here it is adhered to the term⁴⁻⁶ "all-benzenoids" as an abbreviation for all-benzenoid systems,⁷ which, considered as chemical graphs,⁸ correspond to the fully benzenoid hydrocarbons, chemically known or unknown.

The present work was prompted by a recent paper of Dias⁹ dealing with "total resonant sextet benzenoids", a concept which actually is synonymous with "all-benzenoids".¹⁰ Among the interesting findings of Dias⁹ is the existence of constant-

isomer series of all-benzenoids in correspondence with the ordinary constant-isomer series of benzenoids.¹¹⁻¹⁸ In the present work these findings are extended by some general formulations. Also the numerical data are supplemented.

RESULTS AND DISCUSSION

Notation. Let the formula C_nH_s for a benzenoid hydrocarbon be denoted alternatively as

$$C_nH_s \equiv (n; s)$$

The class of benzenoids with this formula, viz., the C_nH_s benzenoid isomers, also has a fixed number of hexagons (h) and a fixed number of internal vertices (n_i). A benzenoid

(isomer) belonging to this class may be denoted by

$$B(n; s) \equiv B(h, n_i)$$

The cardinality of C_nH_s , viz.^{16,18}

$$|C_nH_s| \equiv |n; s|$$

is the number of isomers for the formula $(n; s)$, or strictly: the number of nonisomorphic benzenoid systems compatible with the particular formula or with the pair of invariants (h, n_i) .

Assume now that $S(n; s)$ is an all-benzenoid, S . Then, for $h > 1$, there exist invariably benzenoids which do not belong to all-benzenoids but have the same formula. On the other hand, there are formulas $(n; s)$ pertaining to benzenoids, but not compatible with any S . A necessary (but not sufficient) condition that $S(n; s)$ may be an all-benzenoid is that⁵ n is divisible by 6 and s is divisible by 2. In that case, introduce

$$\nu = n/6 \quad \sigma = s/2 \quad (1)$$

We shall also write

$$(n; s) = (6\nu; 2\sigma) \equiv [(\nu; \sigma)]$$

and occasionally $S(n; s) \equiv S[(\nu; \sigma)]$.

The *supercardinality* of C_nH_s , viz.

$$||C_nH_s|| \equiv ||n; s||$$

is now defined as the number of all-benzenoid (or fully benzenoid) isomers; more strictly: the number of nonisomorphic all-benzenoid systems compatible with the formula $(n; s)$. To take the numbers from Introduction of Dias⁹ as examples, one has

$$|C_{42}H_{18}| = 187 \quad ||C_{42}H_{18}|| = 1 \quad (2)$$

$$|C_{60}H_{22}| = 5726 \quad ||C_{60}H_{22}|| = 1 \quad (3)$$

$$|C_{84}H_{26}| = 123790 \quad ||C_{84}H_{26}|| = 1 \quad (4)$$

Another example, where the supercardinality is greater than unity:

$$|C_{36}H_{18}| = 416 \quad ||C_{36}H_{18}|| = 3 \quad (5)$$

Associated All-Benzenoid. Let $B'(n'; s')$ symbolize an all-benzenoid. Its formula can always be deduced from the formula of a benzenoid, say $B(n; s)$, so that

$$(n'; s') = (3n - 3s + 6; 2s - 6) \quad (6)$$

In this connection it is said that $B'(n'; s')$ is an all-benzenoid *associated* with $B(n; s)$, and one may write $B' = \text{assoc-B}$. From eq 6 it is obtained:

$$n = (n'/3) + (s'/2) + 1 \quad s = (s'/2) + 3 \quad (7)$$

If $B(n; s) \equiv B(h, n_i)$ and $B'(n'; s') \equiv B'(h', n'_i)$, then:

$$h' = h + n_i \quad n'_i = 4n_i - 2h + 2 \quad (8)$$

The correspondence between B and $B' = \text{assoc-B}$ reflects the correspondence between constant-isomer series of benzenoids in general and the constant-isomer series of all-benzenoids. This correspondence was detected by Dias⁹ and is treated in some of the subsequent sections.

Which Formulas Are Compatible with All-Benzenoids? For an all-benzenoid $S(n; s)$ the possible values of s are $s = 6$ and all even integers $s \geq 12$:

$$s = 6, 12, 14, 16, 18, \dots$$

Now the problem is to find the upper and lower bounds of n in $S(n; s)$ when s is given.

A general formulation for the possible values of n in terms of s is known for benzenoids $B(n; s)$.¹⁹ Care must be taken, however, since not every benzenoid formula $(n; s)$ is permitted in eq 6 in order to produce an all-benzenoid formula $(n'; s')$;

see also below. Nevertheless, the upper bound of n in $S(n; s)$ for all-benzenoids is found straightforwardly from the corresponding upper bound for benzenoids¹⁹ in conjunction with eq 6, while the lower bound calls for a special treatment. The net result was achieved as:

$$3s - 6(1 + \lfloor s/6 \rfloor) \leq n \leq 6[(1/48)(s^2 + 12)] \quad (9)$$

Here the "floor" function is employed: $\lfloor a \rfloor$ is the largest integer smaller than or equal to a . In eq 9, when s assumes one of the permitted values which are specified above, the upper and lower bounds (which coincide for $s = 6, 12, 14, 16$) are always realized for all-benzenoids. The possible values of n (between the two bounds) should be taken in steps by 6 units. Examples: (i) $s = 20$ gives $36 \leq n \leq 48$; the possible formulas are $C_{36}H_{20}$, $C_{42}H_{20}$, $C_{48}H_{20}$; (ii) $s = 30$ gives $54 \leq n \leq 114$; the possible formulas are $C_{54}H_{30}$, $C_{60}H_{30}$, ..., $C_{114}H_{30}$ (11 formulas). Altogether, the possible values for n in all-benzenoids $S(n; s)$ are

$$n = 6, 18, 24, 30, 36, \dots$$

Introduce $S(n; s) \equiv S[(\nu; \sigma)]$, where ν and σ are given by eq 1. In terms of these coefficients eq 9 becomes

$$\sigma - (1 + \lfloor \sigma/3 \rfloor) \leq \nu \leq [(1/12)(\sigma^2 + 3)] \quad (10)$$

where

$$\sigma = 3, 6, 7, 8, 9, \dots$$

and the possible values of ν come out as

$$\nu = 1, 3, 4, 5, 6, \dots$$

Assume now, conversely, that we wish the possible values for s in $S(n; s)$ when n is given. For the sake of brevity the final result, which was deduced, is given below immediately:

$$2[(2n - 3)^{1/2}] \leq s \leq (2n/3) - 2[\lfloor n/12 \rfloor - 1] \quad (11)$$

Here, in addition to the floor function, also the "ceiling" function is employed; $\lceil a \rceil$ is the smallest integer larger than or equal to a . The upper and lower bounds (which coincide for $n = 6, 18, 24$) are always realized for the permitted n values already specified above. The intermediate s values should be taken in steps by 2 units. Examples: (i) $n = 30$ gives $16 \leq s \leq 18$; only the formulas for the two extremes are possible, viz., $C_{30}H_{16}$ and $C_{30}H_{18}$; (ii) $n = 60$ gives $22 \leq s \leq 32$; the possible formulas are $C_{60}H_{22}$, $C_{60}H_{24}$, ..., $C_{60}H_{32}$ (6 formulas).

The inequalities for $S[(\nu; \sigma)]$, in analogy with eq 11, are given by

$$\lceil (12\nu - 3)^{1/2} \rceil \leq \sigma \leq 2\nu + 1 - \lfloor \nu/2 \rfloor \quad (12)$$

Other Inequalities. From eq 9 and the known connections between different invariants of benzenoids^{5,7,19,20} it is readily obtained for all-benzenoids $S(n; s) \equiv S(h, n_i)$:

$$s + 1 - 3(1 + \lfloor s/6 \rfloor) \leq h \leq 1 - (s/2) + 3[(1/48)(s^2 + 12)] \quad (13)$$

The possible values of h are

$$h = 1, 4, 6, 7, 8, 9, \dots$$

Furthermore

$$s - 6\lfloor s/6 \rfloor \leq n_i \leq 6 - 2s + 6[(1/48)(s^2 + 12)] \quad (14)$$

and for n_i

$$n_i = 0, 2, 4, 6, \dots$$

In eqs 13 and 14, of course, s could be substituted by σ . The Dias parameter,²⁰⁻²² d_s , viz.

$$d_s = h - n_i - 2 = (1/2)(3s - n) - 7 \quad (15)$$

is also of interest in connection with benzenoid isomers. Its

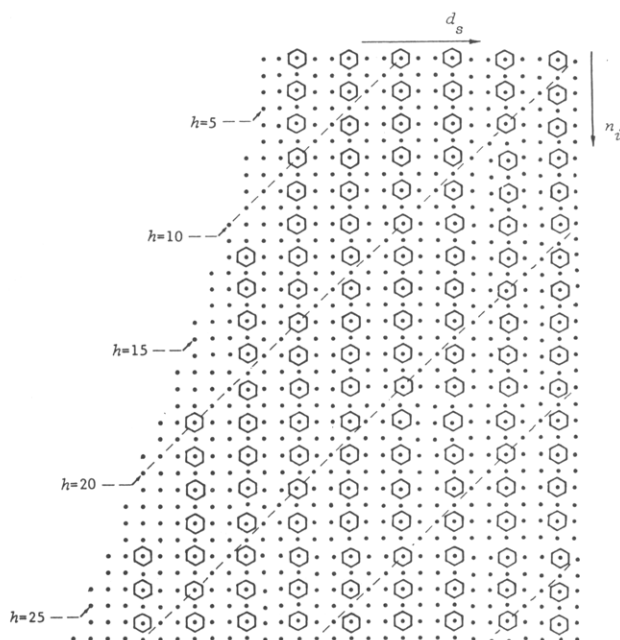


Figure 1. Dot diagram of the Dias periodic table for benzenoid hydrocarbons; each dot represents a C_nH_s formula. The sites of formulas which also pertain to all-benzenoids are marked by hexagons.

upper and lower bounds for all-benzenoids were determined as:

$$(3s/2) - 7 - 3[(1/48)(s^2 + 12)] \leq d_s \leq 3[s/6] - 4 \quad (16)$$

The possible values of d_s appear to be

$$d_s = \dots, -7, -4, -1, 2, 5, 8, \dots$$

where this invariant steps by 3 units each time. For obvious reasons, define

$$\delta_s = (1/3)(d_s + 7) \quad d_s = 3\delta_s - 7 \quad (17)$$

Then eq 16 can be reduced to

$$\sigma - [(1/12)(\sigma^2 + 3)] \leq \delta_s \leq 1 + [\sigma/3] \quad (18)$$

and

$$\delta_s = 0, \pm 1, \pm 2, \pm 3, \dots$$

With the aid of eq 11 also the inequalities for different invariants such as h , n_i , and d_s could be written up as functions of n . For the sake of brevity this part of the analysis is omitted here.

Periodic Table for Fully Benzenoid Hydrocarbons. The title object^{9,23} is a subset of the Dias periodic table for benzenoid hydrocarbons.¹⁹⁻²² It is an array of chemical formulas $C_nH_s \equiv (n; s)$ for the nontrivial ($h \geq 4$) all-benzenoid systems, which correspond to fully benzenoid hydrocarbons. Notice that C_6H_6 benzene ($h = 1$), which is reckoned among the all-benzenoids, is excluded from the table. The formulas of the periodic table are entered in a coordinate system (d_s, n_i).

Figure 1 shows a dot diagram²³ for the Dias periodic table, where each dot represents a benzenoid formula. Apart from C_6H_6 , all the C_nH_s formulas are taken into account,¹⁹ both those where n and s are even^{21,22,24} and those where n and s are odd.²⁴ The dots in Figure 1, which also represent formulas for all-benzenoids, are marked by hexagons surrounding the appropriate dots. These formulas may be identified, in consistency with the listings published previously,^{9,23} by means of the scheme

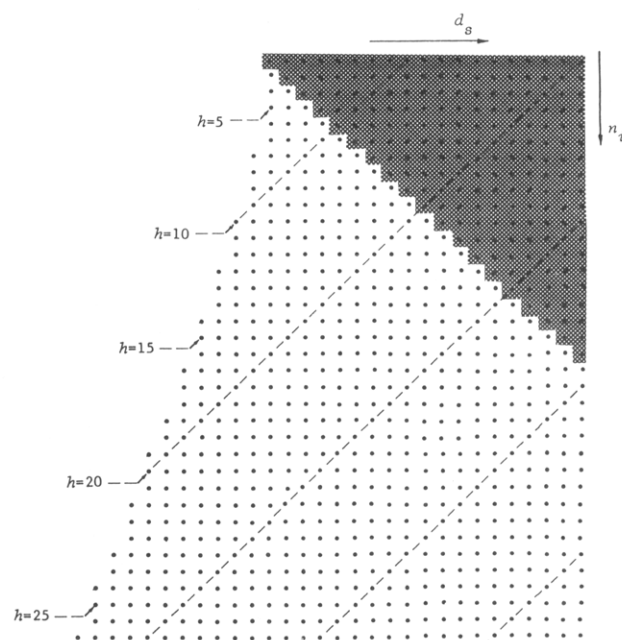
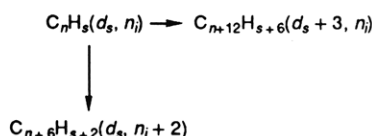
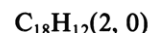


Figure 2. Dot diagram of the Dias periodic table. The formulas for all-benzenoids are produced by $S(n; s) = \text{assoc-B}(n; s)$ when taking all the $(n; s)$ formulas represented by the dots of the unshaded area.

and the initial condition (for the upper-left corner), which is the formula for triphenylene:



A quite different question is: Which formulas for benzenoids, $B(n; s)$, are to be used in order to produce all formulas for all-benzenoids through assoc-B ? The answer is implied in Figure 2, where the appropriate formulas for $B(n; s)$ are indicated in a dot diagram for the Dias periodic table.

Protrusive All-Benzenoids. The periodic table for fully benzenoid hydrocarbons, like the Dias periodic table for benzenoid hydrocarbons, exhibits a staircase-like boundary at its extreme left-hand edge.²⁵ A specification of this boundary is a nontrivial problem. The solution is actually implied in the inequalities, eqs 9 or 10. Another solution was presented²³ in terms of a specification of the *protrusive all-benzenoids*, which are defined by having formulas in the periodic table for fully benzenoid hydrocarbons with no other formula to the left of it and no other formula above it. The first of these formulas are: $C_{18}H_{12}$, $C_{42}H_{18}$, $C_{60}H_{22}$, $C_{72}H_{24}$, $C_{84}H_{26}$, The formulas for the pericondensed protrusive all-benzenoids (for $h > 4$), say $S^p(n; s)$, are reproduced by²³

$$\begin{aligned} (n; s) = & (6h + 18 + 6[(12h - 3)^{1/2}]; 12 + 2[(12h - 3)^{1/2}]) \\ = & [(h + 3 + [(12h - 3)^{1/2}]; 6 + [(12h - 3)^{1/2}])] \end{aligned} \quad (19)$$

Here $h = 1, 2, 3, 4, \dots$ is not the number of hexagons for the all-benzenoid in question, but should rather be considered as a running index only.

Circular All-Benzenoid. A circular benzenoid,¹⁹ say O , is defined by having the maximum number of hexagons for a given perimeter length or s value. The circular benzenoids are known to constitute the members of the six different one-isomer series for benzenoids.^{11,20} Let the class of *circular all-benzenoids*, say S^O , be defined by the all-benzenoids associated with the circular benzenoids; $S^O = \text{assoc-O}$. The following expression was found for the formulas of circular benzenoids, given by $S^O(n; s)$:

$$\begin{aligned} (n; s) = & (6[(1/48)(s^2 + 12)]; s) \\ = & [(1/12)(\sigma^2 + 3); \sigma] \end{aligned} \quad (20)$$

Table I. Possible Formulas (n ; s) for All-Benzenoids when $n > 336$

$N_c = n$	$N_H = s$	$N_c = n$	$N_H = s$
342	54-174	402	58-204
348	54-176	408	58-206
354	54-180	414	58-210
360	54-182	420	→ 58-212
366	→ 54-186	426	60-216
372	56-188	432	60-218
378	56-192	438	60-222
384	56-194	444	60-224
390	→ 56-198	450	→ 60-228
396	58-200		

where s and σ may assume all the permitted values for all-benzenoids (see above). From eqs 9 or 10 it is seen that the circular all-benzenoids are exactly those with the maximum n value for a given s ; $n = n_{\max}(s)$.

The above analysis seems to give the best clue as to how to extend the formulas for all-benzenoids in the form they are given by Dias⁹ in his Table II.²⁶ The right-hand column (upper bounds) for s can simply be extended by steps of 2 units and steps of 4 units every second time, underlining the formula after each step of 4 units. This underlining indicates the catacondensed systems. The left-hand column (lower bound) for s represents the nontrivial problem. Herein a given s value is repeated until a maximum n value, which is reached at a formula marked by an arrow in Dias' table. This formula corresponds actually to a circular benzenoid and is therefore accessible through eqs 20 or 9. In continuation of the Dias table we find for $s = 54$: $n_{\max}(54) = 366$. Furthermore: $n_{\max}(56) = 390$, $n_{\max}(58) = 420$, $n_{\max}(60) = 450$, etc. For the sake of clarity an extension of Table II from Dias⁹ is given as Table I.

Of course, the ranges of s are also obtainable directly from eq 11 for each n value. By this approach, however, the circular all-benzenoids (marked with arrows in Table I and in Table II of Dias⁹) are not identified immediately.

Extremal All-Benzenoid. The extremal benzenoids are of great interest in the studies of benzenoid C_nH_s isomers. In fact, the extremal benzenoids constitute exactly the members of constant-isomer benzenoid series. An extremal benzenoid,^{19,27} say A, is defined by having the maximum number of internal vertices (n_i) for a given number of hexagons (h). Now the class of *extremal all-benzenoids*, say S^a , is defined by the all-benzenoids associated with the extremal benzenoids except $C_{10}H_8$ naphthalene; $S^a = \text{assoc-A}$. From eq 6 and the known expression¹⁹ for the formulas of extremal benzenoids, the following simple expressions were deduced for the formulas of $S^a(n; s) \equiv S^a[(\nu; \sigma)]$:

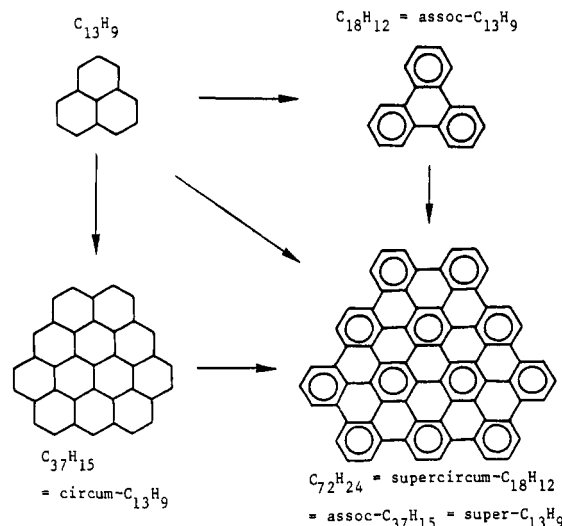
$$(n; s) = (6h; 2[(12h - 3)^{1/2}]) = [(h; [(12h - 3)^{1/2}])] \quad (21)$$

where $h = 1, 3, 4, 5, 6, \dots$, or

$$(n; s) = (n; 2[(2n - 3)^{1/2}]) = [(\nu; [(12\nu - 3)^{1/2}])] \quad (22)$$

Here n and ν may assume all the permitted values for all-benzenoids (see above). From eqs 11 or 12 it is seen that the extremal all-benzenoids are exactly those with the minimum s value for a given n ; $s = s_{\min}(n)$.

Supercircumscribing. Assume that an all-benzenoid $S(n; s)$ can be circumscribed. The circumscribing adds s hexagons along the perimeter, and the resulting benzenoid (which is not an all-benzenoid), circum-S, acquires the formula²⁰ $(n + 2s + 6; s + 6)$. Augment circum-S by adding $(s/2) + 3$ hexagons around the perimeter so that the benzenoid is converted to an all-benzenoid; the added hexagons all become full hexagons. The total process shall presently be referred to as *supercircumscribing*, and the resulting system denoted by supercircum-S. The last part of the process, the adding of hexagons

**Figure 3.** Illustration of the different processes in a "cycle" for benzenoids, starting with the extremal benzenoid $C_{13}H_9$.

to circum-S, adds $(s + 12)$ C atoms and 6 H atoms. Hence the formula for supercircum-S = $S_1(n_1; s_1)$ becomes

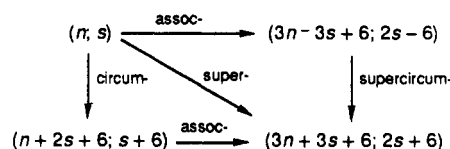
$$(n_1, s_1) = (n + 3s + 18; s + 12) \quad (23)$$

Notice that supercircumscribing is a process which produces an all-benzenoid from another (smaller) all-benzenoid.

Consider now a benzenoid $B(n; s)$ and its associated all-benzenoid, assoc-B, which has the formula given by eq 6. On the other hand, if B can be circumscribed, then circum-B with a known formula can be produced. Proceed now in the two directions: (a) supercircumscribe assoc-B and (b) take the all-benzenoid associated with circum-B. It appears that the net results from these combined processes end up with the same formula, say $(n^*; s^*)$. The corresponding all-benzenoid has been referred to as²³ super-B. In other words, super-B = supercircum-(assoc-B) = assoc-(circum-B). Its formula in terms of $(n; s)$ for the original benzenoid B reads²³

$$(n^*; s^*) = (3n + 3s + 6; 2s + 6)$$

The "cycle" described in this paragraph is illustrated in a schematical way below.



Let us consider the special case when $A(n; s)$ is an extremal benzenoid. Then, if $C_{10}H_8$ (naphthalene) is excluded, all the processes described above (as collected in the above scheme) can be executed, and a unique one-to-one correspondence between any two partners of such a process can be established. This is accomplished by defining assoc-A to any individual of the $A(h, n_i)$ benzenoids: take h hexagons and let them serve as full hexagons arranged in the same pattern as the hexagons are arranged in the original benzenoid A; fill out the "holes" between the full hexagons with n_i empty hexagons. This correspondence between A and assoc-A is exactly the one which was described by Dias.⁹ In Figure 3 an elucidating illustration is given, showing the "cycle" of processes with B = phenylene ($C_{13}H_9$) as example.

An apropos remark to the protrusive all-benzenoids (see above) is warranted here. Let A represent any extremal benzenoid ($h = 1, 2, 3, 4, \dots$). Then it is known that the pericondensed protrusive benzenoids, viz., $C_{24}H_{12}$ (coronene), $C_{32}H_{14}$ (ovalene), $C_{37}H_{15}$ (circumphenylene), $C_{42}H_{16}$ (circumpyrene), $C_{47}H_{17}$, $C_{52}H_{18}$, ..., are covered by the circum-A systems.¹⁹ Let circum-A = P. It appears now that the per-

icondensed protrusive all-benzenoids emerge as associated with the pericondensed protrusive benzenoids; $S^P = \text{assoc-P}$. Therefore also $S^P = \text{assoc-(circum-A)}$, whereafter it is concluded that the pericondensed protrusive all-benzenoids are exactly generated as super-A, where A represents each extremal benzenoid (including naphthalene).

Constant-Isomer Series of All-Benzenoids. A large part of the above material is highly relevant to the constant-isomer series of all-benzenoids. It was stated above that the extremal benzenoids constitute the members of the (ordinary) constant-isomer benzenoid series. Now it is inferred that, in an analogous way, the extremal all-benzenoids constitute members of constant-isomer all-benzenoid series. For the sake of completeness the non-benzenoid $C_{12}H_{10}$, biphenyl, should be included among these members. It is a totally resonant sextet system, but not a benzenoid (or all-benzenoid) according to the strict definition of benzenoid systems. Now with all the extremal all-benzenoids and biphenyl added to them, the members of constant-isomer benzenoid series are covered exactly. The biphenyl formula ($C_{12}H_{10}$) emerges from eqs 21 and 22 by inserting $h = 2$ and $n = 12$ ($\nu = 2$), respectively.

The smallest extremal all-benzenoids (with biphenyl in parentheses), as generated from eq 21, are as follows: C_6H_6 , ($C_{12}H_{10}$), $C_{18}H_{12}$, $C_{24}H_{14}$, $C_{30}H_{16}$, $C_{36}H_{18}$, $C_{42}H_{20}$, All of these formulas are found in Tables III and IV of Dias,⁹ where he has listed the constant-isomer series of all-benzenoids. It is now of interest, of course, to identify specifically the first formulas in each series. These formulas are said to represent the *ground forms* of the all-benzenoids (with biphenyl included) in analogy with the ground forms for the (ordinary) constant-isomer series of benzenoids.^{16,18,20,28} The other formulas represent the *higher members* for the constant-isomer all-benzenoid series.

A general formulation has been derived for the ground forms, say G, of constant-isomer series of benzenoids.^{16,18} Then an expression for the formulas of the ground forms for the constant-isomer series of all-benzenoids, say $S^S(n; s) \equiv S^S[(\nu; \sigma)]$, is readily obtained by $S^S = \text{assoc-G}$. The result is

$$(n; s) = (6 + 6[(1/48)(s^2 - 4s + 16)]; s) \\ = [(1 + [(1/12)(\sigma^2 - 2\sigma + 4)]; \sigma)] \quad (24)$$

where $s = 6, (10), 12, 14, 16, \dots$, or $\sigma = 3, (5), 6, 7, 8, \dots$. Here the parenthesized values ($s = 10, \sigma = 5$) give the formula for the non-benzenoid biphenyl ($C_{12}H_{10}$), which is reckoned among the ground forms. The smallest representatives, according to eq 24, are C_6H_6 , ($C_{12}H_{10}$), $C_{18}H_{12}$, $C_{24}H_{14}$, $C_{30}H_{16}$, $C_{36}H_{18}$, $C_{48}H_{20}$, $C_{54}H_{22}$,

The members of the one-constant isomer series of all-benzenoids coincide with the circular all-benzenoids (see above) with biphenyl included. Their formulas are reproduced by eq 20. The formulas for $s = 6, (10), 12, 14, 16, 20$, viz., C_6H_6 , ($C_{12}H_{10}$), $C_{18}H_{12}$, $C_{24}H_{14}$, $C_{30}H_{16}$, $C_{48}H_{20}$, also found among the formulas listed above, represent the six unique ground forms of all-benzenoids.⁹ Notice that $C_{42}H_{18}$ pertains to a higher member (in the one-isomer series starting with C_6H_6).

In general, when the ground form(s), say $S(n; s)$, of a constant-isomer all-benzenoid series has (have) been identified, then the higher members, say $S_k(n_k; s_k)$ are obtained by k times supercircumscribings of the ground form(s); $S_k = k$ -supercircum-S. For the formulas ($n_k; s_k$) it was found that

$$(n_k; s_k) = (n + 3k(s + 6k); s + 12k) \quad (25)$$

which is a generalization of eq 23.

Three Categories of All-Benzenoid Formulas. A powerful relation for an index, x , was devised in connection with the formulas ($n; s$) for all-benzenoids, viz.

$$x = [(1/48)(s^2 - 4s + 64 - 8n)] \quad (26)$$

This index distinguishes between three categories of such

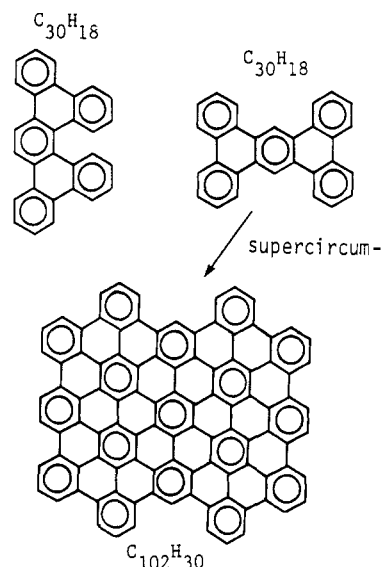


Figure 4. The only two $C_{30}H_{18}$ all-benzenoid isomers, and one of them supercircumscribed, resulting in a ground-form $C_{102}H_{30}$.

formulas, characterized by (a) $x > 0$, (b) $x = 0$, and (c) $x < 0$.

(a) Assume that $S(n; s)$ is an all-benzenoid, for which the coefficients ($n; s$) give a value of $x > 0$ when inserted in eq 26. Then the system is not an extremal all-benzenoid and, therefore, not any member of a constant-isomer all-benzenoid series. However, it can be shown that, if S can be supercircumscribed x times, then the resulting system, x -supercircum- S , is a ground form. It is true that not every all-benzenoid can be supercircumscribed. However, it is reasonable to assume that among the class of $S(n; s)$ all-benzenoids with an arbitrary formula there always exists (at least) one system which can be supercircumscribed k times without limitation.²⁹ Examples: (i) Dias⁹ has depicted the two isomers of the all-benzenoids $C_{30}H_{18}$ (see also Figure 4), of which the strained system cannot be circumscribed and hence neither supercircumscribed. The other one of the systems, viz., tetrabenzo- $[a,c,h,j]$ anthracene can be circumscribed arbitrarily many times. The coefficients of the formula in question ($n = 30, s = 18$) give $x = 1$ when inserted in eq 26. Accordingly, supercircum-tetrabenzo- $[a,c,h,j]$ anthracene is a ground form (see Figure 4). The pertinent formula is found from eqs 23 or 25 for $k = 1$ with the result of $C_{102}H_{30}$. Indeed, this is a formula for the ground forms of a constant-isomer series of all-benzenoids, consistent with Table III of Dias.⁹ As an extra check it is found that $n = 102$ and $s = 30$ obey eq 24. The $C_{102}H_{30}$ system depicted in Figure 4 is one of the nine isomers with this formula. (ii) Dias⁹ has also depicted an all-benzenoid system $C_{54}H_{24}$ (associated with $C_{31}H_{15}$), which can be circumscribed but not supercircumscribed (see also Figure 5). Another $C_{54}H_{24}$ all-benzenoid, also shown in Figure 5, can be supercircumscribed indefinitely. According to eq 26, which gives $x = 2$ for the formula under consideration, two times supercircumscribed $C_{54}H_{24}$ results in a ground form with the formula $C_{270}H_{48}$, as obtained from eq 25. This result is in perfect agreement with Table IV of Dias⁹ and with eq 24. The $C_{270}H_{48}$ system of Figure 5 is one of the 48 all-benzenoid isomers with this formula.

(b) Assume that $S(n; s)$ is an all-benzenoid, for which eq 26 gives $x = 0$. Then S is a ground form of a constant-isomer series of all-benzenoids. This case may be interpreted as a special case of (a) if it is allowed for "zero times supercircumscribing" in the sense of leaving the system as it is.

(c) Assume that $S(n; s)$ is an all-benzenoid for which $x < 0$. Then S is a higher member of a constant-isomer all-

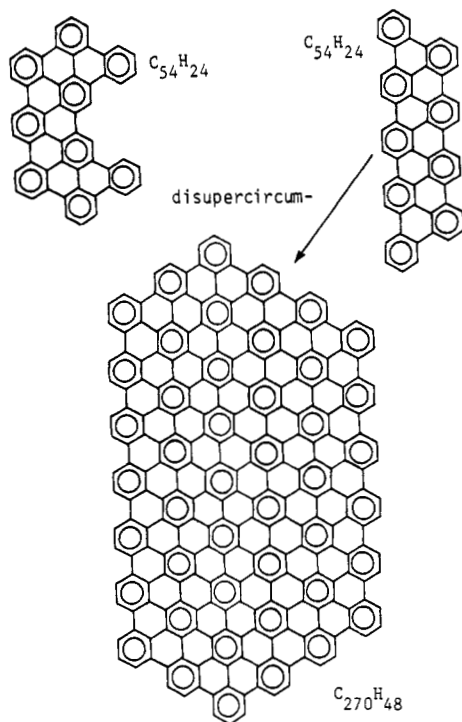


Figure 5. Two C₅₄H₂₄ all-benzenoid isomers, and one of them two times supercircumscribed, resulting in a ground-form C₂₇₀H₄₈.

benzenoid series. The absolute magnitude of x , viz., $|x|$, gives the information of how many times the ground form has been supercircumscribed. Furthermore, eq 25 is also applicable for negative k values in the sense that it gives for $k = -|x|$ the formula of the ground form(s) in the case under consideration. Examples: Dias⁹ has listed for one of the constant-isomer all-benzenoid series the formulas C₁₈H₁₂, C₇₂H₂₄, C₁₆₂H₃₆, C₂₈₈H₄₈, In these four cases eq 26 gives correctly $x = 0$, -1 , -2 , and -3 , respectively. Also eq 24 identifies correctly the ground-form formula, e.g., in the last case with $n = 288$, $s = 48$, and $k = -3$.

Numerical Data. The numerical data of supercardinalities (numbers of all-benzenoid isomers) for the constant-isomer all-benzenoid series are divided, here as in Dias,⁹ into two groups. In the first group (Table II) the data pertain to all-benzenoids associated with even-carbon benzenoids, i.e., those with C _{n} H _{s} formulas where n and s are even integers. These all-benzenoids have each an even number of empty hexagons. In the second group (Table III) the all-benzenoids are associated with odd-carbon (n and s odd integers) benzenoids and have odd-numbered empty hexagons.

The first enumerations of all-benzenoid systems by computer aid are probably due to Knop et al.³⁰ They were extended substantially by Cyvin et al.³¹ and reviewed elsewhere³² with further supplements. In none of these works are the C _{n} H _{s} formulas specified explicitly. Neither are they specified in the enumerations of all-benzenoids with hexagonal symmetries.³³ The C _{n} H _{s} all-benzenoid isomers were explicitly generated and enumerated, without computer aid, probably for the first time by Dias^{34,35} and followed up in the later works.^{36,37} Some of this material is included in reviews.^{22,38} In the most extensive of these enumerations Dias^{36,37} laid emphasis on the strain-free (or minimally strained) all-benzenoids. Although the constant-isomer series of all-benzenoids are not mentioned explicitly in these works, some information about them is contained therein. All extremal all-benzenoids, and hence all members of the constant-isomer all-benzenoid series, are namely strain-free in the sense of Dias. This implicit information about the supercardinalities for constant-isomer series was taken into account under the documentations by footnotes

Table II. Numbers of All-Benzenoid Isomers with Even-Numbered Empty Hexagons for Constant-Isomer Series (Biphenyl Formula in Parentheses)

ground-form formula	D _{6h}	D _{3h}	C _{3h}	D _{2h}	C _{2h}	C _{2v}	C _s	total
C ₆ H ₆	1 ^a	0	0	0	0	0	0	1 ^{a,b}
(C ₁₂ H ₁₀)	0	0	0	1 ^a	0	0	0	1 ^{a,b}
C ₂₄ H ₁₄	0	0	0	1 ^a	0	0	0	1 ^{c,d}
C ₃₆ H ₁₈	0	1 ^a	0	0	1 ^a	1 ^a	0	3 ^{c,d}
C ₅₄ H ₂₂	0	0	0	1 ^a	0	2 ^a	1 ^a	4 ^{c,d}
C ₇₈ H ₂₆	0	0	0	1 ^a	0	2 ^a	1 ^a	4 ^{a,b}
C ₁₀₂ H ₃₀	0	0	0	1 ^a	0	2 ^a	6 ^a	9 ^{a,b}
C ₁₃₂ H ₃₄	0	0	0	1 ^a	2 ^a	4 ^a	9 ^a	16 ^{a,b}
C ₁₆₈ H ₃₈	0	0	0	1 ^a	2 ^a	4 ^a	9 ^a	16 ^{a,b}
C ₂₀₄ H ₄₂	0	1 ^a	0	2 ^a	3 ^a	5 ^a	28 ^a	39 ^{a,b}
C ₂₄₆ H ₄₆	0	0	0	1	1	8	47	57 ^b
C ₂₉₄ H ₅₀	0	0	0	1	1	8	47	57 ^b
C ₃₄₂ H ₅₄	0	1	1	1	2	13	115	133 ^b
C ₃₉₆ H ₅₈	0	0	0	1	8	16	174	199 ^b
C ₄₅₆ H ₆₂	0	0	0	1	8	16	174	199 ^b
C ₅₁₆ H ₆₆	0	0	0	2	11	22	393	428 ^b
C ₅₈₂ H ₇₀	0	0	0	2	4	28	582	616 ^b
C ₆₅₄ H ₇₄	0	0	0	2	4	28	582	616 ^b
C ₇₂₆ H ₇₈	1	0	1	1	6	38	1218	1265 ^b
C ₈₀₄ H ₈₂	0	0	0	2	23	46	1729	1800 ^b
C ₈₈₈ H ₈₆	0	0	0	2	23	46	1729	1800 ^b
C ₉₇₂ H ₉₀	0	1	3	2	32	63	3438	3539
C ₁₀₆₂ H ₉₄	0	0	0	3	11	72	4811	4897
C ₁₁₅₈ H ₉₈	0	0	0	3	11	72	4811	4897

^aDias (1991).⁹ ^bDias (1991).¹⁷ ^cDias (1987).³⁶ ^dDias (1987).²²

Table III. Numbers of All-Benzenoid Isomers with Odd-Numbered Empty Hexagons for Constant-Isomer Series

ground-form formula	D _{3h}	C _{3h}	C _{2v}	C _s	total
C ₁₈ H ₁₂	1 ^a	0	0	0	1 ^b
C ₃₀ H ₁₆	0	0	1 ^a	0	1 ^{b,c}
C ₄₈ H ₂₀	0	0	1 ^a	0	1 ^{b,c}
C ₆₆ H ₂₄	0	0	0	2 ^a	2 ^{a,d}
C ₉₀ H ₂₈	0	0	1 ^a	3 ^a	4 ^{a,d}
C ₁₂₀ H ₃₂	0	0	1 ^a	3 ^a	4 ^{a,d}
C ₁₅₀ H ₃₆	1 ^a	0	3 ^a	9 ^a	13 ^{a,d}
C ₁₈₆ H ₄₀	0	0	4 ^a	16 ^a	20 ^{a,d}
C ₂₂₈ H ₄₄	0	0	4 ^a	16 ^a	20 ^{a,d}
C ₂₇₀ H ₄₈	0	1 ^a	2 ^a	45 ^a	48 ^{a,d}
C ₃₁₈ H ₅₂	0	0	4	70	74 ^d
C ₃₇₂ H ₅₆	0	0	4	70	74 ^d
C ₄₂₆ H ₆₀	0	0	12	162	174 ^d
C ₄₈₆ H ₆₄	0	0	12	246	258 ^d
C ₅₅₂ H ₆₈	0	0	12	246	258 ^d
C ₆₁₈ H ₇₂	0	1	8	541	550 ^d
C ₆₉₀ H ₇₆	0	0	13	783	796 ^d
C ₇₆₈ H ₈₀	0	0	13	783	796 ^d
C ₈₄₆ H ₈₄	2	2	30	1600	1634
C ₉₃₀ H ₈₈	0	0	32	2270	2302
C ₁₀₂₀ H ₉₂	0	0	32	2270	2302

^aDias (1991).⁹ ^bDias (1987).³⁶ ^cDias (1987).²² ^dDias (1991).¹⁷

in Tables II and III. However, the main references to previous works therein are the two recent works by Dias,^{9,17} where the constant-isomer all-benzenoid series are treated explicitly. In particular, Dias has depicted the first^{9,22,34-36} and second^{34,35} higher members from the one-isomer all-benzenoid series starting with C₆H₆, viz., the C₄₂H₁₈ and C₁₁₄H₃₀ systems, respectively. Furthermore, he has depicted the first higher member^{9,36,37} of the one-isomer series starting with (C₁₂H₁₀), viz., C₆₀H₂₂, in addition to other first higher members.^{9,36}

The all-benzenoids pertaining to Table III cannot belong to any symmetry groups other than the four which are listed therein: D_{3h}, C_{3h}, C_{2v}, and C_s. In Table II, on the other hand, all the eight symmetry groups which are possible for benzenoids may occur. Nevertheless, the column for C_{6h} is skipped in Table II. This should be understandable because, if we are not mistaken, the smallest all-benzenoid of C_{6h} symmetry, being a ground form of a constant-isomer series, is a unique

system with the formidable formula $C_{2742}H_{150}$. This system with 1297 hexagons is too big to be depicted here.

CONCLUSION

The present work was inspired by the recent studies of constant-isomer series of benzenoids by Dias,¹¹⁻¹⁷ and especially his extension of these studies to constant-isomer all-benzenoid series.⁹⁻¹⁷ The one-to-one correspondence between the members of these two kinds of series, already foreshadowed in a previous work by Dias,³⁶ was formalized and exploited in the present work. This approach led to a number of general formulations. For instance, an expression (eq 24) was derived that generates precisely the formulas C_nH_x for the ground forms of constant-isomer all-benzenoid series. Also the index x of eq 26 is especially noteworthy. It makes it feasible to decide immediately whether an all-benzenoid formula C_nH_x pertains to a (a) non-extremal system, (b) ground form, or (c) higher member.

Finally, in this work the existing numerical data of all-benzenoid isomers for constant-isomer series are supplemented. All of them follow the presumably general pattern which first was observed by Dias^{12,14,15} and referred to as a "new topological paradigm". It manifests itself in Tables II and III by the progressions of singlets and doublets as $a, b, b, c, d, d, e, f, f, \dots$. This pattern does not apply only to the total numbers but penetrates also into the distributions over the symmetry groups, in consistence with the topological characteristics described by Dias.^{9,12,14,15} A rigorous proof of the general validity of these patterns has so far not been given.

In more general terms, it may be stated that the foundations of the theory of constant-isomer series, including many of the inherent assumptions, which have tacitly been made, are not proved rigorously. Therefore, if only for this reason, there is still much to be done in the theory of constant-isomer series.

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