

Contributions to the Theory of Benzenoid Isomers: Some Properties of Extremal Benzenoids

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Summary. An extremal benzenoid, A, is defined by having the maximum number of internal vertices for the given number of hexagons. A number of properties of A are treated, where the modes of hexagons play an important role. The processes of circumscribing and excising for benzenoids are defined and treated in detail, supported by analytical expressions. It is concluded by stating that A can always be circumscribed an unlimited number of times.

Keywords. Benzenoid hydrocarbon; Extremal benzenoid; Invariants; Circumscribing.

Beiträge zur Theorie von benzenoiden Isomeren. Einige Eigenschaften extremer Benzenoide

Zusammenfassung. Ein extremes Benzenoid A wird durch die maximale Anzahl von internen Vertices für eine gegebene Anzahl von Sechsecken definiert. Es werden einige Eigenschaften von A behandelt, wobei die Erscheinungsformen der Sechsecke eine wichtige Rolle spielen. Der Prozess der Umschreibung und Ausschneidung der Benzenoide wird definiert und im Detail behandelt, wobei analytische Ausdrücke zur Unterstützung herangezogen werden. Es wird geschlossen, daß A stets unbegrenzt oft umschrieben werden kann.

Introduction

A benzenoid system (or shortly benzenoid) consists of mutually connected congruent regular hexagons in a geometrically planar arrangement [1–3]. It has an obvious counterpart in a benzenoid hydrocarbon, C_nH_s , chemically known or unknown. Let the chemical formula (C_nH_s) be denoted alternatively as $(n; s)$ and a benzenoid B with that formula as $B(n; s)$. Then $B(n; s)$ is here referred to as a benzenoid isomer (in a restricted sense). The number of C_nH_s benzenoid isomers is the number of nonisomorphic benzenoid systems compatible with the formula in question. This number is also referred to as the cardinality of C_nH_s and written $|C_nH_s|$ or $|n; s|$.

It is noted that n (the total number of carbon atoms) corresponds to the total number of vertices of the benzenoid system, while s (the number of hydrogens, also the number of secondary carbons) corresponds to the number of vertices of degree two. The benzenoid isomers $B(n; s)$ are also identified by other pairs of invariants, e.g. (h, n_i) , where h is the number of hexagons, and n_i is the number of internal vertices. Correspondingly, a benzenoid B can also be identified by the symbol

$B(h, n_i)$. The connections between the two pairs of invariants referred to above are given by

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

and

$$(h, n_i) = ((1/2)(n - s) + 1, n - 2s + 6). \quad (2)$$

For the catacondensed ($n_i = 0$) benzenoids, viz. $C_{4h+2}H_{2h+4}$, the number of isomers increases with the number of hexagons (h). For $h = 1, 2, 3, \dots, 10$ these numbers (cardinalities) are [4] 1, 1, 2, 5, 12, 36, 118, 411, 1489, 5572, respectively; for $h = 11$ [5], 21115; $h = 12$ [6, 7], 81121; $h = 13, 14$ [8], 314075, 1224528 and finally for $h = 15$ [9]:

$$|C_{62}H_{34}| = 4799205. \quad (3)$$

On the other hand, there exist series of benzenoid formulas for which the number of isomers in each case is the same. Such series, after a strict specification, are referred to as constant-isomer series (of benzenoids) [10].

The extremal benzenoids [11] constitute an important class of benzenoid systems. They are defined precisely in a subsequent section. The present work deals mainly with the properties of extremal benzenoids. These studies represent a contribution to the theory of constant-isomer series since the isomers of such series are supposed to be covered exactly by the extremal benzenoids. This feature is very likely to be true, although it has not yet been proved rigorously.

Results and Discussion

1. Preliminaries on Extremal Benzenoids

Here we give a definition of extremal benzenoids [11] and summarize some well known properties of the systems of this class.

DEFINITION 1.1: An extremal benzenoid is a benzenoid with the maximum number of internal vertices (n_i) for a given number of hexagons (h): $n_i = (n_i)_{\max}(h)$.

Extremal benzenoids exist for all possible h values: $h = 1, 2, 3, \dots$. The maximum number of internal vertices is known as a function of h [11, 12]:

$$(n_i)_{\max}(h) = 2h + 1 - [(12h - 3)^{1/2}]. \quad (4)$$

Here the "ceiling" function is employed: $[a]$ is the smallest integer larger than or equal to a .

A benzenoid system which is not extremal, is also called a non-extremal benzenoid. The two classes of extremal and non-extremal benzenoids cover exactly all the benzenoids.

An extremal benzenoid has also, for a given h : the minimum number of vertices, $n = n_{\min}(h)$; the minimum number of edges, $m = m_{\min}(h)$; the minimum number of external vertices or external edges (equal to the perimeter length), $n_e = (n_e)_{\min}(h)$; the minimum number of vertices of degree two; $s = s_{\min}(h)$. Each of these properties could be used as an alternative definition for the extremal benzenoids.

For an extremal benzenoid $A(h, n_i)$ also the number of hexagons (h) is a minimum for the number of internal vertices (n_i) in question: $h = h_{\min}(n_i)$. However, this property should not be used as a definition for extremal benzenoids without

precaution. When $n_i = 5$, for instance, $h_{\min} = 7$ (realized in $C_{25}H_{13}$), but these isomers are not extremal benzenoids. As a matter of fact there are no extremal benzenoids with $n_i = 5$, but one has $h_{\min} = 7$ also when $n_i = 6$, and this is a pair of invariants for an extremal benzenoid ($C_{24}H_{12}$ coronene).

Also, if in $A(n; s)$ the number of vertices (n) is the maximum for a given number of vertices of degree two (s), viz. $n = n_{\max}(s)$, then A is an extremal benzenoid. However, this property is not necessarily fulfilled for an extremal benzenoid and can therefore not be taken as a definition. Example: $C_{22}H_{12}$ and $C_{24}H_{12}$ are both formulas for extremal benzenoids, but only in the latter case ($C_{24}H_{12}$ coronene) $n = n_{\max} = 24$ for $s = 12$.

Let $A(n; s) \equiv A(h, n_i)$ be an extremal benzenoid. Then, according to Definition 1.1, Eq. (4) and Eq. (1), the formula of A is given by:

$$(n; s) = (2h + 1 + \lceil (12h - 3)^{1/2} \rceil; 3 + \lceil (12h - 3)^{1/2} \rceil). \quad (5)$$

Since a formula $(n; s)$ also determines the pair of invariants (h, n_i) it is clear, when Definition 1.1 is recalled, that all the benzenoid isomers with a given formula $(n; s)$ are either extremal or non-extremal exclusively. This feature is elaborated in the following theorem.

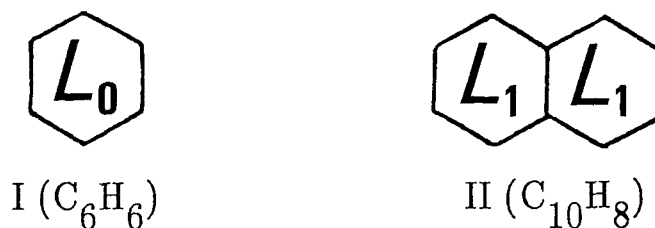
THEOREM 1.1: If $A(n; s)$ is an extremal benzenoid, then all the isomers with the formula $(n; s)$ are extremal. Conversely, if $B(n'; s')$ is a non-extremal benzenoid, then none of the $(n'; s')$ isomers are extremal.

2. Modes of Hexagons in Extremal Benzenoids

For a definition of the modes of hexagons in benzenoid systems two recent monographs may be consulted [3, 13], but also the illustrations in the following are supposed to be self-explanatory. A number of smaller theorems (referred to as propositions) are formulated and proved (more or less completely) below. Herein A is used to designate an extremal benzenoid.

PROPOSITION 2.1: The modes L_0 and L_1 occur for A only when $h = 1$ and $h = 2$, respectively.

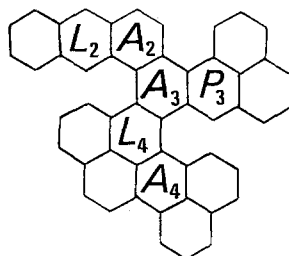
These two cases are illustrated below.



The mode L_0 is specific for benzene (I). In order to demonstrate the second part of the proposition, suppose that A for $h > 2$ had an L_1 -mode hexagon. Then it would be possible to move this hexagon into another position on the perimeter, creating a mode different from L_1 . Hereby h would be unchanged, while n_i would increase – a contradiction.

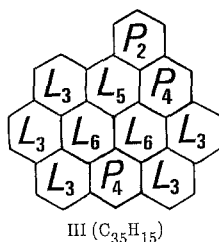
PROPOSITION 2.2: In A the modes L_2 , A_2 , A_3 , P_3 , L_4 and A_4 never occur.

Example:



For most of these modes the validity of this proposition follows from the fact that, if a benzenoid can be separated into two parts by cutting along one edge, it can be put together again in a way so that one or more internal vertices are created. It is noted that the separation along one edge does not affect the internal vertices. Now it remains to prove the proposition for the A_4 -mode. Start by removing the A_4 -mode hexagon. Thereby n_i decreases by 2. Thereafter it is always possible to put the three parts together, the single hexagon and two benzenoids, so that n_i increases by more than 2. The above considerations (especially those for A_4) do not represent a stringent proof of Proposition 2.2.

In summary, it can be said that A can not possess any "thin" part. The remaining modes, which occur in A systems for $h > 2$, are P_2 , L_3 , P_4 , L_5 and L_6 . The first four of these modes (not L_6) are found along the perimeter. Example:



It is of special interest to account for the hexagons with free edges (along the perimeter). A free edge is an edge between two vertices of degree two [3]. For the extremal benzenoids with $h > 2$ it appears from the above statements that the free edges are only found in P_2 - and L_3 -mode hexagons. More details about the properties along the perimeters of extremal benzenoids are treated in the next section.

3. Some Perimeter Properties of Extremal Benzenoids

In preparation of this discussion we shall recall the definition and properties of addition modes. An addition mode [3] is a mode acquired by a hexagon when added to the perimeter of a benzenoid. In general there are the five possibilities L_1 , P_2 , L_3 , P_4 and L_5 . They are associated with the one-, two-, three-, four- and five-contact additions, respectively. A survey is given in Table 1. The account of the increments in the numbers of internal vertices (n_i) during the different types of additions is especially relevant in the present context.

Table 1. The five types of addition of a hexagon to a benzenoid

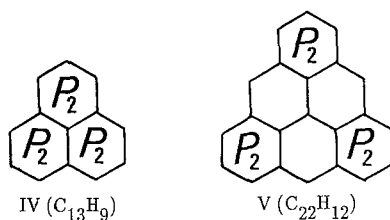
Type of addition	Description*	Acquired mode	Increment in n_i
one-contact	fusion to a free edge (or annelation)	L_1	0
two-contact	filling a fissure	P_2	1
three-contact	embedding in a bay	L_3	2
four-contact	covering a cove	P_4	3
five-contact	immersing in a fjord (fiord)	L_5	4

* For the designations of the different formations (free edge, fissure, bay, cove, fjord) on the perimeter, the cited monographs [3, 13] may be consulted

For extremal benzenoids with $h > 2$ only P_2 and L_3 occur as the addition modes of hexagons with free edges. Normally an extremal benzenoid A possesses either no P_2 -mode hexagon or exactly one P_2 , as we shall see. The exceptions for relatively small systems were found by inspection of the known forms [14] and are specified below.

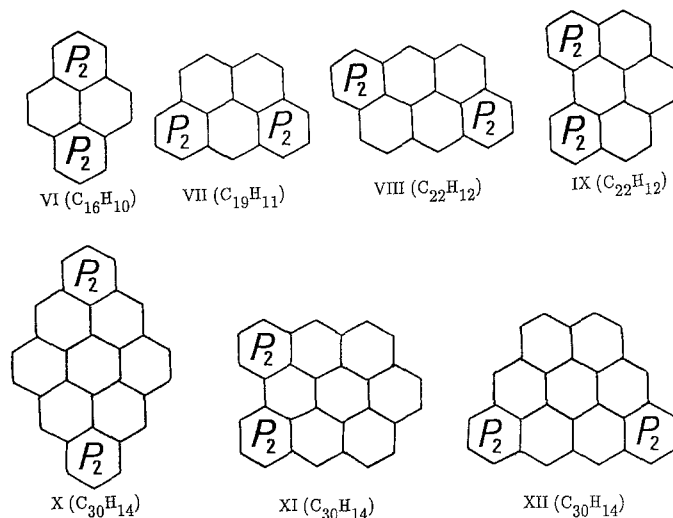
PROPOSITION 3.1: There are exactly two A systems with three P_2 -mode hexagons in each.

These extremal benzenoids are:

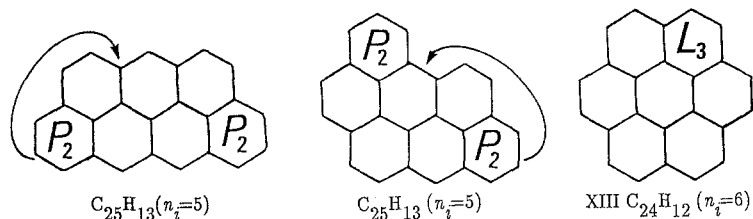


PROPOSITION 3.2: There are exactly seven A systems with two P_2 -mode hexagons in each.

They are:



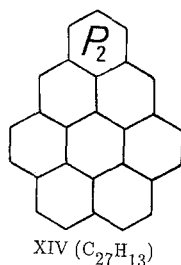
For anyone of the larger extremal benzenoids more than one P_2 -mode hexagon is not possible. Suppose that such a situation occurred. Then it could always be possible to re-arrange the hexagons so that, in the last instance, a P_2 -mode hexagon would be embedded in a bay so as to acquire an L_3 -mode. This process would give a net increment of 1 in the number of internal vertices – a contradiction. Example:



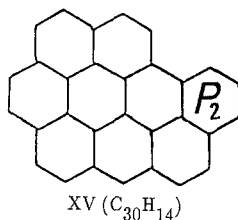
Now it should be explained why this type of reasoning is generally applicable under the given circumstances. Suppose first that A has two P_2 -mode hexagons. These two hexagons must be situated so that a system without any bay is obtained when they are removed. Otherwise one could immediately embed one of these hexagons in a bay to increase n_i . Therefore the initial system (A) must be a generalized hexagon with the two P_2 -mode hexagons added. A generalized hexagon is by definition a benzenoid with exactly six free edges. Furthermore, each P_2 hexagon must be added to a row of two hexagons in one of the six directions as is exemplified by all the systems VI–XII. But under the restrictions of minimum size, as are obeyed in the above example, the generalized hexagon must have at least one row of at least three hexagons, which makes it possible to execute the last step of the procedure. For three P_2 -mode hexagons, after a similar reasoning, one finds that the initial system must be a triangle of the type V. The rest of the reasoning goes by analogy with the first case. Finally, more than three P_2 -mode hexagons are found to be impossible for an extremal benzenoid from the outset. The essence of these considerations is formulated in another proposition.

PROPOSITION 3.3: In any A with $h = 7, 8$ and $h > 9$ there is no or exactly one P_2 -mode hexagon.

To be precise, there is neither any P_2 -mode hexagon in A for $h = 1$ (see System I) or $h = 2$ (System II). For $h = 3$ through 6 the systems IV–IX represent all the extremal benzenoids, including the three isomers of $C_{22}H_{12}$. Coronene (XIII; see above) is the unique extremal benzenoid with $h = 7$ and has no P_2 -mode hexagon. Also for $h = 8$ there is a unique extremal benzenoid; it has one P_2 -mode hexagon:



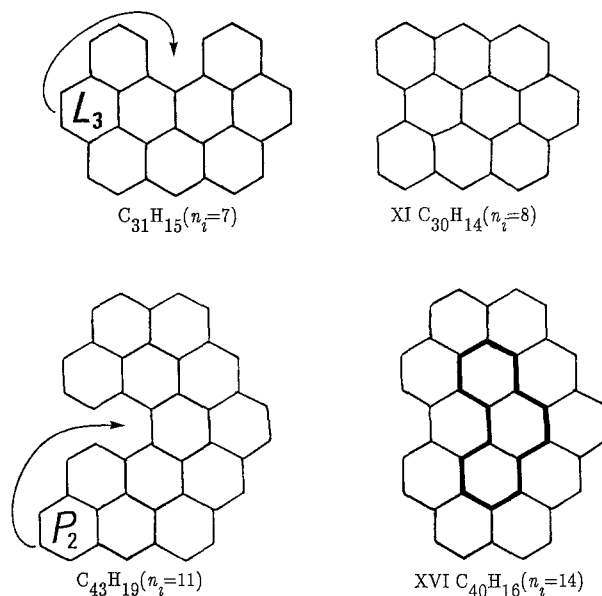
For $h = 9$ there exists, in addition to the three $C_{30}H_{14}$ isomers depicted above (X–XII), a “normal” extremal benzenoid with one P_2 -mode hexagon [14]:



The examples III, IX, XI and XV show that extremal benzenoids may possess bays. In fact, the fissures and bays are the only intruding formations of the perimeter which occur in extremal benzenoids, as is consistent with the following proposition.

PROPOSITION 3.4: An A can never possess a cove or a fjord.

Suppose namely that A had a cove or a fjord. Then it would be possible to move a P_2 - or L_3 -mode hexagon into one of these formations, which would result in a net increment in n_i (cf. Table 1) – a contradiction. Examples:



In XVI (circumphenanthrene) the contour of phenanthrene is indicated in bold.

PROPOSITION 3.5: An A can never possess a bay simultaneously with a P_2 -mode hexagon which is not a part of the bay.

Suppose that the conditions of this proposition were fulfilled. They imply that the bay would still be there if the P_2 -mode hexagon was removed. But then this hexagon could be embedded in the bay, whereby the net number of internal vertices would increase by 1 – a contradiction. The middle system in one of the above diagrams provides an example. The described process generates coronene (XIII), which is depicted in the same diagram.

4. Perimeter Parameters

In connection with the preceding section some parameters associated with the perimeter and relations between them are reported in the following, especially with relevance to the extremal benzenoids.

It is recalled (cf. Section 1) that an extremal benzenoid may be defined (alternatively to Definition 1.1) by having the minimum perimeter length (n_e) or s value for a given h . Here

$$n_e = 2s - 6. \quad (6)$$

The minimum values under consideration are given by [11, 15]

$$(n_e)_{\min}(h) = 2 \lceil (12h - 3)^{1/2} \rceil \quad (7)$$

and

$$s_{\min}(h) = 3 + \lceil (12h - 3)^{1/2} \rceil \quad (8)$$

cf. also Eq. (5).

The perimeter length is obviously given by

$$\begin{aligned} n_e = & 5|L_1| + 4(|L_2| + |A_2| + |P_2|) + 3(|A_3| + |L_3| + |P_3|) \\ & + 2(|L_4| + |A_4| + |P_4|) + |L_5| \end{aligned} \quad (9)$$

in general. Here $|X|$ is used to denote the number of hexagons in mode X . The number of free edges, say f , is in general:

$$f = 3|L_1| + |A_2| + 2|P_2| + |L_3| = b + 6. \quad (10)$$

Similar considerations are also found elsewhere [3, 16–18]. In Eq. (10) b designates the number of bay regions, to which a bay contributes by 1, a cove by 2 and a fjord by 3. Now we consider the special cases of (9) and (10) for extremal benzenoids. Then

$$b = |L_5| \quad (11)$$

signifies simply the number of bays. On neglecting the modes of hexagons which do not occur in extremal benzenoids with $h > 2$ and inserting from (11), Eq. (9) reduces to

$$n_e = 4|P_2| + 3|L_3| + 2|P_4| + b. \quad (12)$$

Furthermore, under the same restrictions,

$$f = 2|P_2| + |L_3| = b + 6. \quad (13)$$

On combining (6), (12) and (13) it was finally arrived at

$$s = 3|P_2| + 2|L_3| + |P_4| = 2b - |P_2| + |P_4| + 12 \quad (14)$$

It is stressed that (12)–(14) are valid for the special cases of extremal benzenoids with $h > 2$. Then, according to the deductions in Section 3, $|P_2|$ is normally 1 or 0, in exceptional cases (IV–XII) 2 or 3.

5. Circumscribing and Excising

The process of circumscribing is defined for many, but not for all benzenoid systems.

DEFINITION 5.1: A benzenoid B is circumscribed when, if possible, a single chain of hexagons is added all the way around the perimeter of B . Each of the added hexagons should share exactly two non-incident edges with its two neighbours among the added hexagons.

Examples: Coronene (XIII) is circumscribed benzene; the system XVI is circumscribed phenanthrene (circumphenanthrene).

Assume that B_1 is circumscribed B (circum- B), and introduce the notation

$$B_1 = c(B). \quad (15)$$

Introduce also the formulas for B and B_1 as given by $B(n; s)$ and $B_1(n_1; s_1)$, respectively. Furthermore, let the numbers of hexagons and numbers of internal vertices be specified by $B(h, n_i)$ and $B_1(h_1, (n_i)_1)$. The number of hexagons which have been added to B during circumscribing, is s , and the number of internal vertices of B_1 , viz. $(n_i)_1$, is the total number of vertices of B , viz. n . Consequently,

$$(h_1, (n_i)_1) = (h + s, n). \quad (16)$$

By means of the known relationships between the different invariants of benzenoids – see, e.g. Eqs. (1) and (2) – one obtains readily [14]

$$\begin{aligned} (h_1, (n_i)_1) &= (3h - n_i + 4, 4h - n_i + 2) \\ &= ((1/2)(n + s) + 1, n). \end{aligned} \quad (17)$$

Similarly [14]:

$$\begin{aligned} (n_1; s_1) &= (n + 2s + 6; s + 6) \\ &= (8h - 3n_i + 16; 2h - n_i + 10). \end{aligned} \quad (18)$$

Assume now that B can be circumscribed k times, and denote the resulting benzenoid by

$$B_k = c_k(B). \quad (19)$$

Introduce also $B_k(h_k, (n_i)_k) \equiv B_k(n_k; s_k)$. The generalization of (17) reads

$$\begin{aligned} (h_k, (n_i)_k) &= (3k^2 + k(2h - n_i + 1) + h, 6k^2 + 2k(2h - n_i - 2) + n_i) \\ &= (3k^2 + k(s - 3) + (1/2)(n - s) + 1, 6k^2 + 2k(s - 6) + n - 2s + 6). \end{aligned} \quad (20)$$

Similarly, for the generalization of (18) [19, 20]:

$$\begin{aligned} (n_k; s_k) &= (6k^2 + 2ks + n; s + 6k) \\ &= (6k^2 + 2k(2h - n_i + 4) + 4h - n_i + 2; 2h - n_i + 6k - 4). \end{aligned} \quad (21)$$

The process of excising is opposite to circumscribing. Here we follow John [18] in a precise definition of this process for an arbitrary benzenoid B .

DEFINITION 5.2: The excised B is obtained by removing all the external vertices (on the perimeter) of B and all their incident edges.

Let the excised B (or excis- B) be denoted by $e(B)$. Notice that $e(B)$ is not always a benzenoid. It may be the empty graph (if and only if B is a catacondensed benzenoid), a non-benzenoid (with one or more edges not belonging to hexagons), and it may be a disjoint system.

Consider now Eq. (15), which implies that B can be circumscribed and defines B_1 . Under this condition $e(B_1)$ is a benzenoid, viz.

$$B = e(B_1). \quad (22)$$

The relations (15) and (22) are compressed to

$$B_1 = c(e(B_1)). \quad (23)$$

More generally, with reference to Eq. (19), B_k can be excised k times, yielding the original benzenoid B , as is expressed by:

$$B = e_k(B_k). \quad (24)$$

Now Eqs. (19) and (24) are compressed to

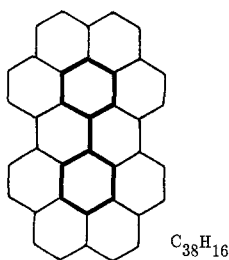
$$B_k = c_k(e_k(B_k)). \quad (25)$$

The relation (23) indicates that B_1 , under the given conditions, is not a core benzenoid; it is sometimes referred to as a non-core benzenoid. The below definition of a core benzenoid is adopted from John [18].

DEFINITION 5.3: A benzenoid B_0 is a core benzenoid if and only if $c(e(B_0)) \neq B_0$.

In our examples of extremal benzenoids, the systems I–XII, XIV, XV are core benzenoids. In all these cases $e(B_0)$ is either an empty set or a non-benzenoid. The systems XIII and XVI are non-core benzenoids.

An observation by John [18] can be translated into the statement: B_0 is a core benzenoid if it contains (at least) a hexagon in the mode $L_0, L_1, L_2, A_2, A_3, P_3, L_4$ or A_4 . We are able to add P_2 to this list, since the presence of this mode guarantees that $e(B_0)$ will be a non-benzenoid. The absence of P_2 in the above list is simply due to a misprint in the cited reference [18]. Now it should be realized that $e(B_0)$ may also be a non-benzenoid (and hence B_0 a core benzenoid) in absence of the modes of hexagons mentioned above. An example is circumbiphenyl:



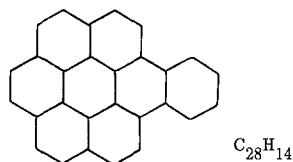
Here biphenyl is drawn in bold. Circumbiphenyl is not an extremal benzenoid.

Some of the above observations are precipitated in the following statement.

PROPOSITION 5.1: The extremal benzenoids benzene (I), naphthalene (II) and all those with one or more P_2 -mode hexagons are core benzenoids.

It may also happen that B_0 is a core benzenoid even if $e(B_0)$ is a benzenoid. In this connection it is important to realize that the benzenoid B_0 is not determined uniquely by $e(B_0)$; one may have $e(B') = e(B'')$ for $B' \neq B''$. This situation is

contrasted by $c(B)$, which determines B uniquely. Consider as an example benzo[a]coronene:



The excised benzo[a]coronene is benzene (I), the same as the excised coronene (XIII). Benzo[a]coronene is a core benzenoid, while coronene is not.

A quite precise statement can be made with regard to the nature of core benzenoids. In preparation to this statement we need the below definition.

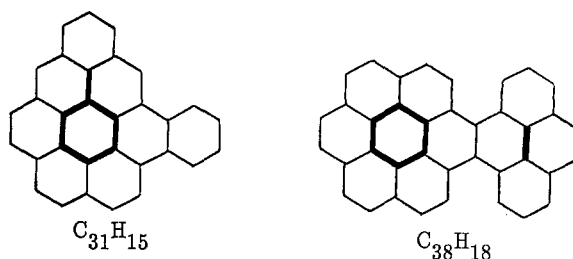
DEFINITION 5.4: A fusing edge of a benzenoid B is an edge between two vertices which both are of the degree three and lie on the perimeter of B .

Loosely speaking, a fusing edge is a short cut on the perimeter. The benzenoid B is split into two smaller benzenoids when cut along a fusing edge. Conversely, B (which possesses a fusing edge) can be interpreted as two smaller benzenoids fused together by one free edge from each of them. Example: The benzenoid of the diagram below Proposition 2.2 has five fusing edges.

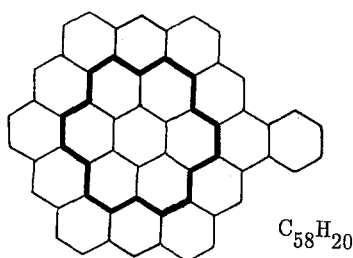
An L_1 -, P_3 - or L_4 -mode hexagon is accompanied by one fusing edge each, an L_2 - or A_2 -mode hexagon by two fusing edges each, and the A_3 -mode is accompanied by three fusing edges. A benzenoid where none of these six modes are present, has no fusing edge.

PROPOSITION 5.2: A benzenoid B_0 is a core benzenoid if and only if (a) $e(B_0)$ is not a benzenoid, or (b) B_0 has a fusing edge, or both (a) and (b) are fulfilled.

The categories (a) and (b) of this proposition are illustrated by the systems $C_{38}H_{16}$ and $C_{28}H_{14}$, respectively, of the above diagrams. Two examples of core benzenoids where both of the conditions (a) and (b) are fulfilled, are shown below.



Here the excised benzenoids are given in bold: excis- $C_{31}H_{15} = C_7H_7$; excis- $C_{38}H_{18} = C_6H_6 + C_2H_4 = C_8H_{10}$. It is noted that $e(B_0)$ very well may be a non-core benzenoid even if B_0 is a core benzenoid; see the below example (excis- $C_{58}H_{20} = C_{54}H_{18}$).



Proposition 5.2 is explained by recalling the nature of excising (cf. Definition 5.2). It is clear that B_0 is a core benzenoid if (a) or (b) of the proposition is fulfilled: if (a) is fulfilled, then $c(e(B_0))$ has no meaning, and B_0 is automatically a core benzenoid (cf. Definition 5.3); if (b) is fulfilled, then obviously B_0 is not restored by circumscribing $e(B_0)$. Finally it should also be explained that B is not a core benzenoid if $B_{-1} = e(B)$ is a benzenoid and B has no fusing edge. In this case B_{-1} can be circumscribed, and $c(B_{-1}) = B$.

Following John [18], let B_0 be called a reproducible benzenoid if and only if

$$B_{p+1} = c(B_p) \quad (26)$$

exists for every $p = 0, 1, 2, \dots$. Also the systems B_1, B_2, B_3, \dots are referred to as reproducible benzenoids (belonging to B_0). A reproducible benzenoid may also be defined in the following way.

DEFINITION 5.5: A benzenoid B is said to be reproducible if and only if B can be circumscribed an unlimited number of times.

Clearly any reproducible non-core benzenoid B_p ($p > 1$) belongs to a unique reproducible core benzenoid. This core benzenoid must eventually be reached by repeated excising of B : $B_{p-1} = e(B_p)$, $B_{p-2} = e(B_{p-1}), \dots$.

It is pointed out that Eqs. (20) and (21) under certain conditions also are applicable to excising when it is allowed for negative k values. Assume that $c_k(B_{-k}) = B$. Then B can be excised k times so that we can write

$$B_{-k} = e_k(B). \quad (27)$$

Under these conditions, from the first part of Eq. (21) for instance, it is obtained [19]

$$(n_{-k}; s_{-k}) = (6k^2 - 2ks + n; s - 6k) \quad (28)$$

when the notation $B_{-k}(n_{-k}; s_{-k})$ is assumed to have been introduced. In the special case of $k = 1$ one has

$$B_{-1} = e(B). \quad (29)$$

On introducing $B_{-1}(n_{-1}; s_{-1})$ it is arrived at a formula similar to the first part of (18), viz. [19, 20]

$$(n_{-1}; s_{-1}) = (n - 2s + 6; s - 6). \quad (30)$$

This relation is valid when $c(B_{-1}) = B$, which is to say that B should be a non-core benzenoid.

It remains to deduce a general expression for the formula coefficients of an excised benzenoid, viz. $B_{-1}(n_{-1}; s_{-1})$, from $B(n; s)$, where B may or may not be

a core benzenoid. Again it is assumed that B and B_{-1} obey Eq. (29). Although being somewhat tedious, we shall follow Definition 5.2 in the following deduction. Let m and m_{-1} denote the number of edges in B and B_{-1} , respectively. We wish to deduce m_{-1} from m . Firstly, subtract the n_e edges on the perimeter of B . Here n_e is used to denote, as usual, the number of external vertices, equal to the number of external edges of a benzenoid [3, 13]. Secondly, subtract the t edges of which (at least) one of the end points is a vertex of degree three on the perimeter of B . This last process subtracts every fusing edge (Definition 5.4) twice. Therefore, if the number of fusing edges of B is m^* , then m^* must be added. The net result is

$$m_{-1} = m - n_e - t + m^* \quad (31)$$

or slightly rewritten as

$$m - m_{-1} = n_e + t - m^*. \quad (32)$$

From the well known connections between different invariants of benzenoids [1, 3, 13, 14, 16] it is easily deduced that $m = (1/2)(3n - s)$, $n_e = 2s - 6$, and $t = s - 6$. Consequently Eq. (32) is rendered into the form

$$(3/2)(n - n_{-1}) - (1/2)(s - s_{-1}) = 3s - m^* - 12. \quad (33)$$

One has also $n - n_{-1} = n_e$ or

$$n - n_{-1} = 2s - 6. \quad (34)$$

When solved with respect to n_{-1} and s_{-1} Eqs. (33) and (34) yield:

$$(n_{-1}; s_{-1}) = (n - 2s + 6; s - 2m^* - 6). \quad (35)$$

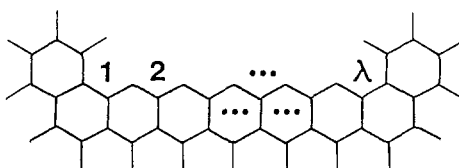
It is seen that Eq. (30) is the special case of (35) for $m^* = 0$. It appears therefore that Eq. (30) is valid even when B is a core benzenoid, if only $m^* = 0$.

In order to exemplify Eq. (35), consider the systems (a) $C_{31}H_{15}$ and (b) $C_{38}H_{18}$ in one of the diagrams above. (a) $n = 31$, $s = 15$, $m^* = 1$ gives $n_{-1} = 7$, $s_{-1} = 7$; (b) $n = 38$, $s = 18$, $m^* = 1$ gives $n_{-1} = 8$, $s_{-1} = 10$. Consider now a catacondensed benzenoid with h hexagons, say $Q_h(n; s)$. It has $m^* = h - 1$ fusing edges, while $n = 4h + 2$ and $s = 2h + 4$. On inserting these expressions into Eq. (35) one obtains $n_{-1} = s_{-1} = 0$ for every h . This reflects the fact that $e(Q_h)$ is the empty graph (see above).

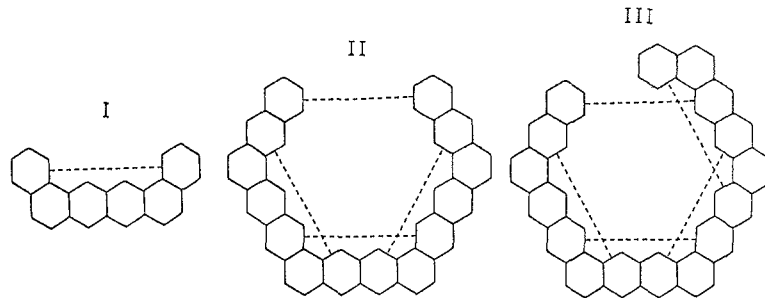
6. Latent Row of Hexagons

DEFINITION 6.1: A latent row (of hexagons) in a benzenoid B is a single chain of hexagons on the hexagonal lattice between two (parallel) edges of the perimeter of B .

It is understood that the hexagons of the latent row are not occupied by hexagons of B . Hence the latent row is only a "gap" connected with the perimeter of B . A latent row of λ hexagons is depicted below. The pendent edges may or may not belong to hexagons of B .



Two types of latent rows of hexagons in B are distinguished; all the hexagons of the latent row, if materialized, may be incident to hexagons of B (along its perimeter), or this may not be the case. The two types shall be referred to as a proper- and improper latent row, respectively. In the below diagram both of these types are illustrated.



PROPOSITION 6.1: A benzenoid B is reproducible if and only if B does not possess any latent row of hexagons.

If B has only one latent row of hexagons, then it must be proper. If B has two or more latent rows, then at least one of them must be proper. Hence the condition of Proposition 6.1 can be sharpened by saying that B has no proper latent row of hexagons. With this modification Proposition 6.1 is a translation of an observation by John [18], although he based his approach on concepts which are largely different from the present ones.

It is obvious that the presence of a latent row in B hinders that B can be circumscribed without limitation. This is seen to be a part of Proposition 6.1 when Definition 5.4 is remembered. A more precise statement is formulated in the following.

PROPOSITION 6.2: If a benzenoid B has a latent row of λ hexagons, then B cannot be circumscribed λ times.

This proposition appears to be evident when the relevant types of the perimeter shape are inspected. It is not implied, however, that B can be circumscribed $\lambda - 1$ times when the shortest latent row in B holds λ hexagons. In the last diagram (see above) some elucidating examples are given. In all cases the shortest latent rows of hexagons (indicated by stippled lines) comply with $\lambda = 3$. The system I can be circumscribed $\lambda - 1 = 2$ times, but not more, II can be circumscribed only once, while III cannot be circumscribed at all.

The remaining part of Proposition 6.1 amounts to saying that B can be circumscribed an unlimited number of times when it does not possess any latent row of hexagons. In order to prove this it should be verified that every feature which hinders an unlimited circumscribing of B entails the presence of (at least) one latent row.

For the sake of completeness a well-known fact [14, 18] is formulated below.

PROPOSITION 6.3: A benzenoid B cannot be circumscribed if it possesses a cove or a fjord.

A cove and a fjord [3, 13] are actually special cases of a latent row when it is allowed for a "row" of one hexagon ($\lambda = 1$). In a cove there is a pair of parallel edges which define the latent row. In a fjord there are two pairs of such edges defining formally two latent rows in terms of the gaps between the edges. However, one and the same hexagon fills both these gaps simultaneously. Under the scope of the above discussion it is clear that the Proposition 6.3 is a special case of Proposition 6.2.

The definition of a latent row is relevant to the extremal benzenoids, which exhibit some important properties reported in the following.

PROPOSITION 6.4: An extremal benzenoid A has no latent row of hexagons.

Proposition 3.4 about the absence of coves and fjords in A , which is proved above, is clearly a special case of Proposition 6.4. A proof of Proposition 6.4 was conducted in detail elsewhere [21] and shall not be repeated here. It follows the same principles as our proof of Proposition 3.4 (see above). It is demonstrated [21] that, by filling a proper latent row of hexagons of a benzenoid B from one side with certain hexagons taken from the perimeter of B , the number of internal vertices of B will inevitably increase sooner or later; hence B cannot be an extremal benzenoid.

An important corollary emerges from Proposition 6.1 and Proposition 6.4 [21]:

COROLLARY 6.1: Every extremal benzenoid A is a reproducible benzenoid.

In other words (cf. Definition 5.5) every A can be circumscribed an unlimited number of times.

Conclusion

The present paper is the first part of a systematic approach to the theoretical studies of extremal benzenoids. This work, which has relevance to the constant-isomer benzenoid series [10, 17] of great chemical interest, is far from ended. It seems to be worth the while to continue this systematic treatment although several contributions to the theory of extremal benzenoids using different approaches, have recently been published [20–24].

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