

**Transfer Matrix Approach to the Wiener Numbers of  
Cata-Condensed Benzenoids**

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**Abstract**

A set of three  $5 \times 5$  transfer matrices,  $I$ ,  $J$ ,  $K$ , associated with the different annellation modes is presented. By multiplying these matrices with an appropriate terminal vector the Wiener numbers of arbitrary unbranched cata-condensed benzenoids can be simply calculated. The matrices required in the case of branched cata-condensed benzenoids are also given: a  $9 \times 5$  matrix  $B$  associated with single branching of a benzenoid chain, and augmented transfer matrices  $I$ ,  $J$ ,  $K$ , of dimension  $9 \times 9$ . By means of these matrices the Wiener numbers of all cata-condensed benzenoids as far, as they have been isolated hitherto, are accessible. More complicated structures are considered, and for these the matrices must again be augmented to dimension  $15 \times 9$  ( $B$ ) and  $15 \times 15$  ( $I$ ,  $J$ ,  $K$ ), respectively. The augmented matrices are explicitly presented and instructions for their further augmentation, if desired, are also given. Further, a particular code for unbranched cata-condensed benzenoids is made applicable to branched ones.

**Introduction**

Among the various invariants which may be derived from molecular graphs the Wiener number plays a significant role historically because it was the first one used in correlations with physico-chemical data. In these early attempts Wiener [1 - 3] empirically introduced two such graph-theoretical invariants: (i) the path number,  $W$  (Wiener number), originally defined as the sum of bonds

separating all pairs of carbon atoms in alkanes, and (ii) the polarity number,  $P$ , which equals the number of those pairs of carbon atoms which are separated by exactly three bonds. Wiener showed that expressions of the type  $aW + bP + c$  reproduce the boiling points, heats of formation and vaporization of numerous alkanes with high accuracy. Similar results have been obtained by Platt [4, 5] for the molecular refraction indices of alkanes. To our knowledge the combination of  $W$  and  $P$  has not been applied since, but Wiener numbers alone have been used in correlations involving densities, viscosities, surface tensions, and gaschromatographic retention times; detailed surveys of that work are found in [6 - 8].

The original definition of the Wiener number,  $W(G)$ , of graph  $G$ , is unique only in the case of acyclic graphs. An extension of the definition has been given by Hosoya [9], who pointed out that  $W(G)$  may be expressed in terms of the entries of the distance matrix,  $D(G)$ , of the graph, by

$$W(G) = \sum_{r < s} d(rs) , \quad (1)$$

where  $d(rs)$  denotes the distance between vertices,  $r$  and  $s$ , i.e. the number of edges of the path with minimal length (= geodesic path) which connects these vertices. By this relation, eq. (1), the Wiener numbers are identified as metric quantities characterizing the graph globally [10, 11]; their basic mathematical properties are outlined elsewhere [7, 12]. As a consequence of their metric character the Wiener numbers provide a suitable basis for describing the features of molecular branching and cyclicity by a series of rules [13 - 21], and this character also allows the Wiener number of a given molecular graph to be expressed in terms of the metric properties of the subgraphs corresponding with the constitutional fragments of the molecule being considered [22]. The metric properties in question are the Wiener number of the subgraph, individual distances,  $d(rs)$ , between its vertices, and the recently introduced distance numbers [12, 22], defined by

$$d(r|G) = \sum_s d(rs) . \quad (2)$$

Since distance numbers play a significant role in the discussion

which follows, we introduce here an important property of distance numbers of adjacent vertices, say  $u$  and  $v$ . With regard to the distances  $d(ur)$  and  $d(vr)$ , the vertex set,  $V(G)$ , can be resolved into three disjoint subsets, namely:

$$\begin{aligned} V_u &= \{r|r \in G, d(ur) < d(vr)\} \quad , \\ V_{uv} &= \{r|r \in G, d(ur) = d(vr)\} \quad , \\ V_v &= \{r|r \in G, d(ur) > d(vr)\} \quad , \end{aligned} \quad (3)$$

where  $V_{uv}$  is non-empty if and only if  $u$  and  $v$  belong to one and the same odd-membered cycle. This means that  $V_{uv}$  is empty for all bipartite graphs and, hence, also for those of benzenoids. It has been proved [11, 12, 22] that the distance numbers of adjacent vertices obey the following relation:

$$d(u|G) - d(v|G) = - |V_u| + |V_v| \quad (4)$$

where  $|V_u|$  and  $|V_v|$  denote the cardinalities of the respective subsets defined above.

In bipartite graphs the parity of Wiener and distance numbers depend on the parities of cardinalities of the colour sets [23]. This general finding has been tightened for benzenoid graphs resulting in modulo 4 and modulo 8 rules, respectively [24].

The Wiener and distance numbers may be derived by means of eqs. (1) and (2), respectively, and the distances may be obtained from the powers of the adjacency matrix  $A(G)$  of the graph according to

$$d(rs) = \min\{v|(A^v)_{rs} \neq 0, 0 \leq v \leq n-1\} \quad (5)$$

where  $n$  denotes the number of vertices of  $G$ . Since with increasing  $n$  this procedure soon becomes clumsy, there is a need for a more efficient method for the evaluation of Wiener numbers. The transfer matrix method offers such an approach.

Very recently we have applied this method to the evaluation of the matching and characteristic polynomials, the topological index  $Z$ , and the number of Kekulé structures of arbitrary unbranched cata-condensed benzenoids [25]. In the transfer matrix approach [26]

the property considered is represented by a particular element of a vector,  $Q_h$ , associated with benzenoid  $B_h$ . The value of the property for  $B_{h+1}$  is obtained by multiplying vector  $Q_h$  with a suitable transfer matrix; all the quantities desired in that multiplication are provided by the other elements of the vector. In the series of unbranched cata-condensed benzenoids each transfer matrix is associated with the annellation of a ring to the benzenoid. According to the different modes of annellation, as explained in the next section, three such matrices, I, J, K, are required, corresponding to the linear (I), the angular clockwise (J), and the angular anti-clockwise mode (K), respectively. It is worth noting that the sequence of transfer matrices applied represents a code word for the benzenoid being considered [25].

In this work we describe the development of transfer matrices by means of which the Wiener numbers of benzenoids can be calculated. We derive the transfer matrices and the vector used in the case of unbranched cata-condensed benzenoids, and then extend this procedure to branched ones. As far as possible the notation used in this paper follows that of [12, 22, 25].

#### Unbranched cata-condensed benzenoids

At first we consider the changes in Wiener and distance numbers which take place due to the formation of benzenoid  $B_h$  (represented by graph H) from  $B_{h-1}$  (represented by graph G) by annellating an additional ring, as shown schematically in Figure 1. Since  $B_{h-1}$  is assumed to be arbitrary, its pattern of annellation cannot be specified; this is indicated by half-circles in Fig. 1.

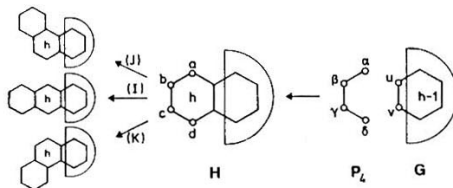


Figure 1: Formation of benzenoid  $B_h$  from  $B_{h-1}$  by annellating a ring, and also the annellation modes corresponding with transfer matrices I, J, and K, respectively.

In graph-theoretical terms, the annellation may be described as a joining of the terminal vertices  $\alpha$  and  $\delta$  of path graph  $P_4$ , with two adjacent vertices  $u$  and  $v$  of the terminal ring of  $G$ . In  $H$  the added vertices are renamed  $a, b, c, d$ . The changes of Wiener and distance numbers due to this process are expressed by eqs. (31) and (32) of [22], and hence we may apply these equations directly to  $H$ . After inserting the respective numerical values of the Wiener and distance numbers of  $P_4$ , we obtain:

$$W(H) = W(G) + 2d(u|G) + 2d(v|G) + 6n(G) + 10 \quad ; \quad (6)$$

$$d(a|H) = d(u|G) + n(G) + 6 \quad , \quad (7a)$$

$$d(b|H) = d(u|G) + 2n(G) + 4 \quad , \quad (7b)$$

$$d(c|H) = d(v|G) + 2n(G) + 4 \quad , \quad (7c)$$

$$d(d|H) = d(v|G) + n(G) + 6 \quad ; \quad (7d)$$

$$n(H) = n(G) + 4 \quad . \quad (8)$$

These equations possess a quite general validity because neither the vertices  $u$  and  $v$ , where annellation takes place, nor the graph to which they belong, are specified in [22].

The terminal ring of a benzenoid has four vertices suitable for annellations which will henceforth always be denoted by  $a, b, c$ , and  $d$ . The vertices  $u$  and  $v$  used in eqs. (6) - (8) are pairs out of that set. As illustrated in Fig. 1 there are three possibilities for selecting  $u$  and  $v$ , each one related to a particular mode of annellation and transfer matrix, namely:

$u = a, v = b$  : angular clockwise mode, J,

$u = b, v = c$  : linear mode, I, (9)

$u = c, v = d$  : angular anti-clockwise mode, K.

From this one might conclude that a vector made up from the 6 left hand side quantities of eqs. (6) - (8) and 1 as multiplier for the natural numbers appearing therein, retains just the quantities required in the next step, but the vector can actually be contracted to 5 elements. Applying eq. (4) to the vertex pairs  $a,b$  and  $c,d$  of  $G$  one obtains

$$d(a|G) = d(b|G) - n(G) + 6 \quad , \quad (10a)$$

$$d(d|G) = d(c|G) - n(G) + 6 \quad . \quad (10b)$$

As a consequence of these relations the vector  $Q(G)$  may be defined without the distance numbers of vertices  $a$  and  $d$ . Thus, it takes the following form:

$$Q(G) = \begin{pmatrix} W(G) \\ d(b|G) \\ d(c|G) \\ n(G) \\ 1 \end{pmatrix} \quad (11)$$

In practice it might be useful to insert a further element into  $Q(G)$  which counts the number,  $h(G)$ , of rings of the benzenoid, but in the following the above form of  $Q(G)$  always will be assumed.

From eqs. (6) - (11) the transfer matrices  $I$ ,  $J$ , and  $K$ , as explicitly given in Table 1, are easily derived. As a consequence of eq. (10), the matrices  $J$  and  $K$  have a zero column each. Further as a consequence of the selection pattern (9) and eq. (10), matrix  $K$  is obtained from  $J$  by interchanging the second and third rows and columns, and vice versa.

$$I = \begin{pmatrix} 1 & 2 & 2 & 6 & 10 \\ 0 & 1 & 0 & 2 & 4 \\ 0 & 0 & 1 & 2 & 4 \\ 0 & 0 & 0 & 1 & 4 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

$$J = \begin{pmatrix} 1 & 4 & 0 & 4 & 22 \\ 0 & 1 & 0 & 1 & 10 \\ 0 & 1 & 0 & 2 & 4 \\ 0 & 0 & 0 & 1 & 4 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

$$K = \begin{pmatrix} 1 & 0 & 4 & 4 & 22 \\ 0 & 0 & 1 & 2 & 4 \\ 0 & 0 & 1 & 1 & 10 \\ 0 & 0 & 0 & 1 & 4 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

Table 1: Transfer matrices  $I$ ,  $J$ ,  $K$  for linear, angular clockwise, and angular anti-clockwise annellation mode, respectively.

According to the formal process shown in Fig. 1 the smallest benzenoid, benzene,  $h = 1$ , is formed from the path graph  $P_4$  and  $G = P_2$ . From that, for the vectors  $Q_0$  and  $Q_1$  one concludes

$$Q_0 = \begin{pmatrix} 1 \\ 1 \\ 1 \\ 2 \\ 1 \end{pmatrix}, \quad Q_1 = I Q_0 = \begin{pmatrix} 27 \\ 9 \\ 9 \\ 6 \\ 1 \end{pmatrix}. \quad (12)$$

Note, that  $Q_1$  can be obtained only by  $I Q_0$ , whilst the products  $J Q_0$  and  $K Q_0$  are undefined. This is because the path graph  $P_2$  consists of two vertices only, and hence eq. (10) cannot be applied to  $P_2$ . In contrast to this the vector  $Q_2$  associated with naphthalene results from  $Q_1$  by applying any one of the three transfer matrices:

$$Q_2 = I Q_1 = J Q_1 = K Q_1 .$$

This result exhibits the symmetry of benzene, but it also follows from eq. (10) and the fact that the benzene graph consists of just 6 vertices.

By means of the vector and the transfer matrices given in this section, the Wiener numbers of arbitrary unbranched cata-condensed benzenoids are very quickly obtained. Thus, the transfer matrix approach is confirmed as an efficient method for calculating Wiener numbers.

Because of eq. (10), transfer matrices  $J$  and  $K$  can only be applied to a pair of adjacent vertices of a terminal six-membered ring, as assumed from the beginning. By contrast, the transfer matrix  $I$  may be generally used for annellating a six-membered ring to two adjacent vertices of any simple graph  $G'$ , provided the vector  $Q(G')$ , corresponding to eq. (11), can be constructed. Starting with  $I Q(G')$  the Wiener numbers of arbitrary sequences of cata-fused six-membered rings with one non-benzenoid terminal group [27] can also be generated.

In principle the Wiener numbers of branched cata-condensed benzenoids could be derived by applying transfer matrix  $I$  to two adjacent vertices of an inner ring of a benzenoid. But the construc-

tion of the required vector  $Q(G')$  would be rather complicated in such a case, and the difficulties involved would be almost insurmountable. We have therefore developed an alternative approach to this problem which is the subject of the next section.

### Cata-condensed benzenoids with single branching

A benzenoid exhibiting a single branching may be interpreted as a derivative of triphenylene from the terminal rings of which branches of cata-condensed benzene rings originate. Viewed in reverse, the annellation of a triphenylene unit to a growing cata-condensed benzenoid produces its branching. In this section, only benzenoids with a single triphenylene unit are considered; multiple branching is the subject of the next section.

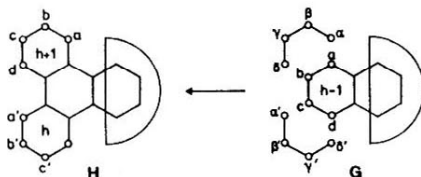


Figure 2: Incorporation of a triphenylene unit into a benzenoid.

The simplest way to incorporate a triphenylene unit into a chain of cata-condensed benzene rings is illustrated by Figure 2. The terminal vertices of two isolated  $P_4$  graphs,  $\alpha, \delta$  and  $\alpha', \delta'$ , respectively, are linked to the vertices  $a, b, c, d$  of the terminal ring of  $G$ . If  $G$  represents the benzenoid  $B_{h-1}$  then the graph  $H$  formed in this way corresponds with the branched benzenoid  $B_{h+1}$ . In  $H$  the added vertices form those peripheric regions where further annellations may take place, hence, in  $H$  they are renamed  $a, b, c, d$  and  $a', b', c', d'$ , respectively (see Fig. 2).

Applying eqs. (31) and (32) of [22] twice one arrives at the following set of equations:



$$W(H) = W(G) + 4d(b|G) + 4d(c|G) + 8n(G) + 124 ; \quad (13)$$

$$d(a|H) = d(b|G) + 32 , \quad (14a)$$

$$d(b|H) = d(b|G) + n(G) + 34 , \quad (14b)$$

$$d(c|H) = d(b|G) + 2n(G) + 24 , \quad (14c)$$

$$d(d|H) = d(b|G) + n(G) + 22 ; \quad (14d)$$

$$d(a'|H) = d(c|G) + n(G) + 22 , \quad (15a)$$

$$d(b'|H) = d(c|G) + 2n(G) + 24 , \quad (15b)$$

$$d(c'|H) = d(c|G) + n(G) + 34 , \quad (15c)$$

$$d(d'|H) = d(c|G) + 32 ; \quad (15d)$$

$$n(H) = n(G) + 8 . \quad (16)$$

Note that b and c on the right hand sides of these equations refer to peripheric vertices of  $G \sim B_{h-1}$ , but on their left hand sides to those of  $H \sim B_{h+1}$ . Note further, that eq. (10) holds for the distance numbers of the vertex pairs (a,b), (c,d), (a',b'), and (c',d') too.

The complete formation of the intended branched benzenoid requires further annellations at ring h and ring h+1, respectively. It is assumed that annellation is begun at ring h+1 and is continued as long as necessary for the complete formation of that branch ("first branch") arriving in such a way at the intermediate benzenoid  $B_h$ . It can be seen that  $B_h$  consists of h'-1 arbitrarily cata-condensed benzene rings and an additional one which is labeled by h and cata-fused with ring h-1. Benzenoid  $B_h$  is the starting material for the formation of the "second branch" which originates from ring h. Performing the first annellation step there, one requires the distance numbers of vertices b' and c' as they actually are in  $B_h$ . Therefore, the vector used during the formation of the first branch must keep these quantities in evidence. Further, the transfer matrices applied in the stepwise formation of the first branch must account for the changes of these distance numbers due to the particular annellations executed. As is shown more fully below, for this purpose the actual values of the distances  $d(bb')$  and  $d(cb')$  will be required, hence, they must also be represented by particular elements of the vector. All this indicates the manner in which the original vector, Q, must be augmented to vector R:

$$R(G) = \begin{pmatrix} W(G) \\ d(b|G) \\ d(c|G) \\ d(b'|G) \\ d(c'|G) \\ d(bb'|G) \\ d(cb'|G) \\ n(G) \\ 1 \end{pmatrix}; \quad (17)$$

where  $G$  denotes the graph of a branched benzenoid, corresponding either with  $B_{h+1}$ , shown in Fig. 2, or with any one of the benzenoids obtained in the course of the stepwise formation of the first branch, including  $B_h$ .

Since the augmented vector  $R$  is generated from  $Q$  when the branched  $B_{h+1}$  is formed from unbranched  $B_{h-1}$  in accordance with Fig. 2, this step may be written as:

$$R(h+1) = B Q(h-1) ,$$

where  $B$  denotes the transfer matrix associated with the incorporation of a triphenylene unit. With regard to the lengths of the vectors involved, matrix  $B$  must consist of 9 rows and 5 columns, respectively. The first rows have to agree with eqs. (13) - (15). For the next two rows by inspection of Fig. 2 one finds  $d(bb') = 6$  and  $d(cb') = 5$ . From that and eq. (16) the last rows of  $B$  are derived. The resulting transfer matrix  $B$  is explicitly given in Table 2.

$$B = \begin{pmatrix} 1 & 4 & 4 & 8 & 124 \\ 0 & 1 & 0 & 1 & 34 \\ 0 & 1 & 0 & 2 & 24 \\ 0 & 0 & 1 & 2 & 24 \\ 0 & 0 & 1 & 1 & 34 \\ 0 & 0 & 0 & 0 & 6 \\ 0 & 0 & 0 & 0 & 5 \\ 0 & 0 & 0 & 1 & 8 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

Table 2: Transfer matrix  $B$  associated with branching of a chain of cata-fused six-membered rings.

The application of transfer matrix B requires a  $P_4$ -like sequence of four vertices suitable for annellations. Such a situation is always realized in the terminal ring of a benzenoid independently from the mode of its annellation. Therefore, matrix B may be applied to any sequence of transfer matrices, i.e. all the combinations, B I ..., B J ..., B K ... are feasible. Since the number of rings,  $h(G)$ , is increased only by 2 when matrix B is applied, the complete triphenylene unit and its annellation mode is represented by (BI), (BJ), and (BK), respectively. As Fig. 2 shows, the two rings introduced by B are angularly annellated, ring  $h+1$  in clockwise, ring  $h$  in anti-clockwise mode.

As assumed above, annellations to  $B_{h+1}$  are continued at ring  $h+1$  to which the vertices  $b$  and  $c$  belong. With regard to the length of vector  $R$ , the transfer matrices applied now must have dimension  $9 \times 9$ . We may denote these matrices again by I, J, and K, respectively, and, because of the difference in size, no confusion with the former ones can occur. As a consequence of their generality, eqs. (6) - (10) are also valid in the case treated here. Therefore, the first three and the last two rows of the augmented matrices are obtained from the former ones if one inserts four zero-columns between their third and fourth column. The final forms of the new matrices are achieved by inserting four rows which produce the elements augmenting the vector. By means of eq. (31) of [22], for the first two quantities in the cases of different annellation modes, one finds:

(i) linear mode (I) :

$$\begin{aligned} d(b'|H) &= d(b'|G) + 2d(bb'|G) + 2d(cb'|G) + 6 , \\ d(c'|H) &= d(c'|G) + 2d(bb'|G) + 2d(cb'|G) + 10 ; \end{aligned} \quad (18a)$$

(ii) angular clockwise mode (J) :

$$\begin{aligned} d(b'|H) &= d(b'|G) + 4d(bb'|G) + 4 , \\ d(c'|H) &= d(c'|G) + 4d(bb'|G) + 8 ; \end{aligned} \quad (18b)$$

(iii) angular anti-clockwise mode (K) :

$$\begin{aligned} d(b'|H) &= d(b'|G) + 4d(cb'|G) + 4 , \\ d(c'|H) &= d(c'|G) + 4d(cb'|G) + 8 . \end{aligned} \quad (18c)$$

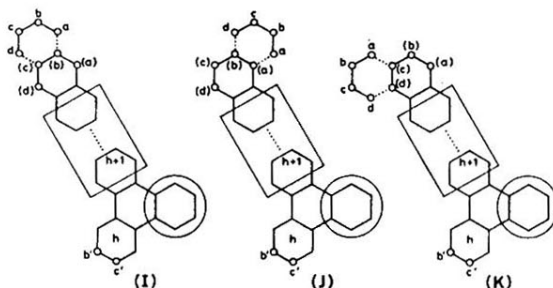


Figure 3: Ring annellations in the formation of the first branch (vertex labels used in G are given in parantheses).

Expression for the distances may be derived from Figure 3 which illustrates the situations met in the course of the formation of the first branch. Areas of arbitrary, i.e. non-specifiable, annellation patterns are marked by light closed lines. Independent from the actual pattern of the first branch, the geodesic paths connecting vertex  $b'$  with vertices  $a, b, c, d$  added in the last step, enter ring  $h$  always at the vertex opposite to  $c'$ . From this one may conclude:

$$\begin{aligned} d(bc') &= d(bb') + 1 \quad , \\ d(cc') &= d(cb') + 1 \quad . \end{aligned} \tag{19}$$

Since these relations are valid for any G or H, the distances to vertex  $c'$  have been omitted in vector R, although they are needed in eqs. (18a,c).

As Fig. 3 further shows, the changes in the distances  $d(bb')$  and  $d(cb')$  due to annellation are fully determined by the local features of the last two rings. Hence, the desired expressions may be directly derived from Fig. 3, and one obtains for the different annellation modes:

(i) linear mode (I) :

$$\begin{aligned} d(bb'|H) &= d(bb'|G) + 2 , \\ d(cb'|H) &= d(cb'|G) + 2 ; \end{aligned} \tag{20a}$$

(ii) angular clockwise mode (J) :

$$\begin{aligned} d(bb'|H) &= d(bb'|G) + 1 , \\ d(cb'|H) &= d(bb'|G) + 2 ; \end{aligned} \tag{20b}$$

(iii) angular anti-clockwise mode (K) :

$$\begin{aligned} d(bb'|H) &= d(cb'|G) + 2 , \\ d(cb'|H) &= d(cb'|G) + 1 . \end{aligned} \tag{20c}$$

By means of eqs. (18) and (20) the missing rows of the augmented transfer matrices I, J, K can now be constructed. The resulting matrices are explicitly given in Table 3. As can be seen by inspection, transfer matrices J and K are obtained from each other by the pairwise interchange of row and column 2 with 3 and 6 with 7.

$$I = \begin{pmatrix} 1 & 2 & 2 & 0 & 0 & 0 & 0 & 6 & 10 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 2 & 4 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 2 & 4 \\ 0 & 0 & 0 & 1 & 0 & 2 & 2 & 0 & 6 \\ 0 & 0 & 0 & 0 & 1 & 2 & 2 & 0 & 10 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 2 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 2 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 4 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

$$J = \begin{pmatrix} 1 & 4 & 0 & 0 & 0 & 0 & 0 & 4 & 22 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 1 & 10 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 2 & 4 \\ 0 & 0 & 0 & 1 & 0 & 4 & 0 & 0 & 4 \\ 0 & 0 & 0 & 0 & 1 & 4 & 0 & 0 & 8 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 2 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 4 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

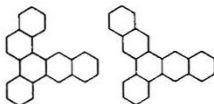
$$K = \begin{pmatrix} 1 & 0 & 4 & 0 & 0 & 0 & 0 & 4 & 22 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 2 & 4 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 1 & 10 \\ 0 & 0 & 0 & 1 & 0 & 0 & 4 & 0 & 4 \\ 0 & 0 & 0 & 0 & 1 & 0 & 4 & 0 & 8 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 2 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 4 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

Table 3: Transfer matrices I, J, and K applied in the formation of the first branch after the incorporation of a triphenylene unit.

As can be seen from matrix B and eq. (20), the distances  $d(bb')$  and  $d(cb')$  always differ by 1. Linear annellation does not alter their difference. After the application of J one always has  $d(bb') < d(cb')$ , but after having applied K, one always finds  $d(bb') > d(cb')$ .

As soon as the first branch is completely formed one turns to the formation of the second branch originating from ring h. For the annellations to be performed now, not all the quantities kept in vector R are required. Consequently, the vector may be contracted to its original length by striking out the second, third, sixth, and seventh element. This procedure also involves vertices  $b'$  and  $c'$  being renamed b and c, respectively. The annellations performed now in order to form the second branch are executed by means of the original transfer matrices I, J, K collected in Table 1.

Clearly, the contraction of  $R(G)$  to  $Q(G)$  may be performed straight after the application of matrix B if no annellations take place at ring h, as for instance in case of the benzenoids shown below:



But note that in these cases the distance numbers of b and c are needed for further annellation. Therefore,  $R(G)$  is contracted to  $Q(G)$  by striking out the fourth, fifth, sixth, and seventh element.

#### Cata-condensed benzenoids with multiple branching

Benzenoids possessing more than one triphenylene unit may be grouped into two classes. The first class is formed from those benzenoids in which all the triphenylene units are incorporated within a single chain (main chain), thus, these benzenoids may be considered as a long chain of cata-condensed benzene rings with some unbranched side chains. The benzenoids of the second class are characterized by the presence of at least one triphenylene unit from the rings of which exclusively branched side chains originate.

The transfer matrices given in Tables 1 - 3 are sufficient for treating benzenoids of the first class: One starts with the

formation of the main chain and, arriving at a triphenylene unit, the unbranched side chain originating from there is completely formed before one continues with annellations in the main chain. Since vector  $R$  is adjusted for persisting with annellations in the angular clockwise branch growing out from ring  $h+1$  (see Fig. 2), its reorganization is necessary if the side chain is annellated in angular anti-clockwise mode, i.e. it originates from ring  $h$ . In some particular cases it may happen that transfer matrix  $B$  must be applied twice, one after the other, as for instance in case of dibenzo-chrysenes shown below:



This benzenoid corresponds to  $B^2 I^2 Q_0$  (the location of vector  $Q_0$  is marked by a heavy bar) and these multiplications can be smoothly performed without difficulties.

For benzenoids of the second class the matrices collected in Tables 1 - 3 are insufficient because in the course of the formation of such a benzenoid, a further triphenylene unit must be incorporated into the growing benzenoid before annellations at the last one can be completed. The situation in question is illustrated by Figure 4. Continuing with annellations at ring

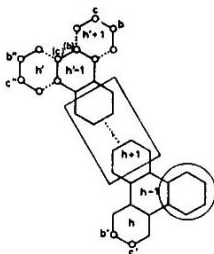


Figure 4: Incorporation of a second triphenylene unit.

$h'+1$ , the actual values of the distance numbers of vertices  $b'$ ,  $c'$ ,

b", c" and also those of the distances  $d(b'b'')$ ,  $d(cb'')$ ,  $d(b'b'')$ ,  $d(c'b'')$  must be kept in evidence. This means that the vector R and consequently also the matrices B, I, J, and K must be augmented. The augmentation of the vector leads to

$$S(G) = \left( \begin{array}{c} W(G) \\ d(b|G) \\ d(c|G) \\ d(b'|G) \\ d(c'|G) \\ d(b''|G) \\ d(c''|G) \\ d(bb'|G) \\ d(cb'|G) \\ d(bb''|G) \\ d(cb''|G) \\ d(b'b''|G) \\ d(c'b''|G) \\ n(G) \\ 1 \end{array} \right) \quad (21)$$

The augmentation of 9x5 matrix B may be performed in two steps. In the first step four zero-columns are inserted between the third and fourth column of B. The rows of the square matrix B formed in such a way are now ready for multiplication with vector R. In that way, the first three rows of B produce  $W(H)$ ,  $d(b|H)$ , and  $d(c|H)$  as desired, thus, they agree with the first three rows of the augmented matrix B. However, the following rows of B now produce  $d(b''|H)$ ,  $d(c''|H)$ ,  $d(bb''|H)$ ,  $d(cb''|H)$ ,  $n(H)$ , and 1, hence, they agree with rows 6, 7, 10, 11, 14, and 15 of augmented matrix B, respectively. For the missing rows one may derive from Fig. 4:



$$\begin{aligned} d(b'|H) &= d(b'|G) + 4d(bb'|G) + 4d(cb'|G) + 8, \\ d(c'|H) &= d(c'|G) + 4d(bb'|G) + 4d(cb'|G) + 16; \end{aligned} \quad (22)$$

$$\begin{aligned} d(bb'|H) &= d(bb'|G) + 1, \\ d(cb'|H) &= d(bb'|G) + 2; \end{aligned} \quad (23)$$

$$\begin{aligned} d(b'b''|H) &= d(cb'|G) + 2, \\ d(c'b''|H) &= d(cb'|G) + 3. \end{aligned} \quad (24)$$

Using these equations for the construction of the rows 4, 5, 8, 9, 12, and 13, the augmented matrix B results, as explicitly given in Table 4. Although, with regard to eq. (19), distances to vertex c' have been omitted in R, d(c'b'') is introduced into vector S, since this distance will be needed in the case of constructing S.

$$B = \begin{pmatrix} 1 & 4 & 4 & 0 & 0 & 0 & 0 & 8 & 124 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 1 & 34 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 2 & 24 \\ 0 & 0 & 0 & 1 & 0 & 4 & 4 & 0 & 8 \\ 0 & 0 & 0 & 0 & 1 & 4 & 4 & 0 & 16 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 2 & 24 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 1 & 34 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 2 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 6 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 5 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 2 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 3 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 8 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

Table 4: Transfer matrix B associated with the incorporation of a second triphenylene unit.

The first step of the augmentation of 9x9 transfer matrices I, J, K also consists in inserting zero-columns, namely two zero-columns between the fifth and sixth columns and four between the seventh and eighth columns of these matrices. Applied to  $S(G)$  the rows of these intermediate matrices produce the quantities  $W(H)$ ,  $d(b|H)$ ,  $d(c|H)$ ,  $d(b'|H)$ ,  $d(c'|H)$ ,  $d(bb'|H)$ ,  $d(cb'|H)$ ,  $n(H)$ , and 1, as desired and, hence, they agree with the rows 1 - 5, 8, 9, 14, and 15 of the respective augmented transfer matrices. The rows 6 and 7 of these matrices have to produce  $d(b''|H)$  and  $d(c''|H)$ , and they can be constructed by means of eq. (18) if there,  $b'$  and  $c'$  are replaced by  $b''$  and  $c''$ , respectively. The rows 10 and 11 producing  $d(bb''|H)$  and  $d(cb''|H)$  are obtained from eq. (20) analogously. Finally, the rows 12 and 13 have to produce the actual values of  $d(b'b'|H)$  and  $d(c'b'|H)$ . Since these distances are not altered by the annellations performed at ring  $h'+1$ , the corresponding rows consist of zeros only, except for the last element, which equals 1. The 15x15 transfer matrices I, J, K obtained in such a way are collected in Table 5. They correspond to the annellations depicted in Figure 5. Once again, matrices J and K are obtained from each other by interchanging particular pairs of rows and columns.

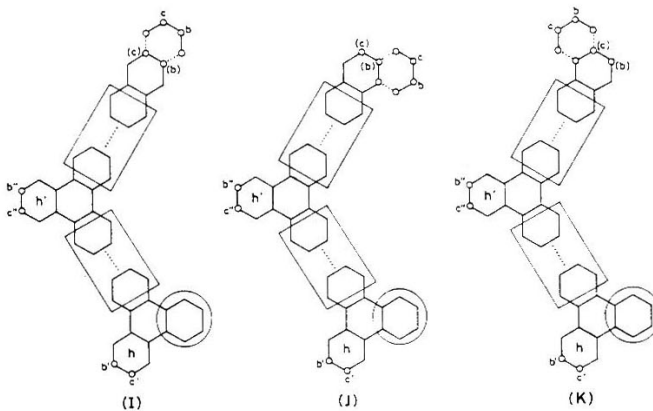


Figure 5: Annellations after the incorporation of two triphenylene units.



After the complete formation of the branch originating from ring  $h'+1$ , vector  $S(G)$  may be contracted by striking out its second, third, eighth, ninth, tenth, and eleventh elements. In this way the resulting vector  $R(G)$  is adjusted for annellations at ring  $h$ . In this contraction, the necessary renaming of vertices suitable for annellations is as follows:  $b'' \rightarrow b'$ ,  $c'' \rightarrow c'$ ,  $b' \rightarrow b$ ,  $c' \rightarrow c$ .

As soon as the branch originating from ring  $h$  is completely formed, the vector  $R(G)$  may be contracted to 5 elements, as has already been considered in the preceding section.

A survey of the augmentations and contractions of the vectors used in the case of branched cata-condensed benzenoids is presented in Table 6. The contraction of  $R(G)$  to  $Q(G)$  is uniquely determined since the intermediate benzenoid possesses only one particular ring where further annellation can take place. For the contraction of  $S(G)$  to  $R(G)$ . Besides the alternative discussed above and also presented in Table 6, one has also to consider the possibility of continuing with annellations at ring  $h'$ . In that case vertices  $b$  and  $c$  are renamed  $b'$  and  $c'$ , respectively, but  $b'$  and  $c'$  keep their meaning. According to

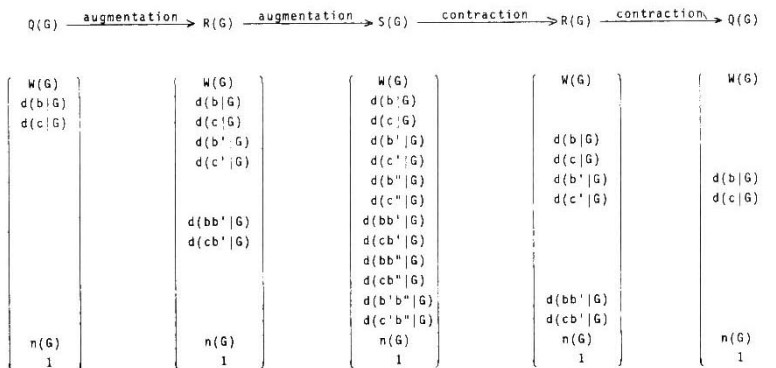


Table 6: Scheme of augmentations and contractions of the vectors used in case of branched cata-condensed benzenoids

this procedure the elements  $d(b''|G)$  and  $d(c''|G)$  of  $S(G)$  are used in  $R(G)$  as  $d(b|G)$  and  $d(c|G)$ , respectively. Similarly  $d(b'b''|G)$  of  $S(G)$  is identified with  $d(bb'|G)$  in  $R(G)$ . But the element  $d(cb'|G)$  required for  $R(G)$  cannot be taken from  $S(G)$  because its precursor,  $d(b'c|G)$ , is not kept in  $S(G)$ . Hence, it must be inserted according to  $d(b'c|G) = d(b'b''|G) - 1$ , as is easily derived from Figs. 4 and 5.

### Applications

By means of the transfer matrices given above the Wiener numbers of even large benzenoids, exhibiting rather complicated annellation and branching patterns, are easily accessible. Thus, this calculation procedure has some advantage compared with other methods [28]. Further, the transfer matrices collected in Tables 1 - 5 form a kit sufficient for the straightforward calculation of the Wiener number of any common cata-condensed benzenoid. Benzenoids, outside of this range have unlikely complex branching patterns. For example, the simplest such benzenoid possesses ten triphenylene units in a particular arrangement; namely, a central unit connected by benzenoid chains to three other units from which exclusively branched side chains originate. In order to treat even structures such as this, the vector  $S(G)$  and transfer matrices given in Tables 4 and 5 must be augmented again by an analogous procedure to that discussed above for  $R(G)$ , and the matrices collected in Tables 2 and 3.

As has been pointed out in the preceding paper [25] in the case of unbranched cata-condensed benzenoids the sequence of applied transfer matrices may be directly interpreted as a code word for the resulting benzenoid. In the case of branched benzenoids such a direct interpretation is impossible. Firstly, one must know by which particular matrix multiplication the formation of each distinct branch has been completed. Further, while matrices I, J, K correspond with the annellation of a single ring, matrix B is related to the addition of two new rings, which must undoubtedly be distinguished from the view-point of further annellations. For all these reasons we prefer to associate matrix B with two letters in the code, say M and N, which refer respectively to the ring annellated

branched side chains originate. In order to treat even structures such as this, the vector  $S(G)$  and transfer matrices given in Tables 4 and 5 must be augmented again by an analogous procedure to that discussed above for  $R(G)$ , and the matrices collected in Tables 2 and 3.

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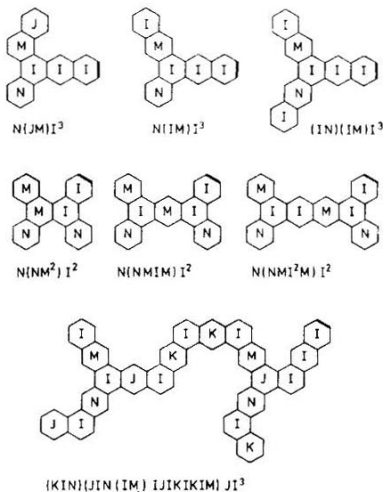


Figure 6: Examples for code words of branched cata-condensed benzenoids. Heavy bars mark the location of the respective starting vectors  $Q_0$ .

Certainly, the most intriguing feature of using transfer matrix approach is its capability of evaluating properties of arbitrary benzenoids. But nevertheless, transfer matrices are also very useful in the study of series of regularly constructed benzenoids such as acenes, fibonaccenes (= zig zag fused benzenoids), helicenes, and others. The Wiener numbers of the members of such a series may be expressed as cubic functions of  $h$  [17, 27, 28] according to

$$W_h = a h^3 + b h^2 + c h + d \quad (25)$$

The constants  $a, b, c, d$  therein are characteristics of the various series. In our experience [29], the derivation of such functions for further families of regularly constructed benzenoids is made noticeably easier by the use of transfer matrices.

In general, such a series  $\{B_t | t=1,2,\dots\}$  is systematically generated by the regularly repeated addition of a particular ben-

zenoid fragment consisting of  $m$  benzene rings. Then the number of benzene rings of the  $t$ -th member of the series is given by  $h = mt+m'$  and eq. (25) may be rewritten as follows:

$$W_t = At^3 + Bt^2 + Ct = D . \quad (25')$$

As eq. (25') indicates, the Wiener numbers,  $W_t$ , of the members of such a family form an arithmetic series of third order. One of the characteristics of a series of that type is that all differences from the fourth order upwards vanish identically to zero. Hence, expressing the fourth order difference in terms of successive members of the series the following recurrence relation results:

$$W_{t+1} = 4 W_t - 6 W_{t-1} + 4 W_{t-2} - W_{t-3} . \quad (26)$$

As outlined in [25], such recurrence relations are also obtained from a combination of transfer matrix and shift operator techniques [30]. Suppose,  $B_t$  and  $B_{t+1}$  are succeeding members of a series of regularly constructed benzenoids for which a shift operator,  $O(+)$ , is defined by

$$B_{t+1} = O(+ ) B_t . \quad (27)$$

Suppose further, that the vector  $Q(B_{t+1})$  is produced from  $Q(B_t)$  by the multiplication

$$Q(B_{t+1}) = X Q(B_t) , \quad (28)$$

where  $X$  denotes the transfer matrix associated with the series considered. Then, a recurrence relation results from

$$D = \det[X - O(+ ) 1] = 0 , \quad (29)$$

where  $1$  denotes the unit matrix of appropriate order. For the series of acenes (where  $X = I$ ), one derives from eq. (29)

$$D = [1 - O(+)]^5 = 0 ; \quad (30a)$$



for all the other series, as for instance  $X = J$  or  $K$  (helicenes),  $X = K J$  or  $J K$  (fibonaccenes),  $X = I J$  or  $I K$ , etc., one obtains

$$D = -O(+) \cdot [1 - O(+)]^4 = 0 \quad . \quad (30b)$$

As is easily proved, eqs. (30a,b) are in agreement with the recurrence relation, eq. (26). In addition, eqs. (30a,b) explain the existence of cubic functions expressing the Wiener numbers in accordance with eq. (25).

#### Concluding remarks

The transfer matrix approach to the Wiener numbers of benzenoids is not limited to cata-condensed benzenoids. As first results [29] indicate there is no difficulty in also constructing transfer matrices associated with the incorporation of peri-condensed units, such as pyrene, perylene, etc., into growing chains of otherwise cata-condensed benzenoids. The number of desired transfer matrices grows with the increasing number of realizable combinations of modes of incorporation and ways of continued annellation; for instance, in the case of pyrene a total of 25 transfer matrices are needed, even when possible branching at the pyrene units is disregarded.

The construction of transfer matrices associated with cata-fusions of benzene rings is relatively simple because the network of geodesic paths in graph  $G$ , representing the starting material, is retained in the fusion process. This is not necessarily true for other procedures generating a larger benzenoid from a smaller one. Thus, for instance, a particular mode of incorporating pyrene units is related to the reorganisation of a few geodesic paths. From the experience hitherto gained, we conclude that, in general, transfer matrices producing Wiener numbers may be constructed for numerous benzenoid and non-benzenoid units, provided their incorporation takes place either with retention of the network of geodesic paths, or only few geodesic paths are reorganized in a well-defined manner.

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