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GRAPH-THEORETICAL TREATMENT OF AROMATIC HYDROCARBONS
III: CORONA-CONDENSED SYSTEMS

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Abstract

We investigate the nature of both the constitutional and characteristic graphs for cata-condensed cycles (coronae) and derive a number of rules regarding their boundaries. We discuss the differing types of angular relationships which exist for nuclei forming a boundary and show that certain special expressions are derived from formulae previously given.

Graphical Representation of Coronae

In Part I of this series[1] we presented a formal graph-theoretical description of aromatic hydrocarbons, and in Part II[2] we made a special study of all-benzenoid systems. We complete our analysis in this Part by investigating systems in which cata-condensation of the benzene rings results in the formation of cyclic structures. This type of condensation we have previously referred to as cyclic cata-condensation or corona-condensation.[1] The definitions and symbols previously employed in Parts I[1] and II[2] will be taken over here without any change in their significance. Thus, a corona-condensed system will be represented by either a constitutional graph A:

$$A = [V, E], \tag{1}$$

or a characteristic graph C:

$$C = [U, K]. \tag{2}$$

The vertices of A represent carbon atoms whilst those of C represent benzene rings. Some corona-condensed species in the form of a single, unbranched cycle are illustrated in Figure 1.

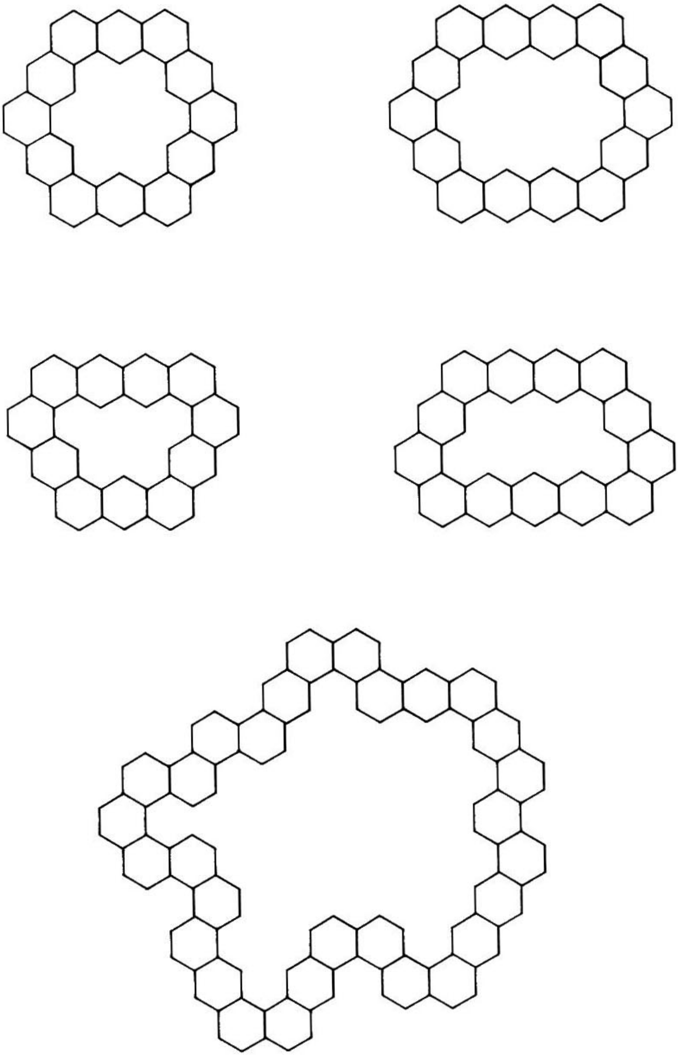

Figure 1. Some examples of cata-condensed aromatic hydrocarbons or coronae.

The characteristic graph C of a corona-condensed species will contain one or more cycles, whose lengths λ_1, λ_2, λ_3, ... will be exactly equal to the number of condensed benzene rings in each of the cycles. As pointed out earlier,[1] for species embeddable within a two-dimensional hexagonally tessellated lattice the length of each cycle must be at least eight. All lengths greater than eight are possible, though for $\lambda \geq 10$ there is more than one way in which the cycle may be formed. It is characteristic of corona-condensed systems that in addition to the outer periphery they also possess at least one inner periphery formed from carbon atoms. These peripheries we shall term respectively the outer and inner boundaries of the system. The number of inner boundaries equals the number of cycles in C. Further condensation of benzene rings onto a corona-condensed species will not change the type of condensation, provided the number of inner boundaries remains fixed.

For simplicity we restrict ourselves at the outset to a consideration of those corona-condensed systems possessing only a single cycle constructed such that the minimum number of benzene rings used; Figure 1 contains exclusively examples of such species. Under these conditions C is a cycle and the cardinalities of U and K are given by:

$$|U| = N \tag{3}$$

and

$$|K| = N, \tag{4}$$

where N represents the number of condensed benzene rings. As the vertices of C correspond to the six-membered cycles of A, two neighbouring vertices of C will correspond to two six-membered cycles in A having one edge and its two vertices in common. The cardinalities of V and E are thus given by

$$|V| = 4N \tag{5}$$

$$|E| = 5N. \tag{6}$$

The A graph will accordingly possess a total of

$$r = N + 1 \tag{7}$$

independent cycles. Using Table 1 in I[1] it is readily seen that the empirical formula of these systems takes the form $C_{4N}H_{2N}$.

<u>The Edge and Vertex Subsets</u>

All the carbon-carbon linkages in a corona species belong either to two adjacent rings or to the inner or outer boundary of the species. The set E may accordingly be written as the union of three disjoint subsets:

$$E = E_i \cup E_o \cup E_s, \tag{8}$$

where E_i is the set of edges representing carbon-carbon linkages in the inner boundary, E_o the set representing those in the outer boundary, and E_s the set of shared carbon-carbon linkages. The cardinality of E will thus be given as the sum of the cardinalities of the three subsets:

$$|E| = |E_i| + |E_o| + |E_s| \tag{9}$$

As every benzene nucleus in a corona species will have two shared carbon-carbon linkages, each nucleus will contribute to E_s a total of $\frac{1}{2}\cdot 2$ edges. It thus follows that

$$|E_s| = N, \tag{10}$$

and, from (6) and (9), that

$$|E_i| + |E_o| = 4N. \tag{11}$$

An analogous partition of the set V representing the carbon atoms would lead to $V = V_i \cup V_o \cup V_s$, where V_i is the set of vertices representing atoms in the inner boundary, V_o is that for atoms in the outer boundary, and V_s is that for atoms belonging to neither of these boundaries. This partitions is, however, reduced to

$$V = V_i \cup V_o \tag{12}$$

because each carbon atom belongs to one of the two boundaries and hence V_s must be empty. It thus follows that V_i and V_o are disjoint subsets and we may therefore write

$$|V| = |V_i| + |V_o| = 4N. \tag{13}$$

Because both boundaries are cycles, each will necessarily have as many edges as vertices. Accordingly, we may write

$$|E_i| = |V_i| = L_i; \; |E_o| = |V_o| = L_o \qquad (14)$$

and therefore

$$L_i + L_o = 4N. \qquad (15)$$

Some Angular Relationships

We come now to a consideration of the angles formed by adjacent edges of the characteristic graph C of a corona-condensed species. In Figure 2 are illustrated the six theoretically possible mutual angles which may be formed at a given vertex of a characteristic graph of a benzenoid hydrocarbon. In corona-condensed species with the minimum number of rings only the types (ii), (iii), and (iv) may occur, for the remaining types (i), and (v) imply the presence of sites of peri-condensation and (vi) does not satisfy the requirement of the minimum number of rings. A collation of the characteristics of each of the six types has been drawn up in Table 1.

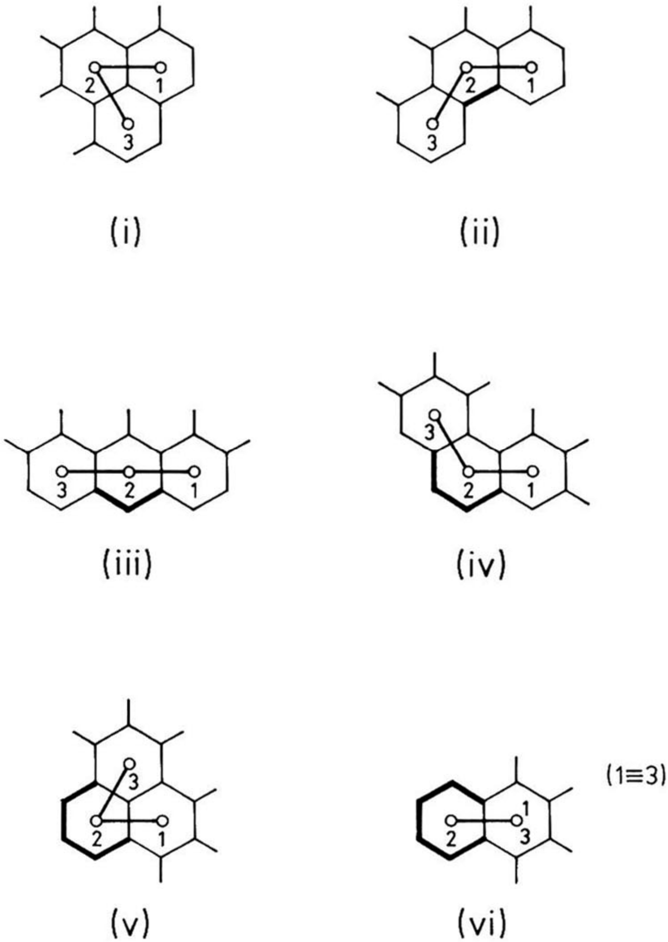

Figure 2. Diagrams of the six theoretically possible arrangements of nuclei around a given nucleus forming part of the boundary of a corona.

Consider the vertex $U_j \in C$, where $1 \leq j \leq N$. Two edges of C terminate on this vertex and form a mutual inner angle which we shall denote as θ_j. In the constitutional graph A the vertex U_j corresponds to a six-membered ring which contributes d_j edges to the inner boundary of A. Evidently a relation of the form

$$\theta_j = \frac{\pi}{3}(1 + d_j) \qquad (16)$$

exists between these two quantities, where it should be stressed that θ_j relates to the characteristic graph C whilst d_j relates to the constitutional graph A.

Table 1: Characteristics of the Six Types of Condensation depicted in Fig. 2.

Type	Mutual Inner Edge Angle (θ)	Number of edges d_j contributed to the inner boundary of A
i	$\pi/3 = 60^{\circ}$	0
ii	$2\pi/3 = 120^{\circ}$	1
iii	$3\pi/3 = 180^{\circ}$	2
iv	$4\pi/3 = 240^{\circ}$	3
v	$5\pi/3 = 300^{\circ}$	4
vi	$6\pi/3 = 360^{\circ}$	5

Now the inner boundary in the constitutional graph of a corona species may be viewed from a purely geometrical standpoint as an irregular N-gon. The sum of the internal angles of this N-gon, ω, will be given by the expression

$$\omega = \sum_{j=1}^{N} \theta_j = (N-2)\pi = 3(N-2)\frac{\pi}{3}. \qquad (17)$$

Using (16) one immediately obtains the result

$$\sum_{1}^{N} d_j = 2N - 6. \qquad (18)$$

Since the length of the inner boundary, L_i, is exactly equal to the left hand side of this equation, it follows that

$$L_i = 2N - 6, \qquad (19)$$

and, because of (15), that

$$L_o = 2N + 6. \qquad (20)$$

It is evident that the lengths L_i and L_o are even. It may be of interest to note that L_i and L_o obey the relations

N odd: $L_i \equiv 0 \pmod 4$

$L_o \equiv 0 \pmod 4$

N even: $L_i \equiv 2 \pmod 4$

$L_o \equiv 2 \pmod 4$.

The Empirical Formula

As pointed out earlier, the empirical formula of any corona species with the minimum number of rings will be of the general form $C_{4N}H_{2N}$. It is of interest here to consider how many of the 2N hydrogen atoms will belong to the inner and outer boundaries of such species. Now the d_j edges belonging to a given peripheral ring will form a path W_j comprising d_j edges from the set E and $d_j + 1$ vertices from the set V. It may be noted in passing that $1 \leq d_j \leq 3$ as only arrangements (ii), (iii), and (iv) shown in Figure 2 can be realized in these corona species. Two of the vertices of W_j will be of degree three whilst the remaining vertices will be of degree two. As the number of C-H linkages in any part of the constitutional graph A is always equal to the number of vertices of degree two in this part, the number of hydrogen atoms, lying on the inner boundary, b_i, must be equal to

$$b_i = \sum_{j=1}^{N}(d_j - 1) = \sum_{1}^{N} d_j - N = L_i - N. \tag{21}$$

Using (19) and b = 2N we now determine the number of hydrogen atoms on the inner and outer boundaries to be

$$b_i = N - 6 \tag{22}$$

$$b_o = N + 6. \tag{23}$$

To summarize, the inner boundary is formed from 2N-6 carbon atoms and has 2N-6 C-C linkages and N-6 C-H linkages. The outer boundary is constructed from 2N+6 carbon atoms and has 2N+6 C-C linkages and N+6 C-H linkages.

In Figure 3 is depicted a corona-condensed species having more than the minimal number of rings and containing all of the typical arrangements of benzene nuclei shown in Figure 2 in both its inner and outer boundaries. The species has the empirical formula $C_{102}H_{44}$. Using the results given in Table 1 of I[1] and remembering that $\bar{\kappa} = 1$, the cardinalities of the sets forming its constitutional and characteristic graphs are seen to be $|V| = 102$, $|E| = 131$, $|U| = 29$, $|K| = 43$, and t = 14. In Figures 3(b) and 3(c) the inner and outer boundaries of the species are sketched. The corresponding partial characteristic

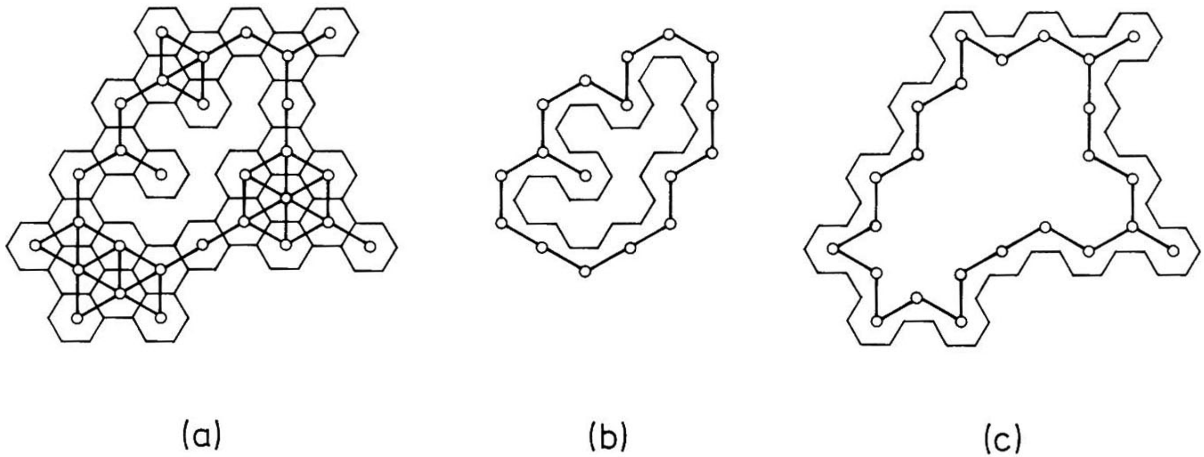

Figure 3. The graphs (a) A and C, (b) C_i and (c) C_o of a given corona.

graphs C_i and C_o also shown contain one cycle each and extra edges: C_i contains a single edge and C_o two such edges. In C_i the length of the cycle is 16 whilst that for C_o is 22; moreover C_i has $|U_i| = 17$ and C_o has $|U_o| = 24$ edges. In both partial graphs the number of edges is equal to the number of vertices.

The Boundaries of Coronae

As arrangement (i) makes no edge contribution to the boundary, only the five remaining arrangements of benzene nuclei, illustrated in Figure 2, are observed in the partial graphs C_i and C_o (Figure 3). Before applying the expressions derived above to C_i and C_o, it is first necessary to consider if this is feasible for arrangements of the type (v) and (vi). Although the arrangement (v) is immediately seen to present no problem in this regard, arrangement (vi) presents the difficulty that the two adjacent nuclei are superimposed. Thus, the nucleus in the boundary has to be counted twice as must the edge connecting the vertex outside the cycle in the characteristic graph C. We illustrate below the procedure to be adopted in this special case.

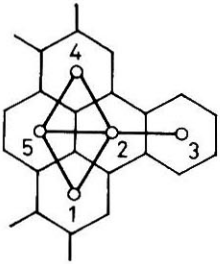

Figure 4. Illustration of a portion of a boundary of a corona in the arrangement (vi) of Figure 2.

In Figure 4 is shown a portion of the boundary of a corona species having the nuclei 2 and 3 in the arrangement (vi). We shall assume for convenience that the nuclei 1 and 4 are condensed on as illustrated in Figure 4. In order to evaluate the summation of the d_j for the portion shown we start from nucleus 1. As the angle $(\widehat{123})$ is 120^o one has the contribution $d_2 = 1$; in the next step, as the angle $(\widehat{232})$ is 360^o, one has $d_3 = 5$; and finally as the angle $(\widehat{324})$ is also 120^o, we have a further contribution $d_2 = 1$. The summation will thus assume the form

$$\sum_{j=1}^{N} d_j = d_1 + 1 + 5 + 1 + d_4 + ...$$

As a consequence of the presence of arrangement (vi) in a corona species it thus becomes necessary to replace the partial characteristic graphs C_i and C_o by the corresponding shortest closed sequence W_i or W_o which embraces all the vertices representing nuclei in the boundary. If Z_i is the length of the cycle in C_i and F_i the number of vertices not lying within this cycle, then the length of the shortest closed sequence, W_i, will be given by

$$|W_i| = Z_i + 2F_i \tag{24}$$

and, analogously, the length of W_o by

$$|W_o| = Z_o + 2F_o. \tag{25}$$

It is to be noted here that it is of no import whether the vertices not contained in the cycles C_i and C_o occur singly or are incorporated within snake or tree-like side chains. We may also write the following general relations

$$|U_i| = Z_i + F_i \tag{26}$$

$$|U_o| = Z_o + F_o \tag{27}$$

From Figure 3 it may be seen that $F_i = 1$ and $F_o = 2$, from which we obtain $|W_i| = 18$ and $|W_o| = 26$. Moreover, equations (19) and (20) enable us to determine the boundary lengths as $L_i = 30$ and $L_o = 58$. The number of hydrogen atoms attached at each of these boundaries is obtained from equations (22) and (23) as $b_i = 12$ and $b_o = 32$. Using equation (14), we also know that $|E_i| = |V_i| = 30$ and $|E_o| = |V_o| = 58$, from whence it follows, using (9) and the result $|E| = 131$, that $|E_s| = 43$. Now, unlike the corona species with the minimum of benzene rings, condensed aromatic hydrocarbons in general have carbon atoms not lying on a boundary. Such atoms will form the disjoint subset $V_s \subset V$. As these carbon atoms correspond to sites of peri-condensation (see equation (22) of I[1]) it follows that

$$|V_s| = |V| - |V_i| - |V_o| = t, \tag{28}$$

which leads, in the case of the species in Figure 3, to the result $|V_s| = t = 14$.

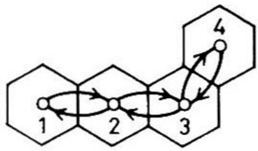

Figure 5. Graph illustrating the shortest closed sequence for a non-cyclic cata-condensed species.

The same process for determining boundary lengths may be employed even when all the benzene nuclei of an aromatic hydrocarbon lie on the boundary, as in the case of ordinary cata-condensation. The partial characteristic graph C_o then assumes the form of a snake (S) or tree (T) graph, and for pure cata-condensation becomes identical with C. For instance, the characteristic graph of tetraphene is a snake having four vertices and three edges. As is clear from Figure 5, the length of the shortest closed sequence traversing all vertices is

$|W| = 6$ here, and so from (20) we obtain the result $L_o = 2|W| + 6 = 18$. For pure cata-condensation the subsets V_s, V_i and E_i are empty. For E_s we have the relation

$$|E_s| = |K| \tag{29}$$

which holds for all aromatic hydrocarbons.

Some Rules for Boundary Lengths

As pointed out above, the boundaries of all cata-condensed aromatic species must be of even length. This is now seen to be true even for the special case in which the partial characteristic graph C_i or C_o is replaced by the shortest closed sequence W_i or W_o.

In deducing (19) and (20) we made use of the fact that in a corona-condensed species with the minimum number of benzene rings we always have $|C_i| = |C_o| = N$. Both of these equations may be generalized to yield

$$L_i = 2|C_i| - 6 \tag{30}$$

and

$$L_o = 2|C_o| + 6. \tag{31}$$

In the more general case still when side chains are present F_i and/or F_o are non zero. As will be seen by reference to Figure 2 (vi), on average each benzene ring depicted by a vertex counted in F_i and/or F_o contributes four edges to the boundary. Taking into account (24) and (25) we therefore may generalize (30) and (31) further to

$$L_i = 2|W_i| - 6 \tag{32}$$

and

$$L_o = 2|W_o| + 6. \tag{33}$$

From this it follows immediately that both L_i and L_o must be even numbers.

In the case of all-benzenoid corona-condensed systems[2] the removal of edges common to two cycles of length three leads to the bipartite partial edge graph $B \subset C$. The open vertices of B are always of degree three, i.e. they represent two-fold branched annelation of the rings. Thus, empty rings in the boundary of an all-benzenoid species will have an edge angle of 120^o and will have an arrangement of type (ii) in our Figure 2. As there is, however, no limitation on the type of arrangement which full rings may assume, all the arrangements (i) to (vi) are possible for these rings. By the removal of seven edges from the characteristic graph shown in Figure 3(a) we obtain the bipartite partial characteristic graph shown in Figure 6. The species depicted in Figure 3(a) is thus an all-benzenoid aromatic hydrocarbon and has the formula $C_{102}H_{44}$.

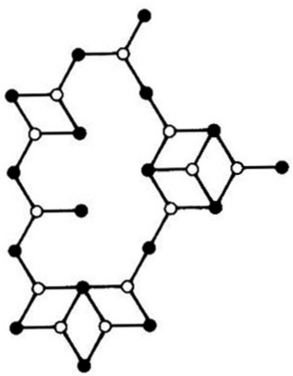

Figure 6. The bipartite characteristic graph B of the corona species illustrated in Figure 3(a).

We conclude with a general rule for the boundaries of all-benzenoid aromatic systems. As in the partial characteristic graph $\mathcal{B}$ of an all-benzenoid species the empty and full vertices alternate, this must also be the case in the partial characteristic graph C_i and C_o. The cycles in both C_i and C_o are thus of even length. From equations (24) and (25) it then follows that $|W_i|$ and $|W_o|$ must also always be even. As a characteristic of all-benzenoid systems, however, equations (19) and (20) reveal that boundary lengths in such species must be of the form $4\mu + 2$ (μ integral).

References

1. O.E. Polansky and D.H. Rouvray, Math. Chem. 2, 63 (1976).

2. O.E. Polansky and D.H. Rouvray, Math. Chem. 2, 91 (1976).