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Graph-Theoretical Treatment of Aromatic Hydrocarbons II: THE ANALYSIS OF ALL-BENZENOID SYSTEMS

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The Aromatic Sextet

In the first paper in this series, hereafter referred to as I, we presented a graph theoretical description of condensed aromatic systems. The present work treats in some detail a special class of these systems, namely those for which the *a* π-electrons present (contributed to the bonding by the *a* carbon atoms in the structure) may be grouped together into sextets in such a way that the sextets can be consistantly associated with particular rings in the structure. Such assignments of electrons will lead to some rings having a full sextet of electrons whereas the remaining rings will have no π-electrons. Systems of this type have been designated by Polansky and Derflinger[1] all-benzenoid aromatic hydrocarbons,

a term we shall employ in the present context. Symbols and definitions given in I will be used here whenever appropriate without further laboration.

The sextet of π-electrons assigned to a given ring in an all-benzenoid hydrocarbon will be referred to as an aromatic sextet. The assignment may be to either an isolated ring, i.e. to a single benzene ring, or to a ring forming an integral part of an aromatic hydrocarbon. Although the notion of the aromatic sextet was first adumbrated in the work of Thomson[2], the expression itself is due to Robinson[3,4]. This latter worker also introduced the symbols of a circle in a hexagon to represent an aromatic sextet, and used the sextet in an attempt to predict the properties of little-known aromatic systems. Numerous investigations expecially by Clar and his co-workers[5-8] on aromatic hydrocarbons brought new insights into the nature of these systems. In particular they stressed the importance of a consistent usage of the cycle symbol when drawing aromatic structures, and Clar was even able to deduce certain criteria[9] to be observed in the construction of these systems. Theoretical support for Clar's deductions was later presented by Polansky and Derflinger[1]; the conclusions reached in this work will serve as the basis of

our present discussion.

Because the number of π-electrons in an aromatic hydrocarbon always equals the number of carbon atoms in the structure, a given structure can be all-benzenoid only if its number of carbon atoms is diversible by 6. This condition is a necessary though insufficient one, as reference to Figure 1 reveals. Therein are

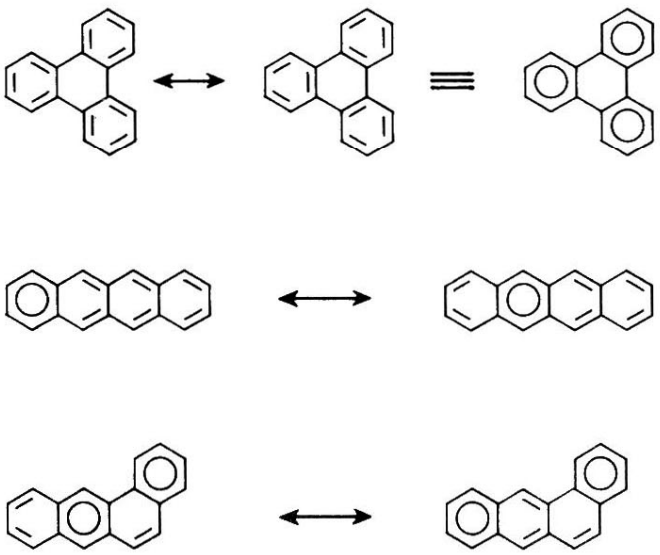

Figure 1

depicted three of the isomers of $C_{18}H_{12}$ namely triphenylene, tetracene and tetraphene. However, only the first of them is all-benzenoid, for three circles

(representing π-sextets) can be consistently assigned to this, whereas for the other two no such consistent assignment is possible. Whether a molecule is all-benzenoid clearly depends upon the way in which its component rings are fused together. In other words, all-benzenoid molecules must be possessed of particular topological structures.

All-Benzenoid Aromatic Systems

It is convenient to designate rings in all-benzenoid systems having an assigned sextet of π-electrons as full, and the others as empty. The simplest possible all-benzenoid system, benzene, is easily characterized as it possesses only one aromatic sextet. In more complex systems having carbon atoms belonging to more than one ring, care must be taken to ensure that a given π-electron is associated with only one ring. Morever, as all rings must be either full or empty, a full ring will always have as immediate neighbours empty rings. In fact, an empty ring must always have three full rings as neighbours, for only then can the π-electrons be properly assigned to sextets in the three adjacent rings. As two full rings may never be adjacent, the above reasoning leads to the conclusion that at each empty ring branching must be present.

Rings in all-benzenoid systems which have one or more attached hydrogen atoms will be designated peripheral rings. This definition implies that every peripheral ring will contain at least one carbon atom belonging solely to that ring. The π-electron from such a carbon atom can be assigned only to the ring in which the carbon atom is found; accordingly rings of this type can never be empty. Circles may therefore be drawn in all the peripheral rings of any all-benzenoid hydrocarbon; this considerably simplifies the assignment of aromatic sextets in general.

The above considerations lead to three basis rules for deciding which rings are to be full and which empty in all-benzenoid systems. These rules are that

(i) only rings which are empty may be condensed on to a full ring;

(ii) exactly three full rings must be condensed at each empty ring, and the condensation must be in the form of a branched annellation;

(iii) all the peripheral rings must be full.

Two rules, which follow automatically from these three are that

(iv) condensation of rings in the form of a linear annellation cannot give rise to an all-benzenoid hydrocarbon, and

(v) there is an upper limit of three on the number of empty rings which may be condensed on to a given empty ring.

The Nature of the Charateristic Graph

The rules given above for deciding which rings are full and which empty in a given all-benzenoid system rest on the fundamental assumption that every ring in such a system may be assigned to only one of two possible classes: the class of empty rings and the class of full rings. A classification of this type automatically implies that the characteristic graph of any all-benzenoid hydrocarbon should be two-colourable. The characteristic graph will be represented as in I by the symbol C, though a full ring will now be represented by a full vertex (•) and an empty ring by an open vertex (o). Our rule (i) stipulates that C may contain no edges connecting two full vertices, whereas rule (v) allows this for the connection of open vertices in C.

Removal from C of all the edges connecting two open vertices will result in the formation of an edge-partial characteristic graph which we shall denote as B. The graph B represents a system in which only empty rings are joined to full rings and vice versa, and as a result B itself must be bipartite. According to

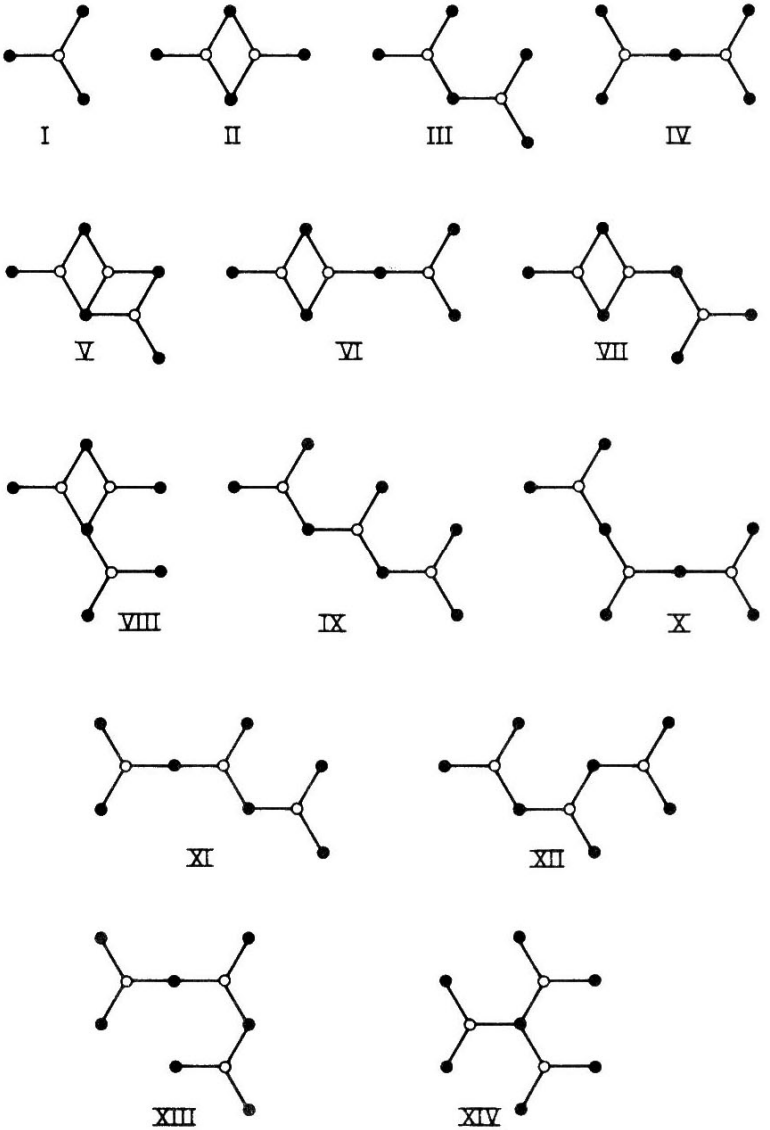

Figure 2

rule (ii) all open vertices in $\mathcal{B}$ must be of degree 3. In Figure 2 the graphs $\mathcal{B}$ for all-benzenoid systems containing up to three empty rings are illustrated. This figure reveals that certain of the bipartite graphs $\mathcal{B}$ contain cycles of length four. These cycles arise from the removal of edges in $\mathcal{C}$ connecting two open vertices. To explore in greater detail the relationships existing between $\mathcal{C}$ and $\mathcal{B}$, a more formal description of each of these graphs is now presented.

The characteristic graph $\mathcal{C}$ defined in I as

$$\mathcal{C} = [U, K, \theta] \tag{1}$$

is not bipartite. The edge-partial characteristic graph $\mathcal{B}$, which is bipartite, we shall define as the graph

$$\mathcal{B} = [U, L, \Omega], \tag{2}$$

where the sets L and Ω are contained within the set K and θ respectively i.e.

$$L \subseteq K, \qquad \Omega \subseteq \theta. \tag{3}$$

The difference in cardinality between sets K and L is given as

$$|K| - |L| = s, \tag{4}$$

where s is the number of cycles of length four in C. Whenever the right hand side of (4) is zero, the two graphs C and B are identical apart from their colouring. When s is greater than zero, C will contain exactly $2s$ cycles of length 3, since a cycle of length 4 appears in B only when an edge common to two cycles of length 3 is removed from C. The number of edges of length 3 in C will thus be given by the expression

$$t = 2s \tag{5}$$

Clearly t can assume only even integral values in all-benzenoid systems.

Some Set-Theoretical Relationships

The vertex set U may be regarded as the union of two disjoint sets:

$$U = F \cup O, \tag{6}$$

where F represents the set of full vertices and O the set of open vertices.

The cardinality of the vertex set U is thus given by the sum of the cardinalities of sets F and O, i.e.

by

$$|U| = |F| + |O|. \tag{7}$$

The number of carbon atoms is clearly equal to

$$a = 6|F|. \tag{8}$$

As all open vertices B are of degree 3 and as no edge can exist which connects two open vertices, we may write for the cardinality of L

$$|L| = 3|O|. \tag{9}$$

From (4) it now follows that the cardinality of K is given by

$$|K| = 3|O| + s. \tag{10}$$

From Table 1 of I and making use of (7) its follows that t may be expressed as

$$t = |K| - |F| - |O| + 1 - \bar{x}. \tag{11}$$

We now write (5) in the form $s = t - s$, and substitute into the right hand side expression (11) for t and ex-

pression (10) for s. The result may be re-written as

$$|F| = 2|O| + 1 - \bar{x} - s \qquad (12)$$

this relationship may be seen to hold from the fact that one needs an extra full vertex to satisfy rule (ii) if a cycle of length 4 were to be opened.

The upper bound of s must depend on $|O|$, since in each cycle of length 4 two open vertices will be required. When B contains as many such cycles as possible we have in the peripheral edge sequence open vertices all of which belong to two cycles (see Figure 3); but the open vertices in the inner region be-

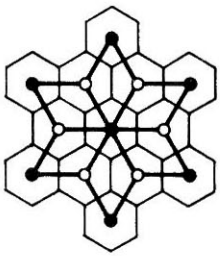

Figure 3

long to three. As each cycle of length 4 requires two open vertices, the range of s may be given as

$$0 \leq s < \frac{3}{2} |O| \tag{13}$$

where it is understood that the upper limit may be attained only when $|O| \to \infty$. In the case where $|O| < 6$ we have the sharper relationship

$$0 \leq s \leq (|O| - 1). \tag{14}$$

From (7) and (11) we may now derive the following expression for the cardinality of U:

$$|U| = 3|O| + 1 - \bar{x} - s \tag{15}$$

This equation enables a further characterization of C.

The number of carbon atoms is given in (8), when there are no cycles in B, b will be given by the difference between a and the number of carbon atoms common to both a full and an empty ring. This latter member is known to be $6|O|$. The number of hydrogens is further reduced by 2 for each corona and by 4 for each cycle of length 4 in B. Hence using (12) we may write the general equation

$$b = 3 \cdot |F| + 3 - s + \bar{x}. \tag{16}$$

A Simplified Construction of All-Benzenoid Aromatic Hydrocarbons

A consequence of rule (ii) is that any all-benzenoid aromatics hydrocarbon may be constructed from triphenylene units. Such a unit is conveniently depicted by a triangle, the vertices of which represent the full rings of the triphenylene unit. Figure 4 shows

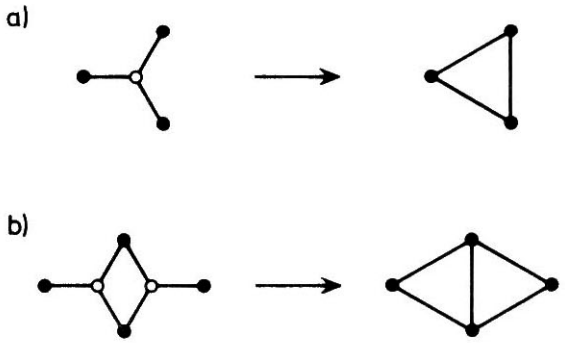

Figure 4

the relationship between the characteristic graphs and these simplified graphs. In Figure 5 we illustrate the graphs of all benzenoid systems containing up to 3 triphenylen units.

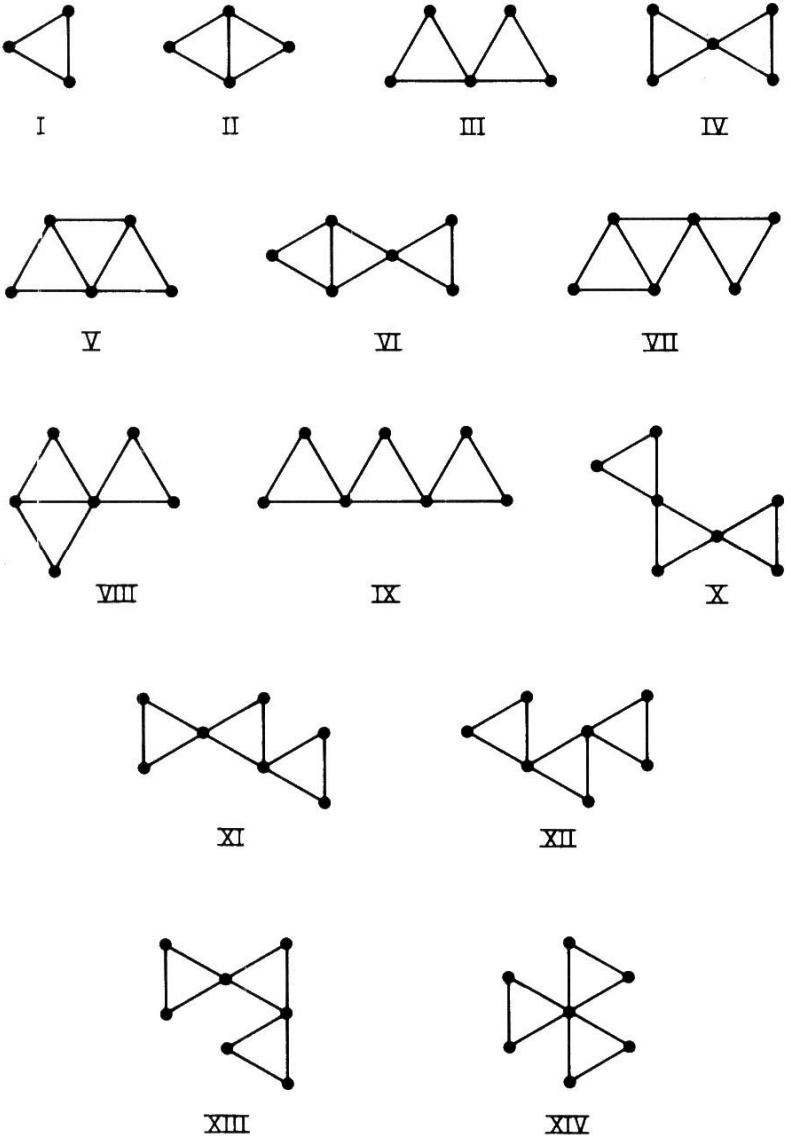

Figure 5

We denote these simplified graphs by P and define them as follows

$$P = [F, Q]. \tag{17}$$

where F has the same significance as in (16) and Q is the edge set.

In order to derive the bipartite graph B from a given P one must place an open vertex at the centre of each triangle and connect this vertex to the three full vertices of the triangle and supress the original edges of P. The number of triangles in P can accordingly not exceed $3 \cdot |O|$; but it will be diminished by the number of cycles present in B because each cycle of B is represented in P by an edge common to two triangles. Thus we may write

$$|Q| = 3|O| - s - \bar{x} = \frac{1}{2}[3|F| - 3 + s + \bar{x}]. \tag{18}$$

Isomerism in All-Benzenoid Aromatics

As inspection of Table 1 shows, the two species designated therein as III and IV are isomeric, as are the triplet VI, VII and VIII, and the sextet IX, X, XI, XII, XIII and XIV. Moreover Figures 2 and 5 bring out the fact that the isomerism arises from differing

Table 1: Characteristic Parameters for the Graphs $\mathcal{B}$ and $\mathcal{P}$ Depicted in Figures 2 and 5 Respectively.

	$\|F\|$	$\|Q\|$	$\|O\|$	s	a	b	p_2	p_3	p_4	p_5	p_6
I	3	3	1	0	18	12	3	0	0	0	0
II	4	5	2	2	24	14	2	2	0	0	0
III	5	6	2	0	30	18	4	0	1	0	0
IV	5	6	2	0	30	18	4	0	1	0	0
V	5	7	3	2	30	16	2	2	2	0	0
VI	6	8	3	1	36	20	3	2	1	0	0
VII	6	8	3	1	36	20	3	2	1	0	0
VIII	6	8	3	1	36	20	4	1	0	1	0
IX	7	9	3	0	42	24	5	0	2	0	0
X	7	9	3	0	42	24	5	0	2	0	0
XI	7	9	3	0	42	24	5	0	2	0	0
XII	7	9	3	0	42	24	5	0	2	0	0
XIII	7	9	3	0	42	24	5	0	2	0	0
XIV	7	9	3	0	42	24	6	0	0	0	1

types of annellation at certain full vertices which serve as articulation points. The isomers are thus to be regarded as a particular sort of geometrical isomer. For the discussion of these isomers we may utilize the graph P, bipartite graph B, or the characteristic graph C. All are equally appropriate for this purpose as P corresponds bi-uniquely with B, and B bi-uniquely with C. Since P has the smallest vertex set, we choose the graph P.

It must be pointed out that P is not uniquely determined by the cardinalities $|F|$ and $|Q|$, neither as regards its type (compare for instance the species XIV with IX up to XIII) nor its topology. We know, however, that these cardinalities do uniquely determine the pair (a, b). In fact, given any one of these two pairs, the magnitudes of the remaining one may be uniquely evaluated. Accordingly, a given pair $(|F|, |Q|)$ can correspond to only one empirical formula C_aH_b, and all species corresponding to these pairs will be isomeric. The actual number of isomers which can exist for an all-benzenoid system characterized by a pair such as $(|F|, |Q|)$ will be determined by two factors. The first is the type of graph involved;

Table 2: The Types of Isomerism Arising in the All-Benzenoid Species Depicted in Figures 2 and 5

						Type					Topological Variations	
$\|F\|$	$\|O\|$	s	$\|Q\|$	a	b	p_2	p_3	p_4	p_5	p_6	Number	Species
3	1	0	3	18	12	3	0	0	0	0	1	I
4	2	1	5	24	14	2	2	0	0	0	1	II
5	2	0	6	30	18	4	0	1	0	0	2	III, IV
5	3	2	7	30	16	2	2	1	0	0	1	V
6	3	1	8	36	20	3	2	1	0	0	2	VI, VII
						4	1	0	1	0	1	VIII
7	3	0	9	42	24	5	0	2	0	0	5	IX, X, XI, XII, XIII
						6	0	0	0	1	1	XIV

this may be characterized in terms of the p_j where p_j denotes the number of vertices in P of degree j. The second is the topological variations associated with each type; these are illustrated in Table 2 in the case of species I to XIV.

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