

Graph-Theoretical Treatment of Aromatic Hydrocarbons I:
THE FORMAL GRAPH-THEORETICAL DESCRIPTION

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Abstract

A detailed graph-theoretical description of both cata- and peri-condensed aromatic hydrocarbons constructed from benzene rings is presented. A discussion of the non-topological features of the characteristic graph is included. Ten parameters have been derived from the constitutional graph, the characteristic graph and the empirical formula; they are all inter-related, but certain triples of them are shown to be mutually independent.

Introduction

In this series of paper we propose to investigate from a mainly topological standpoint the structure and properties of aromatic hydrocarbons. By the term aromatic

hydrocarbon we shall always mean a molecular species consisting only of carbon and hydrogen atoms, constructed in such a way that every carbon atom be incorporated with- in at least one hexagonal carbocycle and every hydrogen atom be attached to a carbon atom belonging to a single carbocycle. From this definition it may be seen that most aromatic hydrocarbons can be embedded bi-uniquely within a regular, two-dimensional, hexagonal lattice. In certain instances, notably for molecules such as triptycene¹ or the helicenes², this is however not always possible.

We shall use the term aromatic throughout the series only in the above structural sense. Originally the word was used to designate organic compounds having a characteristic aroma³. Later the term was associated with a particular type of molecular structure^{4,5}, and, after the proposal of the ring structure for benzene⁶, it came to have the connotation benzenoid. Thereafter the physico-chemical properties of aromatic systems were extensively studied⁷⁻¹¹, and the term became associated with certain of them: a characteristic reactive behaviour, the possession of an additional stabilization energy, and the presence of a considerable ring current.

As a consequence of quantum chemical investigations^{12,13}, the term aromatic is now ascribed to a certain type of the bonding. Ruedenberg¹⁴ has pointed out the existence of relations between the topological structure of a mole-

cule and the eigenvalue and eigenvectors of its MO's. In our present approach however we make no reference to any quantum chemical concept.

The Linkages in Aromatic Hydrocarbons

In order to ensure that our description of aromatic systems will not be influenced by the terminology of quantum chemistry, we shall not refer to bonds but rather to linkages existing between atoms in these systems. In the case of the benzene molecule, it will be evident that three linkages terminate on each carbon atom: two from adjacent carbon atoms and one from an attached hydrogen atom. Thus in benzene, as in other aromatic hydrocarbons, three linkages will always be assumed to radiate from each carbon atom and one from each hydrogen atom. Reference to the other extreme case, namely that for an infinite sheet of graphite with no attached hydrogen atoms, leads to the similar conclusion that three linkages will always terminate on each carbon atom.

A graph-theoretical representation of all the possible different aromatic hydrocarbons containing up to four carbocycles is presented in Figure 1. Each carbon atom is depicted here by a single vertex, though for simplicity in the representation no hydrogen atoms are depicted. Graphs of the type shown in Figure 1 we shall designate as constitutional C-graphs, whereas graphs depicting both carbon and hydrogen atoms will be termed constitutional CH-graphs. Our following characterization of aromatic

hydrocarbons will be carried out without further reference to constitutional CH-graphs. The number of constitutional C-graphs containing a given number of carbocycles which may drawn is in general not known. Studies in pure mathematics, where such systems are known as hexominoes or hexagonal animals, have revealed^{15,16} that a general formula for their number will be difficult to obtain.

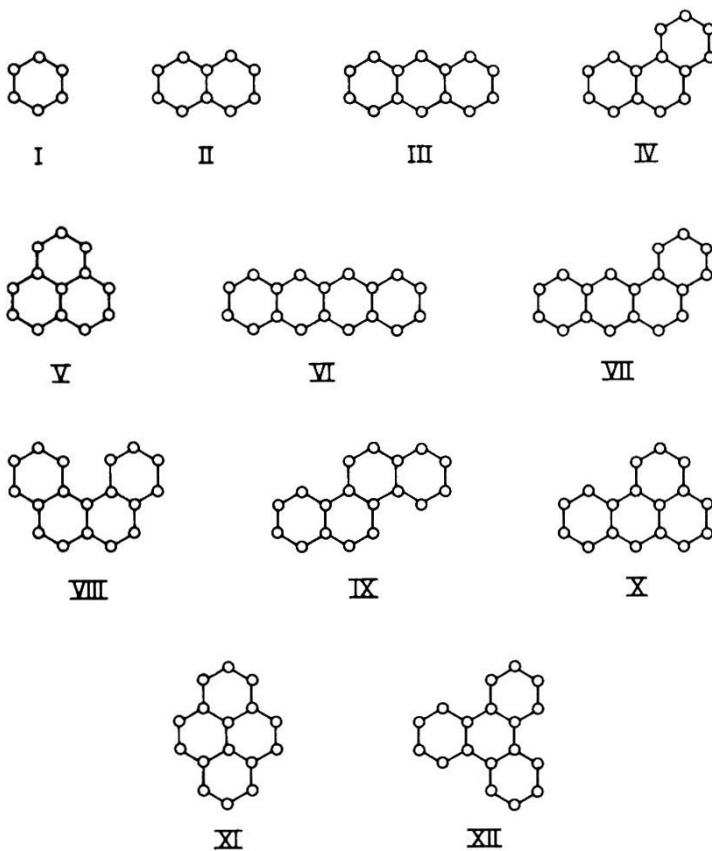


Figure 1

A computer programme due to Lunn¹⁷ has enabled computations to be made for systems containing up to twelve hexagons, and recently a general formula for a particular class of hexagonal animal, i.e. those which are in the form of unbranched chains, has been given by Rouvray¹⁸.

As may be readily verified from inspection of Figure 1, every carbon atom in an aromatic hydrocarbon may belong to either one, two or three carbocyclic hexagonal rings. The whole constitutional C-graph may be constructed from such 6-member rings by edge fusions. As a consequence of this whenever a carbon atom belongs to two or three rings, we know that the rings are condensed together. If the constitutional C-graph contains no vertex common to three rings, the corresponding aromatic hydrocarbon is termed cata-condensed or annellated¹⁹. On the other hand, a vertex belonging to three rings will indicate a site of peri-condensation, and the corresponding aromatic hydrocarbon is then described as peri-condensed²⁰. A discussion of the relevant nomenclature has been given by Balaban and Harary²¹. Whatever the type of condensation present, it is evident that all aromatic hydrocarbons will belong to the class of alternant hydrocarbons, as defined by Coulson and Rushbrooke²². In graph-theoretical terms this means that all the constitutional C-graphs must be two-colourable or bipartite²³.

Formal Graph-Theoretical Description

As indicated above, any aromatic hydrocarbon may be represented by a constitutional C-graph, and such a graph we shall designate by the symbol A . The graph A will be constructed from a set of vertices V , representing the carbon atoms, and a set of edges E , representing the linkages existing between the carbon atoms. We may therefore define A as

$$A = [V, E], \quad (1)$$

where V represents the set $\{V_j\}$ and E the set $\{E_{jk}\}$, and the integers j and k are labels for the j th and k th vertices respectively. All vertices V_j depicting carbon atoms in the CH-graph are of degree three. In the hydrogen-suppressed C-graph A , however, those vertices belonging to only one ring will be of degree two, whereas those belonging to two or three rings will be of degree three. Since each vertex in A must be part of an hexagonal cycle, no vertex therein can be of degree less than two. Accordingly, we may assign the limits

$$2 \leq g_j \leq 3 \quad (2)$$

to any vertex V_j of degree g_j in A .

If we denote the number of vertices of degree two by σ_2 , and that for those of degree three by σ_3 , it follows that the sum of these two numbers must equal the cardinality $|V|$ of set V , i.e.

$$|V| = \sigma_2 + \sigma_3. \quad (3)$$

Since the degree of a vertex indicates the number of edges terminating on it, and as each edge will terminate on two vertices, it is immediately evident that the cardinality $|E|$ of the set E will be

$$|E| = \frac{1}{2} (2\sigma_2 + 3\sigma_3). \quad (4)$$

By combining (3) and (4) it is now possible to obtain the following expressions for σ_2 and σ_3 :

$$\sigma_2 = 3 |V| - 2 |E| \quad (5)$$

$$\sigma_3 = 2 |E| - 2 |V|. \quad (6)$$

The result in (4) is a particular instance of the well-known general theorem that the number of vertices of odd degree in any graph must be even.

Let us suppose that the general aromatic hydrocarbon possesses the empirical formula $C_a H_b$. As the graph A will depict all the carbon atoms present in the species, we may

write according to (3)

$$a = \sigma_2 + \sigma_3. \quad (7)$$

Moreover, since each vertex in A of degree two actually represents a carbon atom bonded to an hydrogen atom, the value of σ_2 gives us directly the number of hydrogen atoms in the hydrocarbon, i.e. we have

$$b = \sigma_2. \quad (8)$$

It is well-known that the number of cycles contained within such a molecular species may be obtained directly²⁴ from the cyclomatic index r of its graph A . The index r is defined as

$$r = |E| - |V| + 1, \quad (9)$$

and for the species C_aH_b may be easily shown to assume the form

$$r = \frac{1}{2} \sigma_3 + 1. \quad (10)$$

It is now possible, by making appropriate substitutions of (7) and (8) into the equations (3) to (6) and (10), to express all the parameters defined in these

latter equations in terms of a and b thus:

$$|V| = a \quad (11)$$

$$|E| = \frac{1}{2} (3a - b) \quad (12)$$

$$\sigma_2 = b \quad (13)$$

$$\sigma_3 = a - b \quad (14)$$

$$r = \frac{1}{2} (a - b) + 1. \quad (15)$$

The Rôle of the Characteristic Graph

To facilitate our further graph-theoretical description, we utilize now the notion of a characteristic graph introduced by Balaban and Harary²¹. For every constitutional graph A there is a corresponding characteristic graph which we shall denote as C . The graph C may be simply constructed from A by placing a vertex in the centre of each hexagonal cycle of A and then connecting those vertices which are in adjacent fused cycles. From its mode of construction C must be a connected graph and accordingly no vertex of degree zero can exist in it. As not more than six hexagonal rings can be arranged around a given central hexagon, the highest possible degree of any vertex in C is six. We therefore obtain for the degree d_k of any vertex in C the range

$$1 \leq d_k \leq 6. \quad (16)$$

As will be explained below, the graphs C cannot be purely topological graphs as the vertices of C are to be placed in the centre of each hexagon in A and their positioning now becomes of importance. More formally we may define A as

$$C = [U, K, \theta], \quad (17)$$

where the vertex set U is the set $\{U_k\}$ created by placing one vertex in each cycle of A , K is the edge set $\{K_{k1}\}$ formed by connecting the vertices U_k and U_1 of adjacent fused cycles, and θ is the set of angles between incident edges [25]. From the construction of C it is evident that the cardinality of the set U must equal the cyclomatic index r for A , and hence we may write

$$|U| = u = r. \quad (18)$$

Similarly, the cardinality of the set K will equal the number of condensation sites for cycles present in A and, remembering that C must always be connected, we obtain the inequality

$$|K| = k \geq u - 1. \quad (19)$$

The reasons of completeness we give the cardinality of the set θ

$$|\theta| = \sum_{j=1}^{|u|} (d_j - 1) = 2 \cdot |K| - |u| \quad (20)$$

In Figure 2 the characteristic graphs C corresponding to each of the constitutional graphs A in Figure 1 are presented. It will be readily seen that certain of the graphs C do not differ in their topological structure, namely the pair C_{III} and C_{IV} and also the quartet C_{VI} , C_{VII} , C_{VIII} , and C_{IX} . The former pair are both constructed on three vertices and have two edges, whilst the latter quartet all have four vertices and three edges and no branching. The topological graph corresponding to the pair is the snake graph S_3 , whereas that for the quartet is the snake graph S_4^\dagger . The differences between the graphs in the pair and those in the quartet are expressed by the difference between the respective angle sets. Using the convention proposed in [25] all the angles are multiples of $\pi/3$ radians. If all edges are depicted by a line of unit length the vertices of C will be sited on the points of a lattice, which may be visualized as an infinite planar array constructed from regular triangles. In this lattice edges can be drawn from a given point to a nearest neighbouring point only.

[†] Snake graphs S_u are unbranched tree graphs, and accordingly may be sufficiently characterized by their number of vertices u .

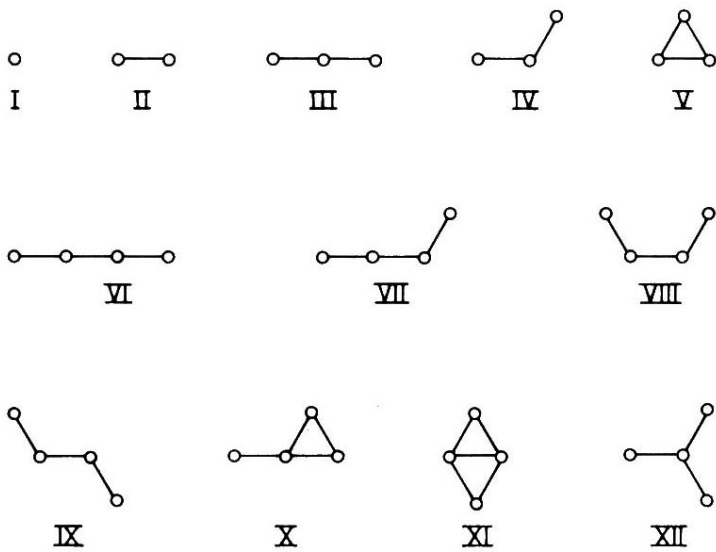


Figure 2

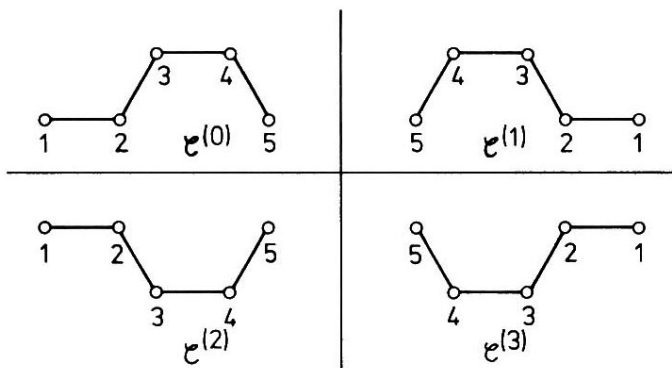


Figure 3

The Equivalence of Characteristic Graphs

Two characteristic graphs are equivalent if and only if there exist a bijective mapping between the respective vertices, edges and angles. The first two conditions are normal for the existence of isomorphism in two graphs and reflect the topological content of the graphs C . On the other hand the third stipulation arises from the fact that the characteristic graphs are truncated geometric duals [25]. The angles formed at the vertices U_2 , U_3 , and U_4 of the graph $C^{(0)}$ will be respectively 120° , 240° , and 240° , if they are read in the clockwise sense (Figure 3). If one maps bijectively $C^{(0)}$ onto $C^{(3)}$ the sense is maintained but if one maps bijectively $C^{(0)}$ onto either $C^{(1)}$ or $C^{(2)}$ the sense is reversed.

The Modes of Condensation

We consider now the possible sites on an aromatic hydrocarbon molecule at which condensation of a new ring may take place. Such condensation can occur in only two ways, namely either at two ortho-located carbon atoms, as illustrated in Figure 4(a), or at two peri-located carbon atoms as shown in Figure 4(b). The first type of condensation we have referred to as annellation or cata-condensation, and the second as peri-condensation. In

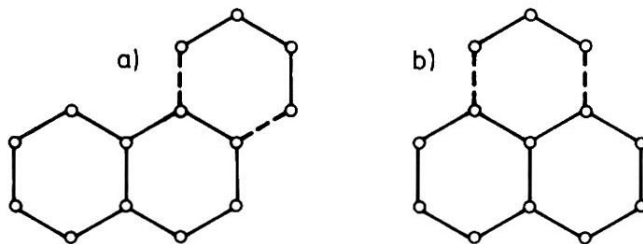


Figure 4

the former case we may speak of a linear or of an angular annellation, according as the new edge in C forms an angle of 180° or $\pm 120^\circ$ with an existing edge. Peri-condensation will always give rise to a mutual angle of $\pm 60^\circ$, and therefore to a cycle of length three in the characteristic graph, as may be seen for instance from inspection of the graphs C_V , C_X , and C_{XI} in Figure 2. Thus, just as a vertex common to three hexagons signifies a site of peri-condensation in A , the presence of a triangle will indicate such a site in C .

By definition the characteristic graphs of cata-condensed systems cannot contain any cycles of length three, and so the only possible mutual edge angles in their graphs C must be 180° or $\pm 120^\circ$. From this fact it follows that the degrees of vertices in such graphs must equal either one (for terminal hexagons), two (for adjacent hexagons with no branching), or three (for adjacent hexagons with branching). Clearly the three edges incident at a vertex of degree three will be at

mutual angles of 120° . As pointed out by Balaban and Harary²¹, cyclic cata-condensed systems may also be constructed (for examples see Figure 5). Since it is not unreasonable to expect that the chemistry of these compounds, the so-called coronaphenes, will be analogous to the well-known acyclic cata-condensed systems rather than to peri-condensed systems, we prefer to call such systems cyclic cata-condensed or corona-condensed²¹.

The number of vertices in the cycles formed in corona-condensed species must always be greater than six. If only six vertices were to be present, these would have to be arranged in the form of a regular hexagon. The lattice point at the centre of this hexagon, however, would also necessarily belong to the graph, and so the resultant characteristic graph would be that of coronene, as may be seen from Figure 5. Since the latter molecule is peri-condensed, a graph constructed in this way clearly could not represent a cata-condensed system.

The above reasoning leads us to the conclusion[†] that the smallest possible cycle which may exist in the charac-

[†] This conclusion is true only for aromatic hydrocarbons which may be embedded within a regular hexagonal, two-dimensional lattice. Non-embeddable species, which in general do not satisfy the above conditions, have been discussed elsewhere by one of the present authors²⁶.

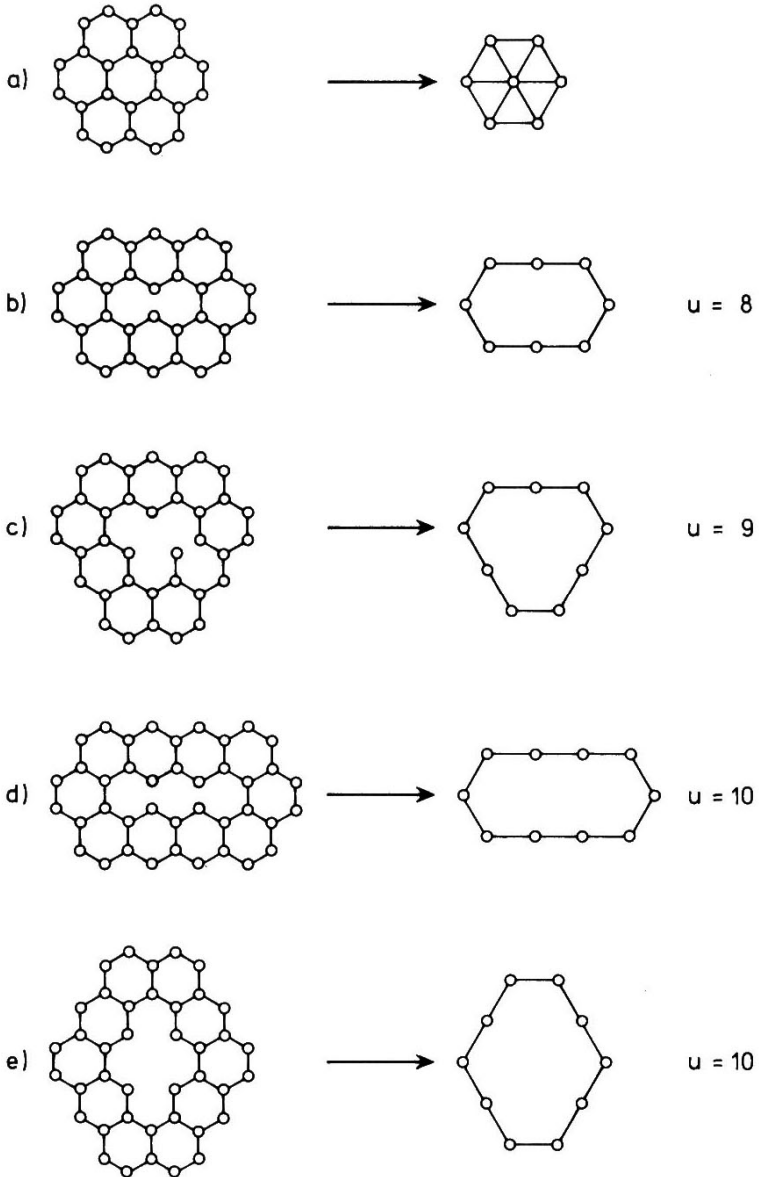


Figure 5

teristic graph of a corona-condensed species must be of length $f = 8$ (see Figure 5(b)). As may be seen, enlargement of the length of a cycle in a corona-condensed species by two may be readily achieved. The vertices of these cycles will lie on at least three pairs of parallel lattice lines, and addition of one extra vertex to each line in such a pair results in the enlargement of the cycle by two vertices. As cycles of length $f = 8$ and $f = 9$ can be drawn, all cycles having $f \geq 8$ can be constructed. To distinguish these cycles from triangles indicating sites of peri condensation, we shall term them coronae.

Some Relationships Between the Constitutional and Characteristic Graphs

We investigate now the relationships existing between the characteristic graph C and the empirical formula $C_a H_b$ of a given aromatic hydrocarbon. Because in the construction of the characteristic graph one vertex is assigned to each hexagonal cycle in the constitutional graph A , the number a of carbon atoms contained within the aromatic hydrocarbon cannot exceed $6u$. Within this $6u$ carbon atoms belonging to two or three rings will have been counted respectively twice or thrice. In the characteristic graph of a cata-condensed aromatic hydrocarbon

each edge K_{1m} represents such a pair of doubly-shared carbon atoms, counted twice; thus we may write for the number of carbon atoms in these systems

$$a = 6u - 2k. \quad (21)$$

The triply-shared carbon atoms represented in the characteristic graph of a peri-condensed system belong to three such pairs. Thus, in subtracting $2k$ from $6u$ each of the triply-shared carbon atoms is taken into account once too often, and we obtain instead the equation

$$a = 6u - 2k + t, \quad (22)$$

where t is the number of sites of peri-condensation.

In order to express both σ_2 and σ_3 of \hat{A} in terms of the parameters k , u , and t , it is necessary first to derive an expression for the number of edges contained in \hat{A} . From our reasoning above we know that this number cannot exceed $6u$. As each edge of the characteristic graph C crosses one edge in \hat{A} which is counted twice in the $6u$, we must subtract from the $6u$ the number of edges in C . We then obtain the result

$$| E | = 6u - k. \quad (23)$$

Use of equations (5), (22) and (23) now enables us to formulate σ_2 as

$$\sigma_2 = 6u - 4k + 3t. \quad (24)$$

The corresponding result for σ_3 is obtained using equations (6), (22) and (23), viz.

$$\sigma_3 = 2k - 2t. \quad (25)$$

Because of the relationship existing between the characteristic graph C and the constitutional graph A , there should be a relation between the parameters k , u , and t . To derive this relation we shall make use of the cyclomatic index μ of C , which is defined as

$$\mu = k - u + 1. \quad (26)$$

The parameter μ yields the number of independent cycles[†]

[†] By an independent cycle is meant any cycle having at least one edge which is not contained in any other cycle in the graph.

in C . Thus, if there are x_f independent cycles of length f in C we may write

$$\sum_f x_f = \mu. \quad (27)$$

From earlier reasoning we know that for any characteristic graph embedded within its triangular lattice f may assume only the values

$$f = 3, 8, 9, 10, \dots \quad (28)$$

We may therefore split the summation in equation (27) into two parts as follows:

$$\sum_f x_f = t + \bar{x}, \quad (29)$$

where t equals x_3 , and \bar{x} is the number of coronae in C . Rearrangement of (29) gives the result that

$$t = k - u + 1 - \bar{x}. \quad (30)$$

The parameter \bar{x} will normally be zero for the simple reason that coronaphenes have not yet been synthesized.

Now the ten parameters which have been introduced above may be assigned to six groups, viz. t ; \bar{x} ; $|E|$ and $|V|$; σ_2 and σ_3 ; u and k ; and a and b . The basis for this classification will be evident from the following reasoning. Both the parameters t and \bar{x} refer to A and C , though \bar{x}

is an independent parameter as it gives the number of coroneae. The two pairs $|E|$ and $|V|$ and σ_2 and σ_3 relate only to A. The pair u and k refers only to C, whereas the latter pair a and b refers to the empirical formula. Since a given aromatic hydrocarbon may be represented by \bar{x} and any of the above pairs, the seven remaining parameters can always be expressed in terms of those chosen for the representation as shown in Table 1.

It should not be forgotten that the sets of equations given in Table 1 are all subject to certain conditions which arise quite naturally from the topology of the systems investigated here. It is in particular necessary that (i) for $t > 0$ we always have $u \geq 3$; (ii) for $\bar{x} > 0$ we have $u \geq 8$; and (iii) for both $t > 0$ and $\bar{x} > 0$ we have $u \geq 9$. It should be mentioned that $\bar{x} = 0$ for all known species.

The Ratio of Carbon to Hydrogen Atoms

We turn our attention at this point to the relative numbers of carbon and hydrogen atoms to be found in the various aromatic hydrocarbons C_aH_b . From the results given in Table 1 for the chosen pair u and k , we know that

$$\frac{b}{a} = \frac{2u + 4 - t - 4\bar{x}}{4u + 2 - t - 2\bar{x}}. \quad (31)$$

Table 1: Relationships between the parameters of the consitutional and characteristic graphs

Chosen pair with \bar{x}	Expressions for the remaining seven parameters	Chosen pair with \bar{x}	Expressions for the remaining seven parameters
$ \bar{E} , V $	$\sigma_2 = 3 V - 2 \bar{E} $ $\sigma_3 = 2 \bar{E} - 2 V $ $u = V - \bar{E} + 1 - \bar{x}$ $k = 5 V - 6 \bar{E} + 6 + 6\bar{x}$ $a = V $ $b = 3 V - 2 \bar{E} $ $t = 4 V - 5 \bar{E} + 6 - 6\bar{x}$	σ_2, σ_3	$ \bar{E} = \sigma_2 + \frac{3}{2}\sigma_3$ $ V = \sigma_2 + \sigma_3$ $u = \frac{1}{2}\sigma_3 + 1 - \bar{x}$ $k = \frac{3}{2}\sigma_3 - \sigma_2 + 6 - 6\bar{x}$ $a = \sigma_2 + \sigma_3$ $b = \sigma_2$ $t = \sigma_3 - \sigma_2 + 6 - 6\bar{x}$
u, k	$ \bar{E} = 6u - k$ $ V = 5u - k + 1 - \bar{x}$ $\sigma_2 = 3u - k + 3 - 3\bar{x}$ $\sigma_3 = 2u - 2 + 2\bar{x}$ $a = 5u - k + 1 - \bar{x}$ $b = 3u - k + 3 - 3\bar{x}$ $t = k - u + 1 - \bar{x}$	a, b	$ \bar{E} = \frac{3}{2}a - b$ $ V = a$ $\sigma_2 = b$ $\sigma_3 = a - b$ $u = \frac{1}{2}a - \frac{1}{2}b + 1 - \bar{x}$ $k = \frac{3}{2}a - \frac{5}{2}b + 6 - 6\bar{x}$ $t = a - 2b + 6 - 6\bar{x}$

Upper and lower limits for this ratio may be obtained in the cases when u equals one or tends to infinity respectively. Thus the quotient (31) has the range

$$1 \geq \frac{b}{a} > 0. \quad (32)$$

The upper limit is attained only in benzene and the lower limit in a single layer of graphite.

It should be pointed out that a particular value of the ratio b/a may correspond to various subclasses of aromatic hydrocarbons. For example with $b/a = 1/2$ we obtain from (31)

$$4u + 8 - 2t - 8\bar{x} = 4u + 2 - t - 2\bar{x}.$$

If both t and \bar{x} have finite values this equality is maintained even for an infinite value of u , and this will correspond to any infinite condensed aromatic system containing only finite numbers of either sites of peri-condensation and/or coronae. For finite u it follows that

$$t + 6\bar{x} = 6. \quad (33)$$

Equation (33) has two acceptable solutions: the first $t = 0$ and $\bar{\chi} = 1$, corresponds to mono-cyclic cata condensed systems (mono-coronae), and the second, $t = 6$ and $\bar{\chi} = 0$, to any non-coronaid condensed aromatic system containing exactly six sites of peri-condensation.

A general expression for the ratio b/a in peri-condensed

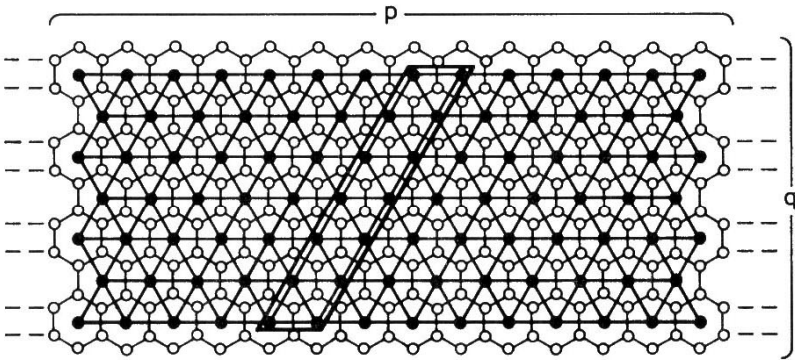


Figure 6

molecules in the form of long strips may be derived in terms of the number of benzene rings p in the top row and the number of rows of benzene rings q in the strip. A typical section of such a strip is illustrated in Figure 6. From inspection of this figure it is evident that the number of sites of peri-condensation t within the strip will be given by the expression

$$t = (2q - 2)p. \quad (34)$$

The number of vertices present in the characteristic graph of the strip molecule will be given by

$$u = q.p. \quad (35)$$

Substitution of these particular values of t and u into (31) yields the general result

$$\frac{b}{a} = \frac{2p + 4 - 4\bar{x}}{(2q + 2)p + 2 - 2\bar{x}}. \quad (36)$$

Clearly when the strip closes on itself to form a single cycle the ratio will assume the simple form

$$\frac{b}{a} = \frac{1}{q + 1}, \quad (37)$$

a result which is independent of the number of rings in the top row.

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