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An Analytical Illustration of the Relevance of Molecular Topology to the *Aufbau* Process*

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The ideas of Mallion and Rouvray (1978), concerning the relevance of molecular topology to the prospects of obtaining, on the basis of the *Aufbau* Principle, a unique, π-electronic ground-state configuration for an existent or hypothetical conjugated-system, are extended by considering a series of networks introduced by Balaban in 1978. It is shown by exploiting the properties of the eigenvalues of circulant matrices that the graph spectrum of a general member of this series may be found analytically in closed form. From this it is further deduced that application of the *Aufbau* process to the »Balaban graphs«, B_N, will lead to the establishment of a unique, ground-state configuration if, and only if, N is divisible by 4. The Balaban graphs are thus shown to constitute a series in which networks that give rise to a unique, ground-state configuration when the *Aufbau* Principle is invoked *alternate* with ones that do not. As a result of these observations, it is emphasised that, despite what is often assumed to the contrary, the existence of a unique and unambiguous »π-electronic, ground-state configuration« for an *arbitrary* network should not be taken for granted.

1. INTRODUCTION

Rouvray and the present author have previously pointed out[1,2] that the σ-bond connectivity of the carbon atoms in a hypothetical, neutral, conjugated hydrocarbon predetermines whether or not it is possible, on the basis of the *Aufbau* Principle, to assign a unique, ground-state configuration from energy levels calculated via Hückel-molecular-orbital (HMO) theory. Such 'molecular topology#' is relevant because it influences the relative ordering amongst the eigenvalues of the associated molecular-graph (see, for example, refs. 9, 5, 7 and 8). It was shown by direct numerical calculation[1] that networks which, on chemical grounds, could not possibly represent actual molecules may, nevertheless, have eigenvalue spectra that constrain application of the *Aufbau* process to occasion a unique π-electronic, ground-state configuration; (naturally, all known conjugated systems are associated with molecular graphs that have this property.) It was speculated[1] that certain hypothetical conjugated-systems may not exist because their very topology# precludes their having an

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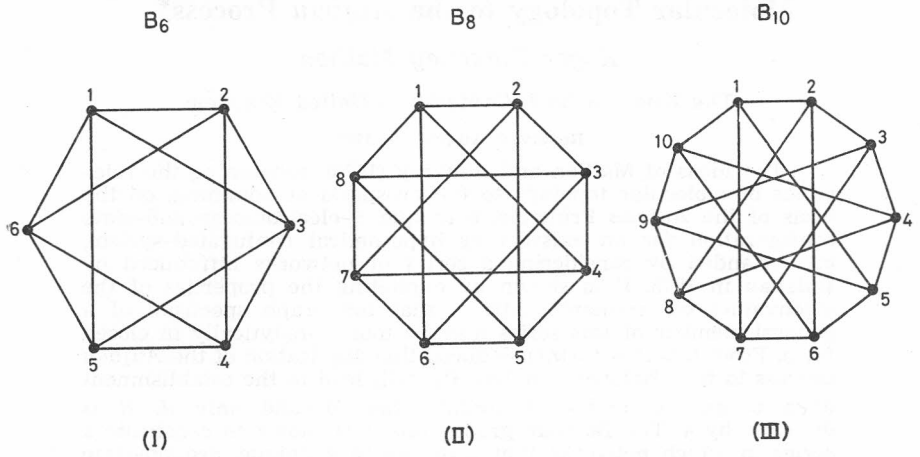
The somewhat unfortunate adjective 'topological' is used in this paper to describe any property or quantity that is derivable solely from the eigenvalues and/or

energy-level family that will lead to a unique, ground-state configuration, when the *Aufbau* Principle is invoked.

Eigenvalues of graphs are, however, somewhat capricious entities (ref. 10 — but see also refs. 11 and 12) and it is not, in general, possible to obtain the latent roots of an arbitrary network in closed form and hence to give an analytical demonstration of the ideas that were introduced in refs. 1 and 2. A specific series of networks that do, however, nicely illustrate these points is one recently discussed, in quite another context, by Balaban[13]. Examples of three members of this series are shown in the Figure. These networks could not,



of course, represent the atom connectivity of conjugated systems, although they indirectly have a chemical significance for they arise in Balaban's graph--theoretical treatment[13] of the constitutional isomers of cyclo-alkanes; because they were introduced by Balaban, I shall for convenience in this discussion call them 'Balaban graphs' and denote the Balaban graph on N vertices by 'B_N'.** (A precise algorithm for the construction of the graph B_N will be given in § 2, below; from this it will be evident that N is always even and that such graphs are defined only for $N \geq 6$).

It will be shown by exploiting the rather pleasant properties of the eigenvalues of circulant matrices (refs. 14 and 7) that the spectrum of a general member of this series may be found analytically in closed form. From this it will be deduced that application of the *Aufbau* process to the Balaban graph B_N will lead to a unique, ground-state configuration if, and only if, N is divisible by 4. As a result of this deduction, the Balaban graphs B_6, B_8, B_{10}, ... etc. will be seen to constitute a pedagogically rather illuminating series in

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eigenvectors of a vertex adjacency-matrix of the graph representing the carbon-atom connectivity of the (extant or hypothetical) conjugated hydrocarbon under discussion. Hence, in the present context, 'molecular topology' is essentially a synonym for 'the σ-bond connectivity of the carbon atoms', and the former term is adopted here not because the author considers it particularly apt, but as a concession to what has become common usage in this field. (See also refs. 1, 3—8).

** I am very grateful to Professor Balaban for his kind permission allowing me to do this; (A. T. Balaban, personal communication, August 17th., 1980). I also thank Professor Frank Harary and Dr. R. J. Wilson for helpful correspondence on the nomenclature of the graphs depicted in the Figure.

which networks that give rise to a unique ground-state configuration on application of the *Aufbau* process *alternate* with ones that do not.

2. CONSTRUCTION OF THE GRAPH B_N

The Balaban graph B_N is a cycle of N vertices (N even, $N \geq 6$) that has, in addition, »... edges between each vertex i and the two vertices adjacent to the vertex opposite to i; thus, each vertex has degree 4«; (this is Balaban's definition, quoted from ref. 13). Effectively, therefore, if the vertices are labelled 1 to N in sequence around the perimeter, each vertex i, in addition to being adjacent to the vertices $i-1$ and $i+1$ (MOD. N), is joined by an edge to the ones labelled

$$(i + \frac{1}{2}N + 1) \qquad \text{and} \qquad (i + \frac{1}{2}N - 1) \qquad \text{(MOD. } N\text{)}.$$

As examples of this construction, the graphs B_6, B_8 and B_{10} are illustrated in the Figure.*** It will be seen that graphs B_N where $\frac{1}{2}N$ is even are bipartite, since they contain no odd-membered cycles, while if $\frac{1}{2}N$ is odd, B_N is non-bipartite; i. e., B_N is bipartite if and only $N = 4p$, p any (odd or even) integer ≥ 2.

3. EIGENVALUES OF THE GRAPH B_N

The k^{th} member of the eigenvalue list of N (not-necessarily-distinct) eigenvalues, $\{\lambda_k\}_{k=1,2,3,\ldots,N}$, of a circulant $N \times N$ matrix (refs. 14 and 7) in which the elements in the first row are

$$a_1, a_2, a_3, \ldots, a_N$$

is given by

$$\lambda_k = a_1 + a_2 \omega_k + a_3 \omega^2_k + \ldots + a_N \omega_k^{N-1} \tag{1}$$

where ω_k is an N^{th} root of unity, — i. e., *one* of the N roots of the scalar equation

$$\omega^N = 1 \tag{2}$$

*** Professor Frank Harary (personal communication, November 15th., 1980) has kindly answered a previous enquiry about the nomenclature of the graphs discussed in this paper by informing me that Frucht[15] has defined the following notation for a certain class of graphs: $n\,(a, b)$ for $a < b < n$ is the graph with vertex set $(0, 1, 2, \ldots, n-1)$ (MOD. n), where each vertex i is adjacent to the vertices $i + a$ and $i + b$ (MOD. n). In this notation:

$$B_6 \equiv 6\,(1, 2)$$
$$B_8 \equiv 8\,(1, 3)$$
$$B_{10} \equiv 10\,(1, 4);$$

in general,

$$B_N \equiv N\,(1, \tfrac{1}{2}N - 1),$$

and the $\{B_N\}$ are thus seen to be a special case of Frucht's more-embracing classification.[15] (Of course, in addition — as a very special member, in its turn, of $\{B_N\}$ — — B_6 is the octahedral graph[2]).

which has solutions $\{\omega_k\}_{k=1,2,3,\ldots,N}$, with

$$\omega_k = \cos\left(\frac{2k\pi}{N}\right) + j\,\sin\left(\frac{2k\pi}{N}\right) \tag{3}$$

(It may be noted that, in spite of the reference to j ($= \sqrt{-1}$) in equation (3), we shall not in this discussion encounter any eigenvalues other than those that are purely real; this is because we are dealing only with graph adjacency--matrices which, being real-symmetric, will necessarily have entirely real characteristic-roots. (See, for example, refs. 9, 5, 7 and 10).)

Armed with equation (1), we now observe that

(i) a vertex adjacency-matrix of a Balaban graph is *circulant;*

(ii) in the graph B_N, the vertex labelled 1 on the labelling scheme adopted in the Figure is joined by an edge to the vertices labelled

$$\text{(a)}\quad 2 \qquad \text{(b)}\quad N \qquad \text{(c)}\quad \frac{1}{2}N \qquad \text{(d)}\quad \frac{1}{2}N + 2;$$

(iii) the elements $(a_1, a_2, a_3, \ldots, a_N)$ of the first row of the vertex adjacency-matrix of the Balaban graph B_N, labelled as in the Figure, are thus

$$a_2 = 1, \quad a_N = 1, \quad a_{\frac{1}{2}N} = 1, \quad a_{\frac{1}{2}N+2} = 1,$$

all the other elements in the first row being *zero.* (It will be recalled that a circulant matrix is completely defined once the elements in the first row have been specified; see, for example, ref. 7).

Insertion of these values into equation (1) gives the k^{th} eigenvalue, λ_k, of the graph B_N as

$$\lambda_k = (\omega_k + \omega_k^{N-1}) + (\omega_k^{\frac{1}{2}N-1} + \omega_k^{\frac{1}{2}N+1}) \tag{4}$$

The first bracket in equation (4) simplifies via equation (3)) to $2\cos\left(\frac{2k\pi}{N}\right)$, exactly as in the case of the circuit graphs, C_N, representing the carbon-atom connectivity of the annulenes[14,7]; the second bracket, after application of equation (3) and some trigonometric identities, amounts to $2\cos\left(\frac{2k\pi}{N} + k\pi\right)$. Hence, equation (4) may more explicitly be written:

$$\lambda_k = 2\left\{\cos\left(\frac{2k\pi}{N}\right) + \cos\left(\frac{2k\pi}{N} + k\pi\right)\right\} \tag{5}$$

or, as a product, rather than a sum, of two cosines:

$$\lambda_k = 4\cos\left(\frac{2k\pi}{N} + \frac{k\pi}{2}\right)\cos\left(\frac{k\pi}{2}\right) \tag{6}$$

This formula has been applied to the graphs $B_6, B_8, B_{10}, \ldots, B_{20}$ and the numerical results obtained are collected and displayed in Table I. It may be

TABLE I

Eigenvalue Spectra of the Graphs B_6 to B_{20}

N	Eigenvalue Spectrum of $B^1{}_N$	Numbers of eigenvalues that are		
		zero	+ ve	— ve
6	{4, 0, 0, 0, —2, —2}[2]	3	1	2
8	{4, 0, 0, 0, 0, 0, 0, —4}[2]	6	1	1
10	{4, 1.2361,[3] 1.2361, 0, 0, 0, 0, 0, —3.2361,[3] —3.2361}	5	3	2
12	{4, 2, 2, 0, 0, 0, 0, 0, 0, —2, —2, —4}	6	3	3
14	{4, 2.4940, 2.4940, 0, 0, 0, 0, 0, 0, 0, —0.8901, —0.8901, —3.6039, —3.6039}	7	3	4
16	{4, 2.8284,[4] 2.8284, 0, 0, 0, 0, 0, 0, 0, 0, 0, 0, —2.8284, —2.8284, —4}	10	3	3
18	{4, 3.0642, 3.0642, 0.6946, 0.6946, 0, 0, 0, 0, 0, 0, 0, 0, 0, —2, —2, —3.7588, —3.7588}	9	5	4
20	{4, 3.2361, 3.2361, 1.2361, 1.2361, 0, 0, 0, 0, 0, 0, 0, 0, 0, —1.2361, —1.2361, —3.2361, —3.2361, —4}	10	5	5

[1] The bipartite Balaban-graphs ($^1/_2N$ even) exhibit 'paired' eigenvalues, in accord with the Coulson-Rushbrooke theorem[17].

[2] These numbers agree with those obtained by 'brute-force' computer-evaluation of the spectra of B_6 and B_8, incidentally reported in refs. 1 and 2.

[3] 1.2361 is the four-decimal-place approximation of $\sqrt{5}-1$; 3.2361 is a similar approximation to $\sqrt{5}+1$.

[4] 2.8284 is the four-decimal-place approximation of $2\sqrt{2}$.

noted in passing that

$$\sum_{k=1}^{N} \lambda_k = 0 \tag{7}$$

in all cases, in accord with the fact that the diagonal elements of an adjacency matrix of a vertex-*un*weighted graph are conventionally — and conveniently — taken to be zero (see, for example, ref. 16); the *trace* of such a vertex adjacency-matrix is thus also zero, and this accounts for equation (7). The latter does, of course, apply equally whether the graph B_N is bipartite ($\frac{1}{2}N$ even) or non-bipartite ($\frac{1}{2}N$ odd). The spectra of the bipartite Balaban-graphs B_8, B_{12}, B_{16}, B_{20}, ...) will be seen to consist of eigenvalues that are symmetrically disposed about zero, as is to be expected from the graph-theoretical generalisation[16] of the Coulson-Rushbrooke[17] 'pairing' theorem. The occurrence of 4 as the highest eigenvalue in all the Balaban graphs — bipartite and non-bipartite — is a natural consequence of (i) the observation (see ref. 13 and § 2) that B_N is a regular graph of degree 4, and (ii) the Perron-Frobenius theorem on non-negative matrices (see, for example, refs. 18 and 19). From equation (6), it is evident that $\lambda_k = 4$ *will* always arise (whether $\frac{1}{2}N$ is odd or even), when the running integer k takes on its final and maximum value, N.

4. MULTIPLICITY OF THE ZERO EIGENVALUES IN THE SPECTRUM OF B_N

A knowledge of how many times the *zero* eigenvalue occurs in the spectrum of B_N will be seen to be particularly material to a discussion of the feasibility of applying the *Aufbau* process to the eigenvalue family belonging to these graphs. Such a discussion will be presented in § 6 but, as a preliminary to this, the multiplicity of the zero eigenvalue in the general Balaban-graph B_N will be established in the present section, and the distribution of positive and negative eigenvalues in the non-bipartite Balaban-graphs will be examined in the next section.

It is immediately evident from equation (6) that an *odd* value of k leads to $\lambda_k = 0$; hence, exactly half the eigenvalues of B_N will always be zero by virtue of the second cosine term in equation (6). To ascertain whether any other zero eigenvalues will arise, via the *first* cosine term in (6), it is necessary to investigate the conditions under which *this* cosine term is zero, for *even* k. This does in fact occur whenever k and N conspire to make

$$\frac{2k\pi}{N} + \frac{k\pi}{2} = r\frac{\pi}{2} \tag{8}$$

where r is an *odd integer* (k is even). Manipulation of equation (8) shows that this requirement is met when there exists k (k even and $2 \leqslant k \leqslant N$) such that

$$\frac{k(N+4)}{N} \text{ is an } \textit{odd integer}.$$

By using arguments that, for integers, odd × odd = odd, odd × even = even, and even × even = even, it is easy to show that this latter constraint is satisfied *only when N is divisible by* 8. Furthermore, if $N = 8p$, where p is an (odd or even) integer, it can be deduced in a similar manner that there are two, and only two, values of (even) k in the range $2 \leqslant k \leqslant N$ that make

$$\frac{k(N+4)}{N}$$

an odd integer: these are $k = \frac{1}{4}N$ and $\frac{3}{4}N$ (both necessarily even, when N is divisible by 8).

This result may be seen in another way, and the equations that are introduced thereby will be of use in § 5. Equation (6) may be expanded as

$$\lambda_k = 4\left\{\cos\left(\frac{2k\pi}{N}\right)\cos\left(\frac{k\pi}{2}\right) - \sin\left(\frac{2k\pi}{N}\right)\sin\left(\frac{k\pi}{2}\right)\right\}\cos\left(\frac{k\pi}{2}\right) \tag{9}$$

As has been observed, when k is odd, this is zero, because of the multiplicative $\cos\left(\frac{k\pi}{2}\right)$ term; but when k is *even*, although λ_k is not in general zero, the term in equation (9) involving the product of two sines *is* zero. For even k, therefore, equation (9) reduces to

$$\lambda_k = 4\cos\left(\frac{2k\pi}{N}\right)\cos^2\left(\frac{k\pi}{2}\right) = 4\cos\left(\frac{2k\pi}{N}\right), \text{ (for } \textit{even } k^{****}) \tag{10}$$

**** This is *superficially* similar (apart from a further factor of 2) to the 'an-

The predictions of equation (6) may thus be simulated by two, simpler equations:

$$\left.\begin{aligned} \lambda_k &= 0 && (k \text{ odd}) \\ \lambda_k &= 4\cos\left(\frac{2k\pi}{N}\right) && (k \text{ even}) \end{aligned}\right\} \tag{11}$$

The argument about when zero eigenvalues arise for *even* k is then entirely analogous to the one used for the circuit-graphs C_N that represent the carbon-atom connectivity of the annulenes.[7,14] λ_k will be zero if there exist values of $k = 2p$ and $k = 2q$ (p, q integers) in the range 2, 4, 6, . . ., k, . . ., N, such that

$$\cos\left(\frac{2(2p)\pi}{N}\right) = 0, \text{ and } \cos\left(\frac{2(2q)\pi}{N}\right) = 0$$

i. e.

$$\text{when } \frac{4p\pi}{N} = \frac{\pi}{2} \text{ (this implies the condition } N = 8p, \text{ as before)}$$

$$\text{and when } \frac{4q\pi}{N} = \frac{3\pi}{2} \text{ (that is, } q = 3\left(\frac{N}{8}\right) = 3p)$$

leading to the values $k = \frac{1}{4}N$ and $k = \frac{3}{4}N$, obtained previously, as the ones that yield $\lambda_k = 0$, when k is even.

It is therefore concluded that, in the spectrum of B_N, there are exactly $\frac{1}{2}N$ zero eigenvalues if $N \neq 8p$, p an odd or even integer, and $(\frac{1}{2}N + 2)$ zeros if $N = 8p$. This result is illustrated numerically in Table I, where the multiplicity of the zero eigenvalue in the spectra of the graphs B_6 to B_{20} is listed in the right-hand section.

5. DISTRIBUTION OF POSITIVE AND NEGATIVE EIGENVALUES IN THE SPECTRA OF THE NON-BIPARTITE BALABAN-GRAPHS

We have seen that the bipartite Balaban-graphs (B_N, $\frac{1}{2}N$ even) have $(\frac{1}{2}N + 2)$ zero eigenvalues if $N = 8p$, and $\frac{1}{2}N$ zero eigenvalues if $N = 4p$ but $N \neq 8p$. Because the eigenvalues of bipartite graphs are symmetrically paired about zero[17], it can be said immediately that the spectrum of B_N, where $N = 8p$, will contain, in addition to its $(\frac{1}{2}N + 2)$ zero eigenvalues, $(\frac{1}{4}N - 1)$ positive eigenvalues and $(\frac{1}{4}N - 1)$ negative ones, and that the spectrum of B_N where

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nulene' (C_N) eigenvalue-formula[14,7]

$$\lambda_k = 2\cos\left(\frac{2k\pi}{N}\right).$$

It should be noted, however, that in the above formula for the spectrum of C_N, k takes on the value 1, 2, 3, . . ., N, but in equation (10), $k = 2, 4, 6, \ldots, N$.

$N = 4p$ but $N \neq 8p$ will comprise $\frac{1}{2}N$ zero eigenvalues, $\frac{1}{4}N$ positive eigenvalues and $\frac{1}{4}N$ negative ones.

Because the Coulson-Rushbrooke 'pairing' theorem[17] does not hold for non-bipartite graphs, the distribution of positive and negative eigenvalues in the spectra of the non-bipartite Balaban-graphs B_N, $\frac{1}{2}$ N odd — i. e., $N = 4p + 2$) is by no means immediately obvious and it will be necessary to state, and prove, the following two Rules.

Rule 1. — If $\frac{1}{4}(N-2)$ is *even* (i. e., $N = 4p + 2$, p even), the spectrum of the non-bipartite Balaban-graph B_N contains

$\frac{1}{2}\left(\frac{1}{2}N - 1\right)$ strictly positive eigenvalues

$\frac{1}{2}\left(\frac{1}{2}N - 1\right)$ strictly negative eigenvalues

(and $\frac{1}{2}N$ zero eigenvalues).

Proof

(a) Consider k-values such that $0 \leqslant \frac{2k\pi}{N} < \frac{\pi}{2}$

For an even k to yield $\frac{2k\pi}{N}$ in this range (which would then give rise, via equation (11), to a strictly *positive* λ_k), k must take on the values $2, \ldots, \frac{1}{4}(N-2)$. There are $\frac{N-2}{8}$ such even values of k.

(b) $\frac{\pi}{2} < \frac{2k\pi}{N} \leqslant \pi$

For an even k to make $\frac{2k\pi}{N}$ lie in the above range (which, via equation (11), would then ocassion a strictly *negative* λ_k), k must assume any of the following values:

$\frac{1}{4}(N+6), \ldots, \left(\frac{1}{2}N - 1\right)$. There are

$\frac{1}{2}\left\{\left(\frac{1}{2}N - 1\right) - \frac{1}{4}(N+6)\right\} + 1 = \frac{N-2}{8}$ such even values of k.

(c) $\pi \leqslant \frac{2k\pi}{N} < \frac{3\pi}{2}$

$\frac{2k\pi}{N}$ will be between π and $\frac{3\pi}{2}$ (giving rise, via equation (11), to strictly *negative* λ_k) when k takes on the values $(\frac{1}{2}N+1), \ldots, \frac{1}{4}(3N-6)$. There are

$$\frac{1}{2}\{\frac{1}{4}(3N-6)-(\frac{1}{2}N+1)\}+1=\frac{N-2}{8}$$ such even values of k.

(d) $\underline{\frac{3\pi}{2}<\frac{2k\pi}{N}\leqslant 2\pi}$

For an even k to give rise to an angle $\frac{2k\pi}{N}$ in this range (thus causing equation (11) to yield a strictly *positive* λ_k), k must be one of $\frac{1}{4}(3N+2)$, $\frac{1}{4}(3N+10), \ldots, N$. There are

$$\frac{1}{2}\{N-\frac{1}{4}(3N+2)\}+1=\frac{N+6}{8}$$

such even values of k.

From (a)—(d), above, it is, therefore, seen that when $\frac{1}{4}(N-2)$ is *even*, the spectrum of B_N contains

$$\frac{N-2}{8}+\frac{N+6}{8}=\frac{1}{2}(\frac{1}{2}N+1)$$ strictly positive eigenvalues

and

$$\frac{N-2}{8}+\frac{N-2}{8}=\frac{1}{2}(\frac{1}{2}N-1)$$ strictly negative eigenvalues

Hence, Rule 1, stated above, is proved.

By an entirely analogous argument, it is possible to prove

Rule 2. — If $\frac{1}{4}(N-2)$ is *odd* (i. e., $N=4p+2$, p *odd*) there are

$\frac{1}{2}(\frac{1}{2}N-1)$ strictly positive eigenvalues,

$\frac{1}{2}(\frac{1}{2}N+1)$ strictly negative eigenvalues

(and $\frac{1}{2}N$ zero eigenvalues) in the spectrum of B_N.

(For brevity, the reader is left to confirm Rule 2). Rules 1 and 2 (and the arguments leading to Rule 1) can be verified in the case of B_8, B_{10}, B_{14}, and B_{18} by consulting Table II, which shows explicitly which values of even k cause equation (11) to occasion positive, and which constrain it to predict negative,

eigenvalues, λ_k, for these graphs. Overall numbers of positive and negative eigenvalues in the spectra of $B_6 - B_{20}$ are given in the right-hand section of Table I.

TABLE II

Distribution of Strictly Positive and Negative Eigenvalues (as Calculated via equation (11)) in the Non-bipartite Balaban-Graphs, B_N ($\frac{1}{2}N$ *odd*)

		Value of k in λ_k								
		2	4	6	8	10	12	14	16	18
Value	6	—	—	+						
of	10	+	—	—	+	+				
N										
in	14	+	—	—	—	—	+	+		
B_N	18	+	+	—	—	—	—	+	+	+

6. FEASIBILITY OF THE *AUFBAU* PROCESS FOR B_N

We now consider the feasibility of applying the *Aufbau* procedure to the eigenvalue ('energy-level') families of the Balaban graphs B_N. Because these networks do not represent the carbon-atom connectivities of actual conjugated--systems, the idea of building up a 'ground-state π-electronic configuration' on the basis of the *Aufbau* Principle is a somewhat academic one; in fact, we do best to regard this whole exercise as a completely abstract process, along the lines described in ref. 1, in which N particles (which will, however, still be called 'electrons') are assigned to the N eigenvalues associated with the graph B_N, the *largest* eigenvalue (numerically equal to 4, in all cases — see § 3) being dealt with first.† In view of the varying multiplicities of zeros in the spectra of B_N (§ 4), and the provisions of the Coulson-Rushbrooke theorem[17] (see also refs. 7, 5 and 16), separate arguments will have to be advanced for the bipartite and non-bipartite Balaban-graphs, as follows:

(i) *The Bipartite Balaban-graphs,* B_N (with $\frac{1}{2}N$ even)

If $N = 4p$ (p any odd or even integer $\geqslant 2$), B_N is bipartite (§ 2); two cases in which this condition is fulfilled must be considered:

(a) $N \neq 8p$, and (b) $N = 8p$.

(a) If $N = 4p$, but $N \neq 8p$, there are precisely $\frac{1}{2}N$ zero eigenvalues in the spectrum of B_N (§ 4); there are thus also $\frac{1}{2}N$ non-zero eigenvalues. By virtue of the Coulson-Rushbrooke 'pairing' theorem[17], exactly one half of those $\frac{1}{2}N$ non-

† The *largest* eigenvalue is considered first in the *Aufbau* process because, on the simple HMO-model (see, for example, refs. 7—10, 5), an eigenvalue λ_k of the associated molecular-graph corresponds to a molecular orbital of energy $\varepsilon_k = \alpha + \lambda_k \beta$; since β is *negative* the *lowest* energy-level arises when λ_k is *largest*. Hence, the highest eigenvalue *is* quite properly the first to be 'filled' in an *Aufbau* scheme.

-zero eigenvalues (i. e., $\frac{1}{4}N$ of them) will be positive and $\frac{1}{4}N$ of them will be negative. The *Aufbau* process does then always yield a unique configuration since, if two 'electrons' are put into each of the $\frac{1}{4}N$ positive eigenvalues, and *one* electron is assigned to each of the $(\frac{1}{2}N)$ zero eigenvalues, this accounts for $(2 \times \frac{1}{4}N) + (1 \times \frac{1}{2}N) = N$ electrons — i. e., the N particles that were to be distributed amongst the available eigenvalues have been used to form a unique and unambiguous ground-state configuration.

(b) If $N = 8p$, there are $(\frac{1}{2}N + 2)$ zero eigenvalues (§ 4), and therefore $(\frac{1}{2}N - 2)$ non-zero ones. As before, though, because of the Coulson-Rushbrooke 'pairing' theorem,[17] there are exactly $\frac{1}{2} \times (\frac{1}{2}N - 2) = (\frac{1}{4}N - 1)$ eigenvalues that are greater than 0. Again ,therefore, placing *two* electrons in each of the positive eigenvalues and assigning *one* to each zero eigenvalue uses up $(2 \times (\frac{1}{4}N - 1)) + (1 \times (\frac{1}{2}N + 2)) = N$ electrons to form a unique, ground--state configuration.

Hence, defining an unambiguous, ground-state, π-electronic configuration by application of the *Aufbau* process *is* possible for both types of bipartite Balaban-graphs, B_N, $N = 4p$.

(ii) *The Non-Bipartite Balaban-Graphs* (with $\frac{1}{2}N$ odd)

If $N = 4p + 2$ (p any odd or even integer $\geqslant 1$), B_N is non-bipartite (§ 2): two cases must be considered (§ 5).

(a) p even, and (b) p odd.

(a) If $N = 4p + 2$, p an *even* integer, the arguments of §§ 4 and 5 determine that the eigenvalue spectrum of B_N is composed as follows:

$$\frac{1}{2}(\frac{1}{2}N - 1) \text{ negative eigenvalues}$$

$$\frac{1}{2}N \text{ zero eigenvalues}$$

$$\frac{1}{2}(\frac{1}{2}N + 1) \text{ positive eigenvalues.}$$

In attempting an *Aufbau* process (with N electrons to dispose of) on *this* family of eigenvalues, the first stage would be to assign two particles to each of the positive eigenvalues; this uses up $2 \times \frac{1}{2}(\frac{1}{2}N + 1) = (\frac{1}{2}N + 1)$ electrons. $(\frac{1}{2}N - 1)$ electrons thus remain to be distributed amongst the $\frac{1}{2}N$ zero

eigenvalues. There is therefore a short-fall of one electron that prevents our being able to half-fill the $\frac{1}{2}N$ zero eigenvalues exactly. Hence, a unique, ground-state electronic-configuration[1] cannot be defined.

(b) If $N = 4p + 2$, p an *odd* integer, the spectrum of B_N contains (see §§ 4 and 5):

$$\frac{1}{2}\left(\frac{1}{2}N + 1\right) \text{ negative eigenvalues}$$

$$\frac{1}{2}N \text{ zero eigenvalues}$$

$$\frac{1}{2}\left(\frac{1}{2}N - 1\right) \text{ positive eigenvalues}$$

Again, an attempted *Aufbau* scheme, with N electrons in hand, would start by assigning $2 \times \frac{1}{2}\left(\frac{1}{2}N - 1\right) = \left(\frac{1}{2}N - 1\right)$ of them to fill completely the $\frac{1}{2}\left(\frac{1}{2}N - 1\right)$ positive eigenvalues. This leaves $\left(\frac{1}{2}N + 1\right)$ particles to be distributed amongst the $\frac{1}{2}N$ zero eigenvalues. There are thus too many to *half*-fill these zero eigenvalues exactly, and yet too few to *fill* them entirely. Again, therefore, an unambiguous, ground-state π-electronic configuration cannot be defined.[1]

Application of the *Aufbau* process to establish a unique ground-state is thus *not* possible with either type of non-bipartite Balaban-graph, B_N ($\frac{1}{2}N$ odd).

7. CONCLUDING REMARKS

In ref. 1, only by direct numerical calculation of the energy levels was it possible to show that some networks which, on chemical grounds, could not conceivably represent actual molecules may, nevertheless, still be assigned a unique »ground-state π-electronic configuration« on the basis of the *Aufbau* Principle, while others — no more unlikely, on the face of it, to represent the carbon-atom connectivity of extant or viable conjugated-systems — may not. In the present paper, this has been done analytically, rather than by 'brute-force' evaluation of eigenvalues. Furthermore, by focussing attention on the Balaban graphs, B_N, we have encountered (albeit serendipitously!) a series of networks which, though arguably somewhat artificial, has the rather entertaining property that members of it giving rise to well-defined ground--state configurations on application of the *Aufbau* process *alternate* with others of the series that do not — a unique, π-electronic, ground-state configuration may be established for the bipartite Balaban-graphs B_N ($\frac{1}{2}N$ even), but not for the non-bipartite Balaban-graphs B_N (with $\frac{1}{2}N$ odd) (§ 6).

The intrinsic pleasure which the author (and, it is hoped, the reader!) has derived from the very aesthetic algebraic properties displayed by the eigenvalues of the Balaban graphs should not, however, be allowed to obscure the essential message of this paper (and that of ref. 1), which is earnestly stated as follows: in the ever-growing Literature on graph-theoretical aspects of simple molecular-orbital calculations, too little attention is paid to the possibility that, even after having calculated the eigenvalues and eigenvectors of the graph that is considered to represent the carbon-atom connectivity of a hypothetical, conjugated system (and these quantities have been properly associated with the HMO energy-levels and LCAO-MO weighting-coefficients, respectively, of that system), we *still* may find that an unambiguous, ground--state configuration is *not* attainable when the *Aufbau* Principle is invoked. In other words, the existence of a unique, well-defined, »π-electronic, ground--state configuration« for an *arbitrary* network should *not* be taken for granted.

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REFERENCES

1. R. B. Mallion and D. H. Rouvray, *Molec. Phys.* **36** (1978) 125.
2. R. B. Mallion and D. H. Rouvray, *Studia Scientiarum Mathematicarum Hungarica* **13** (1978) 229.
3. I. Gutman and N. Trinajstić, *Croat. Chem. Acta* **47** (1975) 507.
4. R. B. Mallion, *Proc. Royal Soc.* (London), **A341** (1975) 429.
5. D. H. Rouvray, »The Topological Matrix in Quantum Chemistry«, in: *Chemical Applications of Graph Theory,* A. T. Balaban (Ed.), Academic Press, London, 1976, Chapter 7 (pp. 175—221).
6. N. Trinajstić, *Croat. Chem. Acta* **49** (1977) 593.
7. C. A. Coulson, B. O'Leary, and R. B. Mallion, *Hückel Theory for Organic Chemists,* Academic Press, London, 1978, Chapter VI (pp. 88—110), Appendix C (pp. 156—158), and Appendix D (pp. 159—166).
8. R. B. Mallion, »Some Chemical Applications of the Eigenvalues and Eigenvectors of Certain Finite, Planar Graphs«, in: *Applications of Combinatorics,* R. J. Wilson (Ed.), Shiva Publishing Co., Nantwich, Cheshire (United Kingdom), 1982, Chapter 7 (pp. 87—114).
9. I. Gutman and N. Trinajstić, »Graph Theory and Molecular Orbitals«, *Fortsch. Chem. Forsch. (Topics Curr. Chem.)* **42** (1973) 49.
10. D. Cvetković, M. Doob, and H. Sachs, *Spectra of Graphs — Theory and Applications, Deutscher Verlag der Wissenschaften,* Berlin (East), 1979 and Academic Press, London, 1980.
11. G. G. Hall, *Molec. Phys.* **33** (1977) 551.
12. U. P. Wild, *Theoret. Chim. Acta* (Berlin (West)) **54** (1980) 245.
13. A. T. Balaban, *Croat. Chem. Acta* **51** (1978) 35.
14. R. B. Mallion, *Bull. Soc. Chim. France* (1974) 2799.
15. R. Frucht, *Annals N. Y. Acad. Sci.* **175** (1970) 159.
16. M. J. Rigby and R. B. Mallion, *J. Combinatorial Theory* (Series B) **27** (1979) 122.
17. C. A. Coulson and G. S. Rushbrooke, *Proc. Cambridge Philos. Soc.* **36** (1940) 193.
18. F. R. Gantmacher, *The Theory of Matrices,* Vols. I and II, Chelsea Publishing Co., New York, 1960.
19. M. J. Rigby, R. B. Mallion, and D. A. Waller, *Chem. Phys. Letters* **59** (1978) **316.**

SAŽETAK

Analitička ilustracija značaja molekularne topologije u Aufbau procesu

R. B. Mallion

Ideja Malliona i Rouvraya (1978) o značaju molekularne topologije za dobivanje jedinstvene π-elektronske konfiguracije osnovnog stanja za postojeće i hipotetske uveo Balaban (1978). Pokazano je da se korištenjem vlastitih vrijednosti cirkulantne konjugirane sustave, na osnovi Aufbau principa, proširene su na niz mreža koje je matrice može odrediti analitički izraz za spektar općeg člana ovog niza. Iz toga je dalje zaključeno da primjena Aufbau postupka na "Balabanove grafove" B_N dovodi do jedinstvene konfiguracije osnovnog π-elektronskog stanja ako i samo ako je N djeljivo s 4. Na taj način pokazuje se da Balabanovi grafovi obrazuju niz u kojem se naizmjenično pojavljuju mreže, koje na osnovi Aufbau principa imaju odnosno nemaju jedinstvenu elektronsku konfiguraciju u osnovnom stanju. Polazeći od ovog zapažanja pokazano je da se (bez obzira što se često pretpostavlja suprotno) ne može opravdati shvaćanje o postojanju jednoznačne konfiguracije osnovnog stanja u proizvoljnom π-elektronskom sustavu.