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The Connection Between the Adjacency Matrix and the Boundary Code of Benzenoid Hydrocarbons

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An algorithm for setting up adjacency matrices of benzenoid hydrocarbons from their boundary sequences is detailed. A recipe for computing the boundary code of a benzenoid structure from its adjacency matrix is also given. Finally, an automatic procedure is devised for computing approximate *TRE* values of benzenoids from their boundary sequences via the Gutman-Petrović formulae.

INTRODUCTION

In this work we wish to report a method for computing the adjacency matrix of benzenoid hydrocarbons from their boundary codes. The carbon skeletons of benzenoids will be depicted by graphs, called *benzenoid graphs*[1,2], which can be constructed in the plane by assembling h regular hexagons in such a way that two hexagons have exactly one joint edge or are disjoint, and the covered area in the plane is simply connected[3,4]. This restriction excludes benzenoid hydrocarbons with a »hole« in the interior, e. g. corannulenes. Since benzenoid graphs represent networks of hexagons[5,6], it is also customary to call them, for brevity, *polyhexes*[7]. Another name used for these structures is *arenes*[8]. In the present report we will use the term polyhex for a benzenoid hydrocarbon.

Here we shall also show how the boundary code of a polyhex can be obtained from its adjacency matrix. The definitions of the boundary and the interior of a polyhex (benzenoid structure) are given in references 4 and 5. Finally, we shall describe a simple way to calculate approximate[9] topological resonance energies[2,10,11] of benzenoid hydrocarbons by using the Gutman-Petrović formulae from eigenvalues of the adjacency matrix.

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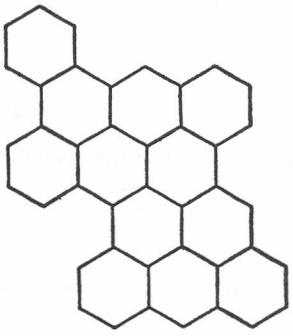
1. *Computing the Adjacency Matrix of a Polyhex from its Bondary Sequence*

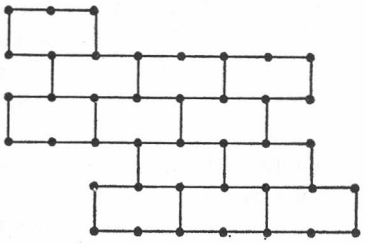
In our earlier work[12-14] we made the statement that the interior of a polyhex is constructable knowing the boundary because of the uniformity of the interior. This statement, which becomes immediately clear on inspection of the polyhex, means that the boundary sequence[12] of a polyhex includes complete information about the structure of the polyhex. On the other hand the adjacency matrix of a polyhex also contains complete information about its structure. Therefore it must be possible to compute the adjacency matrix from the boundary sequence. The adjacency matrix is needed for studying various properties of polyhexes, such as spectra.

Consider the following polyhex denoted by G.



G

To construct the adjacency matrix of G we depict this polyhex in the (x, y)--plane in a very uncommon way:



Since the length of an edge in the plane is defined to be unity, in the above representation of G the vertices, $V(G)$, can be described as a subset of the Cartesian product of the integers Z,

$$V(G) \subset Z \times Z$$

Our first goal is to find the vertex-set $V(G)$ in $Z \times Z$.

Let the polyhex be given in the boundary notation[12] as a sequence of edges,

$$e_1, e_2, \ldots, e_k$$

The mapping f from the set of edge types onto the cartesian product of integers,

$$f : \{1, 2, \ldots, 6\} \rightarrow Z \times Z$$

is defined by,

$$f : \begin{array}{l} 1 \rightarrow (0,1) \\ 2 \rightarrow (1,0) \\ 3 \rightarrow (1,0) \\ 4 \rightarrow (0,-1) \\ 5 \rightarrow (-1,0) \\ 6 \rightarrow (-1,0) \end{array}$$

The set of boundary vertices of the polyhex in $Z \times Z$ can be computed as,

$$V_B := \{v_i : v_i := \sum_{j=1}^{i} f(e_j),\ 1 \leqslant i \leqslant k\} \subset V(G) \subset Z \times Z$$

In this construction of the polyhex two vertices

$$v := (v_1, v_2) \in V(G)$$

$$w := (w_1, w_2) \in V(G)$$

are adjacent if

(i) $v, w \in V_B$ and there is an integer i that

$$w = \sum_{j=1}^{i-1} f(e_j) \quad \text{and} \quad v = \sum_{j=1}^{i} f(e_j) = w + f(e_i)$$

(ii) $v_2 = w_2$ and $|v_1 - w_1| = 1$ and valency v + valency $w > 4$; $v_1 = w_1$ and $|v_2 - w_2| = 1$ and $|v_1 - u_1|$ mod $2 = |v_2 - u_2|$ mod 2 and valency v + + valency $w > 4$

with $u_2 := \max\{u_2' : (u_1', u_2') \in V_B\}$,
$u_1 := \min\{u_1' : (u_1', u_2') \in V_B\}$.

Note the following properties of the vertices of polyhexes:[4,5]

(1) If a vertex has valency 2, it is a boundary vertex.
(2) Some vertices on the boundary have valency 3. They represent points at which the interior of polyhex is connected.
(3) All vertices of the interior have valency 3.
(4) There are only two types of valency 3 vertices possible in our construction,

but in both cases it is true that if,

$$v = (v_1, v_2) \in V(G) \quad \text{and valency } v = 3 \text{ then}$$

$$(v_1 + 1, v_2),\ (v_1 - 1, v_2) \in V(G),$$

This important fact gives us the possibility of constructing all vertices of $V(G)$.

Let $v = (v_1, v_2) \in V(G) \setminus V_B$ be an inner vertex of the polyhex, then there exists a finite sequence of adjacent valency 3 vertices of $V(G)$,

$$v_0 = v, v^{(1)} := (v_1 + 1, v_2), \ldots, v^{(n)} := (v_1 + n, v_2) \quad \text{with} \quad v^{(n)} \in V_B$$

That means each vertex of the interior can be reached from a valency 3 vertex of the boundary by a path of the special type as above.

At this point we can make use of the successor mapping s and the processor mapping p^{12},

$$s: \begin{array}{l} 1 \to 2 \\ 2 \to 3 \\ 3 \to 4 \\ 4 \to 5 \\ 5 \to 6 \\ 6 \to 1 \end{array} \qquad p: \begin{array}{l} 1 \to 6 \\ 2 \to 1 \\ 3 \to 2 \\ 4 \to 3 \\ 5 \to 4 \\ 6 \to 5 \end{array}$$

On the boundary of a polyhex an edge e_i points to a vertex of valency 3 if

$$e_{i+1} = p(e_i) \quad (1 \leqslant i \leqslant k-1), \quad e_1 = p(e_k)$$

and points to a vertex of valency 2 if

$$e_{i+1} = s(e_i) \quad (1 \leqslant i \leqslant k-1), \quad e_1 = s(e_k).$$

The set

$$V_B^3 := \{v_i \in V_B : v_i = \sum_{j=1}^{i} f(e_j) \text{ and } e_{i+1} = p(e_i), \ 1 \leqslant i \leqslant k\}$$

is the set of all valency 3 vertices on the boundary. Starting with a vertex $v = (v_1, v_2) \in V_B^3$ we compute all $v^{(n)} = (v_i + 1, v_2)$ until $v^{(n)} \in V_B$. Thus we generate all boundary vertices and all inner vertices.

As we know from (i) and (ii) which vertices are adjacent it is easy to construct the adjacency matrix. We find canonical labels by ordering the set of vertices in the following way,

$$v = (v_1, v_2), \quad w = (w_1, w_2) \in V(G)$$

$$v < w \text{ if } v_2 > w_2 \text{ or } v_2 = w_2 \text{ and } v_1 < w_1.$$

A FORTRAN program was written to generate the adjacency matrix using the boundary notation of the polyhex. This program may be obtained on request from the authors.

2. *Computing the Boundary Code of a Polyhex from its Adjacency Matrix*

Here we develop an algorithm to compute the boundary code of a polyhex from its adjacency matrix.

Let a polyhex be labeled in an arbitrary way and let A be the adjacency matrix set up according to this labeling. Let $v \in V(G)$ be a vertex and $V(G)$ the vertex-set of the polyhex G. By $h(v)$ we denote the number of different hexagons containing v. Of course,

$$1 \leqslant h(v) \leqslant 3 \text{ for all } v \in V(G)$$

The vertex set of the boundary of a polyhex can be characterized as

$$V_B = \{v \in V(G) : h(v) \neq 3\}.$$

Let t be the number of the terminal vertices equal to paths of lenght 6 starting at v, then,

$$h(v) = \tfrac{1}{2}\, t(v) \quad \text{for all} \quad v \in V(G).$$

So V_B can be determined as

$$V_B = \{v \in V(G) : \tfrac{1}{2}\, t(v) \neq 3\}.$$

We notice here that all vertices of valency $v = 2$ are elements of V_B, i. e. elements of the boundary.

Let v_0 be an element of V_B, $v_0 \in V_B$, with valency $v_0 = 2$. Because of the valency 2 both neighbours of v_0 are elements of the boundary. Let v_1 be one of them.

We consider two cases:

(1) Let the valency of v_1 be 2. From A we find the neighbour $v_{11} \neq v_0$. Because of the valency 2 of v_1, v_{11} must be a boundary vertex.

(2) Let the valency of v_1 be 3. From A we find the neighbours $v_{11} \neq v_0$ and $v_{12} \neq v_0$. If one of them has valency 2, it is the next vertex on the boundary. If both of them have valency 3, we compute all paths of length 5 starting at v_{11} and count the number of terminal vertices equal to v_1. The number of terminal vertices equal to v_1 is the number of different hexagons containing v_1 and v_{11}. Since $v_1 \in V_B$, v_{11} is a boundary vertex if this number is 1. If this number is not 1, v_{12} is a boundary vertex.

By this algorithm we determine the second neighbour of v_1. Now considering v_1 as v_0, we start the algorithm once again and compute with l (the length of the boundary) steps the boundary sequence $v_0, v_1, \ldots, l-1$ for the given polyhex. The code of the boundary sequence is obtained by,

$$\text{code}(v_0) = 1$$

$$\text{code}(v_{i+1}) = \begin{cases} s(\text{code}(v_i)) & \text{if valency } v_i = 2 \\ p(\text{code}(v_i)) & \text{if valency } v_i = 3 \end{cases} \quad 0 \leqslant i \leqslant l-1$$

where s is the successor mapping and p the processor mapping.

3. *A Remark on Computing the Approximate Topological Resonance Energy of Benzenoid Hydrocarbons*

Gutman and Petrović[9] have recently proposed two formulae for the approximate computation of topological resonance energies, *TRE*'s, of benzenoid hydrocarbons. The TRE theory is well described elsewhere[2,9-11,15], so we do not need to detail it here.

The Gutman-Petrović formulae depends on only two topological parameters: the number of hexagons h and the number of Kekulé structures K of a benzenoid hydrocarbon. These formulae are given below,

$$TRE\,(1) = 1.7101\, h^{1/6}\,(K^{1/6} - 1)\,(K-1)^{-1/6} + 0.040$$

and

$$TRE\,(2) = 0.2614\, h^{1/6}\,(\ln K)^{5/6} + 0.077$$

The essential quantity for both formulae is the number of Kekulé structures. There are numerous ways to evaluate K of polyhexes[15,16] One way is from the value of the a_m coefficient of the characteristic polynomial, $P(G; x)$, of G,

$$K = (|a_m|)^{1/2}$$

where m is the number of vertices in G. The value of a_m may be easily obtained since we can set up the adjacency matrix of a polyhex by the algorithm described in section 2 and then can compute the eigenvalues of this matrix $x_1, x_2, \ldots, x_m$ by a suitable programme (*F* ⌽ *AAF* of *NAG*). Thus we obtain,

$$a_m = \prod_{i=1}^{m} x_i$$

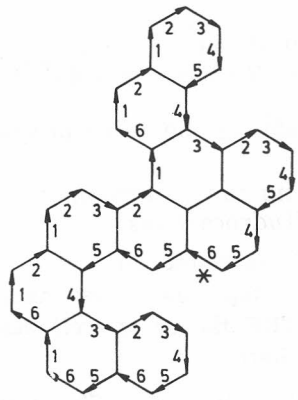
A FORTRAN program is written that produces approximate TRE values of benzenoids from their boundary codes. For most benzenoid hydrocarbons is much easier to set up the boundary sequence than the adjacency matrix. This is the reason why we start our procedure from the boundary sequence and not from the adjacency matrix. Therefore, our procedure consists of the following steps:

1. boundary sequence → 2. adjacency matrix → 3. set of eigenvalues → 4. number of Kekulé structures → 5. *TRE* values

A numerical example is given in the Table

TABLE

Example of Obtaining the Approximate TRE *Values from the Boundary Code for a Given Benzenoid Hydrocarbon* G



G

1. *Boundary Sequence*

(6565432345656161212321612123454323454 5)

Star denotes the bond at which the boundary sequence starts.

2. *Adjacency Matrix*

(copy of the computer output)

```
0100100000000000000000000000000000000000
1010000000000000000000000000000000000000
0100001000000000000000000000000000000000
0000100100000000000000000000000000000000
1001010000000000000000000000000000000000
0000101001000000000000000000000000000000
0010010000000000000000000000000000000000
0001000010000000000000000000000000000000
0000000101000000100000000000000000000000
0000010010100000000000000000000000000000
0000000001010000001000000000000000000000
0000000000101000000000000000000000000000
0000000000010000000010000000000000000000
0000000000001010000000100000000000000000
0000000000000010000000100000000000000000
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0000000000000000000000000000010100010000
0000000000000000000000010000001010000000
0000000000000000000000000000101000000100
0000000000000000000000000000010100000000
0000000000000000000000000010000001000001
0000000000000000000000000001000001000000
0000000000000000000000000000000010100000
0000000000000000000000000000010001010000
0000000000000000000000000000000000000101
0000000000000000000000000000000000100010
```

3. *Set of Eigenvalues*

—2.6660	—2.5096	—2.2942	—2.1995	—1.9706	—1.8464
—1.7207	—1.5023	—1.4673	—1.4355	—1.3075	—1.2195
—1.1633	—1.0532	—1.0000	—0.8442	—0.7110	—0.6446
—0.5827	—0.3700	0.3700	0.5827	0.6446	0.7110
0.8442	1.0000	1.0532	1.1633	1.2195	1.3075
1.4355	1.4673	1.5023	1.7207	1.8464	1.9076
2.1995	2.2942	2.5096	2.6660		

4. *Number of Kekulé Structures*

$K = 109$

5. TRE *Values*

TRE (1) = 1.404
TRE (2) = 1.468

CONCLUSIONS

In this work we have presented an algorithm that can be used for setting up the adjacency matrices of (large) benzenoid hydrocarbons from the boundary sequences[12], which numerically represent benzenoids and are easily available. The algorithm can be straightforwardly programmed in FORTRAN. However, if we have already obtained in some way the adjacency matrix of the benzenoid hydrocarbon, it is shown how the boundary code of a polyhex can be obtained from it. The boundary codes may be used in several ways[14]. For example, the boundary codes may be employed for counting isomeric benzenoid structures. A procedure based on this idea is already developed[12–14]. We have also shown how the Gutman-Petrović formulae for approximating the TRE of benzenoids may be automatically computed from their adjacency matrices, which in turn may be set up from the corresponding boundary sequences, which, as it was shown, fully determine the benzenoid structures.

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SAŽETAK

Odnos između matrice susjedstva i rubnog koda benzenoidnih ugljikovodika

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Prikazan je algoritam za nalaženje matrice susjedstva benzenoidnih ugljikovodika iz njihovih rubnih nizova. Opisan je, također, algoritam za računanje rubnog koda benzenoidne strukture iz njezine matrice susjedstva. Na kraju, izvedena je automatska procedura za računanje vrijednosti TRE benzenoida iz njihovih rubnih nizova s pomoću formule Gutmana i Petrovića.