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GRAPH MODELLING OF CHEMICAL STRUCTURES

Zoiţa BERINDE, Mădălina BERINDE

Abstract. In this paper we describe a mathematical model for representing chemical structures containing multiple bonds, heteroatoms and benzenoid hidrocarbons, using recently developed methods for calculating the weighted electronic distance, w.e.d. We also illustrate the power of w.e.d. in differentiating the chemical bonds according to the context in which they are found in the molecule. For the chemical structures showed here we calculate the ZEP and RZ topological indices using the weighted electronic connectivity matrix, CEP, introduced by the first author in [1].

MSC: 94C15
Key words: molecular graph, weighted electronic distance, topological index, weighted electronic connectivity matrix, correlation

1. Introduction

In 1874 Sylvester [2] introduced the term of graph associated to a molecular structure, based on constitution formulas used by chemists at that time.

The first representation of a graph with a matrix is owed to Sylvester (1878) and he is also the one who showed for the first time the connection between chemistry and algebra..

A single number that is used to characterize a molecule is called its topological index [3]. The first topological index was introduced in 1947 by H. Wiener.

After this date the molecular topology has developed progressively. Today, there are many topological indices described in the literature [4-7].

Recently, the first author [1], [9] proposed a graph theoretical matrix to represent edge-connectivity relationships which is called weighted electronic connectivity matrix, denoted by CEP, while two of the derived topological indices are denoted by ZEP and RZ, respectively [8]. The matrix of weighted electronic connectivity, CEP, can be regarded as a matrix of special adjacency that reproduces the connectivity between atoms much more accurately. The topological distance of the adjacency matrix between two atoms linked covalently was replaced by the weighted electronic distance (w.e.d). By means of matrix CEP one can represent simply, without using other considerations, all chemical structures, both those containing multiple bonds, benzenoid hydrocarbons as well as those containing heteroatoms.

2. The weighted electronic distance and the weighted electronic connectivity matrix

For a molecule having N atoms, whose graph is $G = (V(G), E(G))$, the weighted electronic connectivity matrix CEP (G) is a square $N \times N$ matrix given by

$$CEP(G) = \left\{ [CEP]_{i,j} \; ; \; i, j \in V(G) \right\}, \tag{1}$$

where its entries $[CEP]_{i,j}$ are defined as follows

$CEP_{ij} = \text{d.e.p.}(i,j)$, if $i \neq j$ and $(i,j) \gamma E(G)$ and $CEP_{ij} = 0$, otherwise (2)

and

- $\text{d.e.p.}(i,j)$ denotes the weighted electronic distance between the atoms (vertices) i and j;
- $V(G)$ is the set of all vertices (atoms) of the molecular graph G;
- $E(G)$ is the set of all edges (bonds) of the graph G.

The weighted electronic distance, w.e.d was recently defined in [19] by the formula

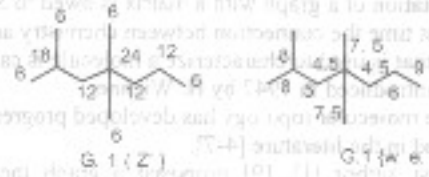
$$\text{w.e.d.}(i,j) = \frac{1}{b_{ij}} \cdot \frac{Z_i' + Z_j'}{v_i \cdot v_j}, \tag{3}$$

where

- b_{ij} is the bond weight (or bond order) with values: 1 for single bond, 2 for double bond, 3 for triple bond like in Barysz at al. [21];
- v_i denotes the degree of vertex i (that is, the number of bonds of the atom i to other atoms);
- Z_i' denotes the formal degree of vertex i, and it is given by

$$Z_i' = Z_i \cdot v_i \tag{4}$$

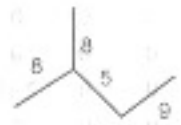
Z_i being the order number of the atom i (that is, the number of electrons in the atom i). In the graph G.1 representing 2,4,4-trimethylheptane we illustrated the notion of formal degree, Z', and weighted electronic distance, w.e.d. We have chosen this structure because it contains all four kinds of carbons: primary, secondary, tertiary and quaternary.



Similar formulas which use the atomic number and the multiplicity order of bonds have been considered in another context by Barysz and collaborators [16], where it is denoted only the presence of multiple bonds and heteroatoms, but their model is not able to reproduce the information related to the neighbourhood of bonds, as in the case of weighted electronic connectivity.

The formal degree Z' of the vertex i is in fact a local invariant on vertex (LOVI), which replaces the classical degree of the vertex, while the weighted electronic distance, w.e.d. (i,j) represents a local invariant on edge (LOEI).

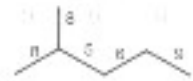
Further on we present, the weighted electronic distances and the corresponding CEP matrices for graphs G.2 - G.7.



G. 2

(2-Methylbutane)

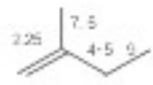
$$CEP(G.2) = \begin{bmatrix} 0 & 8 & 0 & 0 & 0 & 8 \\ 8 & 0 & 5 & 0 & 8 & 21 \\ 0 & 5 & 0 & 9 & 0 & 14 \\ 0 & 0 & 9 & 0 & 0 & 9 \\ 0 & 8 & 0 & 0 & 0 & 8 \end{bmatrix}$$



G.3

(2-Methylpentane)

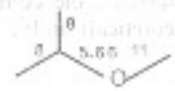
$$CEP(G.3) = \begin{bmatrix} 0 & 8 & 0 & 0 & 0 & 0 & 8 \\ 8 & 0 & 5 & 0 & 0 & 8 & 21 \\ 0 & 5 & 0 & 6 & 0 & 0 & 11 \\ 0 & 0 & 6 & 0 & 9 & 0 & 15 \\ 0 & 0 & 0 & 9 & 0 & 0 & 9 \\ 0 & 8 & 0 & 0 & 0 & 0 & 8 \end{bmatrix}$$



G.4

(2-Methyl-1-butene)

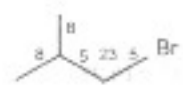
$$CEP(G.4) = \begin{bmatrix} 0 & 2.25 & 0 & 0 & 0 & 2.25 \\ 2.25 & 0 & 4.5 & 0 & 7.5 & 14.25 \\ 0 & 4.5 & 0 & 9 & 0 & 13.5 \\ 0 & 0 & 9 & 0 & 0 & 9 \\ 0 & 7.5 & 0 & 0 & 0 & 7.5 \end{bmatrix}$$



G.5

(2-Methy-isopropylether)

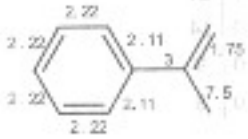
$$CEP(G.5) = \begin{bmatrix} 0 & 8 & 0 & 0 & 0 & 8 \\ 8 & 0 & 5.66 & 0 & 8 & 21.66 \\ 0 & 5.66 & 0 & 11 & 0 & 16.56 \\ 0 & 0 & 11 & 0 & 0 & 11 \\ 0 & 8 & 0 & 0 & 0 & 8 \end{bmatrix}$$



G.6

(3-Methyl-1-bromobutanene

$$CEP(G.6) = \begin{bmatrix} 0 & 8 & 0 & 0 & 0 & 8 \\ 8 & 0 & 5 & 0 & 8 & 21 \\ 0 & 5 & 0 & 23.5 & 0 & 28.5 \\ 0 & 0 & 23.5 & 0 & 0 & 23.5 \\ 0 & 8 & 0 & 0 & 0 & 8 \end{bmatrix}$$



G.7

$$CEP = \begin{bmatrix} 0 & 7.5 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 7.5 & 0 & 3 & 0 & 0 & 0 & 0 & 0 & 1.75 \\ 0 & 3 & 0 & 2.11 & 0 & 0 & 0 & 2.11 & 0 \\ 0 & 0 & 2.11 & 0 & 2.22 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 2.22 & 0 & 2.22 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 2.22 & 0 & 2.22 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 2.22 & 0 & 2.22 & 0 \\ 0 & 0 & 2.11 & 0 & 0 & 0 & 2.22 & 0 & 0 \\ 0 & 1.75 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \begin{matrix} SEP_i \\ 7.5 \\ 12.25 \\ 7.22 \\ 4.33 \\ 4.44 \\ 4.44 \\ 4.44 \\ 4.33 \\ 1.75 \end{matrix}$$

(Isopropenilbenzene)

The sum of all entries on the *i-th* row in CEP(G) is denoted by SEP, (and is written at the matrix right side):

$$SEP_i = \sum_{j=1}^{N} [CEP]_{i,k}, \quad i = 1, N \tag{5}$$

2. The ZEP and RZ topological indices

The electronic connectivity matrix can function as a basis for the construction of several new topological indices. The simplest index is given by the sum of SEP_i

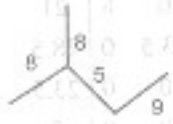
$$\boxed{ZEP = \sum_{i=1}^{N} (SEP)_i^{1/2}} \tag{6}$$

The index was applied in correlation studies to physical properties, the compactness of the molecular branching. Now, we define a new topological (graph-theoretical) index RZ, using the Randić-type [17] graph-theoretical invariant:

$$\boxed{RZ = \sum_{u \neq v} (S_u \cdot S_v)^{-\frac{1}{2}}} \tag{7}$$

where u, v are adjacent edges in the graph and $S_u = \text{d.c.p.}(i, j)$, if $u = (i, j)$

The calculation technique of ZEP and RZ indices is illustrated as follows for the hydrogen-suppressed graphs G.2 - G.7.



G. 2

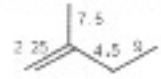
$$ZEP(G.2) = 2 \cdot 8^{\frac{1}{2}} + 2 1^{\frac{1}{2}} + 1 4^{\frac{1}{2}} + 9^{\frac{1}{2}} = 16.98$$

$$RZ = (8 \cdot 8)^{-\frac{1}{2}} + 2(8 \cdot 5)^{-\frac{1}{2}} + (5 \cdot 9)^{-\frac{1}{2}} = 0.295$$

G.3

$$ZEP(G.3) = 2\cdot 8^{\frac{1}{2}} + 2\cdot 1^{\frac{1}{2}} + 1\cdot 1^{\frac{1}{2}} + 1\cdot 5^{\frac{1}{2}} + 1\cdot 9^{\frac{1}{2}} = 20.429$$

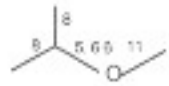
$$RZ = (8\cdot 8)^{\frac{1}{2}} + 2(8\cdot 5)^{\frac{1}{2}} + (5\cdot 6)^{\frac{1}{2}} = 33.494$$



G.4

$$ZEP(G.4) = 2.25^{\frac{1}{2}} + 7.5^{\frac{1}{2}} + 9^{\frac{1}{2}} + 13.5^{\frac{1}{2}} + 14.25^{\frac{1}{2}} = 14.687$$

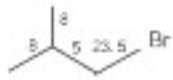
$$RZ = (2.25\cdot 7.5)^{\frac{1}{2}} + (2.25\cdot 4.5)^{\frac{1}{2}} + (7.5\cdot 4.5)^{\frac{1}{2}} + (4.5\cdot 9)^{\frac{1}{2}} = 52.938$$



G.5

$$ZEP(G.5) = 2\cdot 8^{\frac{1}{2}} + 1\cdot 1^{\frac{1}{2}} + 1\cdot 6.66^{\frac{1}{2}} + 1\cdot 21.66^{\frac{1}{2}} = 17.709$$

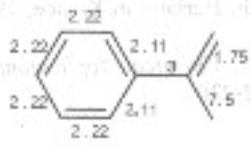
$$RZ = 2\cdot(8\cdot 5.66)^{\frac{1}{2}} + (8\cdot 8)^{\frac{1}{2}} + (5.66\cdot 11)^{\frac{1}{2}} = 29.348$$



G. 6

$$ZEP(G.6) = 23.5^{\frac{1}{2}} + 2\cdot 8^{\frac{1}{2}} + 28.5^{\frac{1}{2}} + 21^{\frac{1}{2}} = 20.425$$

$$RZ = 2\cdot(8\cdot 5)^{\frac{1}{2}} + (8\cdot 8)^{\frac{1}{2}} + (5\cdot 23.5)^{\frac{1}{2}} = 31.488$$



G.7

$$ZEP(G.6) = 1.75^{\frac{1}{2}} + 7.5^{\frac{1}{2}} + 12.25^{\frac{1}{2}} + 7.22^{\frac{1}{2}} + 2\cdot 4.33^{\frac{1}{2}} + 3\cdot 4.44^{\frac{1}{2}} = 41.157$$

$$RZ = (1.75\cdot 7.5)^{\frac{1}{2}} + (3\cdot 7.5)^{\frac{1}{2}} + (3\cdot 1.75)^{\frac{1}{2}} + 2(3\cdot 2.11)^{\frac{1}{2}} + (2.11\cdot 2.11)^{\frac{1}{2}}$$

$$+ 2(2.22\cdot 2.11)^{\frac{1}{2}} + 3(2.22\cdot 2.22)^{\frac{1}{2}} = 28.788$$

3. Concluding remarks

Beside the capacity of differentiating the multiple bonds and those containing heteroatoms, the weighted electronic distance, w.e.d., has the merit of distinguishing even the bonds of the same type between two identical atoms, depending on their connectivity. Thus, the simple bond between two secondary carbon atoms has a w.e.d. different from that of a simple covalent bond between a primary and a secondary atom, as shown in the graphs G.1 - G.7. No other system of representing the chemical bonds

has, as far as we know, this power of differentiating the chemical bonds according to the context they can be found within the molecule.

The presence of double bonds and of heteroatoms in graphs G.1, G.4, G.5 and G.6 is highlighted by the topological indices, ZEP and RZ, which have different values for each of the four graphs.

In order to test the model suggested by us, there have been carried out correlation studies for the class of alkanes [10], ethers [11], alkyl halides [12], amines [13] and other chemical compounds [14,15].

As a result of the studies carried out we can state that the replacement of the common topological distance by the weighted topological distance within the process of representing the chemical structure leads to a viable model, with real correlation qualities.

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Zoita Berinde
Department of Chemistry
North University of Baia Mare
Str. Victoriei 76
4800 Baia Mare ROMANIA
and
National College "Vasile Lucaciu" Baia Mare
Str. Culturii nr. 2
E-mail: zoita_berinde@yahoo.com

Madalina Berinde
Faculty of Mathematics and Computer Science
"Babes-Bolyai" University of Cluj-Napoca
Str. M. Kogalniceanu nr. 1
3400 Cluj-Napoca ROMANIA
E-mail: madalina_berinde@personal.ro