CREATIVE MATH. & INF. **17** (2008), No. 3, 308 - 312
Online version at http://creative-mathematics.ubm.ro/
Print Edition: ISSN 1584 - 286X Online Edition: ISSN 1843 - 441X

Dedicated to Professor Iulian Coroian on the occasion of his 70^{th} anniversary

QSPR modelling of molar volume of alkanes using the ZEP topological index

ZOIŢA BERINDE

ABSTRACT. În this paper it is presented a QSPR study between the molar volume (MV) and molecular structure for a set of 70 alkanes using the ZEP topological index. The ZEP topological index is calculated by using the weighted electronic connectivity matrix, CEP, associated to the chemical graphs of alkanes introduced by the author in a previous paper.

1. INTRODUCTION

A chemical compound can be represented by using the concept of chemical graph. A chemical or molecular graph can itself be represented by several topological matrices [3], [8], [10].

The most frequently matrices used are the adjacency matrix of the graph G, $A = A(G)$, and the distance matrix of the graph G, $D = D(G)$.

The mathematical modelling of the chemical structures using matrices associated to the molecular graphs has developed rapidly, as these matrices provide a source for obtaining some important molecular descriptors [13], [9]. Among these descriptors, the topological indices have been widely used in QSPR (Quantitative Structure- Property Relationship) and QSAR (Quantitative Structure-Activity Relationships) [10].

The alkanes represent a special attractive class of compounds as a starting point for the application of molecular mass and extent of branching, and because the alkanes are nonpolar, a number of complexities that arise with more polar compounds are avoided [12].

By replacing the usual topological distances from the adjacency matrix by the values of the weighted electronic distances (w.e.d.), a local invariant considered by the author in [4] , we obtain a new connectivity matrix, that is, the CEP matrix [4].

2. THE WEIGHTED ELECTRONIC CONNECTIVITY MATRIX AND THE TOPOLOGICAL INDEX ZEP

For a molecule having N atoms, whose graphs is G = (V(G)), E(G)), the weighted electronic connectivity matrix CEP(G) is a symmetric and quadratic

Received: 25.09.2008. In revised form: 26.03.2009. Accepted: 24.05.2009.
2000 *Mathematics Subject Classification.* 92E10.
Key words and phrases. *Molecular graph, topological index, weighted electronic connectivity matrix, molar volume, regression equation.*

$N \times N$ matrix given by:

$$CEP(G) = \{[CEP]_{ij}\,;\, i,j \in V(G)\} \tag{2.1}$$

where $V(G)$ is the set of vertices of the molecular graph G, and $E(G)$ is the set of edges, and

$$CEP_{ij} = w.e.d._{(i,j)}, \text{ if } i \neq j \text{ and } (i,j) \in E(G) \text{ and } CEP_{ij} = 0, \text{ otherwise,} \tag{2.2}$$

where $w.e.d._{(i,j)}$ denotes the weighted electronic distance between the atoms (vertices) i and j. The concept of weighted electronic distance, w.e.d., was defined in [4] by the following formula:

$$w.e.d.(i,j) = \frac{1}{b_r} \cdot \frac{Z_i^{'} + Z_j^{'}}{v_i \cdot v_j}, \tag{2.3}$$

where:
$-b_r$ is the bond weight with values: 1, for single bond, 2 for double bond, 3 for triple bond and 1.5 for aromatic bond, like in Barysz and al. [2];
$-v_i, v_j$ denote the degree of vertices i, and j, respectively;
$-Z_i'$ denotes the formal degree of vertex i, and it is defined by

$$Z_i' = Z_i \cdot v_i; \tag{2.4}$$

$-Z_i$ denotes the order number of atom i in Mendeleev's periodic system.

The formal degree Z_i' represents a local vertex invariant (LOVI) in the molecular graph, while w.e.d.$_{(i,j)}$ represents a local edge invariant (LOEI). Similar formulae which involve the order numbers as well as the multiplicity order of covalent bonds have been used but in a different context by Barysz and collaborators [2] and by Balaban [1]. Their approaches detect the presence of multiple bonds and heteroatoms but are not able to represent the information related to the neighbourhood of bonds, while our method is very sensitive in this respect, see Berinde [5], [6], and Kier [11].

The carbon atom can be itself primary, secondary , tertiary or quaternary having the formal degree Z_j' equal to 6, 12, 18 and 24, respectively. These aspects are illustrated in Figure 1, on the molecular graphs G.1{Z'} representing 2, 2, 3-trimethypentane while the notion of weighted electronic distance, (w.e.d.) is illustrated in the graph G.2 {w.e.d.}

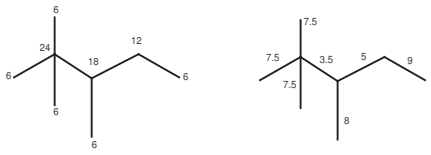
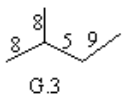


Figure 1. The graphs G.1{Z'}, G.2{w.e.d.}

The weighted electronic distances computed by (2.3) were used to build the weighted electronic connectivity matrix of alkanes.

In Figure 2 is given the corresponding CEP matrix for the hydrogen-deleted graph G.3 of 2-methyl-butane.



$$CEP(G.3) = \begin{array}{c} \\ \begin{bmatrix} 0 & 8 & 0 & 0 & 0 \\ 8 & 0 & 5 & 0 & 8 \\ 0 & 5 & 0 & 9 & 0 \\ 0 & 0 & 9 & 0 & 0 \\ 0 & 8 & 0 & 0 & 0 \end{bmatrix} \end{array} \begin{array}{c} \mathrm{SEP}_i \\ 8 \\ 21 \\ 14 \\ 9 \\ 8 \end{array}$$

Figure 2. The CEP matrix for 2-methyl-butane

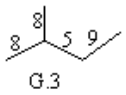
The sum of all entries on the i-th row in CEP (G.3) is denoted by SEP_i (and is written at the matrix right side):

$$SEP_i = \sum_{j=1}^{n} [CEP]_{ij}\,, \quad i = 1, 2, \ldots, n \tag{2.5}$$

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 root square of SEP_i :

$$ZEP = \sum_{i=1}^{n} (SEP_i)^{1/2} \tag{2.6}$$

The calculation technique of ZEP index is illustrated in Figure 3 for the hydrogen-deleted graph G.3 of 2-methyl-butane.



$$ZEP\,(G.3) = 2{\cdot}8^{\frac{1}{2}} + 21^{\frac{1}{2}} + 14^{\frac{1}{2}} + 9^{\frac{1}{2}} = 16.98$$

Figure 3. The calculation of the ZEP indice for 2-methyl-butane.

3. Results and discussions

Values of ZEP index were calculated for a set of 70 alkanes, including pentanes, hexanes, heptanes, octanes and nonanes and their values were correlated with molar volume (MV) and are presented in Table 1. Values for the molar volume were taken from [12]. Regression equation and statistical parameters for monovariable correlation of molar volume using the ZEP index are shown below:

$$MV = 4.298ZEP + 44.185; r = 0.983; s = 3.1; F = 1925 \tag{3.7}$$

were r represents the correlation coefficient, s the standard deviation.

Values of MV predicted by this equation are shown in Table 1.

The quality of this correlation with a single variable is quite remarkable. By considering a linear multivariable correlation for our index ZEP we can improve the correlation coefficient. This task is left for a future paper.

Table 1. Observed and calculated molar volume MV of alkanes correlated with ZEP index

Nr. crt	Alcan	N_C	ZEP	MV Obs	MV Cal.	Res.
1	5	7	17.210	115.205	118.1536	-2.94858
2	2M4	7	16.981	116.426	117.1693	-0.74334
3	22MM3	7	16.432	122.074	114.8097	7.264264
4	6	7	20.674	130.688	133.0419	-2.35385
5	2M5	7	20.429	131.933	131.9888	-0.05584
6	3M5	8	20.554	129.717	132.5261	-2.80909
7	23MM4	8	20.258	130.240	131.2539	-1.01388
8	22MM4	8	20.086	132.744	130.5146	2.229372
9	7	8	24.138	146.540	147.9301	-1.39012
10	2M6	8	23.893	147.656	146.8771	0.778886
11	3M6	8	24.002	145.821	147.3456	-1.5246
12	3E5	8	24.098	143.517	147.7582	-4.2412
13	24MM5	8	23.641	148.949	145.794	3.154982
14	22MM5	8	23.525	148.695	145.2955	3.39955
15	23MM5	8	23.822	144.153	146.572	-2.41896
16	33MM5	8	23.725	144.530	146.1551	-1.62505
17	223MMM4	8	23.388	145.191	144.7066	0.484376
18	8	8	27.602	162.592	162.8184	-0.2264
19	2M7	8	27.354	163.663	161.7525	1.910508
20	3M7	8	27.466	161.832	162.2339	-0.40187
21	4M7	8	27.450	162.105	162.1651	-0.0601
22	25MM6	8	27.112	164.697	160.7124	3.984624
23	3E6	8	27.546	160.072	162.5777	-2.50571
24	24MM6	9	27.214	163.093	161.1508	1.942228
25	22MM6	9	26.989	164.285	160.1837	4.101278
26	23MM6	9	27.270	160.395	161.3915	-0.99646
27	34MM6	9	27.386	158.814	161.89	-3.07603
28	33MM6	9	27.164	160.879	160.9359	-0.05687
29	2M3E5	9	27.354	158.794	161.7525	-2.95849
30	224MMM5	9	26.734	165.083	159.0877	5.995268
31	234MMM5	9	27.086	158.852	160.6006	-1.74863
32	3M3E5	9	27.344	157.026	161.7095	-4.68351
33	223MMM5	9	26.947	159.526	160.0032	-0.47721
34	233MMM5	9	27.020	157.292	160.317	-3.02496
35	234MMM5	9	27.086	158.852	160.6006	-1.74863
36	9	9	31.066	178.713	177.7067	1.006332
37	2M8	9	30.821	179.773	176.6537	3.119342
38	3M8	9	30.931	177.952	177.1264	0.825562
39	4M8	9	30.914	178.150	177.0534	1.096628
40	3E7	9	31.010	176.410	177.466	-1.05598
41	4E7	9	30.994	175.685	177.3972	-1.71221
42	22MM7	9	30.001	180.507	173.1293	7.377702
43	23MM7	9	30.734	176.653	176.2797	0.373268
44	24MM7	9	30.662	179.120	175.9703	3.149724
45	25MM7	9	30.685	179.371	176.0691	3.30187
46	26MM7	9	30.576	180.914	175.6006	5.313352
47	33MM7	9	30.628	176.897	175.8241	1.072856
48	34MM7	9	30.834	175.349	176.7095	-1.36053
49	35MM7	9	30.788	177.386	176.5118	0.874176
50	44MM7	9	30.603	176.897	175.7167	1.180306
51	23ME6	9	30.802	175.445	176.572	-1.127
52	24ME6	9	30.758	177.386	176.3829	1.003116
53	33ME6	9	30.783	173.077	176.4903	-3.41333
54	34ME6	9	30.918	172.844	177.0706	-4.22656
55	223MMM6	9	30.395	175.878	174.8227	1.05529
56	224MMM6	9	30.596	179.220	175.6866	3.533392
57	225MMM6	9	30.208	181.346	174.019	7.327016
58	233MMM6	9	30.459	173.780	175.0978	-1.31778
59	234MMM6	9	30.651	173.498	175.923	-2.425
60	235MMM6	9	30.482	177.656	175.1966	2.459364
61	244MMM6	9	30.372	177.187	174.7239	2.463144
62	334MMM6	9	30.579	172.055	175.6135	-3.55854
63	33EE5	9	30.940	170.185	177.1651	-6.98012
64	223MME5	9	30.472	174.537	175.1537	-0.61666
65	233MME5	9	30.632	170.093	175.8413	-5.74834
66	234MEM5	9	30.605	173.804	175.7253	-1.92129
67	2233(M)5	9	30.160	169.495	173.8127	-4.31768
68	2234(M)5	9	30.209	173.557	174.0233	-0.46628
69	2244(M)5	9	29.824	178.256	172.3686	5.887448
70	2334(M)5	9	30.313	169.928	174.4703	-4.54227

4. CONCLUSIONS

By replacing the usual topological distance between two atoms linked covalently with the weighted electronic distance, we obtain a new matrix representation of the molecular structure that reproduces much more accurately the connectivities between atoms.

Besides the capacity of differentiating the multiple bonds [7] and those containing heteroatoms [5], [6], w.e.d. has the merit of distinguishing even the bonds of the same type between two identical atoms, depending on their connectivities. 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 in which they are in the molecule.

REFERENCES

[1] Balaban, A.T., *Application of graph theory in chemistry*, J. Chem. Inf. Comput. Sci., **25** (1985), 334-343
[2] Barysz, M., Jashari, G., Lall, L.S., Srivastava, V.K. and Trinajsti, N., *On the Distance Matrix of Molecules Containing Heteroatoms*, in "Chemical applications of Graph Theory and Topology", King, R. B. (ed.), Elsevier, Amsterdam, 1983, 222-230
[3] Berge, C., *Teoria grafurilor şi aplicaţiile ei*, Editura Tehnică, Bucureşti, 1969
[4] Berinde, Z., *Applications of molecular topology in the study of physico-chemical properties of organic compounds* (in Romanian), Cub Press 22, Baia Mare, 2001
[5] Berinde, Z., *Consideraţii privind modelarea matricială a compuşilor halogenaţi*, Revista de Chimie (Bucureşti), **52** (2001), No. 12, 788-792
[6] Berinde, Z., *Vertex and edge weighted molecular graphs for amines*, Revue Roumaine de Chimie, **51** (2006), No. 11, 1131-1135
[7] Berinde, Z., *On a local invariant for modelling molecular double bonds graphs,* Chem. Bull."Politehnica" Univ. (Timişoara), **49** (63) (2004), No. 1-2, 8-10
[8] Diudea, M. and Ivanciuc, O., *Topologie moleculară*, Editura Comprex, Cluj-Napoca, 1995
[9] Estrada, E., *Generalization of topological indices*, Chem. Phys. Lett., **336** (2001), 248-252
[10] Kier, L.B., Hall, L.H., *Molecular Connectivity in Structure-Activity Analysis*, J. Willey & Sons, New York, 1986
[11] Kier, L.B., Hall, L.H., *Molecular Connectivity VII: Specific treatment to heteroatoms*, J. Pharm. Sci., **65** (1976), 1806-1809
[12] Needham, D.E., Wei, I.C. and Seybold, P.G., *Molecular modelling of the physical properties of the alkanes*, J. Am. Chem. Soc., **110** (1988), 4186-4194
[13] Randić, M., *Generalized molecular descriptors*, J. Math. Chem., **7** (1991), 155-168

NORTH UNIVERSITY OF BAIA MARE
DEPARTMENT OF CHEMISTRY
VICTORIEI 76
430122 BAIA MARE, ROMANIA
E-mail address: zoitaberinde@ubm.ro
E-mail address: zoita_berinde@yahoo.com