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DESIGN OF TOPOLOGICAL INDICES. PART 11.[1]

DISTANCE-VALENCY MATRICES AND DERIVED MOLECULAR GRAPH DESCRIPTORS

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The distance-valency matrices are defined by using molecular graph distances and atomic valencies. The new matrices are very flexible in representing the chemical structure in a numerical form suitable for use in structure-property, structure-activity and molecular similarity studies. The previously defined distance and reciprocal distance graph matrices are particular cases of the distance-valency matrices. Examples are offered of distance-valency matrices whose elements are integers or real numbers. Nonsymmetric matrices can be generated by using certain combinations of parameters; such matrices are used to define new atomic and molecular descriptors for the chemical structure.

INTRODUCTION

The computation of molecular properties from the molecular structure represents an important problem in theoretical chemistry.[2,3] The molecular structure is considered at various levels of complexity: the molecular graph level, the geometrical level, and the quantum level.[4] The first level of molecular structure description uses the connectivity of atoms, and does not consider the information regarding the three-dimensional structure of the molecule. The structure of the molecular graph determines a large number of molecular properties ranging from physico-chemical and thermodynamic properties to chemical reactivity and biological activity. Among the large class of molecular graph invariants used to describe the chemical structure, we mention here graph theoretic polynomials and spectra, spectral moments, topological indices, distances, walks and paths in graphs.[2,3] The most used molecular graph descriptors in establishing Quantitative Structure-Property Relationships (QSPRs), Quantitative Structure-Activity Relationships (QSARs), and structural similarity models are topological indices (TIs).[2–16]

In this paper we define a new class of matrices, the distance-valency matrices, derived from the distance-valency descriptors **VTI**.[13] After a brief presentation of the molecular graph definitions and structural descriptors used in this study, the distance-valency matrices are defined together with some examples. We present examples of distance-valency matrices whose elements are integers or real numbers, and we demonstrate that the previously defined distance and reciprocal distance graph matrices are particular cases of the distance-valency matrices. Nonsymmetric matrices can be generated by using certain combinations of parameters; such matrices are used to define new atomic and molecular descriptors for the chemical structure. The new matrices are very flexible in representing in a numerical form the chemical structure, and can be used in structure-property, structure-activity and molecular similarity studies.

STRUCTURAL DESCRIPTORS DERIVED FROM THE MOLECULAR GRAPH

A graph $G = G(V,E)$ is an ordered pair consisting of two sets $V = V(G)$ and $E = E(G)$. Elements of the set $V(G)$ are called vertices and elements of the set $E(G)$, involving the binary relation between the vertices, are called edges. The number of vertices N represents the number of elements in $V(G)$, $N = |V(G)|$, and the number of edges M represents the number of elements in $E(G)$, $M = |E(G)|$. The graph vertices are labeled from 1 to N, $E(G) = (v_1, v_2, ..., v_N)$, and the edge connecting vertices v_i and v_j is denoted by e_{ij}. Two vertices v_i and v_j of a graph G are said to be adjacent if there is an edge e_{ij} joining them. The degree of the vertex v_i from the molecular graph G, denoted by $\mathbf{deg}_i = \mathbf{deg}(G)_i$, is equal to the number of vertices adjacent to vertex v_i.

In this paper chemical structures are represented as molecular graphs. By removing all hydrogen atoms from the chemical formula of a compound containing covalent bonds one obtains the hydrogen-depleted (or hydrogen-suppressed) molecular graph of that compound, whose vertices correspond to non-hydrogen atoms and whose edges correspond to covalent bonds. In this study expressions "molecular graph" and "molecule", "vertex" and "atom", "edge" and "bond" are used interchangeably.

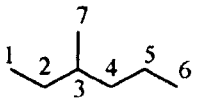
The adjacency matrix $\mathbf{A} = \mathbf{A}(G)$ of a graph G with N vertices is the square $N \times N$ symmetric matrix whose entry in the ith row and jth column is defined as:[10]

$$[\mathbf{A}]_{ij} = \begin{cases} 1 & \text{if } v_i \neq v_j \text{ and } e_{ij} \in E(G) \\ 0 & \text{if } v_i \neq v_j \text{ or } e_{ij} \notin E(G) \end{cases}$$

where $E(G)$ represents the set of edges of G. For alkanes and cycloalkanes the sum of entries over row i or column i in $\mathbf{A}(G)$ represents the degree of vertex v_i, $\mathbf{deg}_i$:

$$\mathbf{deg}_i = \sum_{j=1}^{N} [\mathbf{A}]_{ij} = \sum_{j=1}^{N} [\mathbf{A}]_{ji}$$

The set of degree values for all vertices in a graph gives the vector $\mathbf{Deg} = \mathbf{Deg}(G)$ whose ith element represents the degree of the vertex v_i. The molecular graph of 3-methylhexane **1** and its adjacency matrix, **A(1)**, are presented as an example.



1

A(1)

	1	2	3	4	5	6	7
1	0	1	0	0	0	0	0
2	1	0	1	0	0	0	0
3	0	1	0	1	0	0	1
4	0	0	1	0	1	0	0
5	0	0	0	1	0	1	0
6	0	0	0	0	1	0	0
7	0	0	1	0	0	0	0

The valency of the vertex v_i, $\mathbf{val}(w)_i = \mathbf{val}(w,G)_i$, is defined as the sum of the weights $Ew(w)_{ij}$ of all edges e_{ij} incident with vertex v_i:

$$\mathbf{val}(w)_i = \sum_{e_{ij} \in E(G)} Ew(w)_{ij}$$

where w is the weighting scheme used to compute the Ew parameters. Alternatively, the valency of the vertex v_i may be computed as the sum of the non-diagonal elements in the row i, or column i, of the adjacency

matrix $\mathbf{A}(w) = \mathbf{A}(w,G)$, of a molecular graph G with N vertices:

$$\mathbf{val}(w)_i = \sum_{\substack{j=1 \\ j \neq i}}^{N} [\mathbf{A}(w)]_{ij} = \sum_{\substack{j=1 \\ j \neq i}}^{N} [\mathbf{A}(w)]_{ji}$$

The set of valency values for all vertices in a graph forms the vector $\mathbf{Val} = \mathbf{Val}(G)$ whose ith element represents the valency of the vertex v_i. In alkanes and cycloalkanes the degree of a vertex v_i, $\mathbf{deg}_i$, is identical with the valency of that vertex, $\mathbf{val}_i$, while for molecules containing heteroatoms and/or multiple bonds, represented as vertex- and/or edge-weighted molecular graphs, this equality is not true. As an example, the valency vector of 3-methylhexane **1** is given here: $\mathbf{Val}(\mathbf{1}) = \mathbf{Deg}(\mathbf{1}) = \{1, 2, 3, 2, 2, 1, 1\}$. As explained before, in this case the valency vector is identical with the degree vector.

A walk w in a graph G is a sequence of vertices and edges $w = \{v_a, e_{ab}, v_b, e_{bc}, v_c, \ldots, v_i, e_{ij}, v_j, \ldots, v_m, e_{mn}, v_n\}$ beginning and ending with vertices, in which vertices v_k and v_{k+1} are adjacent, $k = 1, 2, 3, \ldots, n - 1$, and each edge e_{ij} is incident with the two vertices v_i and v_j preceding and following it, respectively. A path is a walk in which all vertices (and thus necessarily all edges) are distinct. The length of a path in a graph is equal to the number of edges along the path. For a given pair of vertices v_i, $v_j \in V(G)$, let d_{ij} denote the topological distance, equal to the length of the shortest path connecting the vertices. The topological distance has the following properties: $d_{ij} \geq 0$ for all v_i, $v_j \in V(G)$, (equality holds if and only if $v_i = v_j$); $d_{ij} = d_{ji}$ for all v_i, $v_j \in V(G)$; $d_{ik} + d_{kj} \geq d_{ij}$ for all v_i, v_j, $v_k \in V(G)$. The reciprocal distance, rd_{ij}, for a pair of vertices v_i, $v_j \in V(G)$ of a graph G, is defined as the reciprocal of the distance d_{ij}, $1/d_{ij}$.[13–15]

THE DISTANCE-VALENCY MATRICES

The distance-valency matrix of a graph G with N vertices, $\mathbf{Dval}(p, q, r) = \mathbf{Dval}(p, q, r; G)$, is a square $N \times N$ matrix, whose entries $[\mathbf{Dval}(p, q, r)]_{ij}$ are equal to:

$$[\mathbf{Dval}(p,q,r)]_{ij} = \begin{cases} d_{ij}^{p}\mathbf{val}_i^{q}\mathbf{val}_j^{r} & \text{if } i \neq j \\ 0 & \text{if } i = j \end{cases}$$

If the parameters p, q, r are natural numbers then the **Dval** matrix has elements natural numbers. In the particular case when $p = 1$ and $q = r = 0$ the $\mathbf{Dval}(p, q, r)$ matrix is identical with the distance matrix **D**. The distance matrix, $\mathbf{D} = \mathbf{D}(G)$, of a connected graph G is a real symmetric matrix whose elements $[\mathbf{D}]_{ij}$ are defined as:

$$[\mathbf{D}]_{ij} = \begin{cases} d_{ij} & \text{if } i \neq j \\ 0 & \text{if } i = j \end{cases}$$

The distance and the $\mathbf{Dval}(1,0,0)$ matrix of 3-methylhexane, $\mathbf{D}(\mathbf{1}) = \mathbf{Dval}(1,0,0,1)$, is:

D(1) = Dval(1,0,0,1)

	1	2	3	4	5	6	7
1	0	1	2	3	4	5	3
2	1	0	1	2	3	4	2
3	2	1	0	1	2	3	1
4	3	2	1	0	1	2	2
5	4	3	2	1	0	1	3
6	5	4	3	2	1	0	4
7	3	2	1	2	3	4	0

If the parameters p, q, r are not natural numbers then one can obtain **Dval** matrices with elements real numbers. If $p = -1$ and $q = r = 0$ then $\mathbf{Dval}(p, q, r)$ is identical with the reciprocal distance matrix **RD**. The reciprocal distance matrix of a graph G with N vertices, $\mathbf{RD} = \mathbf{RD}(G)$, is a square $N \times N$ symmetric matrix, whose entries $[\mathbf{RD}]_{ij}$ are equal to the reciprocal of the distance between vertices v_i

and v_j, $1/d_{ij}$, for non-diagonal elements, and is equal to zero for the diagonal elements:[14]

$$[\mathbf{RD}]_{ij} = \begin{cases} 1/d_{ij} & \text{if } i \neq j \\ 0 & \text{if } i = j \end{cases}$$

The reciprocal distance and the **Dval**(−1,0,0) matrix of 3-methylhexane, **RD(1)** = = **Dval**(−1,0,0,1), is:

RD(1) = Dval(−1,0,0,1)

	1	2	3	4	5	6	7
1	0.000	1.000	0.500	0.333	0.250	0.200	0.333
2	1.000	0.000	1.000	0.500	0.333	0.250	0.500
3	0.500	1.000	0.000	1.000	0.500	0.333	1.000
4	0.333	0.500	1.000	0.000	1.000	0.500	0.500
5	0.250	0.333	0.500	1.000	0.000	1.000	0.333
6	0.200	0.250	0.333	0.500	1.000	0.000	0.250
7	0.333	0.500	1.000	0.500	0.333	0.250	0.000

A nonsymmetric matrix, the detour-distance matrix, was recently defined.[16] It is obvious that a nonsymmetric matrix contains a larger quantity of information regarding the structure of the molecular graph. Because they are relatively recently introduced in the chemical literature only a few molecular graph descriptors (graph invariants) were proposed for the nonsymmetric matrices. In the following sections we will introduce new nonsymmetric matrices and we will propose some graph invariants computed from them.

From the definition of the **Dval** matrix it is clear that nonsymmetric matrices can be generated if $q \neq r$. As an example, we present the distance-valency matrix **Dval**(1,0,1,**1**) of 3-methylhexane **1**:

Dval(1,0,1,1)

	1	2	3	4	5	6	7
1	0	2	6	6	8	5	3
2	1	0	3	4	6	4	2
3	2	2	0	2	4	3	1
4	3	4	3	0	2	2	2
5	4	6	6	2	0	1	3
6	5	8	9	4	2	0	4
7	3	4	3	4	6	4	0

By inspecting the **Dval**(1,0,1,1) matrix it is easy to see that $[\mathbf{Dval}(1,0,1,1)]_{ij} \neq [\mathbf{Dval}(1,0,1,1)]_{ji}$. For two **Dval** matrices **Dval**(p, q, r) and **Dval**(p', q', r') where $p = p'$, $q = r'$ and $r = q'$ the following equality holds: $[\mathbf{Dval}(p, q, r)]_{ij} = [\mathbf{Dval}(p', q', r')]_{ji}$. Consider the **Dval**(1,1,0,**1**) matrix:

Dval(1,1,0,1)

	1	2	3	4	5	6	7
1	0	1	2	3	4	5	3
2	2	0	2	4	6	8	4
3	6	3	0	3	6	9	3
4	6	4	2	0	2	4	4
5	8	6	4	2	0	2	6
6	5	4	3	2	1	0	4
7	3	2	1	2	3	4	0

An inspection of the **Dval**(1,0,1,1) and **Dval**(1,1,0,1) matrices shows that $[\mathbf{Dval}(1,0,1,1)]_{ij} = [\mathbf{Dval}(1,1,0,1)]_{ji}$. Using certain combinations of p, q, r parameters it is possible to generate nonsymmetric **Dval** matrices with elements real numbers. As an example, we present the distance-valency matrix **Dval**(−1,1,0,1) of 3-methylhexane **1**:

Dval(−1,1,0,1)

	1	2	3	4	5	6	7
1	0.000	1.000	0.500	0.333	0.250	0.200	0.333
2	2.000	0.000	2.000	1.000	0.667	0.500	1.000
3	1.500	3.000	0.000	3.000	1.500	1.000	3.000
4	0.667	1.000	2.000	0.000	2.000	1.000	1.000
5	0.500	0.667	1.000	2.000	0.000	2.000	0.667
6	0.200	0.250	0.333	0.500	1.000	0.000	0.250
7	0.333	0.500	1.000	0.500	0.333	0.250	0.000

From the same class of nonsymmetric matrices we present the distance-valency matrix **Dval**(−1,0,−1,1) of 3-methylhexane **1**:

Dval(−1,0,−1,1)

	1	2	3	4	5	6	7
1	0.000	0.500	0.167	0.167	0.125	0.200	0.333
2	1.000	0.000	0.333	0.250	0.167	0.250	0.500
3	0.500	0.500	0.000	0.500	0.250	0.333	1.000
4	0.333	0.250	0.333	0.000	0.500	0.500	0.500
5	0.250	0.167	0.167	0.500	0.000	1.000	0.333
6	0.200	0.125	0.111	0.250	0.500	0.000	0.250
7	0.333	0.250	0.333	0.250	0.167	0.250	0.000

DESCRIPTORS DERIVED FROM THE DISTANCE-VALENCY MATRICES

In this section we present some structural descriptors derived from the **Dval** matrices. The Wiener operator, **Wi**(**M**) = **Wi**(**M**,G), is defined by analogy with the Wiener index:[11,12]

$$\mathbf{Wi}(\mathbf{M},G) = \sum_{i=1}^{N}\sum_{j=i}^{N}[\mathbf{M}]_{ij}$$

where **M** represents the molecular matrix of G. If **M** is the distance matrix, the operator is identical with the Wiener index, while if **M** is the reciprocal distance matrix, this operator gives the Harary index.[14,15] In the case of 3-methylhexane, **Wi**(**D**,1) = **Wi**(**Dval**(1,0,0),1) = 50 and **Wi**(**RD**,1) = = **Wi**(**Dval**(−1,0,0),1) = 11.617.

The Wiener operator can be used only for symmetric **Dval** matrices, and in this way one can generate useful QSPR and QSAR descriptors. For the nonsymmetric **Dval** matrices we define an operator related to **Wi**, the matrix sum operator **MS**. Consider the graph G with N vertices and its nonsymmetric matrix **M** = **M**(G). The matrix sum operator **MS**(**M**) = **MS**(**M**,G) is defined as the sum of the elements of the nonsymmetric matrix **M**:

$$\mathbf{MS}(\mathbf{M},G) = \sum_{i=1}^{N}\sum_{j=1}^{N}[\mathbf{M}]_{ij}$$

For the matrix **Dval**(1,0,1,1) we obtain **MS**(**Dval**(1,0,1),1) = 158. The **MS** operator can be used also for symmetric matrices; in this case, for hydrocarbons **MS**(**M**) = 2**Wi**(**M**). For vertex-weighted molecular graphs this equality is not true.

Many topological indices and graph descriptors are defined with the aid of vertex invariants. An operator that computes vertex invariants from molecular matrices is the vertex sum **VS**. Consider

the vertex v_i from the graph G with N vertices and the symmetric graph matrix $\mathbf{M} = \mathbf{M}(G)$. The vertex sum of the vertex v_i, $\mathbf{VS(M)}_i = \mathbf{VS(M},G)_i$, is defined as the sum of the elements in the column i, or row i, of the molecular matrix $\mathbf{M}$:[1,10]

$$\mathbf{VM(M},G)_i = \sum_{j=1}^{N} [\mathbf{M}]_{ij} = \sum_{j=1}^{N} [\mathbf{M}]_{ji}$$

The vertex sum operator was used to define the Ivanciuc-Balaban topological index **IB**.[1] If **M** is the adjacency matrix the operator **VS** gives the degree vector **Deg**, if **M** is the distance matrix **D** the operator offers the distance sum **DS**, while if **M** is the reciprocal distance matrix **RD**, the operator is identical the reciprocal distance sum **RDS**.[14] Some examples of vertex sum vectors for the molecular graph of 3-methylhexane are: **VS(A,1)** = {1, 2, 3, 2, 2, 1, 1}, **VS(D,1)** = **VS(Dval**(1,0,0),1) = {18, 13, 10, 11, 14, 19, 15} and **VS(RD,1)** = **VS(Dval**(−1,0,0),1) = {2.617, 3.583, 4.333, 3.833, 3.417, 2.533, 2.917}. From its definition it is clear that the VS operator can be applied to symmetric **Dval** matrices.

For the nonsymmetric **Dval** matrices we introduce a related operator, the Vertex Double Sum **VDS**. Consider the vertex v_i from the graph G with N vertices and the nonsymmetric graph matrix $\mathbf{M} = \mathbf{M}(G)$. The vertex double sum of the vertex v_i, $\mathbf{VDS(M)}_i = \mathbf{VDS(M},G)_i$, is defined with the equation:

$$\mathbf{VDS(M},G)_i = \sum_{j=1}^{N} [\mathbf{M}]_{ij} + \sum_{j=1}^{N} [\mathbf{M}]_{ji} - [\mathbf{M}]_{ii}$$

where the diagonal element $[\mathbf{M}]_{ii}$ is subtracted because it is added in both summations. This is not required for simple graphs, when all diagonal elements are zero, but for vertex-weighted graphs that may have certain non-zero diagonal elements. The **VDS** vectors of 3-methylhexane 1 for some **Dval** matrices previously presented are:

VDS(Dval(1,1,0),1) = **VDS(Dval**(1,0,1),1) = {48, 46, 44, 38, 50, 51, 39}

VDS(Dval(−1,1,0),1) = {7.817, 13.583, 19.833, 15.000, 12.583, 7.483, 9.167}

VDS(Dval(−1,0,−1),1) = {4.108, 4.292, 4.528, 4.333, 4.125, 3.969, 4.500}

Consider the distance-valency matrix **Dval**(−1,−1,1,1) of 3-methylhexane 1:

Dval(−1,−1,1,1)

	1	2	3	4	5	6	7
1	0.000	2.000	1.500	0.667	0.500	0.200	0.333
2	0.500	0.000	1.500	0.500	0.333	0 125	0.250
3	0.167	0.667	0.000	0.667	0.333	0.111	0.333
4	0.167	0.500	1.500	0.000	1.000	0.250	0.250
75	0.125	0.333	0.750	1.000	0.000	0.500	0.167
6	0.200	0.500	1.000	1.000	2.000	0.000	0.250
7	0.333	1.000	3.000	1.000	0.667	0.250	0.000

and the distance-valency matrix **Dval**(−1,1,−1,1):

Dval(−1,1,−1,1)

	1	2	3	4	5	6	7
1	0.000	0.500	0.167	0.167	0.125	0.200	0.333
2	2.000	0.000	0.667	0.500	0.333	0.500	1.000
3	1.500	1.500	0.000	1.500	0.750	1.000	3.000
4	0.667	0.500	0.667	0.000	1.000	1.000	1.000
5	0.500	0.333	0.333	1.000	0.000	2.000	0.667
6	0.200	0.125	0.111	0.250	0.500	0.000	0.250
7	0.333	0.250	0.333	0.250	0.167	0.250	0.000

For the above two matrices the **VDS** vectors are identical:

VDS(Dval(–1,–1,1),1) = **VDS(Dval(–1,1,–1),1)** = {6.692, 8.208, 11.528, 8.500, 7.708, 6.386, 7.833}

From the above examples of **VDS** vectors it is clear that different **Dval** matrices can generate identical **VDS** vectors. This situation appears for two matrices **Dval**(p, q, r) and **Dval**(p', q', r') with $p = p'$, $q = r'$ and $r = q'$ when the following equality holds: **VDS(Dval**(p, q, r)) = **VDS(Dval**(p', q', r')).

A matrix with elements real numbers is the χ matrix defined by Randić. The χ matrix can be considered as a weighted adjacency matrix whose elements are 0 and $(\mathbf{deg}_i\mathbf{deg}_j)^{-1/2}$:[17]

$$[\chi]_{ij} = \begin{cases} (\mathbf{deg}_i\mathbf{deg}_j)^{-1/2} & \text{if } e_{ij} \in E(G) \\ 0 & \text{otherwise} \end{cases}$$

The matrix χ**(1)** is presented below:

χ(1)

	1	2	3	4	5	6	7
1	0	0.707	0	0	0	0	0
2	0.707	0	0.408	0	0	0	0
3	0	0.408	0	0.408	0	0	0.577
4	0	0	0.408	0	0.500	0	0
5	0	0	0	0.500	0	0.707	0
6	0	0	0	0	0.707	0	0
7	0	0	0.577	0	0	0	0

Although it is not possible to define a **Dval** matrix in such a way as to obtain the χ matrix, we introduce a somewhat related matrix, the **Xi** matrix:

$$[\mathbf{Xi}]_{ij} = \begin{cases} (\mathbf{val}_i\mathbf{val}_j)^{-1/2} & \text{if } i \neq j \\ 0 & \text{if } i = j \end{cases}$$

The **Xi** matrix is identical with the **Dval**(0, –0.5, –0.5) matrix. For 3-methylhexane **1**, matrix **Xi(1)** = **Dval**(0, –0.5, –0.5,**1**) is:

Xi(1) = Dval(0,–0.5,–0.5,1)

	1	2	3	4	5	6	7
1	0.000	0.707	0.577	0.707	0.707	1.000	1.000
2	0.707	0.000	0.408	0.500	0.500	0.707	0.707
3	0.577	0.408	0.000	0.408	0.408	0.577	0.577
4	0.707	0.500	0.408	0.000	0.500	0.707	0.707
5	0.707	0.500	0.408	0.500	0.000	0.707	0.707
6	1.000	0.707	0.577	0.707	0.707	0.000	1.000
7	1.000	0.707	0.577	0.707	0.707	1.000	0.000

For 3-methylhexane we give here the **VS** and **VDS** vectors for the χ and **Dval**(0, –0.5,–0.5) matrices:

VS(χ,**1**) = {0.707, 1.115, 1.394, 0.908, 1.207, 0.707, 0.577}

VDS(Dval(0,–0.5,–0.5),**1**) = {4.699, 3.530, 2.957, 3.530, 3.530, 4.699, 4.699}

CHARACTERISTIC POLYNOMIALS AND SPECTRAL MOMENTS OF DISTANCE-VALENCY MATRICES

The characteristic polynomial **Ch(M)** = **Ch(M**,G,x) of the molecular matrix **M** = **M**(G) is defined with the following equation:[2,3,10]

$$\mathbf{Ch}(\mathbf{M},G,x) = \mathbf{det}(x\mathbf{I} - \mathbf{M}) = \sum_{n=0}^{N} c_n x^{N-n}$$

where **I** is the unit matrix of order N and c_n is the nth coefficient of the characteristic polynomial **Ch(M)**. An eigenvalue x_i of the molecular matrix **M** = **M**(G) is a zero of its characteristic polynomial, **Ch(M**,G,x_i) = 0, for i = 1 to N. The complete set of graph eigenvalues x_1, x_2, ..., x_N forms the spectrum of the molecular matrix **M**, **Sp(M**,G) = $\{x_i, i = 1, 2, ..., N\}$.

Although used for symmetric molecular matrices, the characteristic polynomial is also an invariant for nonsymmetric matrices, and therefore it can be used for all types of **Dval** matrices. Some examples of characteristic polynomials of the **Dval** matrices are presented here:

$$\mathbf{Ch(Dval}(1,0,1),\mathbf{1}) = \mathbf{Ch(Dval}(1,1,0),\mathbf{1}) = x^7 - 312x^5 - 2936x^4 - 10656x^3 - 18272x^2 - 14848x - 4608$$

$$\mathbf{Ch(Dval}(-1,1,0),\mathbf{1}) = x^7 - 29.436x^5 - 73.003x^4 - 20.169x^3 + 67.616x^2 + 42.183x + 2.100$$

$$\mathbf{Ch(Dval}(-1,0,-1),\mathbf{1}) = x^7 - 2.931x^5 - 2.453x^4 - 0.101x^3 + 0.465x^2 + 0.125x + 0.004$$

$$\mathbf{Ch(Dval}(-1,-1,1),\mathbf{1}) = \mathbf{Ch(Dval}(-1,1,-1),\mathbf{1}) = x^7 - 8.283x^5 - 11.665x^4 - 1.446x^3 + 4.946x^2 + 2.114x + 0.088$$

$$\mathbf{Ch(Dval}(0,-0.5,-0.5),\mathbf{1}) = x^7 - 9.750x^5 - 21.250x^4 - 20.250x^3 - 10.000x^2 - 2.500x - 0.250$$

The Hosoya operator **Ho(M)** = **Ho(M**,G) is defined as the sum of the absolute values of the coefficients of the characteristic polynomial of the matrix **M**:

$$\mathbf{Ho(M)} = \sum_{n=0}^{N} |c_n|$$

For alkanes and if **M** is the adjacency matrix **A** the **Ho** operator is identical with the Hosoya index Z.[18-21] Also, if **M** is the distance matrix **D** the Hosoya operator gives the Z' index.[4] From the definition of the Hosoya operator it is obvious that it can be applied both to symmetric and nonsymmetric matrices. Some values of the Hosoya operator for the **Dval** matrices introduced in the previous sections are: **Ho(Dval(**1,0,1),**1)** = **Ho(Dval(**1,1,0),**1)** = 51633, **Ho(Dval(**−1,1,0),**1)** = 235.507, **Ho(Dval(**−1,0,−1),**1)** = = 7.079, **Ho(Dval(**−1,−1,1),**1)** = **Ho(Dval(**−1,1,−1),**1)** = 29.542, **Ho(Dval(**0,−0.5,−0.5),**1)** = 65.000.

Another molecular graph invariant that can be computed both for symmetric and nonsymmetric matrices is the spectral moment. The spectral moment of order k of the molecular matrix **M** = **M**(G), **SM(M)**$_k$, is defined as:[2,3]

$$\mathbf{SM(M)}_k = \sum_{i=1}^{N} x_i^k = \mathbf{Tr}\ \mathbf{M}^k$$

where the trace of the kth power of the molecular matrix **M** is equal to:

$$\mathbf{Tr}\ \mathbf{M}^k = \sum_{i=1}^{N} [\mathbf{M}^k]_{ii}$$

The spectral moments of some **Dval** matrices are presented below:

SM(Dval(1,0,1),1) = **SM(Dval**(1,1,0),1) = {0, 624, 8808, 237312, 4671520, 106640064, 2259554304}

SM(Dval(−1,1,0),1) = {0.000, 58.872, 219.008, 1813.612, 10406.409, 70307.684, 439141.864}

SM(Dval(−1,0,−1),1) = {0.000, 5.862, 7.358, 17.586, 33.623, 69.436, 139.678}

SM(Dval(−1,−1,1),1) = **SM(Dval**(−1,1,−1),1) = {0.000, 16.566, 34.996, 143.004, 458.390, 1604.021, 5433.119}

SM(Dval(0,−0.5,−0.5),1) = {0.000, 19.500, 63.750, 271.125, 1085.937, 4408.031, 17836.984}

CONCLUSIONS

In this paper we have introduced a new class of molecular graph matrices derived from the distance-valency descriptors **VTI**,[13] the distance-valency **Dval** matrices, defined on the basis of graph matrices and atomic valencies. We have presented examples of distance-valency matrices whose elements are integers or real numbers, and demonstrated that the previously defined distance and reciprocal distance graph matrices are particular cases of the distance-valency matrices. The new matrices are very flexible in representing the chemical structure in a numerical form suitable for use in structure-property, structure-activity and molecular similarity studies. Nonsymmetric matrices can be generated by using certain combinations of parameters; such matrices are used to define new atomic and molecular descriptors for the chemical structure.

We have defined new molecular graph operators, the matrix sum **MS** and the vertex double sum **VDS**, that are invariants for nonsymmetric matrices. New structural descriptors can be obtained with the aid of the Hosoya operator **Ho** applied to the **Dval** matrices. The characteristic polynomial, spectral moments, and the Hosoya operator can be used both for symmetric and nonsymmetric matrices.

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