The Detour Matrix in Chemistry†

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Received November 1, 1996⊗

The detour matrix of a (chemical) graph is defined. The detour matrix is also defined for weighted graphs. A novel method of computing the detour matrix is introduced. Some properties of the detour matrix and the distance matrix are compared. The invariants of the detour matrix (detour polynomial, detour spectrum, and detour index) are discussed, and several methods for computing these quantities are presented. The use of the detour index is analyzed and compared to the application of the Wiener number in the structure−boiling point modeling.

"*...central to an experiment is theory, modelling.*"
Milan Randić[1]

1. INTRODUCTION

The detour matrix, together with the distance matrix, was introduced into the mathematical literature in 1969 by Frank Harary.[2] Both matrices were also briefly discussed in 1990 by Buckley and Harary in their book on the concept of distance in graph theory.[3] The detour matrix was introduced into the chemical literature in 1994 under the name the maximum path matrix of a molecular graph by Ivanciuc and Balaban[4] and independently by us in 1995.[5] One of us (N.T.) learned about this matrix attending a talk by Harary in the Department of Marine Sciences at the Texas A&M University in Galveston, TX, on April 4, 1994. Harary delivered a talk on his work on distance concept in graphs and during the lecture mentioned the detour matrix. After this talk we started our work on the detour matrix and its invariants.

The detour matrix can be used to compute the so-called detour index[6] in the same way as the distance matrix[7,8] can be employed to generate the Wiener index.[9,10] The detour index, which is a Wiener-like index, was also introduced by Ivanciuc and Balaban[4] as the half-sum of the maximum path sums and independently by John[11] and us.[5] Lukovits, who introduced the term the detour index, is also very active in studying the properties of this index and its uses in structure−property studies. He reported some of his results on the detour matrix and detour index in this journal and elsewhere.[6,12,13] Lukovits was also first to use this index in structure−property modeling.[6] He also delivered a very stimulating talk on his work on the detour index and its uses at the Rugjer Bošković Institute in Zagreb on February 29, 1996. Several of his results will be commented on later, and more importantly, we will also try to answer some of his questions. We found very stimulating his remark[12] "*The usefulness of the detour index is deflated by the fact that to date no method (but inspection) is available to compute this index*." Or in another words, there is no method available to compute the detour matrix. Harary[2] already pointed out that there exists no efficient procedure for finding the entries of this matrix. The same was also stated by Buckley and Harary,[3] but they also mentioned that the problem of finding the detour matrix is NP-complete. We will present here our method for constructing the detour matrix for graphs of moderate sizes. Our search for this method was initiated by the above statement of Lukovits.

This report is structured in the following way. In the next section, we give definitions of the distance matrix, detour matrix, and detour/distance matrix for simple and edge-weighted graphs. The third section contains our method for computing the detour matrix of moderately sized graphs. In the fourth section, the detour polynomial and its spectrum are discussed. The fifth section contains the definition of the detour index and an example of its use in structure−property studies. We end the report with our concluding remarks.

2. DEFINITIONS OF THE DISTANCE MATRIX, DETOUR MATRIX, AND DETOUR/DISTANCE MATRIX

The detour matrix $\Delta = \Delta(G)$ of a labeled connected graph G is a real symmetric $N \times N$ matrix whose (i,j) entry is the length of the *longest* path[14a] from vertex i to vertex j:

$$(\Delta)_{ij} = \begin{cases} \delta_{ij} & \text{if } i \neq j \\ 0 & \text{if } i = j \end{cases} \tag{1}$$

where δ_{ij} is the number of steps in a longest path (i.e., the *maximum* number of edges) in G between vertices i and j.

This definition is exactly the "opposite" of the definition of the traditional graph−theoretical distance matrix, whose off-diagonal entries are the lengths of the *shortest* paths

† Dedicated to Professor Milan Randić (Des Moines, IA), the winner of the 1996 Hermann Skolnik Award given by the ACS Division of Chemical Information.

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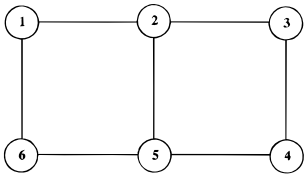
⊗ Abstract published in *Advance ACS Abstracts,* May 15, 1997.

S0095-2338(96)00149-7 CCC: $14.00



G

$$\mathbf{D} = \begin{bmatrix} 0 & 1 & 2 & 3 & 2 & 1 \\ 1 & 0 & 1 & 2 & 1 & 2 \\ 2 & 1 & 0 & 1 & 2 & 3 \\ 3 & 2 & 1 & 0 & 1 & 2 \\ 2 & 1 & 2 & 1 & 0 & 1 \\ 1 & 2 & 3 & 2 & 1 & 0 \end{bmatrix} \quad \Delta = \begin{bmatrix} 0 & 5 & 4 & 5 & 4 & 5 \\ 5 & 0 & 5 & 4 & 3 & 4 \\ 4 & 5 & 0 & 5 & 4 & 5 \\ 5 & 4 & 5 & 0 & 5 & 4 \\ 4 & 3 & 4 & 5 & 0 & 5 \\ 5 & 4 & 5 & 4 & 5 & 0 \end{bmatrix}$$

$$\Delta / \mathbf{D} = \begin{bmatrix} 0 & 5 & 4 & 5 & 4 & 5 \\ 1 & 0 & 5 & 4 & 3 & 4 \\ 2 & 1 & 0 & 5 & 4 & 5 \\ 3 & 2 & 1 & 0 & 5 & 4 \\ 2 & 1 & 2 & 1 & 0 & 5 \\ 1 & 2 & 3 & 2 & 1 & 0 \end{bmatrix}$$

Figure 1. Distance (**D**), detour (Δ), and detour/distance (Δ/**D**) matrices of a labeled bicyclic graph *G*.

between the vertices in *G*:[7,14b]

$$(\mathbf{D})_{ij} = \begin{cases} d_{ij} & \text{if } i \neq j \\ 0 & \text{if } i = j \end{cases} \tag{2}$$

where d_{ij} is the number of steps in a shortest path (i.e., the *minimum* number of edges) in *G* between vertices *i* and *j*.

The upper triangle of the detour matrix and the lower triangle of the distance matrix may be combined in a matrix called the detour/distance matrix. The detour/distance matrix Δ/**D** of a graph *G* is a square $N \times N$ nonsymmetrical matrix whose entries are defined as:

$$(\Delta/\mathbf{D})_{ij} = \begin{cases} \delta_{ij} & \text{if } i > j \\ 0 & \text{if } i = j \\ d_{ij} & \text{if } i < j \end{cases} \tag{3}$$

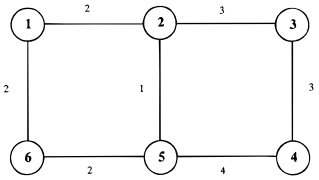
The concept of the distance/distance matrix has been introduced by Randić and co-workers in a different context.[15] They have combined the geometric and topological distance matrices in their attempt to derived an index of molecular folding. The detour/distance matrix is called the maximum/minimum path matrix by Ivanciuc and Balaban.[4]

It is obvious from their definitions that all three matrices presented above are identical for trees. As examples, the distance, detour, and detour/distance matrices of a simple labeled graph *G* are shown in Figure 1.

For edge-weighted graphs G_w, the detour matrix is defined as[16]

$$(\Delta_w)_{ij} = \begin{cases} W_{ij} & \text{if } i \neq j \\ 0 & \text{if } i = j \end{cases} \tag{4}$$

where is W_{ij} the *maximum* sum of edge weights along the path between the vertices *i* and *j*, which is not necessarily the longest possible path between these two vertices in G_w as it would be in terms of just unweighted edges. Hence, the entry $(\Delta_w)_{ij}$ for the weighted detour matrix is the maximum path weight between the vertices *i* and *j* in G_w.



G_w

$$\mathbf{D_w} = \begin{bmatrix} 0 & 2 & 5 & 7 & 3 & 2 \\ 2 & 0 & 3 & 5 & 1 & 3 \\ 5 & 3 & 0 & 3 & 4 & 6 \\ 7 & 5 & 3 & 0 & 4 & 6 \\ 3 & 1 & 4 & 4 & 0 & 2 \\ 2 & 3 & 6 & 6 & 2 & 0 \end{bmatrix} \quad \Delta_w = \begin{bmatrix} 0 & 14 & 11 & 8 & 12 & 14 \\ 14 & 0 & 13 & 10 & 10 & 12 \\ 11 & 13 & 0 & 13 & 9 & 12 \\ 8 & 10 & 13 & 0 & 12 & 10 \\ 12 & 10 & 9 & 12 & 0 & 14 \\ 14 & 12 & 12 & 10 & 14 & 0 \end{bmatrix}$$

$$\Delta_w / \mathbf{D_w} = \begin{bmatrix} 0 & 14 & 11 & 8 & 12 & 14 \\ 2 & 0 & 13 & 10 & 10 & 12 \\ 5 & 3 & 0 & 13 & 9 & 12 \\ 7 & 5 & 3 & 0 & 12 & 10 \\ 3 & 1 & 4 & 4 & 0 & 14 \\ 2 & 3 & 6 & 6 & 2 & 0 \end{bmatrix}$$

Figure 2. Distance ($\mathbf{D}_w$), detour (Δ_w), and detour/distance (Δ_w/$\mathbf{D}_w$) matrices of a labeled edge-weighted bicyclic graph G_w.

The distance matrix $\mathbf{D}_w$ of a labeled edge-weighted graph G_w is a real symmetric $N \times N$ matrix whose elements $(\mathbf{D}_w)_{ij}$ are defined as follows:[14b]

$$(\mathbf{D}_w)_{ij} = \begin{cases} w_{ij} & \text{if } i \neq j \\ 0 & \text{if } i = j \end{cases} \tag{5}$$

where w_{ij} is the *minimum* sum of edge weights along the path between the vertices *i* and *j*, which is not necessarily the shortest possible path between these two vertices in G_w as it would be in terms of just unweighted edges. This is so because the shortest possible path between the two vertices *i* and *j* in G_w may have a greater value of w_{ij} than a longer path.

The detour/distance matrix $\Delta_w/\mathbf{D}_w$ of an edge-weighted graph G_w is a square $N \times N$ nonsymmetrical matrix whose entries are defined as

$$(\Delta_w/\mathbf{D}_w)_{ij} = \begin{cases} W_{ij} & \text{if } i > j \\ 0 & \text{if } i = j \\ w_{ij} & \text{if } i < j \end{cases} \tag{6}$$

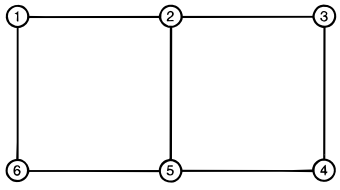
The distance, detour, and detour/distance matrices for an edge-weighted graph G_w are given in Figure 2.

The variants of the distance and detour matrices are their reciprocal matrices. The reciprocal distance matrix $\mathbf{D}^r = \mathbf{D}^r(G)$ is generated by replacing all elements of the distance matrix by their reciprocals:[17,18]

$$(\mathbf{D}^r)_{ij} = 1/(\mathbf{D})_{ij}; \quad i \neq j \tag{7}$$

Similarly, the reciprocal detour matrix $\Delta^r = \Delta^r(G)$ is also generated by replacing all elements of the detour matrix by their reciprocals:

$$(\Delta^r)_{ij} = 1/(\Delta)_{ij}; \quad i \neq j \tag{8}$$



G

$$\mathbf{D}^r = \begin{bmatrix} 0 & 1 & 0.5 & 0.33 & 0.5 & 1 \\ 1 & 0 & 1 & 0.5 & 1 & 0.5 \\ 0.5 & 1 & 0 & 1 & 0.5 & 0.33 \\ 0.33 & 0.5 & 1 & 0 & 1 & 0.5 \\ 0.5 & 1 & 0.5 & 1 & 0 & 1 \\ 1 & 0.5 & 0.33 & 0.5 & 1 & 0 \end{bmatrix}$$

$$\Delta^r = \begin{bmatrix} 0 & 0.2 & 0.25 & 0.2 & 0.25 & 0.2 \\ 0.2 & 0 & 0.2 & 0.25 & 0.33 & 0.25 \\ 0.25 & 0.2 & 0 & 0.2 & 0.25 & 0.2 \\ 0.2 & 0.25 & 0.2 & 0 & 0.2 & 0.25 \\ 0.25 & 0.33 & 0.25 & 0.2 & 0 & 0.2 \\ 0.2 & 0.25 & 0.2 & 0.25 & 0.2 & 0 \end{bmatrix}$$

$$\Delta^r/\mathbf{D}^r = \begin{bmatrix} 0 & 0.2 & 0.25 & 0.2 & 0.25 & 0.2 \\ 1 & 0 & 0.2 & 0.25 & 0.33 & 0.25 \\ 0.5 & 1 & 0 & 0.2 & 0.25 & 0.2 \\ 0.33 & 0.5 & 1 & 0 & 0.2 & 0.25 \\ 0.5 & 1 & 0.5 & 1 & 0 & 0.2 \\ 1 & 0.5 & 0.33 & 0.5 & 1 & 0 \end{bmatrix}$$

Figure 3. Reciprocal distance ($\mathbf{D}^r$) and reciprocal detour (Δ^r) matrices, corresponding to the related distance (**D**) and detour (Δ) matrices, and the reciprocal detour/distance matrix of a labeled bicyclic graph *G* in Figure 1.

The combination of the upper triangle of the reciprocal detour matrix and the lower triangle of the reciprocal distance matrix gives the reciprocal detour/distance matrix ($\Delta^r/\mathbf{D}^r$).

Examples of the reciprocal distance, reciprocal detour, and reciprocal detour/distance matrices are given in Figure 3.

3. COMPUTATION OF THE DETOUR MATRIX

Our procedure for computing the detour matrix of a polycyclic graph *G*, is based on considering the distance matrices of the complete set of spanning trees obtained from *G* by deletion of the appropriate edges. The procedure consist of the following steps:

(1) Labeling of a graph *G* under the consideration.

(2) Generation of labeled spanning trees from *G* and the construction of their distance matrices.

(3) Setting up the detour matrix of *G* by matching the distance matrices of spanning trees and picking up for each element of the detour matrix only that distance matrix element which possesses the highest numerical value.

This procedure is illustrated in in Figure 4 for a simple graph *G*.

A computer program based on this procedure is prepared. For example, the required CPU times to construct the detour matrices for polyhexes G_1 and G_2, shown Figure 5, were 25.7 sand 123.5 s, respectively, on the workstation HP-735.

4. THE DETOUR POLYNOMIAL AND THE DETOUR SPECTRUM

The characteristic polynomial $\pi(G;x)$ of the detour matrix of a graph *G*, called the detour polynomial, is defined as

$$\pi(G;x) = \det|x\mathbf{I} - \Delta| \tag{9}$$

where **I** is the $N \times N$ unit matrix. The coefficient form of the detour polynomial is obtained by the expansion of the above determinant:

$$\pi(G;x) = x^N - c_1x^{N-1} - ... - c_{N-1}x - c_N = x^N - \sum_n c_n x^{N-n} \tag{10}$$

The coefficients of the detour polynomial can be computed using the modified[19] Le Verrier−Faddeev−Frame (LVFF) method.[20−22] The modification consists of using the diagonal forms of the matrices in the method. This is a very convenient computational method for obtaining the characteristic polynomial of any matrix,[7,23] though it has been mostly used to compute the characteristic polynomial of the adjacency matrix.[24−27]

The modified LVFF method works in the following way. The formula for computing the coefficients c_n of the detour polynomials is conveniety expressed as

$$c_n = (1/n)\sum_i (\Delta_n)_{ii} \tag{11}$$

where the diagonal matrix $(\Delta_n)_{ii}$ is given by

$$(\Delta_n)_{ii} = (\Delta)_{ii}(\mathbf{B}_{n-1})_{ii} \tag{12}$$

In eq 12, matrix $(\mathbf{B}_{n-1})_{ii}$ is an auxiliary matrix in the diagonal form. The detour matrix Δ can be diagonalized using the Householder-QL method.[28,29]

The auxiliary matrix in the diagonal form is defined as a difference matrix:

$$(\mathbf{B}_n)_{ii} = (\Delta_n)_{ii} - (c_n\mathbf{I})_{ii} \tag{13}$$

The LVFF method is an iterative procedure which ends when auxiliary matrix vanishes, that is, when $n = N$:

$$(\mathbf{B}_N)_{ii} = (\Delta_N)_{ii} - (c_N\mathbf{I})_{ii} = 0 \tag{14}$$

We give in Table 1, as an illustrative example, the computation of the detour polynomial for the six-cycle.

The detour polynomial of a complete graph K_N with *N* vertices can be given a closed form:

$$\pi(K_N;x) = (x + d)^{N-1}(x - d^2) \tag{15a}$$

where *d* is the degree of a vertex in K_N. Equation 15 follows straightforwardly from the Viete formula[30] (the inventor of this formula Francois Viète (1540−1603) was the greatest French mathematician of the 16th century):[31]

$$\pi(K_N;x) = \prod_i (x - \lambda_i) \tag{15b}$$

where λ_i ($i = 1, ..., N$) are roots of the detour polynomial. Note that, for the complete graphs K_N, $\lambda_1 = (N - 1)^2 = d^2$ and $\lambda_{2,...,N} = -d$. Thus, for example, the detour polynomial of the Kuratowski graph K_5 (see Figure 6) can be easily obtained by applying (15a):

$$\pi(K_5;x) = (x + 4)^4(x - 4^2) = x^5 - 160x^3 - 1280x^2 - 3840x - 4096 \tag{16}$$

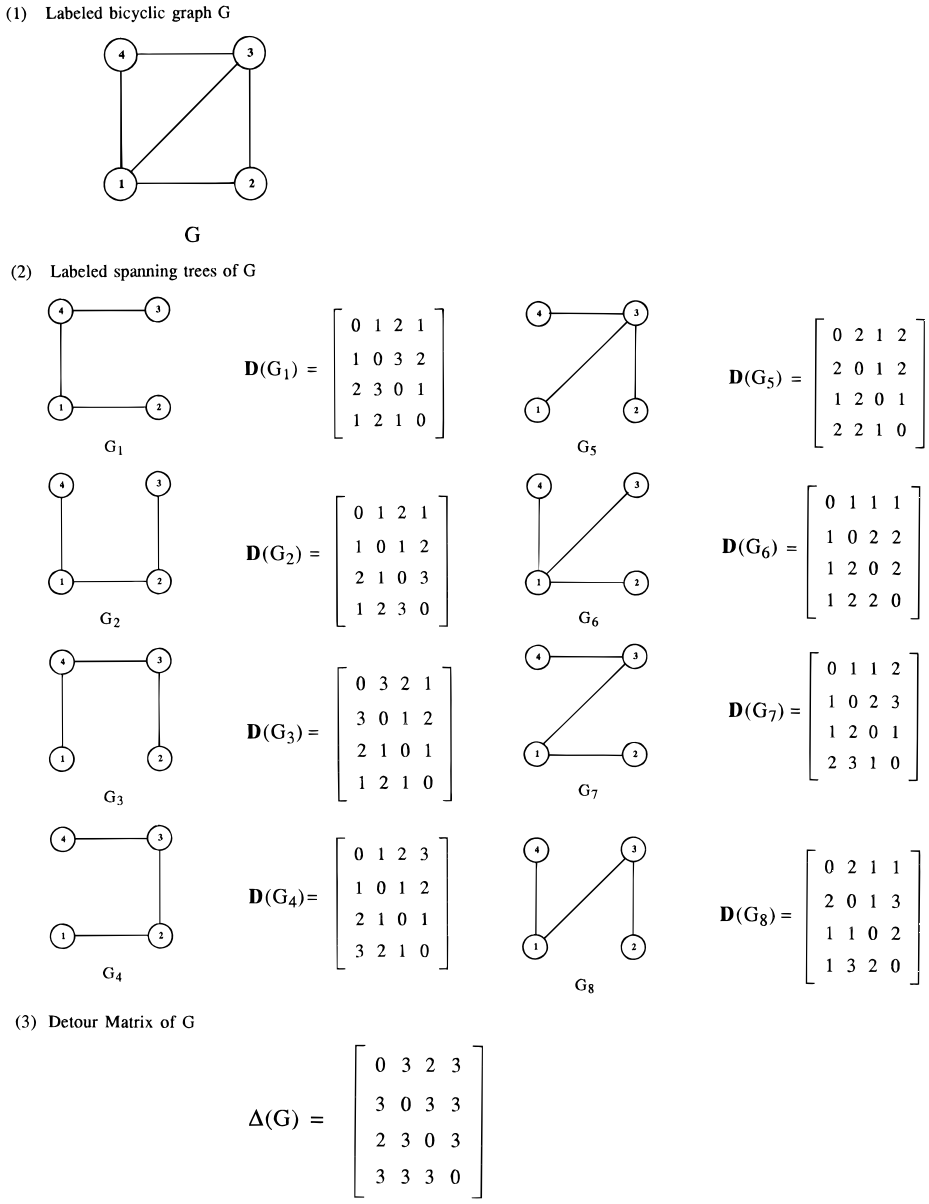


Figure 4. Computation of the detour matrix for the bicyclic graph *G* using the procedure described in the text.

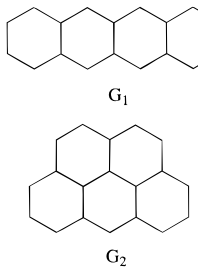


Figure 5. Polyhexes G_1 and G_2.

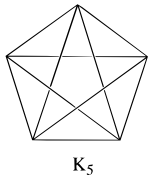


Figure 6. Kuratowski graph.

The coefficients of the detour polynomial show regularities similar to those that the coefficients of the distance polynomial also possess. The first two coefficients of the detour polynomial are equal to one and zero, respectively. The c_1 coefficient is equal to zero since the trace of the detour matrix is zero and the sum of the elements of the detour spectrum is also zero:

$$c_1 = \mathrm{tr}\Delta = \sum_i \lambda_i \tag{17}$$

The c_2 coefficient is equal to the half-sum of the squares of the matrix elements:

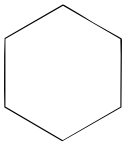
$$c_2 = {}^1/_2 \sum_i \sum_j (\Delta^2)_{ij} \tag{18}$$

The c_N coefficient is, as it is true for all types of characteristic poynomials, given in terms of the determinant of the corresponding matrix:

$$c_N = -\det|\Delta| \tag{19}$$

The roots of the detour polynomial, $\{\lambda_i; i = 1, ..., N\}$, are referred to as the detour spectrum. The detour spectrum consists of one positive and $N - 1$ negative elements (see the detour spectrum of the six-cycle C_6 in Table 1). This

Table 1. Computation of the Detour Polynomial of the Six-Cycle Graph C_6 by the Modified Le Verrier−Faddeev−Frame Method



C_6

(**1**) The detour spectrum of C_6: $\{21, -6, -6, -5, -2, -2\}$

(**2**) $c_1 = \sum_i (\Delta)_{ii} = 0$; $(\Delta)_{ii} = (\Delta_1)_{ii}$

(**3**) $[(\mathbf{B}_1)_{ii} = (\Delta_1)_{ii} - (c_1\mathbf{I})]_{i=1,\dots,6} = \{21, -6, -6, -5, -2, -2\}$
$[(\Delta_2)_{ii} = (\Delta)_{ii} \cdot (\mathbf{B}_1)_{ii}]_{i=1,\dots,6} = \{441, 36, 36, 25, 4, 4\}$
$c_2 = (1/2) \sum_i (\Delta_2)_{ii} = 273$

(**4**) $[(\mathbf{B}_2)_{ii} = (\Delta_2)_{ii} - (c_2\mathbf{I})]_{i=1,\dots,6} = \{168, -237, -237, -248, -269, 269\}$
$[(\Delta_3)_{ii} = (\Delta)_{ii} \cdot (\mathbf{B}_2)_{ii}]_{i=1,\dots,6} = \{3528, 1422, 1422, 1240, 538, 538\}$
$c_3 = (1/3) \sum_i (\Delta_3)_{ii} = 2896$

(**5**) $[(\mathbf{B}_3)_{ii} = (\Delta_3)_{ii} - (c_3\mathbf{I})]_{i=1,\dots,6} = \{632, -1474, -1474, -1656, -2358, -2358\}$
$[(\Delta_4)_{ii} = (\Delta)_{ii} \cdot (\mathbf{B}_3)_{ii}]_{i=1,\dots,6} = \{13272, 8844, 8844, 8280, 4716, 4716\}$
$c_4 = (1/4) \sum_i (\Delta_4)_{ii} = 12168$

(**6**) $[(\mathbf{B}_4)_{ii} = (\Delta_4)_{ii} - (c_4\mathbf{I})]_{i=1,\dots,6} = \{1104, -3324, -3324, -3888, -7452, -7452\}$
$[(\Delta_5)_{ii} = (\Delta)_{ii} \cdot (\mathbf{B}_4)_{ii}]_{i=1,\dots,6} = \{-3184, 19944, 19944, 19440, 14904, 14904\}$
$c_5 = (1/5) \sum_i (\Delta_5)_{ii} = 22464$

(**7**) $[(\mathbf{B}_5)_{ii} = (\Delta_5)_{ii} - (c_5\mathbf{I})]_{i=1,\dots,6} = \{720, -2520, -2520, -3024, -7560, -7560\}$
$[(\Delta_6)_{ii} = (\Delta)_{ii} \cdot (\mathbf{B}_5)_{ii}] = \{15120, 15120, 15120, 15120, 15120, 15120\}$
$c_6 = (1/6) \sum_i (\Delta_6)_{ii} = 15120$

(**8**) $[(\mathbf{B}_6)_{ii} = (\Delta_6)_{ii} - (c_6\mathbf{I})]_{i=1,\dots,6} = \{0, 0, 0, 0, 0, 0\}$

(**9**) The detour polynomial of C_6

$\pi(C_6; x) = x^6 - 273\,x^4 - 2896\,x^3 - 12168\,x^2 - 22464\,x - 15120$

particular distribution of elements in the detour spectrum is a result of the detour polynomial structure, that is, all coefficients, but the first coefficient, possess a negative sign. The sum of spectral elements is, of course, equal to zero. Note that the sum of squares of the elements in the detour spectrum is equal to the trace of Δ^2:

$$\sum_i \lambda_i^2 = \mathrm{tr}\Delta^2 \tag{20}$$

5. THE DETOUR INDEX

The detour index ω is defined in the same way as the Wiener index W, that is, the detour index is equal to the half-sum of the elements of the detour matrix Δ:[4,5]

$$\omega = {}^1/_2 \sum_i \sum_j (\Delta)_{ij} \tag{21}$$

The Wiener index is defined as[9]

$$W = {}^1/_2 \sum_i \sum_j (\mathbf{D})_{ij} \tag{22}$$

The detour/Wiener index ω/W (or in the terminology of Ivanciuc and Balaban[4] the maximum/minimum path sum) is defined as the sum of the detour index and Wiener index:

$$\omega/\mathrm{W} = \omega + \mathrm{W} \tag{23}$$

Table 2. Experimental and Calculated Boiling Points (°C) of 76 Alkanes and Cycloalkanes and Their Wiener and Detour Indices

molecule	W	ω	$(bp)_{exp}$	$(bp)_{calc}$
methane	0	0	−164	−169.6
ethane	1	1	−88.5	−76.6
propane	4	4	−44.5	−36.0
butane	10	10	−0.5	0.1
2-methylpropane	9	9	−10.5	−4.5
pentane	20	20	36.5	33.8
2-methylbutane	18	18	27.9	28.3
2,2-dimethylpropane	16	16	9.5	22.3
hexane	35	35	68.7	65.9
3-methylpentane	31	31	63.2	58.5
2-methylpentane	32	32	60.2	60.4
2,3-dimethylbutane	29	29	58.1	54.6
2,2-dimethylbutane	28	28	49.7	52.5
heptane	56	56	98.4	96.7
3-ethylpentane	48	48	93.5	86.2
3-methylhexane	50	50	91.8	88.9
2-methylhexane	52	52	90	91.6
2,2-dimethylpentane	46	46	89.8	83.3
3,3-dimethylpentane	44	44	86	80.4
2,4-dimethylpentane	48	48	80.5	86.2
2,3-dimethylpentane	46	46	79.2	83.3
2,2,3-trimethylbutane	42	42	80.9	77.4
cyclobutane	8	16	12	5.7
ethylcyclobutane	29	45	70.7	67.8
methylcyclobutane	16	28	36.3	36.9
cycloheptane	42	105	118.5	108.8
cyclohexane	27	63	80.7	76.2
butylcyclohexane	133	217	181.6	186.3
isopropylcyclohexane	88	160	171.3	154.4
sec-butylcyclohexane	121	205	179.3	179.3
tert-butylcyclohexane	114	198	171.5	175.0
1-methyl-4-ethylcyclohexane	90	162	150	155.9
propylcyclohexane	94	166	156.7	158.8
1,1,3-trimethylcyclohexane	82	158	139	150.9
1,2,5-trimethylcyclohexane	84	162	139.5	153.0
cyclooctane	64	160	148.5	141.2
cyclopentane	15	35	49.2	41.2
1,2-diethylcyclopentane	87	151	153.6	151.5
1,1-dimethylcyclopentane	39	75	87.5	94.3
1,2-dimethylcyclopentane	40	79	95.5	96.9
ethylcyclopentane	43	79	103.5	99.5
methylcyclopentane	26	54	71.8	70.1
1-methyl-2-propylcyclopentane	90	151	152.6	152.9
cyclopropane	3	6	−32.7	−33.9
1,1-dimethylcyclopropane	15	22	20.6	28.8
1,2-dimethylcyclopropane	16	24	33	32.8
ethylcyclopropane	17	24	34.5	34.4
methylcyclopropane	8	13	4.5	1.0
1,1,2-trimethylcyclopropane	26	37	52.6	58.6
octane	84	84	125.8	126.4
3-methylheptane	76	76	118.8	118.8
3-ethylhexane	72	72	118.9	114.7
3,4-dimethylhexane	68	68	118.7	110.5
3-ethyl-3-methylpentane	64	64	118.2	106.1
4-methylheptane	75	75	117.7	117.8
2-methylheptane	79	79	117.6	121.7
3-ethyl-2-methylpentane	67	67	115.6	109.4
2,3-dimethylhexane	70	70	115.3	112.7
2,4-dimethylhexane	71	71	109.4	113.7
3,3-dimethylhexane	67	67	112	109.4
2,5-dimethylhexane	74	74	108.4	116.8
2,3,4-trimethylpentane	65	65	113.4	107.2
2,3,3-trimethylpentane	62	62	114.6	103.8
2,2-dimethylhexane	71	71	107	113.7
2,2,3-trimethylpentane	63	63	110.5	105.0
2,2,4-trimethylpentane	66	66	99.3	108.3
2,2,3,3-tetramethylbutane	58	58	106	99.1
1,1-dimethylcyclohexane	59	119	119.5	126.2
1,2-dimethylcyclohexane	60	124	126.6	128.5
1,3-dimethylcyclohexane	61	123	122.3	128.8
1,4-dimethylcyclohexane	62	122	121.8	129.1
ethylcyclohexane	64	124	131.8	131.0
propylcyclopentane	67	111	131	128.5
isopropylcyclopentane	62	106	126.4	123.7
1,1,2-trimethylcyclopentane	56	106	113.5	119.8
1,1,3-trimethylcyclopentane	58	104	115.5	120.4

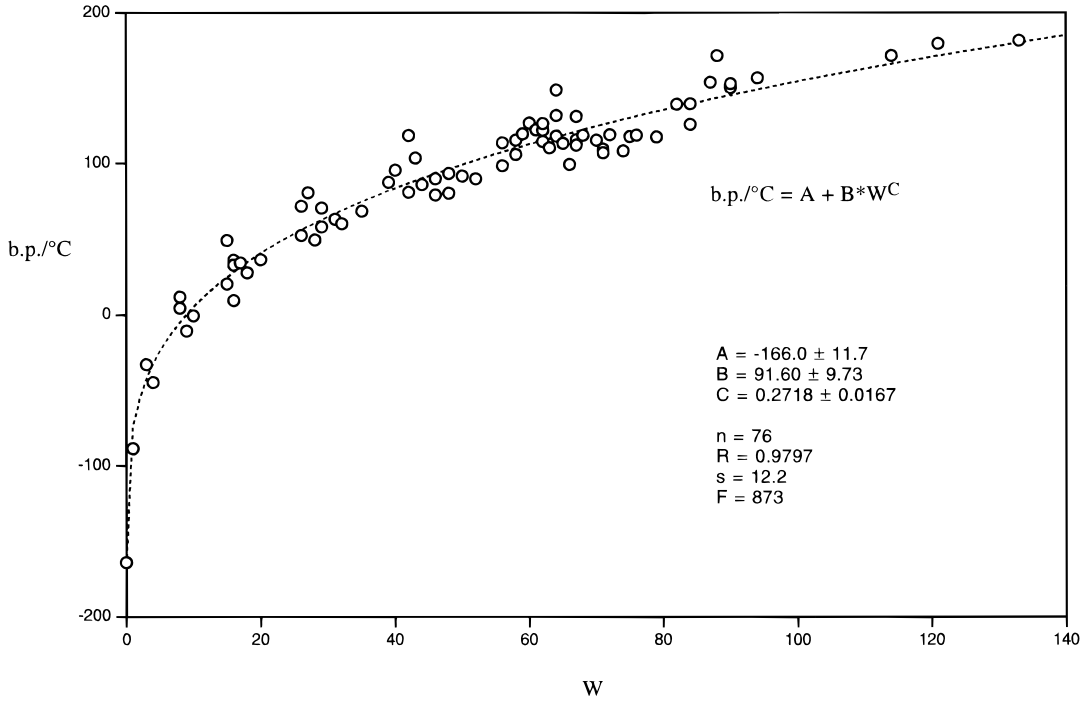


Figure 7. Plot between *W* and bp for 76 alkanes and cycloalkanes from Table 2.

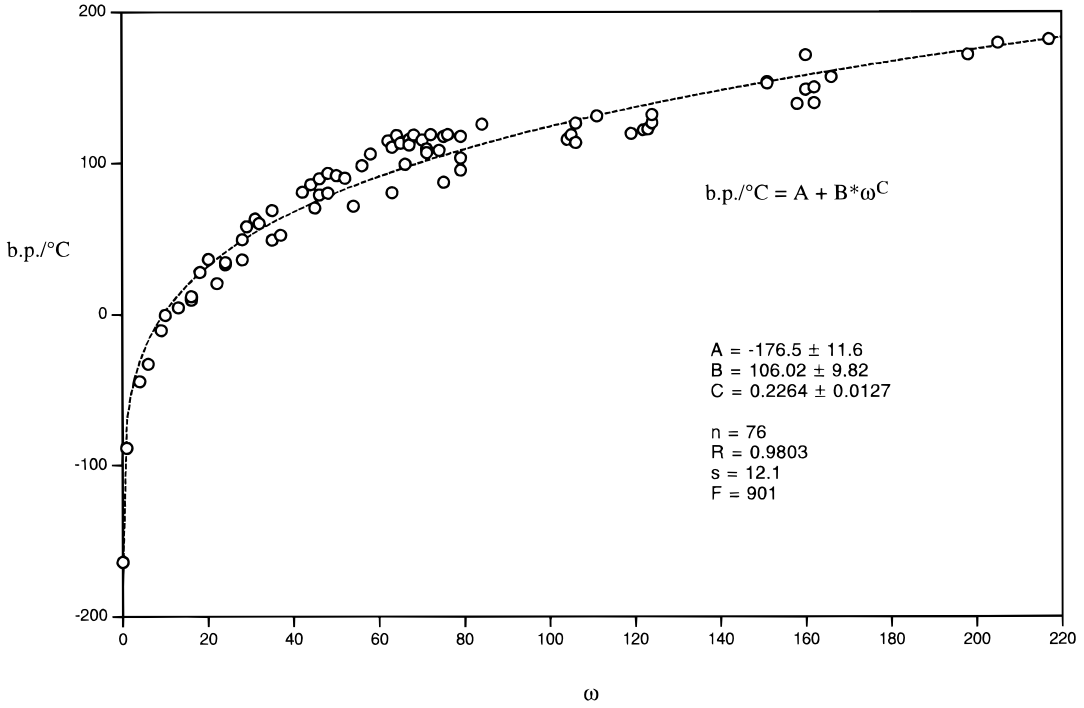


Figure 8. Plot between ω and bp for 76 alkanes and cycloalkanes from Table 2.

For example, the Wiener index, the detour index, and the detour/Wiener index for the graph *G* in Figure 1 are, respectively, 25, 67, and 92.

The Wiener index *W* and the detour index ω are, of course, identical for acyclic structures. For polycyclic structures, *W* and ω are not particularly intercorrelated indices. For example, the linear correlation between *W* and ω ($\omega = aW + b$) for a set of 37 diverse polycyclic graphs has a modest correlation coefficient ($r = 0.79$), while the exponential relationship between *W* and ω ($\omega = aW^b$) produced only a little better correlation between them ($r = 0.86$).

The detour index ω for the complete graph K_N with *N* vertices and *M* edges is given by

$$\omega = M(N - 1) = Md \tag{24}$$

where $d = N - 1$ for complete graphs. In the case of the Wiener index, the expression for computing *W* for complete graphs is even simpler:[32,33]

$$W = M \tag{25}$$

Therefore, the connection between the detour index and the Wiener index for complete graphs is straightforward:[11]

$$\omega = (N - 1)W \tag{26}$$

The detour index for monocycles can be also given in a closed form:[6]

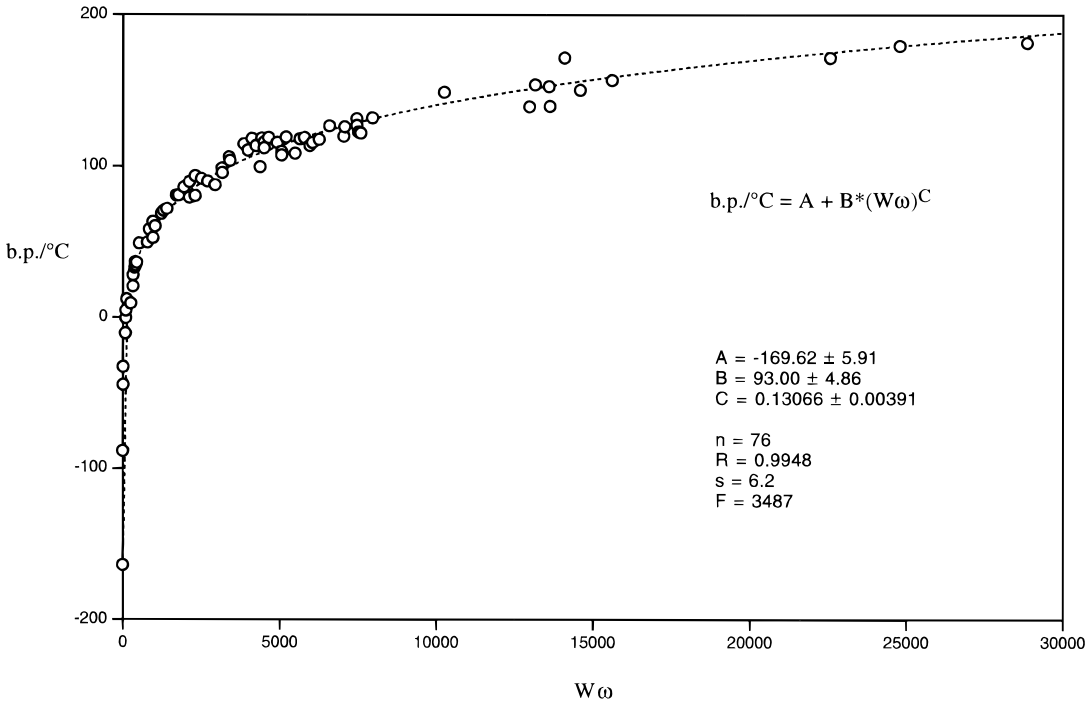


Figure 9. Plot between ωW and bp for 76 alkanes and cycloalkanes from Table 2.

$$\omega = \begin{cases} N^2(3N-4)/8 & N = \text{even} \\ N(3N^2-4N+1)/8 & N = \text{odd} \end{cases} \quad (27)$$

Similarly, the Wiener index for monocycles can be simply given as[34]

$$W = \begin{cases} N^3/8 & N = \text{even} \\ N(N^2-1)/8 & N = \text{odd} \end{cases} \quad (28)$$

It can be easily seen that the detour index and the Wiener index for monocycles are related as follows:[11]

$$\omega = 3W - \begin{cases} N^2/2 & N = \text{even} \\ N(N-1)/2 & N = \text{odd} \end{cases} \quad (29)$$

Lukovits was very enthusiastic when he detected that the detour index combined with the Wiener index is quite efficient in structure−boiling point studies if a series of molecules consists of acyclic and cycle-containing molecules.[6] This is an important result because a typical weakness of most topological descriptors is that they show *no* significant correlation with any physical property of the series of compounds consisting of acyclic and cycle-containing molecules. In order to reinvestigate the Lukovits' results we considered the 76 lowest alkanes and cycloalkanes. Their boiling points, Wiener indices, and detour indices are given in Table 2.

We first studied separately relationships between the Wiener indices (W) and boiling points (bp's), and the detour indices (ω) and boiling points for the collection of 76 alkanes and cycloalkanes. The linear correlations between W and bp and between ω and bp were not particularly good. The polynomial relationship between W and bp and ω and bp was better. The second-order polynomials produced higher values, but still modest, of the correlation coefficients (r = 0.930, r = 0.910). The third-order polynomials improved again, and also equalized, the values of the correlation coefficients for relationships between W and bp (r = 0.952) and ω and bp (r = 0.958). Finally, we considered the exponential structure−boiling point relationship of the type:

$$\text{bp} = A + BI^C \quad (30)$$

where I is a molecular descriptor. In this case the correlation coefficients considerably improved being practically the same (0.98) for both W vs bp and ω vs bp. The corresponding plots W vs bp and ω vs bp and their statistical parameters for the 76 studied alkanes and cycloalkanes are given in Figures 7 and 8.

Then we studied the relationship between the composite index ($W\omega$) and boiling points using the same type of the exponential relationship as above: $\text{bp} = A + B(W\omega)^C$. This time the statistical parameters are much better than when the individual indices were considered. The corresponding plot of ($W\omega$) vs bp is given in Figure 9.

The standard deviation is still high (6.2 °C), but it is the smallest obtained so far for the structure−boiling point relationship for the set of alkanes and cycloalkanes. Besides, it is well-known that the boiling point is a difficult property to model.[35]

6. CONCLUDING REMARKS

The novel distance matrix, called the detour matrix, of a chemical graph G is presented and compared to the related matrix, that is, the traditional distance matrix of G. The combination of both these matrices called the detour/distance matrix is also mentioned. A novel method for the computation of the detour matrix is introduced and illustrated. The detour polynomial and the detour spectrum are discussed and some of their properties summarized.

A novel topological index, called the detour index, is presented and its use in the structure−boiling point relationship is reinvestigated by following an earlier study by Lukovits.[6] It appears that the detour index in combination with the Wiener index is a promising topological index. However, much more work is needed with this index in a

variety of structure−property−activity relationships before it will be possible to assess its usefulness in this kind of chemical computations.

ACKNOWLEDGMENT

This work was supported by the Ministry of Science and Technology of the Republic of Croatia via Grants Nos. 1-07-159 and 1-7-185. We thank the reviewers for their very helpful comments.

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CI960149N