

# The Laplacian Matrix in Chemistry<sup>†</sup>

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The Laplacian matrix, its spectrum, and its polynomial are discussed. An algorithm for computing the number of spanning trees of a polycyclic graph, based on the corresponding Laplacian spectrum, is outlined. Also, a technique using the Le Verrier–Faddeev–Frame method for computing the Laplacian polynomial of a graph is detailed. In addition, it is shown that the Wiener index of an alkane tree can be given in terms of its Laplacian spectrum. Two Mohar indices, one based on the Laplacian spectrum of a molecular graph  $G$  and the other based on the Laplacian  $x_2$  eigenvalue of  $G$ , have been tested in the structure–property relationships for octanes.

## 1. INTRODUCTION

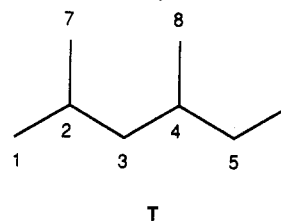
A few years ago Slovenian graph-theoretician Bojan Mohar stated:<sup>1</sup> "...in author's opinion the Laplacian spectrum is much more natural and more important than the adjacency matrix spectrum." This statement motivated the present report. We decided to investigate whether it holds in chemical applications of the Laplacian matrix, because various results in chemical graph theory may be traced back to the adjacency matrix.<sup>2</sup> For example, many topological indices in the current use can be derived from the adjacency matrix or higher order adjacency matrices; e.g. see ref 3. Besides, the second important graph-theoretical matrix from a chemical point of view, that is, the distance matrix of a given graph  $G$ ,<sup>4</sup> can be generated by using powers of the corresponding adjacency matrix of  $G$ .<sup>5</sup> Many topological indices are also based on the distance matrix; e.g. see refs 6 and 7.

The Laplacian matrix is sometimes also called the Kirchhoff matrix<sup>8</sup> of a graph because of its role in the matrix–tree theorem, which is attributed, by some authors,<sup>9</sup> to Kirchhoff.<sup>10</sup> This theorem concerns the number of ways in which a given network can be freed of its cycles by successive removal of an appropriate number of edges from the network. The matrix–tree theorem was proved by a number of authors.<sup>11–13</sup> Another name for the Laplacian matrix is the matrix of admittance,<sup>14,15</sup> which originates in the theory of electrical networks. However, the name Laplacian matrix appears to be more appropriate since this matrix is just the matrix of a discrete Laplacian operator,<sup>8,14</sup> which is one of the basic differential operators in quantum chemistry.<sup>16–19</sup>

Throughout this article we will use the (chemical) graph-theoretical language based on Harary's classic "Graph Theory"<sup>20</sup> and on books on chemical graph theory by one of us.<sup>2,21</sup>

This report is structured as follows. In the next section the Laplacian matrix, its spectrum, and the number of spanning trees of a polycyclic graph are discussed for simple and weighted graphs. In section 3, the Laplacian polynomial is

**Table I.** Laplacian Matrix  $L$  of a Labeled Tree  $T$  Corresponding to the Carbon Skeleton of 2,4-Dimethylhexane



$$L(T) = \begin{bmatrix} 1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 \\ -1 & 3 & -1 & 0 & 0 & 0 & -1 & 0 \\ 0 & -1 & 2 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 3 & -1 & 0 & 0 & -1 \\ 0 & 0 & 0 & -1 & 2 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 1 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 1 \end{bmatrix}$$

presented. Section 4 contains definitions of several topological indices based on the Laplacian spectrum and their use in the structure–property correlations. The report ends with concluding remarks in section 5.

## 2. LAPLACIAN MATRIX AND ITS SPECTRUM

**(a) The Laplacian Matrix.** The Laplacian matrix  $L = L(G)$  of a simple graph  $G$  (i.e., graph without loops and multiple edges) is defined<sup>8,14,15</sup> as the following difference matrix:

$$L = V - A \quad (1)$$

where  $A$  is the adjacency matrix and  $V$  is the degree (valency) matrix. The degree matrix is a diagonal matrix with entries

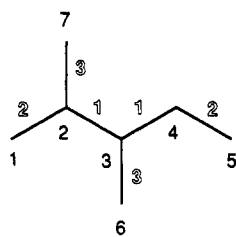
$$(V)_{ii} = D(i) \quad (2)$$

where  $D(i)$  is the degree (valency) of the vertex  $i$  in  $G$  and is also given by  $\sum_j (A)_{ij}$ . For example, the Laplacian matrix of a tree  $T$ , depicting the carbon skeleton of 2,4-dimethylhexane, is given in Table I.

The Laplacian matrix of an edge-weighted graph  $G_{EW}$  is constructed in the same way as the Laplacian matrix for a

<sup>†</sup> Dedicated to the memory of the second Croatian Nobel Prize Laureate Ivo Andrić (1892–1975).

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**Table II.** Laplacian Matrix  $L$  of a Labeled Edge-Weighted Tree  $T_{EW}$ <sup>a</sup> $T_{EW}$ 

$$L(T_{EW}) = \begin{bmatrix} 2 & -2 & 0 & 0 & 0 & 0 & 0 \\ -2 & 6 & -1 & 0 & 0 & 0 & -3 \\ 0 & -1 & 5 & -1 & 0 & -3 & 0 \\ 0 & 0 & -1 & 3 & -2 & 0 & 0 \\ 0 & 0 & 0 & -2 & 2 & 0 & 0 \\ 0 & 0 & -3 & 0 & 0 & 3 & 0 \\ 0 & -3 & 0 & 0 & 0 & 0 & 3 \end{bmatrix}$$

<sup>a</sup> The edge weights are given in outlined style.

simple graph, but the edge weights are taken into account. An illustrative example is shown in Table II.

In the Laplacian matrix of a vertex-weighted graph  $G_{vw}$ , the diagonal entries  $(L)_{ii}$  are equal to the degrees of the weighted vertices minus the weights at these vertices. Note, that the degree of a weighted vertex is defined as the number of (weighted) edges incident with it plus the vertex weight which is usually taken to be nonnegative. Thus, the contribution of vertex weights has no influence on the Laplacian matrix.<sup>8,22</sup>

The most important application of the Laplacian matrix of a graph is in the matrix-tree theorem.<sup>14</sup> This theorem may be stated as follows: Let  $i$  and  $j$  be vertices of a graph  $G$  and let  $L_{ij}$  be the submatrix of the Laplacian matrix of  $G$  obtained by deleting the row  $i$  and the column  $j$ . Then the absolute value of the determinant of  $L_{ij}$  is equal to the number of spanning trees  $t(G)$  of  $G$ .

$$t(G) = |\det(L_{ij})| \quad (3)$$

**(b) The Laplacian Spectrum.** The Laplacian matrix is a real symmetric matrix. The diagonalization of the Laplacian matrix of a graph  $G$  with  $N$  vertices gives  $N$  real eigenvalues  $\{x_i\}_{i=1,\dots,N}$ . The set of eigenvalues is referred to as the spectrum of the Laplacian matrix of a graph  $G$  or the Laplacian spectrum of  $G$ ; e.g. see ref 1. The smallest member of the Laplacian spectrum  $x_1$  is always equal to zero. Conventionally, the Laplacian eigenvalues are given in increasing order:

$$0 = x_1 \leq x_2 \leq \dots \leq x_{N-1} \leq x_N \quad (4)$$

The Laplacian spectrum of a complete graph  $K_N$  shows the following pattern:

$$\{0, N, N, N, \dots\} \quad (5)$$

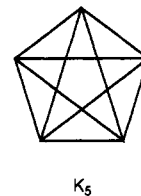
Thus, for example, we can immediately write down the Laplacian spectrum of the Kuratowski  $K_5$  graph (see Figure 1) as

$$\{0, 5, 5, 5, 5\} \quad (6)$$

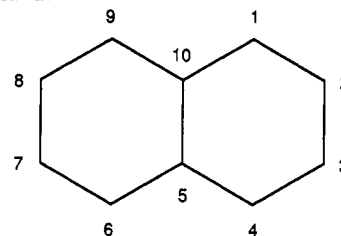
In the case of regular graphs, the eigenvalues  $x_i(L)$  of the Laplacian matrix are related to eigenvalues  $x_i(A)$  of the corresponding adjacency matrix as follows:

$$x_i(L) = D - x_i(A) \quad (7)$$

where  $D$  is the vertex degree in the regular graph.

**Figure 1.** Kuratowski graph.**Table III.** Computation of the Number of Spanning Trees in the Naphthalene Graph Using Formula (8)

(1) Naphthalene Graph  $G$  and the Corresponding Laplacian Matrix

 $G$ 

$$L(G) = \begin{bmatrix} 2 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 \\ -1 & 2 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 2 & -1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 2 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 3 & -1 & 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 0 & -1 & 2 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 & 2 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 2 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 2 & -1 \\ -1 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & -1 & 3 \end{bmatrix}$$

(2) Laplacian Spectrum of the Naphthalene Graph

$$\{0.0000; 0.3820; 0.8851; 1.3820; 1.3820; 2.6180; 3.2541; 3.6180; 3.6180; 4.8608\}$$

(3) Count of Spanning Trees of the Naphthalene Graph

$$t(G) = 0.1 \prod_{i=2}^{10} x_i = 35$$

The Laplacian spectrum has a number of interesting properties.<sup>1</sup> Here we point out that it can be used to compute the number of spanning trees of a polycyclic graph  $G$ . This can be done by the following simple formula based on the matrix-tree theorem:<sup>8</sup>

$$t(G) = (1/N) \prod_{i=2}^N x_i \quad (8)$$

where  $t(G)$  is the number of spanning trees of  $G$ . This formula also holds for weighted graphs.

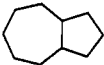
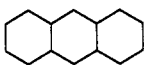
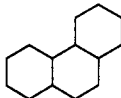
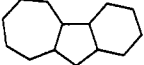
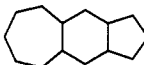
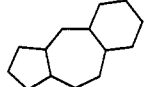
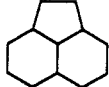
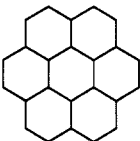
In Table III we give as an example the computation of  $t(G)$  for naphthalene graph by means of (8).

In Figure 2 we depict all spanning trees in the naphthalene graph. Note that 12 among them (those labeled 5, 21, and 26–35) represent Hamiltonian chains.

In Table IV we give the spanning-tree counts for several polycyclic graphs corresponding to carbon skeletons of conjugated polycyclic hydrocarbons.

From the results reported in Table IV we see that the number  $t(G)$  does not depend on the details of fusion, i.e., whether the rings are fused linearly or angularly; a consequence of this

Table IV. Laplacian Spectra and the Spanning-Tree Counts for Several Polycyclic Graphs Computed by Formula 8

							
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.3820	0.1981	0.2162	0.2034	0.1981	0.2014	0.4437	0.2492
0.7717	0.7530	0.5858	0.6914	0.7346	0.6373	0.5456	0.2492
1.3820	0.8402	1.0000	0.8090	0.7530	0.8768	1.3144	0.6472
1.6396	1.1206	1.0914	1.0589	1.1829	1.1984	1.4937	0.6472
2.6180	1.5500	1.5731	1.5626	1.5550	1.5630	1.7475	1.0000
2.8141	1.6207	1.5858	1.8879	1.8333	1.7000	2.4104	1.0000
3.6180	2.4450	2.5856	2.6417	2.4450	2.4838	3.2732	1.4384
4.0000	3.2470	3.0000	2.8459	2.7859	2.8777	3.3342	1.6815
4.7746	3.3473	3.4142	3.3087	3.2470	3.4421	4.0000	1.6815
	3.4919	3.4862	3.4702	3.8019	3.5420	4.3180	1.8397
	3.8019	3.8058	3.8533	4.0000	3.8538	5.1193	1.8397
	4.5321	4.4142	4.6624	4.4475	4.7333		2.7853
	5.0472	5.1417	5.0045	5.0159	4.8903		2.7853
							3.0000
							3.5637
							3.5637
							4.0000
							4.0000
							4.2840
							4.9494
							4.9494
							5.5616
$t = 34$	$t = 204$	$t = 204$	$t = 197$	$t = 198$	$t = 199$	$t = 161$	$t = 423\ 381$

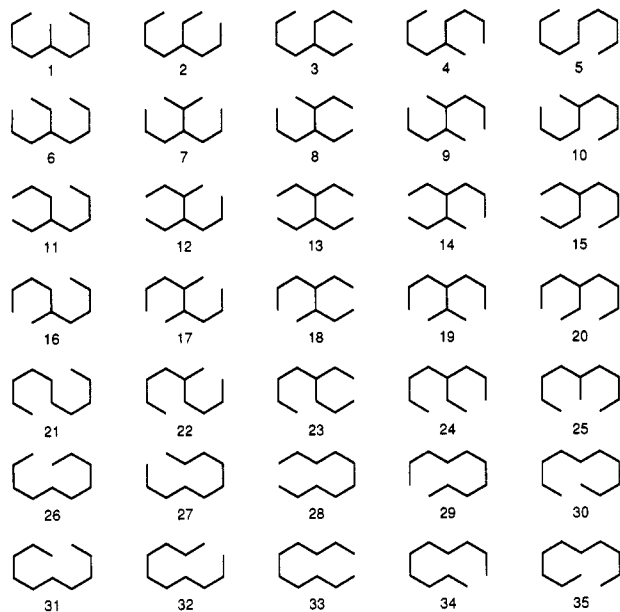
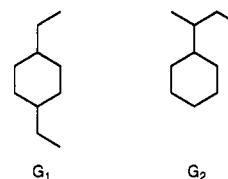


Figure 2. All spanning trees belonging to the naphthalene graph.

is that  $t(\text{anthracene}) = t(\text{phenanthrene})$ . Fusion of five-, six-, and seven-membered rings in different order produces isomeric polycyclic structures with only slightly different  $t$ -numbers.

The number of spanning trees can also be obtained<sup>23</sup> by using the generalized characteristic polynomial of the inner dual.

The  $t$ -numbers find use in calculations of ring current intensities in conjugated polycyclic systems,<sup>24–26</sup> from which <sup>1</sup>H-NMR chemical shifts follow and London contributions to the magnetic susceptibility anisotropies, according to McWeeny's method,<sup>27</sup> can be obtained. Actually Mallion<sup>24</sup> in developing the graph-theoretical framework for ring current calculations made use of the matrix-tree theorem for computing the number of spanning trees in graphs corresponding to conjugated polycyclic systems.

Figure 3. Graphs corresponding to carbon skeletons of 1,4-divinylbenzene ( $G_1$ ) and 2-phenylbutadiene ( $G_2$ ).

For edge-weighted graphs  $G_{EW}$  the spanning-tree count, besides by means of formula (8), can also be carried out by using the following formula:<sup>8</sup>

$$t(G_{EW}) = W t(G^*_{EW}) \quad (9)$$

where  $W$  is equal to the product of the edge weights

$$W = \prod_{j=1}^M w_j \quad (10)$$

and  $G^*_{EW}$  is the dual of  $G_{EW}$ .  $M$  in (10) is the number of edges in  $G_{EW}$ . Since formula (8) is also valid for  $t(G^*_{EW})$ , eq 9 may be rewritten, by employing also (10), as follows:

$$t(G) = (1/N^*) \prod_{i=2}^{N^*} x_i \prod_{j=1}^M w_j \quad (11)$$

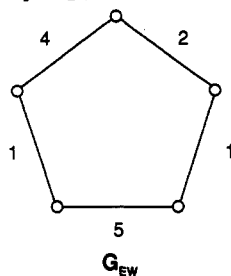
where  $N^*$  is the number of vertices in  $G^*_{EW}$ .

An illustrative example of the use of formula 9 is shown in Table V.

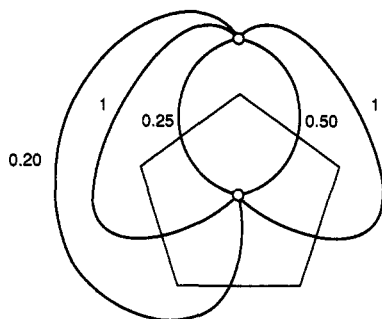
It is also interesting to point out the relationship between the sum of Laplacian eigenvalues and the number  $M$  of edges of a graph:

$$\sum_{i=2}^N x_i = \text{tr } L = 2M \quad (12)$$

The above result, of course, is not surprising because the trace of the Laplacian matrix,  $\text{tr } L$ , is equal to the sum of the vertex degrees which, according to Euler's handshaking lemma, is exactly equal to twice the number of edges of a graph.

**Table V.** Spanning-Tree Count for the Edge-Weighted Graph  $G_{EW}$  Obtained by Formula 9(1) Edge-Weighted Graph  $G_{EW}$ (2) Value of  $W$ 

$$W = \prod_{i=1}^5 w_i = 1 \times 4 \times 2 \times 1 \times 5 = 40$$

(3) The Dual of  $G_{EW}$ (4) Laplacian Spectrum of  $G^*_{EW}$ 

$$\{0.0; 5.9\}$$

(5) Spanning-Tree Count of  $G^*_{EW}$ 

$$t(G^*_{EW}) = 0.5 \times 5.9 = 2.95$$

(6) Spanning-Tree Count of  $G_{EW}$ 

$$t(G_{EW}) = 40 \times 2.95 = 118$$

## 3. LAPLACIAN POLYNOMIAL

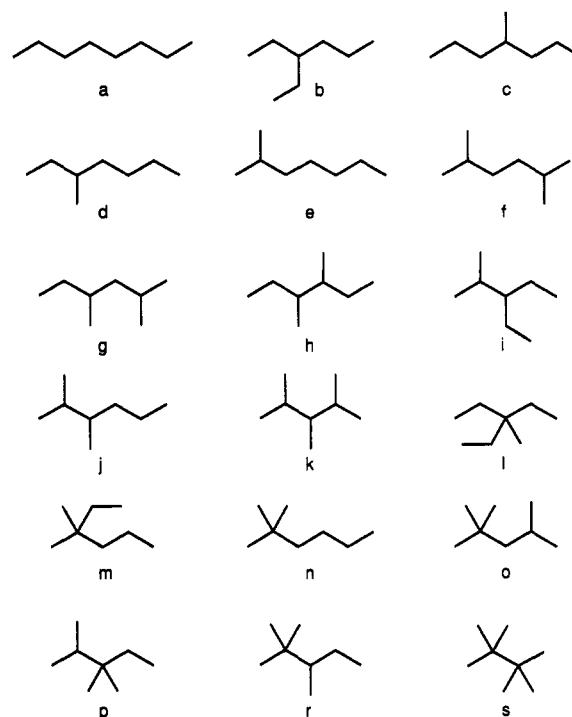
The characteristic polynomial  $\Lambda(G;x)$  of the Laplacian matrix  $L$  of a graph  $G$  is defined as<sup>14</sup>

$$\Lambda(G;x) = \det(xI - L) \quad (13)$$

where  $I$  is the  $N \times N$  unit matrix. We will refer to this polynomial as the Laplacian polynomial. The coefficient form of the Laplacian polynomial is obtained by the expansion of determinant 13

$$\begin{aligned} \Lambda(G;x) &= x^N - c_1 x^{N-1} - c_2 x^{N-2} - \dots - c_{N-1} x - c_N \\ &= x^N - \sum_{n=1}^N c_n x^{N-n} \end{aligned} \quad (14)$$

The Laplacian polynomial may be computed in several ways. The method we use is the modified Le Verrier–Faddeev–Frame (LVFF) method.<sup>28–30</sup> This is a very convenient method for obtaining the characteristic polynomial of any matrix, though it has been introduced to compute the characteristic polynomial of the adjacency matrix. The method was recently resurrected by Balasubramanian,<sup>31–35</sup> Krivka et al.,<sup>36</sup> and Nikolić et al.<sup>4,37,38</sup>

**Figure 4.** Alkane trees corresponding to octanes.

The coefficients  $c_n$  of the Laplacian polynomial can be computed by the LVFF method in the following way:

$$c_n = (1/n) \operatorname{tr} L_n \quad (15)$$

where the matrix  $L_n$  is given by

$$L_n = L B_{n-1} \quad (16)$$

where  $B_{n-1}$  is an auxiliary matrix. This matrix is defined as

$$B_{n-1} = L_{n-1} - c_{n-1} I \quad (17)$$

The LVFF method is an iterative procedure which ends when the auxiliary matrix vanishes, i.e., when  $n = N - 1$ :

$$B_{N-1} = L_{N-1} - c_{N-1} I = 0 \quad (18)$$

The LVFF method was modified by using the proposal by Živković.<sup>39</sup> He proposed the use of the diagonal forms of the matrices in the procedure. Thus, we first diagonalize the Laplacian matrix by means of the Householder–QL method,<sup>40,41</sup> and then the LVFF method is carried out with  $L_n$  and  $B_n$  matrices in the diagonal form. Therefore, instead of multiplying matrices, we multiply sets of numbers representing eigenvalues of these matrices. Therefore, formulas 15–18 can be given in the following forms:

$$c_n = (1/n) \sum_{i=1}^N (L_n)_{ii} \quad (19)$$

$$(L_n)_{ii} = (L)_{ii} (B_{n-1})_{ii} \quad (20)$$

$$(B_n)_{ii} = (L_n)_{ii} - (c_n I)_{ii} \quad (21)$$

$$(B_{N-1})_{ii} = (L_{N-1})_{ii} - (c_{N-1} I)_{ii} = 0 \quad (22)$$

We find this method very convenient for computing the Laplacian polynomial of graphs of moderate sizes. Balasubramanian, however, argues that the above modification is not as universal as the original version of the LVFF method.<sup>42</sup>

**Table VI.** Computation of the Laplacian Polynomial of Benzene by the Modified Le Verrier–Faddeev–Frame Method(i) Laplacian Spectrum of Benzene ( $x_1 = 0$  Is Not Included)

$$\{1, 1, 3, 3, 4\}$$

$$(ii) c_1 = \sum_{i=2}^6 (L)_{ii} = 12$$

$$(iii) \{(B_1)_{ii} = (L)_{ii} - (c_1 I)_{ii} \}_{i=2, \dots, 6} = \{-11, -11, -9, -9, -8\}$$

$$\{(L_2)_{ii} = (L)_{ii}(B_1)_{ii} \}_{i=2, \dots, 6} = \{-11, -11, -27, -27, -32\}$$

$$c_2 = 0.5 \sum_{i=2}^6 (L_2)_{ii} = -54$$

$$(iv) \{(B_2)_{ii} = (L_2)_{ii} - (c_2 I)_{ii} \}_{i=2, \dots, 6} = \{43, 43, 27, 27, 22\}$$

$$\{(L_3)_{ii} = (L)_{ii}(B_2)_{ii} \}_{i=2, \dots, 6} = \{43, 43, 81, 81, 88\}$$

$$c_3 = 0.33 \sum_{i=2}^6 (L_3)_{ii} = 112$$

$$(v) \{(B_3)_{ii} = (L_3)_{ii} - (c_3 I)_{ii} \}_{i=2, \dots, 6} = \{-69, -69, -93, -93, -24\}$$

$$\{(L_4)_{ii} = (L)_{ii}(B_3)_{ii} \}_{i=2, \dots, 6} = \{-69, -69, -93, -93, -96\}$$

$$c_4 = 0.25 \sum_{i=2}^6 (L_4)_{ii} = -105$$

$$(vi) \{(B_4)_{ii} = (L_4)_{ii} - (c_4 I)_{ii} \}_{i=2, \dots, 6} = \{36, 36, 12, 12, 9\}$$

$$\{(L_5)_{ii} = (L)_{ii}(B_4)_{ii} \}_{i=2, \dots, 6} = \{36, 36, 36, 36, 36\}$$

$$c_5 = 0.20 \sum_{i=2}^6 (L_5)_{ii} = 36$$

$$(vii) \{(B_5)_{ii} = (L_5)_{ii} - (c_5 I)_{ii} \}_{i=2, \dots, 6} = \{0, 0, 0, 0, 0\}$$

$$\{(L_6)_{ii} = (L)_{ii}(B_5)_{ii} \}_{i=2, \dots, 6} = \{0, 0, 0, 0, 0\}$$

$$c_6 = 0$$

(viii) Laplacian Polynomial of Benzene

$$\Delta(\text{benzene}; x) = x^6 - 12x^5 + 54x^4 - 112x^3 + 105x^2 - 36x$$

The computation of the Laplacian polynomial of a graph  $G$  by the modified LVFF method may be schematized as follows:

$$G \rightarrow L \rightarrow \{x_i\} \rightarrow \sum_i (L)_{ii} \rightarrow c_1 \rightarrow \sum_i (B_1)_{ii} \rightarrow$$

$$\sum_i (L_2)_{ii} \rightarrow c_2 \rightarrow \dots \rightarrow c_{N-1} \rightarrow \sum_i (B_{N-1})_{ii} \rightarrow$$

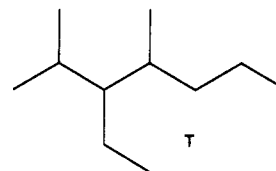
$$\sum_i (L_N)_{ii} \rightarrow c_N = 0$$

As, an example, we give in Table VI the computation of the Laplacian polynomial of benzene via the above scheme.

The Laplacian polynomial is not particularly discriminative; i.e., there exist nonisomorphic graphs with the same Laplacian polynomial (e.g. see ref 15). However, they discriminate some isospectral (cospectral) graphs. Isospectral graphs are nonisomorphic graphs which possess identical spectra (and identical characteristic polynomials) of their adjacency matrices; e.g. see refs 21, 43, and 44. For example, the classic pair of isospectral graphs corresponding to carbon skeletons of 1,4-divinylbenzene ( $G_1$ ) and 2-phenylbutadiene ( $G_2$ ) (see Figure 3) has these Laplacian polynomials and spectra:

$$\Delta(G_1; x) = x^{10} - 20x^9 + 168x^8 - 772x^7 + 2118x^6 - 3552x^5 + 3580x^4 - 2044x^3 + 581x^2 - 60x \quad (23)$$

$$\Delta(G_2; x) = x^{10} - 20x^9 + 168x^8 - 772x^7 + 2118x^6 - 3554x^5 + 3592x^4 - 2066x^3 + 593x^2 - 60x \quad (24)$$

**Table VII.** Computation of the Wiener Index for Alkane Tree  $T$ , Representing the Carbon Skeleton of 2,4-Dimethyl-3-Ethylheptane, by Formula 18(1) Alkane Tree  $T$ (2) Laplacian Spectrum of  $T$ 

$$\{0.0000; 0.1548; 0.3269; 0.5027; 1.0000; 1.3869;$$

$$1.8056; 2.8302; 3.1872; 3.9052; 4.9004\}$$

(3) Wiener Index of  $T$ 

$$W(T) = 10 \sum_{i=2}^{10} x_i^{-1} = 164$$

**Table VIII.** Laplacian Polynomials of Octanes

octane trees <sup>a</sup>	$c_0$	$c_1$	$c_2$	$c_3$	$c_4$	$c_5$	$c_6$	$c_7$	$c_8$
a	1	-14	78	-220	330	-252	84	-8	0
b	1	-14	77	-212	307	-224	72	-8	0
c	1	-14	77	-212	308	-228	75	-8	0
d	1	-14	77	-212	308	-228	76	-8	0
e	1	-14	76	-212	309	-232	79	-8	0
f	1	-14	76	-204	289	-214	74	-8	0
g	1	-14	76	-204	288	-210	71	-8	0
h	1	-14	76	-204	286	-204	68	-8	0
i	1	-14	76	-204	286	-204	67	-8	0
j	1	-14	75	-204	287	-208	70	-8	0
k	1	-14	75	-196	267	-190	65	-8	0
l	1	-14	75	-198	273	-192	64	-8	0
m	1	-14	75	-198	275	-198	67	-8	0
n	1	-14	74	-198	277	-204	71	-8	0
o	1	-14	74	-190	259	-188	66	-8	0
p	1	-14	74	-190	255	-180	62	-8	0
r	1	-14	74	-190	256	-182	63	-8	0
s	1	-14	72	-176	229	-162	58	-8	0

<sup>a</sup> Octane-trees are given in Figure 4.Laplacian spectrum of  $G_1$ :

$$\{0, 0.2243, 0.5188, 1.0000, 1.4108, 2.3111,$$

$$2.7237, 3.0000, 4.1701, 4.6412\} \quad (25)$$

Laplacian spectrum of  $G_2$ :

$$\{0, 0.2037, 0.6275, 1.0000, 1.2493, 2.1875,$$

$$3.0000, 3.1474, 3.8102, 4.7744\} \quad (26)$$

The coefficients of the Laplacian polynomial are related to the structure and to the spectrum of a graph. Some of these relations are summarized as follows:

$$(i) c_1 = 2M \quad (27)$$

$$(ii) c_{N-2} = (-1)^{N-2} [\text{sum of all } (N-2)\text{-tuples of } \{x_1, x_2, \dots, x_N\}] \quad (28)$$

$$(iii) c_{N-1} = (-1)^{N-1} [x_2 x_3 \dots x_N + x_1 x_3 \dots x_N + \dots + x_1 x_2 \dots x_{N-1}]$$

$$= (-1)^{N-1} x_2 x_3 \dots x_N \quad (29)$$

$$(iv) c_N = (-1)^N x_1 x_2 \dots x_N = 0 \quad (\text{since } x_1 = 0) \quad (30)$$

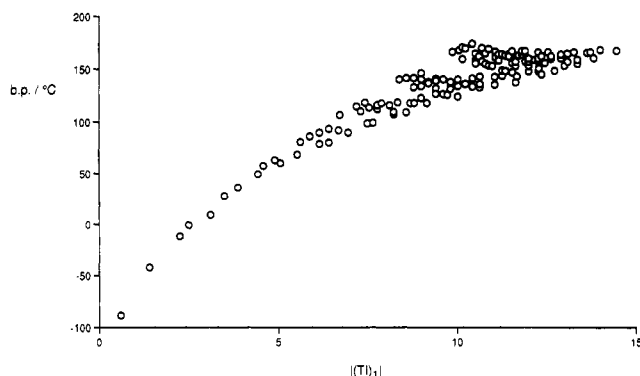
Figure 5. Plot of bp vs |(TI)<sub>1</sub>| for the first 149 alkanes.

Table IX. Laplacian Spectra of Octanes

octane trees <sup>a</sup>	x <sub>1</sub>	x <sub>2</sub>	x <sub>3</sub>	x <sub>4</sub>	x <sub>5</sub>	x <sub>6</sub>	x <sub>7</sub>	x <sub>8</sub>
a	0	0.1522	0.5858	1.2346	2.0000	2.7654	3.4142	3.8478
b	0	0.2434	0.3820	1.1798	2.0000	2.6180	3.1386	4.4383
c	0	0.1981	0.4915	1.3204	1.5550	2.8258	3.2470	4.3623
d	0	0.1864	0.5858	1.0000	2.0000	2.4707	3.4142	4.3429
e	0	0.1667	0.7276	1.0000	1.6353	2.6729	3.5643	4.2332
f	0	0.1864	1.0000	1.0000	1.0000	2.4707	4.0000	4.3429
g	0	0.2137	0.6177	1.0000	1.4977	2.3537	3.8408	4.4763
h	0	0.2509	0.5858	0.7287	2.0000	2.3349	3.4142	4.6855
i	0	0.3065	0.3820	1.0000	1.6703	2.6180	3.3297	4.6935
j	0	0.2243	0.5858	1.0000	1.4108	2.7237	3.4142	4.6412
k	0	0.2679	0.6571	0.7639	1.0000	2.5293	3.7321	4.8136
l	0	0.3820	0.3820	1.0000	2.0000	2.6180	2.6180	5.2361
m	0	0.2538	0.5472	1.0000	1.4689	2.4066	3.1504	5.1732
n	0	0.2023	1.0000	1.0000	1.0000	2.2472	3.4527	5.0979
o	0	0.2384	1.0000	1.0000	1.0000	1.6367	4.0000	5.1249
p	0	0.3187	0.5858	1.0000	1.0000	2.3579	3.4142	5.3234
q	0	0.2888	0.6742	1.0000	1.0000	2.1694	3.5857	5.2819
r	0	0.3542	1.0000	1.0000	1.0000	1.0000	4.0000	5.6458

<sup>a</sup> Octane trees are given in Figure 4.

Table X. Values of the Wiener and Mohar Indices for Octanes

octane <sup>a</sup>	W	(TI) <sub>1</sub>	(TI) <sub>2</sub>
n-octane (a)	84	-9.7426	3.2852
3-ethylhexane (b)	72	-8.3508	2.0542
4-methylheptane (c)	75	-8.6988	2.5240
3-methylheptane (d)	76	-8.8148	2.6824
2-methylheptane (e)	79	-9.1627	2.9994
2,5-dimethylhexane (f)	74	-8.5828	2.6824
2,4-dimethylhexane (g)	71	-8.2349	2.3397
3,4-dimethylhexane (h)	68	-7.8869	1.9928
3-ethyl-2-methylpentane (i)	67	-7.7709	1.6313
2,3-dimethylhexane (j)	70	-8.1189	2.2292
2,3,4-trimethylpentane (k)	65	-7.5390	1.8664
3-ethyl-3-methylpentane (l)	64	-7.4230	1.3089
3,3-dimethylhexane (m)	67	-7.7709	1.9701
2,2-dimethylhexane (n)	71	-8.2349	2.4716
2,2,4-trimethylpentane (o)	66	-7.6549	2.0973
2,3,3-trimethylpentane (p)	62	-7.1910	1.5689
2,2,3-trimethylpentane (q)	63	-7.3070	1.7313
2,2,3,3-tetramethylbutane (r)	58	-6.7271	1.4116

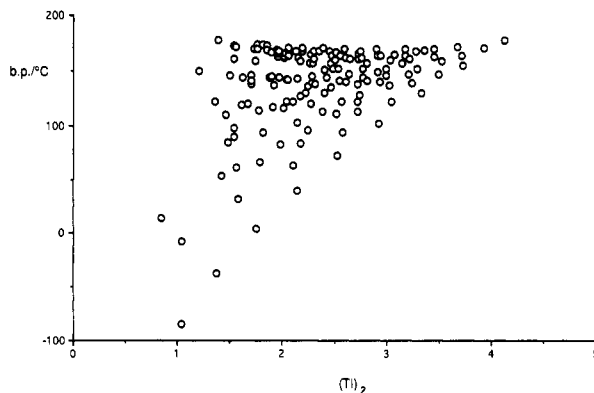
<sup>a</sup> Trees corresponding to octanes are depicted in Figure 4.

#### 4. TOPOLOGICAL INDICES BASED ON THE LAPLACIAN MATRIX

(a) **Wiener Index.** If a graph  $G$  denotes a tree, then the Wiener index of a tree  $T$  can be given in terms of its Laplacian eigenvalues as follows:<sup>8,22,45</sup>

$$W = N \sum_{i=2}^N \frac{1}{x_i} \quad (31)$$

One proof of this formula is recently given in this journal.<sup>45</sup> As an example we give in Table VII the computation of the Wiener index of 2,4-dimethyl-3-ethylheptane.

Figure 6. Plot of bp vs (TI)<sub>2</sub> for the first 149 alkanes.Table XI. Experimental Values for Some Physical Properties of Octanes<sup>a</sup>

octane	BP <sup>b</sup>	MV <sup>c</sup>	MR <sup>d</sup>	HV <sup>e</sup>	CT <sup>f</sup>	CP <sup>g</sup>	ST <sup>h</sup>	MP <sup>i</sup>
a	125.665	162.592	39.1922	41.48	296.20	24.64	21.76	-56.79
b	118.534	160.072	38.9441	39.40	292.00	25.74	21.51	
c	117.709	162.105	39.1174	39.67	290.00	25.60	21.00	-120.95
d	118.925	161.832	39.1001	39.83	292.00	25.60	21.17	-120.50
e	117.647	163.663	39.2316	39.68	288.00	24.80	20.60	-109.04
f	109.103	164.697	39.2596	37.86	279.00	25.00	19.73	-91.20
g	109.429	163.093	39.1300	37.76	282.00	25.80	20.05	-137.50
h	117.725	158.814	38.8453	39.02	298.00	27.40	21.64	
i	115.650	158.794	38.8362	38.52	295.00	27.40	21.52	-114.96
j	115.607	160.395	38.9808	38.79	293.00	26.60	20.99	
k	113.467	158.852	38.8681	37.61	295.00	27.60	21.14	-109.21
l	118.259	157.026	28.7171	37.99	305.00	28.90	21.99	-90.87
m	111.969	160.879	39.0087	37.93	290.84	27.20	20.63	-126.10
n	106.840	164.285	39.2525	37.29	279.00	25.60	19.60	-121.18
o	99.238	165.083	39.2617	35.13	271.15	25.50	18.77	-107.38
p	114.760	157.292	38.7617	37.22	303.00	29.00	21.56	-100.70
q	109.841	159.526	38.9249	36.91	294.00	28.20	20.67	-112.27
r	106.470				270.80	24.50		

<sup>a</sup> Taken from ref 49, p 4186. <sup>b</sup> BP = boiling points in °C. <sup>c</sup> MV = molar volumes in cm<sup>3</sup>/mol at 20 °C. <sup>d</sup> MR = molar refractions in cm<sup>2</sup>/mol at 20 °C. <sup>e</sup> HV = heats of vaporization in kJ/mol at 25 °C. <sup>f</sup> CT = critical temperatures in °C. <sup>g</sup> CP = critical pressures in atm. <sup>h</sup> ST = surface tensions in dyn/cm at 20 °C. <sup>i</sup> MP = melting points in 0 °C.

(b) **Mohar Indices.** Mohar<sup>8</sup> proposed the following two topological indices:

$$(TI)_1 = 2N \log(M/N) \sum_{i=2}^N (1/x_i) \quad (32)$$

$$(TI)_2 = 4/Nx_2 \quad (33)$$

where the symbols have their previous meaning. Since Mohar had "several reasons to strongly believe that these two quantities, especially (TI)<sub>1</sub> correlate high with certain chemical (stability) and physical (thermodynamical) properties" of molecules, we decided to test this statement. However, we note immediately that (TI)<sub>1</sub> of a tree can be given in terms of the Wiener index by using eq 31:

$$(TI)_1 = 2 \log(M/N) W \quad (34)$$

This formula, for example, for octanes reduces to the expression

$$(TI)_1 = -0.11598 W \quad (35)$$

In fact it can be easily seen that each set of isomers will possess the formula similar to eq 35, relating the Mohar (TI)<sub>1</sub> index and the Wiener index. Therefore, Mohar's high expectations concerning (TI)<sub>1</sub> are justified; one can conclude that the (TI)<sub>1</sub> index will be just as good as the Wiener index in the structure-property correlations.

In our recent article on searching for graph invariants of chemical interest<sup>46</sup> we proposed a standard preliminary testing to accompany searching for new invariants. Our view is that

Table XII. Wiener (*W*) and Mohar Indices ((*TI*)<sub>1</sub>, (*TI*)<sub>2</sub>), and Boiling Points (bp, °C) of Alkanes with Up to 10 Carbon Atoms

alkane	<i>W</i>	( <i>TI</i> ) <sub>1</sub>	( <i>TI</i> ) <sub>2</sub>	bp/°C	alkane	<i>W</i>	( <i>TI</i> ) <sub>1</sub>	( <i>TI</i> ) <sub>2</sub>	bp/°C
ethane	1	-0.6021	1.0000	-88.6	2,2,3,3-tetramethylhexane	115	-10.5242	1.9782	158
propane	4	-1.4087	1.3333	-42.1	3-ethyl-2,2,3-trimethylpentane	110	-10.0666	1.5142	168
2-methylpropane	9	-2.2489	1.0000	-11.7	3,3,4,4-tetramethylhexane	111	-10.1582	1.7165	170.5
butane	10	-2.4988	1.7071	-0.5	2,2,3,4,4-pentamethylpentane	111	-10.1582	1.9165	159.29
2,2-dimethylpropane	16	-3.1011	0.8000	9.5	2,2,3,4-tetramethylhexane	118	-10.7988	2.1265	154.9
2-methylbutane	18	-3.4888	1.5420	27.8	3-ethyl-2,2,4-trimethylpentane	115	-10.5242	1.6969	155.3
pentane	20	-3.8764	2.0944	36.1	2,3,4,4-tetramethylhexane	116	-10.6157	1.9847	162.2
2,2-dimethylbutane	28	-4.4342	1.3721	49.7	2,2,3,5-tetramethylhexane	123	-11.2563	2.4396	148.4
2,3-dimethylbutane	29	-4.5925	1.5205	58	2,2,3-trimethylheptane	130	-11.8969	2.7160	158
2-methylpentane	32	-5.0676	2.0521	60.3	2,2-dimethyl-3-ethylhexane	122	-11.1648	1.9785	159
3-methylpentane	31	-4.9092	1.7454	63.3	3,3,4-trimethylheptane	123	-11.2563	2.2611	164
hexane	35	-5.5427	2.4880	69	3,3-dimethyl-4-ethylhexane	118	-10.7988	1.8136	165
2,2,3-trimethylbutane	42	-5.6235	1.4346	80.9	2,3,3,4-tetramethylhexane	115	-10.5242	1.9051	164.59
2,2-dimethylpentane	46	-6.1591	1.9336	79.2	3,4,4-trimethylheptane	122	-11.1648	2.1498	164
3,3-dimethylpentane	44	-5.8913	1.4960	86.1	3,4-dimethyl-3-ethylhexane	117	-10.7073	1.7675	170
2,3-dimethylpentane	46	-6.1591	1.7762	89.8	3-ethyl-2,3,4-trimethylpentane	112	-10.2497	1.4928	169.44
2,4-dimethylpentane	48	-6.4269	1.1326	80.5	2,3,3,5-tetramethylhexane	120	-10.9818	2.2224	153
2-methylhexane	52	-6.9625	2.5354	90	2,3,3-trimethylheptane	127	-11.6224	2.5132	160.1
3-methylhexane	50	-6.6947	2.1951	92	2,3-dimethyl-3-ethylhexane	119	-10.8903	1.8121	169
3-methylpentane	48	-6.4269	1.4960	93.5	3,3-diethyl-2-methylpentane	114	-10.4327	1.3461	174
heptane	56	-7.4980	2.8851	98.4	2,2,4,4-tetramethylhexane	119	-10.8903	2.2537	153.3
2,2,3,3-tetramethylbutane	58	-6.7271	1.4114	106.5	2,2,4,5-tetramethylhexane	124	-11.3479	2.4992	148.2
2,2,3-trimethylpentane	63	-7.3070	1.7313	110	2,2,4-trimethylheptane	131	-11.9885	2.7289	147.7
2,3,3-trimethylpentane	62	-7.1910	1.5690	114.7	2,2-dimethyl-4-ethylhexane	126	-11.5309	2.3594	147
2,2,4-trimethylpentane	66	-7.6549	2.0969	99.2	3,3,5-trimethylheptane	126	-11.5309	2.4599	155.68
2,2-dimethylhexane	71	-8.2349	2.4721	106.8	2,4,4-trimethylheptane	127	-11.6224	2.4270	153
3,3-dimethylhexane	67	-7.7709	1.9702	112	2,4-dimethyl-4-ethylhexane	122	-11.1648	2.1077	158
3-ethyl-3-methylpentane	64	-7.4230	1.3090	118.2	2,2,5,5-tetramethylhexane	127	-11.6224	2.7734	137.46
2,3,4-trimethylpentane	65	-7.5390	1.8660	113.4	2,2,5-trimethylheptane	134	-12.2630	2.9574	148
2,3-dimethylhexane	70	-8.1189	2.2293	115.6	2,5,5-trimethylheptane	131	-11.9885	2.7734	152.8
3-ethyl-2-methylpentane	67	-7.7709	1.6315	115.6	2,2,6-trimethylheptane	139	-12.7206	3.2486	148.2
3,4-dimethylhexane	68	-7.8869	1.9930	117.7	2,2-dimethyloctane	146	-13.3612	3.4844	155
2,4-dimethylhexane	71	-8.2349	2.3399	109.4	3,3-dimethyloctane	138	-12.6291	3.0363	161.2
2,5-dimethylhexane	74	-8.5828	2.6825	109	4,4-dimethyloctane	134	-12.2630	2.6848	157.5
2-methylheptane	79	-9.1627	2.9991	117.6	3-ethyl-3-methylheptane	129	-11.8054	2.4172	163.8
3-methylheptane	76	-8.8148	2.6825	118	4-ethyl-4-methylheptane	126	-11.5309	2.0196	167
4-methylheptane	75	-8.6988	2.5245	117.7	3,3-diethylhexane	121	-11.0733	1.7257	166.3
3-ethylhexane	72	-8.3508	2.0542	118.5	2,3,4,5-tetramethylhexane	121	-11.0733	2.2324	161
octane	84	-9.7426	3.2843	125.7	2,3,4-trimethylheptane	128	-11.7139	2.4782	163
2,2,3,3-tetramethylpentane	82	-8.3890	1.5734	140.27	2,3-dimethyl-4-ethylhexane	123	-11.2563	2.0838	164
2,2,3,4-tetramethylpentane	86	-8.7982	1.8695	133	2,4-dimethyl-3-ethylhexane	122	-11.1648	1.9268	164
2,2,3-trimethylhexane	92	-9.4121	2.1977	131.7	3,4,5-trimethylheptane	125	-11.4394	2.3134	164
2,2-dimethyl-3-ethylpentane	88	-9.0028	1.6587	133.83	2,4-dimethyl-3-isopropylpentane	117	-10.7073	1.4928	157.04
3,3,4-trimethylhexane	88	-9.0028	1.8312	140.5	3-isopropyl-2-methylhexane	124	-11.3479	1.8574	163
2,3,3,4-tetramethylpentane	84	-8.5936	1.6587	141.5	2,3,5-trimethylheptane	131	-11.9885	2.6906	157
2,3,3-trimethylhexane	90	-9.2075	1.9909	137.7	2,5-dimethyl-3-ethylhexane	127	-11.6224	2.2573	157
2,3-dimethyl-3-ethylpentane	86	-8.7982	1.4587	141.6	2,4,5-trimethylheptane	130	-11.8969	2.6053	157
2,2,4,4-tetramethylpentane	88	-9.0028	2.1295	122.7	2,3,6-trimethylheptane	136	-12.4460	2.9895	155.7
2,2,4-trimethylhexane	94	-9.6167	2.3595	126.5	2,3-dimethyloctane	143	-13.0866	3.2369	164.31
2,4,4-trimethylhexane	92	-9.4121	2.1759	126.5	3-ethyl-2-methylheptane	134	-12.2630	2.5535	166
2,2,5-trimethylhexane	98	-10.0259	2.6948	124	3,4-dimethyloctane	137	-12.5376	2.8622	166
2,2-dimethylheptane	104	-10.6397	2.9880	132.7	4-isopropylheptane	131	-11.9885	2.0196	160
3,3-dimethylheptane	98	-10.0259	2.5050	137.3	4-ethyl-3-methylheptane	129	-11.8054	2.1518	167
4,4-dimethylheptane	96	-9.8213	2.2440	135.2	4,5-dimethyloctane	135	-12.3545	2.6906	162.1
3-ethyl-3-methylhexane	92	-9.4121	1.8537	140.6	3-ethyl-4-methylheptane	130	-11.8969	2.3532	167
3,3-diethylpentane	88	-9.0028	1.1636	146.2	3,4-diethylhexane	125	-11.4394	1.9165	162
2,3,4-trimethylhexane	92	-9.4121	2.0986	139	2,4,6-trimethylheptane	135	-12.3545	2.8737	144.8
2,4-dimethyl-3-ethylpentane	90	-9.2075	1.6587	136.73	2,4-dimethyloctane	142	-12.9951	3.1062	153
2,3,5-trimethylhexane	96	-9.8213	2.4281	131.3	4-ethyl-2-methylheptane	134	-12.2630	2.4388	160
2,3-dimethylheptane	102	-10.4351	2.7318	140.5	3,5-dimethyloctane	138	-12.6291	2.9025	160
3-ethyl-2-methylhexane	96	-9.8213	2.0051	138	3-ethyl-5-methylheptane	133	-12.1715	2.5626	158.3
3,4-dimethylheptane	98	-10.0259	2.3865	140.1	2,5-dimethyloctane	143	-13.0866	3.1814	156.8
3-ethyl-4-methylhexane	94	-9.6167	1.9234	140.4	5-ethyl-2-methylheptane	138	-12.6291	2.8737	159.7
2,4-dimethylheptane	102	-10.4351	2.6813	133.5	3,6-dimethyloctane	141	-12.9036	3.1318	160
4-ethyl-2-methylhexane	98	-10.0259	2.2758	133.8	2,6-dimethyloctane	146	-13.3612	3.4116	158.54
3,5-dimethylheptane	100	-10.2305	2.5704	136	2,7-dimethyloctane	151	-13.8188	3.6771	159.87
2,5-dimethylheptane	104	-10.6397	2.8895	136	2-methylnonane	158	-14.4594	3.8880	167
2,6-dimethylheptane	108	-11.0489	3.1930	135.2	3-methylnonane	153	-14.0018	3.6367	167.8
2-methyloctane	114	-11.6628	3.4486	142.8	4-methylnonane	150	-13.7272	3.4116	165.7
3-methyloctane	110	-11.2536	3.1651	143.3	3-ethyloctane	145	-13.2697	3.1318	166
4-methyloctane	108	-11.0489	2.9517	142.4	5-methylnonane	149	-13.6357	3.3163	165.1
3-ethylheptane	104	-10.6397	2.6015	143	4-ethyloctane	141	-12.9036	2.7047	163.637
4-ethylheptane	102	-10.4351	2.2440	141.2	4-propylheptane	138	-12.6291	2.0196	162
nonane	120	-12.2766	3.6848	150.77	decane	165	-15.1000	4.0863	174.119
2,2,3,3,4-pentamethylpentane	108	-9.8836	1.6876	166.05					

the set of 18 octane isomers can serve this purpose. Some other authors have used heptanes for the same purpose; e.g.

see ref 47. Octane isomers show a visible variation in their molecular skeletons (see Figure 4), while they remain all of

the same size, i.e., the same number of atoms and bonds (thus, the size effect is avoided). This is, of course, too narrow a class of molecules. To suggest them for preliminary testing will thus tell little if the use of considered invariants can be extended to more general chemical structures. Nevertheless, if invariants fail to show reasonable correlations with properties of octanes (or any other class of alkanes), they are not likely to be of use in more general situations; thus, the role of this preliminary testing is to filter out unpromising topological indices. However, if the testing is successful, the invariants need to fulfill a number of properties<sup>48</sup> before being considered as a topological index of chemical interest.

The Laplacian polynomials and spectra of octanes are given in Tables VIII and IX.

The values of the Mohar indices for octanes are given in Table X. Table XI contains experimental values (taken from Needham et al.<sup>49</sup>) for boiling points (BP), molar volumes (MV), molar refractions (MR), heats of vaporization (HV), critical temperatures (CT), critical pressures (CP), surface tensions (ST), and melting points (MP) of octanes.

The following algebraic relationships between the Mohar  $(TI)_1$  [or the Wiener index] and  $(TI)_2$  indices and experimental values of octanes have been tested: linear, quadratic, cubic, and the fourth-order polynomial. The regression models were not particularly good judging by their  $s$ - and  $r$ -values, which, according to Randić,<sup>50,51</sup> are criteria for goodness of a regression. However, the above properties are also listed by Randić<sup>51</sup> as "difficult"; i.e., they are hard to represent by a single-variable expression. Therefore, we also tested the two-variable structure-property relationship of the type  $P = a + b(TI)_1 + c(TI)_2$ , where  $P$  = property. The regression models did not improve much.

Finally, we decided to investigate the structure-property relationships when the requirement that the size effect is constant is relaxed. We considered models for boiling points of alkanes with up to 10 carbon atoms (methane was not taken into account because of the obvious reason). The Wiener and Mohar indices and boiling points of the first 150 alkanes are reported in Table XII. The Wiener indices are included in this table because we used them for computing the Mohar  $(TI)_1$  index via eq 34.

We give in Figures 5 and 6 plots of bp vs  $|(TI)_1|$  (i.e., the absolute value of  $(TI)_1$ ) and bp vs  $(TI)_2$ , respectively. The plot of bp vs  $W$  is, of course, identical to the plot in Figure 5.

The statistical characteristics of the quadratic model between bp and  $|(TI)_1|$  are as follows:

$$\text{bp} = 109.6(\pm 10.3) + 17.0(\pm 1.9)|(TI)_1| - 1.4(\pm 0.1)|(TI)_1|^2 \quad (36)$$

$$n = 149; \quad s = 10.0; \quad r = 0.97; \quad F = 1262$$

There is practically no correlation between bp and  $(TI)_2$ . However, it appears that for  $n$  alkanes there is a good correlation between bp and  $(TI)_2$ .

A Walker-type relationship<sup>52</sup>

$$\text{bp} = a(TI)_2^b + c \quad (37)$$

possesses very good statistical characteristics:  $a = 524.8$  ( $\pm 20.8$ ),  $b = 0.288$  ( $\pm 0.009$ ),  $c = -612.8$  ( $\pm 21.0$ ),  $s = 0.47$ ,  $r = 0.999\,990$ , and  $F = 146\,215$ .

It is interesting to note that the correlation between bp of  $n$ -alkanes and  $|(TI)_1|$  is not as good when the Walker-type model given above is used, the standard deviation being 1.39 and the correlation coefficient 0.999 91. A better correlation

is obtained between the  $n$ -alkane boiling points and  $|(TI)_1|$  when the following model is used:

$$\text{bp} = a|(TI)_1| + b)^c + d \quad (38)$$

The statistical characteristics of this model are  $a = 630.6$  ( $\pm 43.3$ ),  $b = 0.532$  ( $\pm 0.029$ ),  $c = 0.131$  ( $\pm 0.007$ ),  $d = -729.7$  ( $\pm 45.5$ ),  $s = 0.14$ ,  $r = 0.999\,9992$  and  $F = 1057\,721$ .

The structure-property model formalized as (38) is also used to correlate bp vs  $N$ , the number of atoms in an  $n$ -alkane. The statistical characteristics of this correlation ( $a = 164.92$  ( $\pm 10.28$ ),  $b = 0.48$  ( $\pm 0.02$ ),  $c = -319.0$  ( $\pm 12.3$ ),  $s = 0.96$ ,  $r = 0.999\,96$ ,  $F = 34\,860$ ) are inferior to structure-property correlations with  $|(TI)_2|$ .

The above results confirm that the boiling point is a difficult property to model and much more involved models are required to increase the accuracy of the prediction, as shown, for example, by Needham et al.<sup>49</sup>

## 5. CONCLUDING REMARKS

This work shows that the Laplacian matrix has a potential for use in chemical graph theory, but not on the same level as the adjacency matrix. The adjacency matrix appears to be more important for applications in chemistry; e.g. see ref 2. In formal graph theory, may as well be so that the Laplacian matrix is more interesting and natural than the adjacency matrix as advocated by Mohar. However, two books on graph-spectral theory by Cvetković et al.<sup>14,15</sup> have shown the versatility of the adjacency matrix which might be difficult to match by any other graph-theoretical matrix.

We have also shown that the Mohar indices are not particularly promising topological indices. In this respect the  $(TI)_2$  index appears to be even less promising than the  $(TI)_1$  index. However, a lot more work is needed with these two indices in a variety of structure-property-activity relationships before it will be possible to give a more definitive answer about their applicability. At present the potentiality of the  $(TI)_1$  index seems to be through its connection with the Wiener index.

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