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LAPLACIAN AND MODIFIED LAPLACIAN MATRICES FOR QUANTIFICATION OF CHEMICAL STRUCTURES

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ABSTRACT. The paper presents the application of Laplacian matrix and its modifications in the characterization of the chemical graphs associated to chemical structures. The eigenvalues of these matrices and some derived topological descriptors were computed. The alkane series C_3 to C_9 was used as the benchmark set in the ordering/discriminating analysis as well as in the QSPR with the normal boiling points.

Keywords: *graphs, Laplacian matrix, chemical structure, topological indices, QSPR*

INTRODUCTION

The chemical formula of a given molecule contains a lot of information which can be directly or, by computational methods, related to topological [1], geometrical [2] and quantum [3,4] descriptors. The basic level of the structural information is the topological one, when the molecule is reduced to a mathematical object called graph *G*, that is a collection of vertices (atoms) and edges (bonds) of the hydrogen depleted molecule (the "molecular" graph [1]). The main relation between the vertices of *G* is the connectivity and, in a first approximation, the nature of atoms is not important. As chemical structures, the molecules have some properties (physical, chemical and biological). At this basic level of molecular modeling, these properties can be correlated with various computed parameters, local and global invariants, the last ones also called topological indices TIs. The topological indices can be computed directly from the molecular graphs [5,6] or better from some matrices associated to molecular graphs [7]. Among the many global invariants calculable from the

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topological matrices, the eigenvalues and eigenvectors of the adjacency matrix **A**(*G*) [8-10] or the distance matrix **D**(*G*) [11,12] are the most studied. Another matrix used to characterize the molecular graphs is the Laplacian matrix **L**(*G*)[13].

Recall the definition of these square matrices of $n \times n$ elements:

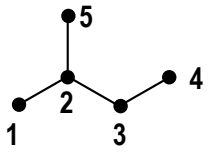
$$[\mathbf{A}(\mathrm{G})]_{ij} = \begin{cases} 1 & \text{if} \quad i \neq j \quad \text{and} \quad (i,j) \in E(G) \\ 0 & \text{if} \quad i = j \quad \text{or} \quad (i,j) \notin E(G) \end{cases} \tag{1}$$

$$\left[\mathbf{D}(G)\right]_{ij} = \begin{cases} \min l(p_{i,j}), \text{if} \quad i \neq j \\ 0 \ \text{if} \quad i = j \end{cases} \tag{2}$$

$$\mathbf{L}(G) = \mathbf{V}(G) - \mathbf{A}(G) \tag{3}$$

In (2) *min* $l(p_{i,j}) = d_{i,j}$ is the minimum length of the path $p_{i,j}$ that joints the atoms *i* and *j*, or the topological distance $d_{i,j}$ measured in the number of edges/bonds on the shortest path between the two atoms. In (3) V(G) is the diagonal matrix of atom valences and **A** is the adjacency matrix.

Let *G* be a graph on 5 vertices/atoms (the molecular graph of 2-Methylbutane, numbered according to IUPAC rules) and **A** the corresponding adjacency matrix (Figure 1); we have the Laplacian matrix **L**(*G*) as in Figure 1, right.

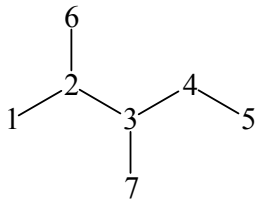


$$\mathbf{A} = \begin{array}{c} \\ 1 \\ 2 \\ 3 \\ 4 \\ 5 \end{array} \begin{array}{c} \begin{array}{ccccc} 1 & 2 & 3 & 4 & 5 \end{array} \\ \left\| \begin{array}{ccccc} 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 1 & 0 & 1 \\ 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \end{array} \right\| \end{array} \begin{array}{c} \text{sum} \\ \left\| \begin{array}{c} 1 \\ 3 \\ 2 \\ 1 \\ 1 \end{array} \right\| \end{array} \qquad \mathbf{L} = \left\| \begin{array}{ccccc} 1 & -1 & 0 & 0 & 0 \\ -1 & 3 & -1 & 0 & -1 \\ 0 & -1 & 2 & -1 & 0 \\ 0 & 0 & -1 & 1 & 0 \\ 0 & -1 & 0 & 0 & 1 \end{array} \right\|$$

Figure 1. A graph on 5 vertices/atoms (2-methylbutane, left) and it's adjacency A (middle) and Laplacian L (right) matrices

Let now consider the remote valences *V*(*r*) as the number of neighbors at distance *d*(*i*,*j*)=*r*, *r*=1,2,...*d*(*G*), where *d*(*G*) is the largest distance in *G*. The sums on the rows of the remote adjacency matrix $\mathbf{A}_r(G)$ are just the *remote valences*. The corresponding graphs/subgraphs can be connected or not. Figure 2 shows examples for the graph associated to 2,3-Dimethylpentane. The matrices $\mathbf{A}_r(G)$ (and their powers) were used to define some others one, mainly based on **L**(*G*) matrix definition[14].

The spectrum *Sp*(**M**) represents the collection of all eigenvalues of the matrix **M**(*G*) (or the solutions of its related polynomial *P*(**M**,*x*)).



2,3-Dimethylpentane

A_1

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

A_2

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

A_3

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

A_4

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

Figure 2. Remote adjacency matrices for the graph of 2,3-dimethylpantane

In this paper, the eigenvalues of **L**(*G*) and its modifications (and some topological indices) were computed on the graphs representing 73 alkanes C_3 to C_9. The calculated TIs were correlated with the values of their boiling points at normal pressure.

RESULTS AND DISCUSSION

Modified matrices and topological indices

Let G be an acyclic graph (tree) with *N* vertices, and **A**, **D**,and **L** the matrices described above. Applying the same method used to define the Laplacian **L** we define the modified laplacian $\mathbf{L_k}$ as follows:

Let $\mathbf{A_k}$ be the k^{th} power of the adjacency matrix:

$$\mathbf{A_k} = \mathbf{A}\times\mathbf{A}\times\mathbf{...}\times\mathbf{A} \ , \ k \text{ times} \tag{4}$$

Let $\boldsymbol{v_k}$ be the vertex valence obtained from $\mathbf{A_k}$ and the corresponding diagonal matrix $\mathbf{V_k}$:

$$\mathbf{V}_k = \{v_{k\,i,j}\} = \begin{cases} 0, & \text{if } i \neq j \\ \sum_{j=1}^{n} a_{k\,i,j}, & \text{if } i = j \end{cases} \tag{5}$$

The modified Laplacian:

$$\mathbf{L}_k = \mathbf{V}_k - \mathbf{A} \tag{6}$$

The matrices $\mathbf{L}_k$ (k=1 to 4) and the eigenvalues and their sum for each graph of the selected alkanes were computed. A first set of topological indices are defined in Table 1. Recall that the first eigenvalue of the Laplacian matrix has already been used to characterize some graph properties [15].

Table 1. New topological indices defined on $\mathbf{L}_k$ matrices: k=1 to 4

No	Definition	TI
1	Le_k	First eigenvalue of L_k matrix
2	Se_k	Sum of all eigenvalues of L_k matrix
3	La_k=Sum(Le_k);$_{k=1\text{ to }4}$	Sum al all first eigenvalues (k=1 to 4)
4	Sa_k=Sum(Se_k);$_{k=1\text{ to }4}$	Sum of all sums (k=1 to 4)

Another way to derive molecular descriptors for the characterization of topological structure of the chemical compounds is based on the remote adjacency matrix $\mathbf{A}_r$ [14] (see above). The algorithm is similar to that described for modified Laplacian matrices $\mathbf{L}_k$ but instead of the powers of **A** matrix we use the corresponding remote adjacency matrices $\mathbf{A}_r$ and the diagonal remote valence $\mathbf{V}_r$ matrix. The new modified Laplacian matrices $\mathbf{L}_r$ are:

$$\mathbf{L}_r = \mathbf{V}_r - \mathbf{A}_r \tag{7}$$

where r represent the r^{th} modification of the Laplacian matrix and r$\in$[1, d_{max}] with d_{max} being a maximum chosen distance in G. Obviously, for r=1, the classical Laplacian matrix $\mathbf{L}(G)$ is recovered.

On $\mathbf{L}_r$ matrix and its eigenvalues λ_i, a new topological index was defined:

$$LaR = \sum_{r=1}^{d_{\max}} \sum_{i=1}^{n} (\lambda_i)^r \tag{8}$$

Note that Diudea [16] computed this index up to $d_{max}=d(G)$, with $d(G)$ being the diameter of the graph (i.e. the largest distance in G). On the other hand, the LaR index values increase with the distance in a graph, so, for large graphs the values became too big to be used in correlations or in topological analysis. We tried some normalizations of this index:

$$LaRd = \frac{LaR}{d_{\max}} \tag{9}$$

$$LaRnd = \frac{LaR}{n \cdot d_{\max}} \tag{10}$$

$$LaRl = \log(LaR) \tag{11}$$

All the computed TIs for the alkanes C_3 to C_9 are listed in Table 2.

Table 2. The topological indices as defined in Table 1 and formulae (9) - (12)

Nr.	Alkane	bp °C	Le1	Se1	Le2	Se2	Le3	Se3	Le4	Se4	La	Sa	LaR	LaRd	LaRnd	LaRl
1	C3	-44.5	3.00	4.00	3.41	6.00	4.73	8.00	5.41	12.00	16.56	30.00	8	4.00	1.33	0.903
2	C4	-0.5	3.41	6.00	4.41	10.00	6.30	16.00	9.24	26.00	23.37	58.00	22	7.33	1.83	1.342
3	2-M-C3	-10.5	4.00	6.00	4.73	12.00	9.46	18.00	10.73	36.00	28.93	72.00	24	12.00	3.00	1.380
4	C5	36.5	3.62	8.00	5.11	14.00	7.53	24.00	12.58	42.00	28.84	88.00	54	13.50	2.70	1.732
5	2M-C4	27.9	4.17	8.00	5.56	16.00	10.53	28.00	15.25	54.00	35.52	106.00	58	19.33	3.87	1.763
6	22MM-C3	9.5	5.00	8.00	6.00	20.00	16.32	32.00	18.00	80.00	45.32	140.00	56	28.00	5.60	1.748
7	C6	68.7	3.73	10.00	5.46	18.00	8.44	32.00	14.24	58.00	31.88	118.00	118	23.60	3.93	2.072
8	3M-C5	63.2	4.30	10.00	6.28	20.00	11.60	38.00	19.56	74.00	41.75	142.00	122	30.50	5.08	2.086
9	2M-C5	60.2	4.21	10.00	6.06	20.00	11.50	36.00	18.44	72.00	40.21	138.00	158	39.50	6.58	2.199
10	23MM-C4	58.1	4.56	10.00	6.56	22.00	12.27	42.00	22.18	86.00	45.58	160.00	126	42.00	7.00	2.100
11	22MM-C4	49.7	5.09	10.00	6.74	24.00	17.34	44.00	23.29	102.00	52.46	180.00	128	42.67	7.11	2.107
12	C7	98.4	3.80	12.00	5.64	22.00	9.12	40.00	15.51	74.00	34.07	148.00	258	43.00	6.14	2.412
13	3E-C5	93.5	4.41	12.00	7.05	24.00	12.66	48.00	24.36	96.00	48.49	180.00	330	82.50	11.79	2.519
14	3M-C6	91.8	4.33	12.00	6.53	24.00	12.55	46.00	20.88	92.00	44.29	174.00	254	50.80	7.26	2.405
15	2M-C6	90	4.23	12.00	6.18	24.00	11.57	44.00	19.49	88.00	41.48	168.00	434	86.80	12.40	2.637
16	23MM-C5	89.8	4.63	12.00	7.17	26.00	13.29	52.00	26.40	108.00	51.48	198.00	276	69.00	9.86	2.441
17	33MM-C5	86	5.16	12.00	7.46	28.00	18.36	56.00	28.55	126.00	59.53	222.00	242	60.50	8.64	2.384
18	223MMM-C4	80.9	5.26	12.00	7.65	30.00	18.40	60.00	31.17	138.00	62.48	240.00	246	82.00	11.71	2.391
19	24MM-C5	80.5	4.41	12.00	6.86	26.00	12.66	48.00	24.25	104.00	48.18	190.00	404	101.00	14.43	2.606
20	22MM-C5	79.2	5.10	12.00	7.12	28.00	18.32	52.00	26.39	122.00	56.93	214.00	406	101.50	14.50	2.609
21	C8	125.8	3.85	14.00	5.75	26.00	9.46	48.00	16.44	90.00	35.49	178.00	526	75.14	9.39	2.721
22	3E-C6	118.9	4.44	14.00	7.19	28.00	13.59	56.00	25.43	114.00	50.64	212.00	674	134.80	16.85	2.829
23	3M-C7	118.8	4.34	14.00	6.58	28.00	12.61	54.00	21.86	108.00	45.39	204.00	606	101.00	12.63	2.782
24	34MM-C6	118.7	4.69	14.00	7.52	30.00	14.28	62.00	28.16	130.00	54.64	236.00	458	91.60	11.45	2.661
25	3E-3M-C5	118.2	5.24	14.00	8.22	32.00	19.37	68.00	34.36	152.00	67.18	266.00	518	129.50	16.19	2.714
26	4M-C7	117.7	4.36	14.00	6.69	28.00	13.49	54.00	22.10	110.00	46.65	206.00	520	86.67	10.83	2.716
27	2M-C7	117.6	4.23	14.00	6.22	28.00	11.58	52.00	20.43	104.00	42.46	198.00	1258	209.67	26.21	3.100
28	3E-2M-C5	115.6	4.69	14.00	7.93	30.00	14.30	62.00	31.26	132.00	58.19	238.00	804	201.00	25.13	2.905
29	23MM-C6	115.3	4.64	14.00	7.28	30.00	13.92	60.00	27.44	126.00	53.28	230.00	620	124.00	15.50	2.792
30	233MMM-C5	114.6	5.32	14.00	8.30	34.00	19.42	72.00	36.38	164.00	69.43	284.00	464	116.00	14.50	2.667
31	234MMM-C5	113.4	4.81	14.00	7.98	32.00	14.59	66.00	33.25	144.00	60.62	256.00	596	149.00	18.63	2.775
32	33MM-C6	112	5.17	14.00	7.65	32.00	19.34	64.00	29.74	146.00	61.90	256.00	552	110.40	13.80	2.742
33	223MMM-C5	110.5	5.28	14.00	8.15	34.00	19.39	70.00	35.34	162.00	68.15	280.00	598	149.50	18.69	2.777
34	24MM-C6	109.4	4.48	14.00	7.07	30.00	13.54	58.00	25.36	124.00	50.44	226.00	712	142.40	17.80	2.852
35	25MM-C6	108.4	4.34	14.00	6.51	30.00	11.81	56.00	21.25	118.00	43.91	218.00	1382	276.40	34.55	3.141
36	22MM-C6	107	5.10	14.00	7.16	32.00	18.33	60.00	27.41	138.00	58.00	244.00	1464	292.80	36.60	3.166
37	2233MMMM-C4	106	5.65	14.00	8.65	38.00	20.23	80.00	41.14	194.00	75.65	326.00	434	144.67	18.08	2.637
38	224MMM-C5	99.3	5.12	14.00	7.79	34.00	19.31	64.00	32.19	156.00	64.42	268.00	928	232.00	29.00	2.968
39	C9	150.6	3.88	16.00	5.81	30.00	9.64	56.00	17.12	106.00	36.45	208.00	1100	137.50	15.28	3.041

Nr.	Alkane	bp °C	Le1	Se1	Le2	Se2	Le3	Se3	Le4	Se4	La	Sa	LaR	LaRd	LaRnd	LaRl
40	33EE-C5	146.2	5.30	16.00	9.03	36.00	20.39	80.00	40.26	180.00	74.98	312.00	1292	323.00	35.89	3.111
41	3E-C7	143	4.44	16.00	7.20	32.00	13.65	64.00	26.40	130.00	51.70	242.00	1710	285.00	31.67	3.233
42	3M-C8	143	4.35	16.00	6.59	32.00	12.61	62.00	22.21	124.00	45.76	234.00	1558	222.57	24.73	3.193
43	4M-C8	142.5	4.37	16.00	6.72	32.00	13.53	62.00	22.98	126.00	47.61	236.00	1000	142.86	15.87	3.000
44	2M-C8	142.5	4.23	16.00	6.23	32.00	11.58	60.00	20.47	120.00	42.52	228.00	3586	512.29	56.92	3.555
45	3E-23MM-C5	141.6	5.38	16.00	9.07	38.00	20.43	84.00	42.26	192.00	77.14	330.00	1084	271.00	30.11	3.035
46	2334MMMM-C5	141.5	5.45	16.00	9.11	40.00	20.48	88.00	44.25	204.00	79.28	348.00	876	219.00	24.33	2.943
47	4E-C7	141.2	4.46	16.00	7.30	32.00	14.53	64.00	26.49	132.00	52.77	244.00	1412	235.33	26.15	3.150
48	3E-3M-C6	140.6	5.24	16.00	8.33	36.00	20.35	76.00	35.39	172.00	69.32	300.00	1040	208.00	23.11	3.017
49	23MM-C7	140.5	4.64	16.00	7.29	34.00	13.96	68.00	28.39	142.00	54.29	260.00	1656	276.00	30.67	3.219
50	334MMM-C6	140.5	5.34	16.00	8.58	38.00	20.40	82.00	37.78	188.00	72.10	324.00	848	169.60	18.84	2.928
51	4E-3M-C6	140.4	4.74	16.00	8.11	34.00	15.29	72.00	32.37	154.00	60.51	276.00	1198	239.60	26.62	3.078
52	2233MMMM-C5	140.3	5.68	16.00	9.23	42.00	21.23	92.00	46.32	222.00	82.45	372.00	878	219.50	24.39	2.943
53	34MM-C7	140.1	4.70	16.00	7.58	34.00	14.90	70.00	29.17	148.00	56.34	268.00	936	156.00	17.33	2.971
54	234MMM-C6	139	4.85	16.00	8.15	36.00	15.42	76.00	34.31	166.00	62.72	294.00	990	198.00	22.00	2.996
55	3E-2M-C6	138	4.70	16.00	8.00	34.00	14.95	70.00	32.28	150.00	59.94	270.00	1930	386.00	42.89	3.286
56	233MMM-C6	137.7	5.33	16.00	8.40	38.00	20.38	80.00	37.41	184.00	71.52	318.00	986	197.20	21.91	2.994
57	33MM-C7	137.3	5.17	16.00	7.67	36.00	19.35	72.00	30.70	162.00	62.89	286.00	1686	281.00	31.22	3.227
58	3E-24MM-C5	136.7	4.87	16.00	8.79	36.00	15.60	76.00	38.19	170.00	67.45	298.00	1822	455.50	50.61	3.261
59	35MM-C7	136	4.52	16.00	7.21	34.00	13.79	68.00	26.47	144.00	52.00	262.00	1096	182.67	20.30	3.040
60	25MM-C7	136	4.41	16.00	6.73	34.00	12.72	66.00	22.95	138.00	46.81	254.00	2238	373.00	41.44	3.350
61	26MM-C7	135.2	4.30	16.00	6.39	34.00	11.67	64.00	21.55	134.00	43.91	248.00	5110	851.67	94.63	3.708
62	44MM-C7	135.2	5.18	16.00	7.79	36.00	20.32	72.00	30.89	166.00	64.18	290.00	1078	179.67	19.96	3.033
63	4E-2M-C6	133.8	4.54	16.00	7.48	34.00	14.55	68.00	27.17	146.00	53.74	264.00	1764	352.80	39.20	3.246
64	3E-22MM-C5	133.8	5.30	16.00	8.87	38.00	20.37	80.00	40.21	188.00	74.76	322.00	1730	432.50	48.06	3.238
65	24MM-C7	133.5	4.49	16.00	7.12	34.00	14.46	66.00	26.35	142.00	52.43	258.00	1780	296.67	32.96	3.250
66	2234MMMM-C5	133	5.33	16.00	8.89	40.00	20.37	84.00	42.19	200.00	76.78	340.00	1224	306.00	34.00	3.088
67	22MM-C7	132.7	5.10	16.00	7.17	36.00	18.33	68.00	28.33	154.00	58.93	274.00	5680	946.67	105.19	3.754
68	223MMM-C6	131.7	5.28	16.00	8.20	38.00	19.41	78.00	36.35	180.00	69.25	312.00	1724	344.80	38.31	3.237
69	235MMM-C6	131.3	4.69	16.00	7.53	36.00	14.74	72.00	28.68	158.00	55.63	282.00	1710	342.00	38.00	3.233
70	244MMM-C6	126.5	5.20	16.00	8.08	38.00	20.32	76.00	33.39	180.00	66.98	310.00	1286	257.20	28.58	3.109
71	224MMM-C6	126.5	5.13	16.00	7.89	38.00	19.32	74.00	33.22	176.00	65.55	304.00	2018	403.60	44.84	3.305
72	225MMM-C6	124	5.10	16.00	7.27	38.00	18.35	72.00	28.45	168.00	59.17	294.00	3974	794.80	88.31	3.599
73	2244MMMM-C5	122.7	5.30	16.00	8.66	42.00	20.39	80.00	40.13	210.00	74.49	348.00	1886	471.50	52.39	3.276

Alkane branching ordering

In a topological analysis, the above defined indices were tested for the branching ordering of graphs. Various ordering of alkanes was reported by Bertz [17], Balaban [18] and others. For instance, the C_7 alkanes (all heptanes) are ordered in an identical way by both Bertz and Balaban J-index. Differences appear in the set of C_8 (all octanes): the J index induces a permutation of values: 2,2-2,3-3,4-dimethyl instead of 2,3-3,4-2,2-dimethyl in comparison to the Bertz index. Our indices reproduce the Bertz ordering for C_7 alkanes and dimethyl-C_6 alkanes. Tables 3 and 4 list these alkanes together with their J-index, Le_k indices, two of sum indices (Se4 and Sa) and LaR index.

Analyzing the data in Tables 3 and 4, one observes that LaR index is not suitable for the branching study due to the random ordering. On the other hand, the values of LaR index increase with the maximum distance taken in computation and also with the degree of branching. The other three indices obtained from LaR have a similar behavior as the original index. This interesting behavior of LaR index and its derivatives is under study and will be analyzed in a further paper [19]. Among the other indices, the first eigenvalue of the second modified Laplacian matrix (Le2) induces the same ordering of heptanes as J index and Bertz index. For dimethyl-hexanes, the same index Le2 behaves similarly to J index, with one permutation in comparison to the Bertz results.

Other two indices (Le1 and Le3) based on the first eigenvalue of corresponding matrices gave the same ordering of the tested molecules as the Bertz data, with a single difference for heptanes: the ordering determined by these indices consider the 3-ethylpentane and 2,4-dimethylpentane as having the same degree of branching (degeneracy of the index values). The same degeneracy is observed in the ordering of heptanes based on the sum of adjacency eigenvalues [10].

The ordering of heptanes based on the fourth index Le4 considers the vicinal branching (2,3-dimethylpentane) as slightly more important than the branching at the given atom (2,2-dimethylpentane). For dimethyl-hexanes one gets another type of inversion: 3,4-2,2-2,3 (compared to the Bertz results: 2,3-3,4-2,2).

Table 3. Topological indices of Heptanes

Alkane	N	J	Le1	Le2	Le3	Le4	La	LaR	Sa	Se4
C7	7	2.448	3.801	5.64	9.12	15.51	34.07	258	148	74
2M-C6	7	2.678	4.228	6.18	11.57	19.49	41.78	434	168	88
3M-C6	7	2.832	4.334	6.53	12.55	20.88	44.29	254	174	92
24-MMC5	7	2.953	4.414	6.86	12.66	24.25	48.18	404	190	104
3E-C5	7	2.992	4.414	7.05	12.66	24.36	48.49	330	180	96
23MM-C5	7	3.144	4.629	7.17	13.29	26.4	51.48	276	198	108
22MM-C5	7	3.155	5.097	7.12	18.32	26.39	56.93	406	214	122
33MM-C5	7	3.360	5.164	7.46	18.36	28.55	59.53	242	222	126
223MMM-C4	7	3.541	5.262	7.65	18.4	31.17	62.48	246	240	138

Table 4. Topological indices of dimethyl-hexanes

Alkane	N	J	Le1	Le2	Le3	Le4	La	LaR	Sa	Se4
2,5-MM-C6	8	2.298	4.34	6.51	11.81	21.25	43.91	1382	218	118
2,4-MM-C6	8	3.099	4.48	7.07	13.54	25.36	50.44	712	226	124
2,3-MM-C6	8	3.171	4.64	7.28	13.92	27.44	53.28	620	230	126
3,4-MM-C6	8	3.293	4.69	7.52	14.28	26.18	54.64	458	236	130
2,2-MM-C6	8	3.112	5.10	7.16	18.33	27.41	58.00	1464	244	138
3,3-MM-C6	8	3.373	5.17	7.65	19.34	29.74	61.90	552	256	146

For the two series of analyzed alkanes, the summative index (Sa – the sum of all first eigenvalues of the $\mathbf{L_k}$ matrices, k=1,2,…,4) as well as Se4 index provide the same ordering as that given by the Bertz theory. One can conclude that all these matrices encode information about size and branching of molecular graphs, as already stated by other authors[15,20].

The indices based on the sum of eigenvalues of $\mathbf{L_k}$ matrices show degeneracy (especially Se and Se2) and they could not be analyzed in the same manner as those corresponding to first eigenvalues. Important exceptions are Sa and Se4 which show only one inversion in heptanes ordering (3-ethylpentane is less branched than 2,4-dimethylpentane), the dimethyl-hexanes ordering being the normal one.

Correlating ability

Despite their ability to discriminate the alkane isomers, the computed topological indices give poor correlation with the normal boiling point of these compounds, similar with the J index (frequently used to discriminate isomers). In correlational studies on chemical or physical properties, the J index is used together with the number of atoms (N) meaning that this index expresses more the shape than the size of molecules. A first statistical analysis is done to determine if there is any correlation between the number of atoms in the set of 73 molecules and our topological indices. The data on correlation between N and topological indices based on the first eigenvalue and of LaR type indices are listed in Table 5.

Table 5. Intercorrelation data

	N	LaR	LaRd	LaRnd	LaRl	Le1	Le2	Le3	Le4	La
N	1.000	0.583	0.610	0.927	0.952	0.548	0.736	0.576	0.693	0.674
LaR	0.583	1.000	0.973	0.763	0.756	0.180	0.204	0.204	0.206	0.209
LaRd	0.610	0.973	1.000	0.809	0.772	0.307	0.343	0.329	0.352	0.351
LaRnd	0.927	0.763	0.809	1.000	0.983	0.570	0.692	0.582	0.658	0.652
LaRl	0.952	0.756	0.772	0.983	1.000	0.472	0.620	0.494	0.575	0.566
Le1	0.548	0.180	0.307	0.570	0.472	1.000	0.897	0.982	0.905	0.952
Le2	0.736	0.204	0.343	0.692	0.620	0.897	1.000	0.885	0.987	0.979
Le3	0.576	0.204	0.329	0.582	0.494	0.982	0.885	1.000	0.895	0.950
Le4	0.693	0.206	0.352	0.658	0.575	0.905	0.987	0.895	1.000	0.990
La	0.674	0.209	0.351	0.652	0.566	0.952	0.979	0.950	0.990	1.000

One can see that none of the indices based on the first eigenvalue of Laplacian and modified Laplacian (Le_k) matrices show a significant correlation with the number of atoms N (i.e. the size of molecules). The value 1.00 is obtained in case of the sum of eigenvalues of the Laplacian matrix, this index clearly encoding the molecular size.

Stronger correlations are between the sum of eigenvalues (La) and the Le1, Le2, Le3, Le4 indices which means that these indices encode similar information and cannot be used together in correlations. The correlation coefficients for the dependency of N with sum indices (Se_k) lie between 0.80 and 1.00.

Among all the computed indices, the best monovariate linear correlation is obtained in case of the logarithm of LaR index (i.e. LaRl index):

$$\mathrm{BP} = 68.000(\pm 3.404) \cdot LaRl - 81.512(\pm 8.393)$$

N=73, R=0.9214, R^2=0.8490, adj R^2=0.8468, F(1,71)=399.05, s=15.84 (12)

The correlations of the normal boiling point of alkanes C_3 to C_9 with the Laplacian matrices derived topological indices are listed below.

Le1 $$\mathrm{BP} = 29.130(\pm 0.665) \cdot N - 6.224(\pm 1.7310) \cdot Le1 - 92.469(\pm 6.902)$$ (13)

N=73, R=0.9863, R^2=0.9729, adj R^2=0.9721, F(2,70)=1255.72, s=6.759

Le2 $$\mathrm{BP} = 28.869(\pm 0.878) \cdot N - 1.756(\pm 1.081) \cdot Le2 - 106.989(\pm 5.486)$$ (14)

N=73, R=0.9844, R^2=0.9690, adj R^2=0.9681, F(2,70)=1095.70, s=7.222

Le3 $$\mathrm{BP} = 29.383(\pm 0.666) \cdot N - 0.962(\pm 0.236) \cdot Le3 - 109.116(\pm 4.415)$$ (15)

N=73, R=0.9869, R^2=0.9740, adj R^2=0.9733, F(2,70)=1312.90, s=6.614

Le4 $$\mathrm{BP} = 29.102(\pm 0.810) \cdot N - 0.306(\pm 0.134) \cdot Le4 - 113.107(\pm 4.763)$$ (16)

N=73, R=0.9849, R^2=0.9701, adj R^2=0.9693, F(2,70)=1135.90, s=7.097

La $$\mathrm{BP} = 29.343(\pm 0.774) \cdot N - 0.230(\pm 0.079) \cdot La - 110.870(\pm 4.604)$$ (17)

N=73, R=0.9856, R^2=0.9714, adj R^2=0.9705, F(2,70)=1187.20, s=6.946

LaR $$\mathrm{BP} = 29.208(\pm 0.689) \cdot N - 0.003(\pm 0.0009) \cdot LaR - 118.871(\pm 4.999)$$ (18)

N=73, R=0.9862, R^2=0.9726, adj R^2=0.9718, F(2,70)=1241.1, s=6.798

The contribution of the number of atom is quite the same in all equations. However, the contribution of topological indices is different. The greatest value of the correlation coefficient is obtained for Le1 index. For the rest of indices, the correlation coefficient values are smaller.

Concerning the degeneracy of the computed topological indices, an analysis has been carried out for the set of 73 alkanes and the computed indices listed in Table 2. In the case of the summative type indices (S type) the degeneracy is high except for Sa (sum of all eigenvalues sums) that shows only three pair of degenerated values: compounds 11 and 13 with Sa=180, compounds 24 and 43 with Sa=236 and compounds 31 and 32 with Sa=256. Three indices have no degeneracy within this set: Le2, Le4 and La. The LaR index and the three other indices based on LaR do not degenerate for the 73 alkanes. The Le3 index has two pairs with the same

value: 13 and 19 with Le3=12.6601 and 40 and 73 with 20.3875. The index based on the first eigenvalue of the Laplacian matrix shows the highest degeneracy, with three pairs: 8 and 61 with Le1=4.3028, 13 and 19 with Le1=4.4142, 23 and 35 with Le1=4.3429 and a triple degeneracy: 40, 64 and 73 with Le1=5.3028.

CONCLUSIONS

In this paper, we studied 14 topological indices computed on 73 molecules (alkane isomers of C_3 to C_9). The Laplacian eigenvalue Le and the LaR index were already used as molecular descriptors[14,16]. The eigenvalues of the modified Laplacian matrices have also been used but only to characterize some special graphs [21] and not in correlating studies. We proved here that these indices present a proper behavior in ordering of alkanes, similar to that provided by Bertz index or Balaban's J index, with minor differences.

Using these descriptors as variables in a correlational analysis, no strong intercorrelation between them and the number of atoms in the structures (except the indices based on the sum of eigenvalues) was observed. They can be used in structure – property analysis to describe the molecular branching, together with N (i.e. the number of heavy atoms) with good results.

The degeneracy of the topological indices is not very high for those based on the first eigenvalue. For the sum-type indices this phenomenon is rather present, excepting for Sa.

The LaR index and other normalized indices do not degenerate within the selected set of alkanes.

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