Walk Numbers $^{e}W_{M}$: Wiener-Type Numbers of Higher Rank†

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Definitions of Wiener ***W***,[1] and hyper-Wiener ***R***[2] numbers are reanalyzed and defined from a matrix-theoretical point of view. Thus, **D** and $\mathbf{W}_1$ (distance and Wiener,[3,4] of paths of length 1) matrices are recognized as a basis for calculating ***W***, whereas $\mathbf{D_P}$ and $\mathbf{W_P}$ (distance-path [this work] and Wiener-path,[4] of paths of any length) are recognized as a basis for the calculation of ***R***. Weighted walk degrees $^{e}W_{M,i}$ generated by an iterative additive algorithm[5] are considered as local vertex invariants (LOVIs) whose half-sum in graph offers walk numbers $^{e}W_{M}$ which are Wiener-type numbers of rank ***e***; for $e = 1$, the classical ***W*** and ***R*** numbers are obtained. New matrix invariants, Δ, $\mathbf{D_P}$ ("combinatorial" matrices constructed on **D**), *K* (of reciprocal $[\mathbf{D_P}]_{ij}$ entries), and $\mathbf{W_U}$ (of unsymmetrical weighted distance) are proposed as a basis for weighting walk degrees and whence for devising novel numbers of Wiener-type.

INTRODUCTION

Wiener[1] has defined his number ***W*** as "the sum of the distances between any two carbon atoms in the molecule, in terms of carbon−carbon bonds". ***W*** number (or the *path number*) can be calculated[1] as the sum of bond contributions W_e of all edges, in an acyclic graph, **G**

$$W = W(G) = \sum_{e} W_e = \sum_{e} \mathbf{N_{L,e}} \cdot \mathbf{N_{R,e}} \tag{1}$$

with

$$\mathbf{N_{L,e}} + \mathbf{N_{R,e}} = \mathbf{N(G)} \tag{2}$$

$\mathbf{N_L}$, $\mathbf{N_R}$ being the number of vertices lying to the left ant to the right of edge **e**, and the summation runs over all edges in **G**.

Lukovits[6−8] extended the "bond contribution" definition (or method of calculation) for cycle-containing graphs, giving for W_e the following relation

$$W_e = \sum_{\mathbf{i<j}} \mathbf{C^e_{ij}}/\mathbf{C_{ij}} \tag{3}$$

where $\mathbf{C_{ij}}$ denotes the number of the shortest paths between vertices **i** and **j**, and $\mathbf{C^e_{ij}}$ is the number of those shortest paths between **i** and **j** which contain the edge **e**.

W can be obtained as the half-sum of entries in the distance matrix **D**, as Hosoya[9] proposed

$$W = (^1/_2)\sum_{\mathbf{i}}\sum_{\mathbf{j}}[\mathbf{D}]_{\mathbf{ij}} \tag{4}$$

relation valid both for acyclic structures and cycle-containing graphs. It is also calculable from the Laplacian eigenvalues, $\mathbf{x_i}$,[10−12] in acyclic structures

$$W = \mathbf{N}\sum_{\mathbf{i}=2}^{\mathbf{N}} 1/\mathbf{x_i} \tag{5}$$

For other definitions, modifications and computational methods of ***W***, the reader can consult two excellent recent reviews.[13,14]

Randić[2] extended the relation (1) for all paths of an acyclic graph, thus resulting a new Wiener-related index, denominated "hyper-Wiener", ***R*** (or ***WW***)[3,4]

$$R = R(G) = \sum_{p} R_p = \sum_{p} \mathbf{N_{L,p}} \cdot \mathbf{N_{R,p}} \tag{6}$$

The path contributions R_p or R_{ij} (**i** and **j** being the endpoints of path **p**) are just the entries in the Wiener matrix $\mathbf{W_P}$[3,4]. Thus, ***R*** can be calculated[4] by

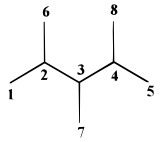
$$R = \sum_{\mathbf{i<j}} [\mathbf{W_P}]_{\mathbf{ij}} \tag{7}$$

a relation which is analoguous to eq 4. When path length equals unity, (case in which the Wiener matrix is denoted by $\mathbf{W_1}$) the relation (7) offers just the Wiener number

$$W = \sum_{\mathbf{i<j}} [\mathbf{W}_1]_{\mathbf{ij}} \tag{8}$$

The Wiener matrices for the graph 234M3C5 (2,3,4-trimethylpentane) are exemplified in Figure 1. Notice that the numbers (*i.e.*, topological indices) are marked here by italic letters, whereas the matrix symbols are marked by right bold letters.

Recall that the eqs 6−8 are valid only for acyclic structures. Lukovits and Linert[6] used the definition (6) to calculate ***R*** for cycles. Klein, Lukovits, and Gutman[15] have



234M3C5

$\mathbf{W_1}$

	1	2	3	4	5	6	7	8
1	0	7	0	0	0	0	0	0
2	7	0	15	0	0	7	0	0
3	0	15	0	15	0	0	7	0
4	0	0	15	0	7	0	0	7
5	0	0	0	7	0	0	0	0
6	0	7	0	0	0	0	0	0
7	0	0	7	0	0	0	0	0
8	0	0	0	7	0	0	0	0

$\mathbf{W_P}$

	1	2	3	4	5	6	7	8
1	0	7	5	3	1	1	1	1
2	7	0	15	9	3	7	3	3
3	5	15	0	15	5	5	7	5
4	3	9	15	0	7	3	3	7
5	1	3	5	7	0	1	1	1
6	1	7	3	5	1	0	1	1
7	1	3	7	3	1	1	0	1
8	1	3	5	7	1	1	1	0

Figure 1. $\mathbf{W_1}$ and $\mathbf{W_P}$ matrices for the graph 234M3C5 (2,3,4-trimethylpentane).

† This work is dedicated to professor Milan Randić for his bright contribution to the development of chemical graph theory.

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decomposed $\boldsymbol{R}$ by a relation equivalent to

$$\boldsymbol{R} = (\mathbf{Tr}(\mathbf{D}^2)/2 + \boldsymbol{W})/2 \tag{9}$$

where $\mathbf{Tr(D^2)}$ is the trace of distance matrix raised at the second power (and is twice D_2 or unnormalized second moment of distance, in ref 15). The relation (9) becomes valid for cycle-containing graphs when $\boldsymbol{W}$ is evaluated by the Hosoya relation.[9]

NEW MATRIX INVARIANTS

Randić has stated[16] that matrix graph invariants can be taken as a rational ground for defining numerical graph invariants, also called topological indices. In this respect, we propose here four new matrices, defined by their entries

$$[\Delta]_{\mathbf{ij}} = \binom{[\mathbf{D}]_{\mathbf{ij}}}{2} \tag{10}$$

$$[\mathbf{D}_\mathrm{P}]_{\mathbf{ij}} = \binom{[\mathbf{D}]_{\mathbf{ij}} + 1}{2} \tag{11}$$

$$[\mathbf{K}]_{\mathbf{ij}} = 1/[\mathbf{D_P}]_{\mathbf{ij}} \tag{12}$$

$$[\mathbf{W}_{\mathrm{U}(\mathrm{M}_1,\mathrm{M}_2,\mathrm{M}_3)}]_{\mathbf{ij}} = {}^{[\mathrm{M}_2]_{\mathbf{ij}}}\boldsymbol{W}_{M_1,i}[\mathbf{M}_3]_{\mathbf{ij}} \tag{13}$$

We limit here to a matrix defined on the **A**, **D**, and **D** matrices

$$[\mathbf{W}_{\mathrm{U(A,D,D)}}]_{\mathbf{ij}} = {}^{[\mathrm{D}]_{\mathbf{ij}}}\boldsymbol{W}_{A,i}[\mathbf{D}]_{\mathbf{ij}} \tag{14}$$

which herein will be denoted simply $\mathbf{W_U}$. Their meaning is as follows: $[\Delta]_{\mathbf{ij}}$ count all paths of length larger than unity included into a path (or distance) **(i,j)**; $[\mathbf{D_P}]_{\mathbf{ij}}$ (distance path) count all paths included into a path (or distance) **(i,j)**; $[\mathbf{K}]_{\mathbf{ij}}$ the reciprocal of the entries in the $\mathbf{D_P}$ matrix; $[\mathbf{W_U}]_{\mathbf{ij}}$ are unsymmetrical weights (*i.e.*, the classical walk degree of vertex **i,** of rank equaling $[\mathbf{D}]_{\mathbf{ij}}$) of a path **(i,j)**. Note that the three "combinatorial" matrices are symmetrical, whereas the last one is nonsymmetrical.

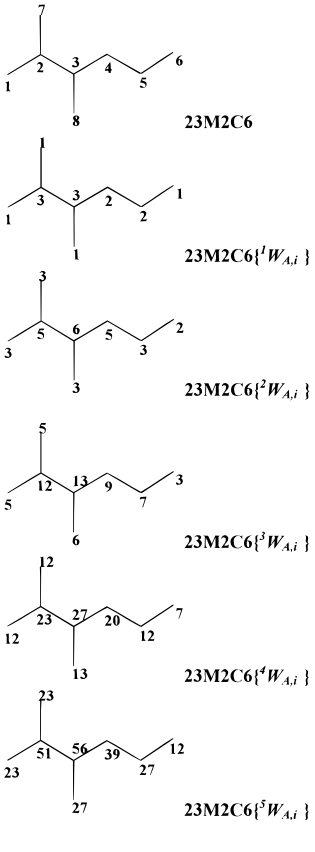
It is easy to reconstruct the graph from the matrices Δ, $\mathbf{D_P}$, and $\mathbf{W_U}$**:** the adjacency is given by nondiagonal zeros, unity, and smallest entries in row, respectively. Figure 2 illustrates the Δ, $\mathbf{D_P}$, and $\mathbf{W_U}$ matrices for the graph 23M2C6 (2,3-dimethylhexane), along with its weighted graphs 23M2C6 $\{{}^e\boldsymbol{W}_{A,i}\}$.

WALK NUMBERS ${}^e\boldsymbol{W}_M$

Walk W in a graph $\mathbf{G = G(V,E)}$ (with $\mathbf{V = V(G)}$ − the set of vertices and $\mathbf{E = E(G)}$ − the set of edges) is defined[17] as **a continuous sequence of vertices, $\mathbf{v_1, v_2, ..., v_m}$, ; it is** allowed edges and vertices to be **revisited**. If the two terminal vertices coincide ($\mathbf{v_1 = v_m}$), the walk is called a closed (or self-returning) walk, otherwise it is an open walk. If its vertices are distinct, the walk is called a path. The number **e** of edges traversed is called the elongation or length of walk. Walks of length **e,** starting at the vertex $\mathbf{i} \in \mathbf{V(G)}$ can be counted by summing the entries in the row **i** of the $\mathbf{e}^{th}$ power of the adjacency matrix **A**

$${}^e\boldsymbol{W}_i = \sum_{\mathbf{j}\in\mathbf{V(G)}}[\mathbf{A}^\mathbf{e}]_{\mathbf{ij}} \tag{15}$$

${}^e\boldsymbol{W}_i$ is called the **walk degree** (of rank **e**) of vertex **i** (or atomic walk count[18]). Local and global invariants based on walks in graph were considered for correlating with physicochemical properties.[5,18]



Δ

	1	2	3	4	5	6	7	8
1	0	0	1	3	6	10	1	3
2	0	0	0	1	3	6	0	1
3	1	0	0	0	1	3	1	0
4	3	1	0	0	0	1	3	1
5	6	3	1	0	0	0	6	3
6	10	6	3	1	0	0	10	6
7	1	0	1	3	6	10	0	3
8	3	1	0	1	3	6	3	0

$\mathbf{D_P}$

	1	2	3	4	5	6	7	8
1	0	1	3	6	10	15	3	6
2	1	0	1	3	6	10	1	3
3	3	1	0	1	3	6	3	1
4	6	3	1	0	1	3	6	3
5	10	6	3	1	0	1	10	6
6	15	10	6	3	1	0	15	10
7	3	1	3	6	10	15	0	6
8	6	3	1	3	6	10	6	0

$\mathbf{W_U}$

	1	2	3	4	5	6	7	8
1	0	1	6	15	48	115	6	15
2	3	0	3	10	36	92	3	10
3	12	3	0	3	12	39	12	3
4	27	10	2	0	2	10	27	10
5	48	21	6	2	0	2	48	21
6	60	28	9	4	1	0	60	28
7	6	1	6	15	48	115	0	15
8	18	6	1	6	18	52	18	0

Figure 2. Graph 23M2C6 (and weighted graphs 23M2C6$\{{}^e\boldsymbol{W}_{A,i}\}$) and its matrices Δ, $\mathbf{D_P}$, and $\mathbf{W_U}$.

Weighted walk degrees can be easily calculated by means of the algorithm proposed by Diudea *et al.*[5] It evaluates a local (topological) property by iterative summation of vertex contributions over all neighbors (see also[18−20])

$$\mathbf{M} + {}^\mathbf{e}\mathbf{W} = {}^\mathbf{e}\mathbf{W_M} \tag{16}$$

$$[{}^{\mathbf{e}+1}\mathbf{W_M}]_{\mathbf{ii}} = \sum_\mathbf{j}([\mathbf{M}]_{\mathbf{ij}}[{}^\mathbf{e}\mathbf{W_M}]_{\mathbf{jj}}); \quad [{}^0\mathbf{W_M}]_{\mathbf{jj}} = 1 \tag{17}$$

$$[{}^{\mathbf{e}+1}\mathbf{W_M}]_{\mathbf{ij}} = [{}^\mathbf{e}\mathbf{W_M}]_{\mathbf{ij}} = [\mathbf{M}]_{\mathbf{ij}} \tag{18}$$

where **M** is a square matrix and ${}^\mathbf{e}\mathbf{W}$ is a diagonal matrix of walk degrees. Equation 18 means that the off diagonal entries of ${}^\mathbf{e}\mathbf{W_M}$ matrix do not change during the iteration and are just the entries of **M** matrix.

The diagonal entries $[{}^\mathbf{e}\mathbf{W_M}]_{\mathbf{ii}}$ represent the sum of elements of the matrix $\mathbf{M}^\mathbf{e}$ on the row **i**, or weighted walk degrees, ${}^e\boldsymbol{W}_{M,i}$

$$[{}^\mathbf{e}\mathbf{W_M}]_{\mathbf{ii}} = \sum_{\mathbf{j}\in\mathbf{V(G)}}[\mathbf{M}^\mathbf{e}]_{\mathbf{ij}} = {}^e\boldsymbol{W}_{M,i} \tag{19}$$

and the global value ${}^e\boldsymbol{W}_M$ will be a **Walk number of rank e**

$${}^e\boldsymbol{W}_M = {}^e\boldsymbol{W}_M\boldsymbol{(G)} = (1/2)\sum_\mathbf{i}{}^e\boldsymbol{W}_{M,i} \tag{20}$$

where the subscript **M** denotes the square matrix used for weighting the walk.

When $\mathbf{M = D}$ then ${}^e\boldsymbol{W}_\mathbf{D}$ denotes a **Wiener-(Hosoya)** number; when $\mathbf{M = W_1}$, then ${}^e\boldsymbol{W}_{\mathbf{W1}}$ represents a **Wiener-(Wiener)** number; when $\mathbf{M = W_P}$, then ${}^e\boldsymbol{W}_{\mathbf{WP}}$ denotes a

Table 1. Topological Indices in Octane Isomers: M = Methyl; E = Ethyl

graph	^1W_D	^2W_D	$^1W_{W1}$	$^2W_{W1}$	$^1W_{WP}$	$^2W_{WP}$	$^1W_{DP}$	$^2W_{DP}$
C8	84	1848	84	2100	210	12054	210	12726
2MC7	79	1628	79	2000	185	9829	185	9711
3MC7	76	1512	76	1892	170	8338	170	8256
4MC7	75	1476	75	1848	165	7815	165	7830
3EC6	72	1360	72	1740	150	6460	150	6412
25M2C6	74	1420	74	1900	161	7825	161	7171
24M2C6	*71*	1312	*71*	1792	147	6536	147	6023
23M2C6	70	1280	70	1748	143	6163	143	5772
34M2C6	68	1208	68	1684	134	5426	134	5050
3E2MC5	*67*	1172	*67*	1640	129	4992	129	4646
22M2C6	*71*	1316	*71*	1808	149	6779	149	6277
33M2C6	*67*	1176	*67*	1664	131	5221	131	4878
234M3C5	65	1096	65	1648	122	4700	122	4076
3E3MC5	64	1072	64	*1564*	118	4222	118	3916
224M3C5	66	1128	66	1708	127	5165	127	4406
223M3C5	63	1032	63	1600	115	4220	115	3653
233M3C5	62	1000	62	*1564*	111	3917	111	3402
2233M4C4	58	868	58	1516	97	3169	97	2521

hyper-Wiener-(Randić) number. Thus, $^eW_{M,i}$ represent local vertex invariants (**LOVI**s) whose half-sum over all vertices in graph provides Wiener-type numbers.

We enlarge the set of Wiener-type walk numbers by those constructed on Δ, $\mathbf{D_P}$, **K**, **H** ("the Harary" matrix, of the reciprocal distances), and $\mathbf{W_U}$ matrices, *i.e.*, the $^eW_\Delta$, $^e\mathbf{W_{DP}}$ (a hyper-Wiener number—see below), ^eW_K, ^eW_H, and $^eW_{WU}$ numbers.

Walk numbers of rank 1 and 2 are listed in Tables 1 and 2 for the octane isomers. The degenerate values are italicized.

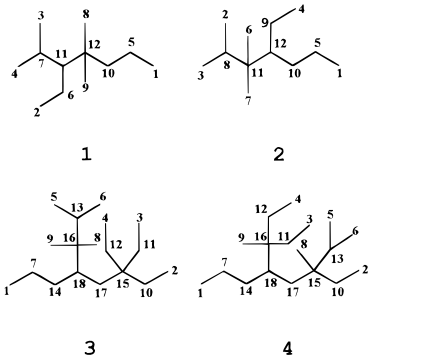
In view of testing the discriminating ability of the novel walk indices, two pairs of graphs which show pairwise identical distance degree sequence[21,22] were selected (Figure 3). The results are listed in Table 3.

NEW DEFINITION OF HYPER-WIENER NUMBER

We define $\boldsymbol{R}$ on the basis of $\mathbf{D_P}$ matrix as

$$\boldsymbol{R} = \sum_{\mathbf{i<j}} [\mathbf{D}_\mathrm{P}]_{\mathbf{ij}} = \sum_{\mathbf{i<j}} \binom{[\mathbf{D}]_{\mathbf{ij}}+1}{2} \tag{21}$$

its meaning being the number of all paths included into all shortest paths in graph. The expansion of the right member



Distance Degree sequence :

Graph 1 and 2 :

27; 27; 29; 33; 33; 35; 41; 43; 43; 43; 45; 51.

Graph 3 and 4 :

43; 45; 49; 49; 55; 61; 63; 63; 63; 65; 65; 69; 77; 77; 79; 79; 79; 85.

Figure 3. Pairs of graphs having identical distance degree sequence.[21,22]

enables the decomposition of $\boldsymbol{R}$ into two terms

$$\boldsymbol{R} = \sum_{\mathbf{i<j}} [\mathbf{D}]_{\mathbf{ij}} + \sum_{\mathbf{i<j}} \binom{[\mathbf{D}]_{\mathbf{ij}}}{2} \tag{22}$$

where the former term is just the Wiener number $\boldsymbol{W}$. The latter term is the "non-Wiener" part of the hyper-Wiener number, which is denoted by Δ (after the Δ matrix)

$$\Delta = \sum_{\mathbf{i<j}} [\Delta]_{\mathbf{ij}} = \sum_{\mathbf{i<j}} \binom{[\mathbf{D}]_{\mathbf{ij}}}{2} \tag{23}$$

It signifies the number of all paths (larger than unity) included into all shortest paths (larger than unity) in graph. Thus, $\boldsymbol{R}$ can be written as

$$\boldsymbol{R} = \boldsymbol{W} + \Delta \tag{24}$$

or in walk number notation

$$^1\boldsymbol{W}_{\mathbf{Dp}} = {}^1\boldsymbol{W}_{\mathbf{D}} + {}^1\boldsymbol{W}_{\Delta} \tag{25}$$

and the corresponding matrix relation

$$\mathbf{D_P} = \mathbf{D} + \Delta \tag{26}$$

Table 2. Topological Indices in Octane Isomers: M = Methyl; E = Ethyl

graph	^1W_H	^2W_H	^1W_K	^2W_K	$^1\boldsymbol{W}_\Delta$	$^2\boldsymbol{W}_\Delta$	$^1W_{WU}$	$^2W_{WU}$
C8	13.74286	48.27930	10.56429	29.03985	126	4998	1181	459906
2MC7	14.10000	51.05028	10.86191	31.15268	106	3473	1072	305722
3MC7	14.26667	52.49472	10.98095	32.12544	94	2780	803	196874
4MC7	14.31669	52.94667	11.01429	32.41052	90	2586	783	193619
3EC6	14.48334	54.37695	11.13333	33.37334	*78*	1924	569	94465
25M2C6	14.46666	53.93945	11.16667	33.34333	87	2259	752	165174
24M2C6	14.65000	55.56028	11.30000	34.45445	76	1759	653	123690
23M2C6	14.73334	56.31723	11.36667	35.02445	73	1668	599	103799
34M2C6	14.86667	57.48166	11.46667	35.84667	66	1362	517	78179
3E2MC5	14.91668	57.92361	11.50001	36.12445	62	1186	471	62066
22M2C6	14.76666	56.49972	11.43333	35.42556	*78*	1903	721	146162
33M2C6	15.03333	58.87751	11.63333	37.10667	64	1312	553	87420
234M3C5	15.16668	59.88889	11.73333	37.79111	57	970	482	65468
3E3MC5	15.25001	60.79167	11.79999	38.49333	54	924	388	42172
224M3C5	15.16666	59.77084	11.76667	37.91111	61	1102	643	114858
223M3C5	15.41667	62.04167	11.96667	39.62111	52	829	454	57150
233M3C5	15.50000	62.79862	12.03334	40.19111	49	738	383	40650
2233M4C4	16.0000	67.0000	12.50000	43.74999	39	441	322	27406

Table 3. Walk Numbers ${}^{e}W_{M}$ (of Rank 1−3) for the Graphs **1**−**4**

	e	1	2	3	4
${}^{e}W_{D}$	**1**	196	196	583	583
	2	6692	6692	39173	39173
	3	227288	227252	2625203	2625299
${}^{e}W_{W1}$	**1**	196	196	583	583
	2	10686	10686	70137	70097
	3	592184	592292	9051023	9066815
${}^{e}W_{\Delta}$	**1**	254	254	1055	1055
	2	13215	13175	142874	142874
	3	666113	661463	19164920	19169360
${}^{e}W_{DP}$	**1**	450	450	1638	1638
	2	38171	38119	329089	329089
	3	3186855	3176484	65720352	65729760
${}^{e}W_{WP}$	**1**	450	450	1638	1638
	2	45940	45946	464101	463865
${}^{e}W_{H}$	**1**	29.33333	29.35001	55.23572	55.23572
	2	149.82250	150.01529	353.43560	353.43560
	3	762.56399	764.13899	2258.69928	2258.66741
${}^{e}W_{K}$	**1**	20.74287	20.76191	35.48334	35.48334
	2	79.35440	79.53998	154.70112	154.70112
	3	300.62484	301.76187	671.90912	671.89416
${}^{e}W_{WU}$	**1**	3780	3491	33851	33896
	2	2979036	2373482	155875988	155261932

For linear graphs, Δ can be expressed as

$$\boldsymbol{\Delta_N = W_1 + W_2 + ... + W_{N-1}} \tag{27}$$

a relation analoguous to that reported by Lukovits[23] for $\boldsymbol{R}$ number. The number Δ can be related to the $\mathbf{Tr(D^2)}$ by

$$\Delta = (\mathbf{Tr(D^2)} - 2\boldsymbol{W})/4 \tag{28}$$

FORMULAS FOR *W*, Δ, AND *R* NUMBERS IN SIMPLE CYCLES

The examination of **D,** Δ, and $\mathbf{D_P}$ matrices of the simple cycles (of **N** vertices) leads to the following combinatorial formulas for $\boldsymbol{W_N}$, Δ_N, and $\boldsymbol{R_N}$

$$\boldsymbol{W_N} = \mathbf{N}\binom{(\mathbf{N}-\mathbf{z}+2)/2}{2} - \mathbf{(1-z)}\frac{\mathbf{N}^2}{4} \tag{29}$$

$$\Delta_N = \mathbf{N}\sum_{\mathbf{i}=1}^{(\mathbf{N}-\mathbf{z}-2)/2}\binom{\mathbf{i}+1}{2} - \mathbf{(1-z)}\frac{\mathbf{N}}{2}\binom{\mathbf{N}/2}{2} \tag{30}$$

$$\boldsymbol{R_N} = \mathbf{N}\sum_{\mathbf{i}=1}^{(\mathbf{N}-\mathbf{z})/2}\binom{\mathbf{i}+1}{2} - \mathbf{(1-z)}\frac{\mathbf{N}}{2}\binom{\mathbf{N}/2+1}{2} \tag{31}$$

where $\mathbf{z} = 1$ when **N** is odd and $\mathbf{z} = 0$ when **N** is even.

The expansion of the above relations gives

$$\boldsymbol{W_N} = [\mathbf{N}^3 + \mathbf{N(z}^2 - 2\mathbf{z)}]/8 \tag{32}$$

$$\Delta_N = \mathbf{(N}^2 - \mathbf{z)(N}^2 - 3\mathbf{N} + 2 - 2\mathbf{z)}/48 \tag{33}$$

$$\boldsymbol{R_N} = \{\mathbf{N}^4 + 3\mathbf{N}^3 + \mathbf{(}2 - 3\mathbf{z)N}^2 + \mathbf{z[(}2\mathbf{z} - 3\mathbf{)(}3\mathbf{N} + 1\mathbf{)} + 1]\}/48 \tag{34}$$

Recurrences for the next term in a homologous series of simple cycles are easily derived

$$\boldsymbol{W_{N+1}} = \boldsymbol{W_N} + \frac{\boldsymbol{W_N}}{\mathbf{N}} + \binom{\mathbf{N}+1}{2}\binom{\mathbf{N}+\mathbf{z}}{2} = \boldsymbol{W_N} + \boldsymbol{W_{e+1}} \tag{35}$$

$$\Delta_{N+1} = \Delta_N + \frac{\Delta_N}{\mathbf{N}} + \binom{\mathbf{N}+1}{2}\binom{(\mathbf{N}+\mathbf{z})/2}{2} = \Delta_N + \Delta_{e+1} \tag{36}$$

$$\boldsymbol{R_{N+1}} = \boldsymbol{R_N} + \frac{\boldsymbol{R_N}}{\mathbf{N}} + \binom{\mathbf{N}+1}{2}\binom{(\mathbf{N}+\mathbf{z})/2+1}{2} = \boldsymbol{R_N} + \boldsymbol{R_{e+1}} \tag{37}$$

where it is obvious that

$$\boldsymbol{R_{e+1}} = \boldsymbol{W_{e+1}} + \Delta_{e+1} \tag{38}$$

The quantities $\boldsymbol{W_{e+1}}$, Δ_{e+1}, and $\boldsymbol{R_{e+1}}$ represent the edge contribution of the newly introduced edge, $\boldsymbol{e}+\mathbf{1}$, within the corresponding number. From the eqs 37 and 38 it is easily seen that

$$\boldsymbol{R_{N+1}} = \boldsymbol{R_N} + \boldsymbol{R_{e+1}} = \boldsymbol{W_{N+1}} + \Delta_{N+1} = \boldsymbol{W_N} + \boldsymbol{\Delta_N} + \mathbf{W}_{e+1} + \Delta_{e+1} \tag{39}$$

DISCUSSION

We discuss here the two main definitions of Wiener number, $\boldsymbol{W}$: (*i*) as sum of "bond contributions" and (*ii*) as half-sum of the entries in the **D** matrix. In our opinion, Wiener's original definition[1] of $\boldsymbol{W}$ (as "sum of the distances" between any two atoms in the molecule) does not express the meaning of eq 1 (which defines the bond contributions whose sum gives the number $\boldsymbol{W}$). Wiener's definition rather accounts for the eq 4, and it is the merit of Hosoya[9] to express that definition in graph-theoretical terms. He replaced the term "distance" with "shortest path" so that the definition (eq 4) is valid for any graph. In fact, "bond contributions" represent the sum of all "external" paths passing through a given edge **e**, whose sum in **G** (cf. eq 1) equals the sum of all "internal" paths (of length 1) included in all paths **(i,j)** in **G** (cf. eq 4), as stated Klein, Lukovits, and Gutman.[15]

In defining the hyper-Wiener number $\boldsymbol{R}$, Randić[2] extended the definition *(i)*−*eq*(1) by replacing the term bond with path, and summation running over all paths in **G** (cf. eq 6). The use of Wiener matrices, $\mathbf{W_P}$ and $\mathbf{W_1}$ for defining $\boldsymbol{R}$ and $\boldsymbol{W}$ numbers (cf. eqs 7 and 8) does not bring anything new, since they are constructed on the ground of eqs 1 and 6 (*i.e.*, the "bond/path contributions"). Thus, the quantities $\sum_{\mathbf{i}<\mathbf{j}}[\mathbf{W_1}]_{\mathbf{ij}}$ and $\sum_{\mathbf{i}<\mathbf{j}}[\mathbf{W_p}]_{\mathbf{ij}}$, count all the "external" paths passing through any path **(i,j)**, of length **1** and |**(i,j)**|, respectively. Note that eqs 1 and 6−8 are valid only for acyclic structures.

Klein, Lukovits, and Gutman[15] have recently given a new definition for $\boldsymbol{R}$, as half-sum of $\boldsymbol{W}$ and half of trace of square **D** matrix, $\mathbf{Tr(D^2)}$, (eq 9). Since the definition is based on **D** matrix, it is valid both for acyclic and cycle-containing structures. However, $\mathbf{Tr(D^2)}$ is not a quantity, but a result of operator application, so that the meaning of eq 9 is not so transparent.

Our definition of $\boldsymbol{R}$ (eq 21) is based, in fact, by eq 6 in ref 15, combinatorial matrix rearranged. $\mathbf{D_P}$ (eq 11) is the first matrix which enables the direct calculation of $\boldsymbol{R}$ in any graph. Formally, the definition of $\boldsymbol{R}$ cf. eq 21 is analoguous to Hosoya's definition of $\boldsymbol{W}$, cf. eq 4. Thus, the quantities $\sum_{\mathbf{i}<\mathbf{j}}[\mathbf{D}]_{\mathbf{ij}}$ and $\sum_{\mathbf{i}<\mathbf{j}}[\mathbf{D_P}]_{\mathbf{ij}}$ count all distinct "internal" paths (of length 1, and lower than |**(i,j)**|, respectively), included into any path **(i,j)**, in **G**.

Although the overall sums of the "internal" and "external" paths are identical, they count distinct quantities. This fact

is reflected in the entries of the corresponding matrices and results in different walk numbers of rank higher than one (*i.e.*, different Wiener-numbers of higher rank). Thus, any graph shows $^{1}W_D = {}^{1}W_{W1}$ and $^{1}W_{DP} = {}^{1}W_{WP}$ but different walk numbers of rank two $^{2}W_M$ (see below and Tables 1 and 3). As a consequence, the composition of R (eq 25) is not maintained between the corresponding walk numbers of rank 2 (*i.e.*, $^{2}W_{DP} \neq {}^{2}\mathbf{W}_{\mathrm{D}} + {}^{2}\mathbf{W}_{\Delta}$).

By using a known combinatorial property, R can be split into two terms (eqs 22 and 24), one being the classical Wiener number W and the second, the "non-Wiener" part of hyper-Wiener number R, denoted by Δ. Equation 24 represent the first *linear decomposition* of R and eqs 25 and 26 its walk number and matrix transcription, respectively. The number Δ gets the status of a Wiener-type number, both by its matrix definition (eq 23) and participation to the composition of hyper-Wiener number (eq 24). It correlates 0.99975 with R. Δ can be related to $\mathbf{Tr(D^2)}$ as in eq 28.

Formulas and recurrences for the evaluation of W, Δ and R numbers in simple cycles were derived. Note that eqs 32 and 34 are equivalent to those reported in ref 15.

The idea of Wiener-type indices of higher rank raised from the following facts: (*i*) the occurrence of degeneracy (since C7 isomers) among the values of classical Wiener indices; (*ii*) the higher rank Wiener indices ^{k}W, (*i.e.*, Wiener numbers counting all paths of length $k = 1, 2, 3,...$), proposed by Randić[4] show no good separating ability (*i.e.*, a spectrum of values is necessary for discriminating pairs of isomers like 2,2-dimethylhexane (^{k}W sequence: 71, 43, 22, 10, 3) and 2,4-dimethylhexane (^{k}W sequence: 71, 43, 22, 9, 2)); and (*iii*) the use of a square matrix ($\mathbf{D^2}$) in the definition of R (eq 9).

The algorithm[5] given in eqs 16−19 offers walk degrees of various ranks $^{e}W_{M,i}$, whose half-sum in **G** (*i.e.*, walk numbers $^{e}W_M$) are just Wiener-type indices of rank e. The subscript **M** denotes the matrix on which the algorithm runs, thus giving walk degrees weighted with the property collected into that matrix. In fact, the above algorithm eludes the raising at power e of the matrix **M**, and in addition puts into the light the significance of the walk degree $^{e}W_{M,i}$: it equals the sum of walk degrees of rank $e-1$ of all first neighbors of vertex **i**. Usually a rank of two suffices in discriminating, i.e., the octane isomers (Tables 1 and 2). Special graphs, like those illustrated in Figure 3, need however a rank higher than two (see Table 3).

The graphs **1** to **4** were selected for testing the separating ability of walk numbers. They were designed[21,22] to show identical pairwise distance degree sequence, **DDS** (*i.e.*, the sequence of sums on row of entries in **D** or in walk notation $^{1}W_D\ S$). Moreover, these graphs show identical sequence for various $^{1}W_{M,i}$ descriptors. The immediate consequence of this fact is the pairwise degeneracy of the corresponding Wiener-type numbers. The results are listed in Table 3.

The pair **1** and **2** shows the following identical sequences: $^{1}W_A\ S$, $^{1}W_D\ S$, $^{1}W_{W1}\ S$, $^{1}W_{\Delta}$ S, $^{1}W_{WP}\ S$, and $^{1}W_{DP}\ S$ but different sequences $^{1}W_H\ S$, $^{1}W_K\ S$ (*i.e.*, walk numbers which count reciprocal quantities) and $^{1}W_{WU}S$ (the vector of an unsymmetrical matrix). These graphs show identical walk numbers of rank 1, $^{1}W_M$ (and also degenerate numbers MTI[24] = 704 and J[25] = 4.25251). The identity is maintained even for the walk numbers of rank 2, $^{2}W_D$ and $^{2}W_{W1}$, but not for $^{2}W_{\Delta}$, $^{2}W_{DP}$, and $^{2}W_{WP}$.

The graphs **3** and **4** are even more similar, showing identical walk numbers of rank 1, $^{1}W_M$ for all the properties (and also identical $MTI = 2108$ and $J = 5.01668$) except the unsymmetrical weighted distance (*i.e.*, the $^{1}W_{WU}$ number). These graphs show the following identical walk numbers of rank two: $^{2}W_D$, $^{2}W_{\Delta}$, $^{2}W_{DP}$, $^{2}W_H$, and $^{2}W_K$ (*i.e.*, those properties based on **D** and its derived matrices, Δ and $\mathbf{D_P}$) but different $^{2}W_{W1}$ and $^{2}W_{WP}$. This result suggests that the count of "external" paths (by means of $\mathbf{W_1}$ and $\mathbf{W_P}$ matrices) within the pair **3** and **4** is more different than the count of "internal" paths (given by the distance-based matrices). Finally, all walk numbers of rank 3 succeeded in separating these isomers.

As shown above, the basis of walk numbers is represented by square matrices. Indeed, the newly proposed matrices (eqs 10−14) enlarge that basis, and all together enlarge the basis of graph/molecular descriptors useful in QSPR/QSAR studies.

Among the novel matrices herein proposed $\mathbf{W_U}$ deserves a special attention. It is a nonsymmetrical matrix which, in a particular definition cf eq 14 has the meaning of a weighted distance. The weight is given by the classical walk degree of one of the two endpoints **(i,j)** (see also ref 26). Properties of such matrices will be discussed in a future paper.

It is known that the Wiener number shows good correlation with several physicochemical and biological properties.[14,27]

Walk numbers, as the classical W, exhibit good correlation with octane numbers, ON:[16] $^{1}W_D$ (0.9569); $^{2}W_D$ (0.9660); $^{1}W_{\Delta}$ (0.9566); $^{2}W_{\Delta}$ (0.9682); $^{2}W_{DP}$ (0.9685) in single variable regression and in two variables one, 0.99099 with $^{2}W_{\Delta}$ and $^{1}W_{WU}$. The walk number $^{1}W_{WU}$ exhibits a correlation of 0.9733 *vs* van der Waals cavity areas of heptane isomers (see ref 28). Further investigation of correlating capability of walk numbers is in progress.

CONCLUSIONS

Wiener W and hyper-Wiener R numbers were reanalyzed about their intrinsic meaning, by considering the matrices on which they are constructed. Thus distance-based matrices, **D** and $\mathbf{D_P}$ (counting "internal" bonds/paths of any path **(i,j)** in **G**) provide W and R, respectively, for any graph whereas the matrices based on "bond/path contributions", $\mathbf{W_1}$ and $\mathbf{W_P}$ (which count "external" paths of any bond/path in **G**) give W and R, particularly for acyclic structures.

Hyper-Wiener number R was decomposed into two terms: the classical W and Δ number, as the non-Wiener part of R. Δ and R can be directly calculated by means of Δ and $\mathbf{D_P}$ matrices, whose elements are combinatorial constructed from the entries of **D** matrix.

Walk numbers $^{e}W_M$ are Wiener-type numbers (of rank **e**) constructed on any square matrix **M** by means of an additive algorithm which eludes the raising at a power **e** the matrix **M**. They can serve for correlation studies or for discriminating pairs of nonisomorphic graphs which show degenerate values of the classical Wiener-numbers. The best separating ability was shown by the unsymmetrical matrix $\mathbf{W_U}$ whose walk number of rank one, $^{1}W_{WU}$ suffices for solving pairs of graphs with identical distance degree sequences.

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