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Molecular Topology 23*. Novel Schultz Analogue Indices

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Abstract: *Novel Schultz analogue indices: DI and HI are defined via matrix algebra, by using weighted (with distance and reciprocal distance, respectively) walk degrees. They are related to the well known indices: molecular topological index, **MTI**, Wiener index, W and hyper-Wiener index, R, and numerical comparisons are made for the set of octane isomers and other selected graphs.*

Introduction.

In 1989 Schultz has introduced the so called Molecular Topological Index, MTI (known also as the Schultz index), by the relation [89Sch]

$$MTI = MTI(G) = \sum_{i=1}^{N} |v(A + D)|_i \qquad (1)$$

where A and D are the adjacency and the distance matrices, respectively and $v = (v_1, v_2, \ldots, v_N)$ is the vector of the vertex valencies / degrees in the graph G. This index has received much attention from both its originator [90Sch, 91Sch, 92Sch1, 92Sch2, 93Sch1, 93Sch2, 94Sch] and other scientists [92Kle, 92Mih, 93Pla, 94Gut].

* part. 22, ref. [95Diu].

By applying the matrix algebraic operations, the MTI can be decomposed [92Mih, 93Sch2, 94Gut] as

$$MTI = \sum_{i=1}^{N}\sum_{j=1}^{N}[A^2 + AD]_{ij} = A_2 + S_D \qquad (2)$$

where

$$A_2 = A_2(G) = \sum_{i=1}^{N}\sum_{j=1}^{N}[A^2]_{ij} = \sum_{i=1}^{N}(v_i)^2 \qquad (3)$$

$$S_D = S_D(G) = \sum_{i=1}^{N}\sum_{j=1}^{N}[AD]_{ij} \qquad (4)$$

The term A_2 represents the sum of the entries of the square adjacency matrix and equals the squares of the vertex valencies in G. It is a well known graph invariant [75Gut, 94Gut, 83Tri] but trivially related to the molecular structure. The nontrivial part of MTI is the term S_D, for which Gutman [94Gut] found some interesting relations, *i.e.*

$$S_D = \sum_{i=1}^{N} v_i DS_i = \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}[v_i + v_j]D_{ij} \qquad (5)$$

where DS_i stands for the sum of distances from the vertex i to all vertices of G.

For acyclic structures, there is a linear correlation between the quantity S_D and the Wiener index, W [94Gut]

$$S_D = 4W - N(N-1) \qquad (6)$$

and also between MTI and W [92Klc]

$$MTI = 4W + 2P_2 - (N-1)(N-2) \qquad (7)$$

where P_2 is the number of paths of length 2 (or the number of Platt [47Pla], or also the number of Gordon - Scantlebury [64Gor]).

Recall that the Wiener index, in acyclic structures, can be calculated [47Wie] by

$$W = \sum_{e} N_{L,e} N_{R,e} \tag{8}$$

where

$$N_{L,e} + N_{R,e} = N(G) \tag{9}$$

$N_{L,e}$, $N_{R,e}$ being the number of vertices lying to the left ant to the right of edge e, and the summation runs over all edges of acyclic graph G.

Randić [93Ran] extended the definition (8) for all paths of G, thus resulting a new Wiener - related index, denominated " hyper-Wiener ", R :

$$R = \sum_{p} N_{L,p} N_{R,p} \tag{10}$$

$N_{L,p}$, $N_{R,p}$ being the number of vertices to the left ant to the right of the two ends of the path p, and the sum is over all paths of G.

Note that none of the eqs (6) to (10) holds for cycle-containing graphs.

Very recently, Klein, Lukovitz and Gutman [95Kle] gave the straight relation between R and W

$$R = [MOM(D^2) + W]/2 \tag{11}$$

where $MOM(D^2)$ is the unnormalized second moment of distance. When W is calculated by Hosoya relation [71Hos]

$$W = W(G) = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} [D]_{ij} \tag{12}$$

it is obvious that eq (11) also holds for cycle-containing graphs.

In this paper, two Schultz analogue indices are proposed and compared with the well-know W, MTI and R indices, within the octane isomers and other selected graphs.

Distance Walk Degrees and the Wiener Index

A walk, $W^{(e)}$ is a continuous sequence of edges $e \in E(G)$ [83Tri]; it is allowed that its edges and vertices to be revisited. The number (e) of edges traversed is called the length of walk. The number of walks, of length (e), starting at the vertex i is called the walk degree, $W_i^{(e)}$ [94Diu] (or atomic walk count [92Iva, 93Rüc]). This quantity can be easily obtained [69Har] from the e^{th} power A^e of the adjacency matrix, as

$$W_i^{(e)} = \sum_{j \in V(G)} [A^e]_{ij} \qquad (13)$$

Walk degrees $W_i^{(e)}$ can be also evaluated from vertex degrees / valences v_i (which equal the walk degree of elongation 1, $W_i^{(e)}$) by iterative summation over all neighbours, as Morgan [65Mor] proposed for his extended connectivities, ECs. Several authors [82Raz, 93Rüc, 93Fig] demonstrated the identity between EC_i and $W_i^{(e)}$. In a recent paper, [94Diu1], we presented an additive algorithm which, implemented on the adjacency matrix (or other quadratic topological matrix), offers walk degrees (or weighted walk degrees) of various length. When the base matrix is D, a matrix $(D)W^{(e)}$ is defined, as the sum between D and a diagonal matrix, $W^{(e)}$ (of walk degrees) :

$$D + W^{(e)} = (D)W^{(e)} \qquad (14)$$

whose elements are

$$[(D)W^{(e+1)}]_{ii} = \sum_j ([D]_{ij} * [(D)W^{(e)}]_{jj}); \qquad [(D)W^{(0)}]_{jj} = 1 \qquad (15)$$

$$[(D)W^{(e+1)}]_{ij} = [(D)W^{(e)}]_{ij} = [D]_{ij} \qquad (16)$$

The diagonal entries $[(D)W^{(e)}]_{ii}$ represent the sum of elements of the matrix D^e on the row i, or the " distance walk " degrees, $(D)W_i^{(e)}$

$$[(D)W^{(e)}]_{ii} = \sum_{j \in V(G)} [D^e]_{ij} = (D)W_i^{(e)} \qquad (17)$$

and the global value, ^eW, will be a Wiener number of rank e

$$^eW = ^e W(G) = \frac{1}{2}\sum_i (D)W_i^{(e)} \qquad (18)$$

Note that $(D)W_i^{(1)}$ equals the distance sum DS_i.

When the base matrix is that with elements the reciprocals of distances (denoted here H, in the honour of Frank Harary, [93Iva1]) the resultant weighted walk we denote by $(H)W_i^{(e)}$. In this case, the eq (18) becomes

$$^eH = ^e H(G) = \frac{1}{2}\sum_i (H)W_i^{(e)} \qquad (19)$$

with ^eH being the Harary number (of rank e).

Schultz analogue indices

By using the walk degree vector $W^{(1)} = (W_1^{(1)}, W_2^{(1)}, \ldots, W_N^{(1)})$, the Schultz index can be written as

$$MTI = MTI(G) = \sum_{i=1}^{N} [W^{(1)}(A + D)]_i \qquad (20)$$

Now it is conceivable to substitute, in eq. (20), the vector $W^{(1)}$ by the weighted walk degree vectors $(D)W^{(1)}$ and $(H)W^{(1)}$ (and their corresponding matrices), to obtained two indices : DI and HI, respectively

$$DI = DI(G) = \sum_{i=1}^{N} [(D)W^{(1)}(A + D)]_i \qquad (21)$$

$$HI = HI(G) = \sum_{i=1}^{N} [(H)W^{(1)}(A + H)]_i \qquad (22)$$

For DI, eq (21) can be expanded as

$$DI = \sum_{i=1}^{N} [(1,1,\ldots,1)D(A + D)]_i = \sum_{i=1}^{N}\sum_{j=1}^{N} [DA + D^2]_{ij} = S_D + 2^2W \qquad (23)$$

where S_D is the same quantity as in MTI (see eqs (2) and (4)), with the specification that, in nonsymmetric graphs, it equals the arithmetic mean of the sums on the matrix product both to the left and to the right of A and D matrices. When the vector is $(H)W^{(1)}$, the eq. (22) becomes

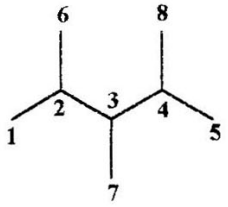
$$HI = \sum_{i=1}^{N}\sum_{j=1}^{N} [HA + H^2]_{ij} = S_H + 2^2H \qquad (24)$$

where S_H is a quantity similar to S_D. By considering eqs (6) and (24), the eq (23) can be written as

$$DI = S_D + 2^2W = 4^1W - N(N-1) + 2^2W = 2[2^1W - \binom{N}{2} + {}^2W] \qquad (25)$$

which is a result comparable to eq (7). However, eq (6) can not be extended for calculating the quantity S_H, questioning that it is of general validity. FIGURE 1 exemplifies the calculation of the two indices, DI and HI.

FIGURE 1. Calculation of DI and HI for the graph 234M3C5 (2,3,4-trimethylpentane).



234M3C5

	$(D)W^{(1)}$	A + D							
		1	2	3	4	5	6	7	8
1	19	0	2	2	3	4	2	3	4
2	13	2	0	2	2	3	2	2	3
3	11	2	2	0	2	2	2	2	2
4	13	3	2	2	0	2	3	2	2
5	19	4	3	2	2	0	4	3	2
6	19	2	2	2	3	4	0	3	4
7	17	3	2	2	2	3	3	0	3
8	19	4	3	2	2	2	4	3	0
	DI_i	328	272	238	272	328	328	302	328

(a) $DI = \sum_i [(D)W^{(1)}(A+D)]_i = \sum_i DI_i = 2396$

(b) $DI = [\ (1/2)\ (\ \sum_i \sum_j [DA]_{ij} + \sum_i \sum_j [AD]_{ij}\ )\ ] + \sum_i \sum_j [D^2]_{ij} =$

$= [\ (1/2)\ (\ 256 + 152\ )\ ] + 2192 =$

$= 204 + 2192 = 2396$

(c) $DI = S_D + 2^2W = 4^1W - N(N-1) + 2^2W =$

$= 4*65 - 8(8-1) + 2*1096 =$

$= 204 + 2192 = 2396$

FIGURE 1 (continued)

	$(H)W^{(1)}$	A + H							
		1	2	3	4	5	6	7	8
1	3.16667	0.000	2.000	0.500	0.333	0.250	0.500	0.333	0.250
2	4.66667	2.000	0.000	2.000	0.500	0.333	2.000	0.500	0.333
3	5.00000	0.500	2.000	0.000	2.000	0.500	0.500	2.000	0.500
4	4.66667	0.333	0.500	2.000	0.000	2.000	0.333	0.500	2.000
5	3.16667	0.250	0.333	0.500	2.000	0.000	0.250	0.333	0.500
6	3.16667	0.500	2.000	0.500	0.333	0.250	0.000	0.333	0.250
7	3.33333	0.333	0.500	2.000	0.500	0.333	0.333	0.000	0.333
8	3.16667	0.250	0.333	0.500	2.000	0.500	0.250	0.333	0.000
	HI_i	17.667	28.779	31.668	28.779	17.667	17.667	18.889	17.667

(a) $HI = \sum_i [(H)W^{(1)}(A+H)]_i = \sum_i HI_i - 178.77778$

(b) $HI = [(1/2) (\sum_i \sum_j [HA]_{ij} + \sum_i \sum_j [AH]_{ij})] + \sum_i \sum_j [H^2]_{ij} =$

$= [(1/2) (65.66668 + 52.33332)] + 2 * 59.88889 =$

$= 59.00000 + 119.77778 = 178.77778$

(c) $HI = S_H + 2^2H \neq 4^1H - N(N-1) + 2^2H =$

$= 4 * 15.16668 - 8(8-1) + 2 * 59.88889 =$

$= 4.66672 + 119.77778 = 124.44450$

Numerical results

The novel indices were calculated for the set of octane isomers and compared with the well known indices : Wiener, W, hyper-Wiener, R, and Schultz, MTI (TABLE **1** and **2**). The intercorrelating matrix of these indices within the set of octanes is given in TABLE **3**.

TABLE 1. Topological indices in octane isomers : M = methyl; E = ethyl.

	^1W	^2W	S_D	DI	^1H	^2H	S_H	HI
C8	84	1848	280	3976	13.74286	48.27930	49.78565	146.34425
2MC7	79	1628	260	3516	14.10000	51.05028	52.16633	154.26689
3MC7	76	1512	248	3272	14.26667	52.49472	53.02004	158.00948
4MC7	75	1476	244	3196	14.31669	52.94667	53.36657	159.25991
3EC6	72	1360	232	2952	14.48334	54.37695	54.29989	163.05379
25M2C6	74	1420	240	3080	14.46666	53.93945	54.59980	162.47870
24M2C6	71	1312	228	2852	14.65000	55.56028	55.63319	166.75375
23M2C6	70	1280	224	2784	14.73334	56.31723	55.85813	168.49259
34M2C6	68	1208	216	2632	14.86667	57.48166	56.89984	171.86316
3E2MC5	67	1172	212	2556	14.91668	57.92361	56.29156	172.13878
22M2C6	71	1316	228	2860	14.76666	56.49972	56.69974	169.69918
33M2C6	67	1176	212	2564	15.03333	58.87751	58.23310	175.98812
234M3C5	65	1096	204	2396	15.16668	59.88889	59.00000	178.77778
3E3MC5	64	1072	200	2344	15.25001	60.79167	59.49985	181.08319
224M3C5	66	1128	208	2464	15.16666	59.77084	59.33315	178.87483
223M3C5	63	1032	196	2260	15.41667	62.04167	60.83316	184.91650
233M3C5	62	1000	192	2192	15.50000	62.79862	61.33311	186.93035
2233M4C4	58	868	176	1912	16.0000	67.0000	64.99982	198.99982

The above mentioned indices were tested for correlation with four physico-chemical properties of octanes : boiling points (BP), enthalpy (ΔHF), critical pressure (CP) and molar volume (MV) (TABLE **2**). The monovariable regression statistics are given in TABLE **4**.

TABLE 2. Topological indices and physico-chemical properties in octane isomers

	MTI	R	BP[a]	ΔHF[b]	CP[c]	MV[d]
C8	306	210	125.8	-49.90	24.54	162.605
2MC7	288	185	117.6	-51.47	24.52	163.653
3MC7	276	170	118.8	-50.79	25.13	161.845
4MC7	272	165	117.7	-50.66	25.09	162.120
3EC6	260	150	118.9	-50.36	25.74	160.076
25M2C6	270	161	108.4	-53.18	24.54	164.715
24M2C6	258	147	109.4	-52.40	25.23	163.093
23M2C6	254	143	115.3	-51.10	25.94	160.413
34M2C6	246	134	118.7	-50.87	26.57	158.653
3E2MC5	242	129	115.6	-50.44	26.65	158.807
22M2C6	260	149	107.0	-53.67	24.96	164.289
33M2C6	244	131	112.0	-52.58	26.19	160.887
234M3C5	236	122	113.4	-51.19	26.94	158.851
3E3MC5	232	118	118.2	-51.35	27.71	157.039
224M3C5	242	127	99.3	-53.54	25.34	165.096
223M3C5	230	115	110.5	-52.57	26.94	159.517
233M3C5	226	111	114.6	-51.69	27.83	157.298
2233M4C4	214	97	106.0	-53.95	28.30	138.595

(a) Boiling Points, from ref. [93Bal]; (b) Enthalpy, from ref. [91Ran1]; (c) Critical Pressure, from ref. [93Bal]; (d) Molar Volume, calculated from molecular weight and densities, ref. [94Ran].

Table 3. Intercorrelation matrix within the set of octane isomers

	^1W	^2W	DI	S_D	^1H	^2H	HI	S_H	MTI	R
^1W	1.00000	0.99810	0.99856	1.00000	0.98777	0.98741	0.98431	0.97332	0.99853	0.99718
^2W		1.00000	0.99999	0.99840	0.98068	0.97933	0.97617	0.96507	0.99783	0.99910
DI			1.00000	0.99856	0.98111	0.97981	0.97666	0.96556	0.99794	0.99908
S_D				1.00000	0.98777	0.98741	0.98431	0.97332	0.99853	0.99718
^1H					1.00000	0.99974	0.99963	0.99602	0.97856	0.97392
^2H						1.00000	0.99961	0.99530	0.97861	0.97305
HI							1.00000	0.99761	0.97428	0.96891
S_H								1.00000	0.96029	0.95552
MTI									1.00000	0.99877
R										1.00000

Table 4. Monovariable regression statistics.

	TI	BP	AHF	CP	MV
1	^1W	0.53122	0.49706	0.88429	0.62783
2	^2W	0.55224	0.50746	0.86388	0.59476
3	DI	0.55121	0.50697	0.86498	0.59648
4	S_n	0.53122	0.49706	0.88429	0.62783
5	^1H	0.56700	0.56916	0.87529	0.67590
6	^2H	0.55061	0.55513	0.88449	0.68665
7	HI	0.56366	0.57347	0.87588	0.68401
8	S_H	0.59411	0.61699	0.85160	0.67519
9	MTI	0.50028	0.45732	0.89220	0.61839
10	R	0.52798	0.47613	0.87060	0.59226

TABLE 5 lists the statistics of the two variable regression. This table includes a compact index, DIFMTI, which is the residual of DI *vs.* MTI (see refs. [91Ran1,91Ran2]).

Four additional graphs (1 to 4, FIGURE 2) were chosen to test the discriminating ability of the novel indices, by comparison with other known indices: the Schultz indices MTI and S_n, the Balaban index J [82Bal] and our centric index [94Diu1,94Diu2], constructed on layer matrices of weighted walk degrees, $C(L(D)W^{(e)})$ and $C(L(H)W^{(e)})$ according to eq

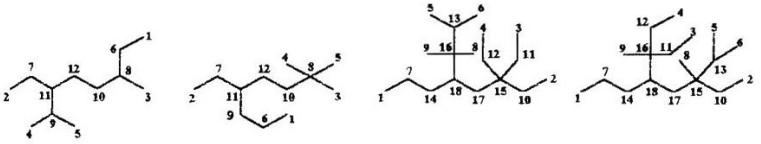
$$C(LM) = \sum_{i=1}^{N}\left[\sum_{j=1}^{ecc_i}([LM]_{ij})^{j/dsp}\right]^{-1} \qquad (26)$$

where M stands for the type of the layer matrix ($(D)W^{(e)}$ and $(H)W^{(e)}$, respectively), $[LM]_{ij}$ are the elements of the layer matrix LM, ecc_i is the eccentricity of vertex **i** and **dsp** is a specified topological distance, usually larger than the diameter of the graph (here **dsp** = 20). The graphs 1 to 4 are labelled in the canonical ordering given by $L(D)W^{(1)}$ [94Diu2] (*i.e.* a more central vertex labelled by a larger number). The results are listed in TABLE 6.

Table 5. Two variable regression statistics.

Y=BP	X_1	X_2	R	S	F
1	DI	MTI	0.95251	2.01109	73.378
2	^{2}W	MTI	0.94836	2.09479	67.044
3	^{1}W	MTI	0.76979	4.21538	10.909
4	R	MTI	0.75842	4.30436	10.155
5	DI	A_2	0.74832	4.38078	9.545
6	^{2}W	A_2	0.74735	4.38801	9.489
7	S_D	A_2	0.76979	4.21538	10.909
8	S_D	^{2}W	0.65709	4.97829	5.699
9	DIFMTI	^{1}W	0.95510	1.95660	77.945
10	DIFMTI	^{2}W	0.95235	2.01453	73.126
11	DIFMTI	^{1}H	0.95790	1.89598	83.496
12	DIFMTI	^{2}H	0.95794	1.89519	83.573
13	DIFMTI	HI	0.95734	1.90830	82.325
Y=ΔHF					
14	DI	^{1}W	0.53502	1.11577	3.008
15	DI	^{2}W	0.53502	1.11577	3.008
16	DI	R	0.87091	0.64905	23.554
17	DI	HI	0.62449	1.03150	4.795
18	DI	MTI	0.91288	0.54150	37.114
19	^{1}W	MTI	0.87549	0.63820	24.618
20	R	MTI	0.60092	1.05564	4.239
21	R	^{1}W	0.56118	1.09313	3.448
Y=CP					
22	DI	^{1}W	0.94592	0.41316	63.770
23	DI	^{2}W	0.94592	0.41316	63.770
24	DI	R	0.87781	0.61008	25.187
25	DI	HI	0.87701	0.61195	24.987
26	DI	MTI	0.97609	0.27684	51.248
27	^{1}W	MTI	0.90050	0.55386	32.159
28	R	MTI	0.98295	0.23417	214.367
29	R	^{1}W	0.88177	0.60076	26.209
30	R	^{2}W	0.88177	0.60076	26.209
31	DIFMTI	^{1}W	0.98103	0.24693	192.024
32	DIFMTI	^{1}H	0.98858	0.19196	322.677
33	DIFMTI	^{2}H	0.98828	0.19441	314.406
34	DIFMTI	HI	0.98787	0.19777	303.542
Y=MV					
35	DI	^{1}W	0.84595	3.32702	18.873
36	DI	^{2}W	0.84595	3.32702	18.873
37	^{1}W	^{2}W	0.84595	3.32702	18.873
38	DI	R	0.60261	4.97883	4.277
39	DI	MTI	0.69711	4.47306	7.090
40	HI	MTI	0.71646	4.35242	7.910
41	^{1}W	MTI	0.64726	4.75569	5.408
42	^{2}W	MTI	0.70495	4.42499	7.409
43	^{1}H	MTI	0.70744	4.40948	7.514
44	^{2}H	MTI	0.73437	4.23466	8.779
45	R	MTI	0.80192	3.72733	13.513
46	R	^{1}W	0.77285	3.95915	11.124

FIGURE 2. $W^{(1)}$, $(D)W^{(1)}$ and $(H)W^{(1)}$ sequences in the graphs 1 to 4 (labelled in the canonical ordering given by $L(D)W^{(1)}$ - see text)



1 2 3 4

$W^{(1)}$ **sequence :**

Graph 1 : 1, 1, 1, 1, 1, 2, 2, 2, 2, 3, 3, 3

Graph 2 : 1, 1, 1, 1, 1, 2, 2, 2, 2, 2, 3, 4

Graph 3 and 4 : 1, 1, 1, 1, 1, 1, 1, 1, 2, 2, 2, 2, 2, 2, 3, 3, 4, 4

$(D)W^{(1)}$ **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.

$(H)W^{(1)}$ **sequence :**

Graph 1 :

3.37857; 3.59286; 3.81667; 3.84286; 3.84286; 4.48333;
4.81667; 5.25000; 5.41667; 5.43333; 5.48333; 6.03333.

Graph 2 :

3.32857; 3.56667; 3.95952; 3.95952; 3.95952; 4.36667;
4.76667; 5.01667; 5.36667; 5.41667; 5.90000; 5.91667.

Graph 3 and 4 :

4.39524; 4.74524; 4.74524; 4.74524; 4.99524; 4.99524; 5.63333; 5.63333; 5.66667;
6.30000; 6.30000; 6.30000; 6.68333; 6.96667; 7.58333; 8.25000; 8.26667; 8.26667.

TABLE 6. Topological indices (TIs) for the graphs 1 to 4

TI	1	2	3	4
S_D	768	768	2026	2026
^1W	225	225	583	583
^2W	8778	8778	39173	39173
^3W	340843	340939	2625203	2625299
DI	18324	18324	80372	80372
S_H	109.25714	109.99047	229.33809	229.33809
^1H	27.69523	27.76191	55.23572	55.23572
^2H	132.30896	132.87408	353.43560	353.43560
^3H	630.55058	634.27632	2258.69928	2258.66741
HI	373.87506	375.73863	936.20929	936.20929
MTI	816	818	2108	2108
J	3.57526	3.57526	5.01668	5.01668
$C(L(D)W^{(1)})$	1.00403	1.02266	1.15383	1.15375
$C(L(D)W^{(2)})$	0.49014	0.50396	0.48045	0.48047
$C(L(D)W^{(3)})$	0.23076	0.23997	0.19278	0.19280
$C(L(H)W^{(1)})$	1.52377	1.54493	1.89667	1.89628
$C(L(H)W^{(2)})$	1.14077	1.15834	1.31404	1.31325
$C(L(H)W^{(3)})$	0.85073	0.86722	0.90670	0.90660

* **dsp** = 20 (see text).

Discussion

The Schultz analogue indices, DI and HI, are constructed (eqs (21) and (22)) on the basis of weighted walk degrees, $(D)W^{(1)}$ and $(H)W^{(1)}$, respectively, by following Schultz's original formula (eq (1)). This extension of the vertex degree / valency resulted in composition formulas (eqs (23) and (25) equivalent to that for MTI (eq (2)). The difference is that DI and HI enhance the contribution of the large distances in the graph whereas in MTI adjacency is more important. DI shows decreasing values as the molecular branching increases), which parallel those of the Wiener-type indices, ^1W and ^2W and also those of MTI (see TABLE 1). In the opposite sense, the HI values (and the corresponding ^1H and ^2H ones) show values which increases as the branching increases. Their corresponding local values, Di_i and Hi_i (*i.e.*

the elements of the product between the walk degree vector and the sum of matrices) can serve for vertex ordering .

As mentioned above, HI can not be expressed by an equation similar to eq (6) (see FIGURE 1) so that the HI values are available only by matrix calculation.

The above discussed indices are highly interrelated within the set of octane isomers (TABLE 3). They show a rather poor correlation (TABLE 4) with four of the physico-chemical properties of octanes : boiling points (BP), enthalpy of formation (ΔHF), critical pressure (CP) and molar volume (MV). However, our indices perform at least as well as good as the known indices. In two variable regression (TABLE 5) the correlations vary with the property :

Boiling points exhibit a very good correlation (R = 0.95251; S = 2.01109) with DI and MTI. The residual DIFMTI shows correlation over 0.95 for the Wiener-type indices and HI (entries 9 to 13 - TABLE 5). Note that the regressions including DIFMTI are equivalent to a three variable regression (see refs. [91Ran1, 91Ran2]).

Enthalpy shows the best correlation with DI and MTI (R = 0.91288; S = 54150), the other combinations correlating less well.

Critical pressure is well described by MTI and R (R = 0.9829; S = 23417), by MTI and DI (R = 0.97609; S = 0.27684) and again by DIFMTI and other Wiener type indices (entries 31 to 34 - TABLE 5).

Molar volume is a rather poor correlating property. However, within the studied indices, it is the best correlated with DI and the Wiener-type indices (entries 35 to 37).

It is known that topological distance indices are not particularly discriminating descriptors [92Mih, 93Iva2]. Within the set of octanes, MTI shows two pairs of degenerate values, within nonanes there are six pairs for MTI and one for DI, and within decanes, 16 pairs and a triplet for MTI, and only two pairs for DI. In contrast with these indices, HI shows no degeneracy up to decanes.

There are nonisomorphic graphs with the same (weighted) degree sequence, which show degenerate values for the indices based on that sequence (*i.e.*the distance degree sequence, DDS - in our notation $(D)W^{(1)}S$ - and distance based indices: ^1W, J, U, V, X, Y... [93Iva2]).

FIGURE 2 and TABLE 6 show two pairs of such graphs. The pair 1 and 2 [92Mih], with identical $(D)W^{(1)}S$ but different $W^{(1)}S$ and $(H)W^{(1)}S$, shows degenerate S_D, ^1W, ^2W and DI and nondegenerate MTI, S_H, ^1H, ^2H and HI values.The pair 3 and 4 [93Iva2] shows all

the $W^{(1)}S$, $(D)W^{(1)}S$ and $(H)W^{(1)}S$ sequences identical. Consequently, the corresponding indices are degenerate. However, the higher rank indices ^3W and ^3H are nondegenerate. Because of their large values, a logarithmic scale would be welcome.

For comparison, TABLE 6 includes values of our indices $C(L(D)W^{(e)})$ and $C(L(H)W^{(e)})$ [94Diu1,94Diu2], which show no degeneracy within the graphs **1** to **4**, since $(e)=1$.

Conclusions

The extension of the vertex degree / valency by the weighted walk degree within the Schultz formula resulted in two Schultz analogue indices, **DI** and **HI**. They showed good correlating ability with some physico - chemical properties of octanes, comparable to that of other topological distance indices. The discriminating power of these indices and also of the Wiener analogue indices, ^cW and ^cH, was tested on two pairs of graphs (with degenerate distance degree sequence) and compared with that of J, MTI and the centric index constructed on layer matrices of weighted walk degrees. Since also our indices show low (or none) degeneracy up to decanes, one can conclude that they are promising candidates to the status of topological indices.

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