A Novel Definition of the Overall Hyper-Wiener Index for Unsaturated Hydrocarbons

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Received May 20, 2002

By replacing the distances between pairs of vertices with the relative distances, we define a novel overall hyper-Wiener index (*NOR*); the novel overall hyper-Wiener index extends the usefulness of the hyper-Wiener index and the overall hyper-Wiener index to unsaturated hydrocarbons.

1. INTRODUCTION

The hyper-Wiener index $R(G)$ was proposed by Randić,[1] the generalization of the much studied Wiener index (W) of graph invariant.[2−4] Recall that W is defined as the sum of distances between pairs of vertices of the graph under study. Randić generalized W to R by considering paths p instead of edges e in the Wiener index; in his definition, R is the sum of contributions K_{ij}, where subscripts i and j denote a pair of vertices. K_{ij} may be obtained[5,6] by using the following two-step algorithm. (1) Remove the path (for trees there is only one path) between vertices i and j; two nonconnected subgraphs will be obtained. (2) Multiply the number of vertices of the first subgraph by the number of vertices of the second one. R may be obtained by adding K_{ij} for all pairs of vertices i and j. There are $N(N-1)/2$ terms altogether, where N denotes the number of vertices (i.e., the number of carbons in H-suppressed graphs).

Klein et al.[7,8] provide an interpretation of R for a tree, they show that

$$R = \frac{1}{2}[\sum_{i<j} d_{ij}^{\,2} + \sum_{i<j} d_{ij}] = \frac{1}{2}\sum_{i<j} d_{ij}^{\,2} + \frac{1}{2}W \qquad (1)$$

Thus the hyper-Wiener index is proportional to the Wiener index plus the sum of squared distances between the pairs of vertices. There have been many studies on the hyper-Wiener index in recent years,[9−10] especially that of Tratch and co-workers who introduced their index similar to the hyper-Wiener index, but earlier,[11] and also suggested to extend the Wiener number to sequences of number invariants.[12−13]

But the usefulness of the hyper-Wiener index is not as popular as the molecular connectivity index, as some limits prevent the usefulness of this index; for example, it can only be used for saturated hydrocarbons. There is a further factor that is not accounted for by the hyper-Wiener index.[14] Recently, Bonchev proposed a new approach to the topological characterization of molecules.[15−17] It proceeds from the total number of subgraphs $K(G)$ of molecular graph G and their presentation in a complete series of classes of order e, with $e = 0, 1, 2, ..., E$ being the constant number of edges in each subgraph of a certain class, and E being the number of edges in the entire graph. We use the Wiener numbers of each subgraph, extending the seminal molecular descriptor to its most complete version, the overall Wiener index.[18] According to this approach we use the hyper-Wiener indices of each subgraph, extending this seminal molecular descriptor to the overall hyper-Wiener index.[19] In this study, we continue to extend the usefulness of the overall hyper-Wiener index to unsaturated hydrocarbons by replacing the distances between the pairs of vertices with the relative distances.

2. METHOD

As the Wiener index weights edges in chemical graphs of saturated hydrocarbons by unity, and the distances between two adjacent vertices of unsaturated hydrocarbons are different from those of saturated hydrocarbons, the overall hyper-Wiener number cannot be used for unsaturated hydrocarbons, as it limits the usefulness of the overall hyper-Wiener index. As we know, the distances are determined by chemical bonds, so the distances between two adjacent vertices may have relationships with the bond lengths between two atoms. The bond lengths of some types of chemical bonds[20] are shown in Table 1.

In this work, according to the bond length, we define a novel distance between two adjacent vertices bonded by different types of chemical bonds, called the relative distance. The relative distance defines the distance of a C−C single bond (sp^3-sp^3 type) as 1, and then the relative distance of another type of chemical bond is defined as the ratio of its bond length and the bond length of a C−C single bond (sp^3-sp^3 type) and is equal to 1.544. For example, the relative distance of a C−C single bond (sp^3-sp^2 type) is 1.501/1.544 = 0.972. The relative distances of some types of chemical bonds are shown in Table 1.

Replacing the distances of definition 1 by the relative distances, we can obtain a novel type of hyper-Wiener index for unsaturated hydrocarbons, called the novel hyper-Wiener indexes (*NR*).[21] Then, we can define the novel overall hyper-Wiener index (*NOR*).

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10.1021/ci025541h CCC: $27.50
Published on Web 01/13/2004

Table 1. Bond Length and Relative Distances of Some Types of Chemical Bonds

C-C single bond	type	bond length	C-C multiple bond	type	bond length
	sp^3-sp^3	1.544	plumbago	sp^2-sp^2+π /3	1.421
	sp^3-sp^2	1.501	benzene	sp^2-sp^2+π /2	1.397
	sp^3-sp	1.459		sp^2-sp^2+π	1.339
	Sp^2-sp^2	1.483		sp^2-sp+π	1.309
	Sp^2-sp	1.426		sp-sp+π	1.284
	sp-sp	1.377		sp-sp+2π	1.205
C-C single bond	type	relative distances	C-C multiple bond	type	relative distances
	sp^3-sp^3	1.000	plumbago	sp^2-sp^2+π /3	0.920
	sp^3-sp^2	0.972	benzene	sp^2-sp^2+π /2	0.905
	sp^3-sp	0.945		sp^2-sp^2+π	0.867
	Sp^2-sp^2	0.960		sp^2-sp+π	0.848
	Sp^2-sp	0.924		sp-sp+π	0.832
	sp-sp	0.892		sp-sp+2π	0.780

Table 2. Novel Overall Hyper Wiener Index *NOR* and Its *e*th-Order Components, Calculated for the 42 Alkanes

no.	molecules[a]	^1NOR	^2NOR	^3NOR	^4NOR	^5NOR	*NOR*
1	C2	1.000					1.000
2	C3	2.000	5.000				7.000
3	nC4	3.000	10.000	15.000			28.000
4	2MC3	3.000	15.000	12.000			30.000
5	nC5	4.000	15.000	30.000	35.000		84.000
6	2MC4	4.000	20.000	42.000	28.000		94.000
7	22MMC3	4.000	30.000	48.000	22.00		104.00
8	nC6	5.000	20.000	45.000	70.000	70.000	210.000
9	2MC5	5.000	25.000	57.000	98.000	58.000	243.000
10	3MC5	5.000	25.000	72.000	91.000	54.000	247.000
11	23MMC4	5.000	30.000	84.000	112.000	47.000	278.000
12	22MMC4	5.000	35.000	93.000	106.000	44.000	283.000
13	ethylene	0.809					0.809
14	propene	1.767	4.378				6.145
15	1-butene	2.767	9.267	13.758			25.792
16	*cis*-2-butene	2.725	8.756	13.304			24.785
17	2-M-propene	2.725	13.534	10.809			27.068
18	1-pentene	3.767	14.267	28.549	32.949		79.532
19	*cis*-2-pentene	3.725	13.645	27.062	31.851		76.283
20	2-M-1-butene	3.725	18.423	39.081	25.994		87.223
21	3-M-1-butene	3.767	19.156	39.335	26.138		88.396
22	2-M-2-butene	3.683	17.912	37.417	25.090		84.102
23	1-hexene	4.767	19.267	43.549	67.615	66.951	202.149
24	*cis*-2-hexene	4.725	18.645	41.853	64.800	65.020	195.043
25	*cis*-3-hexene	4.725	18.534	40.820	63.702	64.376	192.157
26	2-M-1-pentene	4.725	23.423	53.872	93.109	56.838	231.967
27	3-M-1-pentene	4.767	24.156	69.126	86.809	51.329	236.187
28	4-M-1-pentene	4.767	24.267	55.340	93.592	55.140	233.106
29	2-M-2-pentene	4.683	22.801	51.175	88.792	52.805	220.256
30	3-M-*cis*-2-pentene	4.683	22.801	65.698	82.935	49.443	225.560
31	4-M-*cis*-2-pentene	4.725	23.534	52.639	89.840	53.398	224.136
32	2-E-1-butene	4.725	23.312	67.353	85.988	50.929	232.307
33	2,3-MM-1-butene	4.725	28.312	79.172	105.376	44.179	261.764
34	3,3-MM-1-butene	4.767	34.045	88.731	100.164	41.518	269.225
35	2,3-MM-2-butene	4.641	27.068	74.834	100.360	42.233	249.136
36	acetylene	0.694					0.694
37	1,3-butadiene	2.559	8.666	12.700			23.925
38	1-butyne	2.613	8.747	12.903			24.263
39	2-butyne	2.532	7.928	12.132			22.592
40	propadiene	1.568	3.852				5.420
41	propyne	1.613	3.964				5.577
42	1-pentyne	3.613	13.747	27.495	31.512		76.367

[a] M and E stand for methyl and ethyl, respectively; the numbers denote the position of the methyl and ethyl branches.

Table 3. Path(p), Cluster(c), and Pathcluster(pc) Terms of Novel Overall Hyper Wiener Index *NOR* of the 42 Alkanes

no.	molecules[a]	$^3NOR_P$	$^3NOR_c$	$^4NOR_P$	$^4NOR_c$	$^4NOR_{Pc}$	$^5NOR_P$	$^5NOR_c$	$^5NOR_{Pc}$
1	C2								
2	C3								
3	nC4	15.000	0.000						
4	2MC3	0.000	12.000						
5	nC5	30.000	0.000	35.000	0.000	0.000			
6	2MC4	30.000	12.000	0.000	0.000	28.000			
7	22MMC3	0.000	48.000	0.000	22.000	0.000			
8	nC6	45.000	0.000	70.000	0.000	0.000	70.000	0.000	0.000
9	2MC5	45.000	12.000	70.000	0.000	28.000	0.000	0.000	58.000
10	3MC5	60.000	12.000	35.000	0.000	56.000	0.000	0.000	54.000
11	23MMC4	60.000	24.000	0.000	0.000	112.000	0.000	47.000	0.000
12	22MMC4	45.000	48.000	0.000	22.000	84.000	0.000	0.000	44.000
13	ethylene								
14	propene								
15	1-butene	13.758	0.000						
16	*cis*-2-butene	13.304	0.000						
17	2-M-propene	0.000	10.809						
18	1-pentene	28.549	0.000	32.949	0.000	0.000			
19	*cis*-2-pentene	27.062	0.000	31.851	0.000	0.000			
20	2-M-1-butene	28.272	10.809	0.000	0.000	25.994			
21	3-M-1-butene	27.516	11.819	0.000	0.000	26.138			
22	2-M-2-butene	26.608	10.809	0.000	0.000	25.090			
23	1-hexene	43.549	0.000	67.615	0.000	0.000	66.951	0.000	0.000
24	*cis*-2-hexene	41.853	0.000	64.800	0.000	0.000	65.020	0.000	0.000
25	*cis*-3-hexene	40.820	0.000	63.702	0.000	0.000	64.376	0.000	0.000
26	2-M-1-pentene	43.063	10.809	67.115	0.000	25.994	0.000	0.000	56.838
27	3-M-1-pentene	57.307	11.819	32.949	0.000	53.860	0.000	0.000	51.329
28	4-M-1-pentene	43.340	12.000	65.898	0.000	27.694	0.000	0.000	55.140
29	2-M-2-pentene	40.366	10.809	63.702	0.000	25.090	0.000	0.000	52.805
30	3-M-*cis*-2-pentene	54.880	10.809	31.851	0.000	51.084	0.000	0.000	49.443
31	4-M-*cis*-2-pentene	40.820	11.819	63.702	0.000	26.138	0.000	0.000	53.398
32	2-E-1-butene	56.544	10.809	34.000	0.000	51.988	0.000	0.000	50.929
33	2,3-MM-1-butene	56.544	22.628	0.000	0.000	105.376	0.000	44.179	0.000
34	3,3-MM-1-butene	41.274	47.457	0.000	21.750	78.414	0.000	0.000	41.518
35	2,3-MM-2-butene	53.216	21.618	0.000	0.000	100.360	0.000	42.233	0.000
36	acetylene								
37	1,3-butadiene	12.700							
38	1-butyne	12.903							
39	2-butyne	12.132							
40	propadiene								
41	propyne								
42	1-pentyne	27.495	0.000	31.512	0.000	0.000			

[a] M and E stand for methyl and ethyl, respectively; the numbers denote the position of the methyl and ethyl branches.

Definition 1. The novel overall hyper-Wiener index *NOR(G)* of any graph *G* is defined as the sum of the novel hyper-Wiener indices $NR_i(G_i)$ of all *K* subgraphs of *G*:

$$NOR(G) = \sum_{i=1}^{K} NR_i(G_i \subset G) \tag{2}$$

Definition 2. The *e*th-order novel overall hyper-Wiener index $^eNOR(G)$ of any graph G is defined as the sum of the novel hyper-Wiener indices $NR_j(^eG_j)$ of all ^eK subgraphs $^eG_j \subset G$ that have *e* edges:

$$^eNOR(G) = \sum_{j=1}^{^eK} NR_j(^eG_j \subset G) \tag{3}$$

Definition 3. The *e*th-order novel overall hyper-Wiener index $^eNOR(G)$ can be presented as a sum of terms, $^eNOR_k(G)$, representing the sum of the novel hyper-Wiener indices in the subgraphs of specified type. For acyclic graphs these are the path ($k = p$), cluster ($k = c$), and pathcluster ($k = pc$) type, as defined by Kier and Hall:[22]

$$^eNOR(G) = {}^eNOR_p(G) + {}^eNOR_c(G) + {}^eNOR_{pc}(G)$$

$$= \sum_{j=1}^{^eK_p} NR_{pj} + \sum_{l=1}^{^eK_p} NR_{cl} + \sum_{m=1}^{^eK_p} NR_{pcm} \tag{4}$$

Definition 4. The novel overall hyper-Wiener index vector *NOR□(G)* of any graph *G* is the sequence of all $^eNOR(G)$s listed in ascending order of the number of edges *e*

$$NOR'(G) = NOR\{{}^0NOR, {}^1NOR, {}^2NOR, \cdots, {}^ENOR\} \tag{5}$$

or in more detail for acyclic graphs:

$$NOR'(G) = NOR\{{}^0NOR, {}^1NOR, {}^2NOR, {}^3NOR_p, {}^3NOR_c, \cdots, {}^ENOR_p, {}^ENOR_c, {}^ENOR_{pc}\} \tag{6}$$

The *E*th-order novel overall hyper-Wiener index, $^ENOR(G)$, is the novel hyper-Wiener index *NR(G)* itself:

$$^ENOR(G) = NR(G) \tag{7}$$

Table 4. Experimental Values for the Physical Properties of the 42 Alkanes

no.	molecules[a]	MV	bp	LogP	MR	PC	TC
1	C2	35.522	−8.630	1.810		48.20	32.27
2	C3	48.051	−42.070	2.360		42.01	96.80
3	nC4	61.722	−0.500			37.47	152.01
4	2MC3	61.767	−11.730	2.760		36.00	134.98
5	nC5	74.122	36.074		25.2656	33.31	196.62
6	2MC4	75.032	27.852	2.300	25.2923	32.90	187.80
7	22MMC3	73.917	9.503	3.110	25.7243	31.57	160.60
8	nC6	84.523	8.740	3.000	29.9066	29.92	234.70
9	2MC5	85.259	60.271	2.800	29.9459	29.95	224.90
10	3MC5	85.335	63.282	2.800	29.8016	30.83	231.20
11	23MMC4	84.447	57.988		29.8104	30.99	227.10
12	22MMC4	85.174	49.741	3.820	29.9347	30.67	216.20
13	ethylene	31.203	−103.700				
14	propene	43.031	−47.400			46.00	91.90
15	1-butene	55.659	−6.300	2.460		40.20	146.00
16	*cis*-2-butene	57.756	0.880			42.00	155.00
17	2-M-propene	60.504					
18	1-pentene	67.473	29.900	1.590	24.8580	40.40	191.00
19	*cis*-2-pentene	68.513	36.900	2.200			
20	2-M-1-butene	67.407	31.200	2.200			
21	3-M-1-butene	71.324	20.100	2.070			
22	2-M-2-butene	67.345	38.500		24.9550		
23	1-hexene	81.738	63.300	2.070	29.2080		
24	*cis*-2-hexene	83.430	68.800	2.700			
25	*cis*-3-hexene	80.846	66.400	2.700			
26	2-M-1-pentene	84.001	60.700	2.610	29.3980		
27	3-M-1-pentene	81.181	54.100		29.4850		
28	4-M-1-pentene	80.057	53.900	2.500	29.5420		
29	2-M-2-pentene	83.662	67.300		29.7540		
30	3-M-*cis*-2-pentene	82.132	70.400				
31	4-M-*cis*-2-pentene	79.927	58.600	2.540			
32	2-E-1-butene	80.516	64.700	2.410	29.3910		
33	2,3-MM-1-butene	80.351	55.700		30.0630		
34	3,3-MM-1-butene	79.432	41.200		29.5980		
35	2,3-MM-2-butene	80.025	73.200		29.5900		
36	acetylene	24.778	−84.000			62.40	35.50
37	1,3-butadiene	50.697	−4.400	1.630		43.20	152.00
38	1-butyne	52.013	8.100	1.440			
39	2-butyne	51.282	10.500	1.440			
40	propadiene	37.391				44.20	120.00
41	propyne	37.378				53.50	127.80
42	1-pentyne	68.828		1.980			

[a] M and E stand for methyl and ethyl, respectively; the numbers denote the position of the methyl and ethyl branches.

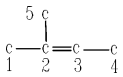
The zero-order novel overall hyper-Wiener index, ${}^0NOR(G)$, is equal to zero:

$$ {}^0NOR(G) = 0 \tag{8}$$

The first-order novel overall hyper-Wiener index, ${}^1NOR(G)$, is equal to the number of graph edges E:

$$ {}^1NOR(G) = E \tag{9}$$

Example:



$e = 1$: 1-2, 2-3, 3-4, 2-5; ${}^1NOR = 30.958 + 0.809 = 3.683$; $e = 2$: 1-2-3, 2-3-4, 1-2-5, 5-2-3; ${}^2NOR = 34.378 + 4.778 = 17.912$; $e = 3$: 1-2-3-4, 5-2-3-4, 1-2-3-5; ${}^3NOR = 213.304 + 10.809 = 37.417$; $e = 3$: the entire graph; ${}^4NOR = 25.090$; $NOR = 3.683 + 17.912 + 37.417 + 25.090 = 84.102$; $NOR\square = 84.102$ (3.683, 17.912, 37.417, 25.090).

3. QUANTITATIVE STRUCTURE−PROPERTY AND STRUCTURE−ACTIVITY RELATIONSHIPS WITH THE NOVEL OVERALL HYPER-WIENER INDEX

The potential usefulness of the novel overall hyper-Wiener index for structure−property and structure−activity studies can be evaluated by performing comparative against molecular connectivity index, the most widely used molecular descriptors in QSAR/QSPR. In this study, we apply multiple regression analysis (MRA) in a QSAR modeling of six physical properties of 42 alkanes and unsaturated hydrocarbons with one to six carbons. The six properties are boiling point,[23] bp; molar volumes (calculated by Gaussian 98), MV; partition coefficient, logP; molecular refractions, MR; critical temperature, TC; and critical pressures, PC.[24−25] Two different sets of novel overall hyper-Wiener indexes were used in the models, the first one include the *NOR* index and its *e*th-order components, ${}^eNOR$, for $e = 1, 2, 3, 4, 5$ (Table 2). The second one is the extended set of novel overall hyper-Wiener indexes including the path(p), cluster(c), and path-cluster(pc) terms of order 3−5 (Table 3). The six physical

Table 5. Comparison of Multilinear Regression Statistics (Correlation Coefficient, Standard Deviation, and the Fischer Ratio) for the 42 Compounds Properties Models Produced by the Two Sets of Topological Indexes χ/*NOR*

	molecular connectivity index χ				novel overall hyper-Wiener index *NOR*			
properties	*n*	*r*	*s*	*F*	*n*	*r*	*s*	*F*
molar volumes	42	0.9943	1.91	610	42	0.9955	1.70	768
boiling point	38	0.9816	8.80	211	38	0.9880	6.95	318
partition coeff	25	0.8705	0.30	15	25	0.8944	0.27	19
molecular refractions	19	0.9672	0.57	72	19	0.9948	0.23	474
critical pressure	20	0.9383	3.11	133	20	0.9227	3.47	103
critical temp	20	0.9709	14.26	82	20	0.9846	10.42	158

Table 6. Cross-Validation Results of the Two Indexes

	${}^{m}\chi_t$		${}^{e}NOR_k$	
properties	r^2_{mean}	s_{mean}	r^2_{mean}	s_{mean}
molar volumes	0.9887	1.91	0.9910	1.70
boiling point	0.9636	8.80	0.9763	6.93
partition coefficient	0.7578	0.30	0.8005	0.27
molecular refractions	0.9361	0.56	0.9896	0.23
critical pressure	0.8814	3.10	0.8519	3.46
critical temperature	0.9429	14.25	0.9695	10.42

properties of the 42 compounds are shown in Table 4, and Table 5 summarizes the statistics (correlation coefficient *r*, standard deviation *s*, and the Fischer ratio *F*) of the molecular connectivity and the novel overall hyper-Wiener index models (10−15) of the 42 compounds.

The best novel overall hyper-Wiener models and the molecular connectivity index models obtained for the six examined properties are given below.

$$\mathrm{MV} = 12.00278 - 2.68226\ln\mathrm{VOR} + 19.95469^{1}\mathrm{VOR} - 0.18025^{3}\mathrm{VOR_p} - 0.03927^{4}\mathrm{OR_p} - 0.21346^{4}\mathrm{VOR_c} \quad (10)$$

$$n = 42,\ r = 0.9955,\ s = 1.70,\ F = 768$$

$$\mathrm{MV} = 12.30299 + 8.2532^{0}\chi_p + 12.51456^{1}\chi_p - 0.0715^{2}\chi_p - 3.70496^{3}\chi_p + 2.00843^{4}\chi_p \quad (10a)$$

$$n = 42,\ r = 0.9943,\ s = 1.91,\ F = 610$$

$$\mathrm{bp} = -96.38561 + 10.47409^{1}\mathrm{VOR} - 3.10339^{2}\mathrm{VOR} + 0.44698^{3}\mathrm{VOR} + 28.43408\ln\mathrm{VOR} \quad (11)$$

$$n = 38,\ r = 0.9880,\ s = 6.95,\ F = 318$$

$$\mathrm{bp} = -169.03513 + 62.4555^{0}\chi_p - 34.60887^{2}\chi_p - 7.80334^{3}\chi_p - 16.92164^{6}\chi_c \quad (11a)$$

$$n = 38,\ r = 0.9816,\ s = 8.80,\ F = 211$$

$$\mathrm{logP} = 2.05966 - 1.71659\ln\mathrm{VOR} + 0.07667^{2}\mathrm{VOR} - 9.06809 \times 10^{-44}\mathrm{VOR_p} + 1.69943^{1}\mathrm{VOR} \quad (12)$$

$$n = 25,\ r = 0.8944,\ s = 0.27,\ F = 19$$

$$\mathrm{logP} = 1.50906 + 0.51803^{2}\chi_p + 0.29145^{4}\chi_c + 2.4264^{5}\chi_p - 1.41545^{5}\chi_{pc} \quad (12a)$$

$$n = 25,\ r = 0.8705,\ s = 0.30,\ F = 15$$

$$\mathrm{MR} = 23.52944 + 0.05308^{2}\mathrm{VOR} + 0.02344^{4}\mathrm{VOR} + 0.04942^{5}\mathrm{VOR} \quad (13)$$

$$n = 19,\ r = 0.9948,\ s = 0.23,\ F = 474$$

$$\mathrm{MR} = 0.86863 + 3.71591^{0}\chi_p + 4.70539^{1}\chi_p - 2.34538^{3}\chi_p \quad (13a)$$

$$n = 19,\ r = 0.9672,\ s = 0.57,\ F = 72$$

$$\mathrm{PC} = 54.46446 - 4.41292\ln\mathrm{VOR} \quad (14)$$

$$n = 20,\ r = 0.\ 9227,\ s = 3.47,\ F = 103$$

$$\mathrm{PC} = 62.2189 - 6.5878^{0}\chi_p \quad (14a)$$

$$n = 20,\ r = 0.\ 9383,\ s = 3.11,\ F = 133$$

$$\mathrm{TC} = 53.25342 + 28.57847\ \ln\mathrm{VOR} + 0.48764^{3}\mathrm{VOR_P} - 0.53499^{3}\mathrm{VOR_C} \quad (15)$$

$$n = 20,\ r = 0.\ 9846,\ s = 10.42,\ F = 158$$

$$\mathrm{TC} = -91.00722 + 134.81177^{0}\chi_p - 75.03106^{1}\chi_p - 69.76575^{2}\chi_p \quad (15a)$$

$$n = 20,\ r = 0.\ 9709,\ s = 14.26,\ F = 82$$

4. RESULTS AND DISCUSSION

It is easy to see that the overall hyper-Wiener index preserves the basic features of the Wiener index and eliminates its pitfalls,[18,19] and it is a complexity measure. From these relations 10−15 we also can see that the novel overall hyper-Wiener index has a good relationship with molecular properties of the 42 unsaturated hydrocarbons with a different type of multiple bonds, and we obtained relatively good statistics results. It is shown that the relative distance duplicates some information contained in unsaturated hydrocarbons, and it is more reasonable to denote the unsaturated bond with a relative distance in the novel overall hyper-Wiener index than simply with 2 or 3 times a single bond in the molecular connectivity index. Besides this, the novel overall hyper-Wiener index also presents some new structural characters of molecules, such as *NOR* and ${}^{2}NOR$ in model 11, which have a good relation to molecular properties. So the models of the novel overall hyper-Wiener index obtained better statistics results, and it means that the novel overall hyper-Wiener index is a potential structure descriptor of unsaturated hydrocarbons with different types of multiple bonds.

To verify the robustness of the models, a cross-validation procedure, leave-one-out, was performed, and the results were listed in Table 6.

From Table 6 we can see that the mean values of the correlation coefficient *r* and the standard deviation *s* are rather close to the results of relations 10−15, and it indicates that the six property models of the two sets of indexes are more stable.

5. CONCLUSION

In this work, according to the bond length, we define a novel distance between two adjacent vertices

Table 7. Valence Molecular Connectivity Indexes of the 42 Alkanes

no.	molecules[a]	$^0\chi_p$	$^1\chi_p$	$^2\chi_p$	$^3\chi_p$	$^3\chi_c$	$^4\chi_p$	$^4\chi_{pc}$	$^4\chi_c$	$^5\chi_p$	$^5\chi_c$	$5\chi_{pc}$	$^6\chi_p$	$^6\chi_c$
1	C2	2.000000	1.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
2	C3	2.707107	1.414214	0.707107	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
3	nC4	3.414214	1.914214	1.000000	0.500000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
4	2MC3	3.577350	1.732051	1.732051	0.000000	0.577350	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
5	nC5	4.121321	2.414214	1.353553	0.707107	0.000000	0.353553	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
6	2MC4	4.284457	2.270056	1.802095	0.816497	0.408248	0.000000	0.408248	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
7	22MMC3	4.500000	2.000000	3.000000	0.000000	2.000000	0.000000	0.000000	0.500000	0.000000	0.000000	0.000000	0.000000	0.000000
8	nC6	4.828427	2.914214	1.707107	0.957107	0.000000	0.500000	0.000000	0.000000	0.250000	0.000000	0.000000	0.000000	0.000000
9	2MC5	4.991564	2.770056	2.182522	0.866025	0.408248	0.577350	0.288675	0.000000	0.000000	0.000000	0.288675	0.000000	0.000000
10	3MC5	4.991564	2.808060	1.921668	1.393847	0.288675	0.288675	0.577350	0.000000	0.000000	0.000000	0.288675	0.000000	0.000000
11	23MMC4	5.154700	2.642735	2.488034	1.333333	0.666667	0.000000	1.333333	0.000000	0.000000	0.333333	0.000000	0.000000	0.000000
12	22MMC4	5.207107	2.560660	2.914213	1.060660	1.560660	0.000000	1.060660	0.353553	0.000000	0.000000	0.353553	0.000000	0.000000
13	ethylene	1.414214	0.500000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
14	propene	2.284457	0.985599	0.408248	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
15	1-butene	2.991564	1.523603	0.696923	0.000000	0.288675	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
16	*cis*-2-butene	3.154701	1.488034	0.666667	0.000000	0.333333	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
17	2-M-propene	3.207107	1.353553	1.207107	0.000000	0.000000	0.353553	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
18	1-pentene	3.698671	2.023603	1.077350	0.000000	0.492799	0.000000	0.204124	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
19	*cis*-2-pentene	3.861807	2.026039	0.977284	0.000000	0.471405	0.000000	0.235702	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
20	2-M-1-butene	3.914214	1.914214	1.310660	0.000000	0.603553	0.250000	0.000000	0.250000	0.000000	0.000000	0.000000	0.000000	0.000000
21	3-M-1-butene	3.861807	1.896282	1.310617	0.000000	0.569036	0.235702	0.000000	0.235702	0.000000	0.000000	0.000000	0.000000	0.000000
22	2-M-2-butene	4.077351	1.866025	1.366025	0.000000	0.577350	0.288675	0.000000	0.288675	0.000000	0.000000	0.000000	0.000000	0.000000
23	1-hexene	4.405777	2.523603	1.430904	0.000000	0.761802	0.000000	0.348462	0.000000	0.000000	0.000000	0.144338	0.000000	0.000000
24	*cis*-2-hexene	4.568914	2.526039	1.357711	0.000000	0.691044	0.000000	0.333333	0.000000	0.000000	0.000000	0.166667	0.000000	0.000000
25	*cis*-3-hexene	4.568914	2.564044	1.287901	0.000000	0.638071	0.000000	0.333333	0.000000	0.000000	0.000000	0.166667	0.000000	0.000000
26	2-M-1-pentene	4.621321	2.414214	1.707107	0.000000	0.676777	0.250000	0.426777	0.176777	0.000000	0.000000	0.000000	0.000000	0.176777
27	3-M-1-pentene	4.568914	2.434287	1.621234	0.000000	1.046319	0.235702	0.166667	0.402369	0.000000	0.000000	0.000000	0.000000	0.166667
28	4-M-1-pentene	4.568914	2.379445	1.918224	0.000000	0.638071	0.408248	0.333333	0.235702	0.000000	0.000000	0.000000	0.000000	0.166667
29	2-M-2-pentene	4.784457	2.404030	1.689723	0.000000	0.612372	0.288675	0.408248	0.204124	0.000000	0.000000	0.000000	0.000000	0.204124
30	3-M-*cis*-2-pentene	4.784457	2.426686	1.488581	0.000000	1.050477	0.204124	0.204124	0.408248	0.000000	0.000000	0.000000	0.000000	0.204124
31	4-M-*cis*-2-pentene	4.732051	2.398718	1.769800	0.000000	0.577350	0.333333	0.384900	0.192450	0.000000	0.000000	0.000000	0.000000	0.192450
32	2-E-1-butene	4.621320	2.474874	1.457107	0.000000	1.000000	0.176777	0.250000	0.353553	0.000000	0.000000	0.000000	0.000000	0.176777
33	2,3-MM-1-butene	4.784457	2.296929	2.001053	0.000000	0.985599	0.492799	0.000000	0.901048	0.000000	0.000000	0.000000	0.204124	0.000000
34	3,3-MM-1-butene	4.784457	2.196923	2.570149	0.000000	0.612372	1.366026	0.000000	0.612372	0.288675	0.000000	0.000000	0.000000	0.204124
35	2,3-MM-2-butene	5.000000	2.250000	2.000000	0.000000	1.000000	0.500000	0.000000	1.000000	0.000000	0.000000	0.000000	0.250000	0.000000
36	acetylene	1.154701	0.333333	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
37	1,3-butadiene	2.568914	1.149830	0.471405	0.000000	0.166667	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
38	1-butyne	2.784457	1.349335	0.557678	0.000000	0.204124	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
39	2-butyne	3.000000	1.250000	0.500000	0.000000	0.250000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
40	propadiene	1.914214	0.707107	0.250000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
41	propyne	2.077350	0.788675	0.288675	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000
42	1-pentyne	3.491564	1.849335	0.954124	0.000000	0.394338	0.000000	0.144338	0.000000	0.000000	0.000000	0.000000	0.000000	0.000000

[a] M and E stand for methyl and ethyl, respectively; the numbers denote the position of the methyl and ethyl branches.

bonded by different types of chemical bonds as relativedistance. By replacing the distances of definition 1 with the relative distances, we defined a novel type of overall hyper-Wiener index for unsaturated hydrocarbons.

Summarizing the results, one may conclude that the novel overall hyper-Wiener index examined shows good potential for QSAR and QSPR studies, and it presents some new structural characters of unsaturated hydrocarbons. The results show that considerably better statistics are obtained when extending the hyper-Wiener index to the novel overall hyper-Wiener index. It provided even the same statistics results as the molecular connectivity indexes in all models, and the standard deviations provided by these two sets of indexes are rather close. This can extend the usefulness of the Wiener number and the hyper-Wiener index and can make them to be a kind of widely used topological index in practice.

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CI025541H