The Valence Overall Wiener Index for Unsaturated Hydrocarbons

Xinhua Li* and Juanjuan Lin

Department of Chemistry, Wenzhou Normal College, Wenzhou, Zhejiang 325027, P.R. China

By replacing the distances between pairs of vertices with the relative distances, we define a novel valence overall Wiener index (VOW); the valence overall Wiener index extends the usefulness of the Wiener index and the overall Wiener index to unsaturated hydrocarbons.

INTRODUCTION

The Wiener number W(G), one of the best descriptors of molecular topology, was introduced in 1947 by Wiener[1] as the path number for saturated acyclic hydrocarbons. The path number was defined as the number of the bonds between all pairs of non-hydrogen atoms in the molecule. The Wiener number $W(G) \equiv W$ of a structure G is equal to the half-sum of distances of the distance matrix between all pairs of vertices:[2]

$$W(G) = W = \frac{1}{2}\sum_i \sum_j d_{ij} \qquad (1)$$

Recently, Bonchev proposed a new approach to the topological characterization of molecules.[3−5] 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. He uses the Wiener numbers of each subgraph, extending thus that seminal molecular descriptor to its most complete version, the overall Wiener index (OW).[6]

THE VALENCE OVERALL WIENER INDEX

But the Wiener index supposed that all the distances between two adjacent vertices are the same and equal to 1. As the distances between two adjacent vertices of unsaturated hydrocarbons are different from those of saturated hydrocarbons, the Wiener number and the overall Wiener index cannot be used for unsaturated hydrocarbons; it limited their usefulness. 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 the two atoms. The bond lengths of some types of chemical bonds[7] 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 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 distances of other types of chemical bonds are defined as the ratio of

* Corresponding author phone: 86-577-88373111; e-mail: lixinhua01@263.net.

their bond lengths; the bond length of a C−C single bond (sp^3-sp^3 type) is 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 2.

Replacing the distances of definition (1) by the relative distances, we obtain a novel type of Wiener index for unsaturated hydrocarbons, called the valence Wiener indexes (VW). Then we can define the valence overall Wiener index (VOW).

Definition 1. The valence overall Wiener index VOW(G) of any graph *G* is defined as the sum of the valence Wiener indices $VW_i(G_i)$ of all *K* subgraphs of *G*:

$$VOW(G) = \sum_{i=1}^{K} VW_i(G_i \subset G) \qquad (2)$$

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

$$^eVOW(G) = \sum_{j=1}^{^eK} VW_j(^eG_j \subset G) \qquad (3)$$

Definition 3. The *e*th-order valence overall Wiener index $^eVOW(G)$ can be presented as a sum of terms, $^eVOW_k(G)$, representing the sum of the valence 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:[8]

$$^eVOW(G) = {}^eVOW_p(G) + {}^eVOW_c(G) + {}^eVOW_{pc}(G)$$

$$= \sum_{j=1}^{^eK_p} VW_{pj} + \sum_{l=1}^{^eK_p} VW_{cl} + \sum_{m=1}^{^eK_p} VW_{pcm} \qquad (4)$$

Definition 4. The valence overall Wiener index vector VOW′(G) of any graph *G* is the sequence of all $^eVOW(G)$s listed in an ascending order of the number of edges *e*:

$$VOW'(G) = \\ VOW\{^0VOW, \ {}^1VOW, \ {}^2VOW, \ \cdots, \ {}^EVOW\} \qquad (5)$$

Table 1. Bond Length 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

Table 2. Relative Distances of Some Types of Chemical Bonds

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

or in more detail for acyclic graphs:

$$VOW'(G) =$$
$$VOW\{^0VOW, \ ^1VOW, \ ^2VOW, \ ^3VOW_p, \ ^3VOW_c \ \cdots,$$
$$^EVOW_p, \ ^EVOW_c, \ ^EVOW_{pc}\} \quad (6)$$

The Eth-order valence overall Wiener index, $^EVOW(G)$, is the valence Wiener index VW(G) itself:
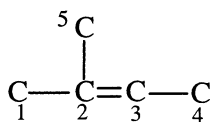
$$^EVOW(G) = VW(G) \quad (7)$$

The zero-order valence overall Wiener index, $^0VW(G)$, is equal to zero:

$$^0VOW(G) = 0 \quad (8)$$

The first-order valence overall Wiener index, $^1VOW(G)$, is equal to the number of graph edges E:

$$^1VOW(G) = E \quad (9)$$

Example:

$$\underset{1}{C}-\underset{2}{C}=\underset{3}{C}-\underset{4}{C}$$

with ^5C attached to C_2.

$e = 1$: 1–2, 2–3, 3–4, 2–5; $^1VOW = 3 \times 0.972 + 0.867 = 3.783$; $e = 2$: 1–2–3, 2–3–4, 1–2–5, 5–2–3; $^2VOW = 3 \times 3.678 + 3.888 = 14.922$; $e = 3$: 1–2–3–4, 5–2–3–4, 1–2–3–5; $^3VOW = 2 \times 9.3 + 8.433 = 27.033$; $e = 4$: the entire graph; $^4VOW = 16.866$; VOW = 3.783 + 14.922 + 27.033 + 16.866 = 62.604; VOW' = 62.604 (3.783, 14.922, 27.033, 16.866).

QUANTITATIVE STRUCTURE-PROPERTY RELATIONSHIPS WITH THE VALENCE OVERALL WIENER INDEX

In this study, we apply multiple regression analysis (MRA) in a QSAR modeling of six physical properties of 48 alkanes and unsaturated alkanes. The properties are boiling point, bp in °C; molecular volumes, V_{cal} in cm^3/mol; partition coefficients, logP; molecular refractions, MR in cm^3/mol; critical temperature, TC in °C; and critical pressures, PC in atm (Table 5).[9–11] The molecular volumes V_{cal} was calculated by Gaussian 98 using 6-31g** basis sets at the Hartree−Fock level. Two different sets of valence overall Wiener indices were used in the modeling, the first one includes the VOW index and its eth-order components, ^{e}-VOW, for e = 1,2,..., 6 (Table 3). The extended set of valence overall Wiener indices include also the path (p), cluster (c), and pathcluster (pc) terms of order 3−6 (Table 4).

Table 3. Valence Overall Wiener Index VOW, and Its *e*th-Order Components, Calculated for the 48 Alkanes

no.	molecule[a]	^{1}VOW	^{2}VOW	^{3}VOW	^{4}VOW	^{5}VOW	^{6}VOW	VOW
1	C2	1.000						1.000
2	C3	2.000	4.000					6.000
3	nC4	3.000	8.000	10.000				21.000
4	2MC3	3.000	12.000	9.000				24.000
5	nC5	4.000	12.000	20.000	20.000			56.000
6	2MC4	4.000	16.000	29.000	18.000			67.000
7	22MMC3	4.000	24.000	36.000	16.000			80.000
8	nC6	5.000	16.000	30.000	40.000	35.000		126.000
9	2MC5	5.000	20.000	39.000	58.000	32.000		154.000
10	3MC5	5.000	20.000	49.000	56.000	31.000		161.000
11	23MMC4	5.000	24.000	58.000	72.000	29.000		188.000
12	22MMC4	5.000	28.000	66.000	70.000	28.000		197.000
13	cyclopropane	3.000	12.000	3.000				18.000
14	cyclobutane	4.000	16.000	40.000	8.000			94
15	cyclopentane	5.000	20.000	50.000	100.000	15.000		305
16	cyclohexane	6.000	24.000	60.000	120.000	210.000	27.000	807
17	ethylene	0.867						0.867
18	propene	1.839	3.678					5.517
19	1-butene	2.839	7.622	9.489				19.950
20	*cis*−2-butene	2.811	7.356	9.300				19.467
21	2-M-propene	2.811	11.244	8.433				22.488
22	1-pentene	3.839	11.622	19.405	19.300			54.166
23	*cis*−2-pentene	3.811	11.300	18.789	18.922			52.822
24	2-M-1-butene	3.811	15.188	27.726	17.188			63.913
25	3-M-1-butene	3.839	15.566	27.894	17.300			64.599
26	2-M-2-butene	3.783	14.922	27.033	16.866			62.604
27	1-hexene	4.839	15.622	29.405	39.189	34.111		123.166
28	*cis*−2-hexene	4.811	15.300	28.705	38.222	33.544		120.582
29	*cis*−3-hexene	4.811	15.244	28.278	37.844	33.355		119.532
30	2-M-1-pentene	4.811	19.188	37.642	56.208	31.915		149.764
31	3-M-1-pentene	4.839	19.566	47.810	54.488	30.111		156.814
32	4-M-1-pentene	4.839	19.622	38.321	56.488	31.111		150.435
33	2-M-2-pentene	4.783	18.866	36.522	54.710	30.299		145.180
34	3-M-*cis*−2-pentene	4.783	18.866	46.326	52.976	29.432		152.383
35	4-M-*cis*−2-pentene	4.811	19.244	37.194	55.144	30.544		146.937
36	2-E−1-butene	4.811	19.132	47.019	54.040	29.887		154.889
37	2,3-MM-1-butene	4.811	23.132	55.935	69.396	27.943		181.217
38	3,3-MM-1-butene	4.839	27.510	64.215	67.788	27.111		191.463
39	2,3-MM-2-butene	4.755	22.488	54.066	67.464	27.243		176.016
40	acetylene	0.780						0.780
41	1,3-butadiene	2.694	7.308	9.042				19.044
42	1-butyne	2.725	7.340	9.120				19.185
43	2-butyne	2.670	6.900	8.790				18.360
44	propadiene	1.696	3.390					5.086
45	propyne	1.725	3.450					5.175
46	1-pentyne	3.725	11.340	18.955	18.790			52.810
47	cyclopentene	4.811	19.244	48.110	96.220	14.433		182.818
48	benzene	5.430	21.720	54.300	108.600	190.050	24.435	404.535

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

Table 4. Path (*p*), Cluster (*c*), and Pathcluster (*pc*) Terms of Valence Overall Wiener Index VOW of the 48 Alkanes

no.	molecule[a]	^{3}VOW$_P$	^{3}VOW$_c$	^{4}VOW$_P$	^{4}VOW$_c$	^{4}VOW$_{Pc}$	^{5}VOW$_P$	^{5}VOW$_c$	^{5}VOW$_{Pc}$	^{6}VOW$_P$
1	C2									
2	C3									
3	nC4	10.000	0.000							
4	2MC3	0.000	9.000							
5	nC5	20.000	0.000	20.000	0.000	0.000				
6	2MC4	20.000	9.000	0.000	0.000	18.000				
7	22MMC3	0.000	36.000	0.000	16.000	0.000				
8	nC6	30.000	0.000	40.000	0.000	0.000	35.000	0.000	0.000	
9	2MC5	30.000	9.000	40.000	0.000	18.000	0.000	0.000	32.000	
10	3MC5	40.000	9.000	20.000	0.000	36.000	0.000	0.000	31.000	
11	23MMC4	40.000	18.000	0.000	0.000	72.000	0.000	29.000	0.000	
12	22MMC4	30.000	36.000	0.000	16.000	54.000	0.000	0.000	28.000	
13	cyclopropane	10.000	0.000							
14	cyclobutane	40.000	0.000	20.000	0.000	0.000				
15	cyclopentane	50.000	0.000	100.000	0.000	0.000	35.000	0.000	0.000	
16	cyclohexane	60.000	0.000	120.000	0.000	0.000	210.000	0.000	0.000	56.000
17	ethylene									
18	propene									
19	1-butene	9.489	0.000							

Table 4 (Continued)

no.	molecule[a]	$^3VOW_P$	$^3VOW_c$	$^4VOW_P$	$^4VOW_c$	$^4VOW_{Pc}$	$^5VOW_P$	$^5VOW_c$	$^5VOW_{Pc}$	$^6VOW_P$
20	*cis*−2-butene	9.300	0.000							
21	2-M-propene	0.000	8.433							
22	1-pentene	19.405	0.000	19.300	0.000	0.000				
23	*cis*−2-pentene	18.789	0.000	18.922	0.000	0.000				
24	2-M-1-butene	19.293	8.433	0.000	0.000	17.188				
25	3-M-1-butene	18.978	8.916	0.000	0.000	17.300				
26	2-M-2-butene	18.600	8.433	0.000	0.000	16.866				
27	1-hexene	29.405	0.000	39.189	0.000	0.000	34.111	0.000	0.000	
28	*cis*−2-hexene	28.705	0.000	38.222	0.000	0.000	33.544	0.000	0.000	
29	*cis*−3-hexene	28.278	0.000	37.844	0.000	0.000	33.355	0.000	0.000	
30	2-M-1-pentene	29.209	8.433	39.020	0.000	17.188	0.000	0.000	31.915	
31	3-M-1-pentene	38.849	8.916	19.300	0.000	35.188	0.000	0.000	30.111	
32	4-M-1-pentene	29.321	9.000	38.600	0.000	17.888	0.000	0.000	31.111	
33	2-M-2-pentene	28.089	8.433	37.844	0.000	16.866	0.000	0.000	30.299	
34	3-M-*cis*−2-pentene	37.893	8.433	18.922	0.000	34.054	0.000	0.000	29.432	
35	4-M-*cis*−2-pentene	28.278	8.916	37.844	0.000	17.300	0.000	0.000	30.544	
36	2-E−1-butene	38.586	8.433	19.664	0.000	34.376	0.000	0.000	29.887	
37	2,3-MM-1-butene	38.586	17.349	0.000	0.000	69.396	0.000	27.943	0.000	
38	3,3-MM-1-butene	28.467	35.748	0.000	15.888	51.900	0.000	0.000	27.111	
39	2,3-MM-2-butene	37.200	16.866	0.000	0.000	67.464	0.000	27.243	0.000	
40	acetylene									
41	1,3-butadiene	9.042								
42	1-butyne	9.120								
43	2-butyne	8.790								
44	propadiene									
45	propyne									
46	1-pentyne	18.955	0.000	18.790	0.000	0.000				
47	cyclopentene	48.110	0.000	96.220	0.000	0.000	33.970			
48	benzene	54.300	0.000	108.600	0.000	0.000	190.050	0.000	0.000	50.680

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

Table 5. Experimental Values for the Physical Properties of the 48 Alkanes

no.	molecule[a]	V_{cal}	bp	LogP	MR	PC	TC
1	C2	35.522	−88.630	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	68.740	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	cyclopropane	41.443	−32.800				
14	cyclobutane	53.857	12.600				
15	cyclopentane	65.711	49.300	2.050		45.10	124.70
16	cyclohexane	77.044	80.700	2.460		41.00	238.60
17	ethylene	31.203	−103.700			51.20	280.40
18	propene	43.031	−47.400			46.00	91.90
19	1-butene	55.659	−6.300	2.460		40.20	146.00
20	*cis*−2-butene	57.756	0.880			42.00	155.00
21	2-M-propene	60.504					
22	1-pentene	67.473	29.900	1.590	24.8580	40.40	191.00
23	*cis*−2-pentene	68.513	36.900	2.200			
24	2-M-1-butene	67.407	31.200	2.200			
25	3-M-1-butene	71.324	20.100	2.070			
26	2-M-2-butene	67.345	38.500		24.9550		
27	1-hexene	81.738	63.300	2.070	29.2080		
28	*cis*−2-hexene	83.430	68.800	2.700			
29	*cis*−3-hexene	80.846	66.400	2.700			
30	2-M-1-pentene	84.001	60.700	2.610	29.3980		
31	3-M-1-pentene	81.181	54.100		29.4850		
32	4-M-1-pentene	80.057	53.900	2.500	29.5420		
33	2-M-2-pentene	83.662	67.300		29.7540		
34	3-M-*cis*−2-pentene	82.132	70.400				
35	4-M-*cis*−2-pentene	79.927	58.600	2.540			
36	2-E−1-butene	80.516	64.700	2.410	29.3910		
37	2,3-MM-1-butene	80.351	55.700		30.0630		
38	3,3-MM-1-butene	79.432	41.200		29.5980		

Table 5 (Continued)

no.	molecule[a]	V_{cal}	bp	LogP	MR	PC	TC
39	2,3-MM-2-butene	80.025	73.200		29.5900		
40	acetylene	24.778	−84.000			62.40	35.50
41	1,3-butadiene	50.697	−4.400	1.630		43.20	152.00
42	1-butyne	52.013	8.100	1.440			
43	2-butyne	51.282	10.500	1.440			
44	propadiene	37.391				44.20	120.00
45	propyne	37.378				53.50	127.80
46	1-pentyne	68.828		1.980			
47	cyclopentene	63.355	44.200	1.750		47.80	232.94
48	benzene	69.303	88.100	2.130		49.20	288.90

The following correlations have been obtained

$$V_{cal} = 1.53095 - 4.39037 \ln VOW + 31.87185 \,^1VOW - 2.69232 \,^2VOW + 1.25316 \,^3VOW - 1.52508 \,^3VOW_p - 0.05523 \,^4VOW_p - 0.97513 \,^4VOW_c \quad (10)$$

$$n = 48, r = 0.9955, s = 1.72, F = 628$$

$$bp = -125.57449 + 25.61543 \ln VOW + 37.19348 \,^1VOW - 7.23669 \,^2VOW + 1.20895 \,^3VOW_c + 0.27420 \,^4VOW_{pc} \quad (11)$$

$$n = 44, r = 0.9906, s = 6.72, F = 398$$

$$\log P = 0.44348 - 0.98301 \ln VOW + 1.57592 \,^1VOW - 0.02702 \,^3VOW - 0.04924 \,^3VOW_P \quad (12)$$

$$n = 29, r = 0.9280, s = 0.22, F = 37$$

$$MR = 3.47989 + 3.73740 \ln VOW + 1.85482 \,^1VOW - 0.03907 \,^3VOW \quad (13)$$

$$n = 19, r = 0.9964, s = 0.19, F = 685 >$$

$$PC = 62.91212 - 9.00299 \,^1VOW + 0.19563 \,^3VOW + 0.18786 \,^4VOW_p \quad (14)$$

$$n = 25, r = 0.9307, s = 3.33, F = 45 >$$

$$TC = 40.59695 + 49.93087 \ln VOW - 5.72402 \,^2VOW + 1.10795 \,^3VOW \quad (15)$$

$$n = 25, r = 0.9906, s = 9.93, F = 366$$

CONCLUSION

From these relations we can see that the valence overall Wiener index has a good relationship with molecular volume, boiling point, partition coefficients, molecular refractions, critical temperature, and critical pressures both for hydrocarbons and unsaturated hydrocarbons with different types of multiple bonds. But the standard deviations are not as good as Bonchev's;[6] however, the ability to include multiply bonded structures compensates for the loss. We obtained relatively good regression coefficients, and it is shown that the relative distance duplicates some information contained in unsaturated hydrocarbons and that the valence overall Wiener index is a potential structure descriptor of unsaturated hydrocarbons with different types of multiple bonds.

REFERENCES AND NOTES

(1) Wiener, H. *J. Am. Chem. Soc.* **1947**, *69*, 17.
(2) Plesnik, J. *J. Graph. Theory* **1984**, *8*, 1.
(3) Bonchev, D. *Bulg. Chem. Commun.* **1995**, *28*, 567.
(4) Bonchev, D. *ASR/QSAR Environ. Res.* **1997**, *7*, 23.
(5) Bonchev, D. *J. Chem. Inf. Comput. Sci.* **2000**, *40*, 934.
(6) Bonchev, D. *J. Chem. Inf. Comput. Sci.* **2001**, *41*, 582.
(7) Yang, P.; Gao, X. H. *Chemical Bonding and Structure−Property Relation*; Higher Education Press: Beijing, 1987.
(8) Kier, L. B.; Hall, L. H. *Molecular Connectivity in Chemistry and Drug Research*; Academic: New York, 1976.
(9) Xu, L.; Hu, C. Y. *Application of Chemical Graph*; Scientific Press: Beijing, 2000.
(10) Wang, L. S.; Zhi, Z. L. *Molecular Connectivity and Molecular Structure−Activity*; Chinese Environment Science Press: Beijing, 1992.
(11) Diane, E. N.; Wei, I. C.; Seybold, P. G. *J. Am. Chem. Soc.* **1988**, *110*, 4186.