

DESIGN OF TOPOLOGICAL INDICES. PART 12.¹

PARAMETERS FOR VERTEX- AND EDGE-WEIGHTED MOLECULAR GRAPHS

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The weighted molecular matrices are the source of important graph theoretic descriptors of the chemical structure. Such descriptors can be used in structure-property studies and in measuring the chemical similarity and diversity of the compounds from chemical databases. Five approaches are presented for the calculation of atom and bond parameters for heteroatom-containing organic compounds represented as vertex- and edge-weighted molecular graphs. The first two weighting schemes compute the atom and bond weights on the basis of the relative atomic mass, using carbon as standard. The other three systems use the relative atom polarizability, radius, and electronegativity to compute atom and bond weights, again with the carbon atom as standard. The new parameter sets can be used to compute the adjacency matrix, the distance matrix, other molecular graph matrices and graph structural descriptors derived therefrom.

INTRODUCTION

Molecular graph descriptors are currently used to develop structure-property models and to measure the similarity and diversity of the compounds from chemical databases. Although the graph model of the chemical structure does not consider the information regarding the three-dimensional structure of the molecule, the molecular graph descriptors are effective parameters in modeling various physical, chemical, and biological properties of organic compounds. Among the large class of molecular graph invariants used to express in a numerical form the chemical structure, we mention here graph theoretic polynomials and spectra, spectral moments, topological indices, distances, walks and paths in graphs, topological indices.²⁻¹⁰

In this paper chemical structures are represented as molecular graphs. By removing all hydrogen atoms from the chemical formula of a compound containing covalent bonds one obtains the hydrogen-depleted (or hydrogen-suppressed) molecular graph of that compound, whose vertices correspond to non-hydrogen atoms and whose edges correspond to covalent bonds. In this study such expressions as "molecular graph" and "molecule", "vertex" and "atom", "edge" and "bond" are used interchangeably.

Chemical compounds containing multiple or aromatic bonds, or heteroatoms are represented as vertex- and edge-weighted (VEW) molecular graphs. The computation of structural descriptors and topological indices from vertex- and edge-weighted molecular graphs requires the development of special parameters. A widely used set of parameters for VEW graphs was developed by Trinajstić and coworkers¹¹ by weighting the contributions of atoms and bonds with parameters based on the atomic number Z and the topological bond order. In the atomic number weighting scheme Z the vertex parameter $Vw(Z)_i$ of the vertex v_i (representing atom i from a molecule) is defined by the following equation:

$$Vw(Z)_i = 1 - Z_c/Z_i = 1 - 6/Z_i, \quad (1)$$

where Z_i is the atomic number Z of the atom i and $Z_C = 6$ is the atomic number Z of carbon. The edge parameter $Ew(Z)_{ij}$ that characterizes the bond between atoms i and j (represented in the molecular graph by the edge e_{ij} between vertices v_i and v_j), is defined as:

$$Ew(Z)_{ij} = Z_C Z_C / Bo_{ij} Z_i Z_j = 6 \cdot 6 / Bo_{ij} Z_i Z_j \quad (2)$$

where Bo_{ij} is the topological bond order of the edge between vertices v_i and v_j . The topological bond order takes the value 1 for single bonds, 2 for double bonds, 3 for triple bonds and 1.5 for aromatic bonds.

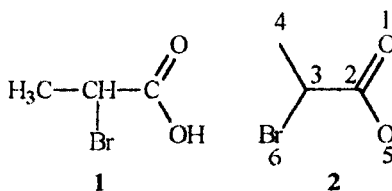
The Z weighting scheme was applied with good results in various QSAR studies.¹²⁻¹⁴ There exist other methods for computing heteroatom parameters,¹⁵ and weights for chemical bonds.¹⁶ A different approach for considering heteroatoms was developed for the Balaban index J , considering electronegativity or covalent radii.^{17,18} The extended index J was applied in QSAR studies.¹⁹ Using the parameters developed for the Balaban index J , two general weighting schemes for the molecular matrices were proposed: X , the relative electronegativity scheme, and Y , the relative covalent radii scheme.²⁰

In this paper five approaches are presented for the calculation of atom and bond parameters in heteroatom-containing organic compounds represented as vertex- and edge-weighted molecular graphs. The first two weighting schemes compute the atom and bond weights on the basis of relative atomic mass, using carbon as standard. The remaining three systems use the relative atom polarizability, radius, and electronegativity to compute atom and bond weights, again with the carbon atom as standard. The new parameter sets can be used to compute the adjacency matrix, the distance matrix, other molecular graph matrices, graph structural descriptors, and topological indices derived from them.

Parameters for molecular graphs

The weighting schemes defined in the present paper will be applied to the computation of some molecular graph descriptors with graph operators. Three molecular matrices will be used to compute graph invariants: the adjacency matrix A , the distance matrix D , and the reciprocal distance matrix RD .²¹⁻²³ An operator uses some mathematical operations performed on a certain molecular matrix computed with a weighting scheme. The operatorial notation of the graph invariants offers a simple way to indicate the weighting scheme and to denote similar descriptors computed with the same mathematical procedure from different molecular matrices.

The characteristic polynomial operator $Ch(M,w,G)$ is the characteristic polynomial for the matrix M of the molecular graph G computed with the weighting scheme w . The graph spectrum operator $Sp(M,w,G)$ is the set of eigenvalues for the matrix M of the molecular graph G computed with the weighting scheme w , or the set of zeros of the characteristic polynomial, $Ch(M,w,G) = 0$.



As examples of structural descriptors computed with the Z weighting scheme we give the characteristic polynomials and spectra for the adjacency, distance, and reciprocal distance matrices of 2-bromopropanoic acid **1** whose molecular graph is represented as graph **2**.

$$Ch(A,Z,2) = x^6 - 1.329x^5 - 2.256x^4 + 3.378x^3 - 0.377x^2 - 0.660x + 0.146$$

$$Ch(D,Z,2) = x^6 - 1.329x^5 - 34.505x^4 - 64.729x^3 - 29.331x^2 + 4.461x + 2.029$$

$$Ch(RD,Z,2) = x^6 - 1.329x^5 - 48.791x^4 - 19.138x^3 + 287.493x^2 + 212.640x + 37.251$$

$$\text{Sp}(A, Z, 2) = \{1.596, 0.840, 0.629, 0.250, -0.449, -1.537\}$$

$$\text{Sp}(D, Z, 2) = \{7.322, 0.257, -0.245, -0.884, -1.305, -3.815\}$$

$$\text{Sp}(RD, Z, 2) = \{7.454, 2.666, -0.288, -0.460, -2.602, -5.442\}.$$

The vertex sum operator for the vertex v_i in a graph G , $\text{VS}(\mathbf{M}, w, G)_i$, is defined as the sum of the elements in the column i , or row i , of the molecular matrix $\mathbf{M}(w) = \mathbf{M}(w, G)$ computed with the weighting scheme w :

$$\text{VS}(\mathbf{M}, w, G) = \sum_{j=1}^N [\mathbf{M}(w)]_{ij} = \sum_{j=1}^N [\mathbf{M}(w)]_{ji}. \quad (3)$$

If \mathbf{M} is the distance matrix, the operator is identical with the distance sum $\text{DS}(w, G)$, while if \mathbf{M} is the reciprocal distance matrix \mathbf{RD} , this operator gives the reciprocal distance sum $\text{RDS}(w, G)$.²²

The Wiener operator, $\text{Wi}(\mathbf{M}, w, G)$, computed from the molecular matrix \mathbf{M} with the weighting scheme w is defined with the equation:

$$\text{Wi}(\mathbf{M}, w, G) = \sum_{i=1}^N \sum_{j=1}^N [\mathbf{M}(w)]_{ij}. \quad (4)$$

If \mathbf{M} is the \mathbf{D} matrix, the Wiener operator gives the Wiener index W ,^{24,25} while if \mathbf{M} is the \mathbf{RD} matrix, the Wiener operator gives the Harary index.^{22,23}

The A Weighting Scheme. The atomic mass weighting scheme A uses the atomic mass A to define the vertex parameter $Vw(A)_i$ for the atom i :

$$Vw(A)_i = 1 - A_c/A_i = 1 - 12.011/A_i \quad (5)$$

and the edge parameter $Ew(A)_{ij}$ for the bond between atoms i and j :

$$Ew(A)_{ij} = A_c A_c / B o_{ij} A_i A_j = 12.011 \cdot 12.011 / B o_{ij} A_i A_j, \quad (6)$$

where A_i is the atomic mass of atom i , A_j is the atomic mass of atom j , and $A_c = 12.011$ is the atomic mass for carbon. Selected values for the atomic mass A , used in eqs. (5) and (6), are presented in Table 1, column 3.

Table 1

Selected set of atomic properties used with different weighting schemes: atomic number Z , atomic mass A , polarizability α_v (\AA^3), radius r_α (\AA), and electronegativity χ_α

Element	Z	A	α_v	r_α	χ_α
B	5	10.811	3.03	1.45	2.02
C	6	12.011	1.76	1.21	2.55
N	7	14.007	1.10	1.03	3.12
O	8	15.999	0.802	0.93	3.62
F	9	18.998	0.557	0.82	4.23
Si	14	28.086	5.38	1.75	1.87
P	15	30.974	3.63	1.54	2.22
S	16	32.066	2.90	1.43	2.49
Cl	17	35.453	2.18	1.30	2.82
As	33	74.922	4.31	1.63	2.11
Se	34	78.960	3.77	1.56	2.31
Br	35	79.904	3.05	1.45	2.56
Te	52	127.60	5.5	1.77	2.08
I	53	126.90	4.7	1.68	2.27

Table 2

Vertex parameters V_w computed with different weighting schemes: $V_w(Z)$, based on the atomic number Z ; $V_w(A)$, based on the atomic mass A ; $V_w(P)$, based on the atomic polarizability α_p ; $V_w(R)$, based on the atomic radius r_a ; $V_w(E)$, based on the atomic electronegativity χ_a

Atom	$V_w(Z)$	$V_w(A)$	$V_w(P)$	$V_w(R)$	$V_w(E)$
B	-0.200	-0.111	0.419	0.166	-0.262
C	0.000	0.000	0.000	0.000	0.000
N	0.143	0.143	-0.600	-0.175	0.183
O	0.250	0.249	-1.195	-0.301	0.296
F	0.333	0.368	-2.160	-0.476	0.397
Si	0.571	0.572	0.673	0.309	-0.364
P	0.600	0.612	0.515	0.214	-0.149
S	0.625	0.625	0.393	0.154	-0.024
Cl	0.647	0.661	0.193	0.069	0.096
As	0.818	0.840	0.592	0.258	-0.209
Se	0.824	0.848	0.533	0.224	-0.104
Br	0.829	0.850	0.423	0.166	0.004
Te	0.885	0.906	0.680	0.316	-0.226
I	0.887	0.905	0.626	0.280	-0.123

Table 2 gives in column 3 the values for the vertex parameters $V_w(A)$ computed from the atomic mass weighting scheme A . For boron the $V_w(A)$ parameter has a negative value because its atomic mass is lower than that of carbon. Carbon has a $V_w(A)$ parameter equal to zero, while for the remaining atoms from Table 2 one can observe a steady increase of the $V_w(A)$ weight with the increase of the corresponding atomic mass. A comparison with the corresponding parameters obtained with the Z weighting scheme, presented in column 2 of Table 2, shows that the $V_w(A)$ parameters are close in numerical value to the $V_w(Z)$ parameters because the ratio Z/A is approximately constant for the atoms presented in Table 2. The edge parameters $E_w(A)$ computed for a selected set of bonds with the atomic mass A weighting scheme are given in Table 3. For a pair of bonded atoms i and j the $E_w(A)$ parameter decreases with the increase of the atomic mass of the two atoms, as one may see in the series of single bonds C-F, C-Cl, C-Br, C-I.

Table 3

Edge parameters $E_w(A)$ computed with the atomic mass weighting scheme A

Atom _i	Atom _j	single	double	triple	aromatic
C	C	1.000	0.500	0.333	0.667
C	N	0.857	0.429	0.286	0.572
C	O	0.751	0.375		
C	F	0.632			
C	Si	0.428			
C	P	0.388			
C	S	0.375	0.187		0.250
C	Cl	0.339			
C	Se	0.152			
C	Br	0.150			
C	Te	0.094			
C	I	0.095			
N	N	0.735	0.368		0.490
N	O	0.644	0.322		0.429
O	S	0.281	0.141		

Table 4

The vertex- and edge-weighted distance matrix $\mathbf{D}(A,2)$ for the molecular graph of 2-bromopropanoic acid **2** computed with the A weighting scheme

		$\mathbf{D}(A,2)$					
		1	2	3	4	5	6
1	0.249	0.375	1.375	2.375	1.126	1.526	
2	0.375	0.000	1.000	2.000	0.751	1.150	
3	1.375	1.000	0.000	1.000	1.751	0.150	
4	2.375	2.000	1.000	0.000	2.751	1.150	
5	1.126	0.751	1.751	2.751	0.249	1.901	
6	1.526	1.150	0.150	1.150	1.901	0.850	

As an example of computation of the vertex- and edge-weighted distance matrix with the A weighting scheme we present in Table 4 the distance matrix $\mathbf{D}(A,2)$ for the molecular graph of 2-bromopropanoic acid **2**. The vertex sum vector of the graph **2** is $\mathbf{VS}(\mathbf{D},A,2) = \{7.027, 5.276, 5.276, 9.276, 8.529, 6.727\}$. The sum of the elements from the upper triangle and the main diagonal of the distance matrix $\mathbf{D}(A,2)$ gives the Wiener index, $\mathbf{Wi}(\mathbf{D},A,2) = 21.730$. We present below some characteristic polynomials and spectra computed with the A weighting scheme for the \mathbf{A} , \mathbf{D} , and \mathbf{RD} matrices of the molecular graph **2**:

$$\mathbf{Ch}(\mathbf{A},A,2) = x^6 - 1.348x^5 - 2.241x^4 + 3.429x^3 - 0.402x^2 - 0.673x + 0.149$$

$$\mathbf{Ch}(\mathbf{D},A,2) = x^6 - 1.348x^5 - 34.263x^4 - 62.882x^3 - 26.107x^2 + 6.377x + 2.331$$

$$\mathbf{Ch}(\mathbf{RD},A,2) = x^6 - 1.348x^5 - 59.063x^4 - 18.574x^3 + 379.874x^2 + 273.629x + 46.311$$

$$\mathbf{Sp}(\mathbf{A},A,2) = \{1.593, 0.857, 0.634, 0.249, -0.450, -1.536\}$$

$$\mathbf{Sp}(\mathbf{D},A,2) = \{7.293, 0.297, -0.245, -0.882, -1.303, -3.812\}$$

$$\mathbf{Sp}(\mathbf{RD},A,2) = \{8.126, 2.801, -0.273, -0.460, -2.599, -6.247\}$$

The AH Weighting Scheme. The structural invariants computed from hydrogen-depleted molecular graphs do not reflect in an explicit way the number of hydrogen atoms attached to a certain atom. In order to define a weighting scheme based on the atomic mass A that gives atom and bond parameters different from those of the Z scheme, we consider the mass of a non-hydrogen atom together with that of the hydrogen atoms connected to it. The AH weighting scheme uses the following equation to define the vertex parameter $Vw(AH)_i$ for the non-hydrogen atom i :

$$Vw(AH)_i = 1 - A_C/(A_i + NoH_i A_H) = 1 - 12.011/(A_i + 1.0079NoH_i). \quad (7)$$

The edge parameter $Ew(AH)_{ij}$ for the bond between atoms i and j is defined with the equation:

$$\begin{aligned} Ew(AH)_{ij} &= A_C A_C / B_{o_{ij}}(A_i + NoH_i A_H)(A_j + NoH_j A_H) = \\ &= 12.011 \cdot 12.011 / B_{o_{ij}}(A_i + 1.0079NoH_i)(A_j + 1.0079NoH_j), \end{aligned} \quad (8)$$

where $A_C = 12.011$ is the atomic mass for carbon, $A_H = 1.0079$ is the atomic mass for hydrogen, NoH_i is the number of hydrogen atoms bonded to the heavy atom i , and NoH_j is the number of hydrogen atoms bonded to the heavy atom j .

Table 5 presents a set of vertex $V_w(AH)$ group parameters computed with the AH weighting scheme. Heavy atoms without adjacent hydrogen atoms have $V_w(AH)$ parameters identical with the corresponding $V_w(A)$ parameters presented in Table 2 column 3. An inspection of the values shows that equation (7) gives parameters that do not parallel the $V_w(A)$ values. A selected set of edge parameters $E_w(AH)$ computed with the AH weighting scheme is given in Table 6. Bonds between atoms that do not have adjacent hydrogen atoms have $E_w(AH)$ parameters equal to the corresponding $E_w(A)$ parameters presented in Table 3.

Table 5

Vertex parameters $V_w(AH)$ computed with the AH weighting scheme. Vertices representing atoms not bonded to hydrogen atoms have $V_w(AH)$ parameters identical with the corresponding $V_w(A)$ parameters presented in Table 2

Group	$V_w(AH)$	Group	$V_w(AH)$
CH ₃	0.201	NH	0.200
CH ₂	0.144	OH	0.294
CH	0.077	PH ₂	0.636
NH ₂	0.250	PH	0.624

Table 6

Edge parameters $E_w(AH)$ computed with the AH weighting scheme. Edges representing bonds between atoms not bonded to hydrogen atoms have $E_w(AH)$ parameters identical with the corresponding $E_w(A)$ parameters presented in Table 3

Bond	$E_w(AH)$	Bond	$E_w(AH)$
CH ₃ -CH ₂	0.684	N-CH ₂	0.734
CH ₃ -CH	0.737	N-CH	0.791
CH ₃ -C	0.799	NH=CH	0.369
CH ₂ -CH ₂	0.733	NH=C	0.400
CH ₂ -CH	0.790	N=CH	0.396
CH ₂ -C	0.856	OH-CH ₂	0.605
CH-CH	0.851	OH-CH	0.652
CH-C	0.923	OH-C	0.706
CH ₂ =CH	0.395	O-CH ₃	0.600
CH ₂ =C	0.428	O-CH ₂	0.643
CH≡C	0.308	O-CH	0.693
NH ₂ -CH ₂	0.642	O=CH	0.346
NH ₂ -CH	0.692	PH ₂ -CH ₂	0.312
NH ₂ -C	0.750	PH ₂ -CH	0.336
NH-CH ₃	0.639	PH ₂ -C	0.364
NH-CH ₂	0.685	PH-CH ₃	0.300
NH-CH	0.738	PH-CH ₂	0.322
NH-C	0.800	PH-CH	0.346
N-CH ₃	0.685	PH-C	0.376

As an example of application of the AH weighting scheme to the computation of molecular matrices, we give in Table 7 the distance matrix $\mathbf{D}(AH,2)$ and reciprocal distance matrix $\mathbf{RD}(AH,2)$ for the molecular graph of 2-bromopropanoic acid **2**. From the two matrices one obtains the following vertex sum vectors: $\mathbf{VS}(\mathbf{D},AH,2) = \{6.476, 4.725, 4.802, 7.874, 7.844, 6.129\}$, and $\mathbf{VS}(\mathbf{RD},AH,2) = \{5.796, 6.709, 11.113, 4.216, 4.237, 11.407\}$. The Wiener operator applied to the above matrices gives the Wiener indices $\mathbf{Wi}(\mathbf{D},AH,2) = 19.761$ and $\mathbf{Wi}(\mathbf{RD},AH,2) = 22.574$. The polynomials and spectra

Table 7

The vertex- and edge-weighted distance matrix $\mathbf{D}(AH,2)$ and reciprocal distance matrix $\mathbf{RD}(AH,2)$ for the molecular graph of 2-bromopropanoic acid **2** computed with the A weighting scheme

$\mathbf{D}(AH,2)$						
	1	2	3	4	5	6
1	0.249	0.375	1.298	2.035	1.082	1.437
2	0.375	0.000	0.923	1.660	0.706	1.061
3	1.298	0.923	0.077	0.737	1.629	0.139
4	2.035	1.660	0.737	0.201	2.366	0.876
5	1.082	0.706	1.629	2.366	0.294	1.768
6	1.437	1.061	0.139	0.876	1.768	0.850

$\mathbf{RD}(AH,2)$						
	1	2	3	4	5	6
1	0.249	2.664	0.770	0.491	0.925	0.696
2	2.664	0.000	1.084	0.603	1.416	0.942
3	0.770	1.084	0.077	1.357	0.614	7.211
4	0.491	0.603	1.357	0.201	0.423	1.142
5	0.925	1.416	0.614	0.423	0.294	0.566
6	0.696	0.942	7.211	1.142	0.566	0.850

computed for the molecular graph **2** with the AH weighting scheme are:

$$\text{Ch}(\mathbf{A},AH,2) = x^6 - 1.671x^5 - 1.115x^4 + 2.782x^3 - 0.950x^2 - 0.163x + 0.064$$

$$\text{Ch}(\mathbf{D},AH,2) = x^6 - 1.671x^5 - 26.197x^4 - 35.341x^3 - 8.381x^2 + 4.800x + 1.233$$

$$\text{Ch}(\mathbf{RD},AH,2) = x^6 - 1.671x^5 - 68.781x^4 - 17.519x^3 + 463.509x^2 + 323.459x + 50.760$$

$$\text{Sp}(\mathbf{A},AH,2) = \{1.463, 0.856, 0.621, 0.259, -0.250, -1.278\}$$

$$\text{Sp}(\mathbf{D},AH,2) = \{6.535, 0.348, -0.240, -0.701, -0.975, -3.296\}$$

$$\text{Sp}(\mathbf{RD},AH,2) = \{8.906, 2.855, -0.238, -0.474, -2.612, -6.766\}.$$

The static electric dipole polarizability is an atomic property that can be experimentally determined and theoretically computed. Recently a relationship was presented between atomic polarizability and electronegativity, leading to a new set of electronegativities for the elements in the periodic table.²⁶ A set of atomic radii was also computed from the atomic polarizabilities. Using the values for polarizability, electronegativity, and radius, we define the following three weighting schemes.

The P Weighting Scheme. The polarizability weighting scheme P uses the polarizability²⁶ α to define the vertex parameter $Vw(P)_i$ for the atom i :

$$Vw(P)_i = 1 - \alpha_c/\alpha_i = 1 - 1.76/\alpha_i. \quad (9)$$

The bond between atoms i and j has an edge parameter $Ew(P)_{ij}$ computed with the equation:

$$Ew(P)_{ij} = \alpha_c\alpha_c/Bo_{ij}\alpha_i\alpha_j = 1.76 \cdot 1.76/Bo_{ij}\alpha_i\alpha_j, \quad (10)$$

where $\alpha_C = 1.76$ is the carbon polarizability, α_i and α_j are the polarizabilities of atoms i and j , respectively. Some values for the polarizability α that may be used in eqs. (9) and (10) are presented in Table 1, column 4.²⁶ Values for the vertex parameters $V_w(P)$ computed with the polarizability weighting scheme P are given in Table 2, column 4. For the elements with a polarizability lower than that of carbon (N, O, and F in Table 1), the corresponding $V_w(P)$ values are negative, while for the elements with α greater than α_C the $V_w(P)$ parameters are positive. From the definition of the P weighting scheme it is clear that the parameter $V_w(P)$ captures the periodicity of the polarizability. Selected values for the edge parameters $E_w(P)$ computed with the polarizability weighting scheme P are presented in Table 8. Several $E_w(P)$ parameters for single bonds have values greater than 1, i.e. C–N, C–O, C–F, N–N, N–O, and O–S. Table 8 presents also several examples of double and aromatic bonds with $E_w(P)$ values greater than 1.

Table 8

Edge parameters $E_w(P)$ computed with the molecular polarizability weighting scheme P

Atom _i	Atom _j	single	double	triple	aromatic
C	C	1.000	0.500	0.333	0.667
C	N	1.600	0.800	0.533	1.067
C	O	2.195	1.097		
C	F	3.160			
C	Si	0.327			
C	P	0.485			
C	S	0.607	0.303		0.405
C	Cl	0.807			
C	Se	0.467			
C	Br	0.577			
C	Te	0.320			
C	I	0.374			
N	N	2.560	1.280		1.707
N	O	3.511	1.756		2.341
O	S	1.332	0.666		

Table 9

The vertex- and edge-weighted distance matrix $D(P,2)$ for the molecular graph of 2-bromopropanoic acid **2** computed with the P weighting scheme

$D(P,2)$		1	2	3	4	5	6
1		-1.195	1.097	2.097	3.097	3.292	2.674
2		1.097	0.000	1.000	2.000	2.195	1.577
3		2.097	1.000	0.000	1.000	3.195	0.577
4		3.097	2.000	1.000	0.000	4.195	1.577
5		3.292	2.195	3.195	4.195	-1.195	3.772
6		2.674	1.577	0.577	1.577	3.772	0.423

The polarizability weighting scheme P was used to compute the distance matrix of the molecular graph **2**; the matrix $D(P,2)$, presented in Table 9, offers the vertex invariants $VS(D,P,2)$, $VS(D,P,2) = \{11.063, 7.869, 7.869, 11.869, 15.452, 10.600\}$, and the Wiener index, $Wi(D,P,2) = 31.378$. Some polynomials and spectra of the graph **2** computed with the polarizability weighting scheme P are:

$$\text{Ch}(A,P,2) = x^6 + 1.966x^5 - 7.936x^4 - 9.976x^3 + 9.758x^2 + 8.246x - 3.041$$

$$\text{Ch}(D,P,2) = x^6 + 1.966x^5 - 90.913x^4 - 552.991x^3 - 1055.969x^2 - 741.117x - 147.939$$

$$\text{Ch}(\mathbf{RD}, P, 2) = x^6 + 1.966x^5 - 7.468x^4 - 25.497x^3 - 25.295x^2 - 8.660x - 0.752$$

$$\text{Sp}(\mathbf{A}, P, 2) = \{2.308, 1.001, 0.302, -1.120, -1.195, -3.261\}$$

$$\text{Sp}(\mathbf{D}, P, 2) = \{11.259, -0.328, -0.979, -1.600, -4.137, -6.180\}$$

$$\text{Sp}(\mathbf{RD}, P, 2) = \{3.331, -0.130, -0.457, -1.341, -1.621, -1.749\}.$$

The R Weighting Scheme. The atomic radius weighting scheme R uses the atomic radius r_α computed from the atomic polarizability²⁶ to define the vertex parameter $Vw(R)_i$ for the atom i :

$$Vw(R)_i = 1 - r_C/r_i = 1 - 1.21/r_i \quad (11)$$

and an edge parameter $Ew(R)_{ij}$ computed for the bond between atoms i and j :

$$Ew(R)_{ij} = r_C r_C / B_{ij} r_i r_j = 1.21 \cdot 1.21 / B_{ij} r_i r_j, \quad (12)$$

where $r_C = 1.21$ is the carbon radius, r_i and r_j are the atomic radii of atoms i and j , respectively. Selected values for the atomic radius r that may be used in eqs. (11) and (12) are reported in Table 1, column 5;²⁶ these values were used to compute the vertex parameters $Vw(R)$ from Table 2, column 5. The $Vw(R)$ parameters may have negative values, as is the case with N, O, and F. Using formula (12) one may obtain the edge parameters $Ew(R)$ included in Table 10. The same six single bonds that have $Ew(P)$ parameters greater than 1 have also $Ew(R)$ parameters greater than 1. On the other hand, the variation of $Ew(R)$ parameters does not parallel that of $Ew(P)$ parameters; for example, while $Ew(P)$ is greater than 1 for the bonds C=O, N=N, and N=O, the parameter $Ew(R)$ is lower than 1 for the same set of bonds.

Table 10

Edge parameters $Ew(R)$ computed with the atomic radius weighting scheme R

Atom _i	Atom _j	single	double	triple	aromatic
C	C	1.000	0.500	0.333	0.667
C	N	1.175	0.587	0.392	0.783
C	O	1.301	0.651		
C	F	1.476			
C	Si	0.691			
C	P	0.786			
C	S	0.846	0.423		0.564
C	Cl	0.931			
C	Se	0.776			
C	Br	0.834			
C	Te	0.684			
C	I	0.720			
N	N	1.380	0.690		0.920
N	O	1.528	0.764		1.019
O	S	1.101	0.550		

An example of a molecular matrix computed with the R weighting scheme is presented in Table 11; the distance matrix $\mathbf{D}(R, 2)$ for the molecular graph of 2-bromopropanoic acid **2** is used to compute the vertex sum vector $\mathbf{VS}(\mathbf{D}, R, 2) = \{9.087, 6.786, 6.786, 10.786, 11.689, 10.290\}$, and the Wiener index $\mathbf{Wi}(\mathbf{D}, R, 2) = 27.494$. Using the \mathbf{A} , \mathbf{D} , and \mathbf{RD} matrices of the molecular graph **2** and the

Table 11

The vertex- and edge-weighted distance matrix $D(R,2)$ for the molecular graph of 2-bromopropanoic acid **2** computed with the R weighting scheme

		$D(R,2)$					
		1	2	3	4	5	6
1		-0.301	0.651	1.651	2.651	1.952	2.485
2		0.651	0.000	1.000	2.000	1.301	1.834
3		1.651	1.000	0.000	1.000	2.301	0.834
4		2.651	2.000	1.000	0.000	3.301	1.834
5		1.952	1.301	2.301	3.301	-0.301	3.136
6		2.485	1.834	0.834	1.834	3.136	0.166

R weighting scheme one obtains the following characteristic polynomials and spectra:

$$\text{Ch}(\mathbf{A},R,2) = x^6 + 0.437x^5 - 4.821x^4 - 1.594x^3 + 3.650x^2 + 0.760x - 0.105$$

$$\text{Ch}(\mathbf{D},R,2) = x^6 + 0.437x^5 - 61.310x^4 - 279.460x^3 - 460.116x^2 - 302.458x - 64.628$$

$$\text{Ch}(\mathbf{RD},R,2) = x^6 + 0.437x^5 - 8.559x^4 - 14.596x^3 - 5.939x^2 + 1.245x + 0.798$$

$$\text{Sp}(\mathbf{A},R,2) = \{1.931, 0.900, 0.096, -0.301, -1.027, -2.035\}$$

$$\text{Sp}(\mathbf{D},R,2) = \{9.575, -0.419, -0.843, -1.757, -2.335, -4.659\}$$

$$\text{Sp}(\mathbf{RD},R,2) = \{3.432, 0.323, -0.469, -0.680, -1.283, -1.760\}.$$

The E Weighting Scheme. The electronegativity weighting scheme E uses the atomic electronegativity²⁶ χ to define the vertex parameter $Vw(E)$ for atom i :

$$Vw(E)_i = 1 - \chi_C/\chi_i = 1 - 2.55/\chi_i \quad (13)$$

The bond between atoms i and j has an edge parameter $Ew(E)_{ij}$ computed with the formula:

$$Ew(E)_{ij} = \chi_C\chi_C/Bo_{ij}\chi_i\chi_j = 2.55 \cdot 2.55/Bo_{ij}\chi_i\chi_j \quad (14)$$

where $\chi_C = 2.55$ is the carbon electronegativity, χ_i and χ_j are the electronegativities of atoms i and j , respectively. Values for the electronegativity χ that may be used to compute vertex and edge parameters $Vw(E)$ and $Ew(E)$ are presented in Table 1, column 6;²⁶ using these values one obtains the vertex parameters $Vw(E)$ from Table 2, column 6 and the edge parameters $Ew(E)$ presented in Table 12. All ele-

Table 12

Edge parameters $Ew(E)$ computed with the atomic electronegativity weighting scheme E

Atom _i	Atom _j	Single	double	triple	aromatic
C	C	1.000	0.500	0.333	0.667
C	N	0.817	0.409	0.272	0.545
C	O	0.704	0.352		
C	F	0.603			
C	Si	1.364			
C	P	1.149			
C	S	1.024	0.512		0.683
C	Cl	0.904			
C	Se	1.104			
C	Br	0.996			
C	Te	1.226			
C	I	1.123			
N	N	0.668	0.334		0.445
N	O	0.576	0.288		0.384
O	S	0.721	0.361		

ments with electronegativity lower than that of carbon have negative values for the $Vw(E)$ parameters; Table 2 presents several such cases, namely B, Si, P, S, As, Se, Te and I. All other heteroatoms from Table 2 have positive $Vw(E)$ values. The closer the electronegativity of an atom to that of carbon, the closer to zero the corresponding $Vw(E)$ parameter. A number of single bond $Ew(E)$ parameters for have values greater than 1, i.e. C-Si, C-P, C-S, C-Se, C-Te, and C-I. For the same set of bonds, the $Ew(Z)$, $Ew(A)$, $Ew(P)$, and $Ew(R)$ parameters have values lower than 1, showing that the electronegativity weighting scheme E gives a numerical representation of the chemical structure different from that of the other schemes.

Table 13

The vertex- and edge-weighted distance matrix $\mathbf{D}(E,2)$ for the molecular graph of 2-bromopropanoic acid **2** computed with the E weighting scheme

$\mathbf{D}(E,2)$	
	1 2 3 4 5 6
1	0.296 0.352 1.352 2.352 1.057 2.348
2	0.352 0.000 1.000 2.000 0.704 1.996
3	1.352 1.000 0.000 1.000 1.704 0.996
4	2.352 2.000 1.000 0.000 2.704 1.996
5	1.057 0.704 1.704 2.704 0.296 2.701
6	2.348 1.996 0.996 1.996 2.701 0.004

We have to mention here that whereas the atom and bond parameters computed the Z and A weighting schemes show a monotonous variation with the atomic number Z or with the atomic mass, the new parameter scales P , E , and R show a periodicity in their variation.

The distance matrix of the molecular graph **2**, $\mathbf{D}(R,2)$, computed with the electronegativity E weighting scheme, is presented in Table 13; the sum of the elements on its columns (or rows) give the vertex invariants $\mathbf{VS}(\mathbf{D},E,2)$, $\mathbf{VS}(\mathbf{D},E,2) = \{7.757, 6.053, 6.053, 10.053, 9.166, 10.041\}$, while the sum of the application of the formula (4) gives the Wiener index, $\mathbf{Wi}(\mathbf{D},E,2) = 24.859$. Some polynomials and spectra of the graph **2** computed with the electronegativity weighting scheme E are:

$$\mathbf{Ch}(\mathbf{A},E,2) = x^6 - 0.595x^5 - 3.523x^4 + 1.962x^3 + 0.969x^2 - 0.367x + 0.001$$

$$\mathbf{Ch}(\mathbf{D},E,2) = x^6 - 0.595x^5 - 46.996x^4 - 149.490x^3 - 164.036x^2 - 68.456x - 8.138$$

$$\mathbf{Ch}(\mathbf{RD},E,2) = x^6 - 0.595x^5 - 16.169x^4 - 18.386x^3 + 5.339x^2 + 10.864x + 2.776$$

$$\mathbf{Sp}(\mathbf{A},E,2) = \{1.813, 0.768, 0.296, 0.002, -0.497, -1.786\}$$

$$\mathbf{Sp}(\mathbf{D},E,2) = \{8.488, -0.194, -0.627, -0.958, -1.994, -4.120\}$$

$$\mathbf{Sp}(\mathbf{RD},E,2) = \{4.746, 0.776, -0.450, -0.499, -1.214, -2.764\}$$

The Wiener operator is used to compute a series of topological indices with the Z , A , P , R , and E weighting schemes. Table 14 presents the Wiener indices computed from the distance matrix \mathbf{D} for butane and related molecules with the molecular graph CCCHet, where Het represents a heteroatom, while Table 15 presents the Wiener indices computed from the reciprocal distance matrix \mathbf{RD} for the same set of compounds. The inspection of the values in Tables 14 and 15 shows that $\mathbf{Wi}(\mathbf{D},Z)$ and $\mathbf{Wi}(\mathbf{D},A)$ increase with increasing atomic number, while $\mathbf{Wi}(\mathbf{RD},Z)$ and $\mathbf{Wi}(\mathbf{RD},A)$ decrease with increasing atomic number. The topological indices computed with the P , R , and E weighting schemes show a periodicity in their values; obviously, the three weighting schemes can generate molecular descriptors which express both the effect of topology and of polarizability, atomic radii, or electronega-

Table 14

Topological indices computed with the Wiener operator for the distance matrix and the *Z*, *A*, *P*, *R*, and *E* weighting schemes

Compound	Wi(D,Z)	Wi(D,A)	Wi(D,P)	Wi(D,R)	Wi(D,E)
CH ₃ -CH ₂ -CH ₂ -CH ₃	10.000	10.000	10.000	10.000	10.000
CH ₃ -CH ₂ -CH ₂ -SiH ₃	8.857	8.855	8.654	9.383	10.727
CH ₃ -CH ₂ -CH ₂ -NH ₂	9.714	9.715	11.200	10.350	9.635
CH ₃ -CH ₂ -CH ₂ -PH ₂	8.800	8.776	8.970	9.571	10.297
CH ₃ -CH ₂ -CH ₂ -AsH ₂	8.364	8.321	8.817	9.485	10.417
CH ₃ -CH ₂ -CH ₂ -OH	9.500	9.501	12.389	10.602	9.409
CH ₃ -CH ₂ -CH ₂ -SH	8.750	8.749	9.214	9.692	10.048
CH ₃ -CH ₂ -CH ₂ -SeH	8.353	8.304	8.934	9.551	10.208
CH ₃ -CH ₂ -CH ₂ -TeH	8.231	8.188	8.640	9.367	10.452
CH ₃ -CH ₂ -CH ₂ -F	9.333	9.264	14.320	10.951	9.206
CH ₃ -CH ₂ -CH ₂ -Cl	8.706	8.678	9.615	9.862	9.809
CH ₃ -CH ₂ -CH ₂ -Br	8.343	8.301	9.154	9.669	9.992
CH ₃ -CH ₂ -CH ₂ -I	8.226	8.189	8.749	9.440	10.247

Table 15

Topological indices computed with the Wiener operator for the reciprocal distance matrix and the *Z*, *A*, *P*, *R*, and *E* weighting schemes

Compound	Wi(RD,Z)	Wi(RD,A)	Wi(RD,P)	Wi(RD,R)	Wi(RD,E)
CH ₃ -CH ₂ -CH ₂ -CH ₃	4.333	4.333	4.333	4.333	4.333
CH ₃ -CH ₂ -CH ₂ -SiH ₃	6.517	6.523	7.413	5.218	3.590
CH ₃ -CH ₂ -CH ₂ -NH ₂	4.698	4.697	3.187	3.951	4.811
CH ₃ -CH ₂ -CH ₂ -PH ₂	6.731	6.830	6.154	4.906	4.005
CH ₃ -CH ₂ -CH ₂ -AsH ₂	10.123	10.902	6.666	5.043	3.883
CH ₃ -CH ₂ -CH ₂ -OH	5.018	5.016	2.313	3.705	5.172
CH ₃ -CH ₂ -CH ₂ -SH	6.940	6.944	5.547	4.729	4.277
CH ₃ -CH ₂ -CH ₂ -SeH	10.300	11.254	6.262	4.937	4.099
CH ₃ -CH ₂ -CH ₂ -TeH	13.421	15.421	7.494	5.246	3.849
CH ₃ -CH ₂ -CH ₂ -F	5.308	5.442	1.091	3.394	5.564
CH ₃ -CH ₂ -CH ₂ -Cl	7.145	7.287	4.841	4.503	4.571
CH ₃ -CH ₂ -CH ₂ -Br	10.476	11.337	5.678	4.762	4.343
CH ₃ -CH ₂ -CH ₂ -I	13.592	15.362	6.945	5.117	4.058

tivity. For the elements in the first row of the Periodic System, $Wi(D,P)$, $Wi(D,R)$, and $Wi(RD,E)$ increase, whereas $Wi(D,E)$, $Wi(RD,P)$, and $Wi(RD,R)$ decrease from carbon to fluorine. For the halogen series, $Wi(D,E)$, $Wi(RD,Z)$, $Wi(RD,A)$, $Wi(RD,P)$, and $Wi(RD,R)$ increase and $Wi(D,Z)$, $Wi(D,A)$, $Wi(D,P)$, $Wi(D,R)$, and $Wi(RD,E)$ decrease from fluorine to iodine.

We have presented five new approaches for the calculation of atom and bond parameters in organic compounds containing multiple bonds and heteroatoms. The first two weighting schemes compute the atom and bond weights on the basis of relative atomic mass, using carbon as standard. The remaining three systems use the relative atom polarizability, radii, and electronegativity to compute atom and bond weights, again with the carbon atom as standard. The new parameter sets may be used to compute molecular graph matrices such as the adjacency matrix, the distance matrix, or the reciprocal distance matrix. With these molecular matrices one may compute a large number of descriptors that express in a numerical form the molecular structure. Such descriptors may be polynomials, spectra, spectral moments, walk counts, or various topological indices.

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