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ON THE THREE-DIMENSIONAL WIENER NUMBER*

B. BOGDANOV

Department of Chemistry, The University of Skopje, 91001 Skopje, Macedonia

S. NIKOLIĆ and N. TRINAJSTIĆ

The Rugjer Bošković Institute, 41001 Zagreb, Croatia

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> "Wanted, new concepts"
> C.A. Coulson (1960)☆

Abstract

A novel approach to the Wiener number is described. It is based on the distance matrix in which topographic (geometric) distances rather than topological (graph-theoretical) distances are the input entries. The Wiener number defined in this novel way is thus the representative of 3D (topographic) molecular descriptors. This novel Wiener number is tested in quantitative structure-property relationships (QSPR) with enthalpy functions of the lower alkanes. Its performance is compared to that of the traditional 2D Wiener number. The statistical analysis favours the QSPR models with the 3D Wiener numbers over the related QSPR models with the 2D Wiener numbers. Among the considered models with the 3D Wiener numbers, the best agreement with experimental enthalpy functions is obtained with the logarithmic QSPR model.

1. Introduction

In recent years, there has been considerable interest in the Wiener number (the Wiener index) and its uses in quantitative structure-property relationships (QSPR) and in quantitative structure-activity relationships (QSAR) [1 – 4]. The Wiener number W was introduced in 1947 by Wiener as the path number [15]. The path number was defined

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as the number of bonds between all pairs of atoms in an acyclic molecule. Wiener also introduced the polarity number of an acyclic structure, which is equal to the number of pairs of atoms separated by three bonds. By using a linear combination of the path number and the polarity number, Wiener was able to obtain a fair prediction of alkane boiling points. In subsequent studies [16–19], Wiener extended the application of path number and polarity number to other physical properties of alkanes such as heats of formation, heats of vaporization, molar volumes and molar refractions. In view of the pioneering contribution of Wiener in recognizing the significance of the number of paths in a molecular skeleton, the term 'the Wiener number' (e.g. [20]) or 'the Wiener index' (e.g. [21]) has been adopted for the number of distances in all chemical structures. We should note here that the one-to-one correspondence between the (graph-theoretical) distance and the path number holds only for acyclic systems. Since the graph-theoretical distance is defined [1–4] as the smallest number of bonds, i.e. the shortest path between the pair of atoms in a structure, the distance and the smallest path number between atoms coincide in cyclic structures.

The Wiener number measures the compactness of a molecule [22]. Note that the smaller the Wiener number, the larger the compactness of the molecule. Hence, it can reliably be used for correlations with those physical and chemical properties which depend on the ratio of the volume to the surface of the molecule. Chromatographic retention data for a homologous series of hydrocarbons are typical molecular properties for which QSPR models with the Wiener number should lead to trustworthy predictions [2,23,24]. Extensive bibliographies on the use of the Wiener number in QSPR and QSAR can be found in several reviews [1,3,4,20–22,25–29].

Graph-theoretical language will be used in this note because the same was employed in most of the fundamental work on the Wiener number (e.g. [1,13,20,30]). We give the graph-theoretical definition of the 2D Wiener number in section 2. The topographic definition of the 3D Wiener number will be presented in section 3. Section 4 contains a selected example of application of the 3D Wiener number to QSPR, and section 5 contains concluding remarks.

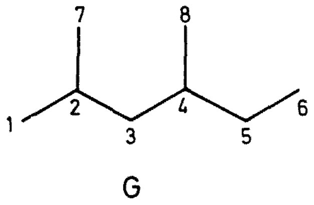
2. The 2D Wiener number

In the original work by Wiener, the Wiener number was not, strictly speaking, formulated in graph-theoretical terms. It was defined within the framework of chemical graph theory later (in 1971) by Hosoya [30], who pointed out that the Wiener number can be obtained from the distance matrix [20,31–34] for the structure (graph) in question.

The Wiener number may be defined for an arbitrary connected graph (structure) G in the following way. Let us assume that G has vertices $1, 2, \ldots, N$. For each pair k, l of vertices, let $(\underline{D})_{kl}$ denote the distance in G between k and l; i.e. the length of the shortest path between k and l. The distances $(\underline{D})_{kl}$ represent the elements of the distance matrix $\underline{D} = \underline{D}(G)$ of the graph G. The Wiener number $W = W(G)$ of G is therefore given by [30]:

$$W = \sum_{k=1}^{N} \sum_{l=1}^{k} (\underline{D})_{kl} = \frac{1}{2} \sum_{k=1}^{N} \sum_{l=1}^{N} (\underline{D})_{kl} \, . \tag{1}$$

In other words, the Wiener number W of G is equal to the half-sum of the elements of $\underline{D}$. Since the distance matrix in the above formulation contains information only about the 2D structure of a molecule, we named the corresponding number representing the sum of all graph-theoretical distances in G the 2D Wiener number. We denote it by ${}^{2\mathrm{D}}W$. In fig. 1, we give as an example the distance matrix and the 2D Wiener number for the graph corresponding to the carbon skeleton of 2,4-dimethylhexane.



$$\underline{D} = \begin{bmatrix} 0 & 1 & 2 & 3 & 4 & 5 & 2 & 4 \\ 1 & 0 & 1 & 2 & 3 & 4 & 1 & 3 \\ 2 & 1 & 0 & 1 & 2 & 3 & 2 & 2 \\ 3 & 2 & 1 & 0 & 1 & 2 & 3 & 1 \\ 4 & 3 & 2 & 1 & 0 & 1 & 4 & 2 \\ 5 & 4 & 3 & 2 & 1 & 0 & 5 & 3 \\ 2 & 1 & 2 & 3 & 4 & 5 & 0 & 4 \\ 4 & 3 & 2 & 1 & 2 & 3 & 4 & 0 \end{bmatrix}$$

$${}^{2\mathrm{D}}W = 71$$

Fig. 1. The graph-theoretical distance matrix and the Wiener number of a 2,4-dimethylhexane tree.

In the literature, there are many algorithms available for computing the distance matrix and consequently the 2D Wiener number for any structure [9,13,35,36]. Some of these algorithms are even applicable to more complicated problems, where vertices and edges are allowed to carry weights (e.g. [9,13,37]).

The 2D Wiener number has interesting properties [1,3,4,13,14,20,21, 26–29,32]. Since at a constant number of atoms the Wiener number has a maximum

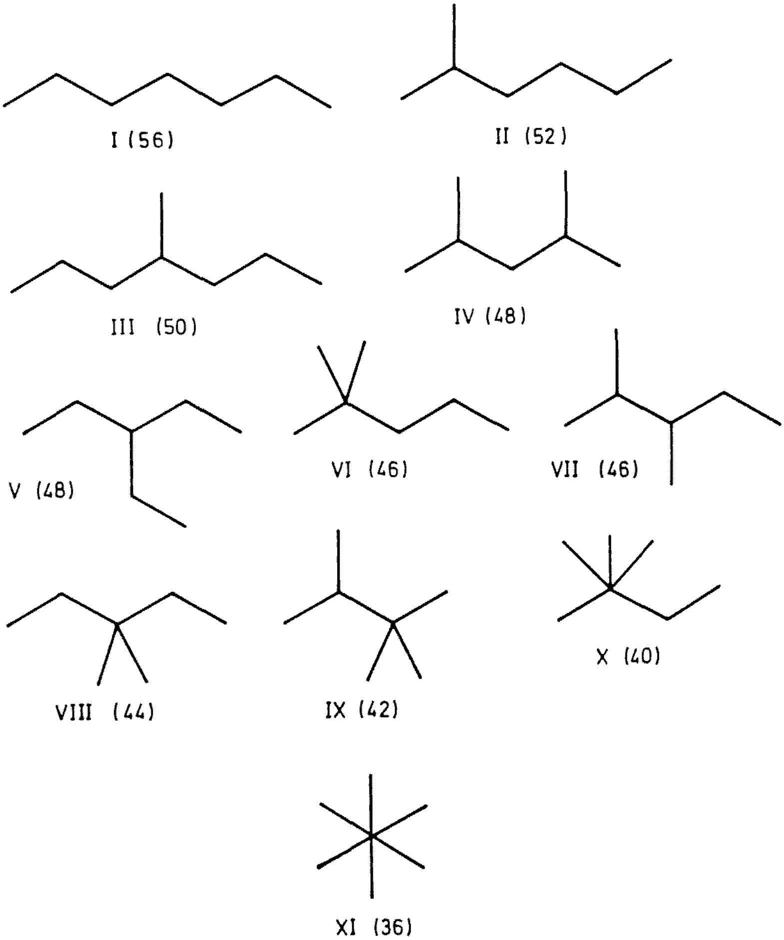


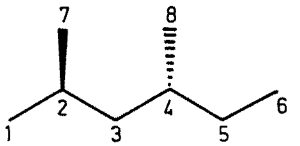
Fig. 2. Ordering of trees with seven vertices according to their 2D Wiener numbers (in parentheses).

for the linear n-alkane and a minimum for the most compact (most branched and cyclic structures [22]), it appears to be a convenient measure of molecular branching and cyclicity [38–46]. As an example, in fig. 2 we give Wiener numbers for all trees with seven vertices.

The Wiener number ordered trees with seven vertices according to the increased mode of branching. The linear structure, a seven-membered chain, has the largest value of the Wiener number, while the six-point star structure has the smallest. All other branched structures lie in between these two extremes. Since the 2D Wiener number is not a very discriminative quantity, two pairs of trees with seven vertices have degenerate values of *W*.

3. The 3D Wiener number

The distance matrix of a structure may also be based on the topographic (geometric) distances, i.e. the matrix elements $(\underline{D})_{kl}$ represent "true" spatial distances between atoms k and l in a molecule expressed in some units of length [2,3,47]. This topographic (geometric) distance matrix contains information on the 3D structure of a molecule. The corresponding Wiener number is termed the 3d Wiener number, and it is representative of topographic invariants [48,49]. We denote it by ^{3D}W. In fig. 3, we give the topographic distance matrix (denoted by $^{3D}\underline{D}$) and the related 3D Wiener number for 2,4-dimethylhexane. Only the carbon skeleton of 2,4-dimethylhexane is considered.



C–C : 1.54 Å
$C_1C_2C_3$: 112°

$$^{3D}\underline{D} = \begin{bmatrix} 0 & 1.54 & 2.55 & 3.93 & 5.11 & 6.38 & 2.55 & 4.42 \\ & 0 & 1.54 & 2.55 & 3.92 & 5.11 & 1.54 & 2.98 \\ & & 0 & 1.54 & 2.55 & 3.93 & 2.55 & 2.55 \\ & & & 0 & 1.54 & 2.55 & 2.98 & 1.54 \\ & & & & 0 & 1.54 & 4.42 & 2.55 \\ & & & & & 0 & 5.30 & 2.98 \\ & & & & & & 0 & 3.43 \\ & & & & & & & 0 \end{bmatrix}$$

$^{3D}W = 86.08$

Fig. 3. The topographic distance matrix (only upper triangle is given) and the related 3D Wiener number for the carbon skeleton of 2,4-dimethylhexane.

The optimal spatial geometry of 2,4-dimethylhexane was constructed by using for CC bond lengths uniformly the value of 1.54 Å, for the bond angles between CC bonds in the chain the value of 112°, the two methyl groups are taken to be in "anti" position to each other and both to be out on opposite sides of the plane in which lies the six-membered chain for 56° each. We considered this idealized "frozen" geometry because we could not find an experimentally determined structure of 2,4-dimethylhexane in the literature. We will construct, in the same way, structures of other alkanes that will be considered in this work.

The 3D Wiener number appears to be more discriminative than the 2D Wiener number. For example, the degeneracy of two pairs of trees with seven vertices that have the same 2D Wiener numbers is resolved when the 3D Wiener numbers are used:

Tree	${}^{2D}W$	${}^{3D}W$
IV	48	58.19
V	48	56.61
VI	46	57.14
VII	46	57.02

4. Application

We used both ${}^{2D}W$ and ${}^{3D}W$ numbers to set up, as an example of their application, QSPR models for predicting enthalpy functions $(H^0 - H_0^0)/T$ (in cal K^{-1} mol^{-1})* of lower alkanes. The enthalpy functions and Wiener numbers for the first 21 alkanes (except methane) are given in table 1.

We examined three types of correlations between enthalpy functions EF and Wiener numbers W of alkanes:

(i) linear least-squares fit

$$EF = aW + b\ , \tag{2}$$

(ii) quadratic least-squares fit

$$EF = aW^2 + bW + c\ , \tag{3}$$

(iii) logarithmic least-squares fit

$$\ln EF = \ln a + b \ln W\ . \tag{4}$$

The statistical characteristics of the above correlations are given in tables 2, 3 and 4. The calculated enthalpy functions by the six models from the above are given in table 5. The agreement between the experimental enthalpy functions $(EF)_{\mathrm{exp}}$ and calculated enthalpy functions $(EF)_{\mathrm{calc}}$ is analyzed via the linear correlation for each model considered:

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*Calories may be converted to SI units (joules) by use of the relation: 1 cal/mol = 4.184 J/mol.

Table 1

The enthalpy functions $(H^0 - H_0^0)/T$ (in cal K^{-1} mol^{-1}) and Wiener numbers ${}^{2D}W$ and ${}^{3D}W$ for the first 21 alkanes (methane is not included)

	Alkane	$(H^0 - H_0^0)/T$	$\ln(H^0 - H_0^0)/T$	${}^{2D}W$	$\ln({}^{2D}W)$	${}^{3D}W$	$\ln({}^{3D}W)$
1	Ethane	9.5	2.2513	1	0.0000	1.54	0.4318
2	Propane	11.8	2.4681	4	1.3863	5.63	1.7281
3	Isobutane	14.4	2.6672	9	2.1972	12.16	2.4982
4	n-butane	15.8	2.7600	10	2.3026	13.65	2.6137
5	2,2-dimethylpropane	18.5	2.9178	16	2.7726	21.25	3.0564
6	2-methylbutane	17.6	2.8679	18	2.8904	23.17	3.1429
7	n-pentane	19.3	2.9601	20	2.9957	26.78	3.2877
8	2,2-dimethylbutane	20.1	3.0007	28	3.3322	35.23	3.5619
9	2,3-dimethylbutane	19.6	2.9755	29	3.3673	36.53	3.5981
10	2-methylpentane	21.1	3.0493	32	3.4657	40.68	3.7057
11	3-methylpentane	20.8	3.0350	31	3.4340	39.27	3.6705
12	n-hexane	23.0	3.1355	35	3.5553	46.35	3.8362
13	2,2,3-trimethylpentane	22.4	3.1091	42	3.7377	51.48	3.9412
14	2,2-dimethylpentane	23.4	3.1527	46	3.8286	57.14	4.0455
15	3,3-dimethylpentane	23.2	3.1442	44	3.7842	54.32	3.9949
16	2,4-dimethylpentane	23.4	3.1527	48	3.8712	58.19	4.0637
17	2,3-dimethylpentane	22.7	3.1224	46	3.8286	57.02	4.0434
18	2-methylhexane	24.7	3.2068	52	3.9512	65.58	4.1833
19	3-methylhexane	24.3	3.1905	50	3.9120	63.23	4.1468
20	3-ethylpentane	25.1	3.2229	48	3.8712	56.61	4.0362
21	n-heptane	26.6	3.2809	56	4.0254	73.57	4.2982

$$(EF)_{\text{exp}} = a\,(EF)_{\text{calc}} + b\,. \tag{5}$$

The statistical parameters for these correlations are given in table 6.

The statistical analysis favours for all three types of investigated correlations QSPR models with 3D Wiener numbers over the related QSPR models with 2D Wiener numbers. Among all six models considered, the best agreement with experimental enthalpy functions is obtained with the logarithmic QSPR model with 3D Wiener numbers. Thus, it appears that the use of the 3D Wiener number in structure-property correlations is rather promising. However, much more work is needed before the range of its usability is determined. Research in this direction is already in progress.

Table 2

Statistical characteristics for the linear correlation between the enthalpy functions and Wiener numbers of lower alkanes

Wiener number	Statistical data					
	a	b	r	s	F-ratio	r^2 (adjusted)
^{2D}W	0.2515 (±0.0167)	12.3839 (±0.5986)	0.960	1.2777	226.0269	0.918
^{3D}W	0.2049 (±0.0129)	12.1574 (±0.5783)	0.965	1.2114	253.5775	0.927

Table 3

Statistical characteristics for the quadratic correlation between the enthalpy functions and Wiener numbers of lower alkanes

Wiener number	Statistical data						
	a	b	c	r	s	F-ratio	r^2 (adjusted)
^{2D}W	– 0.0034 (±0.0009)	0.4501 (±0.0542)	10.5082 (±0.6770)	0.978	0.9809	198.8769	0.952
^{3D}W	– 0.0021 (±0.0005)	0.3584 (±0.0375)	10.2459 (±0.6171)	0.982	0.8811	248.6394	0.961

Table 4

Statistical characteristics for the logarithmic correlation between the enthalpy functions and Wiener numbers of lower alkanes

Wiener number	Statistical data					
	ln *a*	*b*	*r*	*s*	*F*-ratio	r^2 (adjusted)
^{2D}W	2.1709 (±0.0327)	0.2568 (±0.0099)	0.986	0.0442	676.4595	0.973
^{3D}W	2.0543 (±0.0346)	0.2717 (±0.0098)	0.988	0.0413	775.0237	0.975

Table 5

Calculated enthalpy functions (in cal K^{-1} mol^{-1}) of lower alkanes by six models

Alkane	Calculated enthalpy function					
	Model 1[a]	Model 2[b]	Model 3[c]	Model 4[d]	Model 5[e]	Model 6[f]
1	12.64	12.47	10.95	10.79	2.1709	2.1716
2	13.39	13.31	12.25	12.20	2.5269	2.5238
3	14.65	14.65	14.28	14.29	2.7352	2.7330
4	14.90	14.95	14.66	14.75	2.7623	2.7644
5	16.41	16.51	16.83	16.92	2.8830	2.8847
6	16.91	16.91	17.49	17.43	2.9132	2.9082
7	17.41	17.64	18.13	18.34	2.9403	2.9475
8	19.43	19.38	20.41	20.28	3.0267	3.0220
9	19.68	19.64	20.66	20.55	3.0357	3.0319
10	20.43	20.49	21.38	21.37	3.0610	3.0611
11	20.18	20.20	21.15	21.10	3.0529	3.0515
12	21.19	21.65	22.04	22.37	3.0840	3.0966
13	22.95	22.71	23.33	23.15	3.1309	3.1251
14	23.95	23.87	23.92	23.90	3.1542	3.1534
15	23.45	23.29	23.64	23.54	3.1428	3.1397
16	24.46	24.08	24.17	24.02	3.1652	3.1584
17	23.95	23.84	23.92	23.88	3.1542	3.1528
18	25.46	25.60	24.59	24.76	3.1857	3.1909
19	24.96	25.11	24.40	24.55	3.1756	3.1809
20	24.46	23.76	24.17	23.83	3.1652	3.1509
21	26.47	27.23	24.91	25.29	3.2048	3.2221

[a] $EF = 0.2515\ ^{2D}W + 12.3839$

[b] $EF = 0.2049\ ^{3D}W + 12.1574$

[c] $EF = -0.0034\ (^{2D}W)^2 + 0.4501\ ^{2D}W + 10.5082$

[d] $EF = -0.0021\ (^{3D}W)^2 + 0.3584\ ^{3D}W + 10.2459$

[e] $\ln EF = 2.1709 + 0.2568 \ln (^{2D}W)$

[f] $\ln EF = 2.0543 + 0.2717 \ln (^{3D}W)$.

Table 6

Statistical parameters for the linear correlation between the experimental and calculated (by six models) enthalpy functions of lower alkanes

Model	Statistical parameters a	b	r	s	F-ratio	r^2 (adjusted)
1	− 0.0012 (±1.3823)	1.0000 (±0.0665)	0.960	1.2780	225.9089	0.918
2	0.0046 (±1.3049)	0.9998 (±0.0628)	0.965	1.2117	253.4422	0.927
3	0.0050 (±1.0134)	0.9998 (±0.0487)	0.978	0.9538	420.7393	0.955
4	0.0010 (±0.9078)	0.9999 (±0.0437)	0.982	0.8578	524.6664	0.963
5	0.0000 (±0.1151)	1.0000 (±0.0384)	0.986	0.0442	676.9083	0.971
6	0.0002 (±0.1076)	0.9999 (±0.0359)	0.988	0.0413	775.2907	0.975

5. Concluding remarks

We introduced a novel molecular descriptor named the 3D Wiener number which is based on the topographic distance matrix of a molecule. This index captures the 3D structure of a molecule. However, the structure and the index are not isomorphic: the index can be generated from the structure, but the inverse is not possible; the structure is not reconstructable from the index. This is a common weakness of all graph-theoretical and topographic indices.

The 3D Wiener number possesses many of the advantageous features of the related and very much studied descriptor known as the 2D Wiener number, but it also has its own additional attractive characteristics such as high discriminative power. Its use in QSPR studies appears to be encouraging, but more work is needed before the conditions of its applicability can be established.

References

[1] D.H. Rouvray, in: *Chemical Applications of Topology and Graph Theory*, ed. R.B. King (Elsevier, Amsterdam, 1983) p. 159.

[2] E.R. Canfield, R.W. Robinson and D.H. Rouvray, J. Comput. Chem. 6(1985)598.

[3] D.H. Rouvray, in: *Mathematics and Computational Concepts in Chemistry*, ed. N. Trinajstić (Horwood, Chichester, 1986) p. 295.

[4] D.H. Rouvray, Sci. Amer. 254(1986)40.

[5] N. Bošnjak, N. Adler, M. Perić and N. Trinajstić, in: *Modelling of Structure and Properties of Molecules*, ed. Z.B. Maksić (Horwood, Chichester, 1987) p. 103.

[6] M.P. Hanson and D.H. Rouvray, in: *Graph Theory and Topology in Chemistry*, ed. R.B. King and D.H. Rouvray (Elsevier, Amsterdam, 1987) p. 201.

[7] P.G. Seybold, M.A. May and M.L. Gargas, Acta Pharm. Jugosl. 36(1986)253.

[8] D.E. Needham, I.-C. Wei and P.G. Seybold, J. Amer. Chem. Soc. 110(1988)4186.

[9] P. Sen, Comput. Chem. 12(1988)218.

[10] I. Lukovits, J. Chem. Soc. Perkin Trans. II (1988)1667.

[11] M. Randić, P.J. Hansen and P.C. Jurs, J. Chem. Inf. Comput. Sci. 28(1988)60.

[12] P.J. Hansen and P.C. Jurs, J. Chem. Educ. 65(1988)574.

[13] B. Mohar and T. Pisanski, J. Math. Chem. 2(1988)267.

[14] D. Horvat, K. Kovačević, D. Plavšić and N. Trinajstić, in: *MATH/CHEM/COMP 1988*, ed. A. Graovac (Elsevier, Amsterdam, 1989), in press.

[15] H. Wiener, J. Amer. Chem. Soc. 69(1947)17.

[16] H. Wiener, J. Amer. Chem. Soc. 69(1947)2636.

[17] H. Wiener, J. Chem. Phys. 15(1947)766.

[18] H. Wiener, J. Phys. Chem. 52(1948)425.

[19] H. Wiener, J. Phys. Chem. 52(1948)1082.

[20] I. Gutman and O.E. Polansky, *Mathematical Concepts in Organic Chemistry* (Springer-Verlag, Berlin, 1986) p. 124.

[21] D. Bonchev, *Information Theoretic Indices for Characterization of Chemical Structures* (Wiley, Chichester, 1983) p. 71.

[22] D. Bonchev and N. Trinajstić, J. Chem. Phys. 67(1977)4517.

[23] D. Bonchev, O. Mekenyan, G. Protić and N. Trinajstić, J. Chromatogr. 176(1979)149.

[24] N. Adler, D. Babić and N. Trinajstić, Fresenius Z. Anal. Chem. 322(1985)426.

[25] A. Sabljić and N. Trinajstić, Acta Pharm. Jugosl. 31(1981)189.

[26] N. Trinajstić, *Chemical Graph Theory*, Vol. II (CRS, Boca Raton, FL, 1983) Ch. 4.

[27] A.T. Balaban, I. Motoc, D. Bonchev and O. Mekenyan, Topics Curr. Chem. 114(1983)21.

[28] P.G. Seybold, M. May and U.A. Bagal, J. Chem. Educ. 64(1987)575.

[29] N. Trinajstić, CRC Reports on Molecular Theory, in press.

[30] H. Hosoya, Bull. Chem. Soc. Japan 44(1971)2332.

[31] F. Harary, *Graph Theory*, 2nd printing (Addison-Wesley, Reading, MA, 1971) p. 203.

[32] D.H. Rouvray, in: *Chemical Applications of Graph Theory*, ed. A.T. Balaban (Academic Press, London, 1976) p. 175.

[33] D.M. Cvetković, M. Doob and H. Sachs, *Spectra of Graphs* (Academic Press, New York, 1980) p. 283.

[34] N. Trinajstić, *Chemical Graph Theory*, Vol. I (CRC, Boca Raton, FL, 1983) pp. 44–46.

[35] M. Bersohn, J. Comput. Chem. 4(1982)110.

[36] W.R. Müller, K. Szymanski, J.V. Knop and N. Trinajstić, J. Comput. Chem. 8(1987)170.

[37] M. Barysz, G. Jashari, R.S. Lall, V.K. Srivastava and N. Trinajstić, in: *Chemical Applications of Topology and Graph Theory*, ed. R.B. King (Elsevier, Amsterdam, 1983) p. 222.

[38] D. Bonchev and N. Trinajstić, Int. J. Quant. Chem.: Quant. Chem. Symp. 12(1978)293.

[39] D. Bonchev, O. Mekenyan, J.V. Knop and N. Trinajstić, Croat. Chem. Acta 52(1979)361.

[40] I. Gutman, Croat. Chem. Acta 54(1980)81.

[41] D. Bonchev, J.V. Knop and N. Trinajstić, Math. Chem. (Mülheim/Ruhr) 6(1979)21.

[42] O. Mekenyan, D. Bonchev and N. Trinajstić, Math. Chem. (Mülheim/Ruhr) 6(1979)93.

[43] D. Bonchev, O. Mekenyan and N. Trinajstić, Int. J. Quant. Chem. 17(1980)845.

[44] O. Mekenyan, D. Bonchev and N. Trinajstić, Int. J. Quant. Chem. 19(1981)929.

[45] O. Mekenyan, D. Bonchev and N. Trinajstić, Math. Chem. (Mülhein/Ruhr) 11(1981)145.

[46] O. Mekenyan, D. Bonchev and N. Trinajstić, Croat. Chem. Acta 56(1983)237.

[47] G.M. Crippen, J. Comput. Phys. 24(1977)96.

[48] M. Randić, in: *MATH/CHEM/COMP 1987*, ed. R.C. Lacher (Elsevier, Amsterdam, 1988) p. 101.

[49] M. Randić, Int. J. Quant. Chem.: Quant. Biol. Symp. 15(1988)201.