Wiener Indices and Molecular Surfaces

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A correlation between the Wiener index (*W*) and the molecular surface of the respective alkane is established for the first time. This correlation is curvilinear and not particularly good. *W* is only weakly correlated to molecular volume of saturated hydrocarbons and does not reflect at all their surface-to-volume ratio. By this a long-existing controversy concerning the physico-chemical interpretation of *W* is resolved.

Introduction

The Wiener index or Wiener number, *W*, is one of the most frequently employed molecular-graph-based descriptors of the structure of organic molecules. Its applications in the study of structure-property relations of organic compounds are quite numerous. Since the pioneering times of Harold Wiener [1], correlations were established between *W* and a plethora of physico-chemical properties: boiling point, molar volume, refractive index, heat of isomerization, heat of vaporization, density, critical pressure, surface tension, viscosity, chromatographic retention time and sound velocity, to mention just a few. Several reviews [2–9] outline the present state of the art of the theory of the Wiener index.

W is defined as the sum of distances between all pairs of vertices of the skeleton graph [10] of the respective organic molecule. An immediate consequence of this definition is that compact, e.g. ball-shaped, molecules will have small, whereas molecules with extruded features, e.g. rod-shaped, will have large *W*-values. Combining this observation with the fact that so many physico-chemical properties are correlated with *W*, many authors concluded that *W* measures certain geometric characteristics of the respective molecule. For instance, Platt [11] expressed the opinion that $W^{1/3}$ measures the mean molecular diameter; similar ideas were put forward also by Altenburg [12]. In some of his papers Rouvray [13, 14] says that *W* is related to molecular size; in [6] he explicitly claims that *W* "offers primarily a measure of the molecule's volume, although it does give some indication of the molecule's shape". In another paper Canfield, Robinson and Rouvray [15] hypothesize that *W* "provides a measure of the mean external contact area of the molecules". A seemingly related opinion is [9, 16] that *W* reflects the ratio of the surface and the volume of a molecule.

None of these assertions was checked so far.

The aim of this paper is to fill this gap. We calculated the van der Waals volumes and surfaces of a number of alkanes with up to 9 carbon atoms. By means of these data it is possible to judge on the quality of correlations between *W* and molecular volume, *W* and molecular surface, as well as *W* and the surface-to-volume ratio.

Numerical Work

Van der Waals volumes, V_W, and van der Waals surfaces, S_W, of alkanes were estimated by several authors [17–20]. For the purpose of this study, the geometries of 58 alkanes (19 nonanes, 17 octanes and all the isomers with seven and fewer carbon atoms) were optimized at the AM1 level. The values of S_W and V_W were then computed for a stable conformer, by means of the Gavezotti method [21, 22] using the PcMOL program package [23]. The total molecular surface (volume) was calculated from the sum of the free atomic surfaces (volumes). The van der Waals radii employed were 118.5 pm for hydrogen and 175.0 pm for carbon; 15,000–20,000 points were used per atom. The average estimated errors in the calculation of S_W and V_W were below 1.5 and 0.5%, respectively [21, 22]. Additional computational details are outlined elsewhere [20].

The Wiener indices of alkanes are easily calculated [9, 15] and are also available in tabulated form [7].

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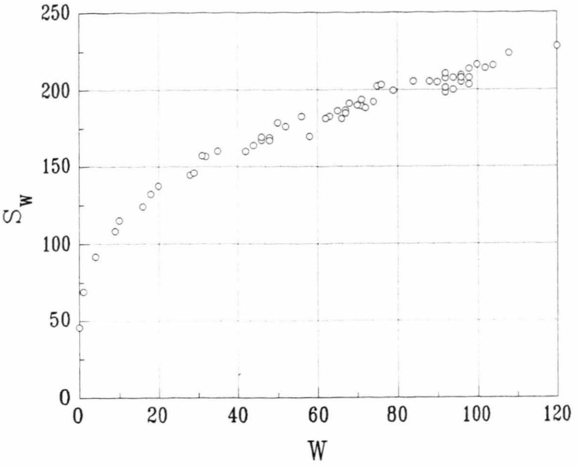

Fig. 1. Van der Waals surfaces of alkanes (in units of 10^4 pm^2) vs. the respective Wiener indices.

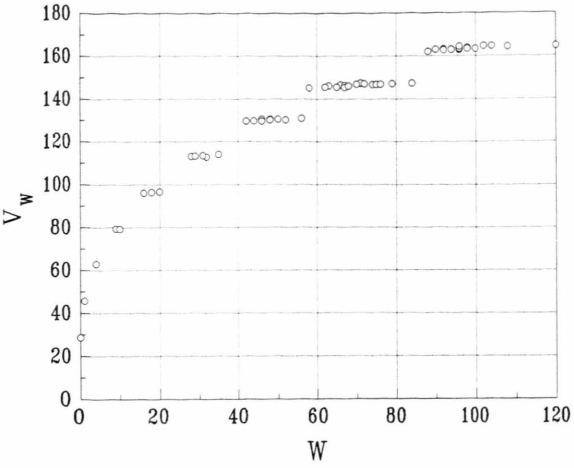

Fig. 2. Van der Waals volumes of alkanes (in units of 10^6 pm^3) vs. the respective Wiener indices.

Results

The way in which the Wiener index is correlated with S_W, V_W and S_W/V_W is shown in Figs. 1, 2 and 3.

From Fig. 1 we see that a curvilinear correlation exists between S_W and W although the spread of the points is quite large. The form of this curve can be approximated by

$$S_W = a\,W^p + b\,. \tag{1}$$

The optimal value of the exponent p was found to be around 0.4, or more precisely: to belong to the interval (0.38, 0.42). For $p=0.4$ the correlation coefficient becomes maximal (0.994), whereas the average relative error and the maximal observed relative error reach their minimal values (1.83% and 6.0%, respectively). The quality of the S_W/W-correlation is best judged by inspecting Figure 1. Although in average S_W increases with W, numerous cases of violation from monotonicity are encountered, some being quite large.

It is worth noting that the calculated value of the exponent p is far from the value $p=2/3$ which could have been expected on the basis of the belief that W measures molecular volume or that $W^{1/3}$ measures mean molecular diameter.

From Fig. 2 is clear that V_W is almost independent of the Wiener index. The points in Fig. 2 are separated into groups, each group corresponding to a set of isomers and lying on an almost horizontal line. Within each group the variation of V_W with W is negligible, and numerous (slight) violations from monotonicity occur.

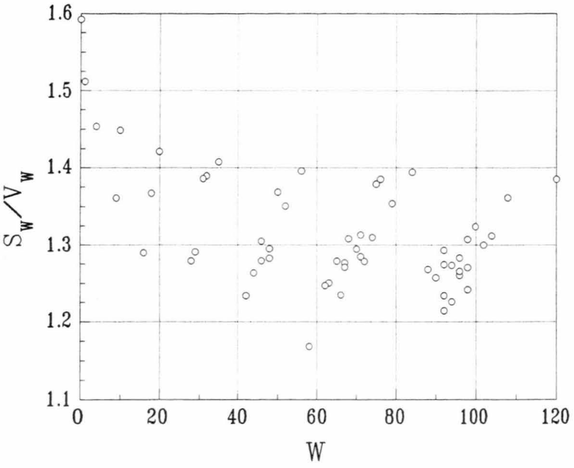

Fig. 3. Ratios of van der Waals surfaces and volumes of alkanes (in units of 10^2 pm^{-1}) vs. the respective Wiener indices.

Even if one restricts the consideration to sets of isomers, the V_W/W-correlation of the form (2)

$$V_W = a'\,W^{p'} + b' \tag{2}$$

is found to be much inferior to the S_W/W-correlation of the form (1). In Table 1 are presented some comparative data.

Figure 3 convincingly shows that the claim that the Wiener index measures the surface-to-volume ratio is a blunder. Within sets of isomers one can observe some rough regularity between the points, which could be approximated by means of

$$S_W/V_W = a''\,W^{p''} + b''\,. \tag{3}$$

Table 1. The correlation coefficients for the correlations between the Wiener index and the van der Waals surfaces (1), volumes (2) and surface-to-volume ratios (3) for sets of isomeric alkanes

	Sample size	(1) $p=0.4$	(2) $p'=0.4$	(2) $p'=1.0$	(3) $p''=0.4$	(3) $p''=1.0$
pentanes	3	0.996	0.976	0.971	0.997	0.995
hexanes	5	0.927	0.652	0.661	0.911	0.904
heptanes	9	0.949	0.819	0.816	0.939	0.938
octanes	17	0.934	0.807	0.798	0.914	0.910
nonanes	19	0.858	0.807	0.797	0.814	0.816

The data given in Table 1 show that within sets of isomers the approximation (3) is somewhat better than (2), but considerably worse than (1).

Concluding Remarks

The testing of the existence of possible relations between the Wiener index and molecular surface, volume or surface-to-volume ratio in saturated hydrocarbons should have been undertaken long time ago. Such a testing would have prevented the appearance of several unwarranted hypotheses concerning the physico-chemical basis of the success of the Wiener index in the study of structure-property dependencies.

We now showed that, contrary to some previous expectations, the Wiener index cannot be considered as either a measure of molecular volume or of the volume-to-surface ratio. On the other hand, the Wiener index does provide a rough measure of the molecular surface of saturated hydrocarbons. Although not without exceptions, the rule is that the molecular surface increases as the Wiener index increases. The variation of molecular surface with the Wiener index is not linear and is approximately reproduced by (1), $p \approx 0.4$. This finding, together with the plausible assumption that in the case of non-polar molecules, intermolecular interactions are proportional to their surfaces [6], may be accepted as a qualitative explanation of why the Wiener index is correlated with so numerous physico-chemical parameters.

Acknowledgement

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[1] H. Wiener, J. Amer. Chem. Soc. **69,** 17 (1947).
[2] D. H. Rouvray, in: A. T. Balaban (Ed.), Chemical Applications of Graph Theory, Academic Press, London 1976, p. 175.
[3] D. H. Rouvray, in: R. B. King (Ed.), Chemical Applications of Topology and Graph Theory, Elsevier, Amsterdam 1983, p. 159.
[4] A. T. Balaban, I. Motoc, D. Bonchev, and O. Mekenyan, Topics Curr. Chem. **114,** 21 (1983).
[5] D. H. Rouvray, in: N. Trinajstić (Ed.), Mathematics and Computational Concepts in Chemistry, Horwood, Chichester 1986, p. 295.
[6] D. H. Rouvray, Sci. Amer. **255**(9), 40 (1986).
[7] Z. Mihalić, D. Veljan, D. Amić, S. Nikolić, D. Plavšić, and N. Trinajstić, J. Math. Chem. **11,** 233 (1992).
[8] Z. Mihalić and N. Trinajstić, J. Chem. Educ. **69,** 701 (1992).
[9] I. Gutman, Y. N. Yeh, S. L. Lee, and Y. L. Luo, Indian J. Chem. **32A,** 651 (1993).
[10] N. Trinajstić, Chemical Graph Theory, CRC Press, Boca Raton 1993.
[11] J. R. Platt, J. Phys. Chem **56,** 328 (1952).
[12] K. Altenburg, Kolloid Z. **178,** 112 (1961).
[13] D. H. Rouvray and W. Tatong, Z. Naturforsch. **41a,** 1238 (1986).
[14] D. H. Rouvray, J. Comput. Chem. **8,** 470 (1987).
[15] E. R. Canfield, R. W. Robinson, and D. H. Rouvray, J. Comput. Chem. **6,** 598 (1985).
[16] I. Gutman, Y. L. Luo, and S. L. Lee, J. Chin. Chem. Soc. **40,** 195 (1993).
[17] A. Bondi, J. Phys. Chem. **68,** 441 (1964).
[18] F. S. Calixto and A. G. Raso, Chromatographia **15,** 521 (1982).
[19] D. Ben-Amot and K. G. Willis, J. Phys. Chem. **97,** 7736 (1993).
[20] T. Körtvélyesi, M. Görgényi, and L. Seres, Chromatographia, to appear.
[21] A. Gavezotti, J. Amer. Chem. Soc. **105,** 5220 (1983).
[22] A. Gavezotti, J. Amer. Chem. Soc. **107,** 962 (1985).
[23] G. Tasi, I. Pálinkó, J. Halász, and G. Náray-Szabó, Semi-empirical Quantum Chemical Calculations on Microcomputers; PcMOL Version 3.1, CheMicro Ltd., Budapest 1992.