

NOTE

**Note on the Hyper-Wiener Index**

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*Abstract:* The hyper-Wiener index  $WW$  of a chemical tree  $T$  is defined as the sum of the products  $n_1n_2$ , over all pairs  $u, v$  of vertices of  $T$ , where  $n_1$  and  $n_2$  are the number of vertices of  $T$ , lying on the two sides of the path which connects  $u$  and  $v$ . We examine a slight modification  $WWW$  of the hyper-Wiener index, defined as the sum of the products  $n_1n_2n_3$ , over all pairs  $u, v$  of vertices of  $T$ , where  $n_3$  is the number of vertices of  $T$ , lying between  $u$  and  $v$ . It is found that  $WWW$  correlates significantly better with various physico-chemical properties of alkanes than  $WW$ . Lower and upper bounds for  $WWW$ , and an approximate relation between  $WWW$  and  $WW$  are obtained.

*Keywords:* hyper-Wiener index, Wiener index, chemical trees, alkanes.

INTRODUCTION

The hyper-Wiener index is one of the recently introduced distance-based molecular structure–descriptors.<sup>1</sup> It was put forward<sup>2</sup> in 1993 and since then it has attracted much attention of theoretical chemists.<sup>3–20</sup> In parallel with the symbol  $W$  for the Wiener index,<sup>21,22</sup> the hyper-Wiener index is traditionally denoted by  $WW$ .

Let  $u$  and  $v$  be two vertices of a (chemical) tree  $T$  and let  $\pi_{uv}$  be the unique path connecting  $u$  and  $v$ . Let  $n_1$  and  $n_2$  be the counts of vertices lying on the two sides of  $\pi_{uv}$ . The vertices  $u$  and  $v$  are included in these counts, and therefore  $n_1$  and  $n_2$  are always greater than or equal to unity.

The hyper-Wiener index of a tree  $T$  is defined as

$$WW = \sum_{u,v} n_1n_2 \quad (1)$$

with the summation going over all pairs of vertices of  $T$ .

By slightly changing the right-hand side of Eq. (1), one arrives at a modified version of the hyper-Wiener index, which is denoted by  $WWW$ :

$$WWW = \sum_{u,v} n_1n_2n_3. \quad (2)$$

Here  $n_3$  is the number of vertices of  $T$ , lying between the endpoints of the path  $\pi_{uv}$ . Note that if the tree  $T$  has  $n$  vertices, then for all pairs of its vertices,  $n_1 + n_2 + n_3 = n$ . Further, if  $u$  and  $v$  are adjacent, then  $n_3 = 0$ . A mathematical reason for defining the hyper-Wiener index via Eq. (2) is outlined elsewhere.<sup>23</sup>

COMPARING THE PHYSICO-CHEMICAL APPLICABILITY OF THE OLD AND NEW  
HYPER-WIENER INDICES

The first question that should be asked when  $WW$  is modified into  $WWW$  is whether the new variant has a better correlating ability, as far as the physico-chemical properties of alkanes are concerned. In order to obtain comparative results on  $WW$  and  $WWW$ , the standard data base of Needham, Wei, and Seybold,<sup>24</sup> in which experimental values for boiling point ( $BP$ ), molar volume ( $MV$ ), molar refraction ( $MR$ ), heat of evaporation ( $HE$ ), critical temperature ( $CT$ ), critical pressure ( $CP$ ), surface tension ( $ST$ ) and melting point ( $MP$ ) of alkanes with up to 10 carbon atoms have been collected, was employed.

For  $MR$  and  $MP$  no correlation between either  $WW$  or  $WWW$  could be established, and therefore these two physico-chemical properties have not been considered any further. The remaining six sets of experimental data were correlated with polynomials of various degrees of either  $WW$  or  $WWW$ . Eventually, the optimal value  $p$  for the degree of these polynomials was established. The correlation coefficients thus obtained are given in Table I.

TABLE I. Correlation coefficients,  $R(WW)$  and  $R(WWW)$ , for the correlation between various physico-chemical properties of alkanes<sup>24</sup> and a  $p$ -th degree polynomial in the parameters  $WW$  and  $WWW$ , respectively. The value of  $p$  was chosen so as to be optimal from the point of view of the  $F$ -test, at 95 % confidence level

| Property | $p$ | $R(WW)$ | $R(WWW)$ |
|----------|-----|---------|----------|
| $BP$     | 5   | 0.9809  | 0.9816   |
| $MV$     | 2   | 0.9687  | 0.9862   |
| $HE$     | 3   | 0.9722  | 0.9804   |
| $CT$     | 3   | 0.9560  | 0.9444   |
| $CP$     | 5   | 0.9657  | 0.9296   |
| $ST$     | 2   | 0.8310  | 0.8762   |

As can be seen from Table I, the new hyper-Wiener index  $WWW$  is significantly better correlated with the boiling point, molar volume, heat of evaporation, and surface tension than the older version  $WW$ . The new hyper-Wiener index is found to be (slightly) inferior to  $WW$  only in the case of the critical temperature and critical pressure.

The polynomial approximation for the boiling point could be much improved by means of the expressions:

$$\ln BP \approx A_1 \ln WW + B_1$$

$$\ln BP \approx A_2 \ln WWW + B_2$$

resulting in  $R = 0.9867$  (for  $WW$ ) and  $R = 0.9911$  (for  $WWW$ ). In these formulas  $BP$  is expressed in Kelvin units; by least squares fitting one obtains  $A_1 = 0.154 \pm 0.004$ ,  $B_1 = 0.52 \pm 0.02$  and  $A_2 = 0.103 \pm 0.002$ ,  $B_1 = 5.41 \pm 0.01$ .

In summary: The new hyper-Wiener index  $WWW$ , Eq. (2), outperforms the previous version  $WW$ , Eq. (1), in correlations with almost all physico-chemical properties of alkanes. Therefore, when applying the hyper-Wiener index in QSPR and QSAR studies,<sup>25</sup> preference should be given to  $WWW$ .

ESTIMATING THE NEW HYPER-WIENER INDEX

It is first shown that the new hyper-Wiener index is bounded from both below and above by simple functions of the old hyper-Wiener index and the ordinary Wiener index:

$$WW - W \leq WWW \leq (n - 2)(WW - W). \tag{3}$$

The summations in (1) and (2) go over all pairs of vertices. They can be divided into two parts as:

$\sum_{u,v} = \sum_{adj} + \sum_{n,adj}$

where  $\sum_{adj}$  and  $\sum_{n,adj}$  indicate summation over adjacent and non-adjacent vertex pairs. As  $n_3 = 0$  whenever the vertices  $u$  and  $v$  are adjacent, formula (2) reduces to

$$WWW = \sum_{n,adj} n_1 n_2 n_3 \tag{4}$$

If  $u$  and  $v$  are not adjacent, then  $n_3$  is at least 1 and at most  $n - 2$ . Replacing  $n_3$  in (4) by its minimal possible value, one obtains a lower bound for  $WWW$ :

$$WWW \geq \sum_{n,adj} n_1 n_2 = \sum_{u,v} n_1 n_2 - \sum_{n,adj} n_1 n_2 \tag{5}$$

From Eq. (1), the first summation on the right-hand side of (5) is just  $WW$ . According to a well known result of Wiener,<sup>22,26,27</sup> the second summation on the right-hand side of (5) is equal to the Wiener index  $W$ . Thus one arrives at the lower bound in (3).

Replacing  $n_3$  in (4) by its maximal possible value ( $= n - 2$ ), one obtains

$$WWW \leq (n - 2) \sum_{n,adj} n_1 n_2$$

which, using the same arguments as above, leads to the upper bound in (3).

By means of an analogous, yet somewhat more complicated, reasoning, one can also deduce the following estimates:

$$v(v - 1)/2 + (WW - W) \leq WWW \leq v(v - 1)/2 + (n - 3)(WW - W)$$

where  $\nu$  is the number of vertices of degree one in the chemical tree  $T$ , *i.e.*, the number of methyl groups in the underlying molecule.

#### APPROXIMATING THE NEW HYPER-WIENER INDEX

In order to deduce an approximate expression for the new hyper-Wiener index  $WWW$ , Eq. (2) is rewritten as:

$$WWW \approx \sum_{u,v} n_1 n_2 \langle n_3 \rangle$$

where  $\langle n_3 \rangle$  is the arithmetic mean of  $n_3$ . Then,

$$WWW \approx \langle n_3 \rangle \sum_{u,v} n_1 n_2 = \langle n_3 \rangle WW. \quad (6)$$

In order to apply (6), the value of  $\langle n_3 \rangle$  must be known (at least approximately). In order to achieve this goal, one starts with:

$$\begin{aligned} \langle n_3 \rangle &= \langle n - n_1 - n_2 \rangle = n - \langle n_1 + n_2 \rangle \\ &= n - 2 \langle (n_1 + n_2)/2 \rangle \approx n - 2 \langle \sqrt{n_1 n_2} \rangle \end{aligned}$$

where the arithmetic mean of  $n_1$  and  $n_2$  has been replaced by their geometric mean. Using another plausible approximation, one obtains:

$$\langle n_3 \rangle \approx n - 2 \sqrt{\langle n_1 n_2 \rangle} \quad (7)$$

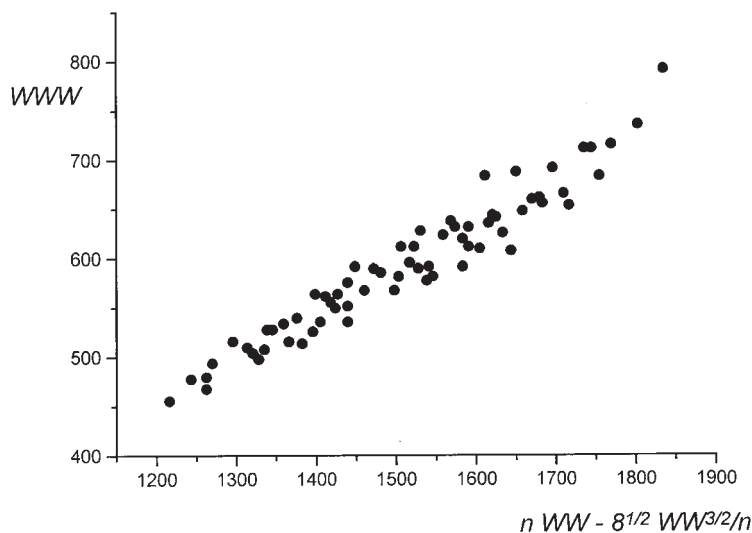


Fig. 1. The new hyper-Wiener index ( $WWW$ , Eq. (2)) vs. the right-hand side of Eq. (9), which is a function of the old hyper-Wiener index ( $WW$ , Eq. (1)). The data points pertain to isomeric decanes,  $C_{10}H_{22}$ , *i.e.*,  $n = 10$ . The correlation coefficient is 0.966.

In view of Eq. (1), the mean value of the product  $n_1 n_2$  is directly related to the hyper-Wiener index  $WW$ :

$$WW = \frac{n(n-1)}{2} \langle n_1 n_2 \rangle \quad (8)$$

where the fact that in an  $n$ -vertex graph there are  $n(n-1)/2$  vertex pairs has been taken into account.

By combining the relations (6)–(8), one finally obtains the expression:

$$WWW \approx n WW - \frac{2\sqrt{2}}{n} WW^{3/2} \quad (9)$$

which relates the old and the new hyper-Wiener index.

The quality of the approximate formula (9) is seen from Fig. 1.

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#### ИЗВОД

#### БЕЛЕШКА О ХИПЕР-ВИНЕРОВОМ ИНДЕКСУ

ИВАН ГУТМАН, БОРИС ФУРТУЛА И ЈАСМИНА БЕЛИЋ

*Природно-математички факултет у Крагујевцу*

Хипер-Винеров индекс  $WW$  хемијског стабла  $T$  дефинисан је као сума производа  $n_1 n_2$ , преко свих парова  $u, v$  чворова стабла  $T$ , где  $n_1$  и  $n_2$  означавају број чворова који леже са две стране пута који повезује  $u$  и  $v$ . У раду испитујемо једну модификацију  $WWW$  хипер-Винеровог индекса, дефинисану као сума производа  $n_1 n_2 n_3$ , преко свих парова  $u, v$  чворова стабла  $T$ , где  $n_3$  означава број чворова који леже између  $u$  и  $v$ . Нађено је да је  $WWW$  значајно боље корелиран са разним физичко-хемијским особинама алкана него  $WW$ . Добивене су доње и горње границе за  $WWW$  као и једна апроксимативна релација између  $WWW$  и  $WW$ .

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