# Wiener-type topological indices of phenylenes

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The Wiener index $W$ of a phenylene (PH) has earlier been shown to depend in a mathematically exact manner on the Wiener indices of its hexagonal squeeze (HS) and inner dual (ID). We now examine the analogous dependency for a class of Wiener-type indices $W_\lambda$, where $\lambda$ is a variable parameter ($W_\lambda = W$ for $\lambda=1$) is examined now. It is shown that some features of the dependency of $W(PH)$ on $W(HS)$ and $W(ID)$ are maintained for all values of $\lambda$, $-5 \leq \lambda \leq +5$, whereas some are violated.

Phenylenes are a class of conjugated molecules that recently attracted much attention of both experimental and theoretical chemists. Most of the experimental work on phenylenes (synthesis and measurement of physico-chemical properties) was accomplished by Peter Vollhardt and his group[1-3]. The main topological (= molecular-graph-based) properties of phenylenes were determined by one of the present authors and his group[4-16]. Among these results is a peculiar formula[12-14], relating the Wiener index of a phenylene (PH) with the Wiener index of its hexagonal squeeze (HS) and inner dual (ID):

$$W(PH) = \frac{9}{4}\left[W(HS) + 16\, W(ID) - (2h+1)(4h+1)\right] \quad \dots (1)$$

In formula (1) and later throughout this paper $h$ denotes the number of hexagons in either the phenylene or its hexagonal squeeze; in the same time $h$ is equal to the number of vertices of the inner dual.

A self-explanatory example, illustrating the structure of phenylenes and the way in which the corresponding hexagonal squeeze and inner dual are constructed, is depicted in Fig. 1. More details on these mutually related molecular graphs can be found elsewhere[5,12-14].

The Wiener index $W(G)$ is equal to the sum of distances between all pairs of vertices of the respective (molecular) graph $G$. If $d(u,v)$ denotes the distance between the vertices $u$ and $v$ (= number of edges in a shortest path connecting $u$ and $v$), then
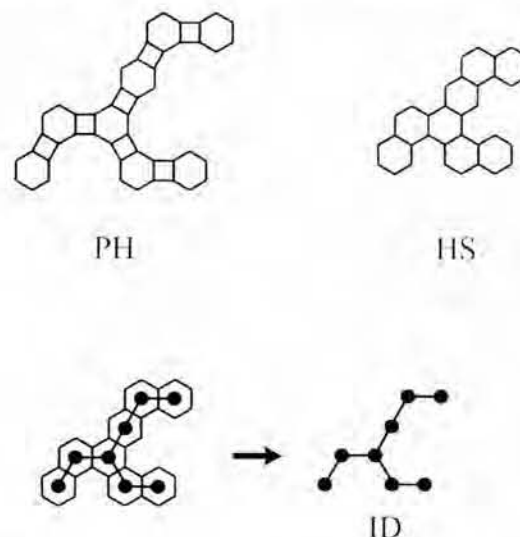
$$W(G) = \sum_{u<v} d(u,v) \quad \dots (2)$$



Fig. 1—A phenylene (PH), its hexagonal squeeze (HS) and inner dual (ID); both PH and HS have $h$=8 hexagons, whereas ID (which is a tree) has 8 vertices. Note that HS is a benzenoid system.

The Wiener index is the oldest and one of the most thoroughly studied molecular structure-descriptors. More details on it can be found in our earlier works[17-19], as well as in the chemical[20,21] and mathematical reviews[22,23].

Recently, a variety of different generalizations of the Wiener index were put forward. One important class of such Wiener-type topological indices is formed by the quantities $W_\lambda(G)$, defined as[18,24]

$$W_\lambda(G) = \sum_{u<v} d(u,v)^\lambda \quad \dots (3)$$

where $\lambda$ is a pertinently chosen exponent. For $\lambda=1$ this Wiener-type index reduces to the original Wiener index. For other choices of the exponent, $W_\lambda(G)$ becomes equal to, or closely related with, a number of other previously (and independently) introduced molecular structure-descriptors; details and further references can be found elsewhere[24,25]. For instance, $W_{-2}$ is the so-called Harary index[26], $(1/2)W_1 + (1/2)W_2$ coincides with the hyper-Wiener index[27], and $(1/3)W_1 + (1/2)W_2 + (1/6)W_3$ coincides with the Tratch-Stankevich-Zefirov index[28]. In view of this it may be of some interest to examine what happens to the relation (1) if $W$ is replaced by its generalization $W_\lambda$

Formula (1) implies the following: For any fixed value of $h$, the Wiener indices of the isomeric phenylenes with $h$ hexagons, plotted versus the Wiener indices of the corresponding hexagonal squeezes, form a set of parallel straight lines. The points belonging to the same line pertain to phenylenes having the same $W(ID)$-values. Figure 2 shows this regularity for the case of $h=8$. This quite unusual relation between $W(PH)$ and $W(HS)$ was first observed within an empirical study,[12] and was eventually proven in a mathematically rigorous manner[13,14].

In this paper we examine the relation between $W_\lambda(PH)$ and $W_\lambda(HS)$ in the case when the parameter $\lambda$ differs from unity. In particular, we seek for answers to the following questions:

1. If $\lambda\neq1$, do the $(W_\lambda(PH), W_\lambda(HS))$-points still form straight lines, and are these lines determined by the respective $W(ID)$-values?
2. If yes, are these lines still parallel?
3. If not, how their slopes vary with $\lambda$ and what is the mutual relation between the slopes of different lines?

## Numerical Work

In order to learn about the $\lambda$-dependence of the $(W_\lambda(PH), W_\lambda(HS))$-correlation, we examined samples consisting of all phenylenes with $h$ hexagons for $h=4,5,6,7,8$. The size of these samples is 5, 12, 37, 122, and 439, respectively[29]. The exponent $\lambda$ was varied between $-5$ and $+5$, an interval embracing all its chemically significant values. Two typical $(W_\lambda(PH), W_\lambda(HS))$-plots are shown in Figs. 3 and 4

As seen from Figs 3 and 4, if $\lambda \neq1$, then the $(W_\lambda(PH), W_\lambda(HS))$-points are no more *exactly* lying on straight lines, but there still exists a good linear *correlation*. The quality of this correlation is remarkably good, not only for near-unity, but also for large (positive or negative) values of the exponent $\lambda$. For $h=4,5,6,7,8$ there is a total of 20 such lines formed by 3 or more $(W_\lambda(PH), W_\lambda(HS))$-data points. Their correlation coefficients are given in Table 1.
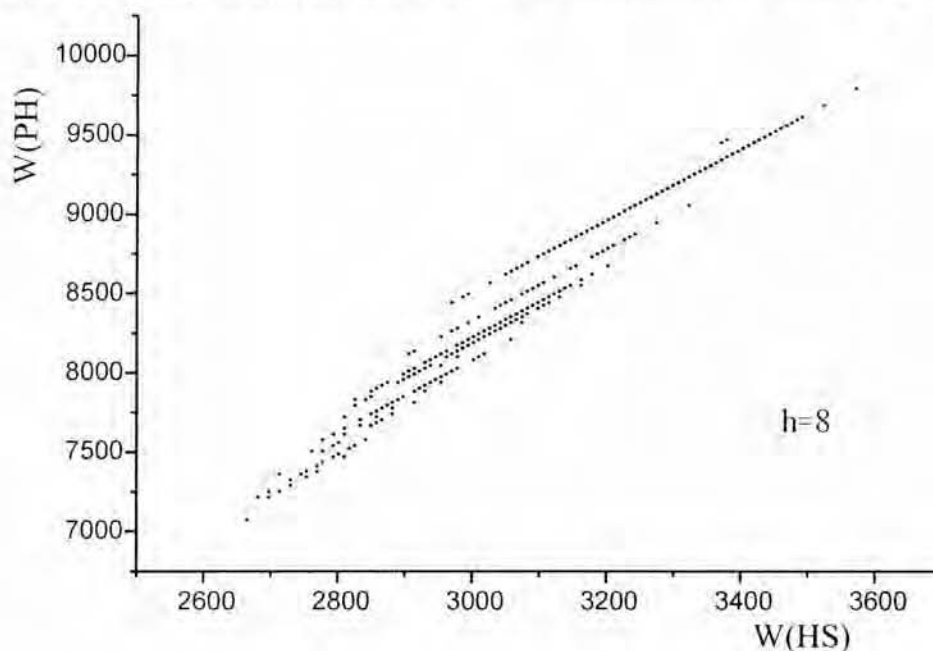


Fig. 2—Relation between the Wiener indices of the phenylenes with 8 hexagons and the Wiener indices of their hexagonal squeezes. This relation is *exactly* described by means of formula (1). Note that Fig. 2 shows the $(W_\lambda(PH), W_\lambda(HS))$-points for $\lambda=1$ (cf. Figs. 3 and 4).
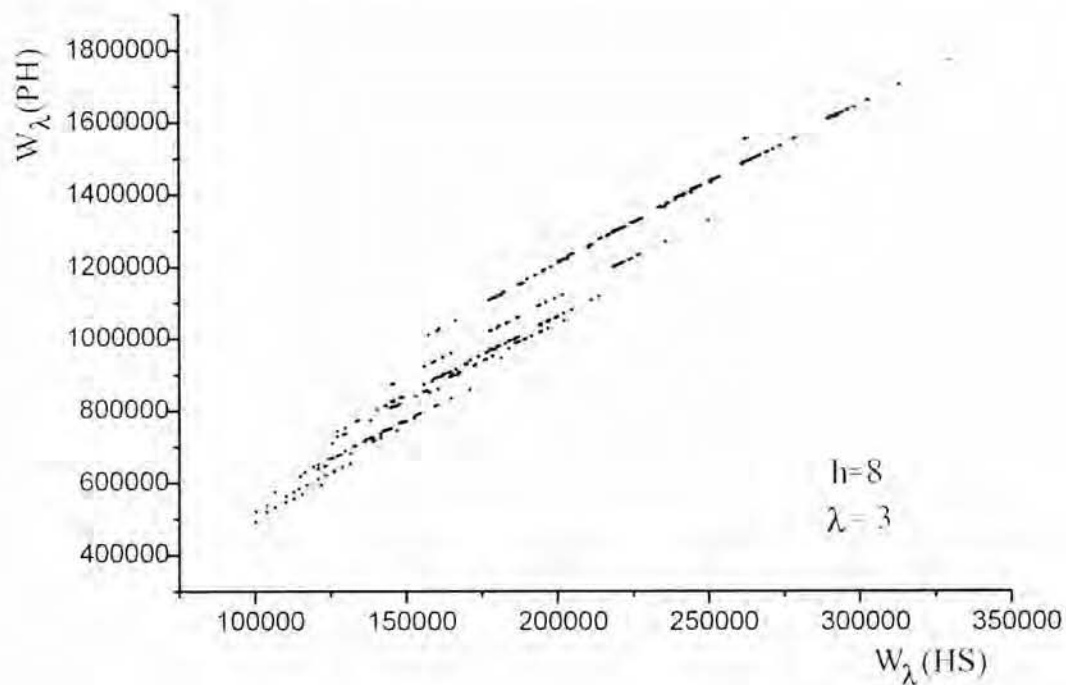
Fig. 3—The correlation between $W_\lambda(PH)$ and $W_\lambda(HS)$ for phenylenes with $h=8$ and $\lambda=+3$; cf. Figs 2 and 4.
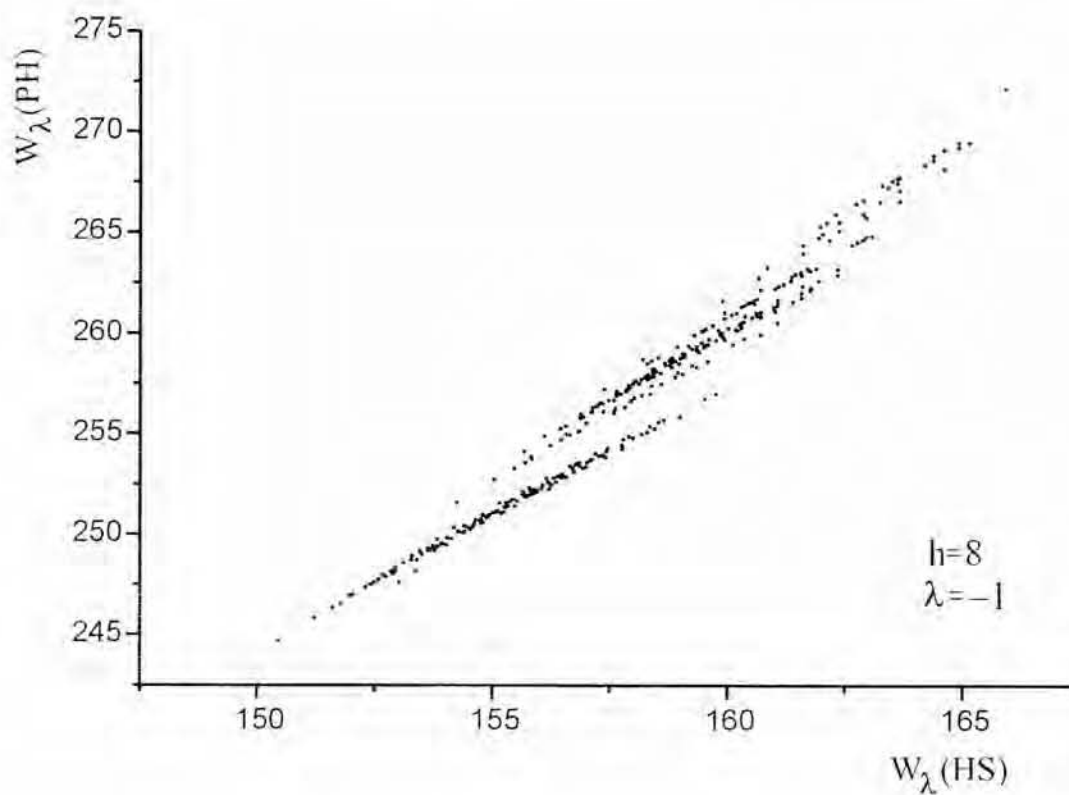


Fig. 4—Same data as in Fig. 3 for $\lambda=-1$.

For each line of the form

$$W_\lambda(PH) \approx a\,W_\lambda(HS) + b$$

the coefficients $a$ and $b$ were determined by least-squares fitting and their dependence on $\lambda$ established. The respective results for the line no. 20 are shown in Figs 5 and 6. The results for all other lines are analogous.

The lines formed by the $(W_\lambda(PH), W_\lambda(HS))$-data points are certainly not mutually parallel (except for $\lambda=1$). The mutual arrangement of these lines depends in a complicated manner on $\lambda$. This is illustrated in Fig. 7 for the lines no. 19 and 20: we see that for some values of $\lambda$ (roughly, those between $-1$ and $+1$) line no. 19 increases faster than line no. 20, whereas for other values of $\lambda$ line no. 20 increases faster than line no. 19. The general rule is that for sufficiently large $\lambda$ (both positive and negative), the slopes of the lines increase with the increasing $W(ID)$-values.

Another noteworthy feature of the $\lambda$-dependence of the slopes $a$ is that their mutual variation is linear. A characteristic example is shown in Fig. 8 for the lines no. 19 and 20.
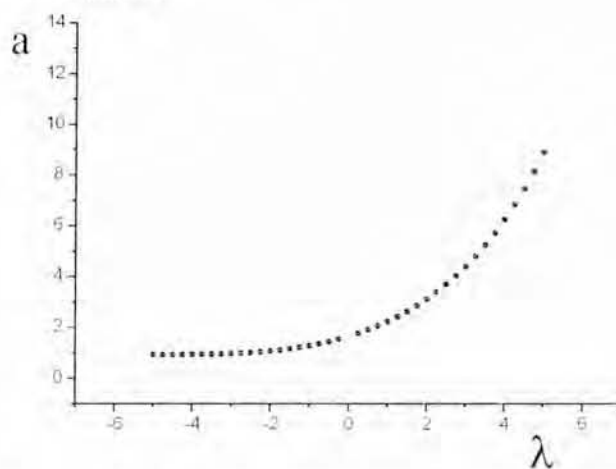


Fig. 5—A characteristic dependence of the slope $a$ of a line $W_\lambda(PH) = a\,W_\lambda(HS) + b$ on the exponent $\lambda$. Here data for the line no. 20 are shown.

Table 1—The correlation coefficients for the lines formed by the $(W_\lambda(PH), W_\lambda(HS))$-points, for various values of the exponent $\lambda$. Note that for $\lambda=1$ the correlation coefficients are always equal to 1. Each group of points is determined by a given $W(ID)$-value, i. e., for $\lambda=1$, these points lie exactly on a straight line, Eq. (1). The number of points in a group is denoted by p. Only lines with $p \geq 3$ were considered. For a fixed value of hexagons ($h$) these lines are numbered according to increasing $W(ID)$. Thus lines no. 11, 12, ..., 20 pertain to $h=8$ and $W(ID) = 67, 68, 70, 71, 72, 74, 75, 76, 79,$ and $84$, respectively, and embrace $p = 6, 12, 9, 10, 42, 4, 44, 80, 40,$ and $188$ points, respectively, cf. Fig. 2.

| line | $h$ | $p$ | $\lambda=-5$ | $\lambda=-3$ | $\lambda=-1$ | $\lambda=3$ | $\lambda=5$ |
|---|---|---|---|---|---|---|---|
| 1 | 4 | 4 | 0.9974 | 0.9973 | 0.9991 | 0.9996 | 0.9993 |
| 2 | 5 | 10 | 0.9940 | 0.9940 | 0.9984 | 0.9996 | 0.9993 |
| 3 | 6 | 6 | 0.9994 | 0.9986 | 0.9991 | 0.9993 | 0.9986 |
| 4 | 6 | 5 | 0.9946 | 0.9957 | 0.9991 | 0.9998 | 0.9995 |
| 5 | 6 | 25 | 0.9917 | 0.9917 | 0.9982 | 0.9997 | 0.9992 |
| 6 | 7 | 9 | 0.9825 | 0.9746 | 0.9878 | 0.9941 | 0.9893 |
| 7 | 7 | 3 | 0.9976 | 0.9955 | 0.9982 | 0.9996 | 0.9994 |
| 8 | 7 | 27 | 0.9940 | 0.9941 | 0.9985 | 0.9996 | 0.9991 |
| 9 | 7 | 14 | 0.9911 | 0.9923 | 0.9986 | 0.9998 | 0.9995 |
| 10 | 7 | 69 | 0.9909 | 0.9902 | 0.9980 | 0.9998 | 0.9994 |
| 11 | 8 | 5 | 0.9993 | 0.9988 | 0.9996 | 0.9998 | 0.9996 |
| 12 | 8 | 12 | 0.9967 | 0.9934 | 0.9976 | 0.9996 | 0.9994 |
| 13 | 8 | 9 | 0.9895 | 0.9908 | 0.9983 | 0.9997 | 0.9995 |
| 14 | 8 | 10 | 0.9974 | 0.9971 | 0.9991 | 0.9996 | 0.9992 |
| 15 | 8 | 42 | 0.9957 | 0.9961 | 0.9991 | 0.9997 | 0.9991 |
| 16 | 8 | 4 | 0.9933 | 0.9944 | 0.9991 | 0.9999 | 0.9997 |
| 17 | 8 | 44 | 0.9916 | 0.9974 | 0.9982 | 0.9996 | 0.9993 |
| 18 | 8 | 80 | 0.9911 | 0.9909 | 0.9982 | 0.9997 | 0.9994 |
| 19 | 8 | 40 | 0.9902 | 0.9904 | 0.9983 | 0.9998 | 0.9996 |
| 20 | 8 | 188 | 0.9904 | 0.9894 | 0.9980 | 0.9998 | 0.9993 |
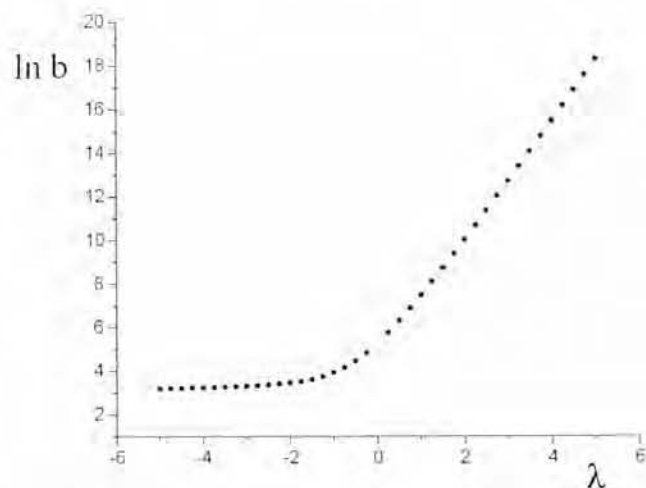
Fig. 6—A characteristic dependence of the intercept $b$ of a line $W_\lambda(PH) \approx a\, W_\lambda(HS) + b$ on the exponent $\lambda$. Here data for the line no. 20 are shown.
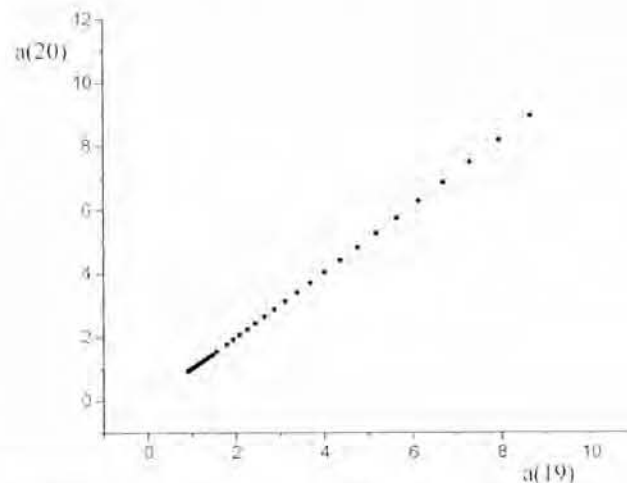


Fig. 8—In spite of what is seen in Fig. 7, the mutual variation of the slopes of two lines $W_\lambda(PH) \approx a\, W_\lambda(HS) + b$ is almost perfectly linear. Here the results pertaining to the lines nos. 19 and 20 are shown.
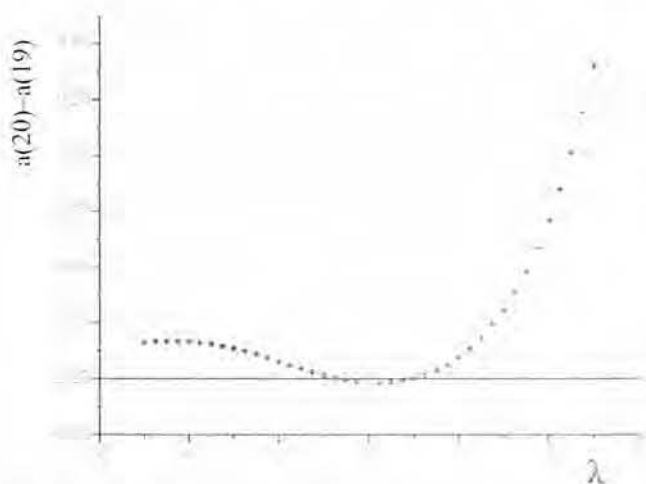


Fig. 7—The $\lambda$-dependence of the mutual orientation of the lines $W_\lambda(PH) \approx a\, W_\lambda(HS) + b$ follows a complicated pattern. Here the difference between the slopes of lines nos. 20 and 19 is shown.

Further details of the numerical studies of the correlation between the Wiener-type indices $W_\lambda$ of phenylenes and their benzenoid analogues are available from the authors (from B. F.), upon request.

## Results and Concluding Remarks

The analysis outlined in the previous section reveals that the exact relation between the Wiener indices of a phenylene, its hexagonal squeeze and its inner dual (stated as Eq. (1)) is violated when the Wiener index $W$ is replaced by its generalization $W_\lambda$, $\lambda \neq 1$. Yet, even for very large positive and negative values of $\lambda$ (namely for $\lambda$ between $-5$ and $+5$, at least)

the basic features of Eq. (1) are preserved: the $(W_\lambda(PH), W_\lambda(HS))$-points lie on a set of (nearly) straight lines, each line being determined by the respective $W(ID)$-value. However, contrary to the case $\lambda = 1$, these straight lines are no more parallel, and their deviation from mutual parallelism rapidly increases as $\lambda$ deviates from unity. The way in which the slopes of individual lines vary with $\lambda$ and in which these slopes vary mutually is difficult to rationalize and to describe by some simple mathematical model. Least-squares fitting of the curves shown in Figs. 5, 6 and 7 (as well as of the numerous other curves of the same kind, not shown in this paper) required polynomials of order 4 and higher.

In spite of these difficulties, we were able to establish the main general regularity governing the structure-dependency of the Wiener-type topological indices of phenylenes: *For all chemically relevant values of the parameter $\lambda$, there is a good linear correlation between $W_\lambda(PH)$ and $W_\lambda(HS)$, whose particular form depends on $\lambda$ and on the inner dual. In other words, for all chemically relevant values of the parameter $\lambda$, the Wiener-type indices $W_\lambda$ of phenylenes are determined by, and can be predicted from, the analogous indices of the corresponding hexagonal squeezes and the inner duals.*

### An application: The hyper-Wiener index

One of the main applications of the Wiener-type topological indices $W_\lambda$ is in connection with the hyper-Wiener index $WW$. This important structure-

Table 2—The parameters required for the calculation of the hyper-Wiener index of phenylenes by means of Eq. (4). These were determined by employing samples of 100 randomly chosen phenylenes with $h$ hexagons. $ARE$ = average relative error (in %), $MRE$ = maximal relative error observed (in %) within the sample considered.

| $h$ | $a$ | $b$ | $c \cdot 10^{-3}$ | $ARE$ | $MRE$ |
|---|---|---|---|---|---|
| 10 | 3.142 | 94.14 | −15.06 | 0.072 | 0.38 |
| 20 | 3.277 | 97.23 | −102.00 | 0.070 | 0.41 |
| 30 | 3.310 | 98.94 | −301.99 | 0.048 | 0.24 |
| 40 | 3.339 | 98.86 | −630.55 | 0.045 | 0.17 |
| 50 | 3.366 | 98.27 | −1101.51 | 0.038 | 0.15 |

descriptor was conceived some ten years ago[27] and, in the meantime, found numerous chemical applications (see the books[30-32] and the references quoted therein). As already mentioned, $WW = (1/2)W_1 + (1/2)W_2$ and therefore we expect that $WW(PH)$ will depend in a (nearly) linear manner on $WW(HS)$ and $WW(ID)$. That this indeed is the case was checked on samples consisting of 100 randomly selected phenylenes with $h$=10, 20, 30, 40, and 50 hexagons. The parameters $a$, $b$, $c$ in the formula

$$WW(PH) \approx a\, WW(HS) + b\, WW(ID) + c \qquad \dots\ (4)$$

determined by least-squares fitting, as well as the precision of the respective approximation are shown in Table 2.

## References

1  Vollhardt K P C, *Pure appl Chem*, 65 (1993) 153.
2  Vollhardt K P C & Mohler D L, *The phenylenes: Synthesis, properties, and reactivity*, in: *Advances in strain in organic chemistry*, Vol. 5, edited by B Halton (JAI Press, London), 1996, pp. 121-160.
3  Bong D T Y, Gentric L, Holmes D, Matzger A J, Scherhag F & Vollhardt K P C, *Chem Commun*, (2002) 278.
4  Gutman I, *Indian J Chem*, 32A (1993) 281.
5  Gutman I, *J chem Soc Faraday Trans*, 89 (1993) 2413.
6  Gutman I, *South Afr J Chem*, 47 (1994) 53.
7  Gutman I, *Commun math Chem (MATCH)* 31 (1994) 99.
8  Gutman I, Stajkovič A, Markovič S, Petkovič P, *J Serb chem Soc*, 59 (1994) 367.
9  Gutman I, *Indian J Chem*, 35A (1996) 909.
10  Gutman I, Markovič S, Stakjovič A & Kamidžorac S, *J Serb chem Soc*, 61 (1996) 873.
11  Gutman I & Ivanov-Petrovič V, *J molec Struct (Theochem)*, 389 (1997) 227.
12  Gutman I, Markovič S, Popovič, L, Spalevič Z & Pavlovič L, *J Serb chem Soc*, 62 (1997) 207.
13  Pavlovič L & Gutman I, *J chem Inf Comput Sci*, 37 (1997) 355.
14  Gutman I & Klavžar S, *ACH Models Chem*, 135 (1998) 45.
15  Gutman I & Tomovič Ž, *Monatsh Chem*, 132 (2001) 1023.
16  Rada J, Araujo O & Gutman I, *Croat chem Acta* 74 (2001) 225.
17  Gutman I, Lee S L, Chu C H & Luo Y L, *Indian J Chem*, 33A (1994) 603.
18  Gutman I, *Indian J Chem*, 36A (1997) 128.
19  Gutman I, *Indian J Chem*, 36A (1997) 644.
20  Gutman I, Yeh Y N, Lee S L & Luo Y L, *Indian J Chem*, 32A (1993) 651.
21  Gutman I & Potgieter J H, *J Serb chem Soc*, 62 (1997) 185.
22  Dobrynin A A, Entringer R & Gutman I, *Acta appl Math*, 66 (2001) 211.
23  Dobrynin A A, Gutman I, Klavzar S & Žigert P, *Acta appl Math*, in press.
24  Gutman I, Vidovič D & Popovič L, *J chem Soc Faraday Trans*, 94 (1998) 857.
25  Klein D J & Gutman I, *J chem Inf Comput Sci*, 39 (1999) 534.
26  Mihalič Z & Trinajstič N, *J chem Educ*, 69 (1992) 701.
27  Randič M, *Chem Phys Lett*, 211 (1993) 478.
28  Tratch S S, Stankevich I M & Zefirov N S, *J comput Chem*, 11 (1990) 899.
29  Gutman I, Cyvin S J & Brunvoll J, *Monatsh Chem*, 125 (1994) 887.
30  Todeschini R & Consonni V, *Handbook of molecular descriptors* (Wiley-VCH, Weinheim), 2000.
31  Diudea M V (editor), *QSPR/QSAR studies by molecular descriptors* (Nova, Huntington), 2001.
32  Diudea M V, Gutman I & Jantchi L, *Molecular topology* (Nova, Huntington), 2001.