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An Algorithm for Computation of Bond Contributions of the Wiener Index

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The Wiener index W is usually obtained by adding distances between all pairs of vertices i and j ($i, j = 1,2,...N$, where N denotes the total number of vertices). The Wiener index may also he obtained by adding all bond contributions W_e, *i.e.* $W = \Sigma\, W_e$, and $W_e = \Sigma\, C^e_{ij} / C_{ij}$, where C^e_{ij} denotes the number of all the shortest paths between i and j that include edge e, and C_{ij} denotes the total number of the shortest paths between vertices i and j. The summation has to be performed for all edges e and for all pairs of indices i and j, respectively. It is easy to calculate the bond contributions W_e for acyclic graphs or for bridges. The present paper introduces an algorithm, which can be used to obtain bond contributions in cycle – containing graphs.

INTRODUCTION

The Wiener index W is the number (graph invariant)[1] that can be calculated for the structural formula (graph) of an acyclic molecule. Due to the algorithm devised by Wiener, W is equal to the sum of bond contributions. The contribution of a particular bond in an acyclic molecular graph (structural formula) equals $N_1 \times N_2$, where N_1 denotes the number of atoms on the »left hand side« of the bond, and N_2 denotes the number of atoms on the »right hand side«, of that bond. For example, $W = 1 \times 2 + 2 \times 1 = 4$ in n-propane. Another (and more popular) method for obtaining W is the Hosoya[2] formula:

$$W = \sum_{i<j} D_{ij} \tag{1}$$

where D_{ij} denotes the length of the shortest paths (the distances) between vertices i and j, and the summation has to be performed for all pairs of atoms (vertices) in a graph ($i < j = 1, 2, \ldots N$).

The bond contribution method proposed by Wiener could be extended to cycle – containing systems. It could be proved[3] that:

$$W = \sum_{e} W_e \tag{2}$$

and

$$W_e = \sum_{i<j} C^e_{ij} / C_{ij} \tag{3}$$

where C_{ij} denotes the number of shortest paths between vertices (atoms) i and j, and C^e_{ij} denotes the number of those shortest paths between vertices i and j which contain edge e. The formula is valid for cyclic graphs, too. Later on, the same theorem was again proved by using different argumentation.[4,5]

No algorithm for the computation of bond contributions W_e of cycle – containing structures has been proposed so far. The aim of the present paper is to introduce such an algorithm. With this algorithm, there are five independent methods that can be used to calculate the Wiener index: I) By using Eq. (1). II) By using Eqs. (2) and (3). III) By using special formulas derived for various kinds of graphs.[6–10] IV) By using a numerical method which gives W directly.[11] V) By calculating the eigenvalues of the Laplacian matrix[12] of a graph (the last two approaches can be used only for trees).

The Wiener index has been extremely popular with researchers interested in quantitative description of steric features of molecules. The reader is advised to consult recent reviews.[13–16] Note that there is a graph theoretical index, the Rouvray index,[17] that is closely related to the Wiener index; in fact, the Rouvray index is equal to $2W$.

THE ALGORITHM

Expressions »graph« and »structural formula«, »edge« and »bond«, »atom« and »vertex« will be used interchangeably hereafter. Only hydrogen suppressed structural formulas will be considered. Edges will be denoted by the vertices they are incident with, *e.g.* (k, m) denotes an edge that is incident with vertices k and m. A graph can be represented by its adjacency matrix $\boldsymbol{A}$. Its ij-th element $A_{ij} = 1$ if vertices i and j are connected by an edge (*i.e.* i and j are adjacent), and $A_{ij} = 0$ if i and j are not connected by an edge. $A_{ii} = 0$ for all i. An introduction to the chemical graph theory has been published recently.[15]

The matrix of shortest distances $\boldsymbol{C}$ will be generated in Steps 1–3. The number of paths which involve edge $e = (k, m)$ is obtained in Steps 4–5. The algorithm is listed below:

Step 1. Set $n = 1$, and set $C_{ij} = A_{ij}$ and set $D_{ij} = A_{ij}$ for all pairs of vertices i, j $(i, j = 1,2,...,N)$.

Step 2. Increase the value of index n by one.

Step 3. If $C_{ij} = 0$ and $(A^n)_{ij} \neq 0$, then $C_{ij} = (A^n)_{ij}$ and $D_{ij} = n$; for $i < j = 1,...,N$. Then go to Step 2.
If for all i and j either $C_{ij} \neq 0$ or $(A^n)_{ij} = 0$, then go to Step 4.

Step 4. For each edge $e = (k, m)$ of G and every i and j repeat: Calculate $h = D_{ik} + D_{mj} + 1$ and $h' = D_{im} + D_{kj} + 1$. If $D_{ij} < h'$, then there is at least one shortest path between i and j that involves edge (k, m), and the order of vertices is i-k-m-j in this path. The number of such paths is $C^e_{ij} = C_{ik}\, C_{mj}$. If $h' = D_{ij} < h$; then there is at least one shortest path between vertices i and j that involves edge (k, m), and the order of the vertices is i-m-k-j in this path. Now $C^e_{ij} = C_{im}\, C_{kj}$. If $\min(h,h') \neq D_{ij}$, then there are no such paths.

Step 5. Add all values C^e_{ij}/C_{ij} to obtain the bond contribution W_e of edge $e = (k, m)$. Add all edge contributions to obtain W.

NUMERICAL EXAMPLES

Table I lists the matrix of the numbers of the shortest paths of cyclohexane (Figure 1). Note that the diagonal elements are $C_{ii} = 1$ for all i. The contribution of bond $e = (1,2)$ may be obtained as follows:

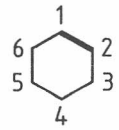

Figure 1. The hydrogen suppressed graph of cyclohexane with the specified bond. The evaluation of the contribution of edge (1,2) has been explained in the text.

For atoms 1 and 2, $C_{12} = 1$ and $C^e_{12} = 1$, $C^e_{12}/C_{12} = 1/1 = 1$,
for atoms 1 and 3, $C_{13} = 1$ and $C^e_{13} = 1$, $C^e_{13}/C_{13} = 1/1 = 1$,
for atoms 1 and 4, $C_{14} = 2$ and $C^e_{14} = 1$, $C^e_{14}/C_{14} = 1/2 = 0.5$,
for atoms 1 and 5, $C_{15} = 1$ and $C^e_{15} = 0$, $C^e_{15}/C_{15} = 0/1 = 0$,
for atoms 1 and 6, $C_{16} = 1$ and $C^e_{16} = 0$, $C^e_{16}/C_{16} = 0/1 = 0$,
for atoms 2 and 3, $C_{23} = 1$ and $C^e_{23} = 0$, $C^e_{23}/C_{23} = 0/1 = 0$,
for atoms 2 and 4, $C_{24} = 1$ and $C^e_{24} = 0$, $C^e_{24}/C_{24} = 0/1 = 0$,
for atoms 2 and 5, $C_{25} = 2$ and $C^e_{25} = 1$, $C^e_{25}/C_{25} = 1/2 = 0.5$,
for atoms 2 and 6, $C_{26} = 1$ and $C^e_{26} = 1$, $C^e_{26}/C_{26} = 1/1 = 1$,
for atoms 3 and 4, $C_{34} = 1$ and $C^e_{34} = 0$, $C^e_{34}/C_{34} = 0/1 = 0$,
for atoms 3 and 5, $C_{35} = 1$ and $C^e_{35} = 0$, $C^e_{35}/C_{35} = 0/1 = 0$,
for atoms 3 and 6, $C_{36} = 2$ and $C^e_{36} = 1$, $C^e_{36}/C_{36} = 1/2 = 0.5$,
for atoms 4 and 5, $C_{45} = 1$ and $C^e_{45} = 0$, $C^e_{45}/C_{45} = 0/1 = 0$,
for atoms 4 and 6, $C_{46} = 1$ and $C^e_{46} = 0$, $C^e_{46}/C_{46} = 0/1 = 0$,
for atoms 5 and 6, $C_{56} = 1$ and $C^e_{56} = 0$, $C^e_{56}/C_{56} = 0/1 = 0$.

The sum of these terms yields 4.5 for edge (1,2). In cyclohexane, the bond contributions of each edge are equal because of symmetry reasons and $W = 6 \times 4.5 = 27$.

TABLE I

The matrix of the numbers of shortest distance
C of cyclohexane

$$C = \begin{matrix} 1\,1\,1\,2\,1\,1 \\ 1\,1\,1\,1\,2\,1 \\ 1\,1\,1\,1\,1\,2 \\ 2\,1\,1\,1\,1\,1 \\ 1\,2\,1\,1\,1\,1 \\ 1\,1\,2\,1\,1\,1 \end{matrix}$$

Table II lists the calculated bond contributions of the various edges of pyrene. The numbering of atoms is shown in Figure 2. The sum of bond contributions is $W = 362$ in pyrene.

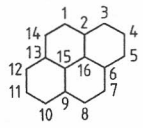

Figure 2. The numbering of carbons in pyrene.

TABLE II

The bond contributions of pyrene (Figure 2)

Bond No.	Atom 1	Atom 2	Contribution	Bond No.	Atom 1	Atom 2	Contribution
1	1	2	17.5	11	11	12	11.666667
2	2	3	19.5	12	12	13	19.5
3	3	4	11.666667	13	13	14	17.5
4	4	5	11.666667	14	1	14	14.5
5	5	6	19.5	15	13	15	26.333333
6	6	7	17.5	16	15	16	35
7	7	8	14.5	17	6	16	26.333333
8	8	9	17.5	18	2	16	26.333333
9	9	10	19.5	19	9	15	26.333333
10	10	11	11.666667				

RESULTS AND DISCUSSION

Inspection of the bond contributions listed in Table II shows that the rule observed for acyclic graphs remains valid in cyclic graphs, namely the maximal values of contributions arise from bonds which are in the centre of the molecule. Indeed, the bond contribution of edge (15,16) is equal to 35. The minimal value 11.6666667 is due to peripheral bonds (3,4), (4,5), (10,11), (11,12). The reason for higher bond contributions of central edges (k, m) is simple: there are more pairs of vertices connected by shortest paths that involve (k, m) than shortest paths which include a peripheral edge.

The present algorithm has already been applied for correlating the logarithms of the partition coefficients of unsaturated hydrocarbons with the sum of bond contributions of single bonds and the sum of bond contributions of double bonds, triple bonds and aromatic bonds.[3,18,19] In principle, this method is appropriate for calculating the bond contributions in heteroatomic molecules, too. In this way, a method for obtaining a more general Wiener number has been obtained.

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SAŽETAK

Algoritam za računanje doprinosa grana Wienerovu indeksu

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Wienerov indeks obično se računa zbrajanjem udaljenosti među svim parovima čvorova i i j (i, j = 1,2,...,N) gdje N označava ukupan broj čvorova u grafu). On se također može dobiti zbrajanjem svih doprinosa po granama W_e, tj. kao $W = \sum W_e$, gdje je $W_e = \sum C_{ij}^e / C_{ij}$, C_{ij}^e predstavlja broj svih najkraćih puteva koji prelaze preko grane e a C_{ij} označuje ukupan broj najkraćih puteva između čvorova i i j. Gornje sumacije idu preko svih grana e, odn. preko svih mogućih parova čvorova i i j u grafu. Doprinose po granama W_e lako je izračunati za acikličke grafove i mostove. U ovom je radu uveden algoritam koji omogućuje račun doprinosa po granama W_e u grafovima koji sadržavaju prstenove.