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Note

On Characterization of Monocyclic Structures

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The sum of topological distances in the molecular graph, the Wiener number, is used for a topological characterization of monocycles. Various other mathematical models based either on the adjacency matrix or on the distance matrix of a system, which were earlier used mostly for studying molecular branching, are now also applied to monocyclic structures in order to learn if they would be of use in characterizing molecular cyclicity.

In this work we wish to describe the application of the topological indices and especially that of the Wiener number, W (G), to monocyclic systems. In the past the Wiener number was used only for studying molecular branching[1]. Wiener[2] in his studies on additive physical parameters of acyclic hydrocarbons has introduced a path number W which is defined as the sum of the distances between any two carbon atoms in the molecule in terms of carbon-carbon bonds. We call this path number the Wiener number of the graph[1], W (G). It can be shown that the Wiener number is equal to half the sum of the off--diagonal elements of the distance matrix of the graph[1], D (G),

$$W(\mathrm{G}) = \frac{1}{2} \sum_{(i,j)} D_{ij}(\mathrm{G}) \tag{1}$$

where D_{ij} are off-diagonal elements of the distance matrix.[3]

The Wiener number is applied to monocyclic structures in order to learn if it is sensitive to the change of ring size since this change is well reflected in their physical and chemical properties[4].

Let the number of atoms in the cycle be denoted by N. The following equations were derived in an inductive way (the method is described in detail elsewhere[1]) for the Wiener number W (G) and the mean value of the Wiener number,

$$\overline{W}(\mathrm{G}) = \frac{2W}{N(N-1)} \tag{1a}$$

(called the mean topological distance), in the cyclic molecular graph[5]:

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(a) $N = 2k + 1$ (for odd cycles)

$$W \text{ (cycle)} = \frac{N^3 - N}{8} \tag{2}$$

$$\overline{W} \text{ (cycle)} = \frac{N + 1}{4} \tag{3}$$

(b) $N = 2k$ (for even cycles)

$$W \text{ (cycle)} = \frac{N^3}{8} \tag{4}$$

$$\overline{W} \text{ (cycle)} = \frac{N^2}{4(N - 1)} \tag{5}$$

Let the mean topological distance in the molecular graph, $\overline{W}$ (G), be taken as the inverse measure of the relative cyclicity. It is easy to conclude that the relative cyclicity decreases with the increase of the number of atoms in the cycle. The increase of the number of atoms in a monocyclic system would make it more and more similar to an infinite chain and eventually its cyclic character would disappear.

Rule 1. — When the number of atoms in a monocyclic system increases, the relative cyclicity decreases, but the decrease is smaller following the transition from even to odd than from odd to even cycles:

$$\Delta \overline{W} \text{ (even} \rightarrow \text{odd)} < \Delta \overline{W} \text{ odd} \rightarrow \text{even)} \tag{6}$$

In order to prove this rule let us consider the subsequent increase of the number of atoms in the three monocyclic structures: odd → even → odd. The following equations hold:

$$\Delta \overline{W} \text{ (odd} \rightarrow \text{even)} = \frac{N}{4(N - 1)} \tag{7}$$

$$\Delta \overline{W} \text{ (even} \rightarrow \text{odd)} = \frac{N - 2}{4(N - 1)} \tag{8}$$

and from these follows the relation,

$$\Delta \overline{W} \text{ (odd} \rightarrow \text{even)} - \Delta \overline{W} \text{ (even} \rightarrow \text{odd)} = \frac{1}{2(N - 1)} > 0 \tag{9}$$

by which the inequality (6) is proven. Here N is the number of atoms in the intermediate even cycle.

It is also of interest to compare the Wiener numbers of the monocyclic compounds with those of their linear carbon skeleton isomers.

Rule 2. — The Wiener numbers of molecular graphs decrease when linear molecules cyclize.

$$W \text{ (cycle)} < W \text{ (chain)} \tag{10}$$

$$\overline{W} \text{ (cycle)} < \overline{W} \text{ (chain)} \tag{11}$$

To prove rule 2 we make the use of the equation for the change upon the cyclization process[6]:

$$W\,(\text{chain}) - W\,(\text{cycle}) = \frac{N^3 - aN}{24} > 0 \qquad (12)$$

where a = 1 for N = odd and a = 4 for N = even, respectively.

Figure 1 ilustrates the two topological rules by a comparison between the boiling points and the Wiener numbers of several chains (representing alkanes, C_nH_{2n+2}) and the corresponding cycles (representing cycloalkanes, C_nH_{2n}). An additional illustration is given later in Table I.

TABLE I

Topological and Information Indices of Monocycles and some Properties of Cycloalkanes

Cycle[a]	N[b]	$\overline{W}$ (G)	$\bar{I}_D$ (G)	Z (G)	S°_{298}	C_p^{298}	ΔH°_{298}
1	3	1.0	—	4	56.75	13.37	12.74
2	4	1.33	0.92	7	63.43	17.26	6.37
3	5	1.5	1.0	11	70.00	19.84	—18.46
4	6	1.8	1.52	18	71.28	25.40	—29.43
5	7	2.0	1.58	28	81.82	29.42	—28.52
6	8	2.29	1.95	43	87.66	33.45	—30.06

[a] Numbers correspond to the cyclic graphs given in Figure 1.

[b] Note, that: $N = \frac{1}{4} M_1\,(G) = \frac{1}{4} M_2\,(G) = \frac{1}{2} F\,(G) = S\,(G) = 2\,\chi_R\,(G)$, and $2W\,(G) = R\,(G)$

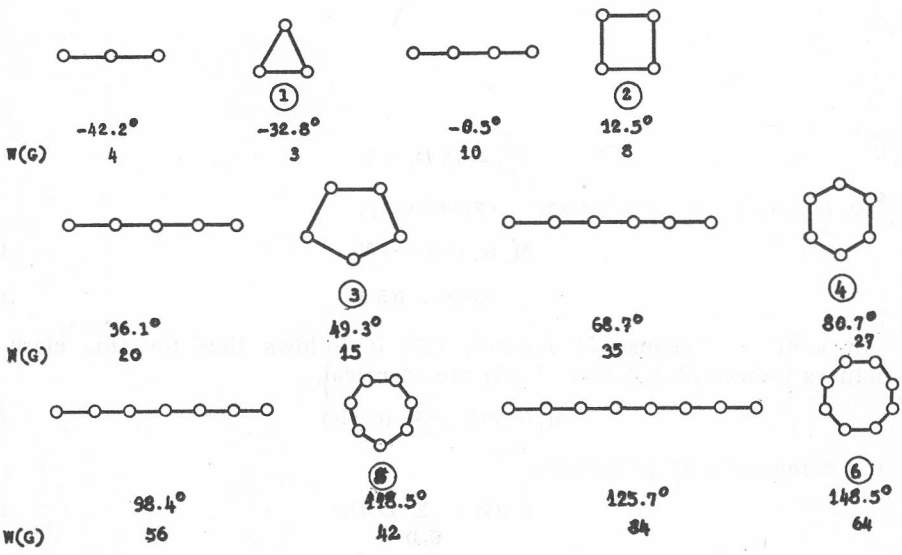


Figure 1. Comparison between the chains (depicting alkanes) and the related cycles (depicting cycloalkanes). Numbers below each structure are boiling points in °C taken from the publication of National Bureau of Standards *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons* (1945).

In what follows we will examine the applicability to monocycles of the other known topological indices introduced in the past mainly for characterization of the acyclic systems. A number of interrelations between the topological indices will be presented.

Rouvray's index[7], R (G), is equal to the sum of all elements of the distance matrix,

$$R\,(\mathrm{G}) = \sum_{(\mathrm{i},\,\mathrm{j})} D_{\mathrm{ij}}\,(\mathrm{G}) \tag{13}$$

Hence, (taking into account eq. (1)) the Rouvray index is connected with the Wiener number by the expression,

$$R\,(\mathrm{G}) = 2\,W\,(\mathrm{G}) \tag{14}$$

Index M_1 (G) is ordinarily obtained from the relation[8],

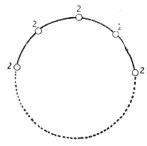
$$M_1\,(\mathrm{G}) = \sum_{\mathrm{j}=1}^{N} D_{\mathrm{j}}^2 \tag{15}$$

while the Randić connectivity index[9], χ_{R} (G) from a similar relation,

$$\chi_{\mathrm{R}}\,(\mathrm{G}) = \sum_{(\mathrm{i},\,\mathrm{j})} (D_{\mathrm{i}}\,D_{\mathrm{j}})^{-1/2} \tag{16}$$

D_{i}, D_{j} denote the degrees (valencies)[5] of the vertices in the graph G, while i, j denote adjacent vertices.

However, the above eqs. (15) and (16) can be simplified for monocycles. Monocycles are represented by connected graphs in which all vertices have valencies 2.



Therefore,

$$D^2_{\mathrm{j}} = D_{\mathrm{i}}\,D_{\mathrm{j}} = 4 \tag{17}$$

Hence, eqs. (15) and (16) become, respectively,

$$M_1\,(\mathrm{cycle}) = 4\,N \tag{18}$$

$$\chi_{\mathrm{R}}\,(\mathrm{cycle}) = 0.5\,N \tag{19}$$

In addition, because of identity (17) it follows that for this class of structures indices M_1 (G) and M_2 (G) are identical,

$$M_1\,(\mathrm{cycle}) = M_2\,(\mathrm{cycle}) \tag{20}$$

M_2 (G) being defined[8] as follows,

$$M_2\,(\mathrm{G}) = \sum_{(\mathrm{i},\,\mathrm{j})} D_{\mathrm{i}}\,D_{\mathrm{j}} \tag{21}$$

Platt[10] proposed an index, F (G), resulting from considering the first neighbour; for each edge the number of adjacent edges is calculated and then these numbers are summed for all the edges to give F (G). Therefore, F (G)

represents the first neighbours sum. Platt has used his index only for paraffins. Here his index is first extended to cyclic systems. For the case of monocyclic structures a simple formula for F (G) is valid,

$$F \text{ (cycle)} = 2N \tag{22}$$

The Platt index F (G) is also related in a simple way to the Gordon and Scantlebury index[11] of the graph, S (G). The index S (G) is equal to the number of distinct ways in which a C_3 acyclic fragment may be embedded on the skeleton of a given molecule. It can be shown[12] that the S (G) index is equal to half the value of F (G),

$$S \text{ (G)} = \frac{1}{2} F \text{ (G)} \tag{23}$$

and consequently for monocycles to a number of atoms within the cycle,

$$S \text{ (cycle)} = N \tag{24}$$

A total interrelation can be thus written for the above topological indices as follows,

$$N = \frac{1}{4} M_1 \text{ (G)} = \frac{1}{4} M_2 \text{ (G)} = \frac{1}{2} F \text{ (G)} = \text{S (G)} = 2 \chi_R \text{ (G)} \tag{25}$$

Since all these indices depend linearly on the number of carbon atoms within the ring they could not provide a basis for the deduction of the rule 1, i. e. these indices do not reflect the difference in the properties of odd- and even--membered cycloalkanes.

Hosoya's index[13] Z (G) is calculated by means of the expression,

$$Z \text{ (G)} = \sum_{k=0}^{m} p \text{ (G; } k) \tag{26}$$

where p (G; k) is the number of ways in which k edges may be selected in such a manner that two of them are never connected, whereas m is the maximum number of k for G. This topological index has already proved its applicability to cyclic systems by providing useful correlations with their molecular properties. One may assume on the basis of the results in Table I that the Hosoya index, after a convenient normalization, could reflect the different molecular properties of odd- and even-membered cycloalkanes. However, the simplest way of normalization by dividing by the number of carbon atoms failed. On the other hand the data from Table II show that the cyclization is accompanied with a regular increase in the Hosoya number, i. e. the rule 2 could be also derived using this topological index.

Statistical analysis of the distance matrix on the basis of information theory[14], taking into account that the distance matrix of a graph is a symmetric matrix with the consequence that its upper triangle preserves all the information about the corresponding system, leads to the relation for the topological index[1] called the information on the distances in the graph G, I_D (G),

$$I_D \text{ (G)} = \frac{N(N-1)}{2} \log_2 \frac{N(N-1)}{2} - \sum_{j=1}^{n} k_j \log_2 k_j \tag{27}$$

TABLE II

Cycle[a]	N	$\Delta W_{cycl.}$ (G)[b]	$\Delta I_D^{cycl.}$ (G)	$-\Delta Z_{cycl.}$ (G)	$-\Delta S_{298}^{cycl.}$
1	3	1	2.58	1	7.7
2	4	2	3.24	2	10.69
3	5	5	8.46	3	13.40
4	6	8	9.40	5	21.55
5	7	14	17.08	7	20.42
6	8	20	18.47	9	23.85

[a] Numbers correspond to the cyclic graphs given in Figure 1.
[b] $\Delta X_{cyclization} = X_{chain} - X_{cycle}$

where n is the number of different sets of matrix elements and $\frac{N(N-1)}{2}$ is the total number of upper off-diagonal elements in D (G). k_j denotes the number of times the distance d_j appears in the off-diagonal triangular submatrix of the distance matrix D (G). The logarithm is taken at basis 2 for measuring the information content in bits.

Eq. (27) can be normalized by dividing I_D (G) with $\frac{N(N-1)}{2}$. The index thus obtained represents the mean value of the information on distances in G, $\bar{I}_D$ (G),

$$\bar{I}_D(G) = -\sum_{j=1}^{n} \frac{2k_j}{N(N-1)} \log_2 \frac{2k_j}{N(N-1)} \tag{28}$$

The calculated values of the topological and information indices of monocycles are given in Table I together with some properties of gaseous cycloalkanes[15].

The change in the Wiener number, information index, and Hosoya index, upon the process of cyclization, $\Delta X_{cyclization} = X$ (chain) $- X$ (cycle), and the change in the entropy of the same process are given in Table II. Values for W (chain)[16] are taken from ref. 1. The positive values of ΔH^0_{298} reflect the ring strain in 3- and 4-membered rings.

Several interesting points may be learned from the Tables. First, the inspection of Tables reveals that the two rules introduced for monocycles are reflected well in the listed molecular properties thus indicating that these properties depend to a certain extent on the topological nature of the molecular skeleton. Secondly, the Wiener number, the information index, and the Hosoya number are thus shown to be sensitive to the change in the ring size. Thirdly, almost all the other investigated indices depend solely on the total number of atoms within the cycle and cannot result in supporting rule 1. Hence, they are less applicable to the cyclic structures than the Wiener number, the information and Hosoya indices, respectively. However, among these three quantities the information indices, as seen from Tables I and II, reflect the two topological rules on monocyclic systems in a more convincing

way than the other two indices. Therefore, the information indices might be very suitable for structural studies and correlations with a variety of molecular properties[17,18].

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SAŽETAK

O karakterizaciji monocikličkih struktura

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Zbroj topoloških udaljenosti u molekulskom grafu, nazivan Wienerovim brojem, upotrijebljen je za karakterizaciju monocikličkih struktura. Različiti matematički modeli koji se temelje na matrici susjedstva ili na matrici udaljenosti dane strukture, ranije upotrebljavani za izučavanje grananja molekule, primijenjeni su također na monocikličke sustave, s ciljem da se ispitaju mogu li se upotrijebiti za karakterizacije prstenastih molekula.

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