match no. 11 pp. 145-168 1981

A TOPOLOGICAL CHARACTERIZATION OF CYCLIC STRUCTURES WITH ACYCLIC BRANCHES

Ov. Mekenyan, D. Bonchev, and N. Trinajstić[a]

Department of Physical Chemistry, Higher School of Chemical Technology, 8010 Burgas, Bulgaria
[a]Institute "Rudjer Bošković", 41001 Zagreb, Yugoslavia

(Received May 1980)

Abstract

The sum of the topological distances in the molecular graph (the Wiener index) is used in the analysis of molecular branching and cyclicity in a large class of compounds, having both a cyclic and an acyclic part, simultaneously. 9 topological rules are proved which reflect the regular change in the topological index upon certain structural changes in groups of isomeric compounds.

Introduction

It is known that, irrespective of the specific geometry and the individual properties of its atoms, the properties of a molecule are basically determined by its topology[1-4]. Molecular topology depends on the adjacency of atoms in the molecule but not on the bond lengths, valence angles, or area encompassed by the cycles. Molecular branching and cyclicity, the Hückel or anti-Hückel character of the π electron circuits in the conjugated cyclic systems[5], the number and parity of the Kekule structures[3,6,7], etc., could be mentioned among the most important topological factors.

Although the hierarchy of the topological structural factors is still an open question, it is out of doubt that some of these factors are determining for the specific molecular properties of many classes of compounds. The basic properties

of acyclic molecules for instance are determined by their branching[8]. This topological factor has been studied in detail for the last 15 years[9-14]. Recently, the molecular cyclicity was also quantitatively defined, its alternation upon certain structural changes being examined in a series of papers on monocyclic[15], and polycyclic condensed[16], spiro-[17], and bridged[18] isomeric structures.

A graph-theoretical approach is used in the above studies which is based on the examining of the changes in a quantitative criterion (a topological index)[19,20], reflecting the essential topological features of molecular graphs. The main point of the approach is in the deduction of equations for the influence that certain structural factors have on the behaviour of the topological index within groups of isomers. Topological rules of molecular branching and cyclicity, reflected in various molecular properties[21-23], are specified by these equations.

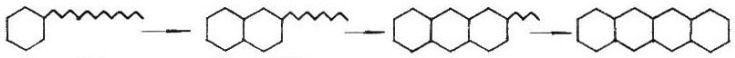
The topological distance matrix D(G) is distinguished, among the many characteristics of molecular graph (G), as a good basis for structural studies[24]. This is a real N x N symmetrical matrix (N is the number of vertices in G). Its off-diagonal entries $D_{ij}(G)$ are equal to the number of bonds along the shortest path between vertices i and j in G, while the diagonal elements are by definition zero. Studying some additive properties of acyclic hydrocarbons Wiener[25] first used the distance number of a graph W (the Wiener number) which he defined as the number of bonds between each pair of carbon atoms. It can be shown that the wiener index W(G) of graph G is half the sum of all distance matrix entries:

$$W(G) = \frac{1}{2} \sum_{ij} D_{ij}(G) \qquad (1)$$

In this way the Wiener number represent the sum of all topological distances in the graph. This topological index demonstrates a high discrimination ability towards isomeric structures and proved to be fruitful as a measure (reverse proportional) of molecular branching[8,14] and cyclicity[15-18].

The studies on molecular branching and cyclicity cited above deal with acyclic molecules and cyclic molecules without branches, respectively, i.e. the two topological factors are investigated in a "pure form". The present paper aims at studying the simultaneous change of the branching and cyclicity in the general case of cyclic structures having acyclic branches. Since the two factors cannot be always demarcated, the quantitative study of this vast class of molecular structures by means of the Wiener index rather characterizes the overall structural complexity within it.

The problem may be illustrated by the following examples:

A) 

$W_1 = 889$ $W_2 = 753$ $W_3 = 625$ $W_4 = 569$

B) 

$W_1 = 195$ $W_2 = 200$ $W_3 = 203$ $W_4 = 207$

One could expect that the increase in cyclicity and the decrease in branching along the first sequence of compounds, will reduce the sum of the topological distances. This is more difficult, however, to be intuitively done for the second series of compounds, as well as for the most branched cyclic chemical structures in Nature. Hence, the necessity of a rigorous mathematical treatment of the change in the Wiener index on certain structural changes in isomeric groups of compounds. The topological rules deduced on this basis could be of practical importance. The ordering of the isomeric structures according to the topological index, reflecting the degree of the structural change in the corresponding isomeric series could in principle be extended on majority of molecular properties. In addition, the topological rules could be used as a convenient basis for quantitative structure-property correlations, specifying the optimal sample of isomeric molecules to be included in a certain correlation.

Structural factors influencing the cyclicity and branching of the cyclic molecules with acyclic branches

The total topological distance in the molecule reflects simultaneously the two topological factors - molecular cyclicity and branching. Since it decreases with the increase in both factors[8,14-18] one should speak in such cases about an increase in the totality of branching and cyclicity. Moreover, it might occur that cyclicity and branching change in opposite directions, as well as the increase in the first of these topological characteristics of molecules to be compensated by the decrease in the second one. Due to the difficulties in demarcating these two molecular features we assume that in this study the Wiener number reflects the totality of cyclicity and branching, i.e. the overall complexity of molecules.

The structural factors that were taken into account in the characterization of cyclicity and branching of the molecules under study, as well as their denotations are listed below.

N_o, the total number of atoms in the molecule. In this paper N_o= const, i.e. isomeric structures are under consideration only;

a , the number of cycles (all cycles are of the same kind of connection - a condensation, or spiro-, or bridged one);

N , the number of atoms in a cycle (all cycles are of the same size);

N_k, the total number of atoms in the acyclic part of the initial structure;

N_{kj}, the length (in number of atoms) of the j-th side chain of the initial structure;

i , the number of the newly-formed side chains to the cyclic part of the structure;

N_i, the length (in number of atoms) of the newly-formed side chains to the cyclic part of the structure;

d_{ij}, the distance (in number of bonds) between the side chains i and j along the cycle;

$\Delta l = N_{kj}' - N_{kj}''$, the difference in the lengths of two

side chains;

p , the number of the newly-formed branches to the single initial side chain;

N_p, the length (in number of atoms) of a newly-formed branch to the initial side chain;

ΔN_p, the distance (in number of atoms) between the cycle and the branch of the initial side chain.

The influence of the above mentioned factors is studied and reflected in the equations, derived in an inductive way for the Wiener number. The results are formulated in rules expressing the nature of molecular cyclicity and branching in the studied molecular structures.

The number of atoms in the acyclic part and the size of the cycle

Rule 1. The sum of the topological distances in isomeric structures composed of a cycle and a non-branched side chain passes through a minimum defined by the condition:

$$N_k = (3N_o - 4 - 2\sqrt{N_o^2 - N_o + 7/3}) / 5 \qquad (2)$$

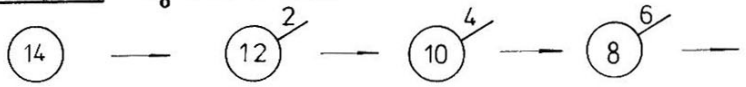
with the increase in the chain length at the cost of a decrease in the cycle size at a constant parity of the cycle membering:

$$W_{N,N_k} > W_{N-1,N_k+1} > \dots > W_{N-n,N_k+n} < W_{N-n-1,N_k+n+1} < \dots$$

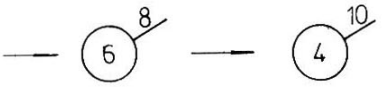
$$\dots < W_{N-n-s,N_k+n+s} \qquad (2')$$

where n and s are positive integers.

Examples: $N_o = 14 = \text{const}$



$N=14, N_k=0$ $W_1=343$ | $N=12, N_k=2$ $W_2=325$ | $N=10, N_k=4$ $W_3=335$ | $N=8, N_k=6$ $W_4=363$



$N=6, N_k=8$ $\qquad$ $N=4, N_k=10$

$W_5=399$ $\qquad$ $W_6=433$

In these and the following examples the number of atoms in the acyclic chains is directly assigned by a number above each chain.

Rule 1 is proved deriving by induction the equation for the Wiener number of a monocyclic system with a single non-branched side chain:

$$W = \left[-5N_k^3 + 3N_k^2(3N_o-4) - N_k(3N_o^2-12N_o+4) + 3N_o^3 + \right.$$
$$\left. + A(N_o+N_k/3)\right] / 24 \qquad (3)$$

where $N_o = (N_k+N) \geqslant 5$; N_o = const; $N_k = 1,2,3,\ldots,n$; $N_k \neq$ const. $A = 0$ and $A = -3$ for even- and odd-membered cycles, respectively.

The second part of the proof is presented below for the case of even-membered rings (it does not essentially differ for odd-membered cycles).

The function W in eqn.(3) has a minimum N' and a maximum N'', respectively, at:

$$N_k^{',''} = \left[(3N_o-4\mp 2\sqrt{D})\right] / 5 \qquad (3')$$

where $D = N_o^2 - N_o + 7/3$.

By condition $N_k = N_o - N$, and $N \geqslant 4$. We shall prove that no maximum of W can occur in the structures under consideration, i.e. $N_k'' > N_o - 4$, or

$$(3N_o - 4 + 2\sqrt{D}) / 5 > N_o - 4 \qquad (3'')$$

Substituting D from (3') into (3'') one obtains

$$N_o \geqslant 37/9 \qquad (3''')$$

which always holds since for even-membered cycles $N_o \geqslant 6$ by condition. Rule 1 is thus proved. The proof can also be extended for the case of a variable cycle-membering.

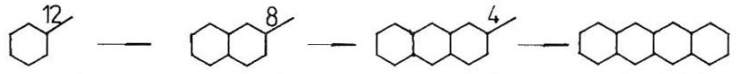
The number of atoms in the acyclic part of the molecule and the number of cycles

Rule 2. The sum of the topological distances in isomeric structures, composed of a linear string of cata-condensed, or spiro-, or bridged linked (with one bridge without atoms in it) cycles and a non-branched side-chain with a length N_k multiple to the number of newly-formed cycles a_k, attached at one and the same position of a terminal ring, decreases when the length of the side chain reduces at the cost of the formation of new cycles:

$$\text{for } N_k = a_k(N-m) \qquad W_{a,N_k} > W_{a+x,N_k-n} \qquad (4).$$

Here x = 1,2,3,..., and n=(N-m)x, where m=2,1, and 0 for condensed, spiro-, and bridged linked cycles, respectively.

Examples:



a=1, N_k=12 a=2, N_k=8 a=3, N_k=4 a=4, N_k=0

W_1=889 W_2=753 W_3= 625 W_4=569

In proving this rule we deal with $\Delta W = W_1 - W_2$, i.e. the difference in the Wiener index W_1 of the initial structure containing only one cycle and a non-branched side chain, and the Wiener index W_2 of the final structure containing only cycles (condensed, spiro-, or bridged linked). We omit the proof for odd N which is analogical to that given below for even-membered rings.

For condensed cycles:

$$W_1 = \left[4a_k^3(N-2)^3 + 12a_k^2N(N-2)^2 + 2a_k(3N^3-14N+4) + 3N^3\right]/24 \qquad (5)$$

$$W_2 = \left[2a_k^3(N-2)^3 + 6a_k^2(N-2)^2(N+1) + a_k(7N^3-6N^2-24N+16) + 3N^3\right]/24 \qquad (6)$$

$$\Delta W = W_1 - W_2 = a_k(N-2)\left[(N-2)^2(2a_k^2+6a_k-1) + 6a_k(N-2) + 8\right]/24 > 0 \qquad (7)$$

For spirosystems:

$$\Delta W = W_1 - W_2 = a_k(N-2)\left[2a_k^2(N-1)^2 + 6a_kN(N-1) - (N^2-6N+2)\right]/24 > 0 \quad (8)$$

For bridged systems:

$$\Delta W = W_1 - W_2 = a_kN(N-2)\left[N(2a_k^2+6a_k-1) + 2\right] / 24 > 0 \quad (9)$$

Rule 2 follows from inequalities (7),(8), and (9).

The length of the side chain in the initial structure and the number of the newly-formed branches to the cycle

Rule 3. The sum of the topological distances decreases when isomers are subsequently formed from a structure, composed of a cycle having up to 10 atoms and a non-branched side chain, by the shortening of the side chain at the cost of the formation of i new, non-branched side chains of equal length N_i to half the atoms of the ring by the condition the length of the initial side chain N_k divided by the maximum number of new branchesincreased by one, to be an integer equal to the length of the newly-formed side chains:

$$\text{for } N_k/i_{max}+1 = N_i : \quad W_{N_{kj},i} > W_{N_{kj}-xN_i,i+x} \quad (10)$$

where x = 1,2,3,..., and i = 1 ÷ N/2.

Examples: $N_k = 4$

$N_{k1}=4, i=0$ $W_1=133$ | $N_{k1}=3, i=1$ $W_2=121$ | $N_{k1}=2, i=2$ $W_3=113$ | $N_{k1}=1, i=3$ $W_4=109$

The proof of the rule is presented below for two cases of structures with even-membered cycles (the similar proof for the case of odd-membered cycles is omitted for brevity).

A) The new side chains are consecutively formed to neighbouring atoms of the cycle proceeding from the initial side chain and moving only in one direction (clockwise or counter-

clockwise).

The following equation is deduced for the Wiener index of the examined type of structures:

$$W = iN_k^2\left[4i^2(2N_k-N-2) + 3i(N+2)(3N-2N_k-2) - (6N^3 + 9N^2 - -16N - 6N_kN - 4N_k - 20)\right] / 3(N+2)^3 + W' \qquad (11)$$

$$W' = \left[4N_k^3 + 12N_k^2N + 2N_k(3N^2 + 6N - 2) + 3N^3\right] / 24 \qquad (11')$$

The specific cases of eqn. (11) for N = 4, 6, 8, and 10, respectively are:

for N=4, i=1,2:

$$W = iN_k^2\left[2i^2(N_k-3) - 9i(N_k-5) + (7N_k-111)\right]/162 + W' \qquad (12)$$

$$W' = (N_k^3 + 12N_k^2 + 35N_k + 48) / 6 \qquad (12')$$

for N=6, i=1,2,3:

$$W = iN_k^2\left[i^2(N_k-4) - 6i(N_k-8) + (5N_k-188)\right] /192 + W' \qquad (13)$$

$$W' = (N_k^3 + 18N_k^2 + 71N_k + 162) / 6 \qquad (13')$$

for N=8, i=1,2,3,4:

$$W = iN_k^2\left[2i^2(N_k-5) - 15i(N_k-11) + (13N_k-875)\right]/750 + W' \qquad (14)$$

$$W' = (N_k^3 + 24N_k^2 + 119N_k + 384) / 6 \qquad (14')$$

for N=10, i=1,2,3,4,5:

$$W = iN_k^2\left[i^2(N_k-6) - 9i(N_k-14) + 8(N_k-105)\right] / 648 + W' \qquad (15)$$

$$W' = (N_k^3 + 30N_k^2 + 179N_k + 750) / 6 \qquad (15')$$

The structures with a six-membered ring are analysed below the analysis of the other cases being quite similar. The Wiener index, defined by eqn. (13) has a minimum and a maximum, respectively, at

$$i_{1,2} = 6(N_k-8) \mp \sqrt{D} \; / \; 3(N_k-4) \qquad (13'')$$

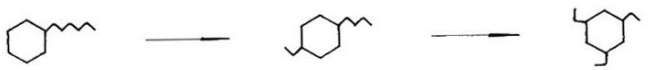
where $D = 3(7N_k^2 + 16N_k + 16)$.

It will be proved that the function is limited within the range from i_1 to i_2. By condition $i = 1, 2, 3$ for $N = 6$. Hence we should prove that $i_1 \leqslant 1$ and $i_2 \geqslant 3$. Substituting $i_1 < 1$ and $i_2 > 3$ in (13') one obtains $(N_k-4)(N_k+26) \geqslant 0$ and $(N_k-4)(N_k+2) \geqslant 0$, respectively. Both the inequalities and equalities are true since $N_k \geqslant 4$. The case $N_k=4$ is also taken under consideration since the Wiener index (13) is defined at this value, irrespective of the uncertainty that appears in its first derivative (13''), (see also the example above).

B) The newly-formed side chains are maximally distant from the main side chain

The proof presented below deals with the specific case when three structures are compared: an initial structure having a cycle and a non-branched side chain of length N_k, where N_k is a multiple of 3, and two other structures in which the initial side chain is shortened at the cost of the formation of one, and respectively two new branches with a length $N_k/3$, the new side chains being maximally distant from the initial one. The Wiener indices of these three types of structures is denoted by W_1, W_2, and W_3, respectively.

Examples:



$N_{k1}=6$, $i=0$ $\qquad$ $N_{k2}=4$, $i=1$ $\qquad$ $N_{k3}=2$, $i=2$

$W_1 = 242$ $\qquad$ $W_2 = 226$ $\qquad$ $W_3 = 198$

$$W_1 = (12N_k^3 + 36N_k^2N + W') / 72 \qquad (16)$$

$$W_2 = \left[12N_k^3 + 4N_k^2(7N+4) + W'\right] / 72 \qquad (17)$$

$$W_3 = \left[28/3N_k^3 + 4N_k^2(5N+6) + W'\right] / 72 \qquad (18)$$

$$W' = 6N_k(3N^2 + 6N - 2) + 9N^3 + A(N + 2N_k) \qquad (18')$$

where A=0, and A=-9, for even- and odd-membered cycles, respectively.

The proof of Rule 3 for this case follows from the inequalities:

$$\Delta W_1 = W_1 - W_2 = N_k^2(N-2) \;/\; 9 > 0 \qquad (19)$$

$$\Delta W_2 = W_2 - W_3 = N_k^2\left[N_k + 3(N-1)\right] \;/\; 27 > 0 \qquad (20)$$

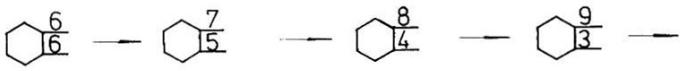
The difference in the length of two side chains

Rule 4. The sum of the topological distances increases when in a structure composed of a cycle and two non-branched side chains the longer chain lengthens at the cost of a shortening of the shorter chain at a fixed distance between them, and a constant cycle size:

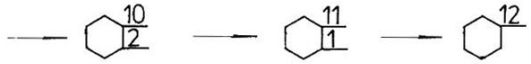
$$W_{N_{kj}',N_{kj}''} < W_{N_{kj}'+1,N_{kj}''-\Delta l} \qquad (21)$$

where $N_{kj}' \geqslant N_{kj}''$, and $\Delta l = 1,2,3,\ldots$, N=const, d=const.

Examples: $d_{12} = 1 = \text{const}$



$\Delta l=0$ $W_1=745$ $\Delta l=2$ $W_2=749$ $\Delta l=4$ $W_3=761$ $\Delta l=6$ $W_4=781$



$\Delta l=8$ $W_5=809$ $\Delta l=10$ $W_6=845$ $\Delta l=12$ $W_7=889$

The equation deduced for the Wiener index of structures composed of constant cycle and two non-branched side chains with a variable length, the chains being distant from each other by a constant number of d bonds along the cycle, is:

$$W = (N-d-1)(\Delta l)^2 \;/\; 4 \;+\; W' \qquad (22)$$

$$W' = \left[4N_k^3 + 6N_k^2(N+d+1) + 2N_k(3N^2+6N-2) + 3N^3 + \right.$$
$$\left. + A(N+2N_k)\right] / 24 \qquad (22)$$

Here A=0, and d=1 ÷ N/2 for structures with even-membered cycles, and A=-3, and d=1 ÷ (N-1)/2 for structures with odd-membered cycles.

Since $N > d+1$, it is evident from eqn. (22) that the increase in the difference of the lengths of the two side chains, Δl, increases the sum of the topological distances W irrespective of the distance d between the two side chains. Rule 4 is thus proved.

Rule 4 could be extended to cycles having more than two side chains.

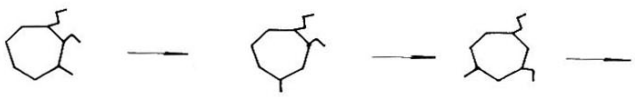
The distance between the side chains along the cycle

Rule 5. In isomeric structures, composed of a cycle and non-branched side chains, the sum of the topological distances W increases with the increase in the distances between the atoms to which the side chains are connected. If the sum of these distances is constant, W increases with the increase in the distances between the longest side chains or , if these distances are also constant the latter is true when the remaining side chains become more distant from the longest ones:

$$W_{N_{k1},N_{k2},N_{k3},\ldots,d_{12},d_{13},\ldots,d_{23},\ldots} >$$
$$> W_{N_{k1},N_{k2},N_{k3},\ldots,d'_{12},d'_{13},\ldots,d'_{23},\ldots} \qquad (23)$$

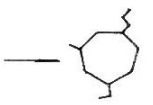
where $d_{12} > d'_{12}$ or (and) $d_{13} > d'_{13}$ or (and) $d_{23} > d'_{23}$, etc.

Examples:



W_1=238 W_2=243 W_3=249

$d_{12}=d_{23}=1, d_{13}=2$ $d_{12}=1, d_{23}=2, d_{13}=3$ $d_{12}=d_{23}=2, d_{13}=3$



$W_4=252$

$d_{12}=3, d_{23}=d_{13}=2$

We present below a part of the proof of this rule for the case of systems composed of a cycle and three non-branched side chains with a different length. The Wiener index for such isomeric structures is:

$$W = d_{12}N_{k1}N_{k2} + d_{13}N_{k1}N_{k3} + d_{23}N_{k2}N_{k3} + W' \qquad (24)$$

$$W' = 6\sum_{\substack{J,J',J''=1 \\ J\neq J'\neq J''}}^{3} N_{kJ}^2(N_{kJ'}+N_{kJ''}+N) + 12\sum_{\substack{J,J'=1 \\ J\neq J'}}^{3} N_{kJ}N_{kJ'} + \qquad (24')$$

$$+ 3N^3 + 2(3N^2 + 6N - 2)\sum N_{ki} + 4\sum N_{ki}^3 + A(N+\sum N_{ki}^3/3)$$

where $A=0$, $d_i = i + N/2$ for even-membered cycles, and $A=-3$, $d_i = i + (N-1)/2$ for odd-membered cycles; $\sum N_{ki} = N_{k1} + N_{k2} + N_{k3}$. W depends linearly on d_{ij}'s and increases when any of them increases at constant N and N_{ki}, which proves the rule.

The size of the cycle and the number of side chains

Rule 6. Consider a consecutive conversion of a monocycle having N_o atoms into isomeric structures in which the cycle, preserving its parity, decreases to N atoms at the cost of the formation of $1,2,3,\ldots,i$ neighbouring, non-branched side chains with the same length N_1, i not exceeding $(N+2)/2$ or $(N+1)/2$ for even- and odd-membered cycles, respectively. In the sequence of isomers thus formed the sum of the topological distances:

a) passes through a minimum:

$$W_{N_1,1_1} > \ldots > W_{N_2,1_2} < \ldots < W_{N_3,1_3} \qquad (25)$$

specified by the condition:

$$\frac{3N_iN_o + 2\sqrt{D}}{3N_i(3N_i + 4)} \geqslant i_{max} - 1 = \frac{N}{2} \qquad (26)$$

b) steadily decreases:

$$W_{N_1,i_1} > W_{N_2,i_2} > W_{N_3,i_3} \qquad (27)$$

when an inequality opposite to (26) occurs;

c) passes through a maximum:

$$W_{N_1,i_1} < \ldots < W_{N_2,i_2} > \ldots > W_{N_3,i_3} \qquad (28)$$

specified by the condition:

$$2N_i + 4 \leqslant N_o \leqslant N_i + 2 + 2N_i\sqrt{B} \qquad (29)$$

where $N_i \geqslant 6$, and $B = (3N_i+10+14/N_i) / 3(3N_i+4)$;

d) increases:

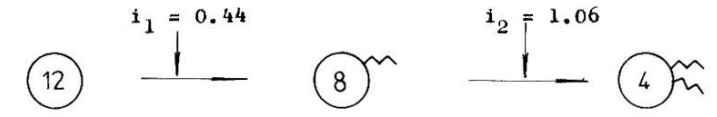
$$W_{N_1,i_1} < W_{N_2,i_2} < W_{N_3,i_3} \qquad (30)$$

when $N_i=2$ and $N_o \leqslant 8$.

The following conditions also holds for Rule 6: $N_i=2k$; $N_o=N+iN_i$; $i \leqslant (N+2)/2$ for $N=2k$, $i \leqslant (N+1)/2$ for $N=2k+1$; $N_1>\ldots>N_2>\ldots>N_3$, and hence $i_1<\ldots<i_2<\ldots<i_3$.

Examples:

$N_k=4$, $N_o=12$

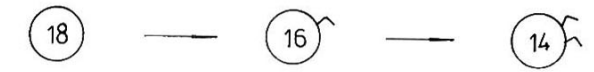


N=12, i=0 $W_1=216$

N=8, i=1 $W_2=183$

N=4, i=2 $W_3=236$

$N_k=2,\ N_o=18$



$N=18, i=0$ $W_1=729$ | $N=16, i=1$ $W_2=689$ | $N=14, i=2$ $W_3=641$

$N=12, i=3$ $W_4=595$ | $N=10, i=4$ $W_5=561$ | $N=8, i=5$ $W_6=549$

$N_k=2, N_o=7$

$N=7, i=0$ $W_1=42$ | $N=5, i=1$ $W_2=43$ | $N=3, i=2$ $W_3=47$

The proof of Rule 6 is based on the analysis of the equation for the Wiener index of the isomeric compounds described above:

$$W = \left[i^3N_i^2(3N_i+4) - 3i^2N_i^2N_o - iN_i(8N_i^2-12N_iN_o+16N_i + \right.$$
$$\left. + 3N_o^2-12N_o+4) + 3N_o^3 + A(N_o+iN_i) \right] / 24 \qquad (31)$$

where A=0, and A=-3, for structures with even- and odd-membered rings, respectively.

At N_o- even, W has a maximum i_1 and a minimum i_2, respectively:

$$i_{1,2} = (3N_iN_o \mp 2\sqrt{D}) / 3N_i(3N_i+4) \qquad (32)$$

where $D = 3N_i\left[6N_i^3-N_i^2(9N_o-20) + N_i(3N_o^2-21N_o+19) + 3(N_o-2)^2\right]$.

The conditions, specified by N_o, N_i, and i, at which W has not an acceptable maximum, i.e. $i_1<0$, can be found from the inequality $2\sqrt{D}>3N_iN_o$. We shall examine however a stron-

ger condition, requiring $i_1 \geqslant 1$. This condition excludes the possibility of the maximum appearing near i=0 (the first example above) since the existence of the maximum requires at least one isomeric structure corresponding to a point on the left to it. Proceeding from these assumptions one arrives at the expressions:

$$3N_o^2(3N_i+4) - 6N_o(3N_i+4)(N_i+2) + (-3N_i^3+8N_i^2+28N_i+48) \leqslant 0 \quad (33)$$

$$N_{o(1,2)} = N_i + 2 \mp 2N_i\sqrt{B} \quad (34)$$

where $B = (3N_i+10+14/N_i) / 3(3N_i+4) < 1$, at each $N_i \geqslant 2$.

From (34) the condition for the appearance of an acceptable maximum of W is

$$N_o \leqslant N_{o(2)} = N_i + 2 + 2N_i\sqrt{B} < 3N_i + 2 \quad (35)$$

Left constraints for N_o also exist as a consequence of its partition into a cycle with N atoms and i side chains each one having N_i atoms: $N_o = N + iN_i$. Taking $N_{min} = 4$ for even-membered cycles and i = 3 (three different isomers are needed for a maximum to be found) we arrive to the condition $N_o \geqslant 3N_i + 4$ which contradicts (35). Therefore, a maximum of the Wiener index never occurs in a sequence of three isomers having side chains. Still, it could occur in another sequence in which the first isomer is a monocycle, and only the second and the third one have side chains. The range of N_o within which the acceptable maximum of W can appear is

$$2N_i + 4 \leqslant N_o \leqslant N_i + 2 + 2N_i\sqrt{B} \quad (36)$$

It follows from (36) that an acceptable maximum of the Wiener index is impossible for $N_i = 2$ and $N_i = 4$, but it can occur for $N_i \geqslant 6$. The narrow range of N_o values specified by (36), however:

N_i	6	8	10
N_o	16-16.14	20-20.44	24-24.74

Hiddens the non-integer maximum between two integer values of

N_o and it will actually appear at very large side chains. When N_i=2 or N_i=4 the Wiener index could have an increasing trend. Condition (36) however narrows the range of N_o values at which this can happen to $N_i = 2$, $N_o \leq 8$, only.

The minimum of the Wiener index is easily obtained as can be seen from the first example above. The condition for the appearance of an acceptable minimum follows from (32), and the initial assumption $i \leq (N+2)/2$ for N=2k:

$$\frac{3N_iN_o + 2\sqrt{D}}{3N_i(3N_i + 4)} \geq i_{max} - 1 = \frac{N}{2} \qquad (37)$$

When the opposite inequality occurs the W function will regularly decrease, being within the range from $W(i=i_1)$ to $W(i=i_2)$.

The distance between the cycle and the branch to the initial side chain

Rule7. In isomeric structures composed of a cycle and a side chain with a branch of arbitrary length, the displacement of the branch from the end of the side chain to the cycle diminishes the sum of the topological distances W, except the cases where the side chain has at least three atoms more than the cycle, in which a minimum of W occurs:

$$a)\ W_{N,N_k,\Delta N_p'} > W_{N,N_k,\Delta N_p''} > W_{N,N_k,\Delta N_p'''} > \ldots. \qquad (38)$$

where $\Delta N_p' > \Delta N_p'' > \Delta N_p''' > \ldots$;

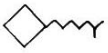
$$b)\ W_{N,N_k,\Delta N_p'} > W_{N,N_k,\Delta N_p''} > \ldots > W_{N,N_k,\Delta N_p^s} < \ldots < W_{N,N_k,\Delta N_p^t} \qquad (39)$$

where $\Delta N_p' > \Delta N_p'' > \ldots > \Delta N_p^s > \ldots > \Delta N_p^t$, and

$$\Delta N_p^s = (N_{kl} - N + 1) / 2 \qquad (40)$$

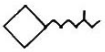
Examples:

N=4, N_k=8



ΔN_p=6

W_1=259

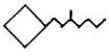


ΔN_p=5

W_2=252

ΔN_p=4

W_3=247

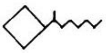


ΔN_p=3

W_4=244

ΔN_p=2

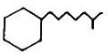
W_5=243



ΔN_p=1

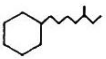
W_6=244

N=6, N_k=8



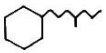
ΔN_p=6

W_1=388



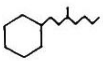
ΔN_p=5

W_2=379



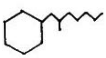
ΔN_p=4

W_3=372



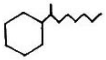
ΔN_p=3

W_4=367



ΔN_p=2

W_5=364



ΔN_p=1

W_6=363

The following equation was obtained for the sum of the topological distances in the isomeric structures obeying Rule 7:

$$W = \Delta N_p . N_p(\Delta N_p - N_{k1} + N - 1) + W' \qquad (40)$$

$$W' = 4N_{k1}^3 + 12N_{k1}^2(N_p+N) + 2N_{k1}(6N_p^2+12N_p+3N^2+6N-2) +$$
$$+ 2N_p(2N_p^2+6N_pN+3N^2+6N-2) + 3N^3 + A(N+2N_p+12N_{k1}^2) \qquad (41)$$

where A=0, and A=-3, for even- and odd-membered cycles, respectively.

The proof of rule 7 follows from the analysis of eqn.(40) showing that W has a minimum at

$$\Delta N_p = (N_{kl} - N + 1) / 2 \qquad (42)$$

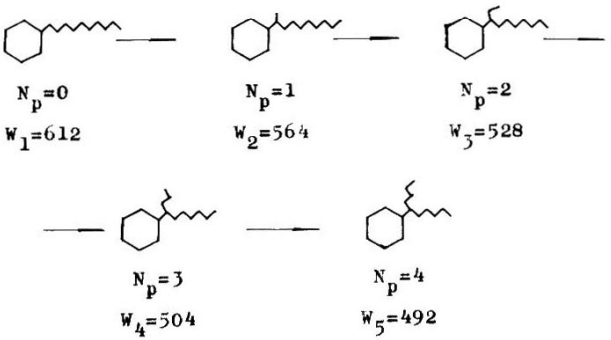
The length of the initial side chain and the length of the newly-formed branches to it

Rule 8. The sum of the topological distances diminishes when in isomeric structures, containing a cycle, a side chain and a branch to an arbitrary atom of the latter, the side chain shortens at the cost of the increase in the branch length without any displacement of the branch:

$$W_{N_k,\Delta N_p,N_{p1}} > W_{N_k,\Delta N_p,N_{p2}} > W_{N_k,\Delta N_p,N_{p3}} > \ldots \qquad (43)$$

where $N_{p1} < N_{p2} < N_{p3} < \ldots$

Example: N_k=10=const, ΔN_p=1=const



N_p=0 W_1=612 N_p=1 W_2=564 N_p=2 W_3=528

N_p=3 W_4=504 N_p=4 W_5=492

The following equation holds for the Wiener index of the structures obeying the above rule:

$$W = \Delta N_p . N_p(\Delta N_p - N_k + N_p + N - 1) + W' \qquad (44)$$

$$W' = \left[4N_k^3 + 12N_k^2 N + 2N_k(3N^2 - 12N_p N + 12N_p + 6N - 2) + 24N_p^2(N-1) + 3N^3 + A(N + 2N_k - 2N_p)\right] / 24 \qquad (44')$$

where $\Delta N_p = 1 \div (N_k - 1)$; A=0, $N_p = 0 \div N_k/2$ for even-membered cycles, and A=-3, $N_p = 0 \div (N_k - 1)/2$ for odd-membered cycles.

From (44) it follows that W has a minimum when the branch length equals the side chain length:

$$\text{for } N_p \text{ - even:} \quad N_p = (N_k - \Delta N_p)/2 \tag{45}$$

$$\text{for } N_p \text{ - odd:} \quad N_p = (N_k - \Delta N_p)/2 - 1/8(\Delta N_p + N - 1) \tag{46}$$

the second term in (46) being approximately equal to zero.

The length of the initial side chain and the number of the newly-formed branches to it

Rule 9. The sum of the topological distances decreases when in isomeric structures, containing a cycle and a side chain (with or without branches), the latter shortens at the cost of the formation to it of new branches with an equal length:

$$W_{N_k,p_1} > W_{N_k,p_2} > W_{N_k,p_3} > \ldots \tag{47}$$

where $p_1 < p_2 < p_3 < \ldots$

Examples:

$p_1=0$ $p_2=1$ $p_3=2$ $p_4=3$

$W_1=399$ $W_2=363$ $W_3=331$ $W_4=311$

(See the proof of Rule 1.4 in ref.8).

Concluding Remarks

This work is a part of a large project for studies on molecular branching and cyclicity[8,14-18]. The latter are characterized by means of a quantitative measure (a topological index) based on the topological distance matrix and mainly by the sum of the topological distances in the molecular graph (the Wiener index). In this series of studies we proceeded from the assumption that the nature of molecular branching and cyclicity could be better understood, only if the contri-

butions made in them by the major structural factors were quantitatively examined. The number, size, and mutual disposition or type of joining of the cycles, chains, and their branches were the important structural features taken into account in the preceding studies. In this study we were interested mainly in the question whether any principal difference in the molecular branching and cyclicity exists when they simultaneously occur in one and the same molecular structure. On the other hand, the mutual influence of branching and cyclicity was also of interest. This is a rather complicated question, indeed, and no study on it has the chance to be complete. Thus, we had to restrict ourselves to a number of typical cases.

The general conclusion possible from the results of this work is that the branching in acyclic and cyclic molecules has a similar behaviour. The similarity of rules 4 and 8 (the decrease in the difference in length of the branches to a cycle or to a side chain decreases the Wiener index), as well as of rule 3 of this paper and rule 2.1 from ref.8 (the conversion of a long branch into several shorter branches decreases the Wiener number) supports this conclusion. The specific nature of the branching in the cyclic structures obeying the above rules is most often expressed by the appearance of a theoretical minimum of W but it cannot be reached in these structures. Quite a similar result follows from the comparison between the conversion of a long chain in acyclic molecules into branches (rule 1.4, ref.8), the analogical conversion of a long side chain in cyclic molecules into branched side chain (rule 9 of this work). In these two cases the above mentioned molecular rearrangements are accompanied by a decrease in the sum of the topological distances W.

The influence of the cycle on branching seems stronger in the case of a displacement of a branch from a terminal to an inner position of the side chain (rule7), as compared with the acyclic chain (rule 4.1 in ref. 8) since a minimum in the Wiener index appears in the first case, instead of a regular decrease. The difference however is not so drastic

since in the acyclic chains the described displacement of a branch actually has also a minimum in the centre of the chain. The case of a side chain to a cycle is similar to the situation described above but the minimum point is displaced nearer to the cycle.

Rule 6 (the conversion of a cycle into branches) is an example of the mutual conversion of the cyclic and acyclic parts of the molecule. One faces here a more complicate situation since, depending on the size of the cycle and the number and size of the branches, the Wiener index can steadily decrease or increase , or can pass through a minimum or a maximum. Rules 1 and 2, dealing with the conversion of a side chain into a larger cycle, or into a larger number of cycles, respectively, are also of this type. The systematic decrease in the sum of the topological distances occuring in the structures that obey rule 2 is however rather an exception than a general trend, since besides rule 6, rule 1 also predicts a minimum of W. The mutual dependence of molecular cyclicity and branching in these cases makes the topological properties of the corresponding structures more complex. Due to this, rules 1,2, and 6, express rather the overall structural complexity of molecules than its components - cyclicity and branching.

The graph-theoretical analysis of molecular branching and cyclicity is not only of theoretical interest. Since most of molecular properties are dependent on the structure (and mainly on the topology) the quantitative scale of branching and cyclicity, specified for different classes of isomeric compounds, might be transferred onto many properties of these compounds. This would help the chemists to order the isomeric molecules (known, as well as non-synthesized ones) according to their stability and reactivity, thermodynamic and spectral properties, et., by means of elementary calculations. The approach can also be applied in a quantitative way deriving correlations between the sum of the topological distances and various molecular properties. High correlations were for instance obtained with some thermodynamic data like heats of for-

mation and combustion, boiling points, et.,[22] as well as with some gas chromatographic retention data[21]. Such results are of more general importance since the topological index of Wiener used in the correlations, is shown to depend in a quantitative way on the different structural features of molecules. Thus, an insight could be provided for the specific contributions of these structural elements (the size and number of cycles, chains, and branches, their mutual disposition or their kind of connection, etc.) in molecular properties. Our approach differs from the classical additivity schemes in the influence of the different structural elements being simultaneously taken into account in a common equation instead of being partitioned into individual contributions. A similar insight could be provided for the changes in some molecular characteristics upon the intramolecular rearrangements obeying the topological rules, by makimg use of the equations derived for the change in the sum of the topological distances. Studies attemting to apply the above ideas to various molecular properties are in progress[26].

Acknowledgements. We gratefully acknowledge helpful comments and recommendations by Prof. Oskar E. Polansky.

References

1. Chemical Applications of Graph Theory, ed. by A. T. Balaban, Academic, New York 1976.
2. D. H. Rouvray, RIC Rev. 4, 173(1971); Chem. Britain 10, 11(1974).
3. I. Gutman and N. Trinajstić, Topics Curr. Chem. 42, 49 (1973); Croat. Chem. Acta 47, 507(1975).
4. O. E. Polansky, Math. Chem. (MATCH) 1, 183(1975).
5. M. Randić, Chem. Phys. Lett. 38, 68(1976); Tetrahedron 33, 1905(1977); J. Am. Chem. Soc. 99, 444(1977).
6. I. Gutman and N. Trinajstić, Croat. Chem. Acta 47, 35 (1975); 45, 539(1973).
7. I. Gutman, N. Trinajstić, and C. F. Wilcox, Jr., Tetrahedron 31, 143(1975).

8. D. Bonchev and N. Trinajstić, J. Chem. Phys. 67, 4517 (1977); Intern. J. Quantum Chem. S12, 293(1978).
9. M. Gordon and G. R. Scantlebury, Trans. Faraday Soc. 60, 605(1964).
10. H. Hosoya, Bull. Chem. Soc. Jpn. 44, 2332(1971).
11. L. Lovasz and J. Pelikan, Period. Math. Hung. 3, 175 (1973).
12. I. Gutman, B. Ruščič, N. Trinajstić, and C. F. Wilcox, Jr., J. Chem. Phys. 62, 3399(1975).
13. M. Randić, J. Am. Chem. Soc. 97, 6609(1975).
14. D. Bonchev, J. V. Knop, and N. Trinajstić, Math. Chem. (MATCH) Symp. 6, 21(1979).
15. D. Bonchev, Ov. Mekenyan, J. V. Knop, and N. Trinajstić, Croat. Chem. Acta 52, 361(1969).
16. D. Bonchev, Ov. Mekenyan, and N. Trinajstić, Internat. J. Quantum Chem., in press.
17. Ov. Mekenyan, D. Bonchev, and N. Trinajstić, Math. Chem.(MATCH) 6, 93(1979).
18. Ov. Mekenyan, D. Bonchev, and N. Trinajstić, J. Chem. Soc. Faraday Trans. II, submitted.
19. A. T. Balaban, Theoret. Chim. Acta (Berl.) 53, 355(1979)
20. A. T. Balaban, in Steric Fit in QSAR, Lecture Notes in Chemistry, Springer, Berlin, in press.
21. D. Bonchev, Ov. Mekenyan, G. Protić, and N. Trinajstić, J. Chrom. 176, 149(1979).
22. Ov. Mekenyan, D. Bonchev, and N. Trinajstić, Internat. J. Quantum Chem. S, in press.
23. D. Bonchev and Ov. Mekenyan, Z. Naturforsch., in press.
24. D. H. Rouvray, in: Chemical Applications of Graph Theory, ed. by A. T. Balaban. Academic, New York 1976.
25. H. Wiener, J. Am. Chem. Soc. 69, 17, 2636(1947); J. Phys. Chem. 52, 425(1948).
26. Ov. Mekenyan, D. Bonchev, and N. Trinajstić, work in progress.