

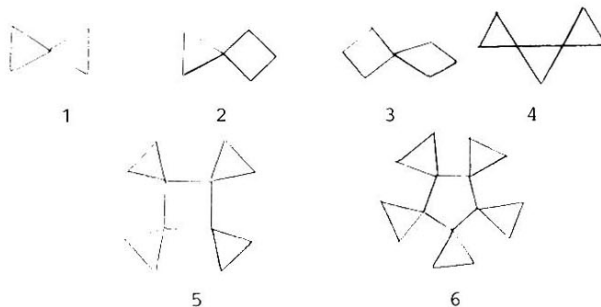
## TOPOLOGICAL RULES FOR SPIROCOMPOUNDS

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INTRODUCTION

A considerable interest in spirocompounds is manifested during the last three decades.<sup>1,2</sup> Quantum chemical calculations are carried out that predict the existence of new spirostructures and their properties.<sup>3</sup> A variety of spirocompounds are synthesized:<sup>4-11</sup>



Spirocompounds have a number of unusual properties. Thus, for instance, the ring strain in most of them is very large and facilitates thermal epimerization and rearrangement processes. Structure 6 above which belongs to the class of spirocompounds called rotanes is distinguished by its ultraviolet

spectrum. Many of heterospirocompounds are easily attacked by electrophilic agents.

Spirostructures are also of great interest to the structural theory of chemistry, because they exhibit very different properties than the related structures with the same number of fused cycles, e.g.,



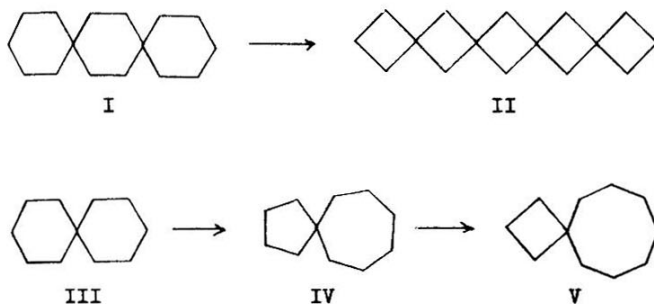
Since the difference in the way of linking two cycles is essentially reflected in their topology, graph theory<sup>12-14</sup> appears to be very useful mathematical tool for the classification of the structural features of spirocompounds and for the analysis of the difference that exist between them and the analogous compounds having fused cycles. Additional advantage of graph theory in such studies is in its generality because it explores the most general geometric properties of chemical compounds.<sup>14</sup> Therefore, the conclusions reached by using the algebraic theory of graphs **refer** not only to carbon chemistry, but to all compounds with a given topology irrespective of the specific nature of the chemical elements in them.

The topological studies of spirocompounds have attracted so far less attention. Mostly they were considered as a part of some more general investigation in which other kinds of structures are also included. Such studies are, for instance, by Hosoya and co-workers<sup>15</sup> on the discrimination of cyclic isomers, by Balaban<sup>16</sup>, and Whitelock and Siefken<sup>17</sup> on the graphs having vertices of order four, etc.

Recently a detailed graph-theoretical investigation on the molecular cyclicity<sup>18</sup> in the systems consisting of condensed cycles of arbitrary size has been carried out by the authors of this report.<sup>19</sup> The main structural factors influencing the molecular cyclicity were specified and the type of their action re-

flecting on the properties of polycyclic hydrocarbons formulated in a number of rules. The present work is an extension of this investigation to molecular structures containing spirocycles without the acyclic fragments. Our aim here is to formulate topological rules reflecting the influence of the diverse structural factors on the properties of spirocompounds. In addition, we wish to make the comparison between the fused cycles and spirocycles.

The essence of the problem of molecular cyclicality can be illustrated by some examples:



The question arises which one out of the isomeric structures above should be viewed as more cyclic: the structure with more cycles of smaller size (II) or the structure having cycles larger in the size but less in the number (I). Chemical intuition gives preference to the structure II. However, the intuition is no help for the comparison of structures III-IV, i.e., for the answering the question what is more favourable for molecular cyclicality: the presence of cycles of smaller or larger size in a given set of iso-

meric spirostructures. The answer to this and similar questions are of importance from the viewpoint of the most general topological properties of molecules. They could also be of direct practical use for predictions of the ordering of isomeric spirocompounds relative to the values of a particular molecular property as shown elsewhere for acyclic<sup>20,21</sup> and condensed polycyclic benzenoid and nonbenzenoid hydrocarbons.<sup>19</sup> The main merit of such an approach is in the offering of the set of general rules for the use by the chemists at large instead of sometimes very difficult calculations producing information not always easy to comprehend. In addition, the topological rules can be also used as a convenient basis for the quantitative correlations between the (observable) molecular properties and (unobservable) algebraic indices.

The topological indices used for the characterization of molecular structures must satisfy a very rigorous restriction. They should provide a mean for the discrimination of the isomeric structures. Our studies have shown that the topological indices introduced on the basis of the distance matrix<sup>22</sup> of a molecular graph satisfy this condition. Especially useful index related to distance matrix appears to be the Wiener number of a given structure,  $W$ . It is defined as the sum of the topological distance between each pair of vertices (atoms) in a molecular graph (structure) or alternatively the sum of the elements  $D_{ij}$  of the upper triangle of the distance matrix,  $D$ :

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

The interested reader should see the detailed discussion about the distance matrix, Wiener number and its relation to other similar indices<sup>20,23-25</sup> in our other report in these Proceedings.<sup>26</sup>

Number of topological rules for isomeric spirocompounds derived in the present work are proved by the deduction of

inequalities for the Wiener number of isomeric structures, a technique we developed in studies on isomeric acyclics.<sup>20</sup> The first step in this procedure is deduction of equations (by the mathematical induction method) for the Wiener number of series of structures each of which reflects the influence of a particular structural factor. (The mathematical part of the work will be published elsewhere<sup>29</sup>). In this way the main feature of the structural distinctions between the isomeric (spiro) compounds are specified which appears to be quite a promising basis for correlating the structures and properties.

#### STRUCTURAL FACTORS INFLUENCING THE MOLECULAR CYCLICITY IN SPIROCOMPOUNDS

In order to avoid the action of additional structural factors which may appear when the acyclic parts are attached to cycles our investigation deals only with the isomeric structures consisting of strings of spirocycles. The following structural factors were taken into account:

1. The total number of the atoms in a molecule,  $N_0$ . In the present paper  $N_0 = \text{const.}$
2. The number of cycles,  $a$ .
3. The number of atoms in a cycle,  $N$  (in the case of equal sized cycles).
4. The mutual position of the cycles in the string of differently sized cycles.
5. The difference in the size of cycles,  $\Delta = N_j - N_i$ .
6. The number of cycles joined by a common vertex,  $a_j$ .
7. The degree of bending in a string of spirocycles.
8. The presence of side-linked spirocycles:
  - 8.1. The number of side-linked cycles.
  - 8.2. The position of side-linking.

8.3. Cis- or trans- character of the side-linking.

8.4. The length of the side string of spirocycles.

One should bear in mind that the first three factors are linearly dependent. For instance, for isomeric acyclic string of equal spirocycles each cycle in which is spiro linked with no more than two other cycles, the following equation holds:

$$N_0 = aN - a + 1 \quad (1)$$

This indicates that, at  $N_0 = \text{const}$ , it is sufficient to examine the influence of either the number of cycles,  $a$ , or the number of atoms in them,  $N$ . In the latter case, the parity of the number of atoms in a cycle is of importance, because of which different subscripts will be used for the Wiener number of odd- and even- membered cycles ( $w^{\text{odd}}$  and  $w^{\text{even}}$ ).

Regarding the mutual position of the neighbouring cycles in a string of spirocycles, unless otherwise stated, we shall restrict our study to the cases for a maximum symmetrical linking of these cycles:



Denoting two subsequent spirovertices by  $i$  and  $j$ , respectively, as well as the two paths between them by  $l_1$  and  $l_2$ , the condition of the maximum symmetrical linking of cycles is given in the form:

$$l_1 - l_2 = 0, \pm 1 \quad (2)$$

where the first value for even-membered, and the second one

for odd-membered rings.

The number of cycles and the cycle size

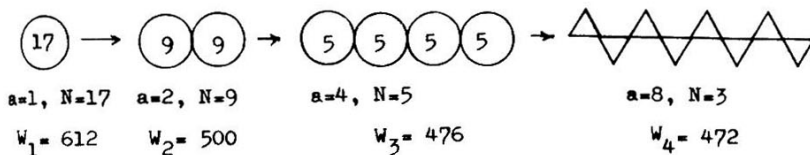
Rule 1.1. The Wiener number decreases when the number of cycles in a string of identical odd-membered spirocycles increases at the cost of a decrease in the number of atoms in the cycles:

for  $N = 3, 5, 7, \dots = 2n+1$ , where  $n = 1, 2, 3, \dots$

$$W_{a,N} > W_{a+x,N-y} \quad (3)$$

where  $x$  and  $y$  are positive integers.

Examples:



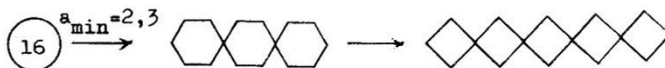
Rule 1.2. In a string of identical even-membered spirocycles the Wiener number changes going through a minimum when the number of cycles increases at the cost of a decrease in the number of atoms in the cycles:

for  $N = 4, 6, 8, \dots = 2n$ , where  $n = 2, 3, 4, \dots$

$$W_{a,N} > \dots > W_{a+x_0,N-y_0}^{\min} < \dots < W_{a+x,N-y} \quad (4)$$

where  $x$  and  $y$  are positive integers,  $x > x_0$ ,  $y > y_0$ .

Examples



$$a = 1$$

$$N = 16$$

$$W_1 = 512$$

$$a = 3$$

$$N = 6$$

$$W_2 = 426$$

$$a = 5$$

$$N = 4$$

$$W_3 = 460$$

Here  $a_{\min}$  is the calculated number of cycles at which the Wiener number has minimum:

$$a_{\min} \approx (N_0 - 1)^3 \sqrt[3]{2 / (N_0^2 + 2N_0 - 1)} \quad (5)$$

Hence, for a  $< a_{\min}$ ,  $W$  decreases, and for a  $> a_{\min}$ ,  $W$  respectively increases with the increase in the number of cycles which proves inequalities (4).

One should expect the different topological features in the series of isomeric spirocompounds composed of odd- and even-membered rings, respectively, expressed by Rules 1.1. and 1.2., to reflect in the physical and chemical properties of these compounds. Rule 1.2. also manifests the great difference which exist between the isomeric spirocompounds and isomeric condensed polycyclic compounds since in the latter the Wiener number always decreases with the increase in the number of cycles.

Inequalities (3) and (5) are valid also for the case  $a=1$ , i.e., Rules 1.1. and 1.2. include as a specific case the conversion of an odd-membered, and respectively an even-membered ring into two such spiro-linked rings.

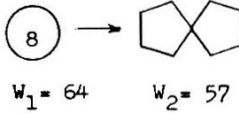
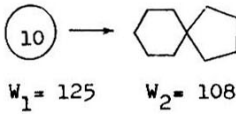
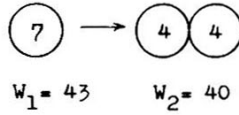
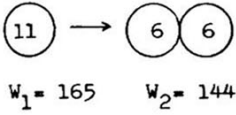
Rule 1.3. The Wiener number decreases when a cycle converts into two **spirocycles**:

$$W_N > W_{N_1, N_2} \quad (6)$$

where  $N_1 + N_2 = N + 1$ .



Examples



The number of cycles joined by a common vertex

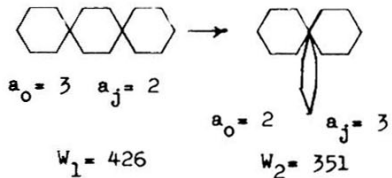
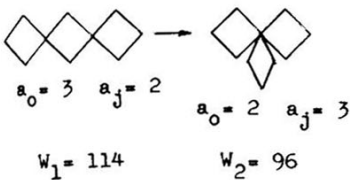
Rule 2.1. The Wiener number decreases when the number of cycles  $a_0$  in a string of equal spirocycles decreases, due to the increase in the number of spirocycles,  $a_j$ , having one and the same common vertex (i.e. when a string of spirocycles converts into a spiropropellane system):

$$W_{a_0, a_j} > W_{a_0-k, a_j+k} \quad (7)$$

where  $k$  is a positive integer.

Examples

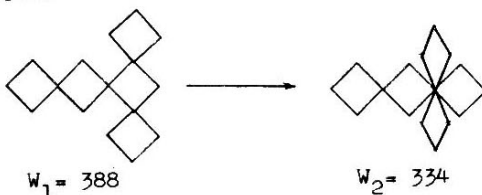
$$N = 4, 6, 8, \dots = 2n, \text{ where } n = 2, 3, 4, \dots$$



Rule 2.2. The Wiener number decreases when the side chains of identical spirocycles, linked to the linear string of spirocycles of the same size, convert into spiropropellane cycles:

$$W_{\text{side-chain cycles}} > W_{\text{propellane cycles}} \quad (8)$$

Examples



Rules analogous to 2.1. and 2.2. hold well for structures with condensed cycles instead of spirocycles.

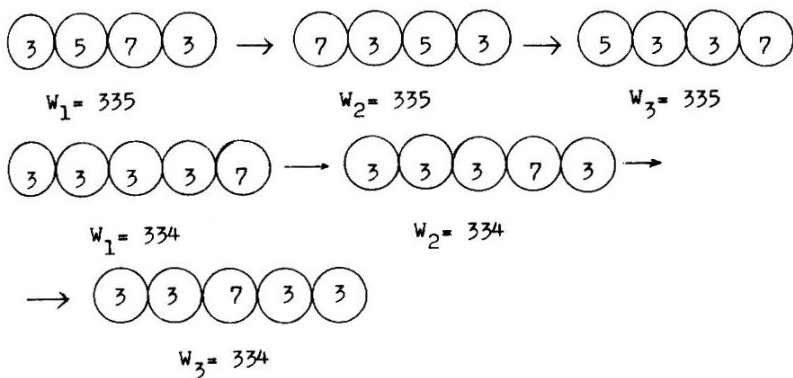
The mutual position of the cycles in the string of different sized cycles

Rule 3. In a string of odd- membered spirocycles of different size, the change in their position does not change the Wiener number:

$$W_{N,N,\dots,N,N_1} = W_{N,N,\dots,N,N_1,N} = W_{N,N,\dots,N,N_1N,N} = \dots \quad (9)$$

for  $N, N_1 = \text{odd}$ .

Examples



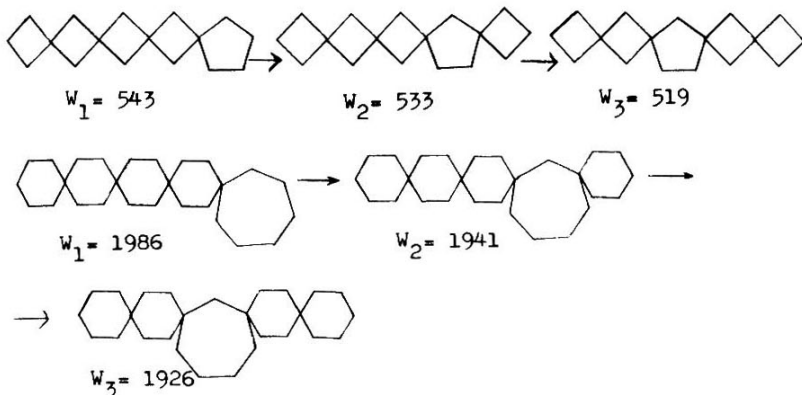
An analogous rule holds well for a chain of linearly condensed even-membered cycles.

Rule 4.1. The Wiener number decreases in a string of identical even-membered spirocycles having one odd-membered cycle, when the latter moves to the middle of the string:

$$W_{N,N,\dots,N,N_1} > W_{N,N,\dots,N,N_1,N} > \dots > W_{N,\dots,N,N_1,N,\dots,N} \tag{10}$$

for  $N$ -even,  $N_1$ -odd,  $N_1 \leq N$ .

Examples



Rule 4.1. holds also well for linear even-membered catafusenes.

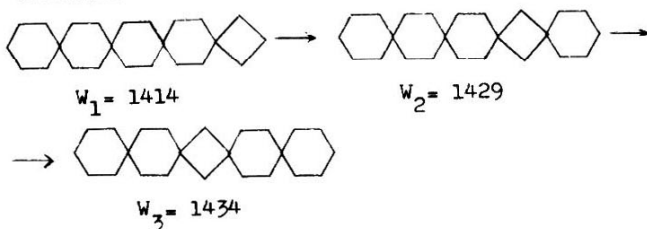
Rule 4.2. In a string of identical even-membered spiro-cycles, having one such cycle of different size, the Wiener number decreases, or respectively increases, when the different cycle (greater, or respectively smaller, than the other cycles) moves to the middle of the string.

for  $N_1 > N$ ;  $N, N_1 = \text{even}$ ,  $N \geq 4$ , inequality (10) holds, and

for  $N_1 < N$ ;  $N, N_1 = \text{even}$ ,  $N \geq 4$ :

$$W_{N, N, \dots, N, N_1} < W_{N, N, \dots, N_1, N} < \dots < W_{N, \dots, N, N_1, N, \dots, N} \quad (11)$$

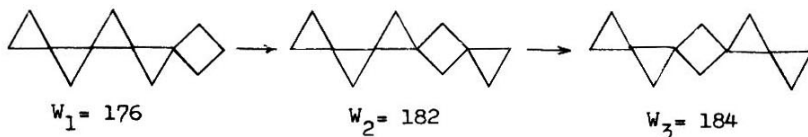
Examples



Rule 5. In a string of identical odd-membered spiro-cycles having one even-membered cycle the Wiener number increases when the different cycle moves to the middle of the string.

for  $N = \text{odd}$ ,  $N_1 = \text{even}$ ,  $N_1 \geq N$ ,  $N_1 \geq 3$ , inequality (11) holds.

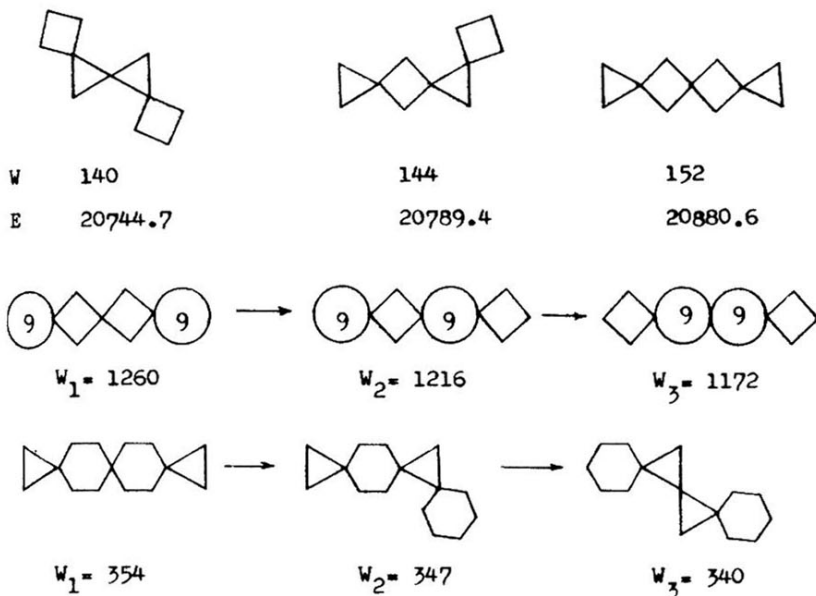
Examples



Inequality (11) is always valid irrespective of the size of the cycle which moves along the string. In this case the behaviour of the analogous systems, having cata-condensed instead of spirolinked cycles, is quite different. The rearrangements within the chain of cata-condensed cycles do not alter the Wiener number which has only two different values for the terminal, and respectively, non-terminal position on the different ring. When this ring is greater than the others the Wiener number is smaller for the ring in terminal position and greater for the one in nonterminal position, and vice versa for the case when the different ring is smaller in size than the others.

Rule 6. In a string consisting of several even- and odd-membered spirocycles the Wiener number decreases when the odd-membered cycles move towards the middle of the string:

$$w_{\text{terminal}}^{\text{odd}} > w_{\text{non-terminal}}^{\text{odd}} > w_{\text{central}}^{\text{odd}} \quad (12)$$



An analogous rule holds for condensed, instead of spirocyclics.

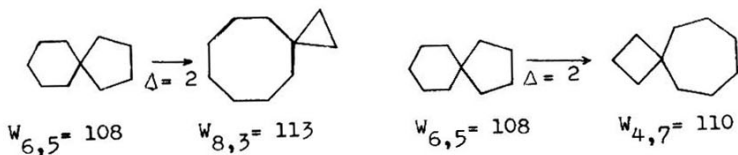
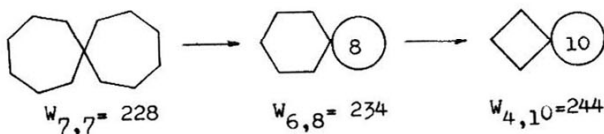
The difference in the size of cycles

Rule 7. The Wiener number almost always increases in a bicyclic spirostructure when the difference in the cycle size increases:

$$W_{N, N_1} < W_{N+\Delta, N_1-\Delta} \quad (13)$$

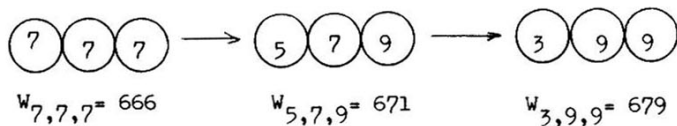
for  $N \geq N_1$ , irrespective of the parity of  $N$  and  $N_1$ .

Examples



Rule 7 also holds for the more complicated structures consisting of a string of more than two spirocycles of different size. Again, the greater the differences in the ring size the greater is the Wiener number.

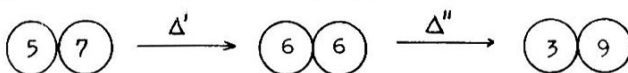
Example:



When the ring size changes occur, the total change in the Wiener number can be calculated by an additive scheme. In the example above  $\Delta W$  on the first conversion is calculated by eqn. (38):

$$W = W_{5,7,9} - W_{7,7,7} = 5.$$

The calculation in the second case includes two stages of conversion of bicyclic structures only, the structure with the equal-membered cycles being intermediate:



Here  $\Delta W = W_{3,9,9} - W_{5,7,9} = \Delta' + \Delta'' = 8$ , where  $\Delta' = 3$ , and  $\Delta'' = 5$ , are calculated by the equations derived for this case.

A large number of isomeric spirocompounds can be compared making use of such a procedure in which intermediate structures are included.

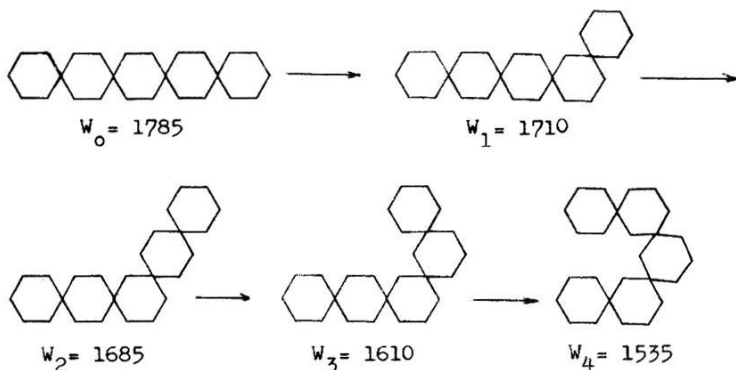
#### The degree of bending in a string of spirocycles

Rule 8. The Wiener number decreases when the bending of a string of spirocycles increases:

$$W_{a_L, a_B} > W_{a_{L-K}, a_{B+K}} \quad (14)$$

Here  $a_L$  and  $a_B$  are the number of cycles in the linear, and respectively bent part of the string,  $a_B = 0, 1, 2, \dots, a$ ; and  $k$  is a positive integer. A cycle in a string of spirocycles is regarded to be of L-, or B-type, respectively, if the characteristic polycyclic subgraph, including this and its two adjacent cycles in the string, is linear, or respectively, bent one. For instance in the following series of isomeric structures:

$$N = 4, 6, 8, \dots = 2n, \text{ where } n = 2, 3, 4, \dots$$



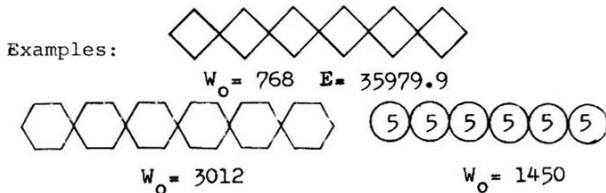
all the cycles in the first structure are of L-type, whilst all the cycles in the last structure are of B-type. The second and third structure have only one cycle of B-type (but differently located in the string), and the fourth structure has three such cycles.

The number of the side-linked spirocycles

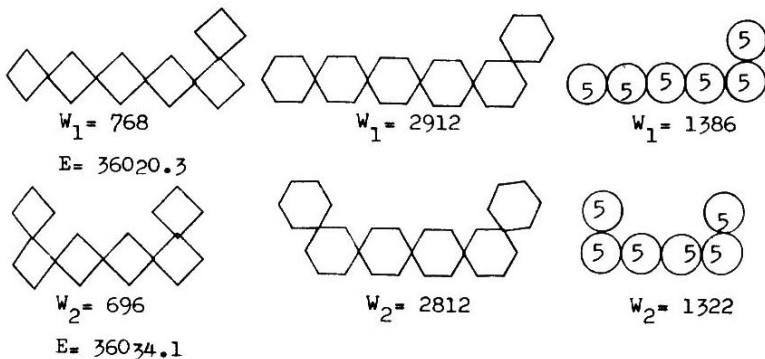
Rule 9. The Wiener number decreases when a string of identical spirocycles shortens at the cost of a side-linking of some cycles:

$$W_0 > W_1 > W_2 > \dots \tag{15}$$

Here the subscripts 0,1,2, etc. are used to denote the number of side-linked spirocycles. In order to prove this rule we shall restrict ourselves to the case when one and two cycles, respectively, are side-linked at a terminal position.

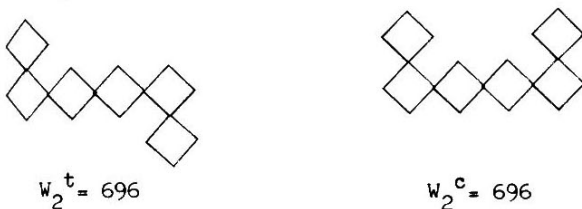




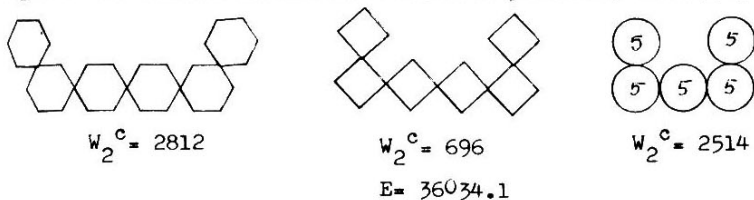


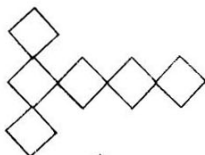
The Cis- Trans Effect

The sum of the all topological distances in the molecular graphs of spirostructures, having a side-linked cycle at each of the two terminal positions of the linear string of identical spirocycles, is the same for the cis- and trans-position of the two cycles. For instance:



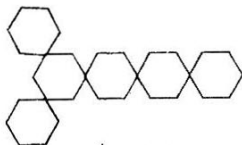
Due to this result a comparison is made below between cis- and another kind of trans-structure in which both side-linked cycles are located at the same terminal position. For instance:



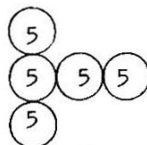


$$W_2^t = 660$$

$$E = 30111.6$$



$$W_2^t = 2612$$



$$W_2^t = 2370$$

The Wiener number of the corresponding cis-, and trans-structures is denoted by  $W_2^c$  and  $W_2^t$ , respectively.

Rule 10. Cis- isomers of the spirostructures with two identical cycles spirolinked at the two terminal positions in a linear string of spirocycles of the same size have higher values of the Wiener number than the corresponding trans- isomer in which the two cycles are linked at the same terminal position:

$$W_2^c > W_2^t \quad (16)$$

The identical rule holds for the structures having condensed cycles instead of spirocycles.

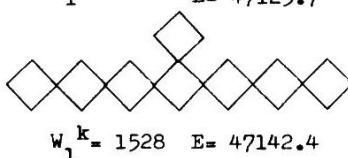
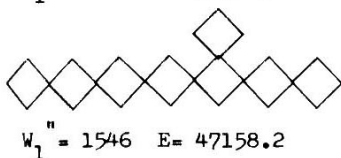
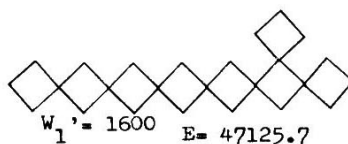
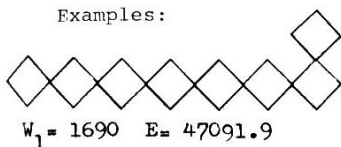
The position of the side-linking

Rule 11. The Wiener number decreases gradually when a spirocycle side-linked to a linear string of identical spirocycles of the same size displaces towards the middle of the string:

$$W_1 > W_1' > W_1'' > \dots > W_1^{k-1} > W_1^k \quad (17)$$

The Wiener numbers for the structures in which the only side cycle is located at a terminal position of the string of cycles, the first and second positions next to the terminal one are denoted above by  $W_1$ ,  $W_1'$ ,  $W_1''$ , respectively. The upper subscripts  $k$  and  $k-1$ , are used for the central and next to it position, respectively.

Examples:



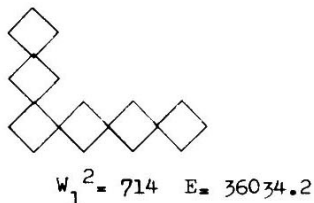
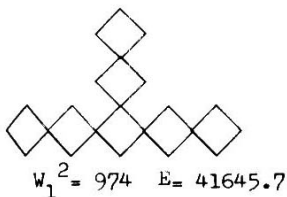
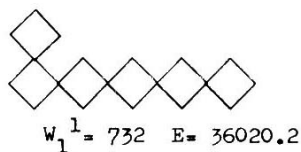
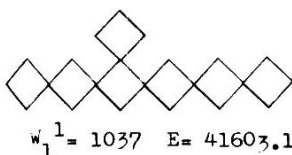
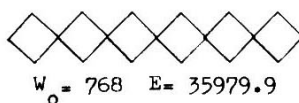
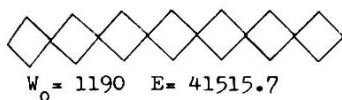
The same rule holds for the analogous type of isomeric structures having condensed cycles instead of spirocycles.

The length of the side-linked branch of cycles

Rule 12. The Wiener number decreases when a side-linked branch of spirocycles increases its length at the cost of the linear string of spirocycles:

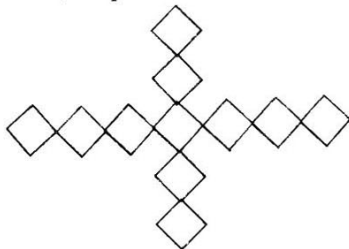
$$W_{a_0, a_1=0} > W_{a_0-1, a_1=1} > W_{a_0-2, a_1=2} \quad (18)$$

Examples:

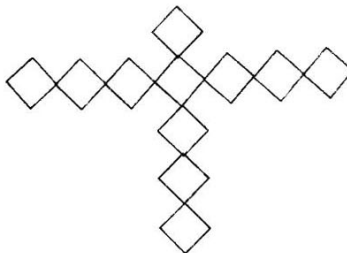


One could also consider here as a specific case of this rule the isomeric branched spirostructures in which the increase in the length of one of the two branches of spirocycles at the cost of the decrease in the length of the other branch is always accompanied with the increase in the Wiener number.

Examples:



$$W_1 = 3082$$



$$W_2 = 3190$$

#### CORRELATION BETWEEN THE WIENER NUMBER AND ELECTRON ENERGIES OF SPIROCOMPOUNDS

It is of importance to examine to what extent the rules on molecular cyclicity, formulated and proved in the previous section, reflect in different molecular properties of spirocompounds. Since the experimental data for spirocompounds are still very scarce indeed we checked some of the rules against the value of electron energies obtained using the extend Hückel method in the form proposed by Hoffmann.<sup>27</sup> The reason behind this effort was the excellent correlation obtained between the Wiener numbers and  $\pi$ -electron energies of polycyclic condensed hydrocarbons.<sup>19</sup> Thus, we wish to examine whether such a correlation exists between the Wiener numbers of spirostructures and their  $\sigma$ -electron energies. The calculations were carried out for 20 spirostructures in the conformation in which the rings were mutually perpendicular. Results (in kcal mole<sup>-1</sup>) are presented in the examples illustrating some of our rules **and elsewhere.**<sup>29</sup>

Six of our rules were examined: rules 5,6,9,10,11 and 12. In all these cases the regular change in the Wiener number of spirocompounds according to one of these rules is associated with a regular change in the EHT-energies. Thus a conclusion can be drawn:

The decrease in the Wiener number within a group of isomeric spirocompounds obeying a certain rule of molecular cyclicity is accompanied by an increase in the EHT-energies of these compounds.

In this way the reverse proportional dependence found earlier between  $\pi$ -electron energies of condensed polycyclic hydrocarbons and their Wiener numbers<sup>19</sup> is now shown to hold also for  $\zeta$ -electron energies of polycyclic spirocompounds.

#### CONCLUDING REMARKS

A number of rules were deduced in this work for the change in the sum of the topological distances (the Wiener number) in molecular graphs of isomeric polycyclic spirocompounds without acyclic branches. It was shown in an analogous study on fused polycyclic structures<sup>19</sup> that the Wiener number decreases regularly with the increase in the molecular cyclicity, i.e., that it could be used as a reverse proportional quantitative measure of molecular cyclicity. On this basis the results of the present work should be viewed as a graph-theoretical formulation of the intuitive ideas of cyclicity in spirocompounds. The chosen criterion for molecular cyclicity is consistent with the practical ideas of experimentalists which indicate that structure out the isomeric ones to be the most cyclic which has the most spirocycles. Moreover, this criterion is in such a state of development that can give a unified scale for the estimation of the influence on the cyclicity that exhibit some more obscure factors like the different size of cycles (thus, for instance, in the example in Introduction the structure III is the most cyclic and the structure V is the least cyclic in the series of structures III - V), their mutual positions, the parity of cycles, etc.

The regularities in the change of molecular cyclicity are similar for the molecules composed of fused cycles and spiro-

cycles, respectively (Rules 1.1, 1.3, 2.1, 4.1, and 6 to 12). The structural factors considered influence in these cases more the sum of topological distances than the kind of linking of cycles. When a string occurs consisting of several identical cycles and one different in the size from them, then the rules devised for even-membered spirocycles maintain their validity also for odd-fused cycles and vice versa (Rules 3 and 4.2; 5 and 4.2). Therefore, the rearrangement of a different cycle within the string of identical cycles does not change the Wiener number if the string is composed either of the odd-membered spirocycles or the even-membered fused cycles.

The importance of the topological rules formulated in this work and the previous one<sup>19</sup> is not limited to the molecular cyclicity only. These rules could be of considerable use as a new approach to the classical problem of the structure-properties relationship. Thus, the large number of structural factors influencing the properties of fused cycles and spirocycles can be classified and examined in detail. Work on establishing the quantitative correlations between the topological indices and various properties of cyclic structures (e.g., boiling points, heats of atomization, heats of vaporization, molecular volumes, etc.) is in progress.<sup>28</sup>

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References

1. A. T. Balaban, Rev. Roumaine Chim. 18, 635 (1973).
2. J. Donohue, G.L. Humphrey, and V. Schomaker, J. Am. Chem. Soc. 67, 332 (1945); see also G. Dallinga, R.K. von der Draai, and L.H. Toneman, Recueil 87, 897 (1968).
3. e.g., R. Hoffmann, A. Imamura, and G.D. Zeiss, J. Am. Chem. Soc. 89, 5215 (1967).
4. D.E. Applequist, G.F. Fanta, and B.W. Henriksen, J. Org. Chem. 23, 1715 (1958).
5. B. Winstein, A. H. Feuselav, and J. G. Trope, J. Chem. Soc., 2281 (1965).
6. H. E. Simmons and T. Fukunaga, J. Am. Chem. Soc. 89, 5208 (1967).

7. L.M. Rice, B.S. Sheth, and T.B. Zalucky, *J. Heterocycl. Chem.* 8, 155 (1971).
8. M.F. Semmelhack and R.J. De Franco, *Tetrahedron Lett.*, 1061 (1971).
9. P. Binger, *Angew. Chem. Int. Edit.* 11, 433 (1972).
10. L. Fitjer and J.M. Conia, *Angew. Chem., Int. Edit.* 12, 761 (1973).
11. J.M. Donis and J.M. Conia, *Tetrahedron Lett.*, 461 (1973).
12. F. Harary, *Graph Theory*, Addison-Wesley, Reading, Mass. 1971, Second printing.
13. M. Behzad and G. Chartrand, *Introduction to the Theory of Graphs*, Allyn and Bacon, Boston 1972.
14. *Chemical Applications of Graph Theory*, Edited by A.T. Balaban, Academic Press, London 1976.
15. K. Kawasaki, K. Mizutani, and H. Hosoya, *Nat. Sci. Reports Ochanomizu Univ.* 24, 27 (1973).
16. A.T. Balaban, *Rev. Roumaine Chim.* 18, 635 (1973).
17. H. W. Whitelock, Jr., and M.W. Siefken, *J. Am. Chem. Soc.* 90, 4929 (1968).
18. Molecular cyclicity is important structural feature of polycyclic systems and equals molecular branching in acyclic structures.
19. D. Bonchev, Ov. Mekenjan, and N. Trinajstić, "On Topological Characterization of Cyclic Structures", work in preparation (preprint available on the request).
20. D. Bonchev and N. Trinajstić, *J. Chem. Phys.* 67, 4517 (1977).
21. D. Bonchev and N. Trinajstić, *Int. J. Quantum Chem., Symposia*, in press.
22. D.H. Rouvray, in: *Chemical Applications of Graph Theory*, Edited by A.T. Balaban, Academic Press, London 1976, p. 175.
23. H. Wiener, *J. Am. Chem. Soc.* 69, 17 (1947); *ibid* 69, 2036 (1947); *J. Phys. Chem.* 52, 425 (1948).
24. J. R. Platt, *J. Chem. Phys.* 15, 419 (1947).
25. D.H. Rouvray, *Mathematical Chemistry* 1, 125 (1975).
26. D. Bonchev, J.V. Knop, and N. Trinajstić, *Mathematical Models of Branching*, These Proceedings.
27. R. Hoffmann, *J. Chem. Phys.* 39, 1397 (1963).
28. D. Bonchev, Ov. Mekenjan, and N. Trinajstić, "On Modelling of Thermodynamic Functions", work in preparation
29. Ov. Mekenjan, D. Bonchev, and N. Trinajstić, *Bremen Briefe Zur Chemie*, in press.