

CCA-1374

YU ISSN 0011-1643

UDC 541/547.28

Original Scientific Paper

## Structural Complexity and Molecular Properties of Cyclic Systems with Acyclic Branches\*

*Ovanes Mekenyan, Danail Bonchev*

*Department of Physical Chemistry, Higher School of Chemical Technology,  
8010 Burgas, Bulgaria*

and

*Nenad Trinajstić*

*The Rugjer Bošković Institute, P.O.B. 1016, 41001 Zagreb, Croatia, Yugoslavia*

Received August 30, 1982

The degree of structural complexity of cyclic molecules with acyclic branches is quantitatively expressed by means of rules based on the change in the sum of the topological distances, i. e. the Wiener number, in the corresponding graphs. It is shown that these topological rules are well reflected in the properties of isomeric alkyl-benzenes.

### INTRODUCTION

The central problem in theoretical chemistry is the deduction of molecular properties from the structural features of molecules. In this the influence of electronic and geometric factors is usually separately treated, i. e. one discriminates between the electronic structure and the structure of the molecular skeleton (or molecular constitution) as defined by the equilibrium state of atomic nuclei.

There are several levels of information about the molecular structure. The first level considers the connectedness (the atom-atom connectivity) or topology of a molecule. Most nearest-neighbours interactions are a consequence of the connectivity in a molecule. This aspect of molecular structure is sometimes called the primary structure of a molecule. The secondary structure of a molecule concerns bond lengths and bond angles and it is commonly referred to as the geometry of the system. The tertiary structure of a molecule results from torsional energetics and it is usually referred to as the conformation of the system.

Different methods compete in studying the dependence of properties on molecular structure. Chronologically the first approach proposed was the increment method, according to which each molecular fragment (an individual atomic group, a bond, a ring, etc.) contributes to the total magnitude of molecular properties. The most complete form of the increment method has been

---

\* Presented at *The IUPAC International Symposium on Theoretical Organic Chemistry*, held in Dubrovnik, Croatia, August 30 — September 3, 1982.

developed by Tatevskii.<sup>1-3</sup> The additive schemes for calculation of molecular properties, however, have their limitations related to accuracy achieved as well as to their applicability to molecular properties originating from intermolecular interactions, such as melting and boiling points, vapour pressure, etc. The very basis of the approach, that individual structural fragments always make the same contribution to various molecular properties, is also debatable. In many cases a complicated combination of individual structural elements means a new quantity that is not reducible to the sum of individual contributions. The last argument has played a major role in the appearance of alternative algebraic approaches to the relation between molecular constitution and properties.

In the work by Dubois<sup>4-7</sup> the diverse structural elements are already variables, their contributions to a certain molecular property are calculated by means of a computer program for correlation analysis. The procedure eliminates those factors with a negligible contribution, thus laying bare the structural fragments dominating the molecular property under consideration. This approach displays a high accuracy and has found considerable application in research on biologically active substances. The difficulties in applying this method to complicated molecular systems are mainly of technical nature: it needs a computer with a large memory, it uses a considerable amount of computer time, etc. From the methodological point of view, however, the computer-oriented description of a molecular property as a function of a very large number of structural parameters seems questionable, since the physical nature of the property is, thus, dissolved in the mass of various parameters.

Quite different is the approach based on a global quantitative estimate of molecular complexity by means of various structural (topological) indices.<sup>8-12</sup> It is supposed that these indices, reflecting the essential features of molecular structure, will correlate well with molecular properties. Chemical graph theory is largely applied in the realization of this approach.<sup>13-17</sup> The approach is based on the idea that molecular properties are mainly dependent on the primary structure of a molecule (molecular topology),<sup>18</sup> while the specific geometrical parameters such as bond lengths and bond angles (molecular metrics) are responsible rather for only moderate deviations in the magnitude of a given property. The structural indices, obtained by graph-theoretical techniques, reflect on a unified scale the gradual increase in the complexity of molecular structures starting from linear acyclic and proceeding through branched acyclic, cyclic, branched cyclic, and finally to cyclic structures with acyclic branches. This order of molecular complexity is reflected in a regular manner in various properties of these molecules thus revealing possibilities for establishing satisfactory correlations between molecular properties and topological indices.<sup>11,19</sup>

Reviewing the results in this field, one should note those obtained for acyclic structures.<sup>20-36</sup> However, in the case of cyclic molecules one faces some difficulties due to ring strain. This is the reason why the topological approach was mainly applied to (poly)cyclic structures containing strain-less rings, e. g. systems consisting of six-membered rings.<sup>37-49</sup> Most frequently, however, attempts to associate the properties of (poly)cyclic molecules with their structure represented correlations within a certain homologue series of components. These correlations for isomeric compounds are, with a few exceptions,<sup>50,51</sup> not satis-

factory. This is understandable when taking into account the numerous factors influencing cyclicity and branching of cyclic molecules, which determine to a large extent their structural complexity. Hence, there is an obvious necessity for general quantitative analysis of the regularities in the changes of molecular topology of these compounds.

The sum of the topological distances in the molecular graph,  $G$ , (the so-called Wiener number of a graph) appears to be a particularly convenient tool<sup>37</sup> for realization of the above-stated aim. It should be recalled that the distances between graph vertices are integers since the distance between two adjacent vertices is by definition a unity.<sup>14,17</sup> This fact points to the connection between the graph distances and the Wiener number of a graph. The easiest way to obtain the Wiener number of a graph,  $W = W(G)$ , is by means of the distance matrix,  $G, D(G)$ . The distance matrix of the graph is a real  $N \times N$  ( $N =$  number of vertices in  $G$ ), symmetric in relation to the principal diagonal. Its elements,  $D_{ij}(G)$ , represent the length of the shortest path (the topological, graph distance) between the  $i$ -th and the  $j$ -th vertices in  $G$ . All the elements of the type  $D_{ii}(G)$  are, by definition, zero. Also, by definition,  $D_{ij}(G) = 1$ , if  $i$  and  $j$  vertices of  $G$  are adjacent. Therefore, all off-diagonal entries of the distance matrix are integers. It is found that the Wiener number of a graph is equal to the sum of all entries of the trigonal off-diagonal submatrix of  $D(G)$ ,

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

It is enough to consider the submatrix of  $D(G)$ , because owing to the symmetry of the distance matrix each  $D_{ij}(G)$  entry is counted twice.

The Wiener number was initially defined for acyclic graphs (acyclic hydrocarbons)<sup>20</sup> as the sum of the paths (bonds) between each pair of vertices (atoms) in the graph (molecule). However, the one-to-one correspondence between a pair of neighbours a certain number of bonds away and the number of paths of the same length holds only for acyclic systems. Hence, in polycyclic structures the Wiener number is associated with distance only, and not with the number of paths, but in acyclic structures the two are the same. Since the sum of the topological distances in the molecular graph is associated in an obvious way with the compactness of the molecules, the Wiener number was used as a reverse proportional measure of molecular branching<sup>8,37,46</sup> and cyclicity.<sup>47,49,52,53</sup> The change in the Wiener number as a result of certain structural changes was reported in a series of papers dealing with isomeric polycyclic structures with different types of ring linkage (fusion-,<sup>49</sup> spiro-,<sup>54</sup> and bridge-type<sup>52</sup> linkage), in which a number of rules of molecular cyclicity were formulated. The latter are of practical interest, since, in principle, they provide a basis for the prediction of the relative order of magnitudes of different molecular properties in a series of isomeric chemical compounds.

In relation to the above, we wish in the present work to report on the influence of topological rules, defined by means of the change in the Wiener number along a series of isomers, on the  $\pi$ -electron energy and on some physical properties of cyclic structures with acyclic branches. Alkylbenzenes will be used as the test molecules.

## TOPOLOGICAL RULES FOR CYCLIC MOLECULES WITH ACYCLIC BRANCHES

In this section we present a set of topological<sup>55</sup> rules for characterization and classification of cyclic molecules with acyclic branches. Each rule deals with a certain molecular rearrangement within an isomeric series of compounds, as well as with the change in the Wiener number upon this transformation. The rules are illustrated by examples accompanied by the Wiener numbers and the Hückel energies in  $\beta$  units. The lengthy mathematical proof of these rules are given elsewhere.<sup>56</sup>

**Rule 1.** — The sum of the topological distances in molecular graphs of isomeric structures composed of a cycle and a non-branched side-chain goes through a minimum, defined by the condition,

$$N_k = (3 N_o - 2 \sqrt{N_o^2 - N_o + \frac{7}{3} - 4})/5 \quad (1)$$

with an increase in chain length at the cost of a decrease in the cycle size at a constant parity of the cycle dimensions,

$$W_{N, N_k} > W_{N-1, N_k+1} > \dots > W_{N-n, N_k+n} < W_{N-n-1, N_k+n+1} < \dots < W_{N-n-s, N_k+n+s} \quad (2)$$

where  $n$  and  $s$  are positive integers. In the above relations  $N_k$  is the number of atoms in the side-chain (or the length of the latter),  $N$  is the number of atoms in a cycle, while  $N_o$  is the total number of atoms in the molecule. Illustrative examples are given in Figure 1.

It is seen from the examples in Figure 1 that the maximum in the Wiener number appears at the beginning of the series of isomeric compounds under consideration. Thus for molecules having smaller rings, which are most frequently encountered in chemical practice, the Wiener number changes smoothly without extremes. The latter may be of use in the search for correlations with molecular properties.

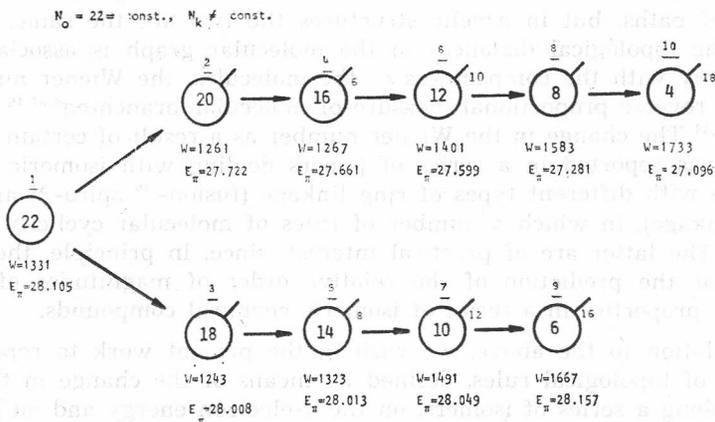
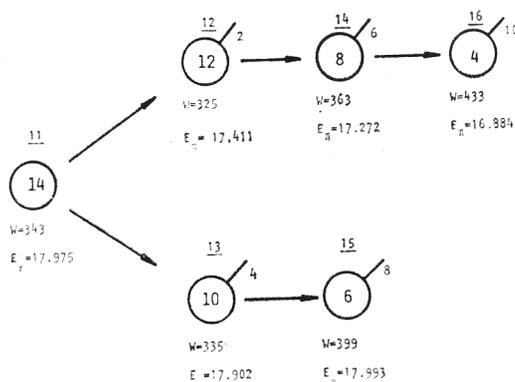


Figure 1. Examples illustrating Rule 1. The superscript 2 on the values of  $E$  (here and in what follows) signifies the number of NBMO's.

$$N_0 = 14 = \text{const.}, N_k \neq \text{const.}$$



**Rule 2.** — The sum of the topological distances in molecular graphs of isomeric structures composed of a linear string of cata-condensed, or spiro-linked rings, or cycles connected by a bridge (a single edge) and 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 the terminal ring, decreases when the length of the side-chain reduces at the cost of formation of new cycles,

$$W_{a, N_k} > W_{a+x, N_k-n} \quad (3)$$

for  $N_k = a_k(N-m)$ . The new symbols in (3) have the following meaning:  $a$  is the number of cycles,  $x = 1, 2, 3, \dots$ , while  $n = x \cdot (N-m)$ , where  $m = 2, 1$ , and  $0$  for cata-condensed, spiro- and bridge-linked cycles, respectively. An explanatory example is presented in Figure 2.

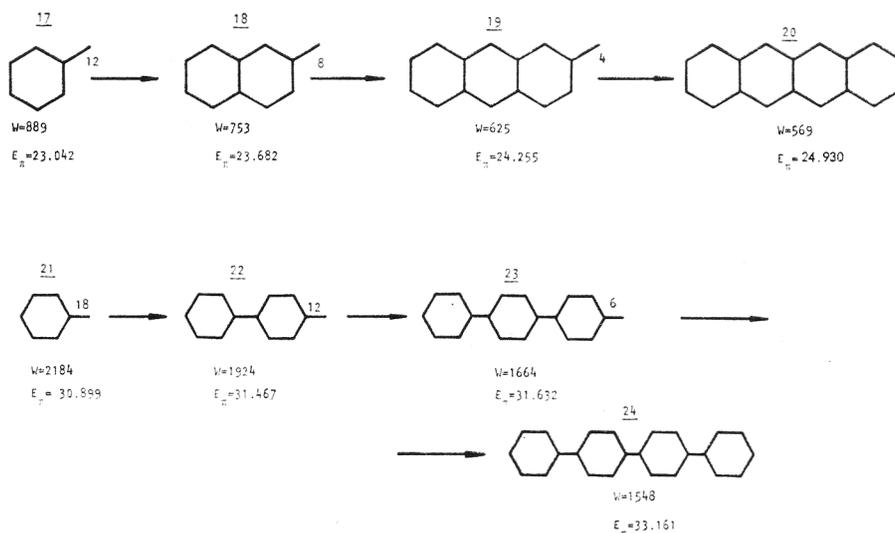


Figure 2. Examples illustrating Rule 2

**Rule 3.** — The sum of topological distances in the molecular graph decreases when isomers are subsequently created from a structure, composed of a cycle having up to 10 atoms and a non-branched side-chain, by shortening the side-chain at the cost of the formation of  $i$  new non-branched side-chains of equal length  $N_i$ , on condition that the length of the initial side-chain  $N_k$ , divided by the maximum number of new branches increased by one, is an integer equal to the length of newlyformed side-chains  $N_i$ ,

$$W_{N_{kj}, i} > W_{N_{kj}-xN_i, i+x} \quad (4)$$

for  $\frac{N_k}{i_{\max} + 1} = N_i$ . In eq. (4)  $N_k$  is the length of the  $j$ -th side-chain of the initial structure, while  $x = 1, 2, 3, \dots$  and  $i = 1 + \frac{N}{2}$ . Examples clarifying

**Rule 3** are shown in Figure 3.

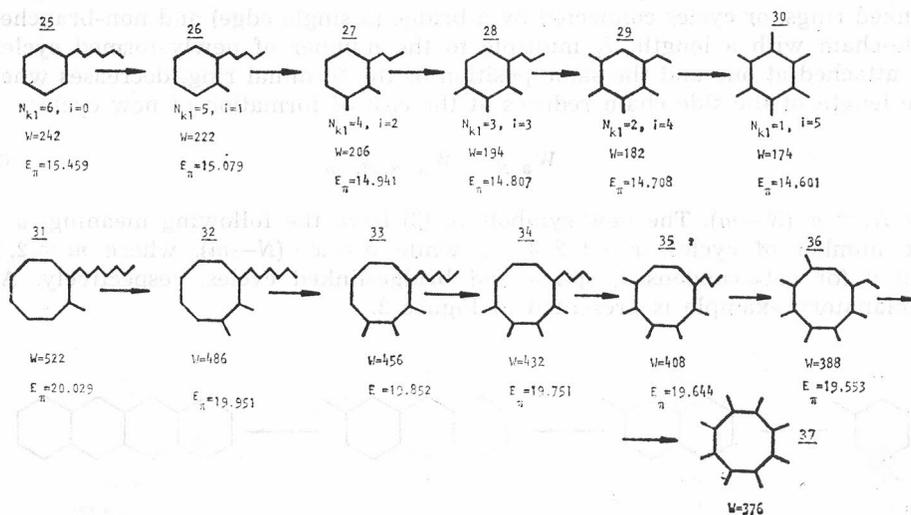


Figure 3. Examples illustrating Rule 3

**Rule 4.** — The sum of topological distances in the molecular graph 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 while keeping a fixed distance between them, and a constant cycle size,

$$W_{N_{jk}', N_{kj}''} < W_{N_{kj}'+\Delta l, N_{kj}''-\Delta l} \quad (5)$$

where  $N_{kj}' \geq N_{kj}''$  and  $\Delta l = 1, 2, 3, \dots$

Examples supporting this rule are given in Figure 4.

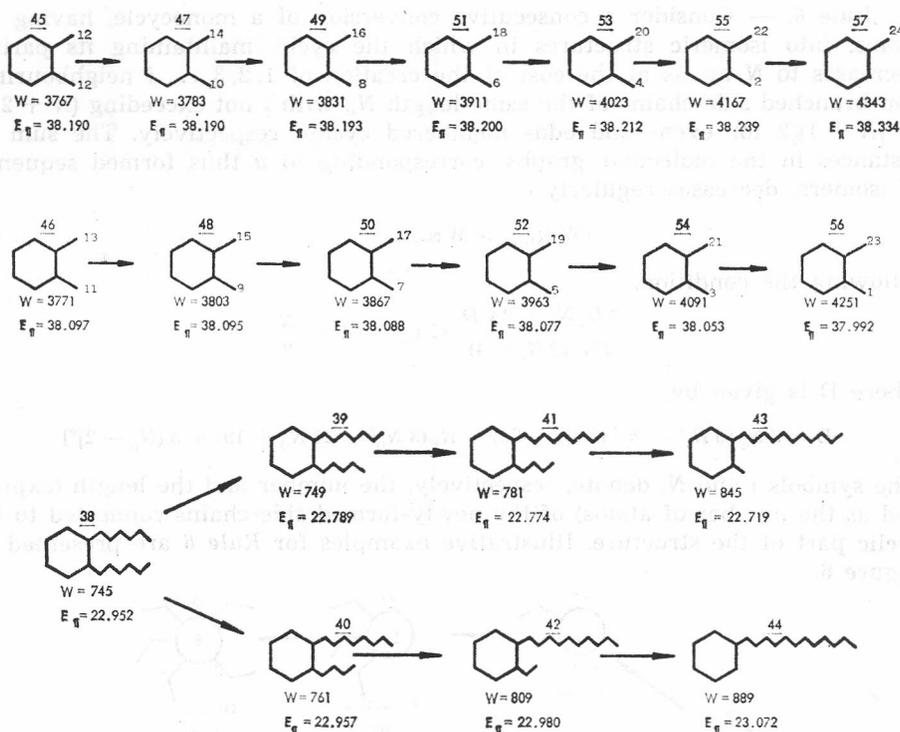


Figure 4. Examples illustrating Rule 4

**Rule 5.** — In isomeric structures composed of a cycle and non-branched side-chains, the sum of the topological distances in the molecular graph increases with an increase in the distance between the atoms to which the side-chains are connected. If the sum of these distances is constant, the Wiener number increases with an 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,

$$W_{N_{k1}, N_{k2}, N_{k3}, \dots, d_{12}, d_{13}, \dots, d_{23}, \dots} > W_{N_{k1}, N_{k2}, N_{k3}, \dots, d'_{12}, d'_{13}, \dots, d'_{23}, \dots} \quad (6)$$

where  $d_{12} > d'_{12}$  and/or  $d_{13} > d'_{13}$  and/or  $d_{23} > d'_{23}$  etc. The distance (expressed as the number of bonds) between the side-chains  $i$  and  $j$  along the cycle is denoted by  $d_{ij}$ . Illustrative examples for Rule 5 are presented in Figure 5.

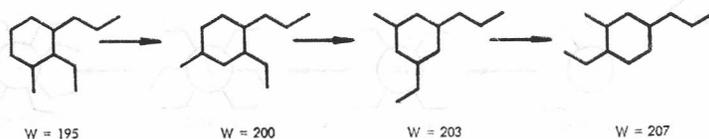


Figure 5. Examples illustrating Rule 5

**Rule 6.** — Consider a consecutive conversion of a monocycle, having  $N_0$  atoms, into isomeric structures in which the cycle, maintaining its parity, decreases to  $N$  atoms at the cost of the creation of 1, 2, 3, ...,  $i$  neighbouring, non-branched side-chains of the same length  $N_i$ , with  $i$  not exceeding  $(N + 2)/2$  or  $(N + 1)/2$  for even- and odd- membered cycles, respectively. The sum of distances in the molecular graphs, corresponding to a thus formed sequence of isomers, decreases regularly,

$$W_{N_1, i_1} > W_{N_2, i_2} > \dots \quad (7)$$

following the condition,

$$\frac{3 N_i N_0 + 2 \sqrt{D}}{3 N_i (3 N_i + 4)} < i_{\max} - 1 = \frac{N}{2} \quad (8)$$

where  $D$  is given by,

$$D = 3 N_i [6 N_i^3 - N_i^2 (9 N_0 - 20) + N_i (3 N_0^2 - 21 N_0 + 19) + 3 (N_0 - 2)^2] \quad (9)$$

The symbols  $i$  and  $N_i$  denote, respectively, the number and the length (expressed as the number of atoms) of the newly-formed side-chains connected to the cyclic part of the structure. Illustrative examples for **Rule 6** are presented in Figure 6.

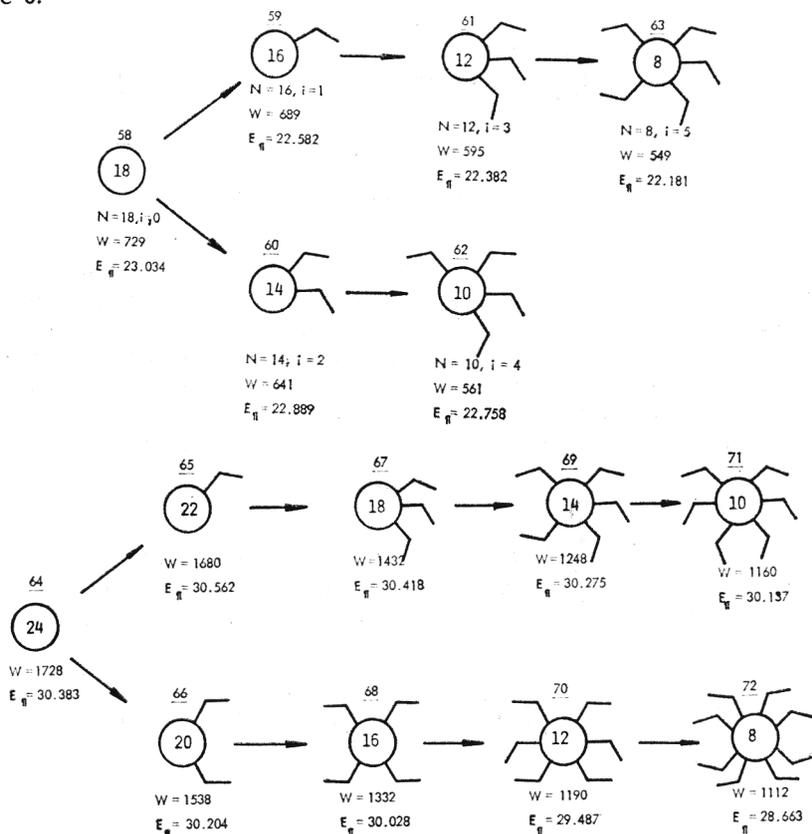


Figure 6. Examples illustrating Rule 6

The other possibilities for the sum of topological distances in the molecular graphs of such a sequence of isomers, which, however, occur much less frequently, are:

(a) to pass through a minimum specified by an inequality opposite to (8),

$$\frac{3 N_i N_o + 2\sqrt{D}}{3 N_i (3 N_i + 4)} > i_{\max} - 1 = \frac{N}{2} \quad (10)$$

(b) to pass through a maximum specified by the condition,

$$2 N_i + 4 \leq N_o \leq N_i + 2 + 2 N_i \sqrt{B} \quad (11)$$

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

(c) to increase when  $N_i = 2$  and  $N_o \leq 8$ .

**Rule 7.** — In isomeric structures composed of a cycle and a side-chain with a branch of arbitrary length, in which the branch is displaced from a position close to the cycle towards the end of the side-chain, the sum of the topological distances in the molecular graph increase, or, when the side-chain has at least three atoms more than the cycle, it passes through a minimum at a displacement.

$$\Delta N_p = (N_k - N + 1)/2 \quad (12)$$

where  $N_p$  is the length (as the number of atoms) of the newly-formed branch attached to the initial side-chain. Examples supporting **Rule 7** are given in **Figure 7**.

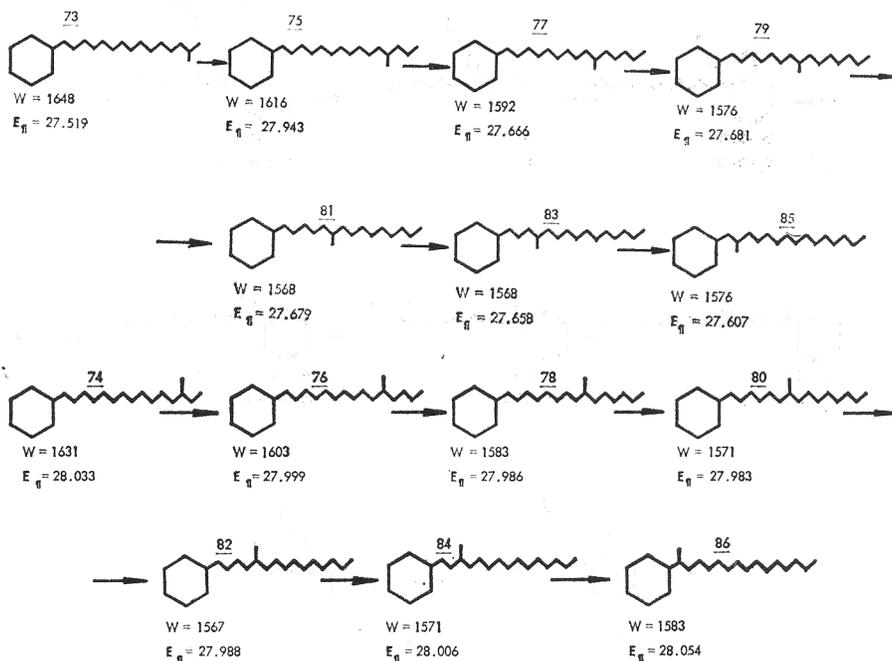


Figure 7. Examples illustrating Rule 7

**Rule 8.** — The sum of topological distances in the molecular graph decreases when in isomeric structures, consisting of a cycle, a side-chain, and a branch attached to an arbitrary atom of the latter, the side-chain shortens at the cost of an increase in branch length at a constant branch position,

$$W_{N_k, \Delta N_p, N_{p1}} > W_{N_k, \Delta N_p, N_{p2} \dots} \quad (13)$$

where  $N_{p1} < N_{p2} < N_{p3} \dots$  Illustrative examples are presented in Figure 8.

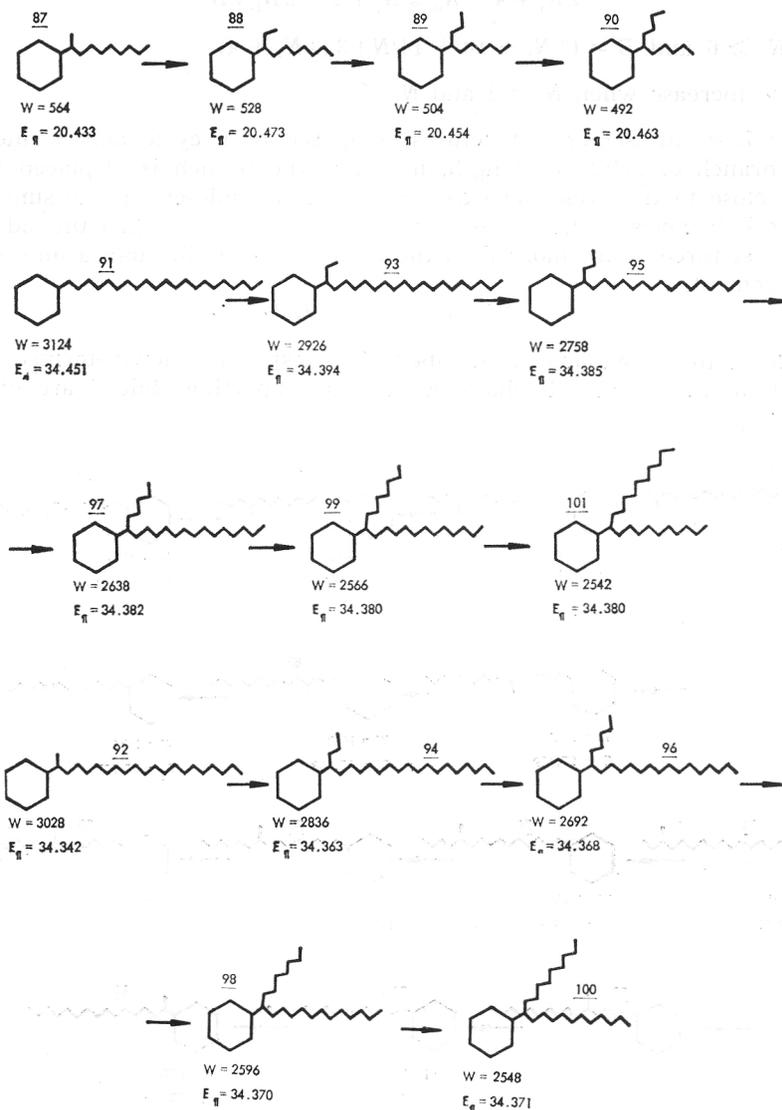


Figure 8. Examples illustrating Rule 8

*Rule 9.* — The sum of the topological distances in the molecular graph decreases when in isomeric structures, composed of a cycle and a side-chain (with or without branches), the latter shortens at the cost of the formation of new branches of equal length attached to the side-chain,

$$W_{N_k, p_1} > W_{N_k, p_2} > \dots \quad (14)$$

where  $p$  is the number of newly-formed branches attached to the single initial side-chain. Note,  $p_1 < p_2 < \dots$ . Examples illustrating *Rule 9* are shown in Figure 9.

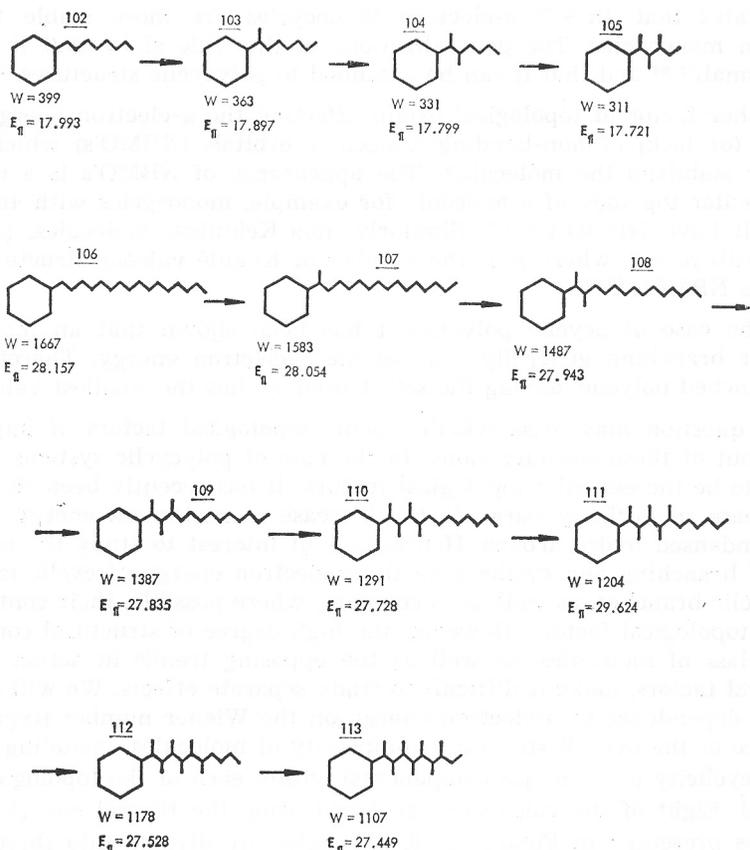


Figure 9. Examples illustrating Rule 9

#### TOPOLOGICAL RULES AND $\pi$ -ELECTRON ENERGY

Total  $\pi$ -electron energy ( $E_{\pi}$ ) is one of the most important parameters characterising conjugated molecules that can be obtained from the Hückel method. Hückel  $E_{\pi}$ 's are often of the same degree of accuracy as those obtained by much more sophisticated (and complicated) SCF  $\pi$ -MO models.<sup>57a,b</sup> In this respect an interesting result was achieved by Hess and Schaad<sup>57b</sup> who demonstrated that in many cases  $E_{\pi}$  (Hückel) follows linearly the total thermodynamically observable energy of conjugated systems.

Since the Hückel model is topological in its origin,  $E_\pi$  (Hückel) depends to certain extent on molecular topology.<sup>58</sup>  $E_\pi$  (Hückel) is not just a topological quantity, because it depends upon a knowledge of a ground-state configuration, and this may only be attained by an application of the *Aufbau* Principle, which is external to the topological aspects of the problem embodied in the adjacency matrix.<sup>58a</sup> Nevertheless,  $E_\pi$  (Hückel) in combination with the *Aufbau* Principle is deducible from the structure of the molecular graph. The influence of some topological factors on the  $\pi$ -electron energy is modestly understood.<sup>17,58,59</sup> In the case of monocyclic conjugated hydrocarbons, the size of the cycle is of major importance for  $E_\pi$ .<sup>60</sup> This is formulated as the Hückel rule<sup>61</sup> which states that  $4n + 2$   $\pi$ -electron monocycles are more stable than  $4n$   $\pi$ -electron monocycles. The generalizations of this rule show that it is valid for  $n = \text{small}$ <sup>62-64</sup> and that it can be extended to polycyclic structures.<sup>65,66</sup>

Another factor of topological origin affecting the  $\pi$ -electron energy is the presence (or lack) of non-bonding molecular orbitals (NBMO's) which destabilize (or stabilize) the molecule.<sup>67</sup> The appearance of NBMO's is a result of the particular topology of a molecule for example, monocycles with  $4n$   $\pi$ -electrons will have NBMO's.<sup>14,17,68</sup> Similarly, non-Kekuléan molecules, (i. e. molecules with  $K = 0$ , where  $K$  is the number of Kekulé valence structures) will also have NBMO's.<sup>69,70</sup>

In the case of acyclic polyenes it has been shown that an increase in molecular branching generally reduces the  $\pi$ -electron energy. Therefore, the most branched polyene, among the set of isomers, has the smallest value of  $E_\pi$ .

The question may arise whether some topological factors of importance are left out of these considerations. In the case of polycyclic systems *cyclicity* appears to be the essential topological feature. It has recently been shown that the increase in cyclicity parallels the increase of  $\pi$ -electron energy of polycyclic condensed hydrocarbons. Hence, it is of interest to study the combined action of branching and cyclicity on the  $\pi$ -electron energy of cyclic molecules with acyclic branches, as well as to compare, where possible, their contribution to other topological factors. However, the high degree of structural complexity in this class of molecules, as well as the opposing trends in action of some topological factors, make it difficult to study separate effects. We will examine here the dependence of  $\pi$ -electron energy on the Wiener number (regarded as a measure of the overall structural complexity of molecules, including branching and cyclicity as its major components) within each of the topological rules presented. Eight of the rules were analyzed using the Hückel energies of 113 structures presented in Figures 1—9. The rules are divided into three groups according to the collective influence of the various topological factors on the  $\pi$ -electron energy.

The first group comprises the rules in which the sum of the distances in the molecular graph (the Wiener number), representing molecular branching or cyclicity is the dominating factor. Within Rules 3 and 9 (structures 25—37 and 102—113, respectively) the Hückel (HMO) energy is directly proportional to the Wiener number  $W$  since in both cases branching increases (we recall here that  $E_\pi$  is reverse proportional to branching<sup>37</sup> and the same is true for  $W$ <sup>37</sup>). This is shown in Figures 10 and 11.

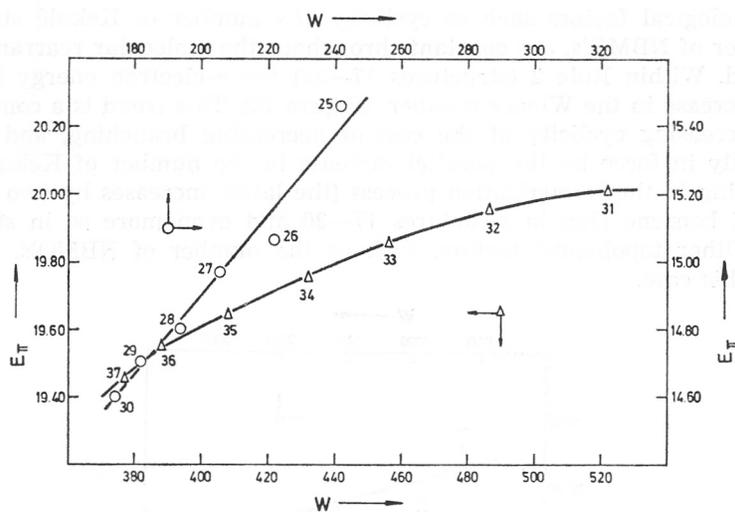


Figure 10. Total  $\pi$ -electron energy vs. the Wiener number for structures 25–37 supporting Rule 3

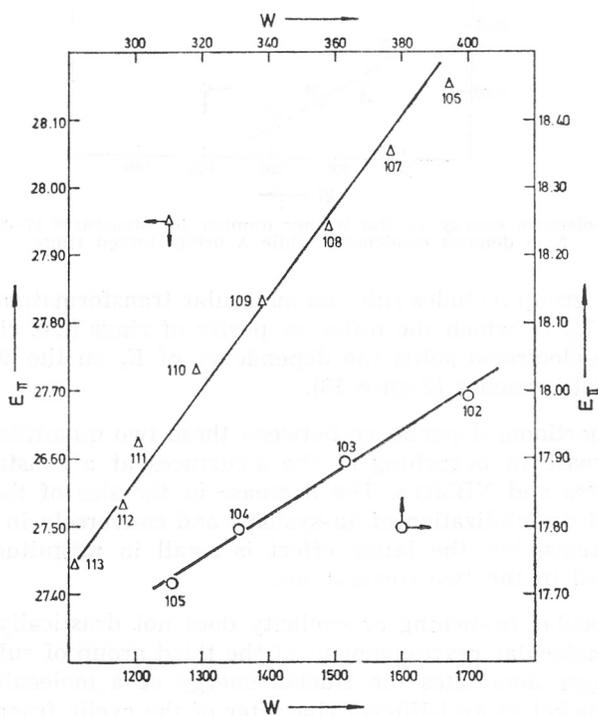


Figure 11. Total  $\pi$ -electron energy vs. the Wiener number for structures 102–113 supporting Rule 9

Other topological factors such as cyclicity, the number of Kekulé structures, the number of NBMO's, are constant throughout the molecular rearrangements considered. Within Rule 2 (structures 17—24) the  $\pi$ -electron energy increases with a decrease in the Wiener number (Figure 12). This trend is a consequence of the increasing cyclicity at the cost of decreasing branching, and it gains additionally in force by the parallel increase in the number of Kekulé structures arising in the isomerization process (the latter increases by two for each additional benzene ring in structures 17—20 and even more so in structures 21—24). Other topological factors, such as the number of NBMO's, are constant in this case.

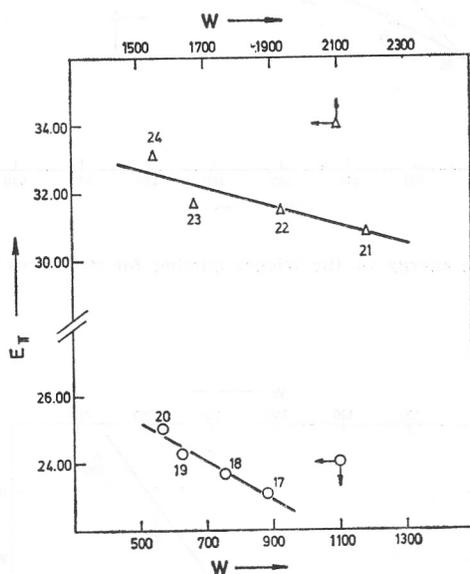


Figure 12. Total  $\pi$ -electron energy vs. the Wiener number for structures 17—24 supporting Rule 2. O denotes condensed, while  $\Delta$  bridge-linked rings

The second group includes rules on molecular transformations, (e. g. Rule 6, structures 58—72) in which the different parity of rings (i. e. rings containing  $4n$  or  $4n + 2$   $\pi$ -electrons) splits the dependence of  $E_\pi$  on the Wiener number into two parallel branches (Figure 13).

The direct proportional dependence between these two quantities is caused by the strong increase in branching of the structures at a constant number of Kekulé structures and NBMO's. The decrease in the size of the cycle results in an additional destabilization of  $4n$ -systems and conversely in a stabilization of  $(4n + 2)$ -systems, but the latter effect is small in magnitude and cannot change the trend in the two correlations.

When molecular branching or cyclicity does not drastically change, as is the case with molecular rearrangement of the third group of rules, the Wiener number no longer dominates the Hückel energy of a molecule. This role is taken by the Hückel or anti-Hückel character of the cyclic fragment, or, when the parity effect is constant, by the number of Kekulé structures. These two topological factors also cause a splitting of the correlation into two branches,

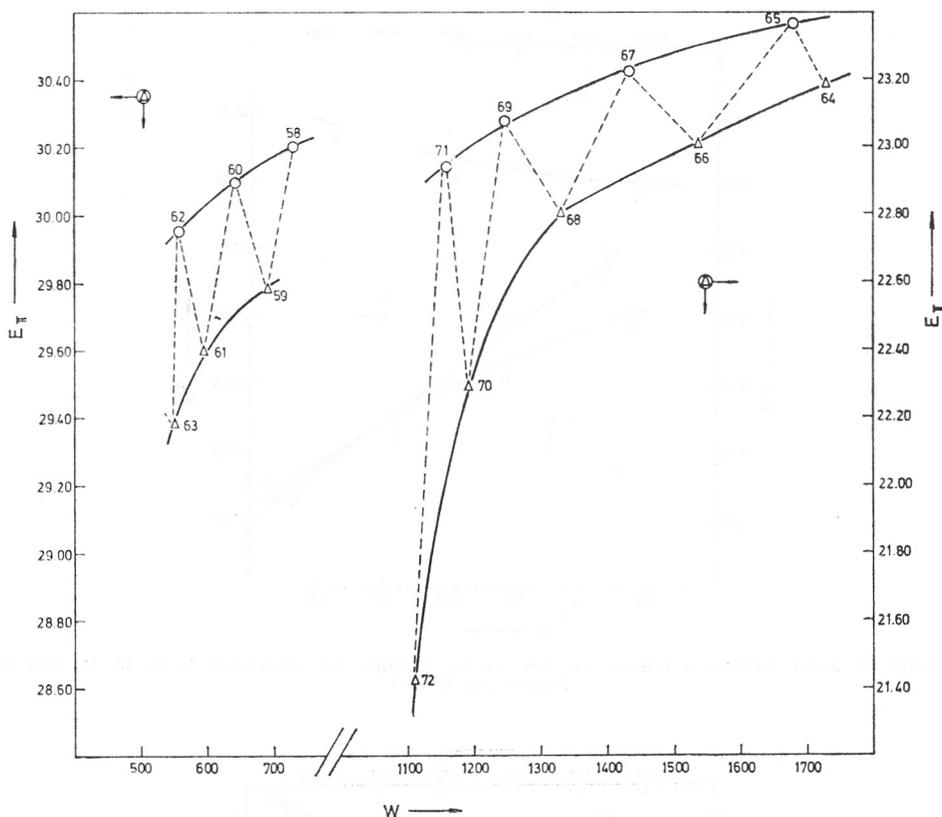


Figure 13. Total  $\pi$ -electron energy vs. the Wiener number for structures 58–72 supporting Rule 6.

but in the opposite direction in comparison with the change in  $\pi$ -electron energy with increase in the Wiener number. Such is the case with Rule 1 (structures 1–16) which is similar to Rule 6 (structures 58–72). Both these rules describe molecular transformations upon which the cyclic fragment reduces at the cost of the increase in the acyclic fragment. The only difference between the two rules is that the acyclic part of the molecules handled by Rule 6 is highly branched whilst for those molecules in the domain of Rule 1 it is linear (or less branched). This difference, however, is sufficient to change the trend in the  $\pi$ -electron energy for  $(4n + 2)$ - and  $4n$ -systems. The increase in the Wiener number is accompanied by an increasing branching of structures or by a decrease in the Hückel energy. However, this effect is not strong and it is counter-balanced in molecules having rings with  $4n + 2$   $\pi$ -electrons by the stronger stabilization effect of the smaller  $(4n + 2)$ -rings (Figure 14).

In the case of molecules whose rings have  $4n$   $\pi$ -electrons, the decrease in the  $\pi$ -electron energy is the result of both increasing branching and the increasing destabilizing effect of the smaller  $4n$ -rings. The superposition of the two effects is reflected as relatively large changes in the  $\pi$ -electron energy.

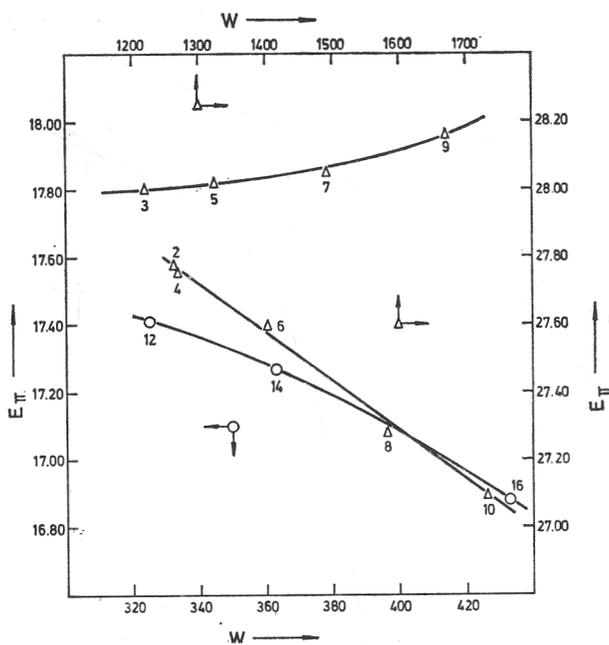


Figure 14. Total  $\pi$ -electron energy vs. the Wiener number for structures 2-10, 12, 14, and 16 supporting Rule 1.

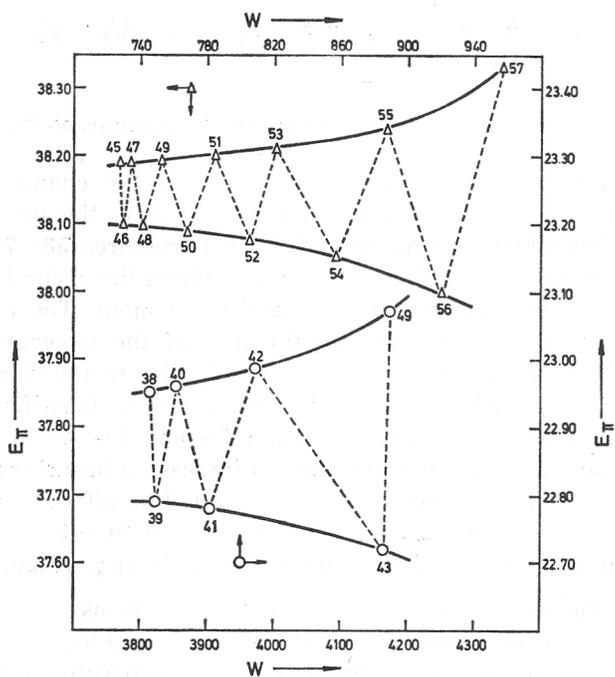


Figure 15. Total  $\pi$ -electron energy vs. the Wiener number for structures 38-57 supporting Rule 4

In the other three rules of this group, i. e. Rule 4, structures 38—57 (Figure 15), Rule 7, structures 73—86, and Rule 8, structures 87—101 (Figure 16), the rearrangements within the acyclic part of the molecules are considered for a constant cyclic part.

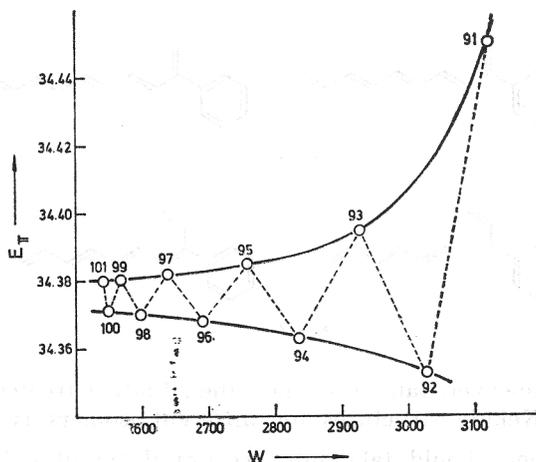
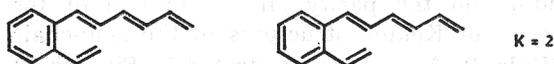
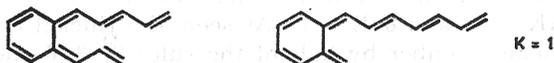


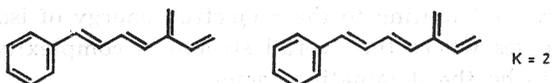
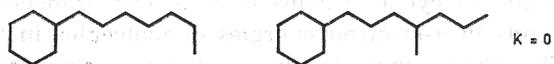
Figure 16. Total  $\pi$ -electron energy vs. the Wiener number for structures 91—101 supporting Rule 8

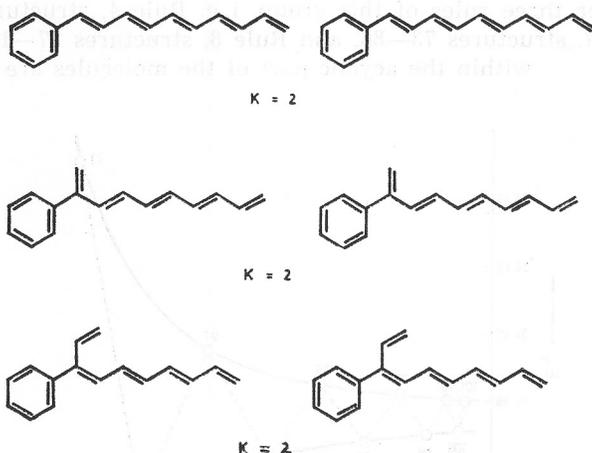
Smaller changes in the sum of topological distances in the molecular graph result in a very weak change in the Hückel energy. One could explain the splitting of the correlation into two sections with opposite trends by the difference in the number of Kekulé structures (and NBMO's). Thus, in the case of Rule 4,  $K = 2$  for branches with an even number of atoms and  $K = 1$  for branches with an odd number of atoms. Similarly, in the case of Rule 7,  $K = 0$  (and NBMO = 2) for the branch linked to even-numbered atoms of the side-chain (counting from the terminal atom of the side-chain), while  $K = 2$  (and NBMO = 0) for the branch linked to odd-numbered atoms of the side-chain. Illustrative example are given below.

#### Rule 4



#### Rule 7





This argument, however, fails to explain the situation treated by Rule 8, since the number of Kekulé structures for different isomers is the same,

Here, perhaps, one should take into account different delocalization in the acyclic parts<sup>57a</sup> depending on their length and parity. The algebraic structure count (ASC) model,<sup>71,72</sup> which takes into account the different parity of the Kekulé structures,<sup>73</sup> however, also fails to reflect this effect. We suppose that the topological factor causing the splitting of the correlation between the Hückel energy and the Wiener number into two individual correlations with opposite trends in the case of the molecular rearrangements following Rule 8 is the alternating number of Kekulé structures in the side-chain ( $K = 0$  for odd and  $K = 1$  for even number of atoms, see examples above).

In concluding this section we wish to summarize the effects that the examined topological rules have on the Hückel energy. The latter increases in parallel with the sum of the distances in the molecular graph upon molecular rearrangement as designated by Rules 3, 9, 6, 1 ( $4n + 2$ ), 4 ( $K = 2$ ), 7 ( $K = 1$ ) and 8 ( $K = 0$ ). An inverse proportional correlation was found between  $E_\pi$  and the Wiener number for molecular transformations described by Rules 2, 1 ( $4n$ ), 4 ( $K = 1$ ), 7 ( $K = 0$ ), and 8 ( $K = 1$ ). As seen, the Hückel energy is uniquely related to the Wiener number by half of the rules (2, 3, 6 and 9). For each of the remaining rules (1, 4, 7 and 8) there are two correlations between the two quantities depending on the parity ( $4n$  or  $4n + 2$ ) of the cyclic fragment (Rule 1), the number of Kekulé structures in the side-chain of the branched cyclic molecule (Rule 8). As was demonstrated in Figures 10—16 the correlations obtained are quite satisfactory. Therefore, the Wiener number used above as a measure of branching and cyclicity, or more generally as a measure of structural complexity of cyclic systems with acyclic branches, can be applied for predicting trends in  $\pi$ -electron energies of molecules in this vast class of hydrocarbons. The above analysis also provides a comparison of different topological factors contributing to the  $\pi$ -electron energy of isomeric molecules. It indicates the cases where the overall structural complexity (branching and cyclicity) seems to be the dominating factor.

In this section we will examine the influence that some of the structural complexity rules formulated above have on eleven properties of alkyl benzenes. These properties are: relative density,  $d_4^{20}$ ; reflection coefficient,  $n_D^{20}$ ; dielectric constant,  $\epsilon$ ; surface tension,  $\sigma$ ; parachor,  $P$ ; molecular volume,  $V_{20}^{\text{mol}}$ ; boiling point,  $T_B$ ; heat of formation,  $-\Delta H_{\text{form}}^{298}$ ; heats of combustion in the liquid and the gas phase,  $(-\Delta H_{\text{comb}}^{298})_{\text{liq}}$  and  $(-\Delta H_{\text{comb}}^{298})_{\text{gas}}$ , respectively; and heat of vaporization,  $L_{298}$ . The data<sup>1-3</sup> for sixteen alkylbenzenes, presented in Table I, allow a detailed examination of Rules 3 and 5, as well as a partial examination of Rules 7 and 9.

Rule 3 can be illustrated by two isomers with 8 carbon atoms and 3 isomers with 9 carbon atoms taken from Table I.



$$W_1 > W_2$$

Let us denote the Wiener numbers for the two neighbouring structures in a sequence of isomers, ordered by the increase in this topological index, by  $W_i$  and  $W_{i+1}$ , respectively. Further, let  $X_i$  and  $X_{i+1}$  be the respective values of the molecular property  $X$  of these isomers. Inspection of Table I shows that for  $W_i < W_{i+1}$  the considered molecular properties of the above two groups of isomers obey the following inequalities,

$$(a) \quad X_i < X_{i+1}, \text{ where } X \equiv P, V_{\text{mol}}^{20}, (-\Delta H_{\text{comb}}^{20})_{\text{liq}}, (-\Delta H_{\text{comb}}^{20})_{\text{gas}}$$

$$(b) \quad X_i > X_{i+1}, \text{ where } X \equiv d_4^{20}, n_D^{20}, \epsilon, \sigma, T_B, -\Delta H_{\text{form}}^{298}, L_{298}$$

One can conclude that the molecular rearrangement by which a side chain attached to a cycle reduces in size at the cost of the formation of new side-chains on neighbouring positions, is reflected in all eleven molecular properties considered.

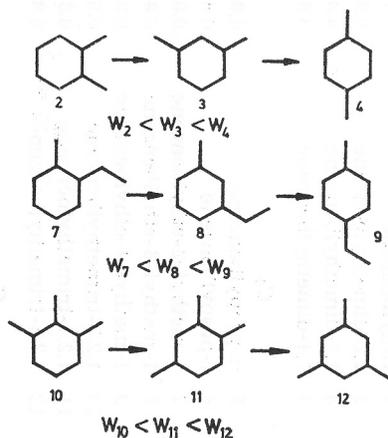


TABLE I  
Molecular Properties<sup>1-3</sup> and the Topological Index of Wiener of some Alkyl Benzenes

No.	Structure	$d_4^{20\text{ a}}$	$n_D^{20\text{ b}}$	$\epsilon^c$	$\sigma \cdot 10^3\text{ d}$	$P^e$	$V_{\text{mol}}^{20\text{ f}}$	$T_B^g$	$-\Delta H_{298}^{\text{O}^h}$	$-\Delta H_{298}^{\text{O}^i}$	$-\Delta H_{298}^{\text{O}^j}$	$L_{298}^k$	W
1	2	3	4	5	6	7	8	9	10	11	12	13	14
<b>C<sub>8</sub></b>													
1	Ethylbenzene	0.86702	1.49588	2.40329	0.4	284.4	122.44	136.19	1524.67	1091.03	1101.13	10.99	64
2	1,2-dimethylbenzene	0.88020	1.50545	2.594	30.03	282.5	120.61	144.41	1527.25	1088.16	1098.54	10.35	60
3	1,3-dimethylbenzene	0.86417	1.49722	2.367	28.63	284.3	122.85	139.10	1527.67	1087.92	1098.12	10.19	61
4	1,4-dimethylbenzene	0.86105	1.49582	2.269	28.31	284.6	123.29	138.35	1527.50	1088.16	1098.29	10.11	62
<b>C<sub>9</sub></b>													
5	n-propylbenzene	0.86204	1.49202	2.372	29.00	323.7	139.42	159.22	1760.46	1247.19	1258.24	10.92	94
6	i-propylbenzene	0.86179	1.49145	2.384	28.20	321.5	139.46	—	1761.39	1246.52	1257.31	—	88
7	1-methyl-2-ethylbenzene	0.88069	1.50456	2.595	30.19	320.0	136.47	165.15	1762.04	1245.26	1256.66	11.22	86
8	1-methyl-3-ethylbenzene	0.86452	1.49660	2.365	29.07	322.9	139.02	161.31	1762.79	1244.71	1255.92	11.10	88
9	1-methyl-4-ethylbenzene	0.86118	1.45500	2.265	28.82	323.3	139.56	161.99	1763.11	1244.45	1255.59	11.07	90
10	1,2,3-trimethylbenzene	0.89438	1.51393	2.636	31.27	317.8	134.38	176.08	1764.62	1272.36	1254.08	11.60	82
11	1,2,4-trimethylbenzene	0.87582	1.50484	2.378	29.71	320.4	137.23	169.35	1765.66	1241.58	1253.04	11.36	84
12	1,3,5-trimethylbenzenes	0.86518	1.49937	2.279	28.83	322.0	138.91	167.72	1766.17	1241.19	1252.53	11.26	84
<b>C<sub>10</sub></b>													
13	n-butylbenzene	0.86013	1.48979	2.359	29.23	362.9	156.04	183.27	1996.17	1403.46	1415.44	—	133
14	i-butylbenzene	0.85321	1.48676	2.319	27.47	360.3	157.30	—	1998.02	1402.04	1413.59	—	126
15	s-butylbenzene	0.86207	1.49020	2.364	28.53	360.0	155.69	—	1997.04	1402.85	1414.57	—	121
16	t-butylbenzene	0.86650	1.49266	2.366	28.13	356.8	154.89	—	1998.29	1401.82	1413.32	—	114

<sup>a</sup> relative density in g.ml<sup>-1</sup>, <sup>b</sup> refraction coefficient, <sup>c</sup> dielectric susceptibility in F.m<sup>-1</sup>, <sup>d</sup> surface tension in Nm<sup>-1</sup>, <sup>e</sup> parachor, <sup>f</sup> molar volume in ml.mol<sup>-1</sup>, <sup>g</sup> boiling point in °C, <sup>h,i,j,k</sup> heats of formation, combustion in liquid and gas state, and vaporization, respectively, all in kcal.mol<sup>-1</sup> (1 cal = 4.185 joule)

Rule 5 is even better demonstrated because of the larger number of isomers for which experimental data are available. 3 isomers with 8 carbon atoms and two sets of 3 isomers with carbon atoms are considered.

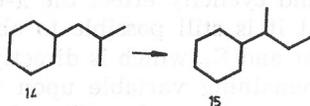
For each  $W_i < W_{i+1}$  within these three groups of isomers two inequalities are again valid,

$$(i) \quad X_i < X_{i+1}, \text{ where } X \equiv P, V_{\text{mol}}^{20}, -\Delta H_{\text{form}}^{298}$$

$$(ii) \quad X_i > X_{i+1}, \text{ where } X \equiv d_4^{20}, n_D^{20}, \epsilon, \sigma, T_B, (-\Delta H_{\text{comb}}^{298})_{\text{liq}}, (-\Delta H_{\text{comb}}^{298})_{\text{gas}}, L_{298}$$

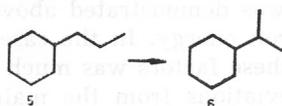
The grouping of molecular properties in the case of Rule 5 is similar to that of Rule 3, the only difference being the interchange of the heat of formation and the heats of combustion.

In the case of Rule 7 one finds exactly the same grouping of molecular properties in inequalities (i) and (ii) as for Rule 5. Although the data for boiling points and heats of vaporization are missing one would expect them to follow a similar trend in the case of Rule 7 as was found for Rule 5. Clearly more examples are needed since only two isomers illustrating Rule 7 are shown in Table I.

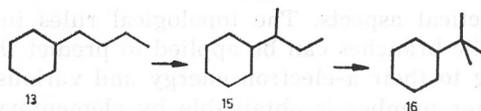


$$W_{14} > W_{15}$$

The situation with Rule 9, which deals with the transformation of a side-chain attached to a cycle into shorter side-chains having more branches, is more complicated than for Rules 3, 5, and 7. Rule 9 can be illustrated by the isomeric structures given below.



$$W_5 > W_6$$



$$W_{13} > W_{15} > W_{16}$$

It follows from inspection of Table I that for each  $W_i < W_{i+1}$  within the above two groups of isomers, a partition is obtained for only some properties,

$$(i) \quad X_i < X_{i+1}, \text{ where } X \equiv \sigma, P, (-\Delta H_{\text{comb}}^{298})_{\text{liq}}, (-\Delta H_{\text{comb}}^{298})_{\text{gas}}$$

$$(ii) \quad X_i > X_{i+1}, \text{ where } X \equiv \epsilon, -\Delta H_{\text{form}}^{298}$$

No data are available for  $T_B$  and  $L_{298}$ . The other three properties, however, are differently grouped for isomers with 9 and 10 carbon atoms:  $d_4^{20}$  and  $n_D^{20}$  are in group (ii) for  $C_9$ -isomers, but in group (i) for  $C_{10}$ -isomers, while

$V_{\text{mol}}^{20}$  is in group (i) for  $C_9$ -isomers, but in group (ii) for  $C_{10}$ -isomers. We assume that the difficulties with Rule 9 regarding these three properties are caused by the singular behaviour of isomers with branches in the next-to-terminal position, as has already been discussed<sup>37</sup> in the case of acyclic branched molecules.

#### CONCLUDING REMARKS

In this work we have examined how deduced topological rules for cyclic structures with acyclic branches are reflected in the  $\pi$ -electron energy and in various molecular properties. Based on the sum of topological distances (Wiener number) in the molecular graph, these rules illustrate to what extent molecular branching and cyclicity determine the properties of this class of molecules.

The analysis of the correlation between the  $\pi$ -electron energy and the Wiener number reveals its complicated nature. In the case of conjugated acyclic compounds one finds that  $E_{\pi}$  decreases with increasing branching. When polycyclic condensed structures are considered, the Hückel energy increases in parallel with increasing cyclicity.<sup>49</sup> In cyclic molecules with acyclic branches both branching and cyclicity effect the  $\pi$ -electron energy. When one of these factors is constant it is still possible to obtain a unique dependence between the Wiener number and  $E_{\pi}$ , which is directly or inversely proportional depending on the factor remaining variable upon the molecular transformations described by the corresponding rules. When both factors, branching and cyclicity, are variable the dependence may have quite a complicated form containing extremes. Clearly in such cases, where the influence of molecular branching and cyclicity cannot be separated, the topological rules describe the overall molecular complexity. In addition, the situation for cyclic systems with acyclic branches is complicated due to the influence of other topological factors, such as the parity of cycles, the number of Kekulé structures, etc, acting in these molecules. As was demonstrated above, the latter often determine the trend in the  $\pi$ -electron energy. In the case of polycyclic condensed hydrocarbons, the potency of these factors was much weaker and was responsible only for insignificant deviations from the main regularity.<sup>49</sup>

In addition to providing a comparative analysis of the different topological contributions to the  $\pi$ -electron energy, the results of the present study also have important practical aspects. The topological rules introduced for cyclic molecules with acyclic branches can be applied to predict the relative ordering of isomers according to their  $\pi$ -electron energy and various molecular properties. Since the Wiener number is obtainable by elementary calculations, such predictions are accessible to every chemist. In addition, the rules based on the sum of topological distances in a molecular graph are of interest as a novel approach to structure-property and structure-activity correlations.<sup>48</sup> The major advantage of this approach is in the optimal selection of isomer samples to be used in a certain correlation. This selection is realized by means of the structural criteria used in the different topological rules. Thus, it seems that a promising way for obtaining pertinent correlations between molecular structure and properties is emerging.

*Acknowledgements.* — The authors are very much indebted to Professor O. E. Polansky (Mülheim/Ruhr) for helpful discussions on the formulation of some of the topological rules presented here. We also thank the referees for their comments.

## REFERENCES

1. V. M. Tatevskii, *Khimicheskoe stroenye uglevodorodov i zakonmernosti v ikh fiziko-khimicheskikh svoistv*, Nauka, Moscow 1953.
2. V. M. Tatevskii, V. A. Benderskii, and S. S. Yaravoi, *Metody rascheta fiziko-khimicheskikh svoistv parafinovykh uglevodorodov*, Nauka, Moscow 1960.
3. *Fiziko-khimicheskie svoistva individualnikh uglevodorodov*, Edited by V. M. Tatevskii, Nauka, Moscow 1960.
4. J.-E. Dubois, D. Laurent, and H. Veillard, *C. R. Acad. Sci. Paris* **263C** (1966) 764.
5. J.-E. Dubois, *DARC System in Chemistry*, in: *Proceedings of the NATO/CNA Advanced Study Institute on Computer Representation and Manipulation of Chemical Information*, Leewenhorst Congress 1973.
6. J.-E. Dubois, in: *Computer Representation and Manipulation of Chemical Information*, Edited by W. T. Wipke, S. Heller, R. Fieldmann, and E. Hyde, Wiley, New York 1974.
7. J. Chretien and J.-E. Dubois, *J. Chromatogr.* **126** (1976) 171.
8. D. Bonchev, J. V. Knop, and N. Trinajstić, *Math. Chem. (Mulheim/Ruhr)* **6** (1979) 21.
9. A. T. Balaban, *Theoret. Chim. Acta* **53** (1979) 355.
10. A. T. Balaban and I. Motoc, *Math. Chem. (Mulheim/Ruhr)* **5** (1979) 197.
11. A. T. Balaban, A. Chiriac, I. Motoc, and Z. Simon, *Lecture Notes in Chemistry*, Vol. 15, Springer-Verlag, Berlin 1980.
12. D. Bonchev, O. Mekenyan, and N. Trinajstić, *J. Comput. Chem.* **2** (1981) 127.
13. D. H. Rouvray, *RIC Rev.* **4** (1971) 173; *Chem. Britain* **10** (1974) 11.
14. I. Gutman and N. Trinajstić, *Topics Curr. Chem.* **42** (1973) 49; *Croat. Chem. Acta* **47** (1975) 507.
15. O. E. Polansky, *Math. Chem. (Mulheim/Ruhr)* **1** (1975) 183.
16. *Chemical Applications of Graph Theory*, Edited by A. T. Balaban, Academic, New York 1976.
17. A. Graovac, I. Gutman, and N. Trinajstić, *Lecture Notes in Chemistry*, Vol. 4, Spinger-Verlag, Berlin 1977.
18. V. Prelog, Nobel Lecture, December 12, 1975; reprinted in *Science* **193** (1976) 17.
19. O. Mekenyan, D. Bonchev, and N. Trinajstić, *Int. J. Quantum Chem.* **18** (1980) 369.
20. H. Wiener, *J. Am. Chem. Soc.* **69** (1947) 17; *ibid.* **69** (1947) 2636; *J. Chem. Phys.* **15** (1947) 766; *J. Phys. Chem.* **52** (1948) 425.
21. J. R. Platt, *J. Chem. Phys.* **15** (1947) 419; *J. Phys. Chem.* **56** (1962) 368.
22. E. Kovats, *Z. Anal. Chem.* **181** (1961) 351.
23. K. Altenburg, *Kolloid. Z.* **178** (1961) 112.
24. B. Gordon and G. R. Scantlebury, *Trans. Faraday Soc.* **60** (1964) 605.
25. H. Hosoya, *Bull. Chem. Soc. Japan* **44** (1971) 2332.
26. I. Gutman, B. Ruščić, N. Trinajstić, and C. F. Wilcox, Jr., *J. Chem.* **62** (1975) 3399.
27. M. Randić, *J. Am. Chem. Soc.* **97** (1975) 6609; *J. Chromatogr.* **161** (1978) 1.
28. L. B. Kier, L. H. Hall, W. J. Murray, and M. Randić, *J. Pharm. Sci.* **64** (1975) 1971.
29. L. B. Kier, W. J. Murray, M. Randić, and L. H. Hall, *J. Pharm. Sci.* **65** (1976) 8.
30. L. B. Kier and L. H. Hall, *Molecular Connectivity in Chemistry and Drug Research*, Academic, New York 1976.
31. R. Kaliszan and H. Foks, *Chromatographia* **10** (1977) 346.
32. R. Kaliszan, *Chromatographia* **10** (1977) 529.
33. R. Kaliszan and H. Lamparczyk, *J. Chromatogr.* **161** (1978) 246.
34. M. Randić, *Int. J. Quantum Chem.* **5** (1978) 245.
35. M. Randić and C. F. Wilkins, *J. Phys. Chem.* **83** (1979) 1525.
36. M. Randić and C. F. Wilkins, *J. Chem. Inf. Comp. Sci.* **19** (1979) 31.
37. D. Bonchev and N. Trinajstić, *J. Chem. Phys.* **67** (1977) 4517.
38. E. Heilbronner, *Helv. Chim. Acta* **37** (1954) 921.

39. V. Sahini, *J. Phys. Chem.* **59** (1962) 1977; *Rev. Roumaine Chim.* **7** (1962) 1265 *Rev. Chim. (Bucuresti)* **15** (1964) 551.
40. A. T. Balaban, *Rev. Roumaine Chim.* **15** (1970) 1243.
41. K. Kawasaki, K. Mizutani, and H. Hosoya, *Science Report of Ochanomizu University* **22** (1971) 181.
42. H. Hosoya, K. Kawasaki, and K. Mizutani, *Bull. Chem. Soc. Japan* **45** (1975) 3415.
43. H. Hosoya, M. Murakimi, and M. Gotoh, *Science Report of Ochanomizu University* **24** (1973) 27.
44. W. England and K. Ruedenberg, *J. Am. Chem. Soc.* **95** (1973) 8769.
45. D. Rouvray, *American Scientist* **61** (1973) 729; *Math. Chem. (Mulheim/Ruhr)* **1** (1975) 125.
46. D. Bonchev and N. Trinajstić, *Int. J. Quantum Chem.* **S12** (1978) 293.
47. D. Bonchev, Ov. Mekenyan, J. V. Knop, and N. Trinajstić, *Croat. Chem. Acta* **52** (1979) 361.
48. D. Bonchev, Ov. Mekenyan, G. Protić, and N. Trinajstić, *J. Chromatogr.* **176** (1979) 149.
49. D. Bonchev, Ov. Mekenyan, and N. Trinajstić, *Internat. J. Quantum Chem.* **17** (1980) 845.
50. H. Hosoya, K. Hosoi, and I. Gutman, *Theoret. Chim. Acta* **38** (1975) 37.
51. W. T. Yee, K. Sakamoto, and Y. J. I'Haya, *Rep. Univ. Electro-Comm.* **27-1** (1976) 53; K. Sakamoto, W. T. Yee, and Y. J. I'Haya, *Rep. Univ. Electro-Comm.* **27-2** (1977) 227.
52. D. Bonchev, Ov. Mekenyan, and N. Trinajstić, *Internat. J. Quantum Chem.* **19** (1981) 929.
53. Ov. Mekenyan, Ph. D. Thesis, Higher School of Chemical Technology, Burgas, 1980.
54. Ov. Mekenyan, D. Bonchev, and N. Trinajstić, *Math. Chem. (Mulheim/Ruhr)* **6** (1979) 93.
55. The term topology is used here (as is occasionally the case in chemical literature) in a »weak« sense, i.e., by recognizing atoms of valency two in molecular graphs. In a »strong« sense, when atoms of valency two are not discriminated, azulene and naphthalene would have the same topology, that of two fused rings (regardless of their size). The latter is sometimes referred to as the basic topology. The reader is reminded that topology is not a synonym for graphs. While metric is not defined for topology it is defined for graphs. As defined, the distance in a graph is topological invariant, but in topology there is no analogous invariant for figures or curves.
56. Ov. Mekenyan, D. Bonchev, and N. Trinajstić, *Math. Chem. (Mulheim/Ruhr)*, in press.
57. (a) B. A. Hess, Jr. and L. J. Schaad, *J. Am. Chem. Soc.* **93** (1971) 305.  
(b) L. J. Schaad and B. A. Hess, Jr., *J. Am. Chem. Soc.* **94** (1972) 3068.
58. N. Trinajstić, in: *Semiempirical Methods of Electronic Structure Calculation. Part A: Techniques*, Edited by G. A. Segal, *Modern Theoretical Chemistry*, Vol. 7, Plenum, New York, 1—27 (1977).
- 58a. R. B. Mallion and D. H. Rouvray, *Mol. Phys.* **13** (1978) 229; see also R. B. Mallion, *Croat. Chem. Acta*, in press.
59. I. Gutman and N. Trinajstić, *Chem. Phys. Lett.* **17** (1972) 535; A. Gravovac, I. Gutman, and N. Trinajstić, *Chem. Phys. Lett.* **35** (1975) 555; *ibid.* **37** (1976) 471.
60. I. Gutman and N. Trinajstić, *Chem. Phys. Lett.* **20** (1973) 257; *J. Chem. Phys.* **64** (1976) 4921.
61. E. Hückel, *Z. Physik* **76** (1932) 628.
62. M. J. S. Dewar and C. J. Gleicher, *J. Am. Chem. Soc.* **87** (1976) 685.
63. T. M. Krygowski, *Tetrahedron Lett.* (1970) 1311.
64. I. Gutman, M. Milun, and N. Trinajstić, *Croat. Chem. Acta* **44** (1972) 207.
65. J. Kruszewski and T. M. Krygowski, *Can. J. Chem.* **53** (1975) 945.
66. I. Gutman and N. Trinajstić, *Can. J. Chem.* **54** (1976) 1789.
67. H. C. Longuet-Higgins, *J. Chem. Phys.* **18** (1950) 265.

68. D. Cvetković, I. Gutman, and N. Trinajstić, *Croat. Chem. Acta* **44** (1972) 365.
69. D. Cvetković, I. Gutman, and N. Trinajstić, *J. Mol. Struct.* **28** (1975) 289.
70. N. Trinajstić, *Chemical Graph Theory*, in press.
71. C. F. Wilcox, Jr., *Tetrahedron Lett.* (1968) 795; *J. Am. Chem. Soc.* **91** (1969) 2732.
72. W. C. Herndon, *Tetrahedron* **29** (1973) 3.
73. M. J. S. Dewar and H. C. Longuet-Higgins, *Proc. Roy. Soc. (London)* **A 214** (1952) 482.

### SAŽETAK

#### Strukturna sastavljenost i molekularna svojstva cikličkih sistema s acikličkim ograncima

*Ov. Mekenyan, D. Bonchev i N. Trinajstić*

Stupanj strukturne sastavljenosti cikličkih molekula s acikličkim ograncima kantitativno je izražen pomoću pravila zasnovanih na promjeni sume topoloških udaljenosti, tj. Wienerovog broja, u odgovarajućim grafovima. Pokazano je da se ova topološka pravila dobro koreliraju sa svojstvima izomernih alkil-benzene.