A Topological Approach to the Calculation of the π-Electron Energy and Energy Gap of Infinite Conjugated Polymers [a]

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A procedure was developed, on the basis of the distance matrix of the graph, for the calculation of the specific π-electron energy and energy gap in polymerhomologous series and infinite polymers. 25 conjugated polymers were examined by this procedure and a fairly good correlation between these energy characteristics and the sum of all distances in the graph (the Wiener index) was found. A zero energy gap was shown to occur in 12 polymers. For polymers composed of condensed benzenoid and non-benzenoid cycles, a linear correlation was found between the Wiener index normalized to infinite polymer chains and the specific π-electron energy thus revealing possibilities for predictions proceeding from monomer topology only.

Introduction

The interest in the polymers having a conjugated π-electron chain has sharply risen during the last decade after the recognition of some of these polymers as potential high-temperature superconductors [1 – 3]. Treated as monodimensional crystals with different topology they are of interest for both theoreticians and experimentalists. The problem of the prediction of the π-electron energy and energy gap in polymers was treated by the conventional Hückel method and more elaborate methods like PPP, the finite differences method [4 – 6], etc. Due to the crucial importance of polymer topology, Graph Theory [7] was used in theoretical studies of this kind [8]. The influence of different structural factors on the existence of forbidden zones in conjugated polymers was studied and a number of general rules and conditions were formulated for such polymers to show high conductivity [9 – 12].

Another topological approach is developed in this paper. It is essentially based on the formulation of a topological index convenient for a quantitative description of infinite polymer chains. As will be shown below this index is likely to be very promicing for the prediction of the electron energy and energy gap in polymers that are potential conductors or semiconductors, as well as to be a reliable basis for more general structural considerations.

The Method

Albeit Graph Theory has various applications in chemistry [13, 14] it is usually applied to the graphical representations of chemical structures (molecules, polymers, crystals, etc.) whose atoms are depicted by points (vertices) while the chemical bonds – by lines (edges) connecting the points. Any arbitrary graph G appropriately labelled may be represented by a matrix. There are a number of ways of assigning a matrix to a graph. Chemists are usually familiar with the vertex adjacency matrix of the graph, $A(G)$, which is closely related to the Hückel hamiltonian matrix [15, 16]. The adjacency matrix A of a graph with N vertices is a $N \times N$ matrix, symmetrical to its principal diagonal, defined as follows:

$$A_{ij} = \begin{matrix} 1 \text{ for } i, j \text{ neighbours,} \\ 0 \text{ otherwise.} \end{matrix}$$

In this paper we make use of another matrix termed distance matrix of the graph, $D(G)$. It is again symmetrical $N \times N$ matrix whose entries d_{ij}, called distances, are equal to the number of bonds connecting two vertices in the shortest path between them. $d_{ij} = 1$ if i, j are neighbours, therefore all d_{ij} are by definition integers.

The distance matrix (N_k) is given [17] by the expression:

$$D(N_k) = d(N_k) + d^2(N_k) + d^3(N_k) + \cdots, \qquad (1)$$

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[a] Dedicated to Professor Oskar E. Polansky on the occasion of his 60th birthday.

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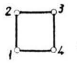
where $d^i(N_k)$ is the partial distance matrix. Each element in $d^i(N_k)$ is set equal to the i-value in the $A^i(N_k)$ matrix, the latter being a matrix of i times the adjacency matrix of the graph:

$$A(N_k)\,A(N_k)\dots A(N_k).$$

The graph of cyclobutadiene, as well as its adjacency and distance matrices, are presented below:



$$\begin{array}{r|l}
\text{Atoms} & 1\ 2\ 3\ 4 \\
\hline
1 & 0\ 1\ 0\ 1 \\
A(G) = 2 & 1\ 0\ 1\ 0 \\
3 & 0\ 1\ 0\ 1 \\
4 & 1\ 0\ 1\ 0
\end{array} \; ; \quad D(G) = \left\|\begin{array}{cccc} 0 & 1 & 2 & 1 \\ 1 & 0 & 1 & 2 \\ 2 & 1 & 0 & 1 \\ 1 & 2 & 1 & 0 \end{array}\right\| .$$

The half-sum of distance matrix elements:

$$W = \frac{1}{2} \sum_{ij=1}^{N} d_{ij} \qquad (2)$$

is said to be the path number or Wiener number of the graph. Wiener, who defined this number for acyclic hydrocarbons as the number of bonds between each pair of atoms in the molecule, found it to correlate well with a number of molecular properties [18]. Hosoya [19] extended this definition to cyclic graphs. Rouvray [20] proposed the sum of all distance matrix elements as a topological index characterizing the molecule. Therefore, his index is twice the Wiener number. In a series of papers Bonchev, Trinajstić et al. demonstrated that the Wiener number is a very appropriate measure of molecular branching [21, 22] and cyclicity [23–26] correlating fairly well with a number of thermodynamic properties [26 b], chromatographic retention data [27], etc.

All this encouraged us to extend the topological approach based on the distance matrix of the molecular graph in order to describe infinite polymer chains and their properties. A procedure was developed with this aim having the following stages:

1. The deduction of an equation for the Wiener number of a polymerhomologous series of compounds.
2. The normalization of the Wiener number.
3. The calculation of the normalized Wiener index for an infinite polymer chain.
4. The correlation between the normalized Wiener index and a certain property of a polymerhomologous series.
5. The prediction of the value which this property will have for an infinite polymer chain.

The first stage of this procedure is essentially based on the mathematical induction method. The distance matrix of the first several members of a polymerhomologous series was analyzed with this aim and the Wiener number was expressed as a polynomial of degree 3 related to the number of atoms N in the oligomers under consideration. This polynomial is obviously not appropriate for infinite polymer chains since it will tend to infinity when $N \to \infty$. Therefore, a modification of the Wiener number is necessary yielding a non-vanishing quantity in the case of infinite chains. This was done multiplying W by the normalized factor F:

$$F = 1/HB, \qquad (3)$$

where

$$H = N(N-1)/2, \qquad (4)$$

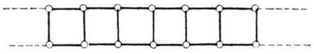
is the number of topological distances in the molecular graph (the half-sum of all entries of the distance matrix), and $B(N)$ is the number of bonds (or edges) of the graph. Evidently, HB is also a polynomial of degree 3. Then the limit of the normalized Wiener index, W, at $N \to \infty$ will be a finite number:

$$\tilde{\tilde{W}} = F\,W = W/HB, \qquad (5)$$

$$\tilde{\tilde{W}}_\infty = \lim_{N\to\infty} \tilde{\tilde{W}} \neq \infty. \qquad (6)$$

As seen from Eqs. (3–5), W is the mean topological distance per bond in the chemical structure under consideration.

The procedure is illustrated below by the infinite polybutadien chain:



for which we obtain:

$$W = (N^3 + 3N^2 - 4N)/12,$$
$$F = 4/(3N^3 - 7N^2 + 4N), \qquad (7)$$

and

$$\tilde{\tilde{W}}_\infty = \lim_{N\to\infty} \frac{N^3 + 3N^2 - 4N}{3(3N^3 - 7N^2 + 4N)} = 0.111. \qquad (8)$$

In order to check if the normalized Wiener index is an appropriate measure for the characterization of polymer chains, and, in particular, for predicting

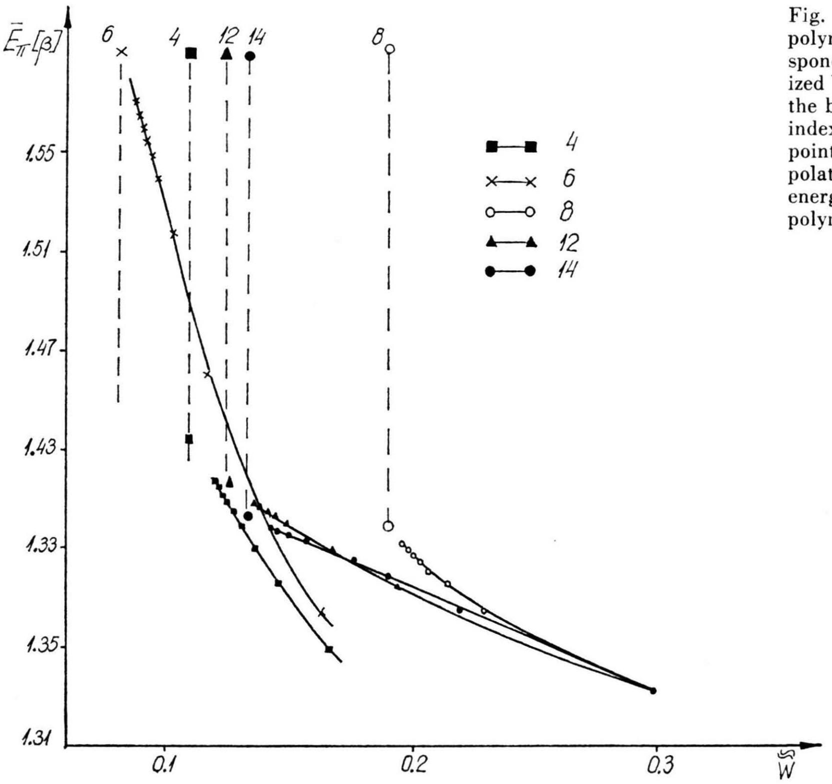


Fig. 1. The specific π-electron energy of 5 polymerhomologous series (Nos. correspond to those of Fig. 2) vs. their normalized Wiener index. The broken lines denote the bound values of the normalized Wiener index for the infinite polymers. The single point on each of these lines is the extrapolated values of the specific π-electron energy of the corresponding infinite polymer.

their π-electron energy and forbidden zone width, we have studied the correlation between these quantities. The least-square fitting resulted in equations in which each of the two polymer characteristics (taken here in the Hückel approximation) is a polynomial of degree one, two, or three of the normalized Wiener index. The program used eliminates the non-significant terms in the polynomial. Substituting the value of $\tilde{\tilde{W}}_\infty$ in these equations one completes the procedure obtaining the specific π-electron energy and energy gap of the infinite polymer under examination.

Thus, for polycyclobutadiene:

$$\bar{E}_\pi = 1.680 - 2.658\,\tilde{\tilde{W}} + 4.042\,\tilde{\tilde{W}}^2\,, \quad R = 1.000\,, \quad \sigma = 0.01\%\,, \qquad (9)$$

$$\Delta E_\pi = -1.545 + 17.633\,\tilde{\tilde{W}} - 32.20\,\tilde{\tilde{W}}^2\,, \quad R = 0.999\,, \quad \sigma = 1.1\%\,, \qquad (10)$$

$\bar{E}_\pi^\infty = 1.434$ (in β units); $\Delta E_\pi^\infty = 0.016$ (or ≈ 0).

Here R and σ are the correlation coefficient and the mean relative error, respectively.

As an illustration of the last two stages of the procedure we present in Fig. 1 the correlation between the specific π-electron energy and the normalized Wiener number for 5 polymerhomologous series. The vertical dashed lines correspond to $\tilde{\tilde{W}}_\infty$-values and indicate where the line of each series will end. As seen, the correlation is very high, being often linear.

Results. Discussion

The topological procedure developed above for the prediction of the specific π-electron energy (per electron) and energy gap of infinite conjugated polymer chains was applied to 25 open chain polymers (Figure 2). All the systems chosen can be viewed as models of a monodimensional crystal. These are mainly alternant benzenoid systems. Some non-benzenoid and non-alternant structures, polyenes and radialenes are also included. These structures differ considerably in their topology but the Wiener number reflects this difference very well.

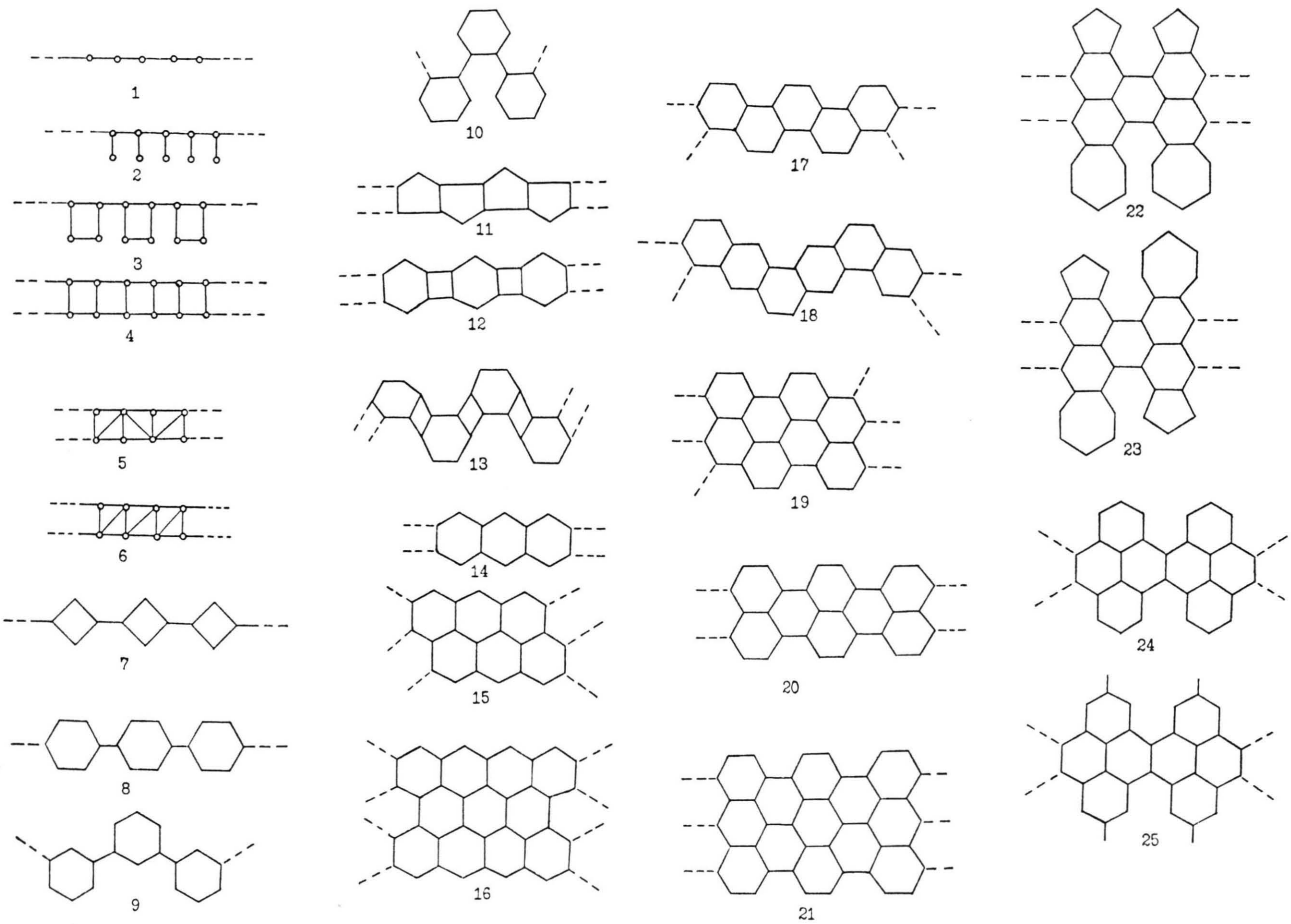


Fig. 2. 25 polymers under study representing quasimonodimensional systems with delocalized electrons.

The accuracy achieved in the prediction of the π-electron energies of polymeres is higher when more monomer units are taken into consideration. Due to this, the Hückel molecular orbital method, which provides calculations of larger oligomers, was preferred to the more accurate methods. Moreover, this enables us to compare our results with those of Polansky and Tyutyulkov [8], obtained as explicit expressions within the Hückel approximation, also using the finite differences method.

The results obtained in the first three stages of the procedure in use are given in Table 1. The Wiener number W and the normalizing factor F are presented there as polynomials of degree three. Some of the coefficients of these polynomials equal zero. In the case of structure 11, $A = 75$ and 72 for the system having odd and even number of cycles, respectively. Equations (19) and (21) hold for structures having more than two naphthalene fragments and more than one anthracene fragment, respectively. The values of the normalized Wiener index for the asymptotic case when $N \to \infty$ are given in the last column of Table 1. As seen, this topological index discriminates satisfactorily the examined polymers. The degeneracy of the index, which appears in several cases, does not practically influence the accuracy of the predictions made below for the electron energy and energy gap of the infinite polymers under study.

In Table 2 the equations are collected representing the specific π-electron energy, $\bar{E}_\pi$, of the 25 examined polymerhomologous series as a function of the normalized Wiener number. Some statistical characteristics of these correlations are also given, namely the correlation coefficient, R, the mean relative error, σ, in %, as well as the cardinality of

Table 1. The Wiener index, W, and the normalizing factor, F, as polynomial functions of the number of atoms, as well as the value of the normalized Wiener number, $\tilde{\tilde{W}}_\infty$, for the infinite polymers of Figure 2.

No.[a] 1	The Wiener number, W 2	Normalizing factor, F 3	$\tilde{\tilde{W}}_\infty$ 4
1	$(N^3-N)/6$	$(N^3-2N^2+N)/2$	0.3333
2	$(N^3+6N^2-10N)/12$	$(N^3-2N^2+N)/2$	0.1667
3	$(N^3+6N^2-16N)/12$	$(5N^3-9N^2+4N)/8$	0.1333
4	$(N^3+3N^2-4N)/12$	$(3N^3-7N^2+4N)/4$	0.1111
5	$(N^3+8N-12)/12$	$(2N^3-5N^2+3N)/2$	0.0833
6	$(2N^3+3N^2-2N)/24$	$(2N^3-5N^2+3N)/2$	0.0833
7	$N^3/8$	$(5N^3-9N^2+4N)/8$	0.2000
8	$(2N^3+9N)/18$	$(7N^3-13N^2+6N)/12$	0.1905
9	$(N^3+6N^2-18N)/12$	$(7N^3-13N^2+6N)/12$	0.1429
10	$(N^3+18N^2-63N)/18$	$(7N^3-13N^2+6N)/12$	0.0952
11	$(2N^3+3N^2+22N-\mathrm{A})/24$	$(4N^3-9N^2+5N)/6$	0.1250
12	$(N^3+3N^2)/12$	$(2N^3-5N^2+3N)/3$	0.1250
13	$(N^3+54N-216)/12$	$(2N^3-5N^2+3N)/3$	0.1250
14	$(N^3+3N^2+2N-12)/12$	$(5N^3-11N^2+6N)/8$	0.1333
15	$(N^3+8N^2+35N-188)/18$	$(4N^3-11N^2+7N)/6$	0.0833
16	$(N^3+15N^2+104N-384)/24$	$(11N^3-39N^2+28N)/16$	0.0606
17	$(N^3+50N-192)/12$	$(5N^3-11N^2+6N)/8$	0.1333
18	$(N^3+62N-264)/12$	$(5N^3-11N^2+6N)/8$	0.1333
19	$(N^3+219N-2580)/18$	$(4N^3-11N^2+7N)/6$	0.0833
20	$(2N^3+235N-1080)/30$	$(13N^3-33N^2+20N)/20$	0.1026
21	$(2N^3+1057N-10080)/42$	$(19N^3-61N^2+42N)/28$	0.0702
22	$(6N^3+108N^2+2907N-31104)/162$	$(23N^3-59N^2+36N)/36$	0.0580
23	$(2N^3+36N^2+993N-10\,800)/54$	$(23N^3-59N^2+36N)/36$	0.0580
24	$(196N^3+2793N^2-1372N-5880)/4116$	$(9N^3-20N^2+11N)/14$	0.0741
25	$(N^3+21N^2-13N-90)/24$	$(5N^3-11N^2+6N)/8$	0.0667

[a] According to Figure 2.

the set of pairs $(\bar{E}_\pi, \tilde{\tilde{W}})$ used in the correlation, i.e. the number of oligomers examined in each series. The correlation coefficient in 22 out of the studied 25 cases is 0.999 or 1.000. This is evidence in favour of the normalized Wiener index as a very appropriate topological index for the calculation of the π-electron energy of polymers. Further evidence is the mean relative error which in 16 cases is $\sigma \leqq 0.02\%$, and only in 4 cases is slightly greater than 0.1%. This high accuracy was achieved in 3 cases with a simple linear function, in 12 – with a quadratic function, and in 12 – by a complete or incomplete polynomial of degree 3. The influence of the degree of polynomial function on the results was studied by comparison of two or three polynomials of a different degree (some of them are shown in Table 2) derived on the same basis set of $(\bar{E}_\pi, \tilde{\tilde{W}})$ values. As expected, the higher the degree of the polynomial the better the results (see for instance structures 6, 11, 12, etc.). It is remarkable, however, that even the simplest linear equations provide a correlation coefficient close to 0.99 and a mean relative error not greater than 0.2%. All this indicates that the procedure developed in this paper for the prediction of the specific π-electron energy of polymer chains is accurate and simple in use thus competing with known Pade-approximation [29] usually applied for this purpose. The values of $\bar{E}_\pi^{\infty}$, calculated by us in β-units, were compared with those calculated from the explicit formulae derived within the Hückel approximation by Polansky and Tyutyulkov [28] (see the last two columns of Table 2). The coincidence achieved by the two methods is very high. The specific π-electron energy differ only in the third figure after the decimal point with the only exception of structure 21 where this difference is 0.012. Taking into account the difficulties in the deduction of the explicit formulae by means of the finite differences method in the more complicated cases, as well as the difficulties in the examination of the asymptotic, case $N \rightarrow \infty$, one comes again to a conclusion in favour of the large applicability of the approach developed in this paper.

Table 3 presents analogous results for the energy gap of the 24 polymerhomologous series under study. Structure 11 is not included here since the exclusive presence of 5-membered rings alters the highest occupied molecular orbital in a way in which no correlation with the normalized Wiener number

Table 2. The specific π-electron energy, E_π, of the 25 polymer-homologous series of Fig. 2 as a polynomial function of the normalized Wiener index, $\tilde{\tilde{W}}$ (R — correlation coefficient, σ — mean relative error).

No. [a] 1	Specific π-electron energy 2	σ, % [b] 3	R 4	$\bar{E}_\pi\infty$ [c] 5	$\bar{E}_\pi\infty$ [d] 6
1	$\bar{E}_\pi=1.532-0.7931\,\tilde{\tilde{W}}$	0.16^8	0.997	1.268	1.274
2	$\bar{E}_\pi=1.267-0.3256\,\tilde{\tilde{W}}+0.1003\,\tilde{\tilde{W}}^2$	0.00^{10}	1.000	1.216	1.216
3	$\bar{E}_\pi=1.454-0.8936\,\tilde{\tilde{W}}-1.085\,\tilde{\tilde{W}}^2$	0.01^8	1.000	1.316	
4	$\bar{E}_\pi=1.680-2.658\,\tilde{\tilde{W}}+4.042\,\tilde{\tilde{W}}^2$	0.01^{10}	1.000	1.435	
5	$\bar{E}_\pi=2.235-9.616\,\tilde{\tilde{W}}+29.17\,\tilde{\tilde{W}}^2$	0.05^{10}	0.999	1.636	
6	$\bar{E}_\pi=1.819-2.855\,\tilde{\tilde{W}}$	0.45	0.987	1.581	
	$\bar{E}_\pi=2.050-5.858\,\tilde{\tilde{W}}+61.82\,\tilde{\tilde{W}}^3$	0.21^{10}	0.998	1.598	
7	$\bar{E}_\pi=1.655-2.056\,\tilde{\tilde{W}}-3.612\,\tilde{\tilde{W}}^2+15.66\,\tilde{\tilde{W}}^3$	0.00^8	1.000	1.225	
8	$\bar{E}_\pi=1.684-2.097\,\tilde{\tilde{W}}+3.091\,\tilde{\tilde{W}}^2$	0.01^{10}	0.999	1.397	1.398
9	$\bar{E}_\pi=1.425-0.1115\,\tilde{\tilde{W}}-0.6513\,\tilde{\tilde{W}}^2$	0.01^{10}	1.000	1.396	
10	$\bar{E}_\pi=1.438-0.5688\,\tilde{\tilde{W}}+2.305\,\tilde{\tilde{W}}^2-5.233\,\tilde{\tilde{W}}^3$	0.01^{10}	0.999	1.400	1.399
11	$\bar{E}_\pi=1.628-1.696\,\tilde{\tilde{W}}$	0.02^8	0.999	1.416	
	$\bar{E}_\pi=1.588-1.299\,\tilde{\tilde{W}}-5.725\,\tilde{\tilde{W}}^3$	0.01	1.000	1.414	
12	$\bar{E}_\pi=1.470-0.4636\,\tilde{\tilde{W}}$	0.17^{10}	0.992	1.412	
	$\bar{E}_\pi=1.521-0.9912\,\tilde{\tilde{W}}+1.212\,\tilde{\tilde{W}}^2$	0.14	0.998	1.416	
13	$\bar{E}_\pi=1.628-2.204\,\tilde{\tilde{W}}+4.528\,\tilde{\tilde{W}}^2+0.6853\,\tilde{\tilde{W}}^3$	0.01^8	0.999	1.425	
14	$\bar{E}_\pi=1.458-0.4188\,\tilde{\tilde{W}}$	0.04^{12}	0.999	1.402	
15	$\bar{E}_\pi=1.502-0.606\,\tilde{\tilde{W}}$	0.02	0.999	1.452	1.455
16	$\bar{E}_\pi=1.506-0.6196\,\tilde{\tilde{W}}$	0.19^7	0.995	1.468	1.483
	$\bar{E}_\pi=1.539-1.115\,\tilde{\tilde{W}}+1.577\,\tilde{\tilde{W}}^2$	0.08	0.999	1.477	
17	$\bar{E}_\pi=1.805-4.961\,\tilde{\tilde{W}}+20.60\,\tilde{\tilde{W}}^2-32.10\,\tilde{\tilde{W}}^3$	0.02^8	0.999	1.434	1.437
18	$\bar{E}_\pi=1.545-0.9046\,\tilde{\tilde{W}}$	0.01^8	0.996	1.424	
	$\bar{E}_\pi=1.803-4.346\,\tilde{\tilde{W}}+11.44\,\tilde{\tilde{W}}^2$	0.01	0.999	1.427	1.429
19	$\bar{E}_\pi=1.645-2.900\,\tilde{\tilde{W}}+12.33\,\tilde{\tilde{W}}^2-22.11\,\tilde{\tilde{W}}^3$	0.05^9	0.999	1.476	1.484
20	$\bar{E}_\pi=1.525-0.7304\,\tilde{\tilde{W}}$	0.24^{12}	0.984	1.450	1.461
	$\bar{E}_\pi=1.634-2.225\,\tilde{\tilde{W}}+4.626\,\tilde{\tilde{W}}^2$	0.07	0.999	1.454	1.461
21	$\bar{E}_\pi=1.708-5.131\,\tilde{\tilde{W}}+33.91\,\tilde{\tilde{W}}^2-89.52\,\tilde{\tilde{W}}^3$	0.03^7	0.999	1.484	1.496
22	$\bar{E}_\pi=1.453-0.5373\,\tilde{\tilde{W}}$	0.12^6	0.995	1.422	
	$\bar{E}_\pi=1.480-1.030\,\tilde{\tilde{W}}+1.979\,\tilde{\tilde{W}}^2$	0.02	0.999	1.427	
23	$\bar{E}_\pi=1.473-0.8935\,\tilde{\tilde{W}}+1.429\,\tilde{\tilde{W}}^2$	0.02	0.999	1.426	
24	$\bar{E}_\pi=1.505-0.6604\,\tilde{\tilde{W}}+1.547\,\tilde{\tilde{W}}^3$	0.00^6	1.000	1.457	
25	$\bar{E}_\pi=1.412-0.5290\,\tilde{\tilde{W}}+4.155\,\tilde{\tilde{W}}^3$	0.01^6	0.999	1.378	

[a] — according to Fig. 2; [b] — the superscript stands for the number of oligomers used in the deduction of the correlation; [c] — calculated in this work; [d] — calculated by [28].

exists ($R=0.187$). In the other 24 cases the accuracy achieved is less than that of the specific π-electron energy but still it is very high. The correlation coefficient is in 16 cases equal to 0.999 or 1.000, and in the other 8 cases it is within the range 0.993 to 0.998. The mean relative error is in 14 cases less than 1%. In the other 10 cases it is greater than 1% due to the large *relative* but not absolute

Table 3. The energy gap, ΔE, of the 25 polymerhomologous series of Fig. 2 as a function of the normalized Wiener index $\tilde{\tilde{W}}$ (R — correlation coefficient, σ — mean relative error).

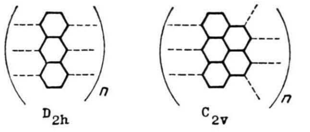
No. [a] 1	Energy gap 2	σ, % 3	R 4	ΔE_∞ [b] 5	ΔE_∞ [c] 6
1	$\Delta E = -4.016 + 13.69\,\tilde{\tilde{W}} - 14.57\,\tilde{\tilde{W}}^3$	0.57	1.000	0.007	
2	$\Delta E = 0.8103 + 3.210\,\tilde{\tilde{W}}^3$	0.18	0.999	0.825	0.828
3	$\Delta E = 0.3570 + 6.773\,\tilde{\tilde{W}}^3$	0.70	0.993	0.373	
4	$\Delta E = -1.545 + 17.63\,\tilde{\tilde{W}} - 32.20\,\tilde{\tilde{W}}^2$	1.10	1.000	0.017	0
5	$\Delta E = 0.7453 + 97.24\,\tilde{\tilde{W}}^3$	0.70	0.995	0.802	
6	$\Delta E = -0.4888 + 4.057\,\tilde{\tilde{W}} + 25.25\,\tilde{\tilde{W}}^2$	3.93	0.999	0.024	
7	$\Delta E = -4.287 + 25.94\,\tilde{\tilde{W}} - 111.7\,\tilde{\tilde{W}}^3$	0.48	1.000	0.007	
8	$\Delta E = -4.585 + 308.1\,\tilde{\tilde{W}}^2 - 849.8\,\tilde{\tilde{W}}^3$	0.72	0.998	0.721	0.828
9	$\Delta E = 1.408 - 20.69\,\tilde{\tilde{W}}^2 + 90.82\,\tilde{\tilde{W}}^3$	0.38	0.999	1.251	
10	$\Delta E = 0.0923 + 11.06\,\tilde{\tilde{W}} - 47.58\,\tilde{\tilde{W}}^2 + 106.3\,\tilde{\tilde{W}}^3$	0.35	0.999	0.806	0.890
12	$\Delta E = -2.573 + 22.82\,\tilde{\tilde{W}} - 25.26\,\tilde{\tilde{W}}^2$	8.35	0.997	0 [d]	0
13	$\Delta E = -0.7466 + 12.20\,\tilde{\tilde{W}} - 100.2\,\tilde{\tilde{W}}^3$	0.50	0.999	0.583	0.494
14	$\Delta E = -2.841 + 21.17\,\tilde{\tilde{W}} - 55.79\,\tilde{\tilde{W}}^3$	6.10	0.999	0 [d]	0
15	$\Delta E = -1.890 + 20.84\,\tilde{\tilde{W}} - 136.8\,\tilde{\tilde{W}}^3$	8.72	0.999	0 [d]	0
16	$\Delta E = -0.9805 + 12.30\,\tilde{\tilde{W}} - 36.30\,\tilde{\tilde{W}}^3$	13.3	0.999	0 [d]	0
17	$\Delta E = -1.439 + 23.00\,\tilde{\tilde{W}} - 49.29\,\tilde{\tilde{W}}^2$	0.23	0.999	0.751	0.764
18	$\Delta E = 0.4951 + 86.75\,\tilde{\tilde{W}}^3$	0.53	0.993	0.701	0.695
19	$\Delta E = -2.350 + 60.71\,\tilde{\tilde{W}} - 389.1\,\tilde{\tilde{W}}^2 + 848.9\,\tilde{\tilde{W}}^3$	0.88	0.998	0.518	0.494
20	$\Delta E = -10.73 + 138.9\,\tilde{\tilde{W}} - 3232\,\tilde{\tilde{W}}^3$	0.34	1.000	0.030	0
21	$\Delta E = -0.6541 + 8.879\,\tilde{\tilde{W}}$	4.37	0.999	0 [d]	0.469
22	$\Delta E = -0.0641 + 11.55\,\tilde{\tilde{W}}^2$	95.2	0.997	0 [d]	
23	$\Delta E = -0.1953 + 2.816\,\tilde{\tilde{W}}$	16.3	0.995	0 [d]	
24	$\Delta E = 0.3366 + 3.551\,\tilde{\tilde{W}} - 2.539\,\tilde{\tilde{W}}^3$	0.09	0.999	0.599	
25	$\Delta E = 0.1083 + 0.5665\,\tilde{\tilde{W}} - 3.244\,\tilde{\tilde{W}}^3$	0.21	0.999	0.145	

[a] — according to Fig. 2; [b] — calculated in this work; [c] — according to Ref. [28]; [d] — approximate value.

deviation from the zero value of the energy gap. Thus, in spite of these high relative errors, the correlation coefficient is usually very high (see for instance structure 22). All this evidences show that the topological index used in our approach reflects quite satisfactorily the magnitude of the energy gaps in polymer chains with delocalized electrons.

It can also be seen from Table 3 that polynomials of degree 3 are usually the ones to provide high accuracy. Still, in some cases quadratic or even linear functions (structures 21 and 23) yield fairly good predictions of the energy gap.

In 12 cases, namely for structures 1, 4, 6, 7, 12, 14, 15, 16, 20, 21, 22, and 23, a zero energy gap was found. (We include here the cases where the energy gap is within the range ± 0.03, i. e. within the error limits of the procedure in use.) In 6 out of 7 cases our predictions coincide with the results of Polansky and Tyutyulkov [28] (the other five polymers are studied only in this paper). In the cases where both calculations show the presence of an energy gap they accord quite well ($\Delta \leqq 0.024$) in the case of 4 polymers (Nos. 2, 17, 18, 19). The unsatisfactory coincidence established in the case of structures 8 ($\Delta = 0.107$), 19 ($\Delta = 0.089$), and 10 ($\Delta = 0.084$) is most probably a consequence of the different symmetry of the infinite polymers which here were taken having an open chain but taken having a closed chain (cyclopolymers) in [28]. The single drastic difference between the two calculations seems to have a similar origin. It refers to polymer 21 for which in this paper we predict a lack of energy gap whereas in [28] a gap of 0.47 was reported. In order to check our arguments we have recalculated structure 21 with an open chain whose elementary link to be of C_{2v}-symmetry like that of the cyclo-polymer:



an open chain polymer; a cyclo-polymer
(this paper) (Ref. [28]).

The correlation thus obtained was very high:

$$\Delta E_\pi^\infty = -0.9556 + 18.32\,\tilde{\tilde{W}} - 350.9\,\tilde{\tilde{W}}^3 \qquad (11)$$

with $\sigma = 0.3\%$, $R = 0.9999$, and $\Delta E_\pi^\infty = 0.209$ which is approximately half the value for the cyclopolymer of the same symmetry, and in any case indicates the presence of an energy gap in this polymer. Still, the three different bounds for the energy gap of infinite polymer 21 seem confusing and need further explanations.

Since the normalized Wiener number appeared as a reliable topological measure of the π-electron characteristics of polymers it was important to check if the results obtained might be generalized in order to provide predictions of such characteristics for a wide range of polymers. We studied the presence of a correlation between the values of the specific π-electron energy and the normalized Wiener index for the infinite polymers under consideration. Naturally, one should not expect all 25 cases to be included in one and the same correlation since these systems differ greatly in their topology (acyclic, condensed polycyclic, bridged polycyclic, and branched polycycli systems) and the Wiener number behaves differently within classes of structures. A good linear correlation was however obtained (Eq. (12) and Fig. 3) for the condensed non-branched benzenoid and non-benzenoid infinite polymers, excluding only the polymers with three-membered rings (Nos. 5 and 6):

$$\bar{E}_\pi^\infty = 1.533 - 0.851\,\tilde{\tilde{W}}_\infty\,, \quad R = 0.902\,, \quad \sigma = 0.01\,. \qquad (12)$$

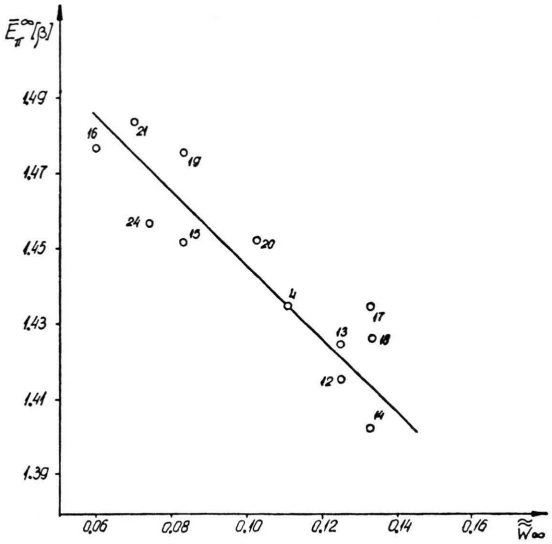
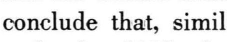


Fig. 3. A linear correlation between the specific π-electron energy and the normalized Wiener index for some benzenoid and non-benzenoid polymers shown in Figure 2.

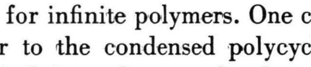
As seen, a reverse proportional dependence exists between the values of the specific π-electron energy and the Wiener index for infinite polymers. One can conclude that, similar to the condensed polycyclic molecules [22], the infinite polymers also have a greater π-electron energy when their cyclicity is greater, i. e. at a smaller value of the Wiener number.

One should also stress the capability of the Wiener number to reproduce very well the great topological similarity between systems having approximately the same specific π-electron energy. Thus, $\tilde{\tilde{W}}_\infty = 0.0580$ for both infinite polymers 22 and 23 which have $\bar{E}_\pi^\infty = 1.427$ and $\bar{E}_\pi^\infty = 1.426$, respectively. Similarly, $\tilde{\tilde{W}}_\infty = 0.0833$ for the pair of polymers 5 and 6 which have $\bar{E}_\pi^\infty = 1.636$ and 1.596, respectively.

Illustrating the possibilities revealed by Eq. (12) we have predicted the specific π-electron energy of the following infinite polymers:



26



27

$$W_{26} = (N^3 + 8\,N^2 - 9\,N)/18\,, \qquad (13)$$

$$W_{27} = (2\,N^3 + 21\,N^2 - 48\,N + 32)/36\,, \qquad (14)$$

Structure 26:

$$\tilde{\tilde{W}}_\infty = 0.0667\,, \quad \bar{E}_\pi{}^\infty = 1.476\,,$$

Structure 27:

$$\tilde{\tilde{W}}_\infty = 0.0870\,, \quad \bar{E}_\pi{}^\infty = 1.459\,.$$

Other infinite polymers having non-branched benzenoid or non-benzenoid condensed cycles can be treated in this way. Thus, Eq. (12) may be of interest since it provides a fast prediction of the π-electron energy of this important class of infinite conjugated polymers.

Concluding Remarks

The results obtained in this paper seem interesting in several aspects. The independent arrival at the same specific π-electron energy and energy gap in polymers by two different approaches (the present one and that developed by Polansky and Tyutyulkov [28]) confirms the reliability of each of them. However, we can cite as an argument in favour of the present approach the possibilities of application to polymers of more complicated topology, including non-alternant structures, as well as the applicability within each MO – LCAO-method. Related to this, Pariser-Parr-Pople type studies are now in progress [30].

This work also demonstrates the capability of a topological index (the normalized Wiener index) to reproduce the electron characteristics of infinite polymers well. Generalization like that presented in Eq. (12) and Fig. 3, could facilitate the calculations of the π-electron energy of infinite polymers making use of monomer topology only. Other physical or chemical quantities could be similarly treated, thus developing a general graph-theoretical scheme for the prediction of polymer properties.

Finally, the present paper might be viewed as evidence that, in the case of polymers, topology is the major factor determining the properties of chemical structures.

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