A Topological Approach to the Predicting of the Electron Energy Characteristics of Conjugated Infinite Polymers.
II. PPP-Calculations

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A topological extrapolation procedure is applied (within the PPP-method) to the predicting of the mean π-electron energy and energy gaps of 10 infinite polymers composed of benzenoid units.

In the first communication of this series [1], a topological extrapolation procedure was proposed for predicting the properties of infinite polymers. In particular, the mean π-electron energy, $\bar{E}_\pi$, and the energy gap, ΔE, of 25 infinite polymers with various topologies were calculated within the Hückel approximation. The same extrapolation procedure is applied in this paper making use of the PPP-method; 10 benzenoid as well as nonbenzenoid alternant polymers (Fig. 1) were treated as models of infinite monodimensional crystals. The program used permitted the investigations of oligomers having up to 50 atoms.

The approach is based on the calculation of the total topological path within the molecule, usually called the Wiener number [2], W, which proved to be a very convenient tool in various structure-property correlations [3–8]. Table 1 contains the intermediate results after the first three stages of our procedure: the polynomials for the Wiener index, the normalizing factor, F, as well as the normalized Wiener numbers, $\tilde{\tilde{W}}_\infty$, that correspond to the infinite polymers.

Within the fourth stage of the extrapolation procedure, the least-square correlations were derived for $\bar{E}_\pi$ and ΔE versus the normalized topological index of Wiener. The results are presented in Tables 2 and 3.

The statistical characteristics of the equations from Tables 2 and 3 are somewhat worse as compared with the previous results, obtained by means of the conventional Hückel-method. This is due to the fact that the Wiener index and the Hückel-method are essentially topological in nature while the use of the specific molecular geometry within the PPP-method causes some deviations. Nevertheless the accuracy achieved in the correlations is quite good. Thus, the correlation coefficient of the equations from Table 2 is within the range $0.973 \leqq R \leqq 0.9996$. This accuracy is achieved in two cases by the use of a simple linear function, and in the eight others by a quadratic function. In Table 3, the correlation coefficient is within the range $0.9851 \leqq R$

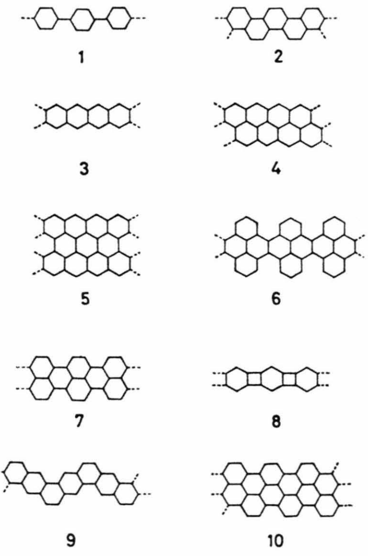
1 2 3 4 5 6 7 8 9 10

Fig. 1. Infinite conjugated polymers under examination.

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Table 1. Equations for the Wiener index, W, the normalizing factor, F, and the values of the normalized Wiener index, $\tilde{\tilde{W}}_\infty$, corresponding to the infinite polymer chains studied.

Structure No.[a]	W[b]	F[b]	$\tilde{\tilde{W}}_\infty$
1	$(2N^3+9N)/18$	$(7N^3-13N^2+6N)/12$	0.1905
2	$(N^3+50N-192)/12$	$(5N^3-11N^2+6N)/8$	0.1333
3	$(N^3+3N^2+2N-12)/12$	$(5N^3-11N^2+6N)/8$	0.1333
4	$(N^3+8N^2+35N-188)/18$	$(4N^3-11N^2+7N)/6$	0.0833
5	$(N^3+15N^2+104N-384)/24$	$(11N^3-39N^2+28N)/16$	0.0606
6	$(196N^3+2793N^2-1372N-5880)/4116$	$(9N^3-20N^2+11N)/14$	0.0741
7	$(2N^3+235N-1080)/30$	$(13N^3-33N^2+20N)/20$	0.1026
8	$(N^3+3N^2)/12$	$(2N^3+5N^2+3N)/3$	0.1250
9	$(N^3+62N-264)/12$	$(5N^3-11N^2+6N)/8$	0.1333
10	$(N^3+291N-2380)/18$	$(4N^3-11N^2+7N)/6$	0.0833

[a] The structure numbers are the same as those of Figure 1. [b] N denotes the total number of carbon atoms.

Table 2. The specific π-electron energy ($\bar{E}_\pi$) of the polymer homologue series of Fig. 1 as a function of the normalized Wiener index ($\tilde{\tilde{W}}$); the predicted values of the specific π-electron energy of the infinite polymers ($\bar{E}_\pi^\infty$); the correlation coefficient (R), and the mean square deviation (σ).

Structure No.	Pairs $\bar{E}_\pi/\tilde{\tilde{W}}$	$\bar{E}_\pi = f(\tilde{\tilde{W}})$	R	σ	$\bar{E}_\pi^\infty$
1	8	$\bar{E}_\pi = 428.991 - 3081.98\,\tilde{\tilde{W}} + 5646.45\,\tilde{\tilde{W}}^2$	0.9874	1.8965	46.7849
2	12	$\bar{E}_\pi = 173.847 - 1247.79\,\tilde{\tilde{W}} + 2375.56\,\tilde{\tilde{W}}^2$	0.9732	2.9469	49.7277
3	12	$\bar{E}_\pi = 176.403 - 1247.61\,\tilde{\tilde{W}} + 2343.45\,\tilde{\tilde{W}}^2$	0.9848	2.0442	51.7371
4	7	$\bar{E}_\pi = 150.136 - 1282.12\,\tilde{\tilde{W}} + 3113.68\,\tilde{\tilde{W}}^2$	0.9946	1.4960	64.9409
5	5	$\bar{E}_\pi = 119.642 - 945.362\,\tilde{\tilde{W}} + 2234.48\,\tilde{\tilde{W}}^2$	0.9966	1.5072	70.6021
6	3	$\bar{E}_\pi = 93.5484 - 425.605\,\tilde{\tilde{W}}$	0.9823	3.3273	62.0111
7	5	$\bar{E}_\pi = 209.534 - 1971.89\,\tilde{\tilde{W}} + 5017.22\,\tilde{\tilde{W}}^2$	0.9938	2.1391	60.0332
8	8	$\bar{E}_\pi = 163.021 - 1179.48\,\tilde{\tilde{W}} + 2260.26\,\tilde{\tilde{W}}^2$	0.9899	1.8696	50.8964
9	4	$\bar{E}_\pi = 153.940 - 757.173\,\tilde{\tilde{W}}$	0.9828	1.4800	53.0088
10	7	$\bar{E}_\pi = 138.376 - 1163.46\,\tilde{\tilde{W}} + 2819.56\,\tilde{\tilde{W}}^2$	0.9928	1.8208	61.0244

$\leqq 1.0000$. A simple linear function is again sufficient in five cases.

Substitution of the $\tilde{\tilde{W}}_\infty$ values in these correlation equations terminates the procedure by obtaining the mean π-electron energy, $\bar{E}_\pi{}^\infty$, and the energy gap, ΔE_∞, of the infinite polymers under examination. These extrapolated values are also given in Tables 2 and 3. In the second column of these tables we present the number of pairs $\bar{E}_\pi$ (or ΔE)/W that were used in the correlation sample. One may note that, due to the large monomer size, for polymers 6 and 9 only 3 and 4 points, respectively, could be computed. Correspondingly, this affects the reliability of the energetic characteristics obtained for these infinite polymers.

In our first communication [1], we have found a good inverse proportional dependence of the Hückel π-electron energy on the normalized Wiener index of the infinite polymers (condensed benzenoid and non-benzenoid ones). Thus, we have examined here the possibility of a similar generalization for the PPP-π-electron energy. The correlation so obtained is given below:

$$\bar{E}_\pi{}^\infty = 90.3624 - 396.916\,\tilde{\tilde{W}}_\infty + 774.396\,\tilde{\tilde{W}}^2_\infty;$$
$$R = 0.9577, \quad \sigma = 2.4055,$$

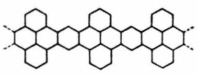
and is illustrated in Figure 2.

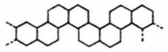
It is seen that also in the case of the more precise PPP-method, an inverse proportional dependence exists between the Wiener index and the mean π-electron energy. Thus, possibilities are revealed for

Table 3. Energy gap (ΔE) of the polymer homologue series of Fig. 1 as functions of the normalized Wiener index ($\tilde{\tilde{W}}$). Predicted values of the gap of the infinite polymers (ΔE^∞); R-correlation coefficient, σ-mean square deviation.

Structure No.	Pairs $\Delta E/\tilde{\tilde{W}}$	$\Delta E = f(\tilde{\tilde{W}})$	R	σ	ΔE^∞
1	8	$\Delta E = 14.5817 + 149.204\,\tilde{\tilde{W}} - 232.485\,\tilde{\tilde{W}}^2$	1.0000	0.0100	5.4047
	8	$\Delta E = -0.5351 + 33.1020\,\tilde{\tilde{W}}$	0.9871	0.1982	5.7708
2	12	$\Delta E = 2.38986 + 22.624\,\tilde{\tilde{W}}$	0.9912	0.1466	5.4056
	12	$\Delta E = 2.72878 + 19.9982\,\tilde{\tilde{W}} + 17.961\,\tilde{\tilde{W}}^2$	0.9915	0.1526	5.4371
3	12	$\Delta E = -2.66282 + 41.3024\,\tilde{\tilde{W}}$	0.9851	0.3321	2.8428
	12	$\Delta E = -7.77305 + 79.6441\,\tilde{\tilde{W}} - 254.308\,\tilde{\tilde{W}}^2$	0.9999	0.02	2.2412
4	7	$\Delta E = -9.00317 + 145.017\,\tilde{\tilde{W}} - 328.065\,\tilde{\tilde{W}}^2$	1.0000	0.0173	0.8003
5	5	$\Delta E = -4.3522 + 90.8315\,\tilde{\tilde{W}} - 171.696\,\tilde{\tilde{W}}^2$	1.0000	0.01	0.5224
6	3	$\Delta E = 3.46937 + 14.2638\,\tilde{\tilde{W}}$	1.0000	0.00	4.5263
7	5	$\Delta E = -7.16645 + 126.464\,\tilde{\tilde{W}} - 281.688\,\tilde{\tilde{W}}^2$	0.9992	0.0781	2.8435
8	8	$\Delta E = -2.6080 + 50.0537\,\tilde{\tilde{W}} - 116.69\,\tilde{\tilde{W}}^2$	1.0000	0.0245	3.4212
	8	$\Delta E = -0.313206 + 32.3152\,\tilde{\tilde{W}}$	0.9962	0.1643	3.7265
9	4	$\Delta E = 2.01919 + 23.0115\,\tilde{\tilde{W}}$	0.9882	0.0374	5.0866
10	7	$\Delta E = 3.39488 + 15.2023\,\tilde{\tilde{W}} + 24.1874\,\tilde{\tilde{W}}^2$	0.9872	0.1470	4.6752
	7	$\Delta E = 3.21483 + 17.114\,\tilde{\tilde{W}}$	0.9870	0.1327	4.6404

predicting PPP-π-electron energies of infinite polymers using their topology only. To illustrate these possibilities, the above equation was used for the following infinite polymers:





$\bar{E}_\pi^{\infty} = 61.69$ eV, $\bar{E}_\pi^{\infty} = 58.41$ eV.

Table 4. Comparison between the predicted energy gaps, obtained by means of the topological extrapolation procedure making use of the conventional Hückel method and the PPP-method.

Structure No.	ΔE^∞ [β] by Hückel[a]	ΔE^∞ [eV] PPP
1	0.721	5.4047
2	0.751	5.4056
3	0.00	2.8428
4	0.00	0.8003
5	0.00	0.5224
6	0.590	4.5263
7	0.00	2.8435
8	0.00	3.4212
9	0.701	5.0866
10	0.518	4.6752

[a] The energy equivalent of [β] lies within the range 1.1 to 4.0 eV [10].

Table 4 indicates that, as anticipated [9], the predicted energy gaps in the polymers studied are always greater when obtained by the PPP-method than those found earlier by the conventional Hückel method. It is seen from this comparison that the structures having zero gap within the Hückel ap-

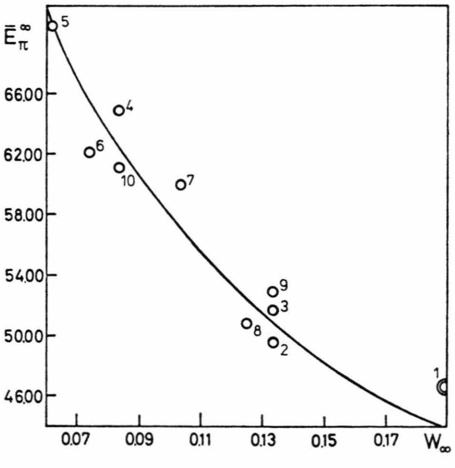


Fig. 2. Correlation between the specific π-electron energy and the topological index of Wiener of infinite alternant polymers composed of benzenoid units. The numbering is the same as in Figure 1.

proximation have, in general, small gaps within the PPP-method while the structures with non-zero gap in the first method have much higher gaps in the second one. Polymers 4 and 5 were obtained with a fairly low gap which is an indication for a possible enhanced conductivity in these polymers. It should be noted that results for polymers 2 and 4 – 10 have previously not been published.

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