# A Topological Approach to the Predicting of the Electron Energy Characteristics of Conjugated Infinite Polymers. III. The Influence of Some Structural Modifications of Polymers

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The influence of acyclic conjugated branches on the $\pi$-electron energy and energy gaps of infinite polymers containing benzene rings is studied applying a graph-theoretical extrapolation scheme. It is found that methylene branches strongly reduce the energy gap of the unmodified polymers.

In the first communications of this series [1, 2], the energy gaps, $\Delta E$, of a number of infinite conjugated polymers containing cycles were obtained applying a graph-theoretical extrapolation procedure within the Hückel approximation. Some of these polymers (see Fig. 1) are subjected in this study to a certain structural modification. Specifically, it includes the formation of acyclic conjugated branches with one and two atoms, preserving the conjugated character of polymers (Figure 2).

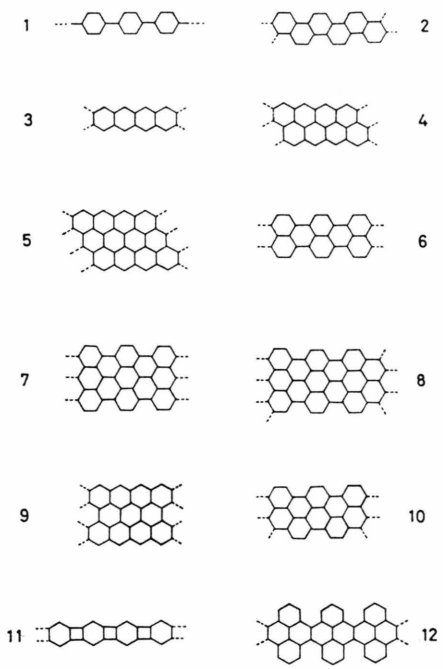


Fig. 1. Unmodified infinite conjugated polymers studied in our first communication.

The polynomials for the Wiener index [3, 4], $W$, as well as for the normalizing factor, $F$, were determined applying the first three stages of the extrapolation procedure (Table 1). The values of the normalized Wiener index, $\tilde{W}^{\infty}$, of the infinite modified polymers are also given in Table 1. As seen, $\tilde{W}_{\infty}$ discriminates in most cases between the polymers studied.

In the fourth stage of the procedure, we have calculated (within the Hückel approximation) the energy gaps of the oligomer chains of the modified structures under examination. The program used in the quantum chemical calculations provided possibilities of dealing with oligomers with up to 160 atoms. The leastsquare fit between the energy gap and the normalized Wiener index of each polymerhomologue series is shown in Table 2 together with the predicted values of the energy gap of the infinite modified polymer chains, obtained in the final stage of the procedure. A total of 35 equations are suggested for the 24 modified polymers under study. In 31 of them, the correlation coefficient is 0.999 or 1.000, and only in 4 cases (polymers 3 b, 5 b, 8 a, 10 b) is it within the range 0.977 – 0.994. In view of previous analysis [1] we conclude that this is convincing evidence of the ability of the normalized Wiener index to predict correctly the calculated energy gap of polymers. The mean-

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Table 1. Polynomials for the Wiener index, $W$, the normalizing factor, $F$, as well as the values of the normalized Wiener index, $\tilde{W}_\infty$, of the infinite polymers from Figure 2.

| Structure[a] No. | The Wiener index polynomial[b c] | The normalizing factor $F$[c] | The normalized Wiener index $\tilde{W}_\infty$ |
|---|---|---|---|
| 1a | $(2N^3 + 12N^2 + 7N - 48)/30$ | $(11N^3 - 23N^2 + 12N)/20$ | 0.1212 |
| 1b | $(2N^3 + 36N^2 - 35N - 144)/42$ | $(15N^3 - 33N^2 + 18N)/28$ | 0.0889 |
| 2a | $(N^3 + 6N^2 + 129N - 1008)/18$ | $(7N^3 - 19N^2 + 12N)/12$ | 0.0952 |
| 2b | $(N^3 + 18N^2 + 224N - 2808)/24$ | $(9N^3 - 27N^2 + 18N)/16$ | 0.0740 |
| 3a | $(2N^3 + 21N^2 - 12N - 40)36$ | $(7N^3 - 15N^2 + 8N)/12$ | 0.0952 |
| 3b | $(N^3 + 24N^2 - 40N)/24$ | $(9N^3 - 19N^2 + 10N)/16$ | 0.0740 |
| 4a | $(7N^3 + 198N^2 - 592N + 2208)/192$ | $(5N^3 - 13N^2 + 8N)/8$ | 0.0583 |
| 4b | $(5N^3 + 162N^2 + 439N - 5568)/150$ | $(6N^3 - 15N^2 + 9N)/10$ | 0.0556 |
| 5a | $(10N^3 + 261N^2 + 2888N - 30984)/300$ | $(13N^3 - 41N^2 + 28N)/20$ | 0.0512 |
| 5b | $(2N^3 + 87N^2 + 780N - 11340)/72$ | $(5N^3 - 15N^2 + 10N)/8$ | 0.0445 |
| 6a | $(2N^3 + 13N^2 + 571N - 4620)/42$ | $(17N^3 - 57N^2 + 40N)/28$ | 0.0784 |
| 6b | $(6N^3 + 110N^2 + 2857N - 33292)/162$ | $(7N^3 - 27N^2 + 20N)/12$ | 0.0634 |
| 7a | $(2N^3 + 12N^2 + 2211N - 32004)/54$ | $(23N^3 - 107N^2 + 84N)/36$ | 0.0580 |
| 7b | $(88N^3 + 1719N^2 + 149990N - 2876112)/290$ | $(27N^3 - 153N^2 + 126N)/44$ | 0.0493 |
| 8a | $(6N^3 + 46N^2 + 6829N - 118356)/162$ | $(23N^3 - 91N^2 + 68N)/36$ | 0.0580 |
| 8b | $(11N^3 + 198N^2 + 22000N - 490083)/363$ | $(27N^3 - 124N^2 + 97N)/44$ | 0.0494 |
| 9a | $(10N^3 + 261N^2 + 2012N - 12264)/300$ | $(13N^3 - 45N^2 + 32N)/20$ | 0.0512 |
| 9b | $(N^3 + 43N^2 + 298N - 2592)/36$ | $(5N^3 - 17N^2 + 12N)/8$ | 0.0445 |
| 10a | $(N^3 + 6N^2 + 650N - 7848)/24$ | $(5N^3 - 13N^2 + 8N)/8$ | 0.0666 |
| 10b | $(N^3 + 18N^2 + 1109N - 17988)/30$ | $(6N^3 - 15N^2 + 9N)/10$ | 0.0556 |
| 11a | ... NBMO | nonbonding MO appears | |
| 11b | $(N^3 + 17N^2 - 20N)/20$ | $(3N^3 - 8N^2 + 5N)/5$ | 0.0833 |
| 12a | $(N^3 + 21N^2 - 13N - 90)/24$ | $(5N^3 - 11N^2 + 6N)/8$ | 0.0666 |
| 12b | $(12N^3 + 371N^2 - 710N + 4376)/324$ | $(11N^3 - 24N^2 + 13N)/18$ | 0.0606 |

[a] The numbering corresponds to that of Figure 2.
[b] The expression for the Wiener index of polymers 5b, 7a, 7b, 8a, 8b are valid for the number of monomer units $Z > 1$, while those of polymers 5a, 10a, 10b — for $Z > 2$, respectively.
[c] $N$ denotes the total number of carbon atoms.

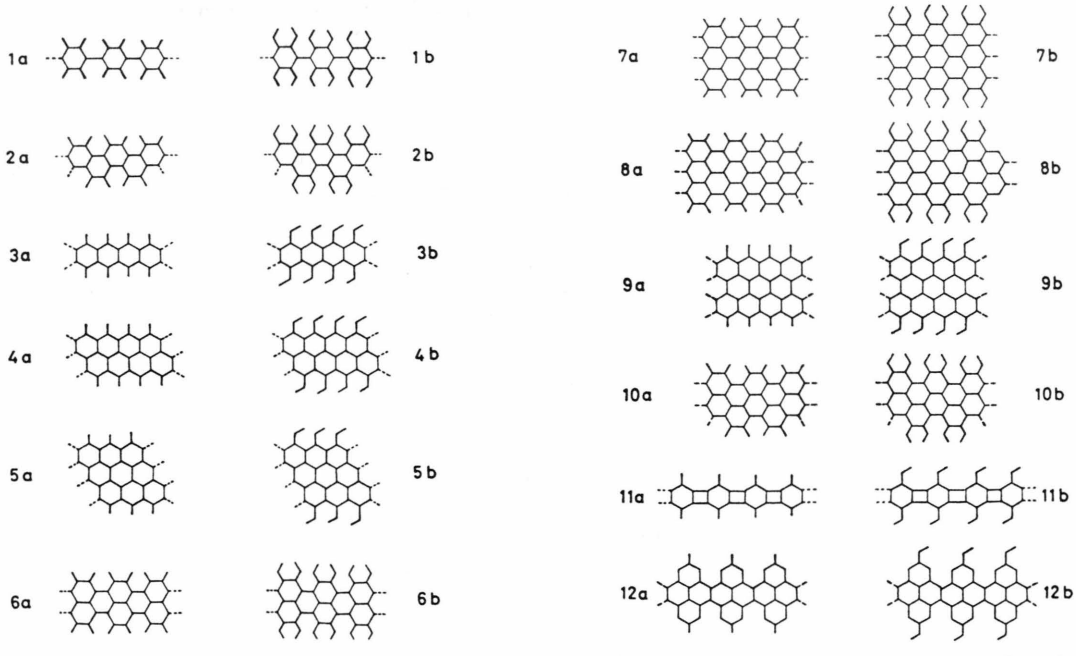


Fig. 2. Infinite conjugated polymers modified by mono- and diatomic conjugated branches studied in this work.

Table 2. The energy gap of the polymerhomologue series of Fig. 2 as a function of the normalized Wiener index, $\tilde{\tilde{W}}$, the predicted values of the energy gaps of the infinite polymers of these series, $\Delta E^{\infty}$, the correlation coefficient, $R$, and the standard deviation, $\sigma$.

| Structure No. | Number of atoms in the largest studied oligomers | Number of pairs $\Delta E/\tilde{\tilde{W}}$ | $\Delta E = f(\tilde{\tilde{W}})$ | $R$ | $\sigma$ | $\Delta E^{\infty}$ |
|---|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| 1a | 82 | 8 | $\Delta E = 0.6160 - 21.436\,\tilde{\tilde{W}}^2 + 117.577\,\tilde{\tilde{W}}^3$ | 0.999 | 0.00 | 0.5104 |
| 1b | 102 | 7 | $\Delta E = 0.0496 + 5.5266\,\tilde{\tilde{W}} - 32.0183\,\tilde{\tilde{W}}^3$ | 1.000 | 0.00 | 0.5184 |
| 2a | 90 | 7 | $\Delta E = 0.6734 + 7.5088\,\tilde{\tilde{W}} - 1.3186\,\tilde{\tilde{W}}^2$ | 0.999 | 0.00 | 0.0295 |
| | | | $\Delta E = -0.6486 + 7.1398\,\tilde{\tilde{W}}$ | 0.999 | 0.00 | 0.0311 |
| 2b | 122 | 7 | $\Delta E = 0.1096 + 4.3002\,\tilde{\tilde{W}} - 50.1289\,\tilde{\tilde{W}}^3$ | 1.000 | 0.00 | 0.4075 |
| 3a | 56 | 9 | $\Delta E = 0.3418 + 3.7718\,\tilde{\tilde{W}}^2 - 0.3988\,\tilde{\tilde{W}}^3$ | 0.999 | 0.00 | 0.3756 |
| | | | $\Delta E = 0.3431 + 3.6466\,\tilde{\tilde{W}}^2$ | 0.999 | 0.00 | 0.3761 |
| 3b | 74 | 9 | $\Delta E = -0.8070 + 9.1492\,\tilde{\tilde{W}} - 30.5801\,\tilde{\tilde{W}}^3$ | 0.999 | 0.00 | 0.00 |
| | | | $\Delta E = -0.4338 + 5.6366\,\tilde{\tilde{W}}$ | 0.989 | 0.05 | 0.00 |
| 4a | 76 | 9 | $\Delta E = 0.1786 - 0.2482\,\tilde{\tilde{W}} + 5.3417\,\tilde{\tilde{W}}^2$ | 0.999 | 0.00 | 0.1823 |
| 4b | 74 | 7 | $\Delta E = 0.7204 + 9.7080\,\tilde{\tilde{W}} - 42.7012\,\tilde{\tilde{W}}^3$ | 0.999 | 0.01 | 0.00 |
| 5a | 96 | 9 | $\Delta E = 0.0734 + 4.8106\,\tilde{\tilde{W}}^2$ | 0.999 | 0.00 | 0.0860 |
| | | | $\Delta E = 0.0848 - 0.2010\,\tilde{\tilde{W}} + 5.5734\,\tilde{\tilde{W}}^2$ | 0.999 | 0.00 | 0.0891 |
| 5b | 90 | 7 | $\Delta E = -0.5167 + 7.9520\,\tilde{\tilde{W}} - 40.6073\,\tilde{\tilde{W}}^3$ | 0.999 | 0.01 | 0.00 |
| | | | $\Delta E = 0.3468 + 5.6530\,\tilde{\tilde{W}}$ | 0.994 | 0.03 | 0.00 |
| 6a | 116 | 8 | $\Delta E = 0.5442 + 5.8956\,\tilde{\tilde{W}} + 3.7339\,\tilde{\tilde{W}}^2$ | 0.999 | 0.01 | 0.00 |
| | | | $\Delta E = -0.6024 + 6.8648\,\tilde{\tilde{W}}$ | 0.999 | 0.01 | 0.00 |
| 6b | 134 | 7 | $\Delta E = -0.5487 + 10.7779\,\tilde{\tilde{W}} - 22.2386\,\tilde{\tilde{W}}^2$ | 0.999 | 0.00 | 0.0452 |
| 7a | 132 | 7 | $\Delta E = -0.0985 - 0.4462\,\tilde{\tilde{W}} + 27.5020\,\tilde{\tilde{W}}^2$ | 0.999 | 0.01 | 0.00 |
| | | | $\Delta E = -0.1205 + 25.4837\,\tilde{\tilde{W}}^2$ | 0.999 | 0.01 | 0.00 |
| 7b | 144 | 6 | $\Delta E = -0.3137 + 5.3626\,\tilde{\tilde{W}}$ | 0.999 | 0.00 | 0.00 |
| | | | $\Delta E = -0.3386 + 5.7838\,\tilde{\tilde{W}} - 13.6344\,\tilde{\tilde{W}}^3$ | 0.999 | 0.00 | 0.00 |
| 8a | 136 | 7 | $\Delta E = 0.2936 - 166.832\,\tilde{\tilde{W}}^2 + 1531.34\,\tilde{\tilde{W}}^3$ | 0.999 | 0.01 | 0.0312 |
| 8b | 125 | 5 | $\Delta E = -0.3888 + 10.8054\,\tilde{\tilde{W}} - 296.913\,\tilde{\tilde{W}}^3$ | 0.999 | 0.00 | 0.1092 |
| 9a | 74 | 7 | $\Delta E = 0.0803 + 3.5450\,\tilde{\tilde{W}}^2$ | 1.000 | 0.00 | 0.0896 |
| | | | $\Delta E = 0.0811 - 0.0120\,\tilde{\tilde{W}} + 3.5838\,\tilde{\tilde{W}}^2$ | 1.000 | 0.00 | 0.0899 |
| 9b | 88 | 7 | $\Delta E = -0.4852 + 6.9090\,\tilde{\tilde{W}} - 10.3706\,\tilde{\tilde{W}}^3$ | 0.999 | 0.02 | 0.00 |
| 10a | 76 | 9 | $\Delta E = -0.1702 + 2.0857\,\tilde{\tilde{W}} + 1.2102\,\tilde{\tilde{W}}^2$ | 0.999 | 0.00 | 0.00 |
| | | | $\Delta E = -0.1224 + 0.9652\,\tilde{\tilde{W}} + 9.4370\,\tilde{\tilde{W}}^2 - 18.8247\,\tilde{\tilde{W}}^3$ | 0.999 | 0.00 | 0.00 |
| 10b | 74 | 7 | $\Delta E = 0.5241 + 53.2020\,\tilde{\tilde{W}}^3$ | 0.977 | 0.04 | 0.5332 |
| 11a | | | NBMO | | | |
| 11b | 140 | 7 | $\Delta E = -0.7611 + 7.4055\,\tilde{\tilde{W}} + 9.3944\,\tilde{\tilde{W}}^2$ | 0.999 | 0.00 | 0.00 |
| | | | $\Delta E = -0.9205 + 9.9236\,\tilde{\tilde{W}}$ | 0.999 | 0.01 | 0.00 |
| 12a | 98 | 6 | $\Delta E = 0.1083 + 0.5666\,\tilde{\tilde{W}} - 3.2444\,\tilde{\tilde{W}}^3$ | 0.999 | 0.00 | 0.1451 |
| 12b | 128 | 7 | $\Delta E = 0.4352 + 2.6839\,\tilde{\tilde{W}} + 0.3815\,\tilde{\tilde{W}}^2$ | 0.999 | 0.00 | 0.5992 |
| | | | $\Delta E = 0.4301 + 2.7764\,\tilde{\tilde{W}}$ | 0.999 | 0.00 | 0.5983 |

square-deviation also supports this statement being $\leqq 0.01$ in all but 4 cases where it is $0.02 - 0.05$. This high accuracy is achieved in 8 cases by means of a linear function, in 14 others by means of a quadratic function, and in 13 using polynomials of degree three (complete or incomplete ones).

Since the normalized Wiener index proved to be a reliable topological measure in the study of polymers energy gaps, a possible generalization of the above results seems worthwhile. With this aim, we have compared in Table 3 the energy gaps of the initial unmodified polymers of Fig. 1 with those of the corresponding modified polymers having one and two atoms in their branches.

The results obtained upon the structural modification under examination exhibit two tendencies:

A) When an unmodified alternant conjugated polymer has a non-zero gap, the monocarbon branches reduce the gap. The appearance of a second atom in each branch increases the gap once again but not to its initial magnitude. Polymers 2 and 10 are the best examples of this tendency. Thus, the gap of polymer 2 drops from $0.75\,\beta$ to zero after the first stage of the modification. It has again a non-zero value after the second stage, but this value ($0.418\,\beta$) is much lower than the initial one.

| No. | Unmodified polymer | Modified polymer | |
|---|---|---|---|
| | | Type a | Type b |
| 1 | 0.760 | 0.510 | 0.518 |
| 2 | 0.751 | 0.030 | 0.408 |
| 3 | 0 | 0.376 | 0 |
| 4 | 0 | 0.182 | 0 |
| 5 | 0 | 0.086 | 0 |
| 6 | 0.030 | 0 | 0.040 |
| 7 | 0 | 0 | 0 |
| 8 | 0.284 | 0.031 | 0.109 |
| 9 | 0 | 0.090 | 0 |
| 10 | 0.609 | 0 | 0.533 |
| 11 | 0 | NBMO | 0 |
| 12 | 0.599 | 0.144 | 0.599 |

Table 3. Energy gap, $\Delta E^{\infty}$, of the initial and modified polymers from Fig. 1 and 2.

B) When an unmodified alternant polymer has a zero gap the modification by means of monoatomic branches is accompanied by a non-zero gap while the subsequent lengthening of the branches with a second carbon atom again reduces the gap to zero value.

This tendency is best expressed in polymers 3 and 4. In the case of polymer 3, for example, the gap sharply rises from 0 to $0.38\,\beta$ and then again drops to 0 for the two stages of modification, respectively. Polymer 7 is the only exception to this regularity. One should, however, recall that the same unmodified polymer displayed a peculiar behaviour [1], the estimate of its energy being essentially different for our extrapolating scheme and the finite differences method used by Tyutyulkov and Polansky [5].

In conclusion, one should emphasize the practical importance of the structural modifications examined in this paper. The strong decrease in the energy gap of the model monodimensional alternant systems studied upon modification by means of methylene branches, could be of interest in the search for high conductivity in polymers.

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[1] D. Bonchev and O. Mekenyan, Z. Naturforsch. **35a**, 739 (1980).
[2] O. E. Polansky, O. Mekenyan, and D. Bonchev, Z. Naturforsch. **36a**, 643 (1981).
[3] H. Wiener, J. Amer. Chem. Soc. **69**, 17 (1947); 2636 (1947); J. Phys. Chem. **52**, 524 (1948).
[4] D. Bonchev and N. Trinajstić, J. Chem. Phys. **67**, 4517 (1977).
[5] N. Tyutyulkov and O. E. Polansky (unpublished results).