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Note

On Acyclic Polynomials of $[N]$ -Heteroannulenes

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It is known that the acyclic polynomial of a graph has real roots. However, it is of some interest to give a direct, graph-theoretical proof. Such a proof is given for heteroannulene graphs.

Acyclic polynomial is essential quantity in the topological theory of aromaticity¹⁻³. It may be defined in several ways⁴. Here we will use the definition based on the Sach formula⁵,

$$P^{\text{ac}}(G; x) = \sum_{n=0}^N a_n^{\text{ac}}(G) x^{N-n} \quad (1)$$

with

$$a_n^{\text{ac}}(G) = \sum_{s \in S_n^{\text{ac}}} (-1)^{c(s)} \quad (2)$$

where G stands for Hückel graph⁶ with N vertices, s , the Sachs graph with n vertices, is a member of S_n^{ac} set consisting of only K_2 graphs⁷, while $c(s)$ is the number of K_2 components, respectively.

In the early work¹⁻³ there was no proof given that the zeros of the acyclic polynomial are always real. This result is needed in order to ensure the meaningful topological resonance energies^{1-3,8,9}. Several chemical papers were published in 1979 considering the problem¹⁰⁻¹².

However, this recent interest in the acyclic polynomial has revealed that it was independently discovered in mathematics¹³, physics¹⁴⁻¹⁷, besides being rediscovered in chemistry by Aihara¹⁸. Altogether the acyclic polynomial was discovered, as far as we know, at least five times; authors being unaware of the previous works. In addition, various authors proposed and used different names for $P^{\text{ac}}(G; x)$, such as acyclic polynomial^{1-3,8,9}, reference polynomial^{10,12,18}, and matching polynomial^{11,13}, respectively.

In our early work we conjectured that the acyclic polynomial of a given structure has real roots; the conjecture being based on the numerical work¹⁹. However, the proof was shown to be true by several authors, e.g., most recently by Godsil and Gutman¹¹. However, the proof, that was given by these authors and others, is obtained using the reasoning of mathematical induction. Therefore, we know that the acyclic polynomials of all graphs have real roots, and, consequently, that the topological resonance energies of conjugated systems are real. However, we feel that it is of some interest to give more direct, graph-theoretical proof. Some initial work is already carried out^{10-12,20,21}.

For example, several »acyclic« graphs are known (Figure 1). »Acyclic« graph G^{ac} , corresponding to a graph G , is defined as the graph whose characteristic polynomial $P(G^{ac}; x)$ equals the acyclic polynomial $P^{ac}(G; x)$ of G .

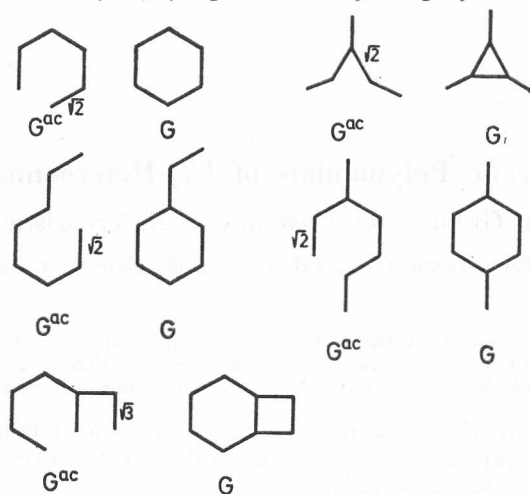


Figure 1. Examples of »acyclic« graphs G^{ac} and the corresponding parent graphs G .

In we could construct »acyclic« graph for every structure, then the problem of proving that the zeros of $P^{ac}(G; x)$ are always real would not exist. In this case we will be able to set up the corresponding adjacency matrix, which is a Hermitian matrix, and the roots of the acyclic polynomial would be immediately proved real. However, this is not the case; »acyclic« graphs are available only for a few simple structures.

Another approach is also based on a construction of a Hermitian matrix but the original molecular skeleton is retained and the complex weights of the form $e^{\pm i\alpha}$ are associated with edges^{10,12,20}. Unfortunately, until now the method is applicable to monocyclic^{10,12} and some bicyclic²⁰ hydrocarbon systems.

In the present note we wish to extend the later approach to the vertex- and edge-weighted graphs, G_{VEW} , which pictorially represent heteroconjugated molecules^{22,23}. Only heteroannulene graphs will be treated here. A vertex- and edge-weighted graph is a graph in which vertices and edges of different »type« are weighted, and their »weights« are identified by parameters h and k for heteroatoms and heterobonds, respectively. Vertex weight h is diagrammatically represented by a loop. In Figure 2 we give as an example the graphical representation of pyrrole.

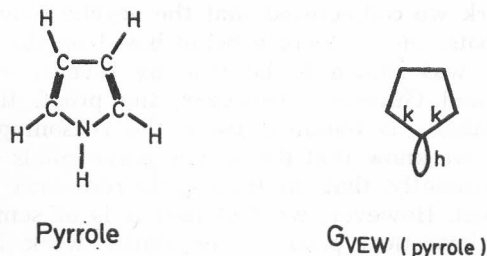


Figure 2. Vertex- and edge-weighted graph of pyrrole.

In our approach the undirected molecular graph G has to be replaced by the corresponding directed graph⁷, namely each edge from G has to be represented by two oppositely directed lines. Moreover, a weight $e^{i\alpha}$ should be associated with the line $i \rightarrow j$ and its complex conjugate weight $e^{-i\alpha}$ should be associated with the line $j \rightarrow i$. In such a way »graph« \vec{G} described by a Hermitian matrix is obtained and it is clear that its characteristic polynomial $P(\vec{G}; x)$ has real roots. Because the edge contributions from G and \vec{G} ($e^{i\alpha} \cdot e^{-i\alpha} = 1$) are the same, it is evident that $P^{ac}(G; x)$ and $P(\vec{G}; x)$ could differ only in contributions originating from cycles. In the case of $[N]$ -annulene, represented by the graph C_N , cycle enters only through the last coefficient:

$$P(C_N; x) = P^{ac}(C_N; x) + a_N^{cyclic}(\vec{G}) \tag{3}$$

where:

$$a_N^{cyclic}(\vec{G}) = (-1)^1 [e^{iN\alpha} + e^{-iN\alpha}] = -2 \cos N\alpha \tag{4}$$

Therefore, for:

$$\alpha = \frac{\pi}{2N} \tag{5}$$

the $a_N^{cyclic}(\vec{G})$ coefficient vanishes thus giving

$$P(C_N; x) = P^{ac}(C_N; x) \tag{6}$$

Now, we go a step further and consider the vertex-weighted graph G_{VW} ,



Our procedure gives,

$$P(G_{VW}; x) = P^{ac}(G_{VW}; x) + a_5^{cyclic}(\vec{G}_{VW}) \tag{7}$$

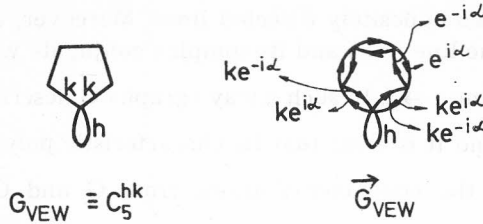
where,

$$a_5^{cyclic}(\vec{G}_{VW}) = -2 \cos 5\alpha, \text{ and for: } 5\alpha = \frac{\pi}{2} \text{ one obtains,}$$

$$P(\vec{G}_{VW}; x) = P(G_{VW}; x) \tag{8}$$

independently on loop h .

Let us now consider the vertex- and edge-weighted graph G_{VEW} corresponding to 5-membered ring,



The relation between $P(G_{VEW}; x)$ and $P(\vec{G}_{VEW}; x)$ is given as before by,

$$P(\vec{G}_{VEW}; x) = P(G_{VEW}; x) + a_5^{cyclic}(\vec{G}_{VEW}) \tag{9}$$

where

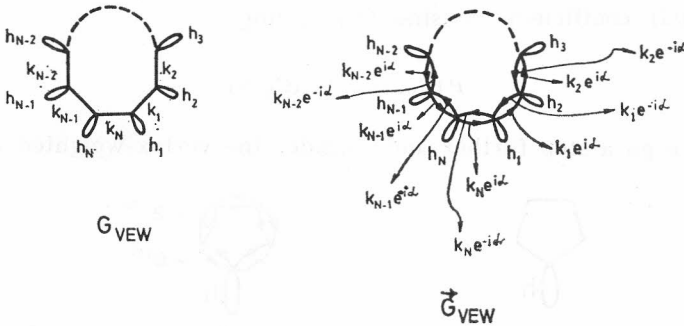
$$a_5^{cyclic}(\vec{G}_{VEW}) = (-1)^1 [k^2 e^{i5\alpha} + k^2 e^{-i5\alpha}] = -2 k^2 \cos 5\alpha \tag{10}$$

For $5\alpha = \pi/2$ we obtain again,

$$P(\vec{G}_{VEW}; x) = P^{ac}(G_{VEW}; x) \tag{11}$$

The conclusion is that the relation (11) is independent on the values for parameters h and k , respectively.

This procedure extends along the same line for $[N]$ -heteroannulenes,



thus giving,

$$P(\vec{G}_{VEW}; x) = P^{ac}(G_{VEW}; x) + a_N^{cyclic}(\vec{G}_{VEW}) \tag{12}$$

where

$$\begin{aligned} a_N^{cyclic}(\vec{G}_{VEW}) &= (-1)^1 [k_1 k_2 \dots k_N e^{iN\alpha} + k_1 k_2 \dots k_N e^{-iN\alpha}] = \\ &= -2 \cos N\alpha \cdot \prod_{i=1}^N k_i \end{aligned} \tag{13}$$

and for $N\alpha = \frac{\pi}{2}$, one obtains as before

$$P(\vec{G}_{VEW}; x) = P^{ac}(G_{VEW}; X) \tag{14}$$

The above result does not depend on the number and values of parameters h and k .

Therefore, the acyclic polynomial of $[N]$ -heteroannulene has real roots. Moreover both for $[N]$ -annulenes and $[N]$ -heteroannulenes the acyclic polynomial equals the characteristic polynomial of a Hermitian matrix for the unique choice:

$$N\alpha = \frac{\pi}{2}$$

The procedure described here although attractive from the graph theoretical point of view should be understood as a rather limited. Namely, the procedure could be generalized to polycyclic hetero-systems only under very restrictive conditions on symmetry of the systems studied.

REFERENCES

1. I. Gutman, M. Milun, and N. Trinajstić, *Math. Chem.* **1** (1975) 171.
2. N. Trinajstić, *Int. J. Quantum Chem.* **S11** (1977) 469.
3. I. Gutman, M. Milun, and N. Trinajstić, *J. Amer. Chem. Soc.* **99** (1977) 1692.
4. J. V. Knop and N. Trinajstić, *Report at the Sanibel-Palm Coast Symposium 1980*, March 10–15, 1980.
5. H. Sachs, *Publ. Math. (Debrecen)* **11** (1964) 119.
6. N. Trinajstić, in: *Semiempirical Methods of Electronic Structure Calculation. Part A: Techniques*, G. A. Segal, (Ed.), Modern Theoretical Chemistry Vol. VII, Plenum, New York 1977, p. 1.
7. F. Harary, *Graph Theory*, Addison-Wesley, Reading, Mass. 1971.
8. P. Ilić and N. Trinajstić, *J. Org. Chem.* **45** (1980) 1738.
9. P. Ilić and N. Trinajstić, *Pure Appl. Chem.* **52** (1980) 1495.
10. L. J. Schaad, B. A. Hess, Jr., J. B. Nation, and N. Trinajstić, (with an appendix by I. Gutman), *Croat. Chem. Acta* **52** (1979) 233.
11. G. D. Godsil and I. Gutman, *Z. Naturforsch.* **34a** (1979) 776.
12. J.-i. Aihara, *Bull. Chem. Soc. Japan* **52** (1979) 1529.
13. E. J. Farrell, *J. Comb. Theory* **27B** (1979) 75.
14. O. J. Heilman and E. H. Lieb, *Phys. Rev. Lett.* **24** (1970) 1412.
15. O. J. Heilman and E. H. Lieb, *Comm. Math. Phys.* **25** (1972) 190.
16. H. Kunz, *Phys. Lett.* **32A** (1970) 311.
17. C. Gruber and H. Kunz, *Comm. Math. Phys.* **22**, 133 (1971).
18. J.-i. Aihara, *J. Amer. Chem. Soc.* **98** (1976) 2750.
19. M. Milun, *Ph. D. Thesis*, University of Zagreb, 1976.
20. A. Graovac, *Chem. Phys. Lett.*, in press.
21. P. Ilić, *Ph. D. Thesis*, University of Zagreb, 1979.
22. A. Graovac, O. E. Polansky, N. Trinajstić, and N. Tyutyulkov, *Z. Naturforsch.* **30a** (1975) 1696.
23. M. J. Rigby, R. B. Mallion, and A. C. Day, *Chem. Phys. Lett.* **51** (1977) 178; erratum *Chem. Phys. Lett.* **53** (1978) 418.

SAŽETAK

O acikličkim polinomima $[N]$ -heteroanulena

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Poznato je da su korijenovi acikličkog polinoma grafa realni. Od praktičnog je interesa ponuditi i izravni, graf-teorijski dokaz. Takav jedan dokaz je dan za grafove pridružene heteroanulenima.