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The spectral radius of the adjacency matrix of benzenoid hydrocarbon

J. Cioslowski*

Department of Theoretical Chemistry, Jagiellonian University, 30060 Cracow, Poland

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The variational treatment of the spectral radius of the adjacency matrix, based on the Rayleigh's quotient and the steepest descent method is presented. The resulting formula, valid for the benzenoid hydrocarbons, gives accurate values for benzene and the linearly condensed benzenoid system of infinite length.

Key words: Benzenoid hydrocarbons — Spectral radius of the adjacency matrix

Introduction

The spectral radius of the adjacency matrix (R) is a quantity equal to the energy of the lowest occupied π-molecular orbital of a particular conjugated system. According to the well-known Frobenius theorem [1], R expressed in β units fulfils the inequalities $2 \leq R < 3$ for the benzenoid hydrocarbons. In this paper a lower bound for R is found.

Theory

Let $\tilde{A}$ be the adjacency matrix of a given benzenoid hydrocarbon having N carbon atoms and M carbon-carbon bonds. Let

$$r = (\vec{x}^{+}\tilde{A}\vec{x})/(\vec{x}^{+}\vec{x}) \tag{1}$$

* *Present address*: Department of Chemistry, Georgetown University, Washington, DC 20057, USA

be the Rayleigh's quotient [2]. Then, for any trial vector $\vec{x}$ the inequality $r \leq R$ holds. The equality is fulfilled only if $\vec{x}$ is the eigenvector of $\tilde{A}$ corresponding to the eigenvalue R. The simplest possibility for constructing a suitable trial $\vec{x}$ is to choose:

$$\vec{x}^{(0)}: x_j^{(0)} = 1 \quad \text{for } j = 1, \ldots, N. \tag{2}$$

For such a choice we have:

$$r^{(0)} = 2M/N. \tag{3}$$

This 0th order approximation can be easily improved using the steepest descent method [2]:

$$\vec{x}^{(1)} = \vec{x}^{(0)} + \lambda \vec{g}, \tag{4}$$

where $\vec{g} = \partial r / \partial \vec{x}^{+}$ and λ fulfils the condition:

$$\frac{\partial r(\lambda)}{\partial \lambda} = 0, \qquad r(\lambda) = (\vec{x}^{(1)+} \tilde{A} \vec{x}^{(1)})/(\vec{x}^{(1)+} \vec{x}^{(1)}). \tag{5}$$

Explicit calculation gives:

$$\vec{g} = 2/N^2 (N\vec{w} - 2M\vec{x}^{(0)}), \tag{6}$$

$$\vec{x}^{(1)+} \vec{x}^{(1)} = N + 2\lambda \sum_i g_i + \lambda^2 \sum_i g_i^2, \tag{7}$$

$$\vec{x}^{(1)+} \tilde{A} \vec{x}^{(1)} = 2M + 2\lambda \sum_{i,j} g_i A_{ij} + \lambda^2 \sum_{i,j} g_i A_{ij} g_j; \tag{8}$$

where: $\vec{w} = (w_1, \ldots, w_N)$ and w_j is the degree of vertex j in the molecular graph corresponding to $\tilde{A}$. Substituting (6) into (7) and (8), then defining:

$$W = \vec{w}^{+} \tilde{A} \vec{w} \tag{9}$$

and taking into account that for benzenoid hydrocarbons:

$$\sum_i w_i = 2M, \tag{10}$$

$$\sum_i w_i^2 = 10M - 6N, \tag{11}$$

we get:

$$\begin{aligned} r(\lambda) = \{&2M + 8\lambda(3N - 2M)(M - N)/N^2 \\ &+ 4\lambda^2 [N^2 W - 8M(5MN - 3N^2 - M^2)]/N^4\}/\{N + 8\lambda^2 (3N - 2M) \\ &\times (M - N)/N^3\}. \end{aligned} \tag{12}$$

λ is a solution of the following equation:

$$\begin{aligned} &8[(3N - 2M)^2 (M - N)^2/N^4]\lambda^2 + [4M(15MN - 9N^2 - 4M^2) - N^2 W]/ \\ &\quad N^2 \lambda - (3N - 2M)(M - N) = 0. \end{aligned} \tag{13}$$

The solution of (13), together with the condition $\partial^2 r(\lambda)/\partial \lambda^2 < 0$ leads to:

$$\begin{aligned} \lambda = N^2 \{&\sqrt{[4M(15MN - 9N^2 - 4M^2) - N^2 W]^2 + 32(3N - 2M)^3 (M - N)^3} \\ &- [4M(15MN - 9N^2 - 4M^2) - N^2 W]\}/16(3N - 2M)^2 (M - N)^2. \end{aligned} \tag{14}$$

Table 1. The lower bounds for the spectral radius R

Compound	R	$r^{(0)}$	$r^{(1)}$	r (Eq. (15))[a]
Benzene	2.0000	2.0000	2.0000	2.0000
Naphthalene	2.3028	2.2000	2.2808	2.2800
Anthracene	2.4142	2.2857	2.3689	2.3684
Phenanthrene	2.4348	2.2857	2.4000	2.3947
Triphenylene	2.5321	2.3333	2.5000	2.4706
Pyrene	2.5321	2.3750	2.4922	2.4894
Coronene	2.6751	2.5000	2.6180	2.6154
∞-acene[b]	2.5616	2.5000	2.5616	2.5385

[a] Hall's lower bound [3]
[b] Polyacene of an infinite length

The Eqs. (4), (6), (12) and (14) determine the approximate values of $\vec{x}$ as well as of $r^{(1)}$, which is a lower bound for R.

Discussion

The problem of the lower bounds for R has been considered by Hall [3]. The formula quoted in his paper has the form:

$$r = W/(10M - 6N) \tag{15}$$

when the Eqs. (9) and (11) are taken into account. In Table 1 the values of R and the bounds $r^{(0)}$, $r^{(1)}$ and r (Eq. (15)) are presented for some benzenoid systems. One can observe that the present approach leads to improved results for pericondensed hydrocarbons, whereas for catacondensed systems the values of $r^{(1)}$ and r (Eq. (15)) are almost the same. It should be also accentuated that only the variational treatment provides r equal to R for the polyacene of an infinite length.

Since the computation of both $r^{(1)}$ and r (Eq. (15)) requires only the knowledge of N, M and W, thus we can say that the spectral radius of the adjacency matrix of benzenoid hydrocarbon is essentially determined by the local structure of its carbon-carbon connections.

References

1. Graovac A, Gutman I, Trinajstić N (1977) Topological approach to the chemistry of conjugated molecules. Springer, Berlin, Heidelberg, New York
2. Ralston A, Rabinovitz P (1978) A first course in numerical analysis. McGraw-Hill, New York
3. Hall G G (1977) Mol Phys 33:551