Upper Bound for Total π-Electron Energy of Benzenoid Hydrocarbons

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Z. Naturforsch. **40a**, 1167–1168 (1985);
received June 4, 1985

A novel upper bound for the π-electron energy (E_π) is described. The formula, valid for benzenoid hydrocarbons yields values closer to the true E_π than the McClelland's or even Gutman's estimates.

Introduction

The present paper deals with an improvement of McClelland's estimate [1] of the π-electron energy of benzenoid systems. A similar task has been tackled recently by Gutman et al. [2]. In their paper a better estimation has been achieved using the number of the Kekulé structures as an additional condition in the variational problem. Here, a similar method is used, however the additional condition is expressed by means of the square of the following Cartesian norm

$$Q = \sum_{ij} (\tilde{A}^2)^2_{ij} = \| \tilde{A}^2 \|^2, \tag{1}$$

where $\tilde{A}$ is the adjacency matrix of the graph G corresponding to the hydrocarbon. This results in an upper bound for the E_π energy.

The Upper Bound for E_π

Let G be a molecular graph [3] of the benzenoid hydrocarbon having N carbon atoms and M carbon-carbon bonds. Let $\tilde{A}$ be a corresponding adjacency matrix [3], and $x_1, x_2, \ldots, x_N$ be the eigenvalues of $\tilde{A}$ labelled in non-increasing order. Since the benzenoid graphs are bipartite, so [4]

$$x_i = -x_{N+1-i} \quad \text{for all } i. \tag{2}$$

Also [5]

$$\sum_{i=1}^{N/2} x_i^2 = M \quad \text{and} \quad 2\sum_{i=1}^{N/2} x_i = E_\pi \tag*{(3), (4)}$$

for all the benzenoid non-charged hydrocarbons having a closed-shell ground state. Let Q be the square of the Cartesian norm of the $\tilde{A}^2$ matrix. Since the Cartesian norm is invariant under any orthogonal transformation of the matrix, one has

$$2\sum_{i=1}^{N/2} x_i^4 = Q. \tag{5}$$

Inspection of the form of Q makes it easy to realize that it is equal to the sum of three terms: the first is a number of the triply bonded vertices of G multiplied by 9, the second is a number of the doubly bonded vertices multiplied by 4, and the third one is a number of the atom triplets multiplied by 2. Taking into account all the possible modes of the ring annelation in benzenoid systems we find

$$Q = 18M - 12N. \tag{6}$$

In consequence we come to

$$\sum_{i=1}^{N/2} x_i^4 = 9M - 6N. \tag{7}$$

We have to find the extremal value of E_π with the constraints (3) and (7). A common approach to deal with such a problem is to use the Lagrange multipliers. However, we can solve it in a different way. Because to the two constraints we have only $N/2-2$ independent variables $x_1, \ldots, x_{N/2-2}$. Thus, differentiating (3), (4) and (7) with respect to some x_k ($k = 1, 2, \ldots, N/2-2$) we get

$$\frac{\partial E_\pi}{\partial x_k} = 2 + 2\,\frac{\partial x_{N/2-1}}{\partial x_k} + 2\,\frac{\partial x_{N/2}}{\partial x_k}, \tag{8}$$

$$0 = 2x_k + 2x_{N/2-1}\,\frac{\partial x_{N/2-1}}{\partial x_k} + 2x_{N/2}\,\frac{\partial x_{N/2}}{\partial x_k}, \tag{9}$$

$$0 = 4x_k^3 + 4x_{N/2-1}^3\,\frac{\partial x_{N/2-1}}{\partial x_k} + 4x_{N/2}^3\,\frac{\partial x_{N/2}}{\partial x_k}. \tag{10}$$

Then we will prove that the choice

$$x_1 = \ldots = x_{N/2-1} = a \neq x_{N/2} = b \tag{11}$$

leads to the extremal value of E_π.

Inserting (11) into (9) and (10) we obtain

$$2a\left(1 + \frac{\partial x_{N/2-1}}{\partial x_k}\right) + 2b\,\frac{\partial x_{N/2}}{\partial x_k} = 0, \tag{12}$$

$$4a^3\left(1 + \frac{\partial x_{N/2-1}}{\partial x_k}\right) + 4b^3\,\frac{\partial x_{N/2}}{\partial x_k} = 0. \tag{13}$$

The equations (12) and (13) can be fulfilled simultaneously only when

$$\frac{\partial x_{N/2-1}}{\partial x_k} = -1 \quad \text{and} \quad \frac{\partial x_{N/2}}{\partial x_k} = 0. \tag{14}$$

This gives $\dfrac{\partial E_\pi}{\partial x_k} = 0$ and completes the proof. One can easily find, calculating the Hessian matrix elements $\dfrac{\partial^2 E_\pi}{\partial x_k\, \partial x_l}$, that the choice described above corresponds to the maximum of E_π.

In order to evaluate a and b we have to solve the system of equations

$$\left(\frac{N}{2} - 1\right) a^2 + b^2 = M, \tag{15}$$

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$$\left(\frac{N}{2}-1\right)a^4+b^4=9M-6N. \tag{16}$$

Except for benzene, this system of equations has exactly one solution ($a>0, b>0$):

$$a=\sqrt{\frac{2M(N-2)-2D}{N(N-2)}}, \tag{17}$$

$$b=\sqrt{\frac{2M+D}{N}}, \tag{18}$$

where

$$D=\sqrt{(N-2)(9MN-6N^2-2M^2)}. \tag{19}$$

Then

$$E_\pi \leqq (N-2)\sqrt{\frac{2M(N-2)-2D}{N(N-2)}}+2\sqrt{\frac{2M+D}{N}}. \tag{20}$$

For benzene, there are two possible solutions of the system (15–16), however solutions (17–18) give the true estimation $E_\pi \leqq 8$.

Discussion

The novel upper bound has been used to estimate E_π's for some benzenoid hydrocarbons. The results are presented in Table 1.

Table 1. Comparison of various upper bounds for the total π-electron energy of some benzenoid hydrocarbons.

Compound	E_π	E_π (upper bound)		
	(exact)	McClelland [1]	Gutman [2]	This work
Benzene	8.00	8.48	8.08	8.00
Naphthalene	13.68	14.83	13.98	14.00
Anthracene	19.31	21.16	19.99	19.97
Phenanthrene	19.45	21.16	20.09	19.97
Triphenylene	25.27	27.49	26.28	26.19
Pyrene	22.51	24.65	23.41	23.42
Perylene	28.25	30.98	29.61	29.54
Coronene	34.57	37.94	36.49	36.26
Ovalene	46.50	51.22	49.65	49.15
Kekulene	68.61	75.84	74.29	73.22

The detailed numerical calculations show that the new formula (20) gives for almost all tested molecules a better estimation of E_π than Gutman's formula. However, the formula (20) requires only a number of carbon atoms and bonds, N and M respectively. This is also a little disadvantage since the formula does not account for energetical effects due to different numbers of the Kekulé structures; therefore it is less appropriate for approximate calculation of E_π through a linear regression.

Acknowledgement

I would like to thank Prof. I. Gutman for his valuable discussions during preparation of manuscript.

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