Upper Bounds for the Total π-Electron Energy of Benzenoid Hydrocarbons and Their Relations

J. Ciosłowski *
Department of Chemistry, Jagiellonian University, 30060 Cracow, Karasia 3, Poland

I. Gutman
Faculty of Science, University of Kragujevac, Yugoslavia

Z. Naturforsch. **41 a,** 861 – 865 (1986); received March 25, 1986

Upper bounds for the total π-electron energy of benzenoid hydrocarbons, depending on the number of carbon atoms and carbon-carbon bonds, are examined and several of their properties established.

Introduction

McClelland's expression [1]

$$E_{MC} = \sqrt{2MN} \tag{1}$$

is an upper bound for the total π-electron energy E_π, i.e. $E_\pi \leqq E_{MC}$ for all conjugated hydrocarbons with N carbon atoms and M carbon-carbon bonds. Some additional upper bounds for E_π, depending on N and M only, have recently been obtained. These are E_T, E_{GTD} and E_C, proposed by Türker [2], Gutman, Türker and Dias [3], and Ciosłowski [4], respectively:

$$E_T = 2\sqrt{M + [N(N-2)\,a_4/2]^{1/2}}\,, \tag{2}$$

$$E_{GTD} = 2\,[\sqrt{3N(N-2)(N-4)\,a_6/4} - \sqrt{8M^3/N} + 3ME_T/2]^{1/3}, \tag{3}$$

$$E_C = 2\sqrt{2M/N + R(N/2-1)^{1/2}} + (N-2)\sqrt{2M/N - R(N/2-1)^{-1/2}}\,. \tag{4}$$

Here a_4 and a_6 denote the fourth and the sixth coefficient of the characteristic polynomial, and

$$R = (18MN - 12N^2 - 4M^2)^{1/2}\,N^{-1}. \tag{5}$$

In the Appendix it will be proved that R is necessarily a real quantity.

It should be pointed out that E_{MC} is an upper bound for the total π-electron energy of an arbitrary conjugated hydrocarbon whereas E_T and E_{GTD} are limited to alternant hydrocarbons. The expression (4) is an upper bound for E_π only in the case of benzenoid hydrocarbons. Since benzenoid systems are necessarily alternant, it is clear that all the formulas (1) – (4) provide upper bounds for their total π-electron energy.

Furthermore, for benzenoid systems,

$$a_4 = (M^2 - 9M + 6N)/2 \tag{6}$$

and therefore in that case Türker's estimate E_T is of (N, M)-type. The dependence of a_6 on the structure of benzenoid molecules is given by [3]

$$a_6 = (M^3 - 27M^2 + 158M + 48)/6 + 3N(M-8) + N_b, \tag{7}$$

where N_b denotes the number of bay regions. Bearing in mind the algebraic form of E_{GTD} and the fact that $N_b \ll a_6$, one concludes that the effect of N_b on the numerical value of E_{GTD} is insignificant. Hence E_{GTD} depends essentially on N and M only.

The expression obtained by formally setting $N_b = 0$ into (7) and (3) is denoted by E^0_{GTD}. Thus E^0_{GTD} is of (N, M)-type. It is clear that E^0_{GTD} cannot exceed E_{GTD}.

Note that any expression of (N, M)-type cannot distinguish between isomers. This is because all conjugated hydrocarbons with N carbon atoms and M carbon-carbon bonds have the formula C_NH_{3N-2M}.

Reprint requests to Professor Dr. Ivan Gutman, P.O. Box 60, YU-34000 Kragujevac, Yugoslavia.

* Present address: Department of Chemistry, Georgetown University, Washington, D.C. 20057, USA.

0340-4811 / 86 / 0600-0861 $ 01.30/0. – Please order a reprint rather than making your own copy.

In the following we shall arrive at a generalization of the formula E_C, viz.

$$E_C(t) = 2t\sqrt{2M/N + RS} + (N - 2t)\sqrt{2M/N - R/S}$$

where R is given by (5) and

$$S = S(t) = [(N - 2t)/(2t)]^{1/2}. \tag{9}$$

It is easy to see that the r.h.s. of (8) is real-valued only if the parameter t does not exceed $M^2/(9M - 6N)$. Since t will be assumed to be an integer, its value lies between 1 and Q, with Q being the integer part of $M^2/(9M - 6N)$. Evidently, $E_C(1) = E_C$.

The main result of the present paper can be formulated as

$$E_\pi < E_C(2) < E_C(1) < E^0_{GTD} < E_{GTD} < E_T < E_{MC}. \tag{10}$$

The above statement hold for all benzenoid systems, expect for benzene and naphthalene (see below). We provide rigorous proofs for the inequalities

$$E_C(1) > E_C(2) > E_C(3) > \ldots > E_C(Q) \tag{11}$$

and

$$E_C < E_{MC}, \tag{12}$$

whereas the remaining relations in (10) are verified by extensive numerical testing (see below). In particular, $E_\pi < E_C(2)$ holds for almost all (but not for all) benzenoid systems the inequality $E_\pi < E_C(3)$ is obeyed by the majority of benzenoid systems, but is violated in a considerable number of cases and is therefore not included into (10). Note that the relation $E_T < E_{MC}$ was proved previously [2].

Generalization of the Bound E_C

In [4] it was shown that (4) is the maximal possible value of the expression

$$2\sum_{i=1}^{N/2} x_i = E_\pi \tag{13}$$

provided the conditions

$$\sum_{i=1}^{N/2} x_i^2 = M \tag{14}$$

and

$$\sum_{i=1}^{N/2} x_i^4 = 9M - 6N \tag{15}$$

are simultaneously obeyed. Here $x_1, x_2, \ldots, x_{N/2}$ are to be understood as unknown variables whose actual value will be determined by the extremality requirement for (13) and by the constraints (14) and (15). By no means should the x_i's be identified with the eigenvalues of a molecular graph (and thus with the HMO energy levels). Of course, these eigenvalues satisfy relations which are fully analogous to (13)–(15) [4].

Applying standard variational calculus to the above problem one immediately deduces that the equation

$$1 + \lambda x_i + \mu x_i^3 = 0 \tag{16}$$

must hold for all $i = 1, 2, \ldots, N/2$. Here λ and μ are pertinent Lagrange multipliers. After multiplication of (16) by x_i, summing over all i and taking into account (13), (14) and (15) one arrives at

$$E_\pi = (12\mu)\,N + (-2\lambda - 18\mu)\,M. \tag{17}$$

If the terms 12μ and $-2\lambda - 18\mu$ were constants, then the right-hand side of (17) would provide a good approximation for E_π. For benzenoid hydrocarbons these constants were estimated as 0.83 and 0.48, respectively [5]. Hence $\mu \approx 0.07$ and $\lambda \approx -0.86$. Because of $\lambda < 0$ and $-\lambda \gg \mu$, all the three roots of (16) are real and two of them are positive.

Let these two positive roots be denoted by a and b, $a > b > 0$. Then the solution of our variational problem is

$$x_1 = x_2 = \ldots = x_t = a, \tag{18}$$

$$x_{t+1} = \ldots = x_{N/2} = b, \tag{19}$$

$$E_C(t) = 2ta + (N - 2t)\,b \tag{20}$$

for some t.

The roots a and b are determined using (14) and (15), namely from the equations

$$t\,a^2 + (N/2 - t)\,b^2 = M, \tag{21}$$

$$t\,a^4 + (N/2 - t)\,b^4 = 9M - 6N. \tag{22}$$

Analysis shows that the solution of (21) and (22), which we are interested in is

$$a = (2M/N + RS)^{1/2}, \quad b = (2M/N - R/S)^{1/2}, \tag{23}$$

resulting in (8). $E_C(t)$ is a real-valued quantity only for $t = 1, 2, \ldots, Q$.

Properties of $E_C(t)$

We prove first the inequalities (11). In order to do this, we differentiate (20), (21) and (22) with respect to t, bearing in mind that a and b are functions of t. We obtain

$$E_C'(t) = 2a + 2ta' - 2b + (N - 2t)\, b', \tag{24}$$

$$a^2 + 2taa' - b^2 + 2(N/2 - t)\, bb' = 0, \tag{25}$$

$$a^4 + 4ta^3 a' - b^4 + 4(N/2 - t)\, b^3 b' = 0. \tag{26}$$

Solving the latter two equations in the unknowns a' and b' one gets

$$a' = -(a^2 - b^2)/(4ta), \tag{27}$$

$$b' = -(a^2 - b^2)/(2Nb - 4tb) \tag{28}$$

which, substituted back into (24) yields

$$E_C'(t) = -(a - b)^3/(2ab). \tag{29}$$

Because $a > b > 0$, $E_C'(t)$ is negative, which means that $E_C(t)$ is a monotonically decreasing function of t.

This proves (11).

We demonstrate now that $E_C(t)$ is necessarily smaller than McClelland's bound (1). To do this one has to consider $E_C(t)$, given by (8), as a function of R.

Setting $R = 0$ into the r.h.s. of (8) one obtains just McClelland's expression (1).

Differentiation of (8) with respect to R with bearing in mind (9) gives

$$\frac{\partial E_C(t)}{\partial R} = t(N/2 - t)[(2M/N + RS)^{-1/2} - (2M/N - R/S)^{-1/2}], \tag{30}$$

which is obviously negative. Hence $E_C(t)$ is a decreasing function of the parameter R. Since for all benzenoid systems $R > 0$ (see the Appendix), we arrive at the inequality (12).

As a final result concerning $E_C(t)$ it will be shown that only the choice $t = 1$ gives rise to a real extremum of E_π.

Assume that the variables $x_1, x_2, \ldots, x_{N/2}$ fulfil the conditions (18) and (19). Only $N/2 - 2$ of these variables, say $x_1, x_2, \ldots, x_{t-1}, x_{t+1}, \ldots, x_{N/2-1}$ are independent. Let us write $x_t = y$ and $x_{N/2} = z$ for the two dependent variables. Then from (13),

$$\frac{\partial E_\pi}{\partial x_i} = 2 + 2\frac{\partial y}{\partial x_i} + 2\frac{\partial z}{\partial x_i} \tag{31}$$

$$\frac{\partial^2 E_\pi}{\partial x_i \partial x_j} = 2\frac{\partial^2 y}{\partial x_i \partial x_j} + 2\frac{\partial^2 z}{\partial x_i \partial x_j}, \tag{32}$$

whereas from (14) and (15),

$$x_i + y\frac{\partial y}{\partial x_i} + z\frac{\partial z}{\partial x_i} = 0, \tag{33}$$

$$\delta_{ij} + \frac{\partial y}{\partial x_i}\frac{\partial y}{\partial x_j} + y\frac{\partial^2 y}{\partial x_i \partial x_j} + \frac{\partial z}{\partial x_i}\frac{\partial z}{\partial x_j} + z\frac{\partial^2 z}{\partial x_i \partial x_j} = 0, \tag{34}$$

$$x_i^3 + y^3\frac{\partial y}{\partial x_i} + z^3\frac{\partial z}{\partial x_i} = 0, \tag{35}$$

$$3\delta_{ij}x_i^2 + 3y^2\frac{\partial y}{\partial x_i}\frac{\partial y}{\partial x_j} + y^3\frac{\partial^2 y}{\partial x_i \partial x_j} + 3z^2\frac{\partial z}{\partial x_i}\frac{\partial z}{\partial x_j} + z^3\frac{\partial^2 z}{\partial x_i \partial x_j} = 0. \tag{36}$$

δ_{ij} denotes the Kronecker delta.

For $i \in \{1, 2, \ldots, t-1\}$, (33) and (35) reduce to

$$a\left(1 + \frac{\partial y}{\partial x_i}\right) + b\frac{\partial z}{\partial x_i} = 0, \tag{37}$$

$$a^3\left(1 + \frac{\partial y}{\partial x_i}\right) + b^3\frac{\partial z}{\partial x_i} = 0. \tag{38}$$

Since $ab^3 - a^3b \neq 0$, from (37) and (38) follows that

$$\frac{\partial y}{\partial x_i} = -1; \quad \frac{\partial z}{\partial x_i} = 0. \tag{39}$$

Combining (31) with (39) one obtains $\partial E_\pi/\partial x_i = 0$. The same conclusion can be reached also for $i \in \{t+1, \ldots, N/2 - 1\}$. Hence $E_C(t)$ is a stationary point for every $t = 1, 2, \ldots, N/2 - 1$.

For $i = j \in \{1, 2, \ldots, t-1\}$, (34) and (36) result in

$$a\frac{\partial^2 y}{\partial x_i^2} + b\frac{\partial^2 z}{\partial x_i^2} + 2 = 0, \tag{40}$$

$$a^3\frac{\partial^2 y}{\partial x_i^2} + b^3\frac{\partial^2 z}{\partial x_i^2} + 6a^2 = 0. \tag{41}$$

Therefore

$$\frac{\partial^2 y}{\partial x_i^2} = -(6a^2 - 2b^2)/a(a^2 - b^2), \tag{42}$$

$$\frac{\partial^2 z}{\partial x_i^2} = 4a^2/b(a^2 - b^2) \tag{43}$$

which, substituted back into (32) gives

$$\frac{\partial^2 E_\pi}{\partial x_i^2} = 2u, \tag{44}$$

where

$$u = 2(2a+b)(a-b)/ab(a+b). \tag{45}$$

By an analogous way of reasoning one can determine all the second partial derivatives of E_π. Thus for $i, j \in \{1, 2, \ldots, t-1\}$, $i \neq j$,

$$\frac{\partial^2 E_\pi}{\partial x_i \, \partial x_j} = u. \tag{46}$$

For $i, j \in \{t+1, \ldots, N/2-1\}$

$$\frac{\partial^2 E_\pi}{\partial x_i \, \partial x_j} = \begin{cases} 2w & \text{if } i = j \\ w & \text{if } i \neq j, \end{cases} \tag{47}$$

where

$$w = -2(a+2b)(a-b)/ab(a+b). \tag{48}$$

All other partial derivatives are found to be equal to zero. Note that because of $a > b > 0$, u is positive whereas w is negative.

The above results mean that the Hessian matrix of E_π has the following structure:

$$\boldsymbol{H} = \begin{pmatrix} \boldsymbol{U} & \boldsymbol{0} \\ \boldsymbol{0} & \boldsymbol{W} \end{pmatrix}, \tag{49}$$

where

$$\boldsymbol{U} = \begin{pmatrix} 2u & u \ldots & u \\ u & 2u \ldots & u \\ \cdot & \cdot \ldots & \cdot \\ u & u \ldots 2u \end{pmatrix}, \quad \boldsymbol{W} = \begin{pmatrix} 2w & w \ldots & w \\ w & 2w \ldots & w \\ \cdot & \cdot \ldots & \cdot \\ w & w \ldots 2w \end{pmatrix} \tag{50}$$

and $\boldsymbol{0}$ denotes a pertinent zero matrix. Note that $\boldsymbol{U}$ and $\boldsymbol{W}$ are square matrices of order $t-1$ and $N/2-t-1$, respectively, and that the order of $\boldsymbol{H}$ is $N/2-2$.

The eigenvalues of $\boldsymbol{H}$ are now easily found: u $(t-2)$ times, w $(N/2-t-2)$ times, $u\,t$ and $w(N/2-t)$. Therefore $\boldsymbol{H}$ has a total of $t-1$ positive and $N/2-t-1$ negative eigenvalues. It follows that only for $t = 1$ we deal with a true extremum (which, of course, is a maximum). For all other choices of t we have only saddle points. A true minimum would be reached for $t = N/2-1$, but then $E_C(t)$ is complex valued.

Numerical Work

All the inequalities given in (10) were tested by numerical calculation. A sample consisting of 106 benzenoid hydrocarbons has been used [6]. All the relations (10) were confirmed in all cases except $E_\pi < E_C(2)$, which was violated for benzene and naphthalene, and $E_{GTD} < E_T$, which was violated for benzene. In addition to this, in all studied cases $E_C(Q)$ was found to have a lower value than E_π.

A very good linear correlation between E_π and $E_C(t)$ could be observed. For $t = 1$, $t = 2$, $t = Q/2$ and $t = Q$ the correlation coefficients found were 0.999843, 0.999831, 0.999826 and 0.987, respectively.

In Table 1 are presented the E_π, E_{MC}, E_T, E_{GTD}, E^0_{GTD}, $E_C(1)$, $E_C(2)$ and $E_C(3)$ values for a number of benzenoid molecules. They illustrate the quality of the estimates (10) as well as the inequalities (11).

Table 1.

Molecule	E_{MC}	E_T	E_{GTD}	E^0_{GTD}	$E_C(1)$	$E_C(2)$	$E_C(3)$	E_π
Benzene	8.49	8.10	8.16	8.16	8.00	6.93	–	8.00
Naphthalene	14.83	14.35	14.19	14.19	14.01	13.65	12.61	13.68
Anthracene	21.17	20.66	20.38	20.38	20.09	19.73	19.28	19.31
Phenanthrene	21.17	20.66	20.39	20.38	20.09	19.73	19.28	19.45
Pyrene	24.66	24.13	23.81	23.81	23.43	23.03	22.61	22.51
Tetracene	27.50	26.98	26.64	26.64	26.19	25.80	24.42	24.93
Triphenylene	27.50	26.98	26.65	26.64	26.19	25.80	24.42	25.27
Perylene	30.98	30.45	30.09	30.08	29.54	29.12	28.73	28.25
Pentacene	33.82	33.30	32.92	32.92	32.32	31.89	31.51	30.54
Picene	33.82	33.30	32.93	32.92	32.32	31.89	31.51	30.94
Coronene	37.95	37.40	36.99	36.99	36.26	35.79	35.38	34.57
Ovalene	51.22	50.67	50.21	50.21	49.15	48.59	48.15	46.50

Appendix

We prove here that R, as defined via (5), is a real-valued quantity for all benzenoid hydrocarbons. In order to do this it is sufficient to show that

$$18MN - 12N^2 - 4M^2 \geqq 0. \tag{51}$$

Consider the left-hand side of (51) as a polynomial in the variable M. Its zeros are equal to $(9 \pm \sqrt{33})\,N/4$. Consequently, the l.h.s. of (51) will be positive whenever

$$(9 - \sqrt{33})\,N/4 < M < (9 + \sqrt{33})\,N/4, \tag{52}$$

i.e.

$$1.6 < 2M/N < 7.4. \tag{53}$$

On the other hand, $2M/N$ is the average vertex degree of a graph with N vertices and M edges. For benzenoid graphs all vertex degrees are either two or three, and thus the average vertex degree lies between two (benzene) and three (graphite). Therefore the inequalities (53) are always fulfilled, and we arive at (51). The same argument shows that equality in (51) will never occur.

[1] B. J. McClelland, J. Chem. Phys. **54,** 640 (1971).
[2] L. Türker, Match (Mülheim) **16,** 83 (1984).
[3] I. Gutman, L. Türker, and J. R. Dias, Match (Mülheim) **19,** 147 (1986).
[4] J. Cioslowski, Z. Naturforsch. **40a,** 1167 (1985).
[5] I. Gutman, Lj. Nedeljković, and A. V. Teodorović, Bull. Soc. Chim. Beograd **48,** 495 (1983).
[6] R. Zahradnik and J. Pancir, HMO Energy Characteristics, Plenum Press, New York 1970.