APPROXIMATING THE TOTAL π-ELECTRON ENERGY OF BENZENOID HYDROCARBONS:

ON AN OVERLOOKED FORMULA OF CIOSLOWSKI

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Abstract: An implicit (n,m)-type approximate topological formula for the total π-electron energy (E) of benzenoid hydrocarbons was deduced by Jerzy Cioslowski in 1987, but attracted little attention so far. We provide here a detailed analysis of this formula and, in particular, show that its precision is slightly better than that of the McClelland's approximation.

INTRODUCTION

In a recently published review [1] the present author reported on the plethora of works devoted to the elucidation of the dependence of the total π-electron energy (E) of benzenoid hydrocarbons on their various structural features and topological (i.e. graph-theoretical) invariants. It has been unequivocally established that the gross part of E is determined by only two such invariants, namely the number of carbon atoms (n) and the number of carbon-carbon bonds (m).

In [1] we collected a total of 24 various (n,m)-type approximate

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expressions $E^{\bullet}$ for total π-electron energy, i.e. expressions depending solely on the parameters n and m, and tested the accuracy and reliability of the approximate formulas:

$$E \approx a_1 E^{\bullet} \tag{1}$$

$$E \approx a_2 E^{\bullet} + b_2 \tag{2}$$

Least-squares fitting and a standardized data-base were used for this purpose (for details see [1] or [2]). One of the conclusions achieved was that the best (n,m)-type formulas are capable of reproducing some 99.5% of E. More precisely, in the case of the most reliable formulas of the type (1) or (2) the mean relative error was about 0.3 %. One of such "best" expressions for $E^{\bullet}$ is the famous McClelland function $\sqrt{2\,m\,n}$ [3].

Recall that in [3] it was shown that the function $\sqrt{2\,m\,n}$ is an upper bound for E (for details see [1]). In addition to this, McClelland observed the (nontrivial) fact that $\sqrt{2\,m\,n}$ is proportional to E and put forward the simple approximation $E \approx a\,\sqrt{2\,m\,n}$ in which the fitting parameter a was about 0.9. Since then, under the name "McClelland approximation" one usually refers to the formula $E \approx a\,\sqrt{2\,m\,n}$.

All the expressions $E^{\bullet}$ studied in [1] were explicit mathematical functions of n and m. In addition to them, however, there exists an (n,m)-type formula for E that can be defined only in an implicit manner. Namely, some time ago Jerzy Cioslowski developed a theoretical approach to the π-electron properties of benzenoid hydrocarbons [4-7], based on certain assumptions on the form of the spectral-density operator. Cioslowski was then able to demonstrate [5] that within the framework of his theory the total π-electron energy obeys (approximately) the following equation:

$$E^4 + 6(2mn - E^2)\left[E^2 + A E (2mn - E^2)^{1/2} + B(2mn - E^2)\right]$$

$$= 6n^3(3m - 2n) \tag{3}$$

where A and B are adjustable constants; in ref. [5] it was proposed to choose $A = 1.1360$ and $B = -1.7600$.

In connection with Eq. (3) Cioslowski stated [5] that "*the result-ing average E's are reproduced with the error which is 4 times smaller than the one of McClelland formula*". In this (somewhat overlooked) claim he had in mind McClelland's upper bound $\sqrt{2\ m\ n}$ and not the McClelland approximation $a\ \sqrt{2\ m\ n}$ [8]. Because this detail was not pointed out in [5] the wrong impression may be obtained that Eq. (3) is claimed to pro-vide an (n,m)-type approximate formula for E that has a mean relative error below 0.1 % . [This, in turn, would then imply that certain gene-ral conclusions [1] about the structure-dependency of E would need to be reconsidered.] The present paper is aimed to clarify this conundrum.

In this paper we report our findings that the accuracy and reliabi-lity of the approximation for E obtained from Eq. (3) are only slightly better than of the McClelland formula, and are tantamount to the preci-sion of several previously examined explicit (n,m)-type expressions.

EXISTENCE OF SOLUTION OF CIOSLOWSKI'S EQUATION

From the form of Eq. (3) it is evident that one cannot expect to solve it solely by means of algebraic manipulations. Nevertheless, a significant simplification is gained by introducing the "reduced total π-electron energy" e, defined via [6,7]:

$$e: = (2mn)^{-1/2} E \quad . \tag{4}$$

Recall that e necessarily lies in the interval (0,1). Substituting (4) back into (3) one obtains

$$f(e) = F(n,m) \qquad (5)$$

where the two auxiliary functions f and F are given by

$$f(e): = e^4 + 6(1 - e^2)\left[e^2 + A e (1 - e^2)^{1/2} + B (1 - e^2)\right]$$

and

$$F(n,m): = 3n(3m - 2n)/(2m^2) \qquad (6)$$

For the solution of Eq. (5) it is essential that the function $f(e)$ has a maximum in the interval (0,1). To see this it is sufficient to realize that $f(0) = 6 B < 0$, $f(1) = 1 > 0$, $f'(0) = 6 A > 0$ and $f'(1) = -8 < 0$. Using the above given values for A and B we found that $f(e) = f_{max} \approx 1.765$ for $e = e_{max} \approx 0.86$. Consequently, Cioslowski's equation (3) will have real-valued solutions only for those combinations of n and m for which $F(n,m)$ is less than $f_{max} \approx 1.765$. Then, however, there will be two such solutions, one lying in the interval $(0, e_{max}]$, the other belonging to $[e_{max}, 1)$. Evidently, the physically meaningful solution is the latter one.

In the Appendix we demonstrate that for all combinations of n and m that may occur in benzenoid systems, $F(n,m) \le 27/16 = 1.6875$. Hence the condition $f_{max} > F(n,m)$ is always obeyed and, consequently, Cioslowski's equation has real-valued solutions for all benzenoid hydrocarbons.

In the Appendix we also show that for benzenoids with more than two hexagons, the function $F(n,m)$ varies in a remarkably narrow interval, namely that it is bounded as follows:

$$105/64 \le F(n,m) \le 108/64 \quad .$$

This implies

$$F(n,m) \approx const \approx 213/128$$

i.e. the value of $F(n,m)$ may deviate from $213/128$ by at most 1.4 % .

NUMERICAL WORK

If one takes Cioslowski's statements concerning Eq. (3) literally, then the respective approximate expression for the total π-electron energy would be of the form

$$E \approx E^* \tag{7}$$

with E^* standing for the pertinent solution of Eq. (3). This certainly yields results better than

$$E \approx \sqrt{2\ m\ n} \tag{8}$$

but its accuracy is still very poor (see below). Therefore in addition to Eq. (7) we also studied approximations of the type (1) and (2).

First the values of the parameters A and B have been determined. We calculated them by minimizing the mean relative errors of Eqs. (7), (1) and (2), respectively. (As in our previous studies [1,2], we employed a data-base consisting of 104 Kekuléan benzenoids possessing more that two six-membered rings.) The values obtained are:

$$A = 1.136 \quad B = -1.33 \qquad \text{for Eq. (7)} \qquad (\alpha)$$

$$A = 1.136 \quad B = -1.97 \qquad \text{for Eq. (1)} \qquad (\beta)$$

$$A = 1.136 \quad B = -1.76 \qquad \text{for Eq. (2)} \qquad (\gamma)$$

Note that the third set of parameters coincides with what originally was proposed in ref. [5]. Whereas the value of A is "stable", there exists a great deal of variation in B, depending on the criterion used for its

determination. Furthermore, B also exhibits a significant sample-depend-ency.

The results of the numerical testing of Eqs. (1), (2), (7) and (8) are presented in Tables 1a and 1b.

Table 1a. Coefficients in the approximate
(n,m)-type formulas (1) & (2)

Parameter set	a_1	a_2	b_2
(α)	1.024	1.025	-0.01
(β)	1.040	1.034	0.24
(γ)	1.032	1.023	0.34

Table 1b. Results of numerical testing of approximate formulas
(1),(2) & (7) for the parameter sets (α), (β) & (γ),
as well as of formula (8)

Equation	mean error (%)	max. error observ.(%)	correlation coefficient
(1) & (α)	0.50	8.2	
(2) & (α)	0.50	8.1	0.9994
(7) & (α)	2.35	3.5	
(1) & (β)	0.33	1.3	
(2) & (β)	0.31	1.2	0.9998
(7) & (β)	3.93	4.6	
(1) & (γ)	0.34	1.2	
(2) & (γ)	0.30	1.1	0.9998
(7) & (β)	3.18	4.1	
(8)	9.99	11.4	0.9998

From the data collected in Table 1b we immediately arrive at the following conclusions:

(a) The solutions of Cioslowski's equation are themselves [i.e. via Eq. (7)] very poor approximations for total π-electron energy. It is true that formula (8) would result in about 4 times greater errors, but - as already pointed out - neither McClelland himself [3] nor anybody else ever purported that (8) be used.

(b) When these solutions are amended by means of one [Eq. (1)] or two [Eq. (2)] least-squares parameters, then the agreement with the total π-electron energy is much better.

(c) Even then the quality of the approximation is comparable with that of the McClelland formula as well as with several other previously known (n,m)-type expressions [1,2]. The mean relative error of (amended) Cioslowski's approximation differs insignificantly from the mean relative error of McClelland's and similar formulas.

A P P E N D I X : ANALYSIS OF THE TOPOLOGICAL FUNCTION F(n,m)

The topological function F(n,m), defined via Eq. (6) can be readily transformed into

$$F(n,m) = <d>^{-2} (9<d> - 12)$$

where $<d> = 2m/n$ is the average vertex degree. Now, for benzenoid systems, $2 \le <d> < 3$ and therefore we are interested in the behavior of the function $G(x): = x^{-2} (9x - 12)$ in the interval [2,3]. Elementary calculus shows that G(x) increases for $x \in [2, 8/3)$, decreases for $x \in (8/3, 3)$ and has a maximum at $x = 8/3$.

Consider now the average vertex degree $<d>$. Denote by n_i and h the numbers of internal vertices and hexagons, respectively, of a benzenoid

system [9]. Then because of [9] $n = 4h + 2 - n_i$ and $m = 5h + 1 - n_i$ we readily arrive at

$$\langle d \rangle = 2 \left(1 + (h - 1)/(4h + 2 - n_i) \right)$$

showing that for a fixed value of h, $\langle d \rangle$ is a decreasing function of n_i. Knowing that [10]

$$0 \leq n_i \leq 2h - \left\lceil (12h - 3)^{1/2} \right\rceil$$

we conclude that the minimum and maximum values of $\langle d \rangle$ are

$$\langle d \rangle_{min} = (5h + 1)/(2h + 1) \tag{9}$$

and

$$\langle d \rangle_{max} = \left\{ 6h + 2 \left\lceil (12h - 3)^{1/2} \right\rceil \right\} \left\{ 2h + 1 + \left\lceil (12h - 3)^{1/2} \right\rceil \right\}^{-1}$$

$$\tag{10}$$

respectively. In the above formulas, $\left\lceil X \right\rceil$ denotes the smallest integer that is not smaller than X. It is easily verified that both $\langle d \rangle_{min}$ and $\langle d \rangle_{max}$ are increasing functions of h. Their limits (as $h \to \infty$) are 2.5 and 3, respectively. Hence, $\langle d \rangle_{min}$ will always belong to the interval [2, 8/3). Because for h = 19, $\langle d \rangle_{max} = 8/3$, $\langle d \rangle_{max}$ will lie in the interval (8/3, 3) only if $h \geq 20$.

The above analysis, combined with the previously established pro-perties of the function G(x), implies that for $h \leq 19$,

$$G(\langle d \rangle_{min}) \leq F(n,m) \leq G(\langle d \rangle_{max}) \tag{11}$$

where $\langle d \rangle_{min}$ and $\langle d \rangle_{max}$ are given by Eqs. (9) and (10). The bounds (11) are the best possible. Observe that practically all benzenoid hydrocar-bons of chemical relevance have fewer than 19 six-membered rings.

For $h \geq 20$ the inequalities (11) have to be modified as

$$G(\langle d \rangle_{min}) \leq F(n,m) \leq G(8/3) = 27/16 \quad .$$

Because $G(8/3)$ is the maximum value of the function $G(x)$, it follows that for all benzenoid systems the value of $F(n,m)$ is less or equal to $27/16 = 108/64$. This is the result that guarantees the existence of real-valued solutions of Cioslowski's equation.

For $h = 3$, $G(\langle d \rangle_{min}) = 105/64$. Consequently for benzenoids with more than two hexagons, $105/64 \leq F(n,m) \leq 108/64$. This means that for all benzenoid systems, the quantity $F(n,m)$ assumes nearly the same value. This value is close to $213/128 = 1.664$.

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