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INVESTIGATION OF THE CIOSLOWSKI FORMULA

I. Gutman, S. Marković and M. Marinković

Faculty of Science, University of Kragujevac, P.O.Box 60,
YU-34000 Kragujevac, Yugoslavia

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Abstract

A result by Cioslowski [Match 20, 95 (1986)], concerning the dependence of total pi-electron energy E_{pi} of benzenoid hydrocarbons on N - the number of carbon atoms, M - the number of carbon-carbon bonds and K - the number of Kekulé structures, is examined. The Cioslowski formula $E_{pi} = (2\ M\ N)^{1/2}\ F[K^{2/N}\ (2M/N)^{-1/2}]$ contains an unspecified function F. By numerical testing of this formula some information is gained about F. Our findings support the relation F(1) = 1, proposed recently by Cioslowski and Polansky.

INTRODUCTION

Total pi-electron energy (as calculated by means of the HMO approximation) and its dependence on molecular structure attract the interest of theoretical chemists over decades[1]. In spite of numerous results obtained[2], this field of research seems not to be completely exhausted[3].

Recently a method has been developed[9] for approximate calculation of various HMO pi-electron indices of benzenoid hydrocarbons. This method, named the universal distribution approach (UDA), is outlined in detail elsewhere[9,17-19]. When applied to the total pi-electron energy (E_{pi}), it leads to the formula

$$E_{pi} = (2\ M\ N)^{1/2}\ F[K^{2/N}\ (2M/N)^{-1/2}]\ . \qquad (1)$$

where N, M and K denote the number of carbon atoms, carbon-carbon bonds and Kekule structures, respectively, of the corresponding benzenoid hydrocarbon. (The notation used in the present paper is the same as in Refs. 9 and 18.) In eq. (1) a function F = F(x) appears which within UDA remains unspecified.

Not much is known about Cioslowski's function F(x). Bearing in mind the very good quality of the McClelland formula[2,12,21]

$$E_{pi} = a_0\ (2\ M\ N)^{1/2} \quad , \quad a_0 = \text{const} \qquad (2)$$

we see that already the crudest assumption about F(x), namely F(x) = const, implies a tolerable approximate topological expression for E_{pi}. In Ref. 9 it has been demonstrated (by numerical testing) that F(x) is fairly well approximated by a linear function $a_0 + a_1\ x$ where $a_0 = 0.7676$ and $a_1 = 0.1775$.

In a later work Cioslowski and Polansky concluded[19] that the function F(x) should obey the condition F(1) = 1.

NUMERICAL WORK

In order to acquire some experience about the actual analytical form of Cioslowski's function we have tested the quality of the approximation (1) for the following seven cases:

$$F(x) = a_0 \tag{3a}$$

$$F(x) = a_0 + a_1 x \tag{3b}$$

$$F(x) = a_0 + a_1 x + a_2 x^2 \tag{3c}$$

$$F(x) = a_0 + a_1 x + a_2 x^{-1} \tag{3d}$$

$$F(x) = a_0 + a_1 x + a_2 \ln x \tag{3e}$$

$$F(x) = a_0 + a_1 x^p \tag{3f}$$

$$F(x) = a_0 \left[(1 + x^2)/2\right]^{1/2} \quad . \tag{3g}$$

Here a_0, a_1, a_2, and p denote constants which, of course, are different for different choices of F(x). These parameters have been determined by least-squares fitting, based on the exact E_{pi} values for a set of 104 polycyclic benzenoid hydrocarbons from the book[22], with naphthalene excluded. (The same data base has been employed also in Refs. 10,12,13 and 21.)

The results obtained are collected in Table 1. The quality of the approximate topological expressions of the type (1), based on the choices (3a)-(3g) of F(x) can be seen from the data presented in Table 2.

Table 1. Optimal values for the parameters a_0,a_1,a_2 and p, calculated by least-squares fitting. Data base: 104 benzenoid hydrocarbons from Ref. 22.

F(x)	a_0	a_1	a_2,p	F(1)
3a	0.9083			0.9083
3b	0.7578	0.1899		0.9477
3c	1.2910	-1.1684	0.8644	0.9870
3d	-0.0821	0.7247	0.3295	0.9721
3e	-0.5923	1.5741	-1.0867	0.9818
3f	0.8934	0.1864	11	1.0798
3g	1.0089			1.0089

Table 2. Results of numerical testing of topological formulas of type (1). Data base same as in Table 1.

F(x)	correlation coefficient	mean error(%)	max.error observed(%)
3a	0.9998	0.372	1.23
3b	0.999983	0.092	0.45
3c	0.999986	0.075	0.42
3d	0.999986	0.078	0.43
3e	0.999986	0.075	0.42
3f	0.999986	0.072	0.42
3g	0.9996	0.434	1.66

DISCUSSION

The test functions (3a)-(3f) have been chosen because of their simple algebraic form. The approximate topological formula for total pi-electron energy, based on the function (3g), has been already considered in Ref. 21 and is included in the present work for sake of completeness. Anyway, the choice (3g) for f(x) yields the worst among all approximate formulas for E_{pi}.

Eq. (3a) results, of course, in the McClelland formula (2) whereas a study of the case (3b) has been previously reported in Ref. 9. The inclusion of a non-linear term (either x^2 or x^{-1} or ln x) into Cioslowski s function only slightly increases the reliability and accuracy of the pertinent approximate topological formula for E_{pi}. Therefore the usage of such non-linear correction terms does not seem to be warrantable. It is a curious finding that all the three functions (3c),(3d) and (3e) result in approximate formulas for E_{pi} having practically the same precision.

Another result worth noting is the large value (11) of the parameter p in eq. (3f). A detailed examination of (3f) showed, however, that the quality of the approximate formula for E_{pi} is not very sensitive to the variation of this parameter. Thus for p = 2,4,6,8,10 and 12, the corresponding correlation coefficients found were 0.9999834, 0.9999848, 0.9999857, 0.9999861, 0.9999860 and 0.9999855, respectively. The corresponding mean errors were 0.088%, 0.083%, 0.078%, 0.074%, 0.072% and 0.073%, respectively. Therefore some caution is necessary with regard to the above given numerical values of the empirical parameters in eq. (3f).

Finally, we wish to point at a fact that in all cases, except in eqs. (3a) and (3b), the value of F(x) for x = 1 is found to be very close to unity (see Table 1). This is in full agreement with the theory put forward some time ago by Cioslowski and Polansky[19].

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The main conclusions of the present investigation are the following two. 1. Cioslowski's function F(x) is essentially linear. Therefore eq. (3b) may be understood as something more than just a plausible Ansatz. A theoretical confirmation of this empirical observation may be a challenging task for the future. 2. Small modifications of eq. (3b) do not significantly improve the accuracy of the corresponding topological formula for E_{pi}, eq. (1). However, by these amendments (no matter what their analytical form is), the value of F(1) becomes very close to unity. This confirms a previous theoretical result and brings it in harmony with empirical findings.

The Cioslowski formula provides a deep insight into the topological factors which determine the thermodynamic stability of benzenoid hydrocarbons. We hope that the present work made this insight somewhat more clear[23].

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