

TOPOLOGICAL PROPERTIES OF BENZENOID SYSTEMS. XLVIIIa.
AN EMPIRICAL STUDY OF TWO CONTRADICTORY FORMULAS
FOR TOTAL π -ELECTRON ENERGY

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Abstract

Some time ago [Match 21, 317 (1986)] an attempt has been made to reconcile two approximate formulas for total π -electron energy (E), namely, that of Hall and Cioslowski, which predict quite different dependence of E on the number of Kekulé structures (K). Whereas Hall's formula is linear in K , Cioslowski's theory relates E with a certain function of $K^{2/n}$ (n = number of vertices). In the present paper we examine classes of isomeric benzenoid hydrocarbons, and show that Cioslowski's formula with a linear dependence of E on $K^{2/n}$ is inferior to Hall's. If a third order polynomial dependence on $K^{2/n}$ is anticipated, then Cioslowski's formula reaches the precision of Hall's formula.

INTRODUCTION

The investigation of the dependence of the Hückel molecular orbital total π -electron energy (E) on the number of Kekulé structures (K) has a relatively long history^{1,2}, and a considerable number of scientific publications are devoted to this problem^{1,3-10}.

Already in 1973 Hall observed³ that within a class of isomeric benzenoid hydrocarbons a fairly good linear correlation between E and K exist. Hall's rule was further elaborated⁴ in 1981 when the formula

$$E = A_n + B_m + CKe^{-D(m-n)} \quad (1)$$

was proposed. Here and later m and n denote the number of edges and vertices, respectively, of the molecular graph. Hence the benzenoid hydrocarbon considered has n carbon atoms, m carbon - carbon bonds, and $3n-2m$ hydrogen atoms, isomeric benzenoid molecules have thus equal values for n and m.

In Eq. (1) A, B, C and D are empirical parameters which are to be determined by least squares fitting. The same is true for the constants A_0 and A_1 in Eq. (1'), as well as A_i , $i = 0, 1, \dots, L$, in the Cioslowski-type formulas (see below).

A result equivalent to (1) was also obtained in Ref. 5.

A completely different approach to the same problem has been put forward in 1986, when Cioslowski formulated his UDA model⁶. This model implies that the total π -electron energy conforms to the formula

$$E = \sqrt{2mn} F(x) \quad (2)$$

where

$$x = \sqrt{\frac{n}{2m}} K^{2/n}. \quad (3)$$

In Eq. (2) F stands for a certain function which, within Cioslowski's approach, remains unspecified. The only known property of this function is the condition⁷

$$F(1) = 1. \quad (4)$$

As a first Ansatz for $F(x)$ Cioslowski proposed⁶ a linear form

$$F(x) = A_0 + A_1 x \quad (5)$$

which, when combined with Eq. (2), yields a fairly good approximation for E . Formula (2)&(5) has been recently deduced¹⁰ without the usage the UDA model.

The contradiction between Hall's formula (1) and Cioslowski's formula (2) was discussed in detail in Ref. 8, where an attempt to reconcile (1) and (2)&(5) was also put forward. The idea advocated in Ref. 8 was that since both (1) and (2)&(5) are approximations, they both may have similar and indistinguishable accuracy and reliability. This indeed seems to be the case when (1) and (2)&(5) are tested on sets of non-isomeric benzenoid molecules. In the present work a more selective test is employed, which shows that the conclusions of Ref. 8 need to be somewhat modified.

When instead of (5) a higher-degree polynomial approximation is used, viz.

$$F(x) = A_0 + A_1 x + \dots + A_L x^L \quad (6)$$

then⁹ in the case of non-isomeric samples only a minor improvement in the precision of Eq. (2) is gained. On the other hand, if $F(x)$ is given by (5), then the condition (4) is poorly satisfied. For $L > 1$ in Eq. (6) the condition (4) was found⁹ to be almost perfectly obeyed.

AN EMPIRICAL TEST OF CIOŚŁOWSKI'S FORMULA

As already mentioned, Hall arrived³ to the linear dependence of E on K by examining sets of isomeric benzenoid hydrocarbons. (Molecules in such sets necessarily have equal n and m .) We decided to repeat the same empirical approach in order to test formula (2).

Several sets of benzenoid isomers have been selected and examined. Preference was given to sets with more than hundred elements; by this the statistical significance of the results obtained is assured.

In the present paper we report only the results obtained for the set of 328 octacyclic benzenoid hydrocarbons of the formula $C_{32}H_{18}$ ($n = 32$, $m = 39$); according to our experience these results are typical.

On Fig 1 the energies of the molecules $C_{32}H_{18}$ versus their number of Kekulé structures are plotted.

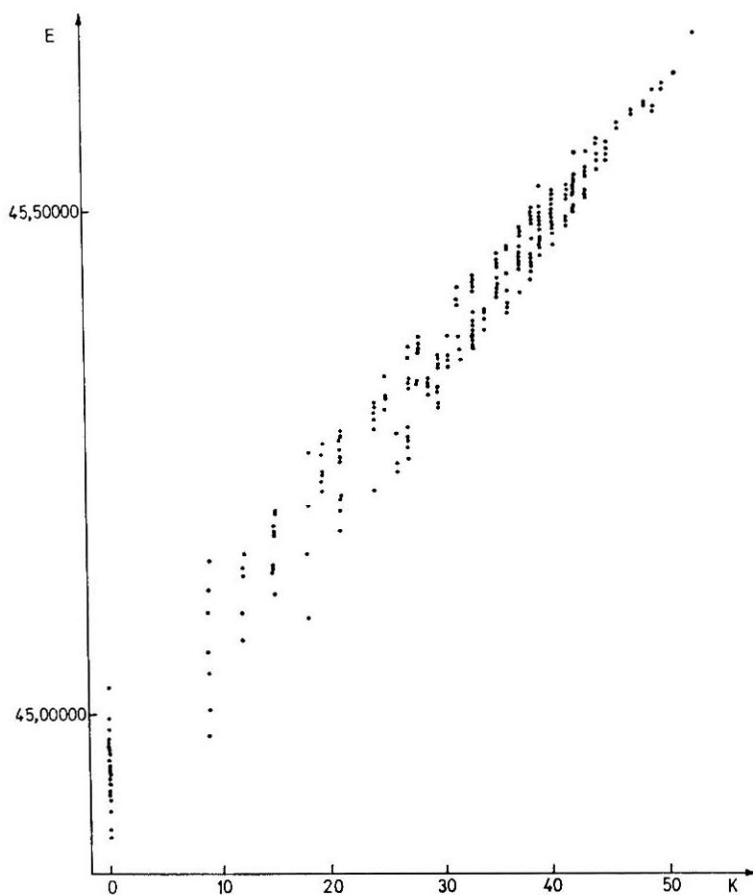


Fig. 1. Correlation between the total π -electron energies (E) and Kekulé structure counts (K) of the 328 benzenoid isomers $C_{32}H_{18}$.

A glance at Fig. 1 reveals that the correlation between E and K is essentially linear, but because of the spread of the points a slightly curvilinear dependence cannot be automatically excluded.

In Tables 1 and 2 the relevant least-squares results for Eqs. (1) and (2)&(6) are collected. Since in our samples n and m are constants, we used the form (1') of Hall's formula:

$$E = \sqrt{2mn} (A_0 + A_1 x^{n/2}) \quad (1')$$

with x being given by (3).

equation	correlation coefficient	average error (%)
(1)	0.9907	0.044
(2)&(6); L=1	0.82	0.201
(2)&(6); L=2	0.98	0.061
(2)&(6); L=3	0.9906	0.045

Table 1. Statistical data enabling the comparison of Hall's and Cioslowski's formulas; calculations based on the sample presented in Fig. 1.

equation	A_0	A_1	A_2	A_3	F(1)
(1')	0.8997	0.3411			
(6); L=1	0.8993	0.0122			0.91
(6); L=2	0.8993	-0.1235	0.1699		0.95
(6); L=3	0.8997	0.8082	-2.2132	1.5227	1.02

Table 2. Least-squares coefficients in Hall's and Cioslowski's formulas; calculations based on the sample presented in Fig. 1.

DISCUSSION

From Table 1 we immediately see that the linear form for Cioslowski's function $F(x)$, namely Eq. (5) or Eq. (6), $L=1$, yields results significantly weaker than those obtained from Hall's formula (1). Thus we may conclude that E must not be represented by a linear function of $K^{2/n}$.

By including a quadratic and a further cubic term into $F(x)$ the quality of Cioslowski's formula becomes significantly better. For $L=3$ Cioslowski's formula reaches the accuracy of Hall's formula. However, whereas Hall's formula (1') contains only two least-squares parameters, the Cioslowski's formula of the same precision requires four such parameters.

In some other samples examined, the accuracy of Eqs. (1) and (2) coincides already for $L=2$. On the other hand, in all cases studied, Eq. (2) for $L=1$ is doubtlessly inferior to Eq. (1).

Thus we may conclude that the linear form (5) is a poor approximation for Cioslowski's function; a cubic polynomial provides a substantially better agreement. This finding is in full harmony with the recently published⁷ plot of $F(x)$ vs. x , which shows an evident non-linearity of Cioslowski's function. The value of $F(1)$ given in Table 2 also indicates that the condition (4) is obeyed only after including the cubic term into formula (6).

The final conclusion of the present empirical study is that:

(a) Hall's formula is better than the linear Cioslowski's formula (2)&(5);

(b) Hall's formula and the cubic Cioslowski's formula (2)&(6); $L=3$ are of equal accuracy. Therefore, on the basis of our samples of isomers it is not possible to decide whether E is a linear function of K or E is a complicated function of $K^{2/n}$.

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