Theoret. Chim. Acta (Berl.) 65, 23–31 (1984)

THEORETICA CHIMICA ACTA

Topological properties of benzenoid systems. Bounds and approximate formulae for total π-electron energy

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A novel variational approach to McClelland's estimate of total π-electron energy (E) is described. An extension of this method yields lower and upper bounds and E of benzenoid hydrocarbons. On the basis of these bounds several approximate topological formulae for E are obtained.

Key words: Benzenoid hydrocarbons—total π-electron energy

1. Introduction

The present paper deals with total π-electron energy of benzenoid hydrocarbons, as calculated within the framework of the Hückel molecular orbital model. Total π-electron energy belongs to the most important and best understood topological properties of conjugated molecules [1], which has been examined in theoretical chemistry for decades.

Graph-theoretical methods, introduced to theoretical chemistry about 1970 and thereafter [2], made the discovery of a number of general and exact results on total π-electron energy possible (e.g. [3–5]). In the present paper we shall derive some more results of this type, valid for benzenoid hydrocarbons.

Let G be a molecular graph [1] with n vertices and m edges. This means that the corresponding conjugated hydrocarbon has n carbon atoms and m carbon-carbon bonds. Let $x_1, x_2, \ldots, x_n$ be the eigenvalues [1] of G, labelled in non-decreasing order. Then the Hückel total π-electron energy (in β units and with reference to the standard carbon-atom Coulomb integral, α, as the zero of energies) is given by

$$E = \sum_{i=1}^{n} g_i x_i \tag{1}$$

where g_i is the occupation number of the ith molecular orbital. In the present work we will consider non-charged conjugated hydrocarbons having a closed-shell ground state. In other words, we will assume that n is even and

$$\begin{aligned} g_i &= 2 \quad \text{for } i=1,2,\ldots,n/2 \\ g_i &= 0 \quad \text{for } i=n/2+1,\ldots,n. \end{aligned} \tag{2}$$

Consequently,

$$\sum_{i=1}^{n} g_i = n$$

and

$$g_i^2 = 2g_i \quad \text{for all } i. \tag{3}$$

Bearing in mind the conditions (2), formula (1) can be understood as a mapping which in a unique manner associates a scalar $E=E(\boldsymbol{x})$ with an ordered n-tuple $\boldsymbol{x}=(x_1, x_2, \ldots, x_n)$. In the following, we will be interested in extremal properties of $E(\boldsymbol{x})$, when $\boldsymbol{x}$ is subject to certain constraints.

If $x_1, x_2, \ldots, x_n$ are eigenvalues of a schlicht graph, then they conform to two well-known identities [6], namely

$$\sum_{i=1}^{n} x_i = 0 \tag{4}$$

and

$$\sum_{i=1}^{n} x_i^2 = 2m. \tag{5}$$

2. An extremal property of total π-electron energy

McClelland [7] has discovered that the total π-electron energy is bounded as follows:

$$E \leq \sqrt{2mn}. \tag{6}$$

The simple expression $\sqrt{2mn}$, which appears on the r.h.s. of McClelland's estimate (6) plays an important role in the topological theory of conjugated molecules [1].

The following observation, related to the McClelland's inequality, served as the starting point for the investigations exposed in the present paper.

Proposition 1. If $\boldsymbol{x}$ satisfies the conditions (4) and (5), then $E(\boldsymbol{x})$ cannot exceed the McClelland limit $\sqrt{2mn}$. Furthermore, $E(\boldsymbol{x})=\sqrt{2mn}$ if and only if $x_1=x_2=\cdots=x_{n/2}=\sqrt{2m/n}$ and $x_{n/2+1}=\cdots=x_n=-\sqrt{2m/n}$.

Proof. Proposition 1 is a special case of a statement which has been proved in the Appendix. In order to obtain Proposition 1, one has simply to set $H=0$ and $M=m$ in Proposition 4.

The above result suggests that improvements of the McClelland bound (6) could be obtained by introducing some more constraints in addition to (4) and (5). In the following, we will solve a related variational problem with three constraints, deducing thus both upper and lower bounds for E of benzenoid hydrocarbons.

3. Bounds for total π-electron energy of benzenoid hydrocarbons

Whereas numerous topological properties of benzenoid hydrocarbons have been examined in detail [8], not much is known about their total π-electron energies. Hall [9] has first noticed that E is a linear function of the number of Kekulé structures. This empirical finding was later further elaborated in [10, 11].

Benzenoid graphs are bipartite and therefore [12]

$$x_i = -x_{n+1-i} \quad \text{for all } i. \tag{7}$$

Consequently, instead of (1) and (5) we have

$$E = 2 \sum_{i=1}^{n/2} x_i \tag{8}$$

and

$$\sum_{i=1}^{n/2} x_i^2 = m. \tag{9}$$

Note that if the relations (7) hold, then the condition (4) is automatically fulfilled.

One of the most distinguished properties of benzenoid systems is the Dewar–Longuet–Higgins theorem [13] which claims that the product of all the eigenvalues of a benzenoid graph is equal to the square of the number of Kekulé structures of the corresponding molecule. Bearing in mind the relations (7), we can write the Dewar–Longuet–Higgins theorem in the form

$$\sum_{i=1}^{n/2} \ln x_i = \ln K \tag{10}$$

where, of course, we assume that $K > 0$.

Proposition 2. Consider the equations

$$a^2 + (n/2-1)b^2 = m, \tag{11a}$$

$$ab^{n/2-1} = K, \qquad K > 0. \tag{11b}$$

Let a_1, b_1 be the solution of (11), such that $a_1 > b_1 > 0$. Let a_2, b_2 be the solution of (11), such that $b_2 > a_2 > 0$. Let $E_{\min} = 2a_1 + (n-2)b_1$ and $E_{\max} = 2a_2 + (n-2)b_2$. Then for a benzenoid hydrocarbon with n carbon atoms, m carbon–carbon bonds and K Kekulé structures,

$$E_{\min} \leq E < E_{\max}.$$

The equality in the left relation holds only for benzene.

Proof. We determine the extremes of the function $E(\boldsymbol{x})$, provided $\boldsymbol{x}$ fulfills the conditions (7), (9) and (10). Because of (7) we may use (8) instead of (1). Hence we must determine the Lagrange multipliers λ and μ, such that the r.h.s. of (12) is maximal or minimal,

$$\sum_{i=1}^{n/2} (2x_i+\lambda x_i^2+\mu \ln x_i)=E+\lambda m+\mu \ln K. \tag{12}$$

Differentiation with respect to $x_i (i=1, 2, \ldots, n/2)$ gives

$$2+2\lambda x_i+\mu/x_i=0. \tag{13}$$

It is not easy to find λ and μ from Eq. (13). Fortunately, this is not at all necessary. Namely, Eq. (13) has just two different solutions:

$$x_i=a=-(1+\sqrt{1-2\lambda\mu})/(2\lambda)$$

and

$$x_i=b=-(1-\sqrt{1-2\lambda\mu})/(2\lambda).$$

We must not select all x_i's equal, because according to Proposition 1, such a choice would result in McClelland's upper bound. Therefore we must choose some x_i to equal a and some x_i to equal b.

It is now obvious that the choice $x_1=a$, $x_2=\cdots=x_{n/2}=b$ will yield a lower bound for $E(\boldsymbol{x})$ if $a>b$, and an upper bound for $E(\boldsymbol{x})$ if $a<b$.

Proposition 2 follows.

In Table 1 are collected the $E_{\min}$, E and $E_{\max}$ values of some typical benzenoid hydrocarbons. More detailed numerical testing showed that $E_{\min}$ is usually 3–4% below and $E_{\max}$ is 4%–5% above the exact E value.

It is not difficult to see that Eq. (11) has exactly two positive solutions. Fig. 1 presents a typical example for the functions (11a) and (11b).

It is not possible to solve (11) explicitly, except in the case of benzene. However, the solutions of (11) are easily obtained by iteration. (In order to obtain a_1, b_1

Table 1. Lower and upper bounds for total π-electron energy of some benzenoid hydrocarbons (according to Proposition 2)

Compound	$E_{\min}$	E	$E_{\max}$
Benzene	8.00	8.00	8.08
Naphthalene	13.48	13.68	13.98
Anthracene	18.69	19.31	19.99
Phenanthrene	19.04	19.45	20.09
Triphenylene	24.70	25.27	26.28
Pyrene	21.80	22.51	23.41
Perylene	27.13	28.25	29.61
Coronene	33.32	34.57	36.49
Ovalene	44.24	46.50	49.65

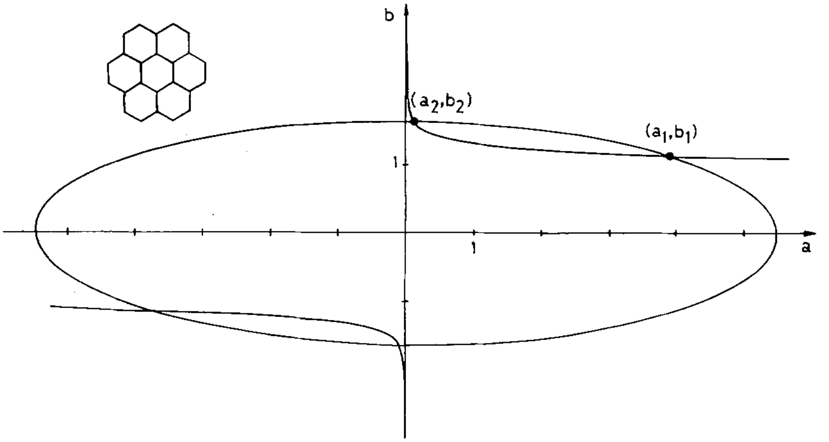

Fig. 1. Functions (11a) and (11b) for the case $n=24$, $m=30$, $K=20$ (coronene)

we start with the guess $b_1^{(0)}=0$, substitute it in (11a) and determine $a_1^{(0)}$. Substituting $a_1^{(0)}$ back into (11b), we determine $b_1^{(1)}$ etc. The solution a_2, b_2 is obtained starting with the guess $a_2^{(0)}=0$. Such an iterative procedure rapidly converges, as can be seen from Fig. 1.) A statisfactory approximate expression for $E_{\min}$ is obtained after three iterations:

$$E_{\min} \approx E_{\min}^{(3)} = 2T + 2q(K/T)^{1/q} \tag{14}$$

where

$$T = \sqrt{m - q\sqrt{\frac{K^2}{m - q(K^2/m)^{1/q}}}}$$

and

$$q = n/2 - 1.$$

Eq. (14) reproduces $E_{\min}$ with an error of only 0.1% or less, what has been established by extensive numerical testing (see also the subsequent section). An equally precise approximtion for $E_{\max}$ requires only one iteration:

$$E_{\max} \approx E_{\max}^{(1)} = 2\sqrt{mq} + 2K(q/m)^{q/2}. \tag{15}$$

Note that $E_{\max}^{(1)}$ is a linear function of K.

Proposition 3. Let $E_{\min}^{(3)}$ and $E_{\max}^{(1)}$ be the topological expressions given by (14) and (15). Then

$$E_{\min}^{(3)} < E < E_{\max}^{(1)}.$$

Exceptionally, the left inequality does not hold for benzene.

According to our experience, even $E_{\min}^{(2)}$ is a lower bound for total π-electron energy of polycyclic benzenoid hydrocarbons.

Propositions 2 and 3 provide relatively narrow lower and upper bounds for total π-electron energy of benzenoid hydrocarbons. These statements are restricted to benzenoid systems because they are based on Eq. (10).

The Dewar–Longuet–Higgins theorem can be extended to non-benzenoid (but alternant) systems by taking into account the parity of Kekulé structures [13, 14]. Therefore Eq. (10) and all its consequences (e.g. Propositions 2 and 3) also hold for non-benzenoid alternant hydrocarbons, provided K is everywhere interchanged by ACS, the algebraic structure count [14, 15].

4. Approximate topological formulae for total π-electron energy of benzenoid hydrocarbons

McClelland [7] found a very good linear correlation between his upper bound $(2mn)^{1/2}$ and E. We examined whether similar correlations can be observed between E, $E_{\min}$ and $E_{\max}$, and arrived at the formulae (16)–(19).

$$E = 1.054 E_{\min}^{(3)}, \tag{16}$$

$$E = 1.091 E_{\min}^{(3)} - 1.377, \tag{17}$$

$$E = 0.940 E_{\max}^{(1)}, \tag{18}$$

$$E = 0.912 E_{\max}^{(1)} + 1.193. \tag{19}$$

The approximate formulae given in the present section are obtained by least squares fitting. The exact E values for 106 benzenoid hydrocarbons are taken from the book [16]. The mean error, the maximal error observed and the correlation coefficient of these formulae are collected in Table 2.

From Table 2 is seen that $E_{\max}^{(1)}$ correlates with E slightly better than $E_{\min}^{(3)}$. This is not surprising if one has in mind the previous finding [9, 10] that in the case of benzenoid hydrocarbons, E is a linear function of K.

Based on Eq. (15), we designed two additional semiempirical formulae, viz.,

$$E = 1.876(mq)^{1/2} + 3.946K(q/m)^{q/2}, \tag{20}$$

$$E = 1.804(mq)^{1/2} + 0.421K(q/m)^{q/2} + 1.686, \tag{21}$$

Table 2. Results of numerical testing of the topological formulae (16)–(22). Asterisk denotes that benzene has been disregarded

Formula	Mean error (%)	Maximal error observed (%)*	Correlation coefficient
16	1.3	4.3	0.99989
17	1.0	3.9	0.998
18	0.78	3.4	0.99997
19	0.37	2.4	0.9998
20	0.50*	2.4	—
21	0.32	1.1	—
22	0.14	0.63	—

which give somewhat more accurate results than Eqs. (18) and (19).

It is necessary to point out here that Hall [10] recently proposed an emprical formula

$$E = 0.442n + 0.788m + 0.34K(0.632)^{m-n} \tag{22}$$

which reproduces E considerably better than Eqs. (16)–(21). An attempt towards a theoretical justification of (22) was reported in [11].

5. Appendix

Generalization of McClelland's formula for conjugated molecules with heteroatoms

In the case of heteroconjugated molecules, instead of Eqs. (4) and (5), we have

$$\sum_{i=1}^{n} x_i = H \tag{A.1}$$

and

$$\sum_{i=1}^{n} x_i^2 = 2M \tag{A.2}$$

where

$$H = \sum_r h_r \quad \text{and} \quad 2M = 2\sum_{r<s} (k_{rs})^2 + \sum_r (h_r)^2$$

and h_r and k_{rs} are the usual HMO parameters for heteroatoms. In particular, if the conjugated system considered possesses just one heteroatom and if the resonance integrals between the heteroatom and the adjacent carbon atoms are assumed to have the standard carbon-carbon value [17], then

$$H = h \quad \text{and} \quad 2M = 2m + h^2.$$

In the case of hydrocarbons, $H = 0$ and $M = m$.

Proposition 4. If the relations (A.1) and (A.2) hold, then $E(\boldsymbol{x})$ cannot be greater than

$$E_{\max} = H + (2Mn - H^2)^{1/2}.$$

Proof. Multiplying (A.1) with λ and (A.2) with μ and adding the obtained equations to (1), we get

$$\sum_{i=1}^{n} (g_i x_i + \lambda x_i + \mu x_i^2) = E + \lambda H + 2\mu M.$$

The r.h.s. of the above expression will be maximal if

$$g_i + \lambda + 2\mu x_i = 0 \tag{A.3}$$

for all values of i. The relation (A.3) can also be written as

$$g_i x_i = -\lambda x_i - 2\mu x_i^2 \tag{A.4}$$

and, taking into account (3),

$$4\mu^2 x_i^2 = 2g_i + 2g_i\lambda + \lambda^2 \tag{A.5}$$

Summing (A.3), (A.4) and (A.5) over all values of i, we obtain

$$n + \lambda n + 2\mu H = 0, \tag{A.6}$$

$$E = -\lambda H - 4\mu M \tag{A.7}$$

and

$$8\mu^2 M = 2n + 2\lambda n + \lambda^2 n. \tag{A.8}$$

From (A.6) and (A.8) the Lagrange multipliers λ and μ are determined as

$$\lambda = -1 + H(2Mn - H^2)^{-1/2} \tag{A.9}$$

and

$$\mu = -\frac{n}{2}(2Mn - H^2)^{-1/2}. \tag{A.10}$$

Substitution of (A.9) and (A.10) back into (A.7) gives the required expression for $E_{\max}$.

Corollary. $E(\boldsymbol{x}) = E_{\max}$ if and only if

$$x_i = \frac{1}{n}[H + (2Mn - H^2)^{1/2}] \quad \text{for } i = 1, 2, \ldots, n/2$$

and

$$x_i = \frac{1}{n}[H - (2Mn - H^2)^{1/2}] \quad \text{for } i = n/2 + 1, \ldots, n.$$

References

1. Graovac, A., Gutman, I., Trinajstić, N.: Topological approach to the chemistry of conjugated molecules. Berlin: Springer-Verlag 1977; and references cited therein
2. Balaban, A. T. ed.: Chemical applications of graph theory. London: Academic Press 1976
3. Gutman, I.: Theoret. Chim. Acta (Berl.) **35**, 355 (1974)
4. Gutman, I.: Theoret. Chim. Acta (Berl.) **45**, 79 (1977)
5. Gutman, I., Polansky, O. E.: Theoret. Chim. Acta (Berl.) **60**, 203 (1981)
6. Graovac, A., Gutman, I., Trinajstić, N., Živković, T.: Theoret. Chim. Acta (Berl.) **26**, 67 (1972)
7. McClelland, B. J.: J. Chem. Phys. **54**, 640 (1971)
8. For review on the topological properties of benzenoid hydrocarbons see: Gutman, I.: Bull. Soc. Chim. Beograd **47**, 453 (1982)
9. Hall, G. G.: Int. J. Math. Educ. Sci. Technol. **4**, 233 (1973)
10. Hall, G. G.: Inst. Math. Appl. **17**, 70 (1981)
11. Gutman, I., Petrović, S.: Chem. Phys. Letters **97**, 292 (1983)
12. Coulson, C. A., Rushbrooke, G. S.: Proc. Cambridge Phil. Soc. **36**, 193 (1940)
13. Dewar, M. J. S., Longuet-Higgins, H. C.: Proc. Roy. Soc. (London) **A214**, 482 (1952)

14. Wilcox, C. F.: Tetrahedron Letters, 795 (1968)
15. Gutman, I., Trinajstić, N., Wilcox, C. F.: Tetrahedron **31**, 143 (1975)
16. Zahradnik, R., Pancir, J.: HMO energy characteristics. New York: Plenum Press 1970
17. Gutman, I.: Theoret. Chim. Acta (Berl.) **50**, 287 (1979)

Received September 20, 1983