

MORE LOWER BOUNDS FOR THE TOTAL π -ELECTRON ENERGY OF ALTERNANT HYDROCARBONS

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Abstract

In a recent paper [MATCH **30**, 243 (1994)] Türker pointed out that for $g = 0.5$ the expression $g\sqrt{2mn}$ is a lower bound for the total π -electron energy of alternant hydrocarbons (as calculated within the HMO approximation); n = number of C-atoms, m = number of C-C bonds. We now deduce better lower bounds of the same type, in particular one with $g = 4\sqrt{2}/9 = 0.628539\dots$.

Introduction

In this paper we are concerned with the total π -electron energy (E) as calculated within the framework of the simple Hückel molecular orbital (HMO) approximation. Upper and lower bounds for E were first investigated by Bernard McClelland [1] and eventually became a traditional field of research in the theory of total π -electron energy [2]. Recently Türker [3] proposed a lower bound for E , valid for all alternant hydrocarbons:

$$g\sqrt{2mn} < E \quad (1)$$

in which $g = 1/2$. In formula (1), n and m stand for the number of vertices and edges, respectively, of the molecular graph [4] (= the number of carbon atoms and carbon-carbon bonds, respectively, of the corresponding conjugated hydrocarbon).

If one thinks of improving Türker's bound [3], i.e., finding g greater than 0.5, for which inequality (1) is still valid, then one first should notice that because of McClelland's upper bound [1,2] $\sqrt{2mn} \geq E$, g cannot exceed unity.

Some improvements of Türker's bound were offered by one of the present authors [5]. In particular, in [5] it was shown that for alternant hydrocarbons with at least n carbon-atoms, for which the condition

$$n > n_3 + 2q \quad (2)$$

is obeyed, the inequality (1) holds for $g = \sqrt{(2n - 2)/(5n)}$. In formula (2), q denotes the number of quadrangles (= four-membered cycles) and n_3 is the number of trivalent vertices in the molecular graph.

In this paper we communicate some further improvements of Türker's lower bound.

Theory

The starting point in our consideration is the inequality

$$E \geq \sqrt{8m^3/(2D_2 - 2m + 8q)} \quad (3)$$

which was deduced in [6], and which holds for all alternant hydrocarbons. In formula (3), D_2 is the sum of the squares of the vertex degrees; as before q counts the quadrangles. If we denote by n_k , $k = 1, 2, 3$, the number of vertices in the molecular graph whose degree is equal to k , then

$$n_1 + n_2 + n_3 = n \quad (4)$$

$$n_1 + 2 n_2 + 3 n_3 = 2 m \quad (5)$$

$$n_1 + 4 n_2 + 9 n_3 = D_2 \quad (6)$$

By comparing (1) and (3) it is immediately seen that (1) will certainly be satisfied if

$$\sqrt{8 m^3 / (2 D_2 - 2 m + 8 q)} \geq g \sqrt{2 m n} .$$

By means of the relations (4)-(6), the above inequality is transformed into

$$\begin{aligned} & x^2 / (2 g^2) + 2 y^2 / g^2 + (1 / g^2 - 5 / 2) x + (2 / g^2 - 7) y + 2 x y / g^2 + \\ & 1 / (2 g^2) - 1 / 2 \geq 4 q / n \end{aligned} \quad (7)$$

where $x = n_2 / n$ and $y = n_3 / n$.

The number q of quadrangles in the graph, may be related to x and y in various ways. Generally one may use

$$4 q / n \leq \alpha x + \beta y \quad \text{i.e.} \quad 4 q \leq \alpha n_2 + \beta n_3 . \quad (8)$$

Then the inequality (7) holds whenever

$$\gamma \geq 0 \quad (9)$$

where

$$\begin{aligned} \gamma = & x^2 / (2 g^2) + 2 y^2 / g^2 + (1 / g^2 - 5 / 2 - \alpha) x + (2 / g^2 - 7 - \beta) y + \\ & 2 x y / g^2 + 1 / (2 g^2) - 1 / 2 . \end{aligned} \quad (10)$$

Hence, (9) is a sufficient condition for the validity of (1).

It is easy to see that the condition (9) is satisfied for $x = y = 0$ and $g \leq 1$. If it is violated for any other value of x and y (for some appropriately

chosen g), then γ , Eq. (10), must vanish for some non-zero values of x and y .

Thus, if the condition (9) is violated by some molecular graphs, then it must be $\gamma = 0$ for some x, y and g , such that $0 < x \leq 1$, $0 < y \leq 1$ and $0 < g < 1$. For $\gamma = 0$, the functional dependence between x and y may be considered as a quadratic function in y . The respective discriminant is then

$$D = -4x(2 + \beta - 2\alpha)/g^2 - 4(6 + \beta)/g^2 + (7 + \beta)^2. \quad (11)$$

If $D < 0$, the equality $\gamma = 0$ has no real zeros. Then the inequality (9) holds for all x and y , and accordingly holds for all graphs of the kind we are considering here.

When $(2 + \beta - 2\alpha) \geq 0$, then the worst condition on the right-hand side of (11) is $x = 0$ and one obtains

$$g \leq 2\sqrt{6 + \beta}/(7 + \beta) \quad \text{for } 2\alpha \leq \beta + 2. \quad (12)$$

When $(2 + \beta - 2\alpha) \leq 0$, the worst condition on the right-hand side is $x = 1$, which leads to

$$g \leq 2\sqrt{8 + 2\beta - 2\alpha}/(7 + \beta) \quad \text{for } \beta + 2 \leq 2\alpha \leq 2\beta + 8. \quad (13)$$

The best possible lower bound for E will be, of course, obtained if one chooses g so that it is equal to the right-hand side of (12) or (13).

In order to determine g (by means of (12) and (13)) we have to find pertinent values for the parameters α and β , Eq. (8). This, on the other hand, depends on the actual structure of the (molecular) graphs under consideration.

In the subsequent considerations a third, auxiliary, class \mathcal{C} will play an important role. \mathcal{C} consists of those graphs from the class \mathcal{A} which have the property that all their edges belong to (at least one) quadrangle.

We first determine the elements of \mathcal{C} . A constructive proof yields the following result:

The class \mathcal{C} contains the ladders L_n , $n = 1, 2, 3, 4, \dots$, the cyclic ladders CL_n , $n = 3, 5, 7, 9, \dots$, the graphs G_1 , G_2 , G_3 , G_4 and G_5 , and only these graphs, see Fig. 1. With the exception of G_5 , all elements of \mathcal{C} are planar and thus belong to class \mathcal{A} .

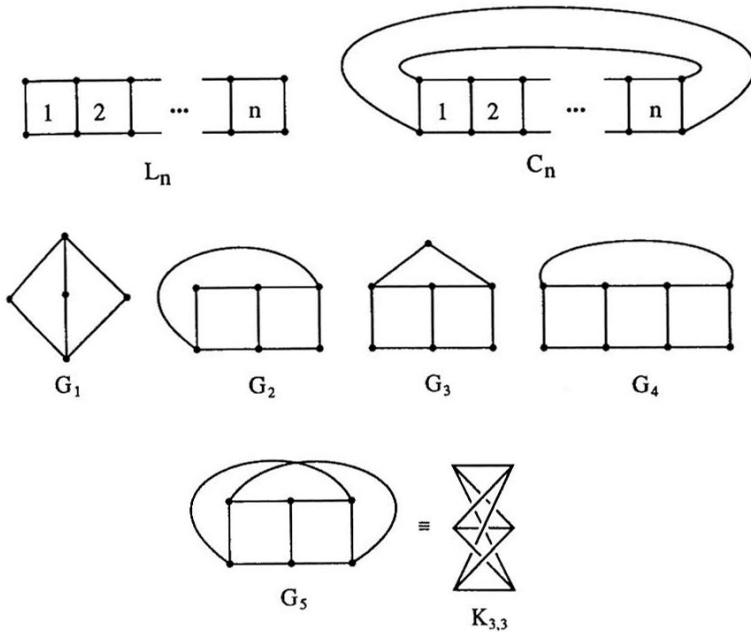


Fig. 1. The elements of the class \mathcal{C} .

A Simple Chemical Application

In the molecules of conjugated hydrocarbons, one carbon atom cannot belong to more than two four-membered rings, because otherwise a drastic violation from planarity would occur, accompanied by an extremely large steric strain. (As a matter of fact, even pairs of fused four-membered rings - when some carbon atoms are shared by two such rings - occur in the chemistry of nonbenzenoid conjugated molecules only in exceptional cases [7-10].) Furthermore, in conjugated hydrocarbons, CH-groups always belong to exactly one ring.

Translated into the language of chemical graph theory [4] the above means that trivalent vertices of a molecular graph belong to at most two quadrangles, whereas bivalent vertices belong to at most one quadrangle. This, in turn, implies that in Eq. (8) we may choose $\alpha = 1$ and $\beta = 2$. For this choice of the parameters α and β , Eq. (12) is applicable and we straightforwardly calculate

$$g = 4\sqrt{2}/9 = 0.628539\dots \quad (14)$$

Hence we reach our first main result: *For all alternant conjugated hydrocarbons, the HMO total π -electron energy is bounded from below by the expression $g\sqrt{2mn}$, where g is given by Eq. (14).*

Extensions to More General Molecular Graphs

In this section we derive lower bounds of the type (1) for two classes of graphs: \mathcal{A} and \mathcal{B} , both embracing the molecular graphs usually considered in chemical applications. Class \mathcal{A} consists of connected bipartite graphs whose maximal vertex degree does not exceed three. Class \mathcal{B} is a subset of \mathcal{A} , containing only those graphs which are planar (in the graph theoretical sense [11]).

One should observe that the "exceptional" graph G_5 is just the complete bipartite graph on $3+3$ vertices, $K_{3,3}$. According to Kuratowski's theorem [11] this graph is non-planar. Because all the vertices of G_5 are trivalent, G_5 cannot be contained as subgraph in any of the graphs from \mathcal{A} .

In order to obtain a value for g , such that the inequality (1) is satisfied for all graphs from \mathcal{A} , we first have to find some pertinent values for α and β , for which the inequality (8) holds, and then to apply Eqs. (12) or (13). Our strategy will be the following:

First observe that for graphs without quadrangles ($q = 0$) inequality (8) is satisfied for any positive α and β . Therefore we may restrict our considerations to those graphs from \mathcal{A} which contain at least one quadrangle.

Let G be such a graph. Denote by $n_{2q}(G)$ and $n_{3q}(G)$ the number of divalent and trivalent vertices, respectively, of G , lying on (at least one) quadrangle. Evidently, $n_{2q}(G) \leq n_2(G)$ and $n_{3q}(G) \leq n_3(G)$. We intend to choose α and β so that $\alpha \leq \beta$, that β is as small as possible and that

$$4 q(G) \leq \alpha n_{2q}(G) + \beta n_{3q}(G) \quad (15)$$

is satisfied. Then, of course, (8) will be satisfied too. Such a choice can always be done.

Construct now a graph G' by deleting from G all edges and all vertices that do not belong to quadrangles. Then G' is a graph whose all components are from \mathcal{A} . Furthermore, $q(G') = q(G)$, $n_{2q}(G') + n_{3q}(G') = n_{2q}(G) + n_{3q}(G)$ and $n_{2q}(G') \geq n_{2q}(G)$. In view of the fact that $\alpha \leq \beta$, we immediately see that if

$$4 q(G') \leq \alpha n_{2q}(G') + \beta n_{3q}(G') \quad (16)$$

is satisfied, then also (15) is satisfied. Let the components of G' be denoted by $G_1'', G_2'', \dots, G_p''$. Then (16) is satisfied whenever

$$4 q(G_i'') \leq \alpha n_{2q}(G_i'') + \beta n_{3q}(G_i'')$$

is satisfied for all $i = 1, 2, \dots, p$. Bearing in mind that all the graphs G_i'' , $i = 1, 2, \dots, p$, belong to the class \mathcal{G} , but that none of them can be isomorphic to G_5 , we arrive at the following important conclusion:

Let α and β be chosen so that the inequality (8) holds for all graphs from the class \mathcal{G} (except, perhaps, for G_5). Let the respective value of g be calculated by means of Eqs. (12) or (13). Then the inequality (1) holds for all graphs from the class \mathcal{A} (except, perhaps, for G_5).

We thus see that the correctness of a choice of α and β needs to be checked only on the few graphs from the class \mathcal{G} .

If we choose $\alpha = \sqrt{6} + 1/2$, $\beta = 2\sqrt{6} - 1$, then application of Eq. (13) gives

$$g = 1/\sqrt{3} = 0.577350\dots \quad (17)$$

The above values for α and β were adjusted so that for the Kuratowski graph G_5 the relation (1) is obeyed in the form of an equality. By direct testing we establish that for all other graphs from the class \mathcal{G} , the inequality (8) is satisfied. We thus conclude: *For g given by Eq. (17), the inequality (1) holds for all graphs from the class \mathcal{A} .*

Furthermore, the above lower bound is the best possible because in the case of the Kuratowski graph it reduces to an equality.

Using an analogous way of reasoning, we establish that the choice $\alpha = 14/5$, $\beta = 18/5$ makes that Eq. (8) is satisfied for all planar molecular graphs. For this choice,

$$g = \sqrt{4800/14045} = 0.584601... \quad (18)$$

and we arrive at the following result: *For g given by Eq. (18), the inequality (1) holds for all graphs from the class \mathcal{B} .*

Another Chemical Application: Alternant Hydrocarbons without Four-Membered Rings

As it is well known, the great majority of conjugated systems known at present are devoid of four-membered rings. For them we obtain further improvements for the lower bound (1). Namely, for such conjugated systems we may select $\alpha = \beta = 0$ and then from (12),

$$g = 2\sqrt{6}/7 = 0.699854... \quad (19)$$

In the case of benzenoid system we further have $x + y = 1$ and then from Eq. (10),

$$g = 4\sqrt{3}/9 = 0.769800... \quad (20)$$

This result was previously obtained in [6], using a different way of reasoning. Finally, for cubic bipartite graph without quadrangles (which, for instance, are the molecular graphs of toroidal polyhexes [12], $x = 0$, $y = 1$ and $\alpha = \beta = 0$. This by means of Eq. (10) yields:

$$g = 3/\sqrt{15} = 0.774597... \quad (21)$$

By comparing Eqs. (14), (19), (20) and (21) we see that for conjugated systems with six- and without four-membered rings, the value of g increases. This is in harmony with the empirical facts about destabilization by 4-membered rings and stabilization by 6-membered ones.

The above results can be summarized as follows: *For alternant conjugated hydrocarbons without four-membered rings, the HMO total π -electron energy is bounded from below by the expression $g\sqrt{2mn}$, where g is given by Eq. (19). For benzenoid hydrocarbons, the same holds for g being given by Eq. (20). For toroidal polyhexes the same holds for g being given by Eq. (21).*

These bounds, valid for special classes of conjugated hydrocarbons, turn out to be significantly better than the general lower bound (1)&(14). This latter bound, on the other hand, is also significantly better than what was recently proposed by Türker [3].

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