A Class of Lower Bounds for Total π-Electron Energy of Alternant Conjugated Hydrocarbons

Ivan Gutman

Institute of Physical Chemistry, Attila Jozsef University,
P. O. Box 105, H-6701 Szeged, Hungary

For alternant hydrocarbons whose molecular graphs possess n vertices and m edges Türker recently put forward a lower bound for total π-electron energy (E), namely $(1/2) (2\ m\ n)^{1/2} \leq E$ (*). The original proof of (*) contains an error. We propose an alternative method for proving (*), which applies to all molecular graphs, except perhaps to some containing very many four-membered cycles. As a byproduct, a class of novel lower bounds for E is obtained.

INTRODUCTION

The theory of total π-electron energy (E), as calculated within the framework of the Hückel molecular orbital approximation, is a traditional and well-elaborated field of research in the chemical graph theory.[1–4] Among other results, a plethora of upper and lower bounds for E is known, especially for alternant or benzenoid hydrocarbons; an exhaustive list of such bounds can be found in the review,[5] of which we mention here only the classical result of McClelland:[6]

$$E \leq (2\ m\ n)^{1/2} \tag{1}$$

where n and m denote the number of vertices and edges, respectively, of the molecular graph. Eq. (1) holds for all conjugated molecules having filled bonding and empty antibonding MO energy levels. In particular, Eq. (1) holds for all alternant hydrocarbons in ground electron states.

In a recent work,[7] Türker came to the conclusion that in the case of alternant hydrocarbons there is a lower bound for E, having a form similar to McClelland's estimate Eq. (1), namely

$$\frac{1}{2} (2\ m\ n)^{1/2} \leq E \ . \tag{2}$$

Although based on an elegant mathematical technique, the proof of Eq. (2) put forward in the paper[7] is technically incorrect.[8] In view of this, we tried to find an alternative route towards Eq. (2). This new proof of Eq. (2) is outlined in the subsequent section. Our analysis made it possible to design a whole class of lower bounds for E, which are better than Eq. (2) and whose form is

$$g \ (2 \ m \ n)^{1/2} \leq E \tag{3}$$

with g being an appropriately chosen constant, greater than $1/2$. Formulas of type Eq. (3) are discussed in the last section of this paper.

TOWARDS THE LOWER BOUND Eq. (2)

First of all, it must be mentioned that relation (2) does not hold for all bipartite graphs. It is, for instance, violated for the star with nine vertices. (The maximal vertex degree in this graph is 8.) Another easily recognizable violation is the graph with 10 vertices and only one edge. (This graph is disconnected.)

Molecular graphs, representing conjugated π-electron systems, are always connected and their vertex degrees never exceed three.[1-3] Alternant hydrocarbons are represented by bipartite graphs.[1-3] It seems that Eq. (2) holds for all connected bipartite graphs whose vertex degrees are less than four.

The starting point in our proof of the inequality Eq. (2) are

$$E \geq (8 \ m^3/M_4)^{1/2} \tag{4}$$

and

$$M_4 = 2 \ D_2 - 2 \ m + 8 \ q \tag{5}$$

where M_4 is the fourth spectral moment of the molecular graph under consideration, q is the number of four-membered cycles in it, and D_2 is the sum of squares of the vertex degrees. Detailed derivations of both relations (4) and (5) were previously publicized.[9,10] Both Eqs. (4) and (5) hold for all alternant hydrocarbons.

Now, from Eq. (4) it is immediately seen that Eq. (2) will certainly be satisfied if

$$(8 \ m^3/M_4)^{1/2} \geq \frac{1}{2} \ (2 \ m \ n)^{1/2} \ . \tag{6}$$

Combining Eq. (6) with Eq. (5), we obtain

$$8 \ m^2/n + m \geq D_2 + 4 \ q \ . \tag{7}$$

Hence, Eq. (7) is a sufficient condition for the validity of Eq. (2).

We now show that Eq. (7) is satisfied for all molecular graphs, except perhaps for some graphs in which q is very large as compared to n.

Denote by n_i the number of vertices of degree i, $i = 1, 2, 3$. Then,[2,3]

$$n_1 + n_2 + n_3 = n$$

$$n_1 + 2\,n_2 + 3\,n_3 = 2\,m$$

$$n_1 + 4\,n_2 + 9\,n_3 + D_2$$

from which

$$D_2 = 6\,m - 2\,n + 2\,n_3\,.$$

Condition Eq. (7) now becomes

$$m\,(8\,m/n - 5) + 2\,n \geq 2\,n_3 + 4\,q\,. \tag{8}$$

Bearing in mind that $2\,m/n$ is just the mean value of the vertex degress,[2,3] which we denote by $<d>$, Eq. (8) is rewritten as

$$m\,(4\,<d> - 5) + 2\,n \geq 2\,n_3 + 4\,q\,. \tag{9}$$

With the only exception of the (two-vertex) molecular graph of ethylene, for all other molecualr graphs, $<d> > 5/4$, *i.e.* $4\,<d> - 5$ is positive-valued. In view of this, condition Eq. (9) will certainly be satisfied if

$$n > n_3 + 2\,q\,. \tag{10}$$

Consequently, if Eq. (10) holds, then also Eq. (7) holds, and then Eq. (2) holds too. On the other hand, it is clear that Eq. (10) is obeyed by all molecular graphs, except by those few which have very many four-membered cycles relative to the number of vertices. Among such graphs are the ladders,[11] the cube and polycube graphs.[12] These, however, do not correspond to any chemically realistic π-electron systems. The cyclobutadieno-annelated phenylenes,[13] for which $n = 6\,h + 4$, $n_3 + 2q = 6\,h + 2$, where h is the number of hexagons, provide a chemically meaningful example with extremely high n_3- and q-values; they nevertheless obey Eq. (10).

Condition Eq. (10) is, of course, satisfied by all conjugated hydrocarbons which do not posses four-membered cycles. Among them are all acyclic polyenes, all benzenoids *etc.*

This shows that the lower bound Eq. (2) holds for practically all, chemically relevant, alternant π-electron systems.

For certain graphs that violate relation (10), in particular for ladders and the cube, as well as for tri(cyclobutadieno)-benzene, direct numerical calculation showed that Eq. (2) is applicable. Bound Eq. (2) holds also for ethylene.

A CLASS OF LOWER BOUNDS FOR TOTAL π-ELECTRON ENERGY

The reasoning outlined in the preceding section can be straightforwardly extended to finding lower bounds for E of the form Eq. (3). Instead of Eq. (9), which is sufficient condition for the validity of Eq. (2), we now have

$$m \ (<d>/g^2 - 5) + 2 \ n \geq 2 \ n_3 + 4 \ q$$

which is a sufficient condition for the validity of Eq. (3).

Next, one has to determine the molecular graphs for which $<d>/g^2 - 5$ is not negative-valued, *i.e.*, for which $<d> \geq 5 \ g^2$. For connected graphs with at least n vertices, $<d> \geq 2(n - 1)/n = <d>_{tree}$. Hence, if we choose g, such that $2(n - 1)/n = 5 \ g^2$, *i.e.*

$$g = [(2 \ n - 2)/(5 \ n)]^{1/2} \qquad (11)$$

then $<d>/g^2 - 5$ will be positive-valued or zero for all connected graphs with n or more vertices. For such graphs, the lower bound is obeyed whenever condition Eq. (10) is fulfilled.

Choosing $n = 3, 4, 5, \ldots$ we arrive at the following sequence of lower bounds for E. They all hold provided condition Eq. (10) is satisfied, which we showed to be the case with practically all molecular graphs of interest in the theory of conjugated π-electron molecules. Hence, for alternant conjugated hydrocarbons with more than two carbon atoms,

$$(4/15)^{1/2} \ (2 \ m \ n)^{1/2} \leq E \ ; \ (4/15)^{1/2} = 0.5163978\ldots$$

for alternant hydrocarbons with more than three carbon atoms,

$$(3/10)^{1/2} \ (2 \ m \ n)^{1/2} \leq E \ ; \ (3/10)^{1/2} = 0.5477226\ldots$$

for alternant hydrocarbons with more than four carbon atoms,

$$(8/25)^{1/2} \ (2 \ m \ n)^{1/2} \leq E \ ; \ (8/25)^{1/2} = 0.5656854\ldots$$

for alternant hydrocarbons with more than five carbon atoms,

$$(1/3)^{1/2} \ (2 \ m \ n)^{1/2} \leq E \ ; \ (1/3)^{1/2} = 0.5773503\ldots$$

etc. We thus arrived at a series of lower bounds for E, all of which represent improvements of the original estimate Eq. (2). Each member of this series is better than the previous one, but applies to a more restricted set of molecular graphs. The greatest value of g which could be obtained by the above reasoning is $(2/5)^{1/2} = 0.6324555\ldots$

In order to gain some numerical experience about the quality of the bounds of the type Eq. (3), we tested them for the set of 106 benzenoid hydrocarbons from the book of Zahradnik and Pancir.[14] (Recall that the same set was used on numerous previous occasions for examining the precision of approximate formulas for total π-electron energy.[5]) The results obtained are collected in Table I.

It is seen from Table I that neither Türker's bound Eq. (2) nor its improvements Eqs. (3) and (11) are very sharp. Bound Eqs. (3) and (11) becomes better than Türker's for n greater than 2. The quality of Eqs. (3) and (11) gradually increases with the increasing value of n.

TABLE I

The quality of McClelland's upper bound Eq. (1), Türker's lower bound Eq. (2) and of the newly deduced lower bounds of the type Eq. (3) and (11) in the case of benzenoid hydrocarbons; if E is the total π-electron energy and E^* the respective bound, then $\delta = |(E - E^*)/E| \times 100$; data for E are taken from[14] the size of the sample employed is 106

formula	average δ	maximal δ observed	minimal δ observed
Eq. (1)	9.94	11.45	6.07
Eq. (2)	45.03	46.97	44.28
Eqs. (3)&(11), $n = 3$	43.23	45.23	42.45
Eqs. (3)&(11), $n = 4$	39.78	41.91	38.96
Eqs. (3)&(11), $n = 5$	37.81	40.00	36.98
Eqs. (3)&(11), $n = 6$	36.53	38.76	35.66
Eqs. (3)&(11), $n = 7$	35.63	37.89	34.74
Eqs. (3)&(11), $n = 8$	34.96	37.25	34.07
Eqs. (3)&(11), $n = 9$	34.45	36.75	33.55
Eqs. (3)&(11), $n = 10$	34.04	36.36	33.13
Eqs. (3)&(11), $n = 20$	32.23	34.62	31.30
Eqs. (3)&(11), $n = 50$	31.17	33.59	30.22
Eqs. (3)&(11), $n = 100$	30.82	33.25	29.87
Eqs. (3)&(11), $n = \infty$	30.47	32.92	29.52

It would be interesting to find the best possible McClelland-type lower and upper bounds for total π-electron energy, of the form

$$g_L \, (2 \, m \, n)^{1/2} \le E \le g_U \, (2m \, n)^{1/2}$$

and to determine the constants g_L and g_U for the case of

(a) conjugated hydrocarbons with filled bonding and empty antibonding MO energy levels,

(b) alternant hydrocarbonds

(c) benzenoid hydrocarbons

(d) species as under (a), (b) or (c), with more than n carbon atoms, n fixed.

These tasks, however, remain to be accomplished in the future.

REFERENCES

1. A. Graovac, I. Gutman, and N. Trinajstić, *Topological Approach to the Chemistry of Conjugated Molecules,* Springer Verlag, Berlin, 1977.
2. N. Trinajstić, *Chemical Graph Theory,* CRC Press, Boca Raton, 1983, 2nd edition, 1992.
3. I. Gutman and O. E. Polansky, *Mathematical Concepts in Organic Chemistry*, Springer Verlag, Berlin, 1986.
4. J. R. Dias, *Molecular Orbital Calculations Using Chemical Graph Theory,* Springer Verlag, Berlin, 1993.
5. I. Gutman, *Topics Curr. Chem.* **162** (1992) 29.

6. B. J. McClelland, *J. Chem. Phys.* **54** (1971) 640.
7. L. Türker, *Commun. Math. Chem.* **30** (1994) 243.
8. In the paper,[7] a quadratic equation for E is obtained, Eq. (6), which in our notation reads:

$$E^2 - (2\ m\ n)^{1/2}\ E + (2\ m\ n)^{1/2}\ \gamma = 0 \qquad\qquad (6)^7$$

Here γ is an auxilliary parameter. Eq. (6)[7] has two solutions:

$$E = \frac{1}{2}\left[(2\ m\ n)^{1/2} + \left\{2\ m\ n - 4\ (2\ m\ n)^{1/2}\gamma\right\}^{1/2} \right] \qquad\qquad (7)^7$$

and

$$E = \frac{1}{2}\left[(2\ m\ n)^{1/2} - \left\{2\ m\ n - 4\ (2\ m\ n)^{1/2}\gamma\right\}^{1/2} \right] \qquad\qquad (!)$$

In the paper,[7] however, only one of these solutions is considered, namely Eq. (7)[7], whereas the other solution (!) is simply ignored. Neglecting in Eq. (7)[7] the positive-valued term $[2\ m\ n - 4\ (2\ m\ n)^{1/2}\ \gamma]^{1/2}$, one indeed arrives at the desired lower bound Eq. (2). If, however, the same argument is applied to the solution (!), then the result is an upper bound for E, namely $E \leq 1/2\ (2\ m\ n)^{1/2}$. Hence, what one actually deduces from Eq. (6)[7] is that E is either underestimated or overestimated by $1/2\ (2mn)^{1/2}$.

9. I. Gutman, *J. Chem. Soc. Faraday Trans.* **86** (1990) 3373.
10. I. Gutman, *J. Chin. Chem. Soc.* **39** (1992) 1.
11. H. Hosoya and F. Harary, *J. Math. Chem.* **12** (1993) 211.
12. H. Narumi and H. Hosoya, *ibid.* **3** (1989) 383.
13. I. Gutman and E. C. Kirby, *Monatsh. Chem.* **125** (1994) 539.
14. R. Zahradnik and R. Pancir, *HMO Energy Characteristics*, Plenum Press, New York, 1970.

SAŽETAK

Klasa donjih granica za ukupnu π-elektronsku energiju alternantnih konjugiranih ugljikovodika

Ivan Gutman

Za alternantne ugljikovodike čiji molekulski grafovi imaju n čvorova i m grana Türker je nedavno predložio donju granicu za ukupnu π-elektronsku energiju (E), naime $(1/2)\ (2\ m\ n)^{1/2} \leq E$ (*). Izvorni dokaz relacije (*) sadržava grešku. U radu se predlaže novi postupak za dokazivanje relacije (*), koji se primjenjuje na sve molekulske grafove izuzev, možda, one koji sadržavaju veoma mnogo četveročlanih ciklusa. Kao sporedni rezultat dobivena je klasa novih donjih granica za E.