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Bounds for Hückel Total π-Electron Energy

I. Gutman

Faculty of Sciences, University of Kragujevac, P.O. Box 60, 34000 Kragujevac, Yugoslavia

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Various lower and upper bounds (eqs 9, 15, 16, 26, 27, 28, 34, 40 and 41 are obtained for the Hückel total π-electron energy. There exists a rather accurate linear correlation between the bounds 16 and 26 and the Hückel total π-electron energy (eqs 31 and 32, correlation coefficients 0.9995).

Total π-electron energy (E) as calculated on the basis of the Hückel molecular orbital (HMO) approximation is a reactivity index, the applicability of which is nowadays firmly established and well documented in theoretical organic chemistry.[1,2] In spite of the fact that the actual physical meaning of E is not yet completely understood,[4] numerous efforts have been made to elucidate its dependence on molecular topology.[5] Mathematical properties of E were also extensively studied.[5]

McClelland[6] was the first who found lower and upper bounds for E. Thereafter various additional bounds have been discovered,[7-9] some of which enable the estimation of E within an interval of only few hunderdths of β.[9] In the present work we offer some further inequalities for E. In addition, some of our estimates exhibit a fairly good linear correlation with the exact values of E.

The following notation and terminology will be used. We consider a conjugated molecule G possessing N conjugated centers and etiher $N = 2n$ or $N = 2n + 1$. Let $P(G, x)$ be the HMO characteristic polynomial of G. For reasons which will become clear later we shall write $P(G, x)$ in the form

$$P(G, x) = \sum_j (-1)^j a_{2j} x^{N-2j} + \sum_j (-1)^j a_{2j+1} x^{N-2j-1} \qquad (1)$$

Let the roots of this polynomial be $x_1 \geqslant x_2 \geqslant \ldots \geqslant x_N$. Then

$$E = \begin{cases} 2 \sum_{j=1}^{n} x_j & \text{for even } N \\ 2 \sum_{j=1}^{n} x_j + x_{n+1} & \text{for odd } N \end{cases} \qquad (2)$$

Of course, in the above formulas E and $P(G, x)$ are expressed in β units (i. e. it is assumed as usual that $\alpha = 0$ and $\beta = 1$). Without losing the generality of our considerations, it can be written[10]

$$E = -a_1 + \sum_{j=1}^{N} |x_j| \tag{3}$$

Note that in the case of hydrocarbons one has $a_1 = 0$. For further details about the meaning of the parameter a_1 see ref. 22.

There exist integral formulas enabling one to express E as a function of the coefficients of the characteristic polynomial.[11] For our purposes the following identity is important.[12]

$$E = -a_1 + \langle x^{-2} \ln [(\sum_j a_{2j} x^{2j})^2 + (\sum_j a_{2j+1} x^{2j+1})^2]^{1/2} \rangle \tag{4}$$

Here and later we use the abbreviated notation

$$\frac{1}{\pi} \int_{-\infty}^{+\infty} F(x) \, dx \equiv \langle F(x) \rangle \equiv \langle F \rangle \tag{5}$$

THE FIRST INEQUALITY

Let us define *the alternant polynomial* $P_{\text{alt}}(G, x)$ of a conjugated system G as

$$P_{\text{alt}}(G, x) = \sum_j (-1)^j a_{2j} x^{N-2j} \tag{6}$$

It is easily seen that $P_{\text{alt}}(G, x)$ is obtained from $P(G, x)$ by formally deleting all coefficients a_{2j+1} in eq 1. We conclude[13] therefrom, that for alternant hydrocarbons (and only for them), the alternant polynomial coincides with the characteristic polynomial.

Let z_j ($j = 1, 2, \ldots, N$) be the roots of the alternant polynomial, which are not necessarily real numbers. Then the quantity

$$E_{\text{alt}} = \sum_{j=1}^{N} | z_j | \tag{7}$$

will be named »the alternant part of the Hückel π-electron energy«. Taking into account the formal analogy between eqs 3 and 7 it follows immediately that

$$E_{\text{alt}} = \langle x^{-2} \ln \sum_j a_{2j} x^{2j} \rangle \tag{8}$$

Comparision of the formulas (4) and (8) yields our *first inequality*

$$-a_1 + E_{\text{alt}} \leqslant E \tag{9}$$

with the equality sign only in the case of alternant hydrocarbons. In other words, the coefficients a_{2j+1} in eq 1 increase the value of E. Therefore,[15] the presence of odd-membered cycles and heteroatoms results in a stabilizing effect in all conjugated molecules. This phenomenon was first discovered by Aihara.[26]

THE SECOND INEQUALITY

In this section lower bounds will be derived for the Hückel π-electron energy of alternant hydrocarbons. However, because of the inequality (9), all our results can be simply extended to arbitrary conjugated systems.

Now, let G be an alternant hydrocarbon containing $N = 2n$ carbon atoms. Eq 4 reduces then to

$$E = \langle x^{-2} \ln \sum_{j=0}^{n} a_{2j} x^{2j} \rangle \tag{10}$$

which, of course, is nothing else but formula (8). Another important property of alternant hydrocarbons is[12] $a_{2j} \geqslant 0$ for all $j = 1, 2, \ldots, n$.

The dependence of a_j's on molecular topology is well known, but is rather complicated in the general case.[15] However, relatively simple topological expressions 11—14 are known for a_2, a_4, a_N and a_{N-2}. In addition $a_0 = 1$.[15]

$$a_2 = M \tag{11}$$

where M is the number of carbon-carbon bonds in the molecule.[15]

$$a_4 = \frac{M(M+1)}{2} - \frac{1}{2} \sum_{j=1}^{N} d_j^2 - 2 n_4 \tag{12}$$

where d_j is the number of carbon atom neighbours of the j-th carbon atom and n_4 is the number of four-membered cycles in the molecule.[16]

$$a_N = (\mathrm{ASC}(G))^2 \tag{13}$$

where ASC(G) denotes the algebraic structure count of the molecule G.[17]

$$a_{N-2} = \sum_{r,s} (\mathrm{ASC}(G_{rs}))^2 \tag{14}$$

where G_{rs} denotes the conjugated system obtained by deletion of the centers r and s, and the summation goes over all pairs of conjugated centers.[18]

Eq 10 shows that E is a monotonously increasing function of all a_j's. We conclude therefrom that for arbitrary parameters ε_j, such that $0 \leqslant \varepsilon_j \leqslant a_{2j}$,

$$\langle x^{-2} \ln \sum_j (a_{2j} - \varepsilon_j) x^{2j} \rangle \leqslant \mathrm{E} \leqslant \langle x^{-2} \ln \sum_j (a_{2j} + \varepsilon_j) x^{2j} \rangle \tag{15}$$

In particular, if we set $\varepsilon_j = a_{2j}$ for certain selected values of j and $\varepsilon_j = 0$ otherwise, the *left hand side* of (15) may become essentially simplified.

We can extend this argument by noting that the main contributions to the integral (10) come from the first coefficients (a_0, a_2, $a_4, \ldots$) when $|x| \ll 1$ and from the last coefficients (a_N, $a_{N-2}, \ldots$) when $|x| \gg 1$. Then it follows

$$E = 2/\pi \int_1^0 + \int_\infty^1 x^{-2} \ln \sum a_{2j} x^{2j} \geqslant I_1 + I_2 \tag{16}$$

where

$$I_1 = 2/\pi \int_0^1 x^{-2} \ln (1 + a_2 x^2 + a_4 x^4)\, dx \tag{17}$$

and

$$I_2 = 2/\pi \int_1^\infty x^{-2} \ln (a_N x^N + a_{N-2} x^{N-2})\, dx \tag{18}$$

The latter two integrals can be calculated by straightforward methods. Hence one derives

$$I_1 = 4/\pi (\mathrm{A} \operatorname{arctg} \mathrm{A} + \mathrm{B} \operatorname{arctg} \mathrm{B}) - 2/\pi \ln (1 + a_2 + a_4) \tag{19}$$

with

$$A = [(a_2 + \sqrt{a_2^2 - 4a_4})/2]^{1/2} \tag{20}$$

$$B = [(a_2 - \sqrt{a_2^2 - 4a_4})/2]^{1/2} \tag{21}$$

and

$$I_2 = 2/\pi\,[N - 2 + \pi T - 2T \text{ arctg } T + \ln(a_{N-2} + a_N)] \tag{22}$$

where

$$T = (a_N/a_{N-2})^{1/2} \tag{23}$$

Substitution of (19) and (22) back into (16) results in our *second bound* for E, which depends exclusively on the coefficients a_2, a_4, a_N and a_{N-2}. Because of the relations 11—14, one can express this lower bound in purely topological terms. The explicit form of this cumbersome expression will, however, not be given here. Because of its rather complex nature one can hardly follow the actual dependence of our estimate on the particular topological invariants of the molecule.

Considerable simplification is gained if one neglects the coefficient a_4 in (17) and/or a_{N-2} in (18). Elementary calculation yields then

$$I_1' = 2/\pi \int_0^1 x^{-2} \ln(1 + a_2 x^2)\, dx = 2/\pi\,[2\sqrt{a_2} \text{ arctg } \sqrt{a_2} - \ln(1 + a_2)] \tag{24}$$

$$I_2' = 2/\pi \int_1^\infty x^{-2} \ln(a_N x^N)\, dx = 2/\pi\,[N + \ln a_N] \tag{25}$$

Now, in addition to the inequality (16) we have also

$$E \geqslant I_1' + I_2 \tag{26}$$

$$E \geqslant I_1 + I_2' \tag{27}$$

$$E \geqslant I_1' + I_2' \tag{28}$$

There is, of course, no physical basis for neglecting the coefficients a_4 and a_{N-2} in eqs 17 and 18. The same is true for the deletion of $a_6, a_8, \ldots, a_{N-4}$ in eq 16. This procedure is, however, justified for purely mathematical reasons. Namely, the integrals I_1, I_2, I_1' and I_2' can be calculated by means of analytical methods, in contrast to the exact integral given by eq 16. It is natural to expect that the coefficients which are omitted have a relatively small contribution to the value of the Hückel π-electron energy. The validity of the obtained bounds and their reliability can be seen from the data given in the Table. The question whether the disregarded coefficients are significant or not will be answered by eqs 31 and 32.

It is to be noted here that for the majority (but not for all) of conjugated systems the term $a_2^2 - 4\,a_4$ is negative and therefore the quantities A and B given by the equations 20 and 21 are complex numbers. Expression 19 has, of course, real values, but in the case of complex A and B it is to be evaluated according to the series expansion[19]

$$I_1 = (a_4)^{1/4} \cos\Theta - \frac{8}{\pi} \sum_{k=0}^{\infty} (-1)^k \frac{\cos 2k\,\Theta}{(2k+1)\,(a_4)^{k/2}} - \frac{2}{\pi} \ln(1 + a_2 + a_4) \tag{29}$$

where

$$\Theta = \text{arctg}\,[(2\sqrt{a_4} - a_2)/(2\sqrt{a_4} + a_2)]^{1/2} \tag{30}$$

This latter formulas are certainly not adequate for hand calculation.

TABLE

Molecule	E	bound (16)	bound (26)
butadiene	4.472	4.432	4.352
hexatriene	6.988	6.848	6.534
2-vinyl-butadiene	6.899	6.744	6.476
benzene	8.000	7.867	7.465
styrene	10.424	10.103	9.466
stilbene	18.878	17.514	16.072
naphthalene	13.683	13.066	12.088
anthracene	19.314	17.878	16.359
phenanthrene	19.448	18.043	16.525
naphthacene	24.931	22.432	20.420
1,2-benz-anthracene	25.101	22.666	20.654
chrysene	25.192	22.785	20.774
triphenylene	25.274	22.892	20.880
pyrene	22.505	20.569	18.759
perylene	28.245	25.162	22.881
coronene	34.572	30.233	27.444
biphenyl	16.383	15.437	14.220
benz-cyclobutadiene	10.381	10.023	9.351
biphenylene	16.505	15.499	14.233
p-xylylene	9.925	9.571	8.961
o-xylylene	9.954	9.604	8.993

The estimates (16) and (26) for an arbitrarily chosen class of 21 alternant hydrocarbons are presented in the Table together with the exact E values. It can be immediately seen that the Hückel total π-electron energies are considerably underestimated and that the difference between E and the lower bounds rapidly increases with increasing size of the molecule. This might be understood as an indication that the practical applicability of our results is poor. Fortunately, a more detailed examination shows that there exists a surprisingly good linear correlation between our bounds and E. Thus we obtain by least squares fitting

$$E = 1.160\ (I_1 + I_2) - 1.197 \tag{31}$$

and

$$E = 1.300\ (I_1' + I_2) - 1.743 \tag{32}$$

The correlation coefficient is in both cases 0.9995.

The high accuracy of the semiempirical formulas (31) and (32) implies that the coefficients a_2, a_4, a_N and a_{N-2} determine the main part of E. Since we know the dependence of these coefficients on molecular topology (eqs 11—14) it is to be expected that the most important topological contributions to E are *quantitatively* reproduced in eqs. (31) and (32). Our results are also in full agreement with previous *qualitative* findings in this area.[20]

THE THIRD INEQUALITY

Let G_r denote the conjugated system obtained by deletion of the atom r from the molecule G. Let E_r be its Hückel π-electron energy. According to the well-known Cauchy inequalities,[21] one has

$$x_1 \geqslant y_1 \geqslant x_2 \geqslant \ldots \geqslant x_{N-1} \geqslant y_{N-1} \geqslant x_N \qquad (33)$$

where x_j's are the roots of $P(G, x)$ while y_j's are the roots of $P(G_r, x)$. From (33) it is evident that for an arbitrary G and G_r,

$$E_r \leqslant E \qquad (34)$$

Let G_h be an alternant conjugated molecule with a (single) heteroatom in the position labeled by r. If the Coulomb integral corresponding to the site r is given by $\alpha_r = \alpha + h\,\beta$, we have[22]

$$P(G_h, x) = P(G, x) - h\,P(G_r, x) \qquad (35)$$

where G denotes the parent hydrocarbon of G_h. Let E_h and E be the Hückel total π-electron energy of G_h and G, respectively. It can be shown that[22]

$$E_h = h + E + 1/2 \langle \ln(1 + h^2 V^2) \rangle \qquad (36)$$

with $V = V(x) = -iP(G_r, ix)/P(G, ix)$ and $i = \sqrt{-1}$. Since G_h was assumed to be alternant, G and G_r represent alternant hydrocarbons and the pairing theorem applies.[13,14] Thus

$$V(x) = \frac{(x^2 + x_1^2) \ldots (x^2 + x_{n-1}^2)(x^2 + x_n^2)}{x(x^2 + y_1^2) \ldots (x^2 + y_{n-1}^2)} \qquad (37)$$

and from the Cauchy inequalities (33) we deduce

$$x/(x^2 + x_1^2) \leqslant V(x) \leqslant x/(x^2 + x_n^2) \qquad (38)$$

for $x \geqslant 0$. Note that x_1 and x_n are the energies of the lowest and the highest occupied molecular orbital, (the so called LOMO and HOMO), respectively. Their topological properties are nowadays extensively studied.[23]

Substitution of inequalities (38) back into (36) yields lower and upper bounds for the energy change caused by the introduction of a heteroatom into an alternant hydrocarbon. Hence,

$$\frac{1}{2}\langle \ln[1 + h^2 x^2/(x^2 + x_1^2)^2] \rangle \leqslant E_h - E - h \leqslant \frac{1}{2}\langle \ln[1 + h^2 x^2/(x^2 + x_n^2)^2] \rangle \qquad (39)$$

which after proper integration results in our *third inequality* (40).

$$(4x_1^2 + h)^{1/2} - 2x_1 \leqslant E_h - E - h \leqslant (4x_n^2 + h^2)^{1/2} - 2x_n \qquad (40)$$

A special case of this result is

$$(36 + h^2)^{1/2} - 6 < E_h - E - h \leqslant h \qquad (41)$$

which is a simple consequence of the fact[24] that $x_1 < 3$ and $x_n \geqslant 0$.

Using the Cauchy inequalities (33) and the relation (38) it is possible to derive bounds for various other reactivity indices of conjugated molecules. These results have been reported elsewhere.[25]

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$$z \operatorname{arctg} z + z^* \operatorname{arctg} z^* = \zeta \pi \cos\Theta - 2 \sum_{k=0}^{\infty} (-1)^k \frac{\cos 2k\,\Theta}{2k+1} \zeta^{-2k}$$

The above formula holds for $\zeta > 1$.
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SAŽETAK

Granice za Hückelovu ukupnu π-elektronsku energiju

Ivan Gutman

Dobiveno je nekoliko donjih i gornjih granica za Hückelovu ukupnu π-elektronsku energiju (jedn. (9), (15), (16), (26), (27), (28), (34), (40). i (41)). Između granica (16) i (26) i točne vrijednosti Hückelove ukupne π-elektronske energije postoji veoma dobra linearna korelacija (jedn. (31) i (32), korelacijski koeficijenti 0,9995).

PRIRODNO-MATEMATIČKI FAKULTET
UNIVERZITETA »SVETOZAR MARKOVIĆ«
34000 KRAGUJEVAC

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