Topological Resonance Energy of Linear Polyacenes

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A method for computation of the topological resonance energy (TRE) of linear polyacenes is described. When the length of the polyacene chain increases, TRE tends to 0.02 β units per π-electron, contrary to a previous prediction [1]. The ionization potential and the energy of the p-band of linear polyacenes are found to be excellently correlated with TRE.

In a recent paper [1] the topological resonance energy of very large (infinitely large) benzenoid hydrocarbons has been estimated using a semi-empirical two-parameter topological formula

$$\mathrm{TRE} = \tfrac{2}{3}\, a \sqrt[6]{2\, n_6 (\log K)^5} + b\,, \tag{1}$$

with n_6 and K being the number of six-membered rings and the number of Kekulé structures, respectively, of the corresponding hydrocarbon. In addition, $a = 0.3541$ and $b = 0.0679$. The validity of the above equation in the case of small and medium size benzenoid systems (i.e. $n_6 \leqq 10$) has been verified on a large number of examples [2].

On the basis of (1) one concluded [1] that the resonance energy per π-electron of linear polyacenes tends to zero when the number of six-membered rings tends to infinity. In the present paper the exact topological resonance energy of linear polyacenes will be determined and it will be shown that, contrary to the previous estimate,

$$\lim_{n \to \infty} \frac{\mathrm{TRE}}{n} = 0.019\,. \tag{2}$$

This result indicates that one must be rather cautious with the application of (1) to very large benzenoid systems.

In the present communication we shall fully follow the notation and terminology of our previous papers [1, 3], where also further references about TRE can be found. Hence, the topological resonance energy will be presented in the form

$$\mathrm{TRE} = E - E^{\mathrm{R}}$$

with E being the total π-electron energy

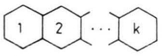
$$E = \sum_{i=1}^{n} g_i\, e_i$$

and E^{R} being the reference energy

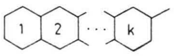
$$E^{\mathrm{R}} = \sum_{i=1}^{n} g_i\, x_i \tag{3}$$

of the pertinent conjugated system.

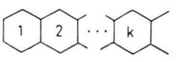
The molecular graph of the linear polyacene with k six-membered rings will be denoted by A_k. In addition, we shall need two auxiliary graphs — Y_k and Z_k.



A_k



Y_k



Z_k

The Total π-Electron Energy of Linear Polyacenes

Closed analytical expressions for the HMO energy levels of linear polyacenes are long known [4] and read (in β units):

$$\begin{aligned} e_i &= (f_i + 1)/2\,, & i &= 1, \ldots, k+1\,, \\ e_{k+1+i} &= (f_i - 1)/2\,, & i &= 1, \ldots, k\,, \\ e_{2k+1+i} &= -\,(f_i - 1)/2\,, & i &= 1, \ldots, k\,, \\ e_{3k+1+i} &= -\,(f_i + 1)/2\,, & i &= 1, \ldots, k+1\,, \end{aligned} \tag{4}$$

where

$$f_i = \sqrt{9 + 8 \cos \frac{i\pi}{k+1}}\,.$$

Note that the number of π-electrons in a linear polyacene with k rings is $n = 4k + 2$.

From (4) it immediately follows that

$$E(A_k) = 2 + 2 \sum_{i=1}^{k} f_i\,. \tag{5}$$

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By numerical calculation it can be easily verified that for k being sufficiently large (say $k \geqq 8$), $E(A_k)$ is practically a linear function of k and

$$E(A_{k+1}) - E(A_k) = 5.611 . \tag{6}$$

In addition, the sum on the right-hand side of (5) can be approximated as

$$\sum_{i=1}^{k} f_i \approx \frac{k}{\pi} \int_0^{\pi} \sqrt{9 + 8 \cos x} \, \mathrm{d}x ,$$

which yields

$$E(A_{k+1}) - E(A_k) \approx \frac{4\sqrt{17}}{\pi} E(\sqrt{16/17}) = 5.622 ,$$

where

$$E(u) = \int_0^{\pi/2} \sqrt{1 - u^2 \sin^2 t} \, \mathrm{d}t$$

is the complete elliptic normal integral of the second kind.

The Matching Polynomial of Linear Polyacenes

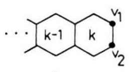
According to (3), in order to calculate E^{R} one has to determine the zeros x_i of the matching polynomial of the molecular graph. The matching polynomial of A_k can be recursively evaluated as follows:

In [3] it has been shown that the matching polynomial of a graph G satisfies the identity

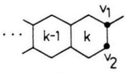
$$\alpha(G) = x \alpha(G - v) - \sum_{j=1}^{d} \alpha(G - v - w_j) .$$

Applying this relation first to the vertex v_1 and then to the vertex v_2 of A_k, we arrive to the equation

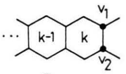
$$\alpha(A_k) = \alpha(A_{k-1}) - 2x\alpha(Y_{k-1}) + (x^2 - 1)\alpha(Z_{k-1}) . \tag{7}$$



A_k



Y_k



Z_k

When a completely analogous procedure is applied to the graphs Y_k and Z_k, one obtains

$$\alpha(Y_k) = x\alpha(A_{k-1}) - (2x^2 - 1)\alpha(Y_{k-1}) + (x^3 - 2x)\alpha(Z_{k-1}) \tag{8}$$

and

$$\alpha(Z_k) = x^2\alpha(A_{k-1}) - (2x^3 - 2)\alpha(Y_{k-1}) + (x^4 - 3x^2 + 1)\alpha(Z_{k-1}) . \tag{9}$$

The Eqs. (7)—(9) form together a system of three coupled recurrence relations. Let us introduce the notation

$$M_k - (x^4 - 5x^2 + 3) M_{k-1} + (x^4 - 3x^2 + 3) M_{k-2} - M_{k-3} \equiv r(M_k)$$

for M_k being an arbitrary function (of the variable x), depending on the parameter k. Then it can be shown that the solution of the system (7)—(9) are the following three recurrence relations:

$$r(A_k) = 0 , \quad r(Y_k) = 0 , \quad r(Z_k) = 0 . \tag{10}$$

The result (10) has been first derived by Farrell and Wahid [5] using a somewhat different way of reasoning.

Using (10) the polynomials $\alpha(A_k)$ can be easily evaluated for relatively large values of k. Their zeros are then readily computed by standard methods. On the other hand, we were not able to find an analytical expression for the zeros of $\alpha(A_k)$. It can, however, be shown [6] that the zeros of $\alpha(A_k)$ are all mutually distinct.

The Reference Energy of Linear Polyacenes

We show first that the reference energy of linear polyacenes is bounded as follows:

$$\sqrt{20} < E^{\mathrm{R}}(A_{k+1}) - E^{\mathrm{R}}(A_k) < \sqrt{20 + 8\sqrt{3}} . \tag{11}$$

The starting point in our proof is the integral expression for E^{R}

$$E^{\mathrm{R}} = \frac{1}{\pi} \int_{-\infty}^{+\infty} \frac{\mathrm{d}x}{x^2} \log[1 + p(G,1)x^2 + p(G,2)x^4 + \cdots + p(G, n/2)x^n] , \tag{12}$$

which is essentially the same result as the formula already used for total π-electron energy [7]. From (12) follows that E^{R} is a monotonically increasing function of all parameters $p(G, j)$, $j = 1, \ldots, n/2$.

The graph A_{k+1} can be obtained from A_k by joining the vertices v_1 and v_2 of A_k with the terminal vertices of a path graph P_4 with four vertices. Hence $A_k \dot{+} P_4$ is a subgraph of A_{k+1}, and consequently

$$p(A_{k+1}, j) \geqq p(A_k \dot{+} P_4, j)$$

for all j. Then because of (12),

$$E^{\mathrm{R}}(A_{k+1}) > E^{\mathrm{R}}(A_k \dot{+} P_4) = E^{\mathrm{R}}(A_k) + E^{\mathrm{R}}(P_4) ,$$

and the left-hand side of (11) follows from the fact that $E^{\mathrm{R}}(P_4) = E(P_4) = \sqrt{20}$.

From the recurrence relation (10) it is immediately seen that $p(A_{k+1}, j)$ is equal to the respective coefficient of $(x^4 - 5x^2 + 3)\,\alpha(A_k)$ minus the respective coefficient of $(x^4 - 3x^2 + 3)\,\alpha(A_{k-1})$ plus the respective coefficient of $\alpha(A_{k-2})$. Since the coefficients of $\alpha(A_{k-2})$ are much smaller than the respective coefficients of $(x^4 - 3x^2 + 3)\,\alpha(A_{k-1})$, we conclude that $p(A_{k+1}, j)$ is smaller than the respective coefficient of $(x^4 - 5x^2 + 3)\,\alpha(A_k)$. Then because of (12),

$$E^{\mathrm{R}}(A_{k+1}) < E^{\mathrm{R}}(A_k) + 2 \cdot \left[\sqrt{(5+\sqrt{13})/2} + \sqrt{(5-\sqrt{13})/2}\right]$$

where $\pm\sqrt{(5 \pm \sqrt{13})/2}$ are the zeros of $x^4 - 5x^2 + 3$. The right-hand side of the inequality (11) follows now after elementary algebraic transformations.

The topological resonance energies of A_k for $k \leqq 6$ were first reported by Aihara [8]. In Table 1 the E, E^{R} and TRE values for the first ten members of the linear polyacene series are presented. It can be seen that for k being sufficiently large, $E^{\mathrm{R}}(A_k)$ is also a linear function of k, and

$$E^{\mathrm{R}}(A_{k+1}) - E^{\mathrm{R}}(A_k) = 5.534\,. \tag{13}$$

Combining (6) and (13) we get

$$\mathrm{TRE}(A_{k+1}) - \mathrm{TRE}(A_k) = 0.077\,,$$

from which the limes (2) follows straightforwardly.

Correlation of TRE with Experimental Data

Quantitative experimental data on ionization potential, electron spectra and chemical reactivity are available for the first six linear polyacenes [9]. These correlate excellently with the computed TREPE values (of course, $\mathrm{TREPE}(A_k) = \mathrm{TRE}(A_k)/(4k+2)$). The following linear relations have been established:

$$\mathrm{IP} = 155.5\,\mathrm{TREPE} + 2.15\,[\mathrm{eV}]\,,$$
$$E_{\mathrm{p}} = 219.5\,\mathrm{TREPE} - 4.06\,[\mathrm{eV}]\,,$$

where IP and E_{p} are the ionization potential and the energy of the p-band (in gas phase), respectively. The correlation coefficients in the above equations are 0.9996 and 0.9995, respectively. Hence the resonance energies of the linear polyacenes with more than six rings (which are given in Table) can be used for a reliable prediction of some of their physico-chemical properties.

Table 1.

k	$E(A_k)$	$E^{\mathrm{R}}(A_k)$	$\mathrm{TRE}(A_k)$
1	8.000	7.727	0.273
2	13.683	13.294	0.389
3	19.314	18.839	0.475
4	24.931	24.378	0.553
5	30.544	29.914	0.630
6	36.156	35.450	0.706
7	41.768	40.985	0.783
8	47.379	46.519	0.859
9	52.990	52.054	0.936
10	58.602	57.589	1.013

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