Topological Resonance Energy of Very Large Benzenoid Hydrocarbons

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An approximate expression is obtained for the resonance energy of benzenoid hydrocarbons. The resonance energy is shown to depend in a simple manner on the number of six-membered cycles and on the number of Kekulé structural formulae of the molecule. By this approach, the resonance energies of very large benzenoid hydrocarbons can be determined.

Introduction

The topological resonance energy (TRE) of a conjugated π-electron system is given by

$$\mathrm{TRE} = \sum_{i=1}^{n} g_i (e_i - x_i)\,, \tag{1}$$

where $x_1, x_2, \ldots, x_n$ are the zeros of the matching polynomial $\alpha(G)$ of the molecular graph G,

$$\alpha(G) = \sum_{k=0}^{[n/2]} (-1)^k\, p(G,k)\, x^{n-2k}\,. \tag{2}$$

The quantities g_i, e_i, n and $p(G,k)$ in Eqs. (1) and (2) are the same as defined in [1]. Here and later TRE is expressed in β units.

According to Eqs. (1) and (2), in order to compute TRE one must first find the polynomial $\alpha(G)$. In spite of several calculation techniques which have been proposed for the determination of the matching polynomial [2–5], this task becomes enormously difficult with the increasing size of the molecular graph. (In fact, the number of arithmetic operations required for the calculation of $\alpha(G)$ increases at least exponentially with the increasing number of edges in G.)

Calculated TRE values of a limited number of benzenoid hydrocarbons have been tabulated [6, 7]. The TRE values of such molecules with 8 and more six-membered cycles are not available in the literature, what is not surprising because of the above mentioned computational difficulties. Nevertheless, the knowledge of the resonance energy of very large benzenoid systems would be of considerable interest for both theoretical and experimental organic chemistry [8].

In the present paper we offer a simple approximate topological formula (3) which enables the calculation of TRE of arbitrarily large benzenoid hydrocarbons.

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

The only two topological invariants which are needed in Eq. (3) are n_6 — the number of six-membered cycles and K — the number of Kekulé valence formulae of the pertinent benzenoid system; a and b are constants (see later). While n_6 is immediately obtained by inspection of the structural formula of the hydrocarbon, the determination of K is slightly more complicated. Fortunately, several combinatorial methods have been developed [9–12] by which K can be readily evaluated.

The Topological Formula for TRE

Let $\Phi(G) = \Phi(G,x)$ be the characteristic polynomial of the graph G. Since benzenoid hydrocarbons are alternant, we can write

$$\Phi(G) = \sum_{k=0}^{[n/2]} (-1)^k\, f(G,k)\, x^{n-2k}\,,$$

where $f(G,0) = 1$ and $f(G,k) \geqq 0$ for all $k = 1, 2, \ldots, [n/2]$. Then TRE conforms to the integral formula [6, 13]

$$\mathrm{TRE} = \frac{2}{\pi} \int_0^\infty T(x)\, \mathrm{d}x\,, \tag{4}$$

where

$$T(x) = T(G,x) = \log \frac{\Phi(G, ix)}{\alpha(G, ix)} = \log \frac{\sum_{k=0}^{[n/2]} f(G,k)\, x^{n-2k}}{\sum_{k=0}^{[n/2]} p(G,k)\, x^{n-2k}}\,.$$

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In the following we will restrict our consideration to benzenoid hydrocarbons for which at least one Kekulé structural formula can be written, $K > 0$. Then, of course, the number n of vertices of the molecular graph G is even. It can be easily verified that for benzene and naphthalene $K = 2$ and $K = 3$, while for all other benzenoid hydrocarbons $K \geqq 4$.

A number of topological relations are known for the coefficients of the characteristic and matching polynomial of a molecular graph of a benzenoid hydrocarbon [14, 15]. We shall need the following properties.

$$f(G,0) = p(G,0) = 1; \tag{5}$$

$$f(G,1) = p(G,1); \tag{6}$$

$$f(G,2) = p(G,2); \tag{7}$$

$$f(G,3) = p(G,3) + 2n_6; \tag{8}$$

$$f(G,n/2) = K^2; \quad p(G,n/2) = K. \tag{9}$$

From Eqs. (5)—(9) it is easy to deduce that

(a) $T(x) = 2n_6 x^{-6} + O(x^{-8})$

for large values of x,

(b) $T(x) = \log K + O(x^2)$

for near-zero values of x, and

(c) the function $T(x)$ has a maximum for $x = 0$,

$$T_{\max} = \log K$$

and monotonically decreases in the interval $(0, \infty)$.

If it is possible to find another function $T^0(x) = T^0(G,x)$ with the properties

(a^0) $T^0(x) = 2n_6 x^{-6} + O(x^{-8})$

for large values of x,

(b^0) $T^0(x) = \log K + O(x^2)$

for near-zero values of x, and

(c^0) the function $T^0(x)$ has a maximum for $x = 0$,

$$T^0_{\max} = \log K$$

and monotonically decreases in the interval $(0, \infty)$, then we can expect that the integral

$$\mathrm{TRE}^0 = \frac{2}{\pi}\int_0^\infty T^0(x)\,\mathrm{d}x$$

will be a good approximation for the right-hand side of Eq. (4). (For further details on this method of approximation see [16].)

A simple analytical function T^0 with the desired properties (a^0)—(c^0) is

$$T^0(x) = \frac{2n_6 \log K}{2n_6 + x^6 \log K}$$

and straightforward integration gives

$$\mathrm{TRE}^0 = \tfrac{2}{3}\sqrt[6]{2n_6(\log K)^5}\,. \tag{10}$$

Numerical testing showed that the formula (10) considerably overestimates the actual TRE values, Equation (4). On the other hand an excellent correlation between TRE and TRE^0 was observed, Equation (3). For 34 benzenoid hydrocarbons (with $K > 2$) a least squares fitting resulted in $a = 0.3541$ and $b = 0.0679$ whereas the correlation coefficient was 0.996.

Linear regression between TRE^0 and the Dewar resonance energy has been already reported [17].

When examining the resonance energies of very large conjugated systems, one should consider the resonance energy per π-electron rather than the total resonance energy. (This latter quantity is often infinitely large when $n \to \infty$.) The topological resonance energy per π-electron (TREPE) can be thus evaluated from the approximate formula

$$\mathrm{TREPE} \doteq \tfrac{2}{3}a\sqrt[6]{2n_6(\log K)^5 n^{-6}} + b/n\,.$$

Let now $H_1, H_2, \ldots, H_k, \ldots$ be a homologous series of benzenoid hydrocarbons and let the number $n(H_k)$ of carbon atoms of H_k become infinitely large when $k \to \infty$. Then for very large benzenoid hydrocarbons we have

$$\mathrm{TREPE}(H_k) \doteq \mathrm{TREPE}(H_\infty) \doteq a\,L(H_\infty)\,, \tag{11}$$

where

$$L(H_\infty) = \lim_{k\to\infty} \tfrac{2}{3}\sqrt[6]{2n_6(H_k)[\log K(H_k)]^5\, n(H_k)^{-6}} \tag{12}$$

and $a = 0.3541$.

The number $n_6(H_k)$ of six-membered cycles in the benzenoid molecule H_k is always a certain linear function of $n(H_k)$. Therefore two cases can arise.

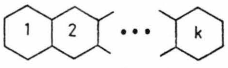
Firstly, if the number of Kekulé structures of H_k is a power function of $n(H_k)$ (i.e. $K(H_k)$ is equal to a polynomial in the variable $n(H_k)$), then $L(H_\infty) = 0$ and consequently the resonance energy per π-electron of H_k tends to zero. Very large benzenoid hydrocarbons of this type are, thus, predicted to be non-aromatic.

Secondly, if the number of Kekulé structures of H_k is an exponential function of $n(H_k)$, then $L(H_\infty)$ is a finite positive number. Consequently, the pertinent TREPE value is positive (but finite) and the corresponding hydrocarbons are predicted to be aromatic.

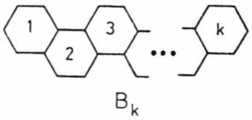
The limes (12) cannot become infinitely large since for a benzenoid hydrocarbon with n_6 six-membered cycles at most 2^{n_6} Kekulé structural formulae can be written.

Applications

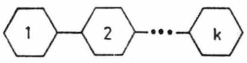
In the present section we shall determine the TREPE values of very large benzenoid hydrocarbons A_k, B_k and C_k with k six-membered cycles and of the system $D_{k,k'}$ with $kk' + (k-1)(k'-1)$ six-membered cycles. (Note that in our notation, $D_{k,1} = A_k$ and $D_{1,k'} = C_{k'}$.)



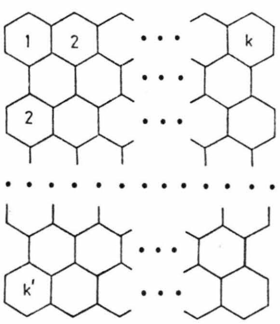
A_k



B_k



C_k



$D_{k,k'}$

It is not difficult to see that A_k, B_k, C_k and $D_{k,k'}$ have $4k+2$, $4k+2$, $6k$ and $(4k+2)k'$ carbon atoms, respectively. The number of Kekulé structures of A_k, C_k and $D_{k,k'}$ is $k+1$, 2^k and $(k+1)^{k'}$, respectively [9, 10]. The number of Kekulé structures of B_k satisfies the recurrence formula

$$K(B_k) = K(B_{k-1}) + K(B_{k-2}) \tag{13}$$

with the initial conditions $K(B_1) = 2$, $K(B_2) = 3$. From (13) we deduce

$$K(B_k) = \frac{1}{\sqrt{5}}\left[\left(\frac{1+\sqrt{5}}{2}\right)^{k+2} - \left(\frac{1-\sqrt{5}}{2}\right)^{k+2}\right].$$

Using the above listed expressions for n, n_6 and K we can calculate from Eq. (12)

$$L(A_\infty) = 0\,,$$
$$L(B_\infty) = \frac{\sqrt[6]{2}}{6}\left(\log\frac{1+\sqrt{5}}{2}\right)^{5/6},$$
$$L(C_\infty) = \frac{\sqrt{2}}{9}(\log 2)^{5/6}\,,$$
$$L(D_{\infty,k'}) = 0\,,$$
$$L(D_{k,\infty}) = \frac{\sqrt[6]{2(2k-1)}}{3(2k+1)}[\log(k+1)]^{5/6}.$$

From Eq. (11) we finally obtain the desired resonance energies of very large (not necessarily infinite) benzenoid hydrocarbons A_k, B_k and C_k:

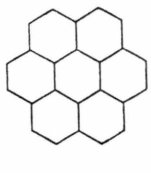
$$\mathrm{TREPE}(A_k) = 0.0000\,,$$
$$\mathrm{TREPE}(B_k) = 0.0360\,,$$
$$\mathrm{TREPE}(C_k) = 0.0325\,.$$

Hence, very large linear polyacenes (A_k) have zero TRE per π-electron and must be therefore classified as non-aromatic species, contrary to angular polyacenes (B_k) and polyphenyls (C_k) which are typical aromatic molecules also if their size is very large. Another interesting chemical prediction is that very large benzenoid hydrocarbons of the type $D_{k,k'}$ will exhibit a strikingly different chemical behaviour, depending on whether k is large (non-aromatic compounds) or k' is large (aromatic compounds).

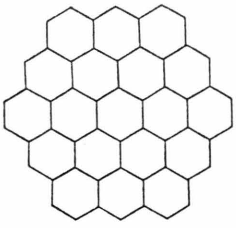
Topological Resonance Energy of the Graphite Lattice

In order to determine the TREPE value for the graphite lattice we will consider the infinite sequence of molecular graphs $G_1, G_2, \ldots, G_k, \ldots$.

G_1



G_2



G_3

It can be shown (c.f. [18]) that the number of vertices and six-membered cycles of G_k are given by

$$n(G_k) = 6k^2\,, \tag{14}$$
$$n_6(G_k) = 1 + 3k(k-1)\,. \tag{15}$$

The number of Kekulé structures of G_k is computed by means of the expression [9, 10]

$$K(G_k) = \frac{\prod_{i=k}^{2k-1}\binom{k+i}{k}}{\prod_{i=1}^{k-1}\binom{k+i}{k}}\,. \tag{16}$$

We show first that

$$\lim_{k\to\infty} k^{-2} \log K(G_k) = \frac{3}{2} \log \frac{27}{16}\,. \tag{17}$$

Equation (16) can be transformed into

$$\frac{K(G_{k+1})}{K(G_k)} = \frac{(3k+2)(3k+1)^2}{(2k+1)^3} \left[\frac{(3k)!\,k!}{(2k)!\,(2k)!}\right]^3,$$

that is

$$\log \frac{K(G_{k+1})}{K(G_k)} = \log \frac{(3k+2)(3k+1)^2}{(2k+1)^3} + 3 \log \frac{(3k)!\,k!}{(2k)!\,(2k)!}\,.$$

For large values of k we may apply the Stirling approximation and thus obtain

$$\log \frac{K(G_{k+1})}{K(G_k)} \sim 3 \log \frac{3}{2} + 3k \log \frac{27}{16}\,,$$

that is

$$K(G_{k+1}) \sim \frac{27}{8} \left(\frac{27}{16}\right)^{3k} K(G_k)\,. \tag{18}$$

Let the relation (18) be applicable for $k \geqq h$, where h is a sufficiently large, but fixed integer. Then

$$K(G_{h+1}) \sim \frac{27}{8} \left(\frac{27}{16}\right)^{3h} K(G_h)\,,$$

$$K(G_{h+2}) \sim \left(\frac{27}{8}\right)^2 \left(\frac{27}{16}\right)^{3(h+1)+3h} K(G_h)\,,$$

etc. The repetition of the above argument gives

$$K(G_{h+k}) \sim \left(\frac{27}{8}\right)^k \left(\frac{27}{16}\right)^{3(h+k-1)+3(h+k-2)+\cdots+3h} K(G_h)\,,$$

that is

$$\log K(G_{h+k}) \sim k \log \frac{27}{8} + \left[3hk + \tfrac{3}{2} k(k-1)\right] \log \frac{27}{16} + \log K(G_h)\,.$$

Since h is fixed, $K(G_h)$ is a finite constant and therefore

$$\lim_{k\to\infty} k^{-2} \log K(G_{h+k}) = \frac{3}{2} \log \frac{27}{16}\,,$$

which then immediately yields (17).

Substituting (14), (15) and (17) back into (12) we obtain

$$L(G_\infty) = \frac{2}{3} \left(\frac{1}{4} \log \frac{27}{16}\right)^{5/6},$$

from which

$$\mathrm{TREPE}(G_k) = 0.0433$$

for sufficiently large k. Thus the topological resonance energy of the graphite lattice is found to be $0.0433\,\beta$ units per π-electron.

This result means that very large benzenoid hydrocarbons of the type G_k and the graphite lattice ($= G_\infty$) are predicted by the TRE criterion to have a high extent of aromaticity, comparable with that of benzene (TREPE = 0.0455 for benzene).

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