

NODAL INCREMENTS APPROACH TO THE TOPOLOGICAL RESONANCE ENERGY  
OF BENZENOID HYDROCARBONS

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Abstract. The concept of the additive nodal increments is applied to analyse the topological resonance energy of benzenoid hydrocarbons.

Preliminaries

Let  $Q(x)$  be a polynomial of a degree  $N$ . We can then define the following functionals :

$$E[Q] = \sum_{i=1}^N |x_i| \quad (1)$$

$$\mu_K[Q] = \sum_{i=1}^N x_i^K \quad (2)$$

where the summation runs over all the roots  $x_i$  of  $Q$ . If we assume that all the  $x_i$ 's lay in the interval  $\langle -a, a \rangle$  , then we can approximate  $E[Q]$  by means of the normalized Legendre polynomials :

$$E[Q] \approx \sum_{i=1}^N \sum_{l=0}^{\infty} c_l P_l(x_i/a) \quad (3)$$

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$$\text{where : } c_1 = \int_{-1}^{+1} |x| P_1(x) dx \quad (4)$$

A truncation of the expansion (3) on the J-th term leads to an approximate formula for  $E[Q]$  :

$$E[Q] \approx a \sum_{i=1}^N \sum_{j=0}^J c_1 P_1(x_i/a) = \sum_{j=0}^J b_{1,j} \mu_1[Q] \quad (5)$$

where  $b_{1,j}$  are appropriate coefficients.

Provided all bonding MOs are doubly occupied and all antibonding MOs are empty , the total pi-electron energy of a particular conjugated system is given by<sup>1</sup> :

$$E_{pi} = E[\tilde{\phi}] \quad (6)$$

while the topological resonance energy (TRE)<sup>2</sup> is given by :

$$TRE = E_{pi} - E_{pi}(\text{ref}) = E[\tilde{\phi}] - E[\alpha] \quad (7)$$

In these formulae  $\tilde{\phi}$  and  $\alpha$  denote the characteristic and the matching polynomial<sup>3</sup> corresponding to the considered molecule , respectively.

In the case of the benzenoid hydrocarbons there is a 1:1 correspondence between the molecular graph and the dualist<sup>1</sup> obtained by the replacement of the ring centers by dots (Fig.1) :

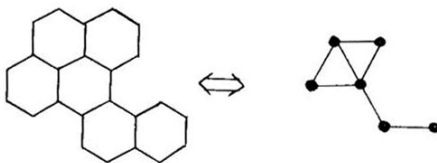


Fig.1

The dualist can be then decomposed into so called nodes<sup>4,5</sup> which describe the local annellations of the rings (Fig.2).

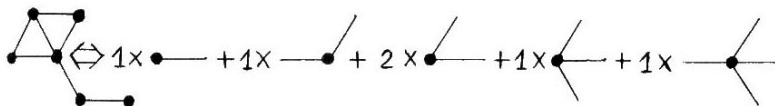


Fig.2

There are only 13 different kinds of the nodes (Fig.3) :

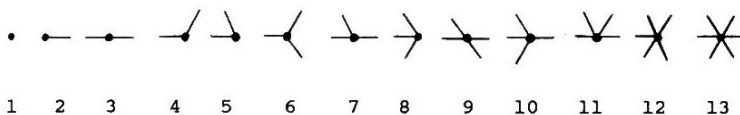


Fig.3

Let  $\underline{n}$  be a vector having the components  $(n_1, \dots, n_{13})$ , where  $n_i$  is the number of the nodes of type  $i$ . For example, the vector  $\underline{n}$  corresponding to the hydrocarbon from Fig.1 has a form  $(0, 1, 0, 1, 2, 0, 0, 1, 0, 1, 0, 0, 0)$ . It should be pointed out, that there are different molecules having the same  $\underline{n}$ . These molecules we call isonodal<sup>4</sup>.

#### The nodally and globally dependent properties

All the properties of benzenoid hydrocarbons can be divided into two general classes. Let  $P$  be a particular property. If there is a function  $p$  for which the relation :

$$P \approx p(\underline{n}) \quad (8)$$

holds with a significant accuracy, then P is called nodally dependent. Otherwise, P is called globally dependent. It should be mentioned that this classification is to some extent arbitrary, depending on the required accuracy of eq.8. For example, it has been found that the total pi-electron energy  $E_{pi}$  is nodally dependent with the accuracy of about 0.2%<sup>4</sup>, whereas the spectral radius of the adjacency matrix (R) :

$$R = \sup_i x_i \quad (9)$$

with the accuracy of about 1%<sup>6</sup>.

The simplest form of eq.8 is encountered when we can write :

$$P \approx g \cdot n \quad (10)$$

If so, then P can be calculated by means of the additive nodal increments represented by the vector  $g = (g_1, \dots, g_{13})$ .

#### The additive nodal increments for TRE

Taking into account equations (5), (6) and (7) we can write (a=3) :

$$E_{pi} \approx \sum_{l=0}^J b_{1,J} \mu_l[\Phi] \quad (11)$$

$$TRE \approx \sum_{l=0}^J b_{1,J} (\mu_l[\Phi] - \mu_l[\alpha]) = \sum_{l=0}^J b_{1,J} \Delta \mu_l \quad (12)$$

It has been shown that the expansion (11) truncated on the 8th term reproduces  $E_{pi}$  up to 98-99%<sup>5</sup>. On the other hand, the moments  $\mu_0$ ,  $\mu_2$ ,  $\mu_4$ ,  $\mu_6$  and the main part of  $\mu_8$  have

been found to be nodally additive. And so , since  $\mu_1=\mu_3=\mu_5=\dots=0$  for benzenoid hydrocarbons ,  $E_{pi}$  can be calculated by means of the additive nodal increments (ANI) with a relatively good accuracy.

The situation with TRE is quite different. Firstly , we have:

$$\Delta\mu_0=\Delta\mu_2=\Delta\mu_4=0 \quad (13)$$

Secondly , the expansion (12) , truncated even on the 10th term , greatly overestimates the TRE. Thus , although the computer simulated ring annellations show that  $\Delta\mu_6$  ,  $\Delta\mu_8$  and  $\Delta\mu_{10}$  are nodally additive (Table 1) :

$$\Delta\mu_l = g_l \cdot n \quad (l=6,8,10) \quad (14)$$

the equations (12) and (14) cannot provide the values for  $g_{TRE}$  :

$$TRE \approx g_{TRE} \cdot n \quad (15)$$

The only way to determine  $g_{TRE}$  is to set together the exact and the calculated (by virtue of eq.15) values of TRE. Such a correlation has been carried out for the trial set of 141 benzenoid hydrocarbons taken from ref.7. The quality of the least-squares fit is described by the standard deviation of 4%. The highest relative error was found to be 28%. The computed increments  $g_{TRE}$  are shown in Table 1 .

### Discussion

The aforementioned considerations lead to the conclusion that the topological resonance energy is a quantity , which is to a great extent nodally dependent , but not so

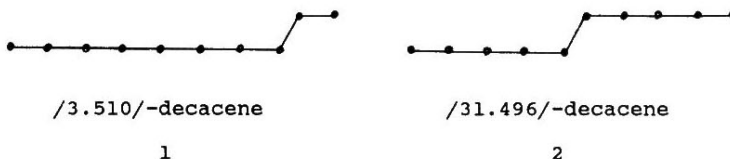
TABLE 1. The additive nodal increments

Node (Fig.3)	$g_6$	$g_8$	$g_{10}$	$g_{TRE}$
1	12	96	540	0.273
2	12	128	970	0.189
3	12	160	1480	0.084
4	12	160	1520	0.149
5	12	144	1240	0.155
6	12	192	2190	0.141
7	12	176	1830	0.080
8	12	160	1530	0.146
9	12	192	2200	0.092
10	12	192	2590	0.116
11	12	176	1840	0.080
12	12	192	2210	0.118
13	12	192	2220	0.076

strictly as for example the total  $\pi$ -electron energy. Three point should be accentuated :

i) The calculation of TRE by means of the ANI approach can serve as a guesstimate for the stability of a given compound when the exact calculation of the TRE is tedious and laborous. For example , the exact/ANI values of the TRE are : for /14.6.7/-octacene (bisanthene) 0.968/0.932 and for /3.7.6/-heptacene (pyranthrene) 0.924/0.985.

ii) In some cases the ANI treatment fails to differentiate the isonodal hydrocarbons with respect to their TRE values. The compounds 1 and 2 can serve as an example :



iii) The ANI approach shows correct asymptotic behaviour of the TRE(PE) (TRE per electron) for the linear and the zig-zag polyacenes with the infinite number of rings. For both classes the TRE(PE) tends to finite values in agreement with the exact ones<sup>8</sup>. Other published formulae<sup>9,10</sup> give wrong estimates in this case.

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