match no. 20 pp. 103-114 1986

FURTHER APPLICATIONS OF THE ADDITIVE NODAL INCREMENTS

J.Cioslowski

Department of Theoretical Chemistry,
Jagiellonian University , 30060 Cracow , Poland
and
Department of Chemistry , Georgetown University ,
Washington , D.C. 20057 , USA

(Received: July 1986)

Abstract: The method of additive nodal increments (ANI) is applied to analyze the dependence of the modified topological index Z and the spectral radius of adjacency matrix R on the topology of benzenoid hydrocarbons. The derived formulae enable these quantities to be calculated with relatively high degree of accuracy.

INTRODUCTION

The dualist[1] of the graph corresponding to a particular benzenoid hydrocarbon comprises whole information needed to calculate any molecular property of the compound. Because of this fact it is guaranteed that there exists some function which relates the structure of the dualist and the property. The question about the form of this function arises in a natural way. A partial answer to this problem has been given by the additive nodal increments approach , which accounts for the topological dependence of some quantities characterizing the molecule. For instance , the total pi-electron energy[2,3] and the topological resonance energy[4] can be expressed in terms of the nodal increments.

A method of the decomposition of the dualist into nodes was described several times[2,3,4,5] and therefore here we recall only the following definitions[4,5] :

1. Let $\underline{n}$ be the vector of the number of nodal increments inherent in the dualist. If the value of some property P can be approximated with reasonable accuracy as :

$$P=p(\underline{n}) \tag{1}$$

then P is called nodally dependent.

2. In the simplest case we deal with the following relation :

$$P=\underline{n}.\underline{g}^{P} \tag{2}$$

Then P is called nodally additive and $\underline{g}^{P}$ is the vector of nodal increments.

It should be accentuated that there exist some properties which cannot be expressed by eq.(1) or (2). These properties we call globally dependent , since they reflect the global structure of the dualist. An example of this type of behavior is the HOMO-LUMO separation.

The advantage of ANI approach lies on its extreme simplicity. One can argue that the method uses a huge number (12) of the parameters to reproduce accurate values of molecular properties. The idea of ANI treatment is , however, not only to provide us with another approximate topological formulae , but also to systematize and study the topological dependencies on the dualist's structure , which is done within this approach in a very clear and straightforward way.

In this paper we present the application of ANI to two important graph invariants : the modified topological index Z and the spectral radius of the adjacency matrix R.

THE MODIFIED TOPOLOGICAL INDEX AND THE ADDITIVE NODAL INCREMENTS

The modified topological index Z has been introduced by Hosoya and Gutman as[6] :

$$Z=i^{-N}\phi(G,i) \tag{3}$$

where $\phi(G,x)$ is the characteristic polynomial[7] of the molecular graph G having N vertices and M edges and $i=\sqrt{-1}$. The importance of Z leans on its relation to the total pi-electron energy (E_{pi})[6,8,9,10].

Z can be also expressed as :

$$\ln Z=\sum_{i=1}^{N/2} \ln(1+x_i^2) \tag{4}$$

where x_i is the i-th eigenvalue of the adjacency matrix $\underline{\underline{A}}$ corresponding to G. Using the reasoning analogous to the one in ref. 3 , the function $\ln(1+x^2)$ can be approximated by means of the Legendre polynomials:

$$\ln(1+x^2)=\sum_{L=0}^{\infty} C_L P_L(x/3)+\ln 9 \quad (x\in<-3,3>) \tag{5}$$

where:

$$C_L=\int_{-1}^{1} P_L(x)\ln(\tfrac{1}{9}+x^2)\,dx \tag{6}$$

A truncation of the series (5) on the 8th term leads to the relation:

$$\ln(1+x_i^2) \approx \sum_{L=0}^{8} b_L x_i^L \qquad (7)$$

with appropriate coefficients b_L. Thus , from eqs.(4) and (7) we have:

$$\ln Z \approx 0.5 \sum_{L=0}^{8} b_L \mu_L \qquad (8)$$

where:

$$\mu_L = \sum_{i=1}^{N} x_i^L = \mathrm{Tr}(\underline{\underline{A}}^L) \qquad (9)$$

is the L-th moment of $\underline{\underline{A}}$. The accuracy of the expansion (8) is even better than in the case of E_{pi}[3] because of a "more smooth" character of the function $\ln(1+x^2)$ than of the function $|x|$. As it was shown in ref. 3 the moments $\mu_0, \dots, \mu_8$ can be expressed in terms of appropriate nodal increments:

$$\mu_L = \underline{n}.\underline{g}^{(L)} \qquad (L=0,2,4,6,8) \qquad (10)$$

$$\mu_1 = \mu_3 = \mu_5 = \mu_7 = 0 \qquad (11)$$

Therefore we can expect , that also Z can be calculated approximately as :

$$\ln Z \approx \underline{n}.\underline{g}^Z \qquad (12)$$

where :

$$\underline{g}^Z = 0.5 \sum_{L=0}^{8} b_L \underline{g}^{(L)} \qquad (13)$$

This result is verified easily by a numerical testing. First , the vector g^Z was computed from analytically derived coefficients b_L and the vectors $g^{(L)}$. Then the obtained values were compared with the increments g^Z determined by means of the least squares fitting and a reasonable agreement was found. Because of that we quote the fitted g^Z's (Table 1) since they give a slightly better result due to higher terms of the expansion (5) included in a semiempirical manner. The test set of molecules covered 1030 possible singlet ground state , planar benzenoid hydrocarbons with 2-8 rings[2]. The accuracy of lnZ is characterized by the average error 0.02% , the standard deviation 0.03% and the maximal error observed 0.10%. These figures are to be compared with the ones for E_{pi} : 0.07% , 0.09% and 0.47%[2].

The nodally dependent character of Z is striking.

TABLE 1. THE NODAL INCREMENTS g^Z AND THE RATIOS g^E/g^Z.

Node*)	g^Z	g^E/g^Z
1	2.568706	2.665
2	2.140404	2.641
3	2.166869	2.654
4	2.267500	2.644
5	1.787431	2.638
6	1.863064	2.622
7	1.971999	2.659
8	1.590606	2.657
9	1.592051	2.655
10	1.667971	2.627
11	1.395820	2.635
12	1.201862	2.575

---

*)the enumeration of nodes as in ref. 2 (see also Fig.1).

As it has been observed first by Aihara[8] and later tested numerically by Gutman et al.[9] there is an approximate linear relationship between E_{pi} and lnZ :

$$E_{pi} \approx 2.650 \ln Z \qquad (14)$$

Since both E_{pi} and lnZ can be computed from the nodal increments $\underline{g}^E$ and $\underline{g}^Z$, respectively , one may be interested how the validity of (14) is reflected by a constant ratio of the components of these vectors. An inspection of Table 1 allows us to draw a conclusion that the ratio varies within the range of 3.5% and thus eq.14 cannot be accurate for all benzenoid compounds.

Finally it should be pointed out that the relationship between Z and the size of the hydrocarbon has been analyzed recently by Gutman and Shalabi[11] and certain exponential increase of Z with the size of molecule has been evidenced , which is in agreement with the results of the present work.

THE SPECTRAL RADIUS R AND THE ANI APPROACH

The spectral radius of the adjacency matrix (R) , equal to the energy of the lowest occupied pi-molecular orbital within Huckel Hamiltonian picture , has been investigated several times[13,14,15]. The approaches to this problem are obviously based on the Rayleigh's quotient technique[12].

For the adjacency matrix $\underline{\underline{A}}$ we define the following quantity :

$$M_k = \underline{u}^+ \underline{\underline{A}}^k \underline{u} \qquad (15)$$

where $\underline{u}$ is the vector of (1,1,...,1). Let us diagonalize the matrix $\underline{\underline{A}}$:

$$\underline{\underline{A}}=\underline{\underline{C}}^{+}\underline{\underline{X}}\underline{\underline{C}} \tag{16}$$

where $\underline{\underline{C}}$ is the matrix of eigenvectors and $\underline{\underline{X}}$ is a diagonal matrix of eigenvalues. Then we can rewrite eq.(15) as :

$$M_k=\underline{w}^{+}\underline{\underline{X}}^{k}\underline{w}=\sum_{i=1}^{N} w_i^2 x_i^k \tag{17}$$

where $\underline{w}=\underline{\underline{C}}\underline{u}$ and $\underline{x}$ is the vector of the increasingly ordered eigenvalues of $\underline{\underline{A}}$. The quantity :

$$r_k=M_{2k+1}/M_{2k} \tag{18}$$

is being used to estimate the R. In particular , Hall has examined the cases for k=0 and 1[13]. A quite different approach has been proposed recently by Cioslowski[14].

The use of such an approximation can lead , however , to incorrect results. Since the benzenoid hydrocarbons are alternant systems , the matrix $\underline{\underline{A}}$ has two eigenvalues of the largest module, namely R and -R. Thus the sequence of numbers r_k converges to :

$$R'=\lim_{k\to\infty} r_k= (-w_1^2R+w_N^2R)/(w_1^2+w_N^2)=R(w_N^2-w_1^2)/(w_N^2+w_1^2) \tag{19}$$

instead to the true R. As pointed out by Polansky and Gutman[16] , an equality R'=R occurs only for the hydrocarbons possessing certain elements of symmetry.

There is a simple method to avoid this difficulty. Let us define the quantity :

$$s_k=M_{k+2}/M_k \tag{20}$$

Then we have :

$$S=\lim_{k\to\infty} s_k=(w_1^2R^2+w_N^2R^2)/(w_1^2+w_N^2)=R^2 \tag{21}$$

One should also note , that for every k , r_k is a lower bound for R , whereas s_k is a lower bound only when k is even. Therefore we have the following sequence of approximations of the rank 0 , 1 and 2 :

$$R^{(0)}=s_0{}^{1/2}=(M_2/M_0)^{1/2}=((10M-6N)/N)^{1/2} \tag{22}$$

$$R^{(1)}=s_1{}^{1/2}=(M_3/M_1)^{1/2}=(M_3/2M)^{1/2} \tag{23}$$

$$R^{(2)}=s_2{}^{1/2}=(M_4/M_2)^{1/2}=(M_4/(10M-6N))^{1/2} \tag{24}$$

The idea of the nodal increments can be applied to calculate N , M , M_3 and M_4 ; and in turn to estimate R. It can be shown that the following relations hold :

$$N=\underline{n}.\underline{g}^{N} \tag{25}$$

$$M=\underline{n}.\underline{g}^{M} \tag{26}$$

$$M_3=\underline{n}.\underline{g}^{M3} \tag{27}$$

$$M_4=\underline{n}.\underline{g}^{M4}+2n_b \tag{28}$$

where : $\underline{g}^N$, $\underline{g}^M$, $\underline{g}^{M3}$ and $\underline{g}^{M4}$ are appropriate nodal increments and n_b is the number of the benzanthracene units present in the dualist of the hydrocarbon[3].

Now , equations (22)-(24) can be rewritten (neglecting a small term $2n_b$ in eq.28) as :

$$R^{(0)}=(\underline{n}.\underline{g}^{U(0)}/\underline{n}.\underline{g}^{L(0)})^{1/2} \tag{29}$$

$$R^{(1)}=(\underline{n}.\underline{g}^{U(1)}/\underline{n}.\underline{g}^{L(1)})^{1/2} \tag{30}$$

$$R^{(2)}=(\underline{n}.\underline{g}^{U(2)}/\underline{n}.\underline{g}^{L(2)})^{1/2} \tag{31}$$

where $\underline{g}^L$ and $\underline{g}^U$ are increments quoted in Table 2. For the sake of convenience , all the g_i's and g_i's are scaled down by g_{12}.

The accuracy of the approximations (29)-(31) , that contains no empirical parameters , was tested numerically on the standard set of 1030 singlet ground state , planar benzenoid hydrocarbons having 2-8 rings. It can be observed (Table 2) that the standard deviation drops from 5.5% to 2.4% when the rank of the approximation raises. However , the best results are achieved when the increments g^U and g^L are found by means of the least squares fitting. The equation of the form :

$$R \approx (\underline{n}.\underline{g}^U/\underline{n}.\underline{g}^L)^{1/2} \qquad (32)$$

where the increments g_i and g_i (i=1,2,...,11) were fitted , g_{12} was assumed to be equal 1 and g_{12} equal to 9 (in order to provide R=3 for the graphite lattice) provides us with R having reasonably small (0.3%) standard deviation from the exact radius. The values of $\underline{g}^U$ and $\underline{g}^L$ are shown in two last columns of Table 2.

TABLE 2. THE NODAL INCREMENTS g^U AND g^L. THE ERRORS CORRESPOND TO THE STANDARD SET OF HYDROCARBONS DESCRIBED IN THE TEXT.

Node*)	Rank 0		Rank 1		Rank 2		Fitted	
	$g^U(0)$	$g^L(0)$	$g^U(1)$	$g^L(1)$	$g^U(2)$	$g^L(2)$	g^U	g^L
1	12.500	2.500	9.500	1.833	7.278	1.389	3.739	0.700
2	13.000	2.000	11.000	1.667	9.444	1.444	4.179	0.612
3	13.000	2.000	11.333	1.667	9.889	1.444	4.557	0.629
4	12.000	2.167	9.667	1.667	7.889	1.333	4.324	0.734
5	13.500	1.500	13.500	1.500	13.167	1.500	8.574	0.908
6	12.500	1.667	11.500	1.500	10.611	1.389	5.904	0.713
7	11.500	1.833	9.833	1.500	8.500	1.278	6.183	0.906
8	12.000	1.333	12.000	1.333	11.778	1.333	10.359	1.165
9	12.000	1.333	12.000	1.333	11.778	1.333	14.456	1.757
10	11.000	1.500	10.000	1.333	9.222	1.222	8.391	1.094
11	10.500	1.167	10.500	1.167	10.389	1.167	13.837	1.666
12	9.000	1.000	9.000	1.000	9.000	1.000	9.000	1.000
average error		5.4%		3.2%		2.4%		.23%
standard dev.		5.5%		3.2%		2.4%		.29%
maximal error		7.8%		4.9%		3.7%		1.52%

---

*)the enumeration of nodes as in ref. 2 (see also Fig.1).

The present approach has been tested also on some large aromatic systems (Table 3). It was found that the method works quite accurately giving the values of R with the error of about 1%. It means , that the spectral radius can be regarded as the nodally dependent property.

TABLE 3. EXAMPLES OF THE ANI AND THE EXACT Rs FOR SOME BENZENOID HYDROCARBONS

Compact name*)	R(exact)	R(ANI)	Error[%]
/8.30.14.15.2/-tridecacene	2.791	2.768	0.83
/7.7.7/-nonacene	2.716	2.711	0.21
/14.15.7/-decacene	2.741	2.733	0.30
/30.31.15/-tridecacene	2.776	2.761	0.55
/28.18.17.9.7/-dodecacene	2.599	2.653	2.07
/7.14.28/-nonacene	2.666	2.672	0.24

---

*) ref.16

CONCLUSIONS

The ANI approach was applied to the topological invariants of the molecular graph. The numerical tests show that both the Z index and spectral radius R can be calculated with a reasonable degree of accuracy from their nodal increments.
This result can be useful in checking some relationships between different graph invariants (as it was shown on the example of the Z/E_{pi} ratios) as well as in studying the dependence of Z and R on topology of the molecules.

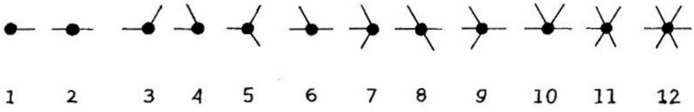

Fig.1

REFERENCES

1 A.T.Balaban , Pure Appl.Chem. 54 (1982) 1075

2 J.Cioslowski , Theor.Chim.Acta (Berlin) 68 (1985) 315

3 J.Cioslowski , Chem.Phys.Lett. 122 (1985) 234

4 J.Cioslowski , MATCH 19 (1986) 163

5 J.Cioslowski , Croat.Chem.Acta , in press

6 H.Hosoya , K.Hosoi and I.Gutman , Theor.Chim.Acta (Berlin) 45 (1977) 45

I.Gutman , T.Yamaguchi and H.Hosoya , Bull.Chem.Soc.Japan 49 (1976) 1811

7 A.Graovac , I.Gutman and N.Trinajstic , Topological Approach to the Chemistry of Conjugated Molecules , Springer-Verlag , Berlin 1977

8 J.Aihara , J.Org.Chem. 41 (1976) 2488

9 I.Gutman , A.V.Teodorovic and Z.Bugarcic , Bull.Soc.Chim. Beograd 49 (1984) 521

10 J.Cioslowski , Z.Naturforsch. 40a (1985) 1169

11 I.Gutman and A.Shalabi , Z.Naturforsch. 39a (1984) 797

12 A.Ralston , A First Course in Numerical Analysis , New York , McGraw-Hill , 1957

13 G.G.Hall , Mol.Phys. 33 (1977) 551

14 J.Cioslowski , Theor.Chim.Acta (Berlin) , in press

15 O.E.Polansky and I.Gutman , MATCH 5 (1979) 149

16 J.Cioslowski and A.M.Turek , Tetrahedron 40 (1984) 2161