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Additive nodal increments for approximate calculation of the total π-electron energy of benzenoid hydrocarbons

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An approximate method that allows efficient calculation of the total π-electron energy (E_π) of benzenoid hydrocarbons is presented. It is based on an additive scheme taking into account the characteristic features of variously annelated benzene rings expressed in terms of the numbers corresponding to the different nodes of the dual graph of the hydrocarbon molecule. The parameters of the model are fitted by a test calculation on 1030 hydrocarbons. The mean square error obtained in E_π is 0.07%. The method provides a connection between the names of hydrocarbons and their stabilities.

Key words: Benzenoid hydrocarbons — Compact naming — Total π-electron energy — Nodal increments

1. Introduction

The total π-electron energy (E_π) is one of the most important topological properties of conjugated molecules [1]. In particular a great deal of effort has been put into the construction of approximate methods to calculate the π-electron energy directly from molecular graphs [2, 3, 4].

The recently developed system for the compact naming of benzenoid hydrocarbons [5] offers a possibility to construct a molecular graph almost directly from the name of molecule. This gives a strong impetus to searching for a simple, but accurate enough method of direct computing the π-electron energy.

The existing approximate formulae [6, 7] use the number of carbon atoms (N), bonds (M) and Kekulé structures (K):

$$E_\pi \simeq 0.442N + 0.788M + 0.34K(0.632)^{M-N} \tag{1}$$

$$E_\pi \simeq 1.804(Mq)^{1/2}+0.421K(q/M)^{q/2}+1.686; \qquad q=\frac{N}{2}-1. \tag{2}$$

Formula (1) was given by Hall [6], whereas formula (2) originates from Gutman [7]. In these formulae the E_π denotes the Hückel total π-electron energy expressed in β units and with reference to the standard integral α as the zero of energies. In that strict sense the E_π quantity will be used in the later parts of this paper. Attention will be turned exclusively to the non-charged hydrocarbons, consisting of only six-membered rings and having a singlet ground state. So, molecules such as for instance perinaphthene or triangulene are left out of consideration.

2. The method of additive nodal increments

Let G be a molecular graph of a given benzenoid hydrocarbon. G' is a dual graph [8] corresponding to the graph G, constructed by replacing all the hexagons of G by dots (Fig. 1). The vertices of the graph G' we will call nodes. Excluding the benzene molecule, there are 12 types of nodes inherent in the benzenoid hydrocarbons (Fig. 2). Then we can observe the following:

1. The linear polyacenes with $n>2$ rings have 2 nodes of the type 1 and $n-2$ nodes of the type 2. As was first found by Gutman [9] the E_π for these polyacenes is in good approximation to a linear function of n

   $$E_\pi \simeq 5.6114n+2.4866. \tag{3}$$

   The largest error which is encountered for naphthalene, is 0.03. Thus, in that case we can compute the E_π energy as a sum of the nodal increments, using the values of 6.8547 and 5.6144 for nodes of type 1 and 2, respectively.

2. There are hydrocarbons, which have equal numbers of nodes of the same type. We shall call these hydrocarbons isonodal. For instance, the hydrocarbons 1, 2, 3 and 4, 5, 6, 7, 8 represent two families of such isonodal molecules (Fig. 3). The first family includes the hydrocarbons with two nodes of type 1 and three nodes of type 3, while another one consists of hydrocarbons with two nodes of type 1 and four nodes of type 3. Extensive numerical testing shows, that isonodal hydrocarbons always have their E_π energies close to each other.

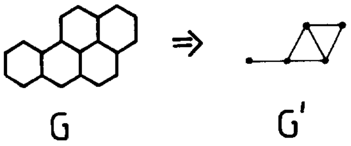

Fig. 1. The molecular graph G and the corresponding dual graph G' of /3.7/-pentacene

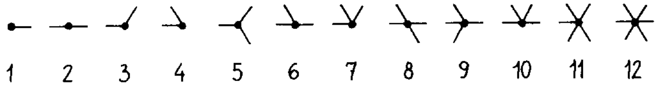

Fig. 2. 12 types of nodes inherent in benzenoid hydrocarbons

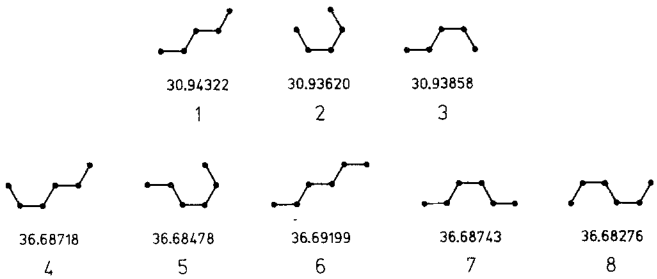

Fig. 3. Examples of the isonodal hydrocarbons

3. It is easy to show, that the values of N and M for a given hydrocarbon can be evaluated exactly using the nodal increments:

$$N=\sum_{j/1}^{12} n_j g_j^N \tag{4}$$

$$M=\sum_{j/1}^{12} n_j g_j^M \tag{5}$$

where: n_j is the number of the nodes of type j; g_j^N and g_j^M-appropriate nodal increments given in Table 1.

Hydrocarbons having at least one node of peritype are peri-ondensed. The cata-condensed hydrocarbons only have cata nodes (e.g. nodes of type 1, 2, 3 or 5).

The aforementioned observations encourage us to suppose that the value of the E_π can be approximately computed in terms of the nodal increments g^E as:

$$E_\pi \simeq \sum_{j/1}^{12} n_j g_j^E . \tag{6}$$

Then, this proposition is to be verified numerically.

Table 1. The nodal increments g^N, g^M and g^E

Node	Type	g^N	g^M	g^E
1	cata	5	5.5	6.845325
2	cata	4	5.0	5.651851
3	cata	4	5.0	5.751298
4	peri	$4\frac{1}{3}$	5.0	5.995198
5	cata	3	4.5	4.715913
6	peri	$3\frac{1}{3}$	4.5	4.885685
7	peri	$3\frac{2}{3}$	4.5	5.243459
8	peri	$2\frac{2}{3}$	4.0	4.225770
9	peri	$2\frac{2}{3}$	4.0	4.227109
10	peri	3	4.0	4.381249
11	peri	$2\frac{1}{3}$	3.5	3.678021
12	peri	2	3.0	3.094499

3. Numerical testing

The validity of the additive nodal increments (ANI) method has been tried out on all the 1030 possible planar, singlet ground state benzenoid hydrocarbons with 2-8 rings. The g^E increments were found by means of least squares fitting. The accuracy of the E_π is characterized by average error: 0.07%, standard deviation: 0.09% and the maximal error observed: 0.47%. It should be pointed out, that this method works better than the Hall and the Gutman formulae, for which the maximal errors were found to be 0.63% and 1.1% [7], respectively.

The success of the ANI approach can be explained by taking into account the Hall formula and the observation 3. The ANI method accounts well for different E_π's due to different values of N and M, since they are exactly computed from their nodal increments g^N and g^M. Differences due to different K values are absorbed into the g^E coefficients. The connection between the nodal treatment and the valence molecular connectivity index [10] can also serve as an explanation for the performance of the ANI method [11].

The ANI approach has been used in approximate calculation of the E_π for some large benzenoid hydrocarbons. The results are given in Fig. 4 and Table 2.

It is quite clear that the proposed algorithm can serve as a "pencil and paper" method for computing the total π-electron energy with relatively high accuracy. The total π-electron energy is directly related to the thermodynamical stability of the hydrocarbon [12] and the compact naming allows us to obtain information on the number of different nodes from its name in an efficient way. Thus, the presented method establishes a straightforward and auspicious connection between the names of hydrocarbons and their stabilities.

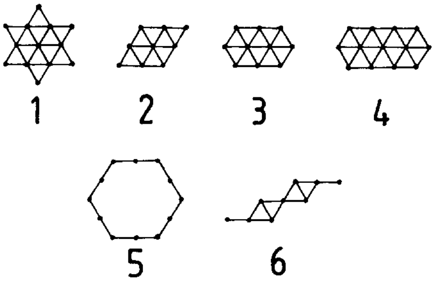

Fig. 4. Examples of the ANI and exact E_π energies for some benzenoid hydrocarbons

Table 2. Examples of the ANI and exact E_π energies for some benzenoid hydrocarbons

Compound	Compact Name	N	M	K	E_π (exact)	E_π (ANI)	Error [%]
1	/8.30.14.15.2/-tridecacene	42	54	250	61.3689	61.1338	0.38
2	/7.7.7/-nonacene	30	38	20	43.1198	43.0968	0.05
3	/14.15.7/-decacene	32	41	50	46.4974	46.4123	0.18
4	/30.31.15/-tridecacene	40	52	105	58.3755	58.2693	0.18
5	/28.18.17.9.7/-dodecacene	48	60	200	68.6102	68.4189	0.28
6	/7.14.28/-nonacene	34	42	40	48.5320	48.6616	0.27

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