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Dependence of Total π-Electron Energy on the Number of Non-Bonding Molecular Orbitals

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Summary. In recent work [*Gutman et al.* (2004) Chem Phys Lett **383**: 171] a method was developed by means of which the influence of non-bonding molecular orbitals (NBMOs) on the value of total π-electron energy (E) can be separated from the multitude of other molecular-structure-dependent effects. We now extend this method and establish the relation between E and the number n_0 of NBMOs. It is shown that E (when computed within the HMO approximation, and expressed in the units of the HMO resonance integral β) is a decreasing function of n_0, and that the dependence of E on n_0 is almost perfectly linear.

Keywords. Total π-electron energy; Non-bonding molecular orbitals; Chemical graph theory.

Introduction

The dependence of total π-electron energy (and therefore of thermodynamic stability) on molecular structure seems to be a perennial problem and topic of research in the theory of conjugated molecules. The first results along these lines were obtained good half a century ago (*e.g.*, [1–4]), but research in the same direction is still going on (for instance, [5–10]). The popularity of this theme may lie in the facts that (a) the structure-dependence of total π-electron energy is rather complex and far from being trivial, but (b) the underlying mathematical formalism is much simpler than in the case of other quantum-chemical π-electron properties, enabling one to formulate and (sometimes) rigorously prove generally valid regularities.

In this work (as well as in Refs. [1–10]) it is assumed that the total π-electron energy is computed within the *Hückel* molecular orbital (HMO) approximation

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[11, 12] and expressed in the units of the resonance integral β. This quantity will be denoted by E. Bearing in mind that β is a negative-valued constant, any structural factor that increases (resp. diminishes) E, causes thermodynamic stabilization (resp. destabilization) of the corresponding conjugated molecule.

In HMO-theoretical considerations it is advantageous to use graph theory [12–14]. If so, then $E = E(G)$, where G is the respective molecular graph. Therefore, in what follows we speak about the dependence of E on the structure of the molecular graph G (recall that the number of vertices and edges of G are equal to the number of carbon atoms and carbon–carbon bonds, respectively, of the underlying conjugated molecule [12, 14]).

The main structural factors determining E have been identified. These are the following:

- The gross part (over 99%) of E is determined by the size of the molecular graph, *i.e.*, by the parameters n (= number of vertices) and m (= number edges) [15, 16]. In order to evade this effect it is customary to examine E within sets of isomeric conjugated species (in which n and m have fixed values).
- The next-important structural features are the cycles, both their number, size, and mutual arrangement [17, 18]; their rather complicated effects are nowadays understood only to a limited extent. A direct consequence of the presence of cycles is the existence of a large number of *Kekulé*-type structural formulas. The relation between E and the *Kekulé* structure count has been much investigated (especially in the case of benzenoid hydrocarbons [19–21]), but – again – the problem is not completely solved [22]. Evidently, in order to be able to disregard the effect of cycles on E one has to consider acyclic systems (whose molecular graphs are referred to as trees).
- In acyclic conjugated systems (with fixed n and $m = n - 1$) the dominant effect influencing E is the extent of branching of the carbon-atom skeleton [23, 24]. It is well established that branching decreases E; *e.g.*, among n-vertex trees the unbranched path and the maximally branched star have minimum and maximum E-values, respectively [25]. However, quantitative relations between E and branching have never been reported, perhaps because there exists no unique numerical measure of (what intuitively is regarded as) "branching" [26–28]. Anyway, empirical observations show that E depends in a complicated manner on the number of branching points, their degrees, their location in the (acyclic) molecular graph, and their mutual constellation.
- In this work we are concerned with the (diminishing) effect of non-bonding molecular orbitals (NBMOs) on total π-electron energy. This effect was also recognized long time ago [12, 24, 29], but could not be properly quantified. The main obstacle seems to be the fact that the presence and number of NBMOs is much influenced by branching. In particular, acyclic systems with large number of NBMOs are necessarily highly branched, although the opposite is not true – highly branched acyclic species may possess no NBMOs. Consequently, it is difficult to separate the effect of branching from the effect of NBMOs.

In what follows we denote the number of NBMOs by $n_0 = n_0(G)$. As well known [12–14], $n_0(G)$ is equal to the number of zero eigenvalues of the molecular graph G.

In order to quantitatively determine the effect of NBMOs on E we have recently developed a pertinent method [10]. We considered molecular graphs $P_N(j)$, obtained by attaching a pendent vertex to the j-th vertex of an N-vertex path P_N $j = 2,3,\ldots,N–1$, *cf.* Fig. 1. These molecular graphs have a fixed number of vertices $(=N+1)$ and edges $(=N)$, possess no cycles, have a single branching point, and thus similar branching patterns. If, in addition, N is chosen to be sufficiently large, and the site j sufficiently distant from the terminal vertices of the N-vertex chain, then the effects of branching in $P_N(j)$ become independent of j. On the other hand, if N is odd, then the number of NBMOs of $P_N(j)$ depends on the parity of j: $n_0(P_N(j)) = 0$ for $j = 3, 5, 7, \ldots$ and $n_0(P_N(j)) = 2$ for $j = 2, 4, 6, \ldots$. Consequently, if N is chosen to be sufficiently large, and the site j sufficiently distant from the terminal vertices of the N-vertex chain, then in the difference $E(P_N(j+1)) - E(P_N(j))$ all (known) effects influencing the total π-electron energy, except the effect of NBMOs, will cancel out. Consequently, $E(P_N(j+1)) - E(P_N(j))$ can be viewed as the effect of two NBMOs on E. Further details are found in Ref. [10].

The obvious questions at this point are: What can one say about the effect of NBMOs in the case when n_0 is not equal to two? What is the effect of n_0 NBMOs on total π-electron energy, if $n_0 = 1, 2, 3, \ldots$? In this work we offer answers to these questions.

Results and Discussion

A Model with Variable Number of NBMOs

The tree with n vertices, in which no vertex has a degree greater than two is called *the path* and is denoted by P_n. The path P_n is the least branched n-vertex tree, because it possesses no branching point at all.

The molecular graphs used for the calculation of the effect of n_0 on E are denoted by $P_N(j_1, j_2, \ldots, j_k)$ and have the structure shown in Fig. 1. This graph is obtained

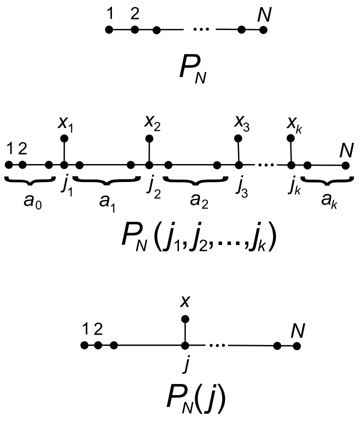

Fig. 1. The N-vertex path (P_N) and the molecular graph $P_N(j_1, j_2, \ldots, j_k)$ studied in this work; according to the notation indicated, the tree $P_N(j_1, j_2, \ldots, j_k)$ has $N+k$ vertices, where $N = a_0 + a_1 + a_2 + \cdots + a_k + k$; for further details see text; note that if $k = 1$, then $P_N(j_1, j_2, \ldots, j_k)$ reduces to the previously studied [10] molecular graph $P_N(j)$

from the N-vertex path P_N (see Fig. 1), by attaching to it k pendent vertices (denoted by $x_1, x_2, \ldots, x_k$) at positions $j_1, j_2, \ldots, j_k$. With the notation indicated in Fig. 1,

$$\left.\begin{array}{lcl} j_1 & = & a_0 + 1 \\ j_2 & = & a_0 + a_1 + 2 \\ j_3 & = & a_0 + a_1 + a_3 + 3 \\ \vdots & & \vdots \\ j_k & = & a_0 + a_1 + a_2 + \cdots + a_{k-1} + k \end{array}\right\} \qquad (1)$$

and

$$N = a_0 + a_1 + a_2 + \cdots + a_k + k. \qquad (2)$$

In Fig. 1 by a_i is denoted the number of vertices of $P_N(j_1,\ j_2, \ldots, j_k)$, lying between the vertices j_i and j_{i+1}, $i = 1,\ 2, \ldots, k-1$. In addition a_0 and a_k are the number of vertices lying left from j_1 and right from j_k, respectively. In view of Eqs. (1) and (2),

$$\begin{array}{l} a_0 = j_1 - 1 \\ a_i = j_{i+1} - j_i - 1; \quad i = 1, 2, \ldots, k-1 \\ a_k = N - j_k. \end{array}$$

From Fig. 1 we see that by deleting from $P_N(j_1,\ j_2, \ldots, j_k)$ the pendent vertices $x_1, x_2, \ldots, x_k$ and their first neighbors $j_1,\ j_2, \ldots, j_k$, a collection of $k+1$ paths $P_{a_0}, P_{a_1}, P_{a_2}, \ldots, P_{a_k}$ will be obtained. Let $\omega(a_0,\ a_1,\ a_2, \ldots, a_k)$ among these paths possess an odd number of vertices.

Let, as before, $n_0(G)$ denote the number of zero eigenvalues of the graph G. A long-known result on zero eigenvalues is the following [13, 31]: If x is a pendent vertex of the graph G, adjacent to vertex j, then

$$n_0(G) = n_0(G - x - j). \qquad (3)$$

By a repeated application of Eq. (3), and bearing in mind that $n_0(P_1) = 1$, $n_0(P_2) = 0$, we immediately obtain the well known result:

$$n_0(P_a) = \begin{cases} 1 & \text{if } a \text{ is odd} \\ 0 & \text{if } a \text{ is even.} \end{cases} \qquad (4)$$

Applying Eq. (3) consecutively to the vertices $x_1,\ x_2, \ldots, x_k$ of $P_N(j_1, j_2, \ldots, j_k)$ we see that the number of zero eigenvalues of $P_N(j_1, j_2, \ldots, j_k)$ is equal to the number of zero eigenvalues of the collection of paths $P_{a_0}, P_{a_1}, P_{a_2}, \ldots, P_{a_k}$, which – in view of Eq. (4) – is equal to $\omega(a_0,\ a_1,\ a_2, \ldots, a_k)$.

The basic idea of our method lies in the observation that if the vertex x_i in $P_N(j_1, j_2, \ldots, j_k)$ is shifted by one (either to the left or to the right), then the parity of the numbers a_{i-1} and a_i is changed and, consequently:

- if both a_{i-1} and a_i are even, then n_0 increases by two,
- if both a_{i-1} and a_i are odd, then n_0 decreases by two, and
- if a_{i-1} and a_i have different parities, then n_0 remains the same.

By pertinently shifting several of the vertices $x_1, x_2, \ldots, x_k$ one can significantly change the value of n_0. If, in addition, the branching points $j_1,\ j_2, \ldots, j_k$ are positioned sufficiently far from each other, and sufficiently far from the terminal vertices of the path P_N, then the respective energy-differences can be assumed to be caused solely by the variations of n_0-values. What is meant under "sufficiently far" is explained below.

In particular, we have constructed the graphs $P_N(j_1, j_2, \ldots, j_k)$ by attaching six pendent vertices ($k = 6$) to the paths P_{174} and P_{175}. Depending on the actual position of the pendent vertices we have $n_0 = 0, 2, 4, 6$ (in the case $N = 174$) and $n_0 = 1, 3, 5, 7$ (in the case $N = 175$).

It is known [10, 23] that in molecular graphs of the type $P_N(j)$ and $P_N(j_1, j_2, \ldots, j_k)$ the energy-effects caused by the branching points depend on the distance between the nearest branching points, and also on the distance between the branching points and the terminal vertices of P_N. These interferences diminish with increasing distance and gradually become negligibly small [10, 23]. In order to eliminate any possible influence of the number of NBMOs, we have examined the differences in the E-values of the graphs $P_N(j_1, j_2, \ldots, j_i, \ldots, j_k)$ and $P_N(j_1, j_2, \ldots, j_i \pm 2, \ldots, j_k)$ because (as explained above) they necessarily have equal n_0-values.

In view of the fact that HMO total π-electron energies give chemically sound results only up to 0.01 β [11–14], our criterion that two neighboring branching points are "sufficiently far" from each other was chosen to be

$$|E(P_N(j_1, j_2, \ldots, j_i, \ldots, j_k)) - E(P_N(j_1, j_2, \ldots, j_i \pm 2, \ldots, j_k))| \leq 0.005. \qquad (5)$$

Table 1. The systems $P_N(j_1, j_2, \ldots, j_6)$ examined (*cf.* Fig. 1), the number of NBMOs (n_0) and total π-electron energy (E); note that n_0 is equal to the number of odd-valued parameters a_i, $i = 0, 1, \ldots, 6$; species having equal numbers of NBMOs insignificantly differ in their E-values

N	$(j_1, j_2, j_3, j_4, j_5, j_6)$	a_0	a_1	a_2	a_3	a_4	a_5	a_6	n_0	E
174	(25, 50, 75, 100, 125, 150)	24	24	24	24	24	24	24	0	227.1087
	(24, 50, 75, 100, 125, 150)	23	25	24	24	24	24	24	2	226.9954
	(26, 50, 75, 100, 125, 150)	25	23	24	24	24	24	24	2	229.9958
	(25, 49, 75, 100, 125, 150)	24	23	25	24	24	24	24	2	226.9995
	(25, 51, 75, 100, 125, 150)	24	25	23	24	24	24	24	2	226.9995
	(24, 50, 74, 100, 125, 150)	23	25	23	25	24	24	24	4	226.8860
	(24, 50, 75, 100, 125, 151)	23	25	24	24	24	25	23	4	226.8821
	(24, 50, 74, 100, 125, 151)	23	25	23	25	24	25	23	6	226.7727
	(26, 50, 76, 100, 126, 150)	25	23	25	23	25	23	24	6	226.7770
175	(25, 50, 75, 100, 125, 150)	24	24	24	24	24	24	25	1	228.3250
	(25, 50, 75, 100, 125, 151)	24	24	24	24	24	25	24	1	228.3287
	(24, 50, 75, 100, 125, 150)	23	25	24	24	24	24	25	3	228.2117
	(25, 49, 75, 100, 125, 150)	24	23	25	24	24	24	25	3	228.2121
	(24, 50, 75, 100, 125, 151)	23	25	24	24	24	25	24	3	228.2154
	(24, 50, 74, 100, 125, 150)	23	25	23	25	24	24	25	5	228.1023
	(24, 50, 74, 100, 125, 151)	23	25	23	25	24	25	24	5	228.1060
	(26, 50, 76, 100, 126, 150)	25	23	25	23	25	23	25	7	227.9931
	(24, 50, 74, 100, 126, 150)	23	25	23	25	25	23	25	7	227.9927

Numerical testing showed that the minimum such distance depends both on the value and parity of N and on the actual (but constant!) value of n_0. In all cases, however, the distance equal to 20 was sufficient for the validity of Eq. (5). This, in turn, means that each of the parameters $a_0, a_1, a_2, \ldots, a_k$ (*cf.* Fig. 1) needs to be 20 or greater. To be on the safe side, we have employed slightly greater a_i-values, see Table 1.

Numerical Work

For technical reasons the number of vertices of the graphs $P_N(j_1, j_2, \ldots, j_k)$, equal to $N+k$, had to be below 185. Therefore, we used as the starting system the graphs $P_N(j_1, j_2, \ldots, j_k)$ with $k=6$, $N=174$, and $a_0=a_1=\cdots=a_6=24$ (for which $\omega(a_0, a_1, \ldots, a_6)=0$ and therefore $n_0=0$), as well as with $k=6$, $N=175$, and $a_0=a_1=\cdots=a_5=24$, $a_6=25$ (for which $\omega(a_0, a_1, \ldots, a_6)=1$ and therefore $n_0=1$). By pertinently varying $(j_1, j_2, \ldots, j_k)$ we could then achieve that n_0 assumes all (integer) values between 0 and 7. Details are given in Table 1.

What first needs to be observed in Table 1 is that the E-values pertaining to the trees $P_N(j_1, j_2, \ldots, j_k)$ with equal n_0 are practically equal, differing by much less than 0.01 β. This detail corroborates the validity of the model employed.

There exists an excellent linear correlations between E and n_0. The data given in Table 1 satisfy the following regression lines: for $N=174$,

$$E = 227.109 - 0.0558\, n_0 \quad \text{and} \quad n_0 = 0, 2, 4, 6$$

whereas for $N=175$,

$$E = 228.381 - 0.0555\, n_0 \quad \text{and} \quad n_0 = 1, 3, 5, 7$$

with correlation coefficients -0.99981 and -0.99987, respectively.

For trees with $N=175$ the E-values are significantly greater than in the case of $N=174$. This is a direct consequence of the fact that the former trees possess 181, whereas the latter only 180 vertices. Therefore, the calculated E-values for even

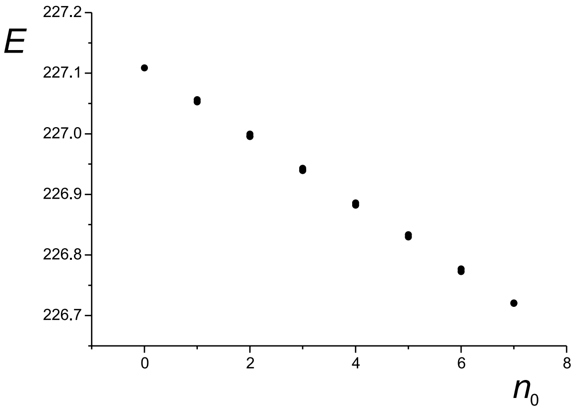

Fig. 2. Correlation between total π-electron energy (E) and the number of non-bonding molecular orbitals (n_0) for the systems $P_N(j_1, j_2, \ldots, j_k)$ specified in Table 1; for odd n_0 the E-values are reduced by 1.2724; the regression line thus obtained is $(227.108 \pm 0.001) - (0.0556 \pm 0.0002)\, n_0$ with correlation coefficient -0.99984

and odd n_0 cannot be directly compared. Fortunately, however, the slopes of the two regression lines are practically identical. This makes it possible to combine the two data sets, by subtracting 1.2724 from the E-values with odd n_0, resulting in the line shown in Fig. 2.

Conclusion

The model elaborated in this work enables us, for the first time, to quantitatively assess the effect of non-bonding molecular orbitals on total π-electron energy. This effect happens to decrease E (and thus to destabilize the respective molecule) and is linearly proportional to the number of NBMOs.

In order to ''extract'' the influence of NBMOs from other structural effects, we pursued the following strategy:

- The systems whose E-values were compared had equal number of vertices (n) and edges ($m = n - 1$). By this size-dependent effects could be disregarded. Exceptionally, because the parity of n_0 is the same as the parity of n, we used $n = 180$ for even n_0, and $n = 181$ for odd n_0.
- The systems whose E-values were compared were acyclic, and thus no cycle-dependent or *Kekulé*-structure-dependent effect could be encountered.
- The systems whose E-values were compared had the same pattern of branching, and the branching points were located sufficiently far from each other. By this we achieved, as much as it was possible, that branching-dependent effects were the same in all species considered.
- Because no other structural feature is known, that would significantly influence the value of E, we anticipate that the energy-differences observed were caused by the difference in the n_0-values. The fact that species having same n_0 have almost coinciding E-values provides a strong argument in favor of this expectation. Another finding pointing at the same direction is the excellent linear correlation between E and n_0, which hardly could happen by mere coincidence.

In summary: we maintain that the results reported here are not restricted to the peculiar molecular graphs of the type $P_N(j_1, j_2, \ldots, j_k)$, but to have a general validity. The regularity established can be formulated as follows:

Provided other effects are kept constant (*which is not easy to achieve*), *the presence of non-bonding molecular orbitals diminishes the total π-electron energy. The effect of NBMOs is linearly proportional to the number of NBMOs.*

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