A Topological Formula for Total π-Electron Energy

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Total π-electron energy E is presented as a sum of first-neighbour interaction terms λ and contributions of cycles ζ [Equation (2)]. The main conclusion of the work is that the total effect of λ's is a constant, independent of the molecular structure. Therefore, E is an additive function of ζ's only.

There have been numerous attempts [2–4] to find formulas expressing the dependence of the total π-electron energy, E, and the closely related resonance energy, RE, on the structural characteristics of conjugated molecules. It was demonstrated recently [4] that an exact explicite functional dependence between E and simple topological parameters (number of atoms, bonds, rings etc.) cannot exist at all. On the other hand, topological formulas relating E with the characteristic polynomial of the molecular graph are long known. They suffer, however, from having a rather complicated, non-linear algebraic structure [5].

In the present communication we derive an exact topological formula for E, which is a linear combination of certain relatively simple graph-theoretical functions. Hence, we offer a linearization and thus a simplification of the problem of total π-electron energy.

Our notation and terminology follows completely that of Ref. [6] and will not be explained here once again. The only difference is that in the present paper $\sum_Z$ denotes summation over all cycles contained in the molecular graph G. In addition, $\sum_{r-s}$ and $\sum_s$ indicate summation over all pairs of adjacent vertices and over all vertices s adjacent to r, respectively.

There is a well-known relation between E and the bond orders, namely

$$E = 2 \sum_{r-s} p_{rs} \,. \tag{1}$$

The substitution of Eq. (6) from [6] into (1) gives after simple transformations,

$$E = 2 \sum_{r-s} \lambda_{rs} + \sum_Z \zeta(Z) \tag{2}$$

where

$$\lambda_{rs} = \langle [A(G-r,s)A + B(G-r,s)B] / (A^2+B^2) \rangle \,,$$
$$\zeta(Z) = 2z \, \langle [A\,\omega_A(Z) + B\,\omega_B(Z)] / (A^2+B^2) \rangle \,.$$

Note that z is the size of the cycle Z. The above formula can be understood as a linear expansion of E into contributions coming from first-neighbour interactions (the first sum) and contributions which can be associated with the cycles Z of the molecular graph (the second sum). It is, however, not legitimate to identify the term $\zeta(Z)$ with the actual effect which a cycle Z has on the value of total π-electron energy [5]. This can be immediately seen from the fact that every integral λ_{rs} and $\zeta(Z)$ in the expansion (2) depends on the polynomials A and B and these, on the other hand, depend on all cycles of the molecular graph.

We prove now an important property of Equation (2). It was shown previously [6] that the integral λ_{rs} is approximately equal to the Pauling bond order between r and s. Taking into account the parity of Kekulé structures [7], the Pauling bond order is given by [8]

$$p_{rs}(\text{Pauling}) = \frac{K_{rs}^+ - K_{rs}^-}{K^+ - K^-}$$

where K_{rs}^+ and K^+ are the number of even Kekulé structures of $G-r,s$ and G, respectively, and K_{rs}^- and K^- are the analogus numbers for odd structures. Of course, K_{rs}^+ (K_{rs}^-) is the number of even (odd) Kekulé structures of G, with a double bond between r and s. Since in a Kekulé structure exactly one double bond terminates at every site r, we have

$$\sum_s K_{rs}^+ = K^+; \quad \sum_s K_{rs}^- = K^- \,.$$

Therefore, for all sites r of a molecular graph it is $\sum_s p_{rs}(\text{Pauling}) = 1$, which can be written also as

$$2 \sum_{r-s} p_{rs}(\text{Pauling}) = \sum_{r=1}^{N} \sum_s p_{rs}(\text{Pauling}) = N \,.$$

Accordingly,

$$2 \sum_{r-s} \lambda_{rs} \doteq 2 \sum_{r=1} p_{rs}(\text{Pauling}) = N = \text{const}$$

and we have the conclusion that *the total contribution of the first-neighbour interaction terms is approximately a constant* and is nearly independent of the structural properties of the molecule.

The importance of the "cyclic contributions" $\zeta(Z)$ is even more stressed by the simple fact that Eq. (2) is now transformed into

$$RE = E - N \doteq \sum_Z \zeta(Z) \,.$$

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Hence, *the resonance energy is experessed as an additive function of the contribution of all cycles* of the molecular graph, *and only of them.*

Formula (2) is essentially simplified for alternant molecules, for which all polynomials B vanish.

$$\lambda_{rs} = \langle A(G-r,s)/A \rangle ,$$
$$\zeta(Z) = (-1)^{z/2-1}\, 2\, z\, \langle A(G-Z)/A \rangle . \quad (3)$$

Since the integrals $\langle A(G-Z)/A \rangle$ are necessarily positive [6], the sign of $\zeta(Z)$ is determined solely by the size of the cycle Z. It is obvious from (3) that for any integer m, (a) *$\zeta(Z)$ is positive and has a stabilizing effect for all $(4\,m+2)$-membered cycles* of the molecular graph, and (b) *$\zeta(Z)$ is negative and has a destabilizing effect for all $(4\,m)$-membered cycles* of the molecular graph.

This rule is closely related to, but is not identic with the Hückel $4\,m+2$ rule. It provides a simple and convincing qualitative explanation of the high stability of conjugated systems composed entirely of $(4\,m+2)$-membered rings (benzenoids, polyphenyls) and of the low stability of structures containing $(4\,m)$-rings (cyclobutadiene derivatives etc.).

Numerical work on the integrals ζ is in progress.

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