

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 recently⁴ 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 structure⁵.

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

$$E = 2 \sum_{r-s} p_{rs}. \quad (1)$$

The substitution of Eq. (6) from⁶ into (1) gives after simple transformations,

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

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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 energy⁵. 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 previously⁶ that the integral λ_{rs} is approximately equal to the Pauling bond order between r and s . Taking into account the parity of Kekulé structures⁷, the Pauling bond order is given by⁸

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

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 analogous 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,

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

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 expressed 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.

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

Since the integrals $\langle A(G-Z)/A \rangle$ are necessarily positive⁶, 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 $(4m+2)$ -membered cycles of the molecular graph, and (b) $\zeta(Z)$ is negative

and has a destabilizing effect for all $(4m)$ -membered cycles of the molecular graph.

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

Numerical work on the integrals ζ is in progress.

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² For some recent work see: J. Aihara, J. Amer. Chem. Soc. **98**, 2750 [1976]; J. Org. Chem. **41**, 2488 [1976]; M. Randić, Chem. Phys. Letters **38**, 68 [1976]; J. Amer. Chem. Soc. **99**, 444 [1977]; I. Gutman, J. Chem. Phys. **66**, 1652 [1977]; for earlier work see references cited in ³, ⁴.

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