An Approximate Method of Calculating Localization Energies in Alternant Hydrocarbons

By Hiroaki BABA

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Since the localization theory was first proposed by Wheland[1], it has been one of the most effective means of dealing with the chemical reactivity in conjugated organic compounds. The only fault found with this theory is that the calculation of localization energies is frequently an arduous task, especially when one is treating a large molecule. By taking into consideration the characteristic property of non-bonding molecular orbitals, Dewar[2] developed a convenient method of obtaining approximate values of localization energies for alternant hydrocarbons, and successfully applied it to some organic reactions[3]. However, the values obtained by this method of approximation are in general numerically far from being the exact values.

In a previous paper[4] it was made clear that in an alternant hydrocarbon the exact value of localization energy has an intimate correlation with Dewar's approximate one, and also with the value of free valence, the latter quantity being an important index of chemical reactivity[5]. In connection with this problem, another approximate method of computing localization energies in alternant hydrocarbons will be described in the present article.

Definition

The present treatment is based on the simple LCAO molecular orbital method with neglect of overlap integrals; the notation is the same as that used in the preceding papers[4,6].

Consider a carbon atom r in an alternant hydrocarbon, and denote the carbon atoms adjacent to atom r by t, t', ……. Suppose that β_{rt}, $\beta_{rt'}$, …… simultaneously change from their initial value β to a certain value β_r, and that the other coulomb and resonance integrals remain unchanged. Then, bond number N_r can be regarded as a continuous function of β_r. If this function is represented by $N_r(\beta_r)$, the localization energy of atom r is expressed as[4]

$$L^{(r)}=\int_{\beta}^{0} 2N_r(\beta_r)\mathrm{d}\beta_r. \quad (1)$$

Next, reference will be made to two known approximate values[4] of $L^{(r)}$. One is

$$L^{(r)\prime}=-2N_r{}^0\beta \quad (2)$$

where $N_r{}^0[\equiv N_r(\beta)]$ is the bond number in the initial state, and is connected with free valence $F_r{}^0$ by the relation $N_r{}^0=\sqrt{3}-F_r{}^0$. The other is

$$L^{(r)\prime\prime}=-2N_r(0)\beta \quad (3)$$

where

$$N_r(0)=\lim_{\beta_r\to 0} N_r(\beta_r)$$

As was proved in the previous paper[4], $L^{(r)\prime\prime}$ defined by Eq. 3 agrees with Dewar's approximate value mentioned in the introductory paragraph.

In the simple molecular orbital procedure, the total energy for the ground state of a system of electrons is obtained as the sum of the energies of the ground-state molecular orbitals to which the individual electrons belong. If the orbital energies are determined by the usual variation method, the total energy obtained in this way corresponds to its absolute minimum under the restriction that the orbitals form

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[1] G. W. Wheland, *J. Am. Chem. Soc.*, **64**, 900 (1942).

[2] M. J. S. Dewar, ibid., **74**, 3357 (1952).

[3] P. M. G. Bavin and M. J. S. Dewar, *J. Chem. Soc.*, **1956**, 164; M. J. S. Dewar, T. Mole and E. W. T. Warford, ibid., **1956**, 3581, and related papers.

[4] H. Baba, This Bulletin, **30**, 154 (1957).

[5] See, for instance, B. Pullman and A. Pullman, "Progress in Organic Chemistry", Vol. 4, edited by J. W. Cook, Butterworths Scientific Publications, London (1958), pp. 31—71.

[6] H. Baba, This Bulletin, **30**, 147 (1957).

an orthonormal set. If one keeps this fact in mind, it is easily verified that N_r decreases monotonously as β_r increases. Hence

$$N_r{}^0 > N_r(\beta_r) > N_r(0) \quad (\beta < \beta_r < 0) \tag{4}$$

so that from Eqs. 1—3

$$L^{(r)\prime} > L^{(r)} > L^{(r)\prime\prime} \tag{5}$$

Let us now consider a new quantity $\boldsymbol{L}^{(r)}$ defined as follows:

$$\boldsymbol{L}^{(r)} = -(N_r{}^0 + N_r(0))\beta \tag{6}$$

Then, from Eqs. 2 and 3

$$\boldsymbol{L}^{(r)} = \frac{1}{2}(L^{(r)\prime} + L^{(r)\prime\prime}) \tag{7}$$

Since both $L^{(r)\prime}$ and $L^{(r)\prime\prime}$ are approximate values of $L^{(r)}$, $\boldsymbol{L}^{(r)}$ will also be an approximation of $L^{(r)}$.

The relation of $\boldsymbol{L}^{(r)}$ with other quantities may be understood by Fig. 1, where the full line curve aeb represents the relation between β_r and $2N_r(\beta_r)$. $L^{(r)}$ is, of course, equal to the area under the curve, $L^{(r)\prime}$ to the area of rectangle agcd, and $L^{(r)\prime\prime}$ to that of rectangle hbcd, while $\boldsymbol{L}^{(r)}$ is equal to the area of trapezoid afbcd.

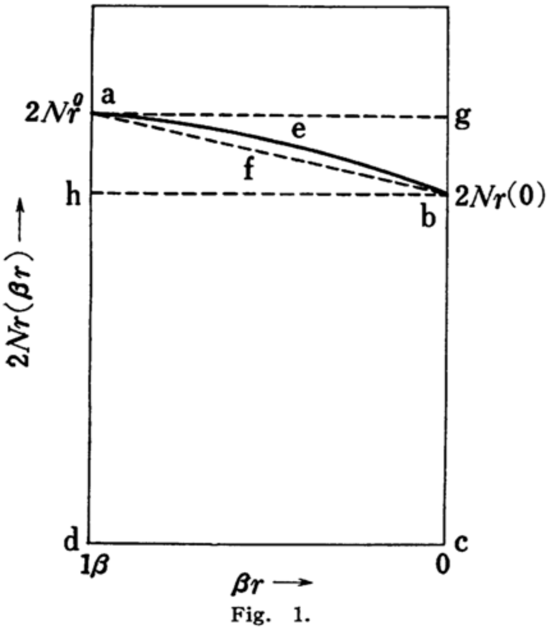

Fig. 1.

Examples and Discussion

In Table I are listed the values of $\boldsymbol{L}^{(r)}$ and other related quantities for three positions of anthracene. In Fig. 2 $\boldsymbol{L}^{(r)}$, $L^{(r)\prime}$ and $L^{(r)\prime\prime}$ are plotted against $L^{(r)}$ for a number of alternant hydrocarbons. The values of $L^{(r)}$ for primary, secondary and tertiary carbon atoms fall within the ranges 1.0 to 1.8, 1.8 to 2.6 and 2.6 to 3.1, respectively. The examples presented in this table and figure clearly show that $\boldsymbol{L}^{(r)}$ is superior to $L^{(r)\prime}$ and $L^{(r)\prime\prime}$ as an approximation of $L^{(r)}$.

TABLE I. LOCALIZATION ENERGIES IN UNITS OF $-\beta$ FOR ANTHRACENE

Position	$L^{(r)}$	$\boldsymbol{L}^{(r)}$	$L^{(r)\prime}$	$L^{(r)\prime\prime}$
1	2.25	2.06	2.55	1.57
2	2.40	2.27	2.65	1.89
9	2.01	1.84	2.42	1.26

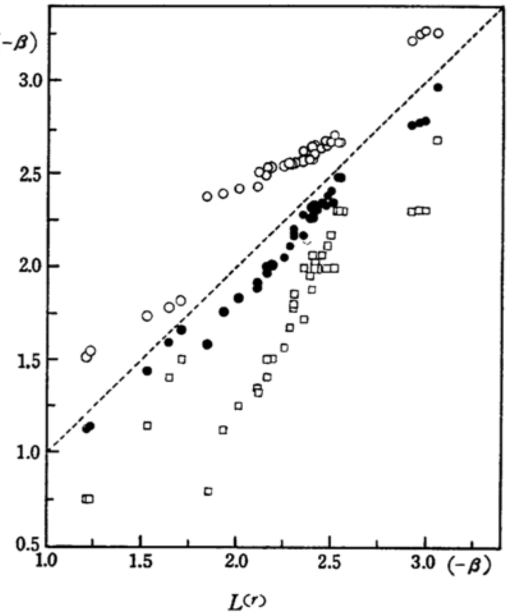

Fig. 2. Relations between $L^{(r)}$ and $\boldsymbol{L}^{(r)}$, $L^{(r)\prime}$ and $L^{(r)\prime\prime}$.
●, $\boldsymbol{L}^{(r)}$; ○, $L^{(r)\prime}$; □, $L^{(r)\prime\prime}$.
$L^{(r)}$ and $L^{(r)\prime}$: Taken from references 5 and 6, and " Dictionary of Values of Molecular Constants ", Vol. II, edited by C. A. Coulson and R. Daudel.
$L^{(r)\prime\prime}$: Taken from reference 2, and calculated by the present author.

Previously it was shown by the present author[4,6] and also by Fukui et al.[7] that under certain conditions there is a definite parallelism among the quantum mechanical quantities, including $L^{(r)\prime}$ and $L^{(r)\prime\prime}$, which are related to the reactivity of an alternant hydrocarbon. Considering the definition of $\boldsymbol{L}^{(r)}$, one may at once reach the conclusion that the same parallelism exists between $\boldsymbol{L}^{(r)}$ and any other quantity mentioned above.

Research Institute of Applied Electricity
Hokkaido University, Sapporo

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[7] K. Fukui, T. Yonezawa and C. Nagata, *J. Chem. Phys.*, **26**, 831 (1957).