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Short Communications

Comments on a MORT treatment of bond length alternations in conjugated hydrocarbons

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It is shown that in treating bond distortions in pentalene and large annulenes in the framework of the Molecular Orbital Resonance Theory (MORT) [1], the variation of the resonance integral with bond length and the σ-bond compression energy should be taken into account. The charge polarization to which the bond disrtortion in pentalene is entirely attributed by Živković [1] is of minor importance.

Key words: Bond length alternation—molecular orbital resonance theory—σ-bond compression energy

Very recently, Živković [1] has proposed the Molecular Orbital Resonance Theory (MORT) for treating electronic structures of conjugated hydrocarbons. This method combines the advantages of the molecular orbital (MO) and valence bond (VB) theories: it retains the concept of resonance from the VB method, but it treats each particular bond in the MO sense. In the simplest variant of this theory, only MORT Kekulé structures are retained and the Hückel Hamiltonian is used. Živković has shown how in this simplest approach one can easily explain the relative stabilities of benzene, pentalene and cyclobutadiene. Using the simplest MORT, he has also treated the bond length alternation in pentalene and expresses the belief that the bond distortion in pentalene is attributed to a charge separation alone, without any further assumption. This contradicts directly the theories of double bond fixation given by Nakajima and Katagiri [2], Binsch *et al.* [3], Binsch and Heilbronner [4] and Nakajima [5], in which the polarization of the electron density plays a very minor role in giving rise to a double bond fixation. In this paper we show within the simplest MORT approach that as in the theory of Nakajima and Katagiri [2], the bond alternation in a conjugated hydrocarbon is successfully explained by taking into account the variation of the resonance integral with bond length and the σ-bond compression energy, both of which are disregarded in Živković's treatment and the energy correction due to the charge polarization is of minor importance.

According to Longuet-Higgins and Salem [6], the total energy which is assumed to be the sum of the π-electronic energy, $E\pi$, and the σ-bond energy, $E\sigma$, of a conjugated hydrocarbon is given by

$$E_{\text{tot}} = E\pi + E\sigma = \frac{2}{ab} \sum_{i<j} \beta_{ij} + \sum_{i} Q^i \alpha_i + \text{const.} \tag{1}$$

where β_{ij} is the resonance integral of the i-j bond, and α_i and Q^i are the Coulomb integral and the π-electron density of the ith C atom, respectively. Parameters a and b appear in the following equations

$$r_{ij}\,(\text{in Å}) = r_0 - aP^{ij} \tag{2}$$

$$\beta_{ij} = \beta_0 \exp\{b(r_b - r_{ij})\} = B \exp(abP^{ij}) \tag{3}$$

where r_{ij} and P^{ij} are the length and the bond order of the i-j bond, respectively, and r_b and β_0 are the bond length and the resonance integral of the bond in benzene, respectively. Using the MORT bond orders of ethylene ($P = 1$) and benzene ($P = 0.6$), one obtains $r_0 = 1.493$ Å and $a = 0.16$ Å, and we use in this paper $b = 3.22\ \text{Å}^{-1}$ proposed by Longuet-Higgins and Salem [6]. We feel that the value of ab thus obtained is somewhat too large, but the precise choice of the value is out of our question. In this connection it is interesting to note that in order for benzene to keep the D_{6h} symmetry, the condition $ab \leq 1$ must be fulfilled [7].

In pentalene, the ground state is assumed to be of the form $\Phi(\theta) = A\phi(\theta)\bar{\phi}(\theta)$, where

$$\phi(\theta) = K_1 \cos\theta + K_2 \sin\theta \tag{4}$$

where K_1 and K_2 are the two equivalent Kekulé structures and θ is to be determined by minimizing the total energy. The bond orders of the peripheral C—C bonds are alternately $\cos^2\theta$ and $\sin^2\theta$ and that of the pinch bond is $(1/8)\sin 2\theta$ [1]. If the second term in Eq. (1) is not considered for the time being, $E_{\text{tot}}(\theta)$ is then given by

$$\begin{aligned} E_{\text{tot}}(\theta) = (2B/ab)[&4\exp(ab\cos^2\theta) + 4\exp(ab\sin^2\theta) \\ &+ \exp\{ab(1/8)\sin 2\theta\}] + \text{const.} \end{aligned} \tag{5}$$

The minimum of $E_{\text{tot}}(\theta)$ is found at $\theta = 2.8°$. The most stable distorted structure of pentalene closely resembles one of the Kekulé structures. The stabilization energy defined as the difference in total energy between the D_{2h} structure ($\theta = 45°$) and the distorted structure (C_{2h}) is calculated to be 12.8 kcal mol^{-1} if we use $\beta_0 = -16$ kcal mol^{-1} [8]. The previously predicted stabilization energies are in the range 6–14 kcal mol^{-1}, depending on the approximations used [3, 9–12]. In Živković's treatment of the bond fixation in pentalene, on the other hand, only the second term in Eq. (1) is taken into account, which is rewritten as

$$\sum_i Q^i\alpha_i = \sum_i Q^i\{\alpha_0 + \omega(Q^i - 1)\beta_0\} \tag{6}$$

where ω is a parameter. Using the value $\omega = 1.4$ given by Streitwieser [13], Živković has shown that the charge polarization, and hence the Coulomb destabilization due to Eq. (6), gives rise to a bond length alternation: the energy minimum is found at $\theta = 22.8°$ and the stabilization energy is calculated to be only 0.23 kcal mol^{-1}. It is thus clear that in causing bond alternation in pentalene, the destabilization due to the second term in Eq. (1) has a very small effect, and at the energy minimum obtained above by considering the first term in Eq. (1) this effect can safely be disregarded. This is in accord with the belief expressed by Binsch et al. [3, 4].

In [2n] annulenes, bond orders are given by

$$\begin{aligned} P^{ij} &= [\cos^2\theta + \{1 + (-1)^{n+1}\}2^{-n}\sin 2\theta]/[1 + \{1 + (-1)^{n+1}\}2^{-n}\sin 2\theta], \\ &\quad ij = 12, 34, \ldots \\ P^{i'j'} &= [\sin^2\theta + \{1 + (-1)^{n+1}\}2^{-n}\sin 2\theta]/[1 + \{1 + (-1)^{n+1}\}2^{-n}\sin 2\theta], \\ &\quad i'j' = 23, 45, \ldots. \end{aligned} \tag{7}$$

If n is even, the total energy is written in the form

$$E_{\text{tot}}(\theta) = (2B/ab)\{n \exp(ab\cos^2\theta) + n \exp(ab\sin^2\theta)\} + \text{const.} \tag{8}$$

The minimum of Eq. (8) is found at $\theta = 0$ (corresponding to one of the Kekulé structures) irrespective of the value of ab. In cases in which n is odd, Eq. (7) indicates that if n becomes large, $P^{ij} \to \cos^2\theta$ and $P^{i'j'} \to \sin^2\theta$. Thus, it is shown that a [$4m + 2$] annulene ($m = 1, 2, \ldots.$) should undergo a bond alternation if θ becomes large enough. This is in agreement with previous predictions and the experimental facts [3, 14]. In Živković's treatment, it is not possible to show that in [$4m$] annulenes and large [$4m + 2$] annulenes the ground state has a distorted structure, since in annulenes the charge separation does not occur. It is concluded from the above results that although the simplest MORT is promising in the sense that physical quantities, such as the π-electronic energy, the charge desnity and the bond order are obtained in analytic forms even for complex molecules, such as pentalene, Živković's theory of bond alternation is insufficient in the sense that he treats only the term of minor importance.

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