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 $\sigma$-bond compression energy should be taken into account. The charge polarization to which the bond distortion in pentalene is entirely attributed by Živković [1] is of minor importance.

Key words: Bond length alternation—molecular orbital resonance theory—$\sigma$-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 $\sigma$-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 $\pi$-electronic energy, $E\pi$, and the $\sigma$-bond energy, $E\sigma$, of a conjugated hydrocarbon is given by

$$E_{\text{tot}} = E\pi + E\sigma = \frac{2}{ab} \sum_{i<j} \beta_{ij} + \sum_i Q^i a_i + \text{const.} \quad (1)$$

where $\beta_{ij}$ is the resonance integral of the $i$-$j$ bond, and $a_i$ and $Q^i$ are the Coulomb integral and the $\pi$-electron density of the $i$th C atom, respectively. Parameters $a$ and $b$ appear in the following equations

$$r_{ij} \ (\text{in } \text{Å}) = r_0 - aP^{ij} \quad (2)$$
$$\beta_{ij} = \beta_0 \exp \{b(r_b - r_{ij}) \} = B \exp \{abP^{ij} \} \quad (3)$$

where $r_{ij}$ and $P^{ij}$ are the length and the bond order of the $i$-$j$ bond, respectively, and $r_b$ and $\beta_0$ 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 $r_0 = 1.493 \ \text{Å}$ and $a = 0.16 \ \text{Å}$, 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

$$\phi(\theta) = K_1 \cos \theta + K_2 \sin \theta \quad (4)$$

where $K_1$ and $K_2$ are the two equivalent Kekulé structures and $\theta$ 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

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

The minimum of $E_{\text{tot}}(\theta)$ is found at $\theta = 2.8^\circ$. The most stable distorted structure of pentalene closely resembles one of the Kekulé structures. The stabilization