Bond Phase Determination of HOMO/LUMO and ‘Ethylene’ in Benzenoid Hydrocarbons

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Classical valence theory suggests the existence of strongly localized bonds (double bonds), *i.e.*, of ethylene-like molecules, in benzenoid hydrocarbons (molecular graphs Bs); such an ‘ethylene’ is an edge in a hexagon that contacts with three hexagon faces in B. The phase of a bond is defined as the sign either plus for bonding or minus for antibonding. By use of perturbation molecular orbital theory we conclude that the phase of each bond that meets at the ethylene has necessarily the minus sign in HOMO of B; the bond phase alters in HOMO and LUMO of B.

Key words: Bond Phase; HOMO and LUMO; Ethylene; Benzenoid Hydrocarbon; Pauling Bond Order.

1. Introduction

Many studies have appeared on the relationship between HOMO/LUMO (highest occupied or lowest unoccupied molecular orbital) and chemical reaction in molecules [1]. In such discussions the ‘form’ of HOMO/LUMO plays a very important role. The form of HOMO/LUMO in a π-electron conjugated molecule is in the first place determined by ‘bond phase’, *i.e.*, by the sign plus for bonding or minus for antibonding, because HOMO/LUMO delocalizes in the whole molecule. The phase between sites (vertices, atoms) t and u in general form is hereafter denoted as either phase$(t, u) > 0$ or phase$(t, u) < 0$.

Let B be a benzenoid hydrocarbon molecule (molecular graph [2]); refer to Figure 1. There is a type of bonds, each of which constitutes a hexagon face that contacts with three hexagon faces, in B. The following discussion suggests that, provided certain conditions are fulfilled, such a bond, which looks like that of an ethylene in a molecule B [3], has a positive phase in HOMO. Let us denote such an ethylene by $r{=}r'$, and let s and s' be two sites, at which $r{=}r'$ meets in B; Figure 2. The existance of the ethylene-in-molecule has been shown by NMR spectra [3]. Removing an $r{=}r'$ from B leads to another benzenoid hydrocarbon molecule B'; *e. g.*, benzo[*a*]pyrene, to chrysene or benzo[*a*]anthracene. After the removal of $r{=}r'$ from B a ‘bay’ region appears in B'; s and s' are then the two capes of the bay. We prove by means of perturbation molecular orbital (PMO) theory [4] that phase$(r, s) < 0$, phase$(r', s') < 0$, and phase$(r, r') > 0$ in HOMO of B, and that the HOMO-LUMO separation of B is smaller than the HOMO-LUMO separation of B'.

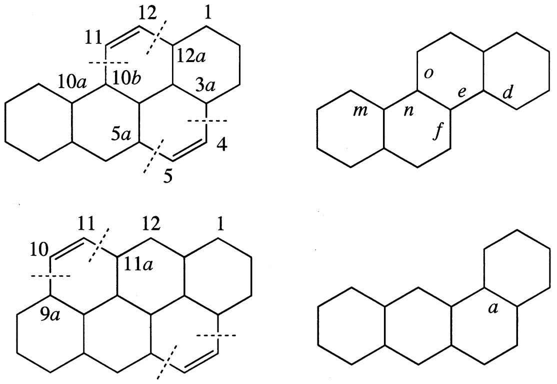

Fig. 1. One benzenoid hydrocarbon, if ethylene is withdrawn / added from / to it, leads to another one; *e.g.*, anthanthrene (dibenzo[*def,mno*]chrysene, left below) to benzo[*a*]pyrene (left above), to chrysene (right above) or benzo[*a*]anthracene (right below).

Let $H = \alpha I + \beta A$ be the Hückel matrix for B, where A is the adjacency matrix (topological matrix) of B; $A_{t,u} = 1$ if two sites t and u are bonded, and $A_{t,u} = 0$

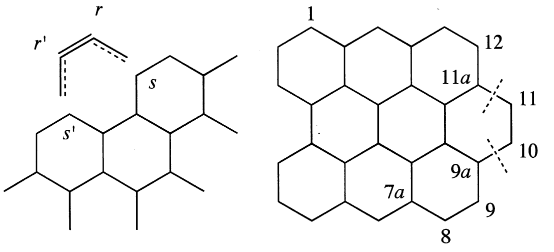

Fig. 2. An ethylene $r{=}r'$ connects with a benzenoid hydrocarbon at the sites s and s' of the bay region (left). The bond 10-11 in dibenzo[*bc,ef*]coronene (right) is an example in which the regularity considered in this work does not apply; the Pauling bond order of the bond 10-11 is equal to 0.875.

otherwise. I is the unit matrix; α and β, respectively, are the Coulomb integral and the resonance integral [5], where $\beta < 0$, *i. e.*, AOs overlap in phase [4]. Let λ_i be an eigenvalue of A; then the energy ϵ_i of the ith MO ϕ_i is given by $\epsilon_i = \alpha + \lambda_i\beta$. Let $C_{t,i}$ and $C_{u,i}$ be the coefficients of linear combinations of AOs of atoms t and u in ϕ_i. The sign of phase(t, u) in ϕ_i is just equal to the sign of the product $C_{t,i} \times C_{u,i}$. When t and u are adjacent, the notation phase$(t, u) > 0$ means bonding in ϕ_i and phase$(t, u) < 0$ antibonding in ϕ_i. No change of the phase occurs in $-\phi_i$. The HOMO-LUMO separation energy of B is expressed by $\Delta\epsilon(B) \equiv \epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}}$.

2. Results and Discussion

Classical valence theory [2] regards the situation of ethylene in B in the following way. B and B' are both stable such that $K(B) > 0$ and $K(B') > 0$. Here $K(B)$ is the number of Kekulé structures in B [6]. The Pauling bond order $P_{t,u}$ [7] is a good index for estimating the degree of π-conjugation between sites t and u. There is, for example, a linear relationship [8] between the bond lengths $d_{t,u}$ and the Pauling bond orders $P_{t,u}$ in B:

$$d_{t,u}/\text{pm} = a - b \times P_{t,u},$$

where a = 146.5, b = 13.0. The average deviation between the experimental and calculated values was ±1.0 pm. It is easy to calculate $P_{t,u}$ of B in small molecules; *e.g.*, $P_{4,5} = 8/9$ and $P_{11,12} = 7/9$ in benzo[*a*]pyrene. $P_{t,u}$ ranges from 0 (single bond) to 1 (double bond); the two limiting bonds are called *essential* in Kekulé structure counting [4]. The large value $P_{11,12} = 7/9$ in benzo[*a*]pyrene implies that the bond 11-12 has doubly bonding character; while two bonds that meet at the bond 11-12 are nearly single because $P_{10b,11} = 1 - 7/9 = 2/9$ and $P_{12,12a} = 1 - 7/9 = 2/9$. In other words, the bond 11-12 (and also 4-5) looks like an ethylene bond in benzo[*a*]pyrene.

The PMO theory interprets in the following way the situation of ethylene-in-B using the interaction of two HOMOs in ethylene and B'. Ethylene $r{=}r'$ and B' are two closed-shell π-electron conjugated systems. When $r{=}r'$ and B' are united at the sites r and s, then HOMO of $r{=}r'$ weakly interacts with HOMO of B'. The HOMO-HOMO interaction yields two MOs; one of lower energy than either the starting MO (*i.e.*, a bonding orbital with phase$(r, s) > 0$), and the other of higher energy (*i.e.*, an antibonding orbital with phase$(r, s) < 0$). Noting that the resultant two MOs are doubly occupied, we obtain phase$(r, s) < 0$ and phase$(r, r') > 0$ in HOMO of B. The second interaction now occurs between r' and s' to form a hexagonal ring. Here we assume that the intra-interaction in the HOMO is weak; *i.e.*, the energy change in the HOMO is the second-order; *i.e.*, both phase$(r, r') > 0$ and phase$(r', s') < 0$ hold in HOMO of B. Note that three of the four phase-relations, phase$(r, s) < 0$, phase$(r, r') > 0$, phase$(r', s') < 0$, and phase$(s, s') > 0$, imply the other one.

In alternant hydrocarbons, phase(t, u) alters in HOMO and LUMO, where t is a starred site, and u is an unstarred one, because the pairing theorem [4] states that

$$C_{t,\text{HOMO}} \times C_{u,\text{HOMO}} = -C_{t,\text{LUMO}} \times C_{u,\text{LUMO}}$$

In other words, for a bond between t and u in even alternant hydrocarbons, if phase$(t, u) < 0$ in HOMO, then phase$(t, u) > 0$ in LUMO; and if phase$(t, u) > 0$ in HOMO, then phase$(t, u) < 0$ in LUMO. Such bond phase implies that the energy ϵ_{HOMO} goes upwards; ϵ_{LUMO}, downwards. Hence, $\Delta\epsilon(B)$ is smaller than $\Delta\epsilon(B')$.

We obtained by Hückel MO calculation for $C_{t,\text{HOMO}} \times C_{u,\text{HOMO}}$ in benzo[*a*]pyrene: (-0.114) $(+0.289) < 0$, $(+0.214)$ $(-0.214) < 0$, $(+0.214)$ $(-0.214) < 0$, and (-0.289) $(+0.114) < 0$ for the bonds 3a-4, 5-5a, 10b-11, and 12-12a, respectively; similarly, (-0.147) $(+0.209) < 0$ for the bond 9a-10, and $(+0.208)$ $(-0.148) < 0$ for the bond 11-11a in anthanthrene. Every bond, crossed by a dotted line in Fig. 1, has a negative phase in HOMO. The HOMO-LUMO separation energy, $\Delta\epsilon(B)$, was calculated for each molecule in Fig. 1 as: -1.04β, -0.904β, -0.695β, and -0.582β for chrysene (right above), benzo[*a*]anthracene (right below), benzo[*a*]pyrene (left above), and anthanthrene (dibenzo[*def,mno*]chrysene, left below), respectively.

The π-electron conjugation of B' after the deletion of ethylene from B should be noted. Cata-condensed Bs include no such ethylene because the deletion of bonds destroys the π-conjugation of B; refer to chrysene and benzo[*a*]anthracene in Figure 1. The present theory cannot be applied to B such that removing an ethylene significantly disturbes the π-conjugation of the resultant molecule, where phase$(s, s') < 0$ in HOMO. Classical valence theory says that the deletion of an ethylene from B may yield two systems of π-electron conjugation that are essentially separated; *e.g.*, the deletion of ethylene from dibenzo[*bc,ef*]coronene gives bisanthene (dibenzo[*fg,op*]anthanthrene) in Fig. 2, which can be regarded as two anthracene molecules because they are connected with each other by only three essential single bonds [9]. Note that the back bond of each bay in bisanthene is essential and single. We obtain $P_{8,9} = 13/15$ and $P_{10,11} = 8/15$ in dibenzo[*bc,ef*]coronene; phase$(7a, 9a) > 0$ in the former case, but in the latter case, phase$(9a, 11a) < 0$, *i.e.*, the condition phase$(s, s') > 0$ disturbes. The Hückel MO calculation for a variety of Bs suggests that the threshold value of $P_{r,r'}$ is about 0.7-0.8 for which the bond between r and r' looks like an ethylene in B; the bond length $d_{r,r'}$ for $P_{r,r'} = 0.8$ is estimated as 136.1 pm.

We conclude that the phase of bonds, each of which connects with a strongly localized (ethylene-like) bond whose Pauling bond order is greater than 0.8, in HOMO of a given benzenoid hydrocarbon, is negative if no deletion of the ethylene disturbes the π-electron conjugation of the benzenoid hydrocarbon; such bond phase alters in HOMO and LUMO of benzenoid hydrocarbons; the HOMO-LUMO separation increases by deleting the ethylene.

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