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Bond-Distorted Orbitals and Effects of Hybridization and Resonance on C–C Bond Lengths

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A localized one-electron orbital base, called bond-distorted orbital, is introduced to study hypothetically localized structures in the framework of valence bond theory. The use of valence bond method with bond-distorted orbitals allows us to evaluate the effects of hybridization and resonance on carbon–carbon bond lengths at the *ab initio* level. Valence bond self-consistent field studies on the delocalized and hypothetically localized structures of 1,3-butadiene and 1,3-butadiyne show that the theoretical C(sp²)–C(sp²) and C(sp)–C(sp) single bond lengths are 1.508 and 1.446 Å, respectively, and that the theoretical resonance energies of 1,3-butadiene and 1,3-butadiyne are –7.9 and –15.8 kcal/mol, respectively.

I. Introduction

Hybridization and resonance (delocalization) are among the oldest and most useful concepts in chemistry. The correlation between hybridization and geometry (sp³ ≈ tetrahedral, sp² ≈ trigonal planar, sp ≈ linear) is well-known.¹ For a given bond, the more s character in the hybridized orbitals (used to form the bond), the shorter the bond length.^{2,3} Indeed, some semiempirical rules have been proposed to account for the s or p character–bond length relationship.^{3,4} Meanwhile, the resonance theory has been popularly used in explaining the tendency of bond equalization in many conjugated systems. However, although the conceptions of hybridization and resonance are routinely used, their effects on bond length have not ever been explored quantitatively at the *ab initio* level. The problem is the difficulty to construct a wave function for a given hypothetically localized structure in the framework of molecular orbital (MO) theory. From the viewpoint of classical valence bond (VB), a bond between A and B atoms can be expressed as the linear combination of two pure unhybridized atomic orbitals (AOs) χ_A and χ_B ($\chi_A + \lambda\chi_B$, also called the Coulson–Fisher orbital⁵). A further improvement to the bond wave function was made by replacing the pure unhybridized AOs with hybridized orbitals. This new bond wave function has been extensively applied by many authors, especially by Harcourt and Weinhold *et al.*^{6,7,10} In the Weinhold *et al.*'s natural bond orbital (NBO) method, natural AOs are used with the advantage of their orthogonality. Indeed, the NBO method is the most general and elaborate way to study the delocalization effect in the framework of MO theory up to now, in which the electronic delocalization energy is estimated by a deletion scheme. Several authors^{8–10} have tried to obtain resonance energies for conjugated systems such as benzene with MO methods. In these attempts, localized wave functions were constructed by replacing those π -symmetry delocalized canonical MOs with non-resonating ethylenic orbitals.

Although the NBO method is now routinely used in studying the electronic delocalization effect in many systems,^{7,10} there are relatively few works based on the VB method.^{11,12} In this paper, the VB method will be used to calculate the energy of a

hypothetically localized structure at an *ab initio* level (using big basis sets and self-consistent field). We will introduce a localized one-electron orbital base, which is basically a form of the Coulson–Fischer orbital,⁵ into the *ab initio* VB self-consistent field (VBSCF) calculations. With the use of this base, the effects of hybridization and resonance on the carbon–carbon bond lengths of ethane, 1,3-butadiene, and 1,3-butadiyne are evaluated quantitatively based on both VB and MO calculations.

II. Methodology

In the VB theory, a system is described by a set of resonance structures (also called VB structures). Correspondingly, the state wave function of a system is expressed as the linear combination of a set of VB functions. In the spin-free quantum chemistry, for a system with N electrons and S spin quantum number, a VB function can be defined as^{13,14}

$$\psi(k) = A_k e_{11}^{[k]} \psi_0(k) = A_k e_{11}^{[k]} [\varphi_1(1)\varphi_2(2)\dots\varphi_N(N)] \quad (1)$$

where A_k is a normalization constant, $e_{11}^{[k]}$ is a standard projection operator, and $\{\varphi_i\}$ is a set of one-electron basis functions. In fact, a VB function as defined in eq 1 corresponds to a VB structure where two basis orbitals φ_{2i-1} and φ_{2i} overlap to form a bond ($i \leq N/2 - S$, and if $\varphi_{2i-1} = \varphi_{2i}$, the bond represents a lone electron pair) and the last $2S$ basis orbitals are unpaired.

In the classical VB method, $\{\varphi_i\}$ takes the form of pure AOs. In such a case, eq 1 is sometimes designated as a canonical Lewis structure.

Unlike in the classical VB method, in the modern VB method, $\{\varphi_i\}$ usually takes the linear combination of all AOs and is now called overlap-enhanced orbitals (OEOs) $\{\chi_i'\}$.^{15,16}

$$\chi_i' = \chi_i + \sum_{j \neq i} d_{ij} \chi_j \quad (2)$$

where χ_i and χ_j are pure AOs and d_{ij} is the expansion coefficient. The most significant advantage of OEOs is that most of the correlation energy can be recovered with only a small number of VB functions. For example, for benzene, only five VB structure (two Kekulé and three Dewar) functions can recover 93% of the correlation energy.¹⁷ However, as noted before by several authors,^{6,12,18} an OEO in fact can only be treated as a

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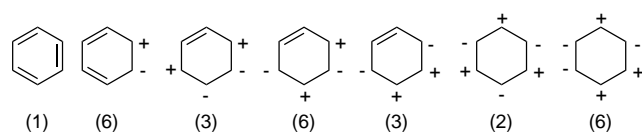
kind of semilocalized basis since it is formed by a distorted AO (mixed with all AOs centered on all near atoms). It is very likely that a resonance structure function constructed with OEOs contains other resonance structure functions. With the use of OEOs, the energy of a given localized structure will be overestimated. Due to this overestimation, the use of only OEO bases in the calculation of resonance energy would be inappropriate. The reason is as follows. Since resonance energy (also called delocalization energy or conjugation energy) is defined as the difference between the energy (E_{tot}) obtained using all possible resonance structures and the reference energy (E_{ref}) of the most stable resonance structure, one has to accurately evaluate E_{ref} . However, the use of OEOs will overestimate E_{ref} and, consequently, underestimate the resonance energy. To eliminate this difficulty, we introduce a basis called the bond-distorted orbital (BDO),¹⁸ which is, for a specific resonance structure, formed by distorting a pure AO only to its bonding partner. In other words, the expansion space of a BDO is the primitive basis functions which are centered on two bonded atoms. Since an OEO is extended to the whole molecule, apparently, a BDO is a constraint form of an OEO and a kind of localized one-electron orbital. The BDO is a direct extension of the Coulson–Fischer orbital, and similar forms have also been used by Harcourt and co-workers in their MO calculations.⁶ It should be pointed out here that different resonance structures use different sets of BDOs.

The BDOs are quite different from the NBOs. The former is nonorthogonal, while the latter is orthogonal. One may be concerned that the nonorthogonal BDOs could also underestimate the relevant REs. In the majority of *ab initio* calculations, basis sets are normally derived by fitting atomic orbital wave functions. Therefore, every subset of primitive AOs is supposed to describe an individual atom well. In our VB program, the expansion space for every BDO is defined in the initial input and the expansion coefficients are then optimized. Since every BDO is restricted to a set of primitive AOs that describe an individual atom well, an underestimation seems unlikely.

III. Discussions on the Bond-Distorted Orbital (BDO) Base

In this section, we will take benzene ($R_{\text{C-C}} = 1.397 \text{ \AA}$, $R_{\text{C-H}} = 1.08 \text{ \AA}$) as an example to illuminate the features of BDOs.

With regard to the theoretical calculation of resonance energy, the key lies in how to derive the reference energy in the classical VB method. Experimentally, one estimates the resonance energy based on a reference molecule containing a pure localized double bond. Therefore, to compare with experimental estimation, one should use the most stable resonance structure, where the bonds are strictly two-center–two-electron, and comparable to the chemically existing ones, as a hypothetical molecule to calculate the reference energy. A hypothetical molecule with n double bonds can be described with 3^n canonical Lewis structures (σ frame is fixed) since every bond is represented by three canonical Lewis structures (one covalent and two ionic). For benzene, if a Kekulé structure is described by the following 27 canonical Lewis structures (the number in the parentheses



represents the number of equivalent structures), the energy of a Kekulé structure is -230.11813 au (using STO-6G), compared

with the total energy of benzene (-230.23840 au) obtained with all 175 VB structure functions. The vertical resonance energy (VRE) is therefore -75 kcal/mol , reasonably close to the value of -66 kcal/mol estimated by Wheland.¹⁹

In the framework of modern VB theory, OEO bases are normally used. As mentioned above, five VB functions, which correspond to two Kekulé and three Dewar structures, that are also self-consistent field (5VBSCF) are accurate enough to calculate the total energy of benzene. Our calculation with STO-6G shows that the energy of benzene is -230.23137 au , indicating that 93.5% of correlation energy is recovered. With regard to the individual structural energy, the energy of the Kekulé structure is as low as -230.19475 au . Consequently, the VRE of benzene is only 27 kcal/mol . Maybe one can claim that this value is close to the well-known experimentally estimated resonance energy 36 kcal/mol . However, this claim apparently ignores the compression energy, which has been discussed in Wheland's book¹⁹ and Mulliken and Parr's paper.⁸ In fact, we believe that the experimentally estimated resonance energy can only be compared with the theoretical resonance energy (TRE) instead of VRE.²⁰ The TRE of a conjugated system is defined as the energy difference between a stable delocalized molecule and its stable hypothetically localized molecule. It should be noted that contrary to the calculation of VRE, in the calculation of TRE, the geometry of the localized molecule usually differs from that of the delocalized molecule. The difference between TRE and VRE is the compression energy.¹¹

If we adopt BDOs as one-electron orbitals to perform 1VBSCF calculations, the energy of the Kekulé structure is now -230.11472 au , very close to the value of -230.11813 au using the 27 canonical Lewis structure functions. Thus, we can conclude that the above 27 canonical Lewis structure functions can excellently converge to only 1 localized VB function when BDOs are used. This result shows that in the 27 canonical Lewis structures, multiionic structures have negligible contribution to the Kekulé structure.

The above discussion clearly indicates that a localized structure function will be contaminated by other localized structure functions when OEOs are used. Alternatively, we can understand the contamination effect produced by OEOs as follows. If we expand a reference structure function with OEOs to canonical Lewis structure functions, we will find that all possible (not only 3^n) canonical Lewis structures will be included. However, if we expand a reference structure function with BDOs as one-electron orbitals to canonical Lewis structure functions with AOs as one-electron orbitals, we will find that only the 3^n canonical Lewis structures discussed above are contained.

It should be noted here that a D_{3h} Kekulé structure was used in our calculations of REs. When another symmetry Kekulé structure, if one exists, is used, the results could be different.

IV. Effects of Hybridization and Resonance on C–C Bond Lengths

To study the relationship among conjugation, hybridization, and carbon–carbon bond lengths, we choose 1,3-butadiene and 1,3-butadiyne as our model molecules. For conjugated systems, we normally utilize a σ – π separation approximation, i.e., the σ electrons are confined in the σ MOs derived from an HF calculation. Although there are two spin couplings in 1,3-butadiene, our preliminary calculations show that using only one VB function with OEOs can account for 92% of the correlation energy. For the sake of simplicity, in this paper, one VB function Ψ_{Del} with OEOs is employed to describe the

TABLE 1: Optimized Carbon–Carbon Bond Lengths (Å) with the 6-31G Basis Set

type	1,3-butadiene		1,3-butadiyne	
	short bond	long bond	short bond	long bond
1VBSCF/OEO	1.347	1.469	1.216	1.387
1VBSCF/BDO	1.342	1.508	1.209	1.446
difference	0.005	−0.039	0.007	−0.059

TABLE 2: Energies of Stable Delocalized and Localized 1,3-Butadiene and 1,3-Butadiyne

	1,3-butadiene	1,3-butadiyne
delocalized structure ^a E_{tot}	−154.92397	−152.54697
localized structure E_{ref}	−154.91138	−152.52172
TRE, kcal/mol	7.9	15.8

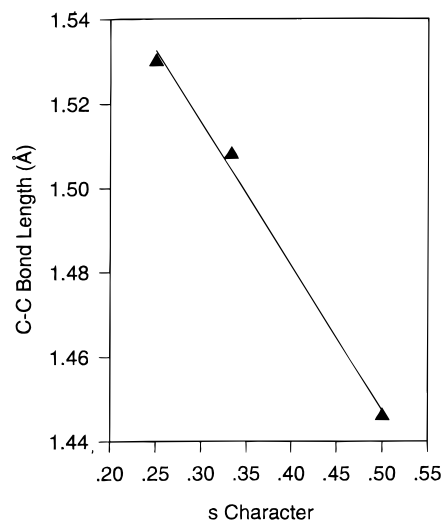
^a The HF energies are −154.863 62 and −152.446 44 hartree for 1,3-butadiene or 1,3-butadiyne respectively.

delocalized 1,3-butadiene or 1,3-butadiyne (1VBSCF/OEO). In the hypothetically localized 1,3-butadiene and 1,3-butadiyne, there is no π electronic delocalization over their central bonds. As mentioned above, the multiionic canonical Lewis structures make negligible contribution. Thus, one VB function Ψ_{Loc} using BDOs is employed to describe the corresponding hypothetically localized structure (1VBSCF/BDO). The energy difference between Ψ_{Loc} and Ψ_{Del} is the relevant delocalization energy.

Since our VB program does not have the geometry optimization function, we estimate the optimal carbon–carbon bond lengths only by varying the relevant bond lengths with single-point calculations and keeping all other structural parameters fixed at the optimized values from the HF/6-31G level. The carbon–carbon bond lengths in the delocalized and localized structures of 1,3-butadiene or 1,3-butadiyne together with their TREs are thus obtained. Tables 1 and 2 show our VBSCF calculation results using the 6-31G basis set.

In the hypothetically localized 1,3-butadiene or 1,3-butadiyne, the C–C multiple bonds should be very similar to those in ethylene or acetylene. This is indeed supported by our calculations. Calculations using BDOs show that the short bond lengths are 1.342 and 1.209 Å for the hypothetically localized 1,3-butadiene and 1,3-butadiyne, respectively, comparable to the experimental values, 1.339 and 1.203 Å, for ethylene and acetylene. The π electronic delocalization (see 1VBSCF/OEO results in Table 1) changes the short bonds only slightly. However, the central bonds are very sensitive to the delocalization and are shortened by 0.039 and 0.059 Å, respectively, due to the π electronic delocalization. Because of no strain energy in the stable localized 1,3-butadiene or 1,3-butadiyne, their central bond lengths represent the theoretical $\text{C}(\text{sp}^2)\text{--C}(\text{sp}^2)$ (1.508 Å) and $\text{C}(\text{sp})\text{--C}(\text{sp})$ (1.446 Å) single bond lengths. The $\text{C}(\text{sp}^3)\text{--C}(\text{sp}^3)$ bond length for ethane is, calculated at the HF level, 1.530 Å. From these theoretical data, we can see that for 1,3-butadiene, the central bond (1.469 Å) is 0.061 Å shorter than a regular C–C single bond (1.530 Å) of ethane. Thus, the π electronic delocalization accounts for about 64% (0.039 Å) of this shortening, while the rehybridization (from sp^3 to sp^2) accounts for the remaining. These results are in good agreement with those obtained by Daudey *et al.* and Kollmar,^{9,21} who estimated the central bond length in the localized *trans*-1,3-butadiene as being 1.510⁹ and 1.521 Å,²¹ respectively. For the 1,3-butadiyne, the π delocalization is only responsible for 41% shortening (0.059 Å) of the central bond, while the rehybridization from $\text{C}(\text{sp}^3)$ to $\text{C}(\text{sp})$ accounts for 59% shortening (0.084 Å).

Though there is no direct experimental proof for our quantitative evaluations above, we can examine the variation of C–H

**Figure 1.** The relationship between C–C single bond length and s character.

bond lengths in ethane, ethylene, and acetylene to see how hybridization changes the C–C single bond length. Because each hydrogen atom uses only the H(1s) orbital, any variation in the C–H bond length can be reasonably attributed to the use of different hybridized orbitals in the relevant carbon atom. The experimental bond lengths of $\text{C}(\text{sp}^3)\text{--H}$, $\text{C}(\text{sp}^2)\text{--H}$, and $\text{C}(\text{sp})\text{--H}$ in the ethane, ethylene, and acetylene are 1.096, 1.085, and 1.061 Å, respectively.²² In other words, the $\text{C}(\text{sp}^2)\text{--H}$ and $\text{C}(\text{sp})\text{--H}$ bond lengths are 0.011 and 0.035 Å shorter than the $\text{C}(\text{sp}^3)\text{--H}$ one. Therefore, we can estimate that the bond lengths of $\text{C}(\text{sp}^2)\text{--C}(\text{sp}^2)$ and $\text{C}(\text{sp})\text{--C}(\text{sp})$ are expected to be around 0.022 and 0.070 Å shorter, respectively, than the $\text{C}(\text{sp}^3)\text{--C}(\text{sp}^3)$ bond length. Our *ab initio* calculations ($\text{C}(\text{sp}^3)\text{--C}(\text{sp}^3)$, 1.530 Å; $\text{C}(\text{sp}^2)\text{--C}(\text{sp}^2)$, 1.508 Å; and $\text{C}(\text{sp})\text{--C}(\text{sp})$, 1.446 Å) indeed prove these estimations.

If we define the s character in a hybridized orbital as x , then the p character is $1 - x$. An approximate linear relationship between the theoretical $\text{C}(\text{s}^x\text{p}^{1-x})\text{--C}(\text{s}^x\text{p}^{1-x})$ single bond length and the s character x is plotted in Figure 1 and can be expressed as

$$R(\text{C--C}) (\text{Å}) = -0.3388x + 1.617 \quad (3)$$

From the above formulation, the $\text{C}(\text{p})\text{--C}(\text{p})$ single bond is supposed to be around 1.617 Å. We can also evaluate the $\text{C}(\text{sp}^3)\text{--C}(\text{sp}^2)$ single bond length as the average of $\text{C}(\text{sp}^3)\text{--C}(\text{sp}^3)$ and $\text{C}(\text{sp}^2)\text{--C}(\text{sp}^2)$ bond lengths, being 1.519 Å. The experimental results in $\text{CH}_3\text{CH}=\text{CH}_2$ show that the long C–C bond length is 1.506 Å,²³ namely, 0.013 Å shorter than 1.519 Å. This shortening could be attributed to a hyperconjugation or σ delocalization resulting from the electron transfer from the C–H bonds of the methyl group to the π antibonding molecular orbital (MO) of propylene.

Our calculations show that the TREs are 7.9 and 15.8 kcal/mol for 1,3-butadiene and 1,3-butadiyne, respectively. These results are expected because in 1,3-butadiene there is one four-center–four-electron Π bond, while in 1,3-butadiyne there are two four-center–four-electron Π bonds.

V. Conclusions

In summary, in VB calculations, one-electron orbitals can take many forms such as OEOs, BDOs, hybrid AOs, or even pure AOs. We believe that the practical usage of a form depends on what the authors want to derive from their calculations. For example, several authors^{24,25} have used the

hybrid AOs to study molecular dynamic processes and the bonding features. Although OEOs have the advantage of recovering most of correlation energy with a very small number of VB functions, BDOs are valuable in the study of hypothetically localized molecules. The combined applications of OEOs and BDOs in this work really present some very interesting and detailed results regarding the relationships among hybridization, resonance, and carbon-carbon bond lengths.

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