A Valence Bond Study of Three-Center Four-Electron π Bonding: Electronegativity vs Electroneutrality[†]

Andrew DeBlase, Megan Licata,[‡] and John Morrison Galbraith*

Department of Chemistry, Biochemistry and Physics, Marist College, Poughkeepsie, New York 12601

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Three-center four-electron (3c4e) π bonding systems analogous to that of the ozone molecule have been studied using modern valence bond theory. Molecules studied herein consist of combinations of first row atoms C, N, and O with the addition of H atoms where appropriate in order to preserve the 3c4e π system. Breathing orbital valence bond (BOVB) calculations were preformed at the B3LYP/6-31G**-optimized geometries in order to determine structural weights, π charge distributions, resonance energies, and π bond energies. It is found that the most weighted VB structure depends on atomic electronegativity and charge distribution, with electronegativity as the dominant factor. By nature, these systems are delocalized, and therefore, resonance energy is the main contributor to π bond energies. Molecules with a single dominant VB structure have low resonance energies and therefore low π bond energies.

Introduction

Though formulated nearly a century ago by Lewis,[1] the idea of the two-electron bond remains central to chemistry.[2] Lewis structures quickly provide a qualitative idea about the electronic and geometrical structure of small molecules, and as a result, most present day chemists became familiar with the two-electron bond and Lewis structures in their first chemistry course. While the conceptual framework of the two-electron bond is simple enough for introductory-level students, it has sound theoretical backing, as first pointed out by Heitler and London[3] and further developed by Pauling.[4]

Another concept that is introduced early on in the chemistry curriculum, though often more difficult to grasp, is that of resonance. In cases where a single Lewis structure fails to describe the molecule, a superposition of structures must be used, as in **I** and **II** for ozone in Figure 1. Ozone is a molecule where the four π electrons (two in the π bond and two in a lone pair on the singly bound terminal O in either **I** or **II**) are distributed throughout three p-type atomic orbitals (AOs) on the oxygens. While **I** and **II** are usually the only structures mentioned when discussing ozone at the introductory level, a more complete description of this three-center four-electron (3c4e) π system requires structures **III**−**VI** as well.

Indeed, previous valence bond (VB) studies of 3c4e π systems[5] have shown that the "singlet diradical", or "long bond", or "Dewar" structure (**III**) is a major contributor to the overall wave function. Although this structure benefits from the lack of atomic formal charge, the energetic stabilization due to spin pairing electrons on the terminal oxygens to form the "long bond" is expected to be small compared to the stabilization upon pairing electrons on adjacent oxygens, as in structures **I** and **II**. Harcourt[6] has shown that the importance of structure **III** lies in its ability to act as a bridge between structures **I** and **II**, thus allowing them to mix. While it is generally accepted that ozone has strong diradical character due to the importance of structure **III**, it is unclear if and when spin pairing takes precedence over minimization of formal charge in general 3c4e π systems.

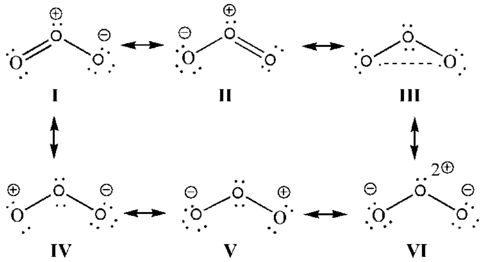
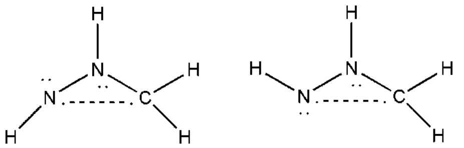


Figure 1. The six resonance structures of ozone used herein. Structures **I** and **II** are referred to as "zwitterionic", **III** is referred to as "singlet diradical" and **IV**−**VI** as are referred to as "co-ionic".



A **B**

Figure 2. Isomers of the $N_2H_2CH_2$ molecule. Isomer **A** is lower in energy and herein designated "NNC".

Although the contribution from structures **IV**−**VI** is expected to be small, Shaik and co-workers have shown that even the seemingly unimportant "ionic" structures can have a major impact on the overall bond energy of two center bonds. This situation, where the bond energy is due to mixing of covalent and ionic structures rather than any one structure alone, has been referred to as charge shift (CS) bonding[7] and has recently been experimentally verified.[8] CS bonding has been shown to be a ubiquitous form of bonding across the periodic table in both σ[9] and π[10] two-center two-electron systems. While 3c4e systems are inherently delocalized, the extent of stabilization due to structure mixing is unknown, and the applicability of the CS concept is unclear.

In the present paper, we seek to elucidate the bonding in three-center four-electron π units such as ozone through VB methods.

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[*] To whom correspondence should be addressed. E-mail: john.galbraith@marist.edu.

[‡] Current address: The University of New Hampshire, College of Engineering and Physical Sciences, Parsons Hall, Durham, NH 03824.

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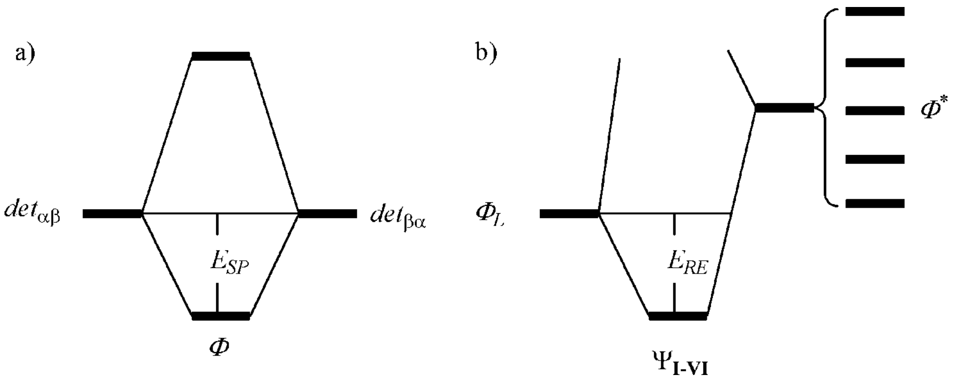

Figure 3. Schematic representation of VB structure and determinant mixing. (a) Mixing of individual spin determinants; $det_{\alpha\beta}$ represents a single determinant, while $det_{\beta\alpha}$ is the corresponding determinant with electron spins flipped. Φ is VB structure **I**, **II**, or **III** from Figure 1 above. (b) Mixing of VB structures. Φ_L is the lowest-energy VB structure, and Φ* represents the higher-energy VB structure. Ψ_{I-VI} is the full six-structure VB wave function.

TABLE 1: BOVB Inverse Overlap Weights of Valence Bond Structures

	$A{=}\overset{\oplus}{B}{-}\overset{\ominus}{C}:$	$:\overset{\ominus}{A}{-}\overset{\oplus}{B}{=}C$	$\cdot A{-}\overset{\cdot\cdot}{B}{-}C\cdot$	$\overset{\oplus}{A}{-}\overset{\cdot\cdot}{B}{-}\overset{\ominus}{C}:$	$:\overset{\ominus}{A}{-}\overset{\cdot\cdot}{B}{-}\overset{\oplus}{C}$	$:\overset{\ominus}{A}{-}\overset{2\oplus}{B}{-}\overset{\ominus}{C}:$
OOO	0.215	0.215	**0.539**	0.006	0.006	0.018
NON	0.149	0.225	**0.584**	0.010	0.021	0.012
NOC	0.078	0.330	**0.501**	0.004	0.078	0.009
COC	0.151	0.151	**0.638**	0.026	0.026	0.07
NNN	0.237	0.298	**0.392**	0.012	0.019	0.042
NNC	0.165	0.362	**0.390**	0.009	0.042	0.033
CNC	0.228	0.228	**0.477**	0.023	0.023	0.022
NOO	**0.490**	0.058	0.358	0.077	0.001	0.016
ONO	**0.305**	**0.305**	0.288	0.010	0.010	0.083
NNO	**0.458**	0.152	0.298	0.033	0.004	0.056
CNO	**0.521**	0.084	0.288	0.072	0.002	0.033
COO	**0.546**	0.020	0.203	0.220	0.000	0.009

Largest weight of each structure indicated in bold.

Although the σ system is more complicated than the localized homopolar bonding picture in Figure 1,[5a,b,11] we have chosen to focus solely on π bonding herein. Valence bond theory is ideally suited for this type of problem due to its ability to break apart the wave function into contributing segments. Furthermore, by changing the atoms that make up the three center system, we will get a better idea of when and why a particular VB structure becomes important. In addition to their theoretical importance, 3c4e π bonding units are analogous to the π system of the TM−O_2 units of many biologically[12] and industrially[13] important molecules.

Theoretical Methods

Computational Details. The 3c4e systems were chosen by mixing isoelectronic CH_2, NH, and O fragments in such a way as to resemble the π system of ozone where the electroneutral structure has two electrons on the central heavy atom and one electron on each terminal heavy atom, as in structure **III** in Figure 1. The geometries of all structures reported herein were optimized by density functional theory (DFT)[14] using the B3LYP functional[15] along with the 6-31G** basis set.[16] All DFT optimizations were preformed with the Gaussian 98 (revision A.11) suite of programs.[17] The lowest-energy structure was used in cases where multiple conformations are possible due to positions of attached H atoms. For example, isomer **A** was found to be the lower-energy form of the $N_2H_2CH_2$ molecules depicted in Figure 2 and is herein designated "NNC". All optimized geometrical parameters can be found in Table 1 of the Supporting Information.

The RHF σ molecular orbitals at the B3LYP/6-31G** geometry were held frozen while the π system was described by VB structures **I**−**VI**. Herein, VB structures **I** and **II** are referred to as "zwitterionic", while **III** is referred to as "singlet diradical", and **IV**−**VI** are referred to as "co-ionic". The π VB orbitals were localized on molecular fragments which consist of a single heavy atom and any attached hydrogens. An alternative approach would be to use semilocalized orbitals as originally proposed by Coulson and Fischer.[18] These semilocalized orbitals (commonly referred to as overlap-enhanced orbitals or bond-distorted orbitals) incorporate ionic character into covalent-type structures through small delocalization tails on neighboring fragments. As a result, some of the interpretability of structural weights is lost in exchange for a more compact wave function.[5e,19] The current study uses orbitals strictly localized on molecular fragments in order to more closely correspond to the Lewis-type structures of Figure 1.

TABLE 2: Energies of Spin Determinants and Spin Pairing Stabilization for Zwitterionic and Singlet Diradical VB Structures

	$\mathrm{A{=}\overset{\oplus}{B}{-}\overset{\ominus}{C}{:}}$		$\mathrm{{:}\overset{\ominus}{A}{-}\overset{\oplus}{B}{=}C}$		$\mathrm{{\bullet}A{-}\overset{\bullet\bullet}{B}{-}C{\bullet}}$	
	E_{det}	E_{sp}	E_{det}	E_{sp}	E_{det}	E_{sp}
OOO	59.7	-17.8	59.7	-17.8	0.0	-0.3
NON	98.1	-23.5	74.3	-26.4	0.0	-0.5
NOC	123.7	-20.3	50.6	-31.8	0.0	-0.5
COC	103.1	-27.8	103.1	-27.8	0.0	-0.3
NNN	50.7	-34.3	36.6	-35.4	0.0	-2.9
NNC	69.5	-34.0	25.3	-39.0	0.0	-3.3
CNC	58.9	-32.5	58.9	-32.5	0.0	-2.5
NOO	6.1	-30.5	127.1	-18.4	0.0	-0.6
ONO	17.7	-37.6	17.7	-37.6	0.0	-3.2
NNO	0.0	-38.4	74.5	-34.0	9.4	-3.1
CNO	0.0	-37.4	111.0	-30.3	20.0	-2.7
COO	0.0	-34.8	165.4	-13.9	17.6	-0.2

All energies in kcal/mol; E_{det} relative to lowest-energy determinant; E_{SP} relative to spin determinant for that VB structure.

Each structure was allowed a unique set of VB orbitals which were allowed to fluctuate independently of the VB orbitals in other structures. This method, known as the breathing orbital valence bond (BOVB),[19b] has been shown to include dynamic correlation effects in a compact VB wave function. All BOVB calculations were performed with the XMVB program.[20]

Analysis of Wave Functions. The weight of each VB structure in the overall wave function was determined by the inverse overlap method of Gallup and co-workers.[21] In the inverse overlap method, the unique contribution of each structure is given by eq 1, where N is a normalization constant, c_i is the coefficient of VB structure i, and $(S^{-1})_{ii}$ is the diagonal component of the inverse of the VB structure overlap matrix.

$$w_i = N\frac{|c_i|^2}{(S^{-1})_{ii}} \tag{1}$$

VB Structure Fragment Charges. The familiar Mulliken population analysis has been slightly modified in order to gage the charge on the fragments of individual VB structures. The gross σ population, $N_{\mathrm{F}\sigma}$, was determined by summing the gross populations over all σ basis functions on a particular fragment, F, as shown in eq 2, where $\mathrm{bsf}_\sigma \in \mathrm{F}$ indicates all σ basis functions on F and N_{bsf} is the gross population of a particular basis function.

$$N_{\mathrm{F}\sigma} = \sum_{\mathrm{bsf}_\sigma \in \mathrm{F}} N_{\mathrm{bsf}} \tag{2}$$

The gross σ population can then be subtracted from the total atomic charge of the fragment, Z_{F}, to give the σ charge of the fragment, $q_{\mathrm{F}\sigma}$, as in eq 3

$$q_{\mathrm{F}\sigma} = Z_{\mathrm{F}} - N_{\mathrm{F}\sigma} \tag{3}$$

Lastly, the number of π electrons localized on the fragment are subtracted to give the overall fragment charge in a particular VB structure, q_{F}. The sum of the absolute values of the fragment charges, $\Sigma|q_{\mathrm{F}}|$, is then an indicator of the overall charge distribution. Large $\Sigma|q_{\mathrm{F}}|$ values indicate charge localization on individual fragments while small values indicate a more even distribution across the whole molecule.

Bond Energies. The idea of a 3c4e bond energy is not as straightforward as that for a two-center bond. Considering a bond to be the difference in energy between the unbound situation and the completely bonded situation, the problem lies in how to define the unbound situation. The zwitterionic and singlet diradical structures are made up of the negative combination two spin-paired determinants ($\alpha\beta - \beta\alpha$). Shaik and co-workers[10,22] have shown that this combination of spin determinants is responsible for the energetic stabilization of spin pairing (Figure 3a). Thus, one can essentially turn the bonding off by considering only a single spin determinant.

In this manner, 3c4e bond energies are defined herein as the energetic difference between the lowest-energy spin determinant and the six-structure BOVB calculation. Furthermore, the contribution to the overall bond energy due to spin paring, E_{SP}, can be taken as the energetic difference between a single determinant and the corresponding VB structure (Figure 3a). Likewise, the resonance energy due to mixing VB structures, E_{RE}, can be taken as the energetic difference between the lowest-energy structure alone, Φ_{L}, and the six-structure BOVB wave function, $\Psi_{\mathbf{I-VI}}$ (Figure 3b).

Results and Discussion

BOVB Structural Weights. It is evident from Table 1 that the VB structure with no formal charge (analogous to **III**) does not always have the greatest inverse overlap weight. The zwitterionic structure (corresponding to **I**) is weighted highest for NOO, ONO, NNO, CNO, and COO. This ordering can be understood by breaking down the zwitterionic and singlet diradical VB structures into energetic contributions from spin determinants, E_{det}, and spin pairing, E_{SP}, as in Table 2.

As expected, E_{SP} is more stabilizing for the zwitterionic structures (~30 kcal/mol) than the singlet diradical structures (<4 kcal/mol) due to the distance between spin-pairing fragments. In most cases, the singlet diradical structure has

TABLE 3: Mulliken charges of Fragments in Individual VB Structures and the Sum of the Absolute Value of Charges on All Fragments

	$A{=}\overset{\oplus}{B}{-}\overset{\ominus}{C}\colon$		$\colon\overset{\ominus}{A}{-}\overset{\oplus}{B}{=}C$		$\cdot A{-}\ddot{B}{-}C\cdot$	
ABC	q_F	$\Sigma\vert q_F\vert$	q_F	$\Sigma\vert q_F\vert$	q_F	$\Sigma\vert q_F\vert$
	A: 0.268		A: -0.732		A: 0.268	
OOO	B: 0.463	1.463	B: 0.463	1.463	B: -0.537	1.074
	C: -0.732		C: 0.268		C: 0.268	
NON	A: 0.401		A: -0.599		A: 0.401	
	B: 0.247	1.297	B: 0.247	1.198	B: -0.753	1.506
	C: -0.648		C: 0.352		C: 0.352	
NOC	A: 0.457		A: -0.543		A: 0.457	
	B: 0.190	1.511	B: 0.190	1.085	B: -0.810	1.619
	C: -0.864		C: 0.352		C: 0.352	
COC	A: 0.417		A: -0.583		A: 0.417	
	B: 0.165	1.165	B: 0.165	1.165	B: -0.835	1.669
	C: -0.583		C: 0.417		C: 0.417	
NNN	A: 0.229		A: -0.771		A: 0.229	
	B: 0.571	1.600	B: 0.571	1.542	B: -0.429	0.858
	C: -0.800		C: 0.200		C: 0.200	
NNC	A: 0.244		A: -0.756		A: 0.244	
	B: 0.445	1.378	B: 0.445	1.512	B: -0.555	1.110
	C: -0.689		C: 0.311		C: 0.311	
CNC	A: 0.338		A: -0.662		A: 0.338	
	B: 0.325	1.325	B: 0.325	1.325	B: -0.675	1.351
	C: -0.662		C: 0.338		C: 0.338	
NOO	A: 0.269		A: -0.731		A: 0.269	
	B: 0.389	1.316	B: 0.389	1.462	B: -0.611	1.223
	C: -0.658		C: 0.342		C: 0.342	
ONO	A: 0.013		A: -0.987		A: 0.013	
	B: 0.974	1.974	B: 0.974	1.974	B: -0.026	0.051
	C: -0.987		C: 0.013		C: 0.013	
NNO	A: 0.162		A: -0.838		A: 0.162	
	B: 0.788	1.900	B: 0.788	1.677	B: -0.212	0.424
	C: -0.950		C: 0.050		C: 0.050	
CNO	A: 0.268		A: -0.732		A: 0.268	
	B: 0.660	1.856	B: 0.660	1.464	B: -0.340	0.680
	C: -0.928		C: 0.072		C: 0.072	
COO	A: 0.290		A: -0.710		A: 0.290	
	B: 0.308	1.196	B: 0.308	1.420	B: -0.692	1.384
	C: -0.598		C: 0.420		C: 0.402	

the lowest-energy spin determinant. However, if the stabilizing effect of E_{SP} is large enough ($|E_{SP}| > |E_{det}|$), the zwitterionic structure can be stabilized below the singlet diradical structure. The ordering of structural weights inversely follows energetic ordering, and thus, in these cases, the zwitterionic structure has the greatest weight.

For example, while the "electroneutral" singlet diradical structure of NOO has no formal charge, Mulliken population analysis (Table 3) revels that the zwitterionic structure has only a slightly greater $\Sigma|q_F|$ value. As a result, the zwitterionic spin determinant is only slightly higher in energy than the singlet diradical spin determinant (6.1 kcal/mol). The zwitterionic spin-

TABLE 4: Resonance and Total π Energies of 3c4e Systems

	E_{RE}	E_{π}
OOO	75.2	75.5
NON	73.1	73.6
NOC	78.6	79.1
COC	63.7	64.0
NNN	110.6	113.5
NNC	97.9	111.7
CNC	84.4	86.9
NOO	80.2	104.7
ONO	153.0	153.6
NNO	93.7	132.1
CNO	76.6	114.0
COO	71.3	106.1

All energies in kcal/mol; E_{π} relative to the lowest-energy determinant and E_{RE} relative to lowest VB structure as in Figure 1.

pairing stabilization, E_{SP}, is large enough to overcome this difference, resulting in a greater structural weight.

ONO has a more extreme difference in $\Sigma|q_F|$ between zwitterionic and singlet diradical spin determinants. However, both zwitterionic determinants place negative charge on the more electronegative oxygen atom. These two factors work in opposite directions, with the lower $\Sigma|q_F|$ value favoring the singlet diradical determinant and electronegativity favoring the zwitterionic determinants. Although the singlet diradical determinant ends up being more stable by 17.7 kcal/mol, spin pairing lowers the energy of the zwitterionic structure below that of the singlet diradical, resulting in a greater structural weight.

The tendency to place negative charge on the more electronegative atom overrides the tendency to lower charge distribution, as can be seen by examining the NON, NOC, COC, CNC, NNO, and CNO molecules. In each of these cases, the VB structure with the greatest negative charge on the more electronegative atom is lowest in energy, even though this structure has a greater $\Sigma|q_F|$ value.

In the case of COO, both electronegativity and charge distribution factors favor the zwitterionic determinant. The lowest-energy zwitterionic structure and the singlet diradical structure both place negative charge on O atoms. The zwitterionic structure has the added benefit of placing negative charge on the terminal O, thus relieving electron−electron repulsion by removing electron density from the center of the molecule. These factors, combined with the added E_{SP} stability, make the zwitterionic structures lowest in energy with the greatest weight.

Contributions to the Bond Energies. It can be seen in Table 4 that the majority of stabilization in the 3c4e π bonding systems studied herein is due to resonance mixing of VB structures rather than any one alone. As a result, trends in bond energies correlate with resonance energies. Harcourt[6] has broken down this resonance mixing into contributions from the off-diagonal Hamiltonian matrix elements, H_{ij}, which are, in turn, affected by atomic orbital overlap integrals, S_{ab} (where where i and j refer to VB structures and a and b refer to AOs). It is shown that the zwitterionic structures, **I** and **II**, alone cannot effectively mix due to small AO overlap between terminal atoms. However, the larger AO overlap between terminal and central atoms allows for effective direct mixing between structure **III** and zwitterionic structures **I** and **II**. Thus, structure **III** can be seen as a bridge between structures **I** and **II**, providing a means by which they can indirectly mix with each other.

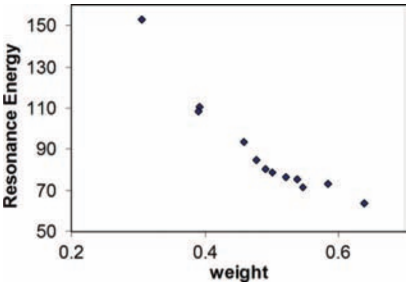

Figure 4. Resonance energy (in kcal/mol; see Table 4) versus the inverse overlap weight of the dominant VB structure (see Table 1).

The resonance energy decreases as a single VB structure dominates the molecular wave function, as seen in Figure 4. For example, ONO has three VB structures with similar weights (Table 1), indicating a highly delocalized π system. Accordingly, ONO also has the largest resonance energy (Table 4) and, therefore, largest π bond energy. In this molecule, resonance serves to spread electron density out of the center of the molecule and onto the highly electronegative terminal O atoms.

The weight of the dominant VB structure (and, thus, the resonance energy) can be understood by looking at the series COC, NON, OOO, NOC. The singlet diradical structure dominates each of these molecules due to the electronegative central O atom. COC has the most singlet diradical character (Table 1) and the lowest resonance energy (Table 4) due to the inability of the terminal C atoms to carry charge in either of the zwitterionic structures. In NON and OOO, the terminal atoms increase in electronegativity, and thus, the zwitterionic structures contribute more, and the resonance energy increases. NOC does not appear to fit this trend. However, the asymmetry of the molecule leads to a greater contribution from VB structure type **II**, which removes charge from the electropositive C atom. As a result, the weight of the singlet diradical structure decreases, and the resonance energy increases.

The effect of electronegativity on VB weights (and, thus, resonance energies) is further elucidated by comparing COO with NOO and CNO with NNO. In these molecules, VB structure **I** dominates the molecular wave function. In going from COO to NOO, structure **II**, which places charge on the more electronegative N, increases in importance. As a result, structure **I** is not as dominant, and NOO has a greater resonance energy. A similar trend is observed in going from CNO to NNO.

Conclusion

The 3c4e π systems are inherently delocalized, and thus, a proper description requires resonance mixing of multiple VB structures. Determination of the dominant VB structure is not as simple as application of the octet rule and/or the electroneutrality principle. Although minimization of charge distribution is an important factor in determining the dominant VB structure, simple calculation of formal charge is an inadequate measure of this factor. Another important factor in determining the dominant VB structure, electronegativity, tends to localize charge on individual fragments. These two factors work in opposite directions, with electronegativity generally overriding the minimization of charge.

Although a direct analogy to the charge shift bonding concept is inapplicable due to the delocalized nature of these systems, 3c4e π bond energies are primarily due to resonance mixing rather than any one VB structure alone. As a result, it follows that molecules with greater resonance energies have greater 3c4e bond energies. Molecules with a single dominant VB structure have lower resonance energies and, thus, lower bond energies.

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Supporting Information Available: Table containing B3LYP/631-G*- optimized geometrical parameters of all molecules studies herein. This material is available free of charge via the Internet at http://pubs.acs.org.

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