

# The Nature of Multiple Bonds. 3. Benzene, Bent Bonds, and Resonance

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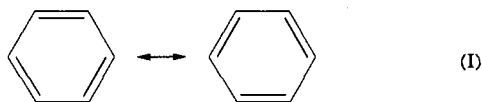
Received March 22, 1993<sup>⊙</sup>

**Abstract:** The phenomenon of resonance, in the classical valence bond sense, is investigated with use of explicitly correlated *ab initio* wave functions of the generalized valence bond form. For molecules exhibiting “resonance”, requiring more than a single classical bonding structure to describe the bonding, the wave function is constructed as the sum of terms, each term being associated with a particular valence bond structure. The interaction of these terms in a nonorthogonal configuration interaction or “structure interaction” calculation results in a wave function lower in energy than provided by any of the terms associated with the individual structures. Although the wave function as a whole cannot be interpreted within an independent particle context, each of the terms that compose it can; in this paper, we examine the nature of the bonding in such a system and probe the relative merits of a  $\sigma, \pi$  symmetry-restricted bond representation and a bent bond representation of the bonding. The results serve to support the conclusions made in previous papers of this series regarding the nature of the bonding in multiple bonds. Based on energetic considerations, the bent bond model serves as a better framework with which to describe the electronic structure in systems exhibiting resonance than the  $\sigma, \pi$  bond model.

## Introduction

There exist many physical systems for which the question of the optimal orbital bonding description within an independent particle (IP) picture cannot be answered. Frequently the nature of the wave function cannot be described in a single valence bond structure with pairs of electrons coupled into singlet bond pairs. The classic example of such a molecule is benzene,  $C_6H_6$ . It is not possible to specify a reasonable bond pairing among the carbon atoms of the ring (excluding the whimsical representation having three carbon–carbon bonds *across* the ring) possessing the 6-fold symmetry of the molecule.

In cases such as these, a more general description consisting of a superposition of alternate bonding structures is called for. A description of this sort for benzene was first proposed in 1872 by August Kekulé to explain the then-unexpected 6-fold symmetry of the benzene molecule with “oscillating” structures.<sup>1</sup> Kekulé postulated the oscillation of a three-fold bonding structure consisting of alternating double (C=C) and single (C–C) bonds around the ring of tetravalent carbon with the equivalent, symmetrically related 3-fold symmetric bonding structure [as in (I)] restoring the overall 6-fold symmetry of the molecule.



While only pedagogical at the time, with the advent of quantum mechanics and subsequent development of the valence bond (VB) theory,<sup>2–8</sup> this description of the benzene molecule and the concept of chemical resonance began to take on a more concrete physical basis. Rather than taking on the character of a particular bonding

structure or an oscillation between bonding structures, the molecule is described as having a quantum mechanical superposition of alternate bonding structures in a “structure interaction” (SI) wave function:

$$\Psi_{SI} = \Psi_A + \Psi_B \quad (1)$$

The many-electron functions  $\Psi_A$  and  $\Psi_B$  correspond to separate bonding structures **A** and **B** such as the two Kekulé structures for benzene.

In addition to rationalizing the symmetry of the ground states of molecules, this description also provides a basis from which to understand the anomalous stability of certain molecules. Benzene, for example, is more stable, by at least 1.6 eV,<sup>5</sup> than would be the hypothetical cyclohexatriene molecule represented by one Kekulé bonding structure (comparing the heats of hydrogenation of cyclohexane and of benzene). This additional stability is attributed to “resonance” between the two Kekulé structures. The total superposition  $\Psi_{SI}$  given by eq 1 is energetically more stable than its components  $\Psi_A$  and  $\Psi_B$ , *i.e.*,

$$E_{SI} = E_A + E_x \quad (2)$$

The quantum mechanical superposition of bonding structures stabilizes the total wave function by an amount  $E_x$ , the quantum mechanical resonance energy.

Classic examples of molecules exhibiting resonance are the conjugated hydrocarbons benzene and the allyl radical and the particularly interesting example of square cyclobutadiene, a molecule considered to be antiaromatic. Standard procedure in such molecules is to separate the electrons into an inactive  $\sigma$  core and a  $\pi$  space of electrons from which the interesting behavior

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<sup>\*</sup> Abstract published in *Advance ACS Abstracts*, October 15, 1993.

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derives.<sup>9-11</sup> This is due in large part to the spectacular early successes enjoyed by the semiempirical  $\pi$  electron molecular orbital (MO) theory of Hückel<sup>9,10</sup> and by other semiempirical derivatives<sup>11</sup> in describing the electronic ground-state and excited-state properties of unsaturated hydrocarbons. In its simplest application, the theory treats the electronic structure as made up of molecular orbitals described as linear combinations of the  $p_x$  orbitals of the participating carbon atoms:

$$\phi_i = \sum_{\mu=1}^{N_C} c_i^{\mu} \chi_{p\pi}^{\mu} \quad (3)$$

The  $\sigma$  electrons are ignored, presumed to be well localized and decoupled from the  $\pi$  space, and the matrix elements among the  $p_x$  atomic orbitals are parametrized. Even within valence bond and resonance theories, the description of the electronic structure of the unsaturated hydrocarbons has been in terms of a  $\pi$  electron description,<sup>12,13</sup> and this presumption of  $\sigma$ - $\pi$  separability has extended to modern *ab initio* valence bond calculations.<sup>14-16</sup>

In this paper, we investigate the relative merits of a  $\sigma, \pi$  bond description *vs* a bent bond description in systems that classically exhibit resonance, *i.e.*, where wave functions of the form of eq 1 are the natural approach to describe the wave function. The SI wave function of eq 1, of course, does not lend itself directly to an IP interpretation; the relevant question instead is the nature of the valence bond terms  $\Psi_I$  making up an SI expansion. Are these terms better represented in terms of a  $\sigma, \pi$  bond framework or a bent bond framework? While the SI wave function is not an IP wave function itself, it is a compact sum of IP wave functions, and as resonance is such an integral part of valence bond theory as a whole, this question is as relevant for resonating systems as it is for molecules interpretable within an IP framework. Detailed *ab initio* configuration interaction (CI) calculations on ethylene<sup>17</sup> and benzene<sup>18</sup> have questioned the validity of  $\sigma$ - $\pi$  separability. In papers 1 and 2 in this series<sup>19,20</sup> we showed that a bent bond model provides a better description of the bonding in simple molecules with multiple bonds than a  $\sigma, \pi$  bond model, using full generalized-valence bond (GVB) wave functions representing the limit of the IP model. As semiempirical MO and VB methods build  $\pi$  electron theories on the foundation of  $\sigma$ - $\pi$  separability, these results invite a reassessment of this assumption for unsaturated hydrocarbons. We examine prototypical conjugated  $\pi$  electron molecules, the allyl radical, benzene, and square cyclobutadiene, finding that these doubts are well-founded: the results show that the bent bond model is a more suitable description of the bonding than the  $\sigma, \pi$  bond model.

Additionally, the nature of aromaticity and the source of the resonance energy within a valence bond context is probed. Resonance, within MO theory, is usually understood as a delocalization phenomenon. Within the VB model, resonance is described as an exchange interaction between alternate structures using localized bonding orbitals. Both viewpoints, given that

they work so well in describing many properties of these systems, must capture certain elements of the same fundamental reality. The SI wave functions defined above, involving patently localized descriptions of the electronic structure, must share some elemental congruence with delocalized molecular orbital descriptions. In the SI calculations, the exchange energy  $E_x$  is broken down into its basic components—the exchange kinetic energy  $T_x$ , the nuclear attraction energy  $V_x^{e-N}$ , and the electron-electron repulsion energy  $V_x^{e-e}$ —in order to derive its nature. The calculated resonance stabilization energies are dominated by the kinetic energy contribution, though the case of the square cyclobutadiene molecule is interestingly different from the others considered. It is shown that the kinetic energy is at the root of the phenomenon of resonance in the valence bond model and thus the congruence between the molecular orbital and valence bond pictures is established.

### Calculation Details

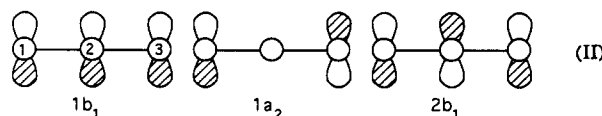
Standard valence double- $\zeta$  Gaussian basis sets were used on all atoms,<sup>21</sup> (9s5p/3s2p) for carbon and (4s/2s) for hydrogen. The calculations for benzene were performed at the experimental geometry ( $D_{6h}$  symmetry,  $R_{C-C} = 1.397$  Å,  $R_{C-H} = 1.084$  Å).<sup>22</sup> The calculations for square cyclobutadiene used a  $D_{4h}$  structure with C-C bond lengths of 1.453 Å and C-H bond lengths of 1.10 Å, and the calculations for the allyl radical used a  $C_{2v}$  ground state with the same bond lengths and 120° bond angles throughout. Single structure calculations used strongly-orthogonal perfect-pairing (SOPP) wave functions computed with use of the GVB-PP method,<sup>6</sup> and SI calculations used our implementation of Voter's resonating-GVB (RGVB) method.<sup>7a</sup> In the SI calculations, the evaluation of the matrix elements between the SOPP wave functions with a large number of pairs proved computationally impractical. As outlined in papers 1 and 2 of this series,<sup>19,20</sup> the SOPP wave function can be written as a conventional CI expansion of  $2^N$  terms,  $N$  being the number of correlated pairs. Many of these terms contribute negligibly to the total wave function, and a truncated configuration list of the leading terms of this CI expansion, sufficient to render a good approximation to the SOPP wave function, was used in some of the calculations. Truncated CI wave functions, denoted SOPPCI( $X$ ), exclude terms differing from the dominant configuration by more than an  $X$ th-order excitation. A further simplification consisted of using the carbon 1s core orbitals derived from a Hartree-Fock calculation in the correlated calculations.

### C<sub>3</sub>H<sub>5</sub>: Allyl Radical and Resonance

**Qualitative.** The allyl radical is the smallest of the  $\pi$  electron systems exhibiting resonance. The electronic ground state is  $^2A_2$ . The MO description consists of a closed-shell  $\sigma$  core, along with three electrons distributed in the three  $p_x$  orbitals of the carbon chain. These orbitals, labeled  $\pi_1, \pi_2$ , and  $\pi_3$  to denote their position along the chain, result in two molecular orbitals of  $B_1$  symmetry and one of  $A_2$  symmetry [see (II)]. The MO ground state can be written as

$$\Psi^{MO} = \mathcal{A}[\Phi_{\sigma} 1b_1^2 \alpha \beta 1a_2^1 \alpha 2b_1^0] \quad (4)$$

where  $\Phi_{\sigma}$  describes the  $\sigma$  electrons, the  $1b_1$  is the in-phase combination of the  $\pi_i$  values, and  $1a_2 \propto (\pi_1 - \pi_3)$  with a node at the central carbon. This leads to a total wave function of  $^2A_2$  symmetry, as required, with a  $^2B_1$  ( $1b_1 \rightarrow 1a_2$ ) excited state.



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Table I. Analysis of SOPP-SI Wave Functions for the Allyl Radical

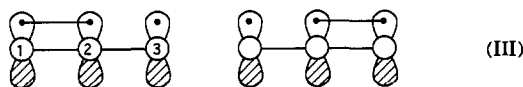
wave function	SOPP energy (hartree)	SI energy (hartree)	$S_{II}$	$E_x$ (eV)	$T_x$ (eV)	$V_x^{e-N}$ (eV)	$V_x^{e-e}$ (eV)
$\sigma, \pi$ Bonds							
HF- ${}^2A_2$	-116.412 90	-116.412 90	-1.0000	0	0	0	0
HF-NSR <sup>a</sup>	-116.413 00	-116.415 80	-0.9562	-0.076	-0.164	+0.022	+0.066
1 pair	-116.429 56	-116.445 20	-0.7534	-0.425	-0.842	+0.110	+0.306
3 pairs	-116.451 88	-116.467 49	-0.7536	-0.425	-0.840	+0.105	+0.309
8 pairs <sup>b</sup>	-116.524 30	-116.539 71	-0.7536	-0.419	-0.830	+0.105	+0.305
Bent Bonds							
3 pairs	-116.450 55	-116.472 03	-0.7821	-0.584	-1.316	+0.680	+0.051
8 pairs <sup>b</sup>	-116.522 62	-116.543 37	-0.7895	-0.565	-1.251	+0.639	+0.048

<sup>a</sup> No symmetry restrictions—yielded a broken-symmetry solution. <sup>b</sup> Using SOPPCI(6) expansions to approximate SOPP to within  $<10^{-5}$  hartree.

Within the VB formulation, the natural description of the allyl radical is  $C=C-C^{\cdot}$ , that is, a  $C=C$  double bond, a  $C-C$  single bond, and an unpaired electron on the terminal carbon with the single bond. Within a  $\sigma-\pi$  principle, each overlapping  $p_x$  hybrid is singly occupied, two neighbors are coupled into a  $\pi$  bond, and the remaining terminal carbon hybrid is occupied by a single unpaired  $\pi$  electron, so that the VB alternatives [see (III)] can be written as (concentrating on the  $\pi$  electrons)

$$\Psi_A^{VB} = \mathcal{A}[\Phi_{\sigma}\pi_1\pi_2(\alpha\beta - \beta\alpha)\pi_3\alpha] \quad (5a)$$

$$\Psi_B^{VB} = \mathcal{A}[\Phi_{\sigma}\pi_1\alpha\pi_2\pi_3(\alpha\beta - \beta\alpha)] \quad (5b)$$



The VB eigenstates are the symmetric and antisymmetric combinations of these two structures:

$$\begin{aligned} \Psi_{sym}^{VB} &= \Psi_A^{VB} + \Psi_B^{VB} \\ &= \mathcal{A}[\Phi_{\sigma}\pi_1\pi_2\pi_3(\alpha\alpha\beta - \beta\alpha\alpha)] \end{aligned} \quad (6a)$$

$$\begin{aligned} \Psi_{asym}^{VB} &= \Psi_A^{VB} - \Psi_B^{VB} \\ &= \mathcal{A}[\Phi_{\sigma}\pi_1\pi_2\pi_3(-\alpha\alpha\beta + 2\alpha\beta\alpha - \beta\alpha\alpha)] \end{aligned} \quad (6b)$$

with the antisymmetric combination being the ground state. This can be deduced by examining the effective pairing among the orbitals. In  $\Psi_{sym}$ , the electrons in the terminal orbitals  $\pi_1$  and  $\pi_3$  are singlet paired as shown in (IV). This bonding is patently



less favorable than the pairing of nearest neighbors within the single structure, indicating that  $\Psi_{sym}$  is the destabilized state and that  $\Psi_{asym}$ , with the terminal atoms triplet coupled, is the stabilized state. Hence, as for the MO description, the VB expression predicts a  ${}^2A_2$  ground state ( $\Psi_{asym}$ ) and a  ${}^2B_1$  excited state ( $\Psi_{sym}$ ).

From the form of eq 6, it is apparent that both the resonant and the antiresonant  $\sigma, \pi$  VB states are representable in an IP framework, *i.e.*, rather than as a resonance of two bonding structures, the wave function can be described as a product of singly occupied orbitals coupled by a general spin function. A full-GVB calculation optimizing the spatial forms of the  $\pi_i$  was done by Levin.<sup>15</sup>

Alternatively, rather than incorporating the resonance in the form of a generalized spin coupling among a shared set of  $\pi$  orbitals, the wave function could be described as the interaction of two separate spatial structures, taking the form:

$$\begin{aligned} \Psi^{VB} &= \Psi_A^{VB} \pm \Psi_B^{VB} \\ &= \mathcal{A}[\{\Phi_{\sigma}^A\pi_1^A\pi_2^A(\alpha\beta - \beta\alpha)\pi_3^A\alpha\} \pm \\ &\quad \{\Phi_{\sigma}^B\pi_1^B\alpha\pi_2^B\pi_3^B(\alpha\beta - \beta\alpha)\}] \end{aligned} \quad (7)$$

where different sets of orbitals are used to describe the two classical valence bond structures A and B. This form of the wave function is more general than eq 6 as it incorporates both bond couplings of the orbitals, simultaneously allowing a set of orbitals optimized for each bond pairing rather than using spatial functions representing a forced compromise of the two couplings.

**Results.** With respect to the general form in eq 7, our calculations are restrictive in two ways: first, the SOPP restrictions on the wave functions are used to represent the individual structures, and second, the orbitals are not reoptimized in the presence of the resonance. Within these two restrictions, all orbitals except the C1s cores (taken from the  ${}^2A_2$  HF calculation) are variationally optimized. We consider alternate representations of the bonding, both enforcing  $\sigma, \pi$  symmetry and also representing the double bond in the individual structures as bent bonds, and compare the resulting energies. The numerical results of the calculations are summarized in Table I.

For reference, the symmetry-restricted  ${}^2A_2$  HF wave function of the form of eq 4 heads the list. This wave function already has the full symmetry of the molecule; therefore, its resonance structure is itself (overlap of -1.0) and gives no calculated resonance energy. If, however, the orbitals are not restricted to irreducible representations of the  $C_{2v}$  point group, the HF wave function spontaneously breaks symmetry (to a more localized  $\pi$  bond pair and an unpaired electron more on one terminal carbon than the other). With no symmetry restrictions (NSR), the HF result is  $10^{-4}$  hartree lower in energy than the symmetry-restricted HF result, and now there can be resonance. The overlap between resonance structures is reduced to -0.96, and the SI stabilization gained using the HF-NSR basis is 0.08 eV.

Correlating one SOPP pair results in a localized  $\pi$  bond (with bond overlap of 0.72) and a localized terminal unpaired  $\pi$  electron and lowers the energy by 0.45 eV from the HF-NSR result. The structure overlap has been reduced from the HF-NSR calculations to -0.75, reflecting the increased localization within the structure induced by the correlation and the consequent enhanced distinction between the two alternate bonding structures. The SI stabilization energy ( $E_x$ ) increases to 0.42 eV. These results reproduce those presented originally by Voter.<sup>7,8</sup>

Now we expand the SOPP-correlated treatment to include more pairs. To measure the bent bond model meaningfully against the  $\sigma, \pi$  bond model, all  $C-C$  bond pairs need to be correlated. The SOPP treatment of the  $\sigma$  bonds (bond overlaps of 0.87) adds 0.30 eV/pair in correlation energy. The SI stabilization energy and structure overlaps do not change from the one-pair value, however. This is understandable as the two  $\sigma$  bonds are almost symmetrically equivalent, while the  $\pi$  bond is almost completely unaffected by correlation of the  $\sigma$  bonds. The net effect is a rigid shift of the reference energy level; the calculated SI parameters are unaffected.

Rather than as a  $\sigma$  and a  $\pi$  bond, the double bond in the single structure could be described as two bent bonds. For the case of three pairs, the SOPP bent bond, single structure wave function is 0.04 eV higher in energy than the  $\sigma, \pi$  bond analog. The bent bond orbitals have an overlap of 0.82, while the single C–C bond ( $\sigma$ ) orbitals have an overlap of 0.87, just as in the  $\sigma, \pi$  bond wave function. The resonance, however, is more effective, by 0.16 eV, in the bent bond representation, so the final SI result favors bent bonds by 0.12 eV.

Additional correlation of the five C–H pairs, while incorporating correlation energy into the individual structures, does not markedly affect the results of the SI calculations. The orbitals of the C–C bonds of the SOPP structures are essentially unchanged, and the calculated resonance energy for both  $\sigma, \pi$  and bent bond representations is slightly reduced. The bent bond model is favored by 0.10 eV over the  $\sigma, \pi$  bond model.

**Analysis.** While the best result does favor bent bonds, the conclusion concerning the optimal bonding model is not definitive. Important considerations have been neglected here that could affect the balance. First, the level of basis set used for the allyl radical did not employ polarization functions. For ethylene, the absence of carbon d-polarization functions biases the final result against the bent bond description by 0.06 eV (see paper 2).<sup>20</sup> If this bias extends to the double bond within the allyl radical, adding polarization functions will increase the 0.10-eV margin, favoring bent bonds. Second, according to the results of paper 1 in this series,<sup>19</sup> the constraints introduced by the use of the SOPP wave function instead of the more general IP wave functions impact the bent bond representation more strongly than the  $\sigma, \pi$  bond representation. This factor would also tend to widen the calculated energy difference. Third, self-consistent calculation of the total SI wave functions could conceivably benefit one of the bonding models more than the other.

Within the  $\sigma, \pi$  representation, results of self-consistent resonance calculations have been published.<sup>7,8</sup> Using a SOPP reference state with one pair, the C–C  $\pi$  bond, correlated, the self-consistent wave function (referred to as G-RVB<sup>7,8</sup>) is 0.34 eV lower than an SI calculation based on SOPP wave functions. Given the constancy of the results of the SI  $\sigma, \pi$  results, it is safe to assume that this value would carry over into calculations correlating the  $\sigma$  bond pairs. The bent bond SI stabilization energy would have to be augmented by  $-0.10 + 0.34 = 0.24$  eV in the self-consistent calculation of the resonating SI wave function in order to have a lower energy than the  $\sigma, \pi$  G-RVB calculation. It is plausible that the bent bond G-RVB stabilization energies would show a similar increase, but this remains to be shown.

In conclusion, the results for the allyl radical do favor a bent bond model of the bonding, but this conclusion cannot be regarded as definitive in light of the above concerns. A calculation examining, for even one molecule, the relative enhancement of the resonance energy *via* the G-RVB for the  $\sigma, \pi$  vs the bent bond representation would be highly desirable in order to gain a measure of the systematic bias incorporated into the analysis because resonance is not self-consistently treated. The allyl radical, because of its small size, would be a good candidate for such a study.

### Benzene and Resonance

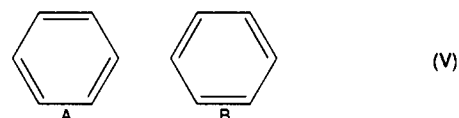
**Qualitative.** As the prototypical aromatic molecule and the canonical  $\pi$  electron system, benzene represents an important test of the bent bond model. Concentrating on the  $\pi$  electrons, the molecular orbital wave function consists of a doubly occupied  $a_{2u}$  orbital and four electrons in a doubly degenerate  $e_{1g}$  level:

$$\Psi_{MO} = \mathcal{A}[\Phi_{\sigma} a_{2u}^2 \alpha \beta e_{1g}^2 \alpha \beta e_{1g}^2 \alpha \beta e_{2u}^0 e_{2u}^0 b_{1g}^0] \quad (8)$$

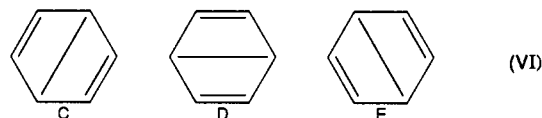
where the molecular orbitals are delocalized onto all the carbon centers. Unlike for the allyl radical, there is no spontaneous symmetry lowering if  $D_{6h}$  symmetry restrictions are removed—the

HF wave function retains its  $D_{6h}$  symmetry. Our calculated HF energy is in almost exact agreement with the results of Hay and Shavitt,<sup>18</sup> Levin,<sup>15</sup> and Voter<sup>8</sup> using essentially the same basis, so we can directly compare our results with the results of full  $\pi$ -CI and full  $\pi$ -GVB results and calculations incorporating the treatment of resonance self-consistently within the constraint of  $\sigma$ - $\pi$  separation.

Within the VB model, assuming  $\sigma$ - $\pi$  separation, the electronic structure of benzene is thought of as a covalently bonded network of  $sp^2$  carbon atoms involved in  $\sigma$  bonds along with six electrons in the  $\pi$  electron space. In the classical description, there is one electron in each of the  $p_x$  atomic orbitals,  $\pi_1$ – $\pi_6$ , of the six carbon atoms in the ring. Given six electrons, five independent singlet spin functions span the spin space. In benzene, the most familiar basis is composed of the two Kekulé structures [see (V)] we denote as A and B



and the three Dewar structures [see (VI)] we denote as C, D, and E



This is not the only basis possible to represent the possible spin couplings; it is merely one in which the spin relationships among the electrons are most physically transparent. The  $\sigma, \pi$  bond wave functions for the Kekulé structures can be written

$$\Psi_A = \mathcal{A}[\Phi_{\sigma} \pi_1^A \pi_2^A (\alpha\beta - \beta\alpha) \pi_3^A \pi_4^A (\alpha\beta - \beta\alpha) \pi_5^A \pi_6^A (\alpha\beta - \beta\alpha)] \quad (9a)$$

$$\Psi_B = \mathcal{A}[\Phi_{\sigma} \pi_6^B \pi_1^B (\alpha\beta - \beta\alpha) \pi_2^B \pi_3^B (\alpha\beta - \beta\alpha) \pi_4^B \pi_5^B (\alpha\beta - \beta\alpha)] \quad (9b)$$

where the bonding structures are related by a  $60^\circ$  rotation about the high-symmetry axis, and the Dewar structure  $\sigma, \pi$  bond wave functions can be written

$$\Psi_C = \mathcal{A}[\Phi_{\sigma} \pi_1^C \pi_4^C (\alpha\beta - \beta\alpha) \pi_2^C \pi_3^C (\alpha\beta - \beta\alpha) \pi_5^C \pi_6^C (\alpha\beta - \beta\alpha)] \quad (9c)$$

$$\Psi_D = \mathcal{A}[\Phi_{\sigma} \pi_2^D \pi_5^D (\alpha\beta - \beta\alpha) \pi_3^D \pi_4^D (\alpha\beta - \beta\alpha) \pi_6^D \pi_1^D (\alpha\beta - \beta\alpha)] \quad (9d)$$

$$\Psi_E = \mathcal{A}[\Phi_{\sigma} \pi_3^E \pi_6^E (\alpha\beta - \beta\alpha) \pi_4^E \pi_5^E (\alpha\beta - \beta\alpha) \pi_1^E \pi_2^E (\alpha\beta - \beta\alpha)] \quad (9e)$$

where the first singlet pair in each case describes the long bond across the ring.

Two independent alternatives exist to construct a totally symmetric ( $^1A_{1g}$ ) ground state: the coherent superposition of the Kekulé terms of eq 9a,b

$$\begin{aligned} \Psi_{A+B} &= \Psi_A + \Psi_B \\ &= \mathcal{A}[\Phi_{\sigma} \pi_1^A \pi_2^A (\alpha\beta - \beta\alpha) \pi_3^A \pi_4^A (\alpha\beta - \beta\alpha) \pi_5^A \pi_6^A (\alpha\beta - \beta\alpha)] \\ &\quad + \mathcal{A}[\Phi_{\sigma} \pi_6^B \pi_1^B (\alpha\beta - \beta\alpha) \pi_2^B \pi_3^B (\alpha\beta - \beta\alpha) \pi_4^B \pi_5^B (\alpha\beta - \beta\alpha)] \quad (10) \end{aligned}$$

and of the Dewar terms of eq 9c,d,e

Table II. Analysis of SOPP-SI Wave Functions for Benzene (E(HF) = -230.640 37 hartree)

wave function	SOPP energy (hartree)	SI energy (hartree)	$S_{11}$	$E_x$ (eV)	$T_x$ (eV)	$V_x^{\sigma-\pi}$ (eV)	$V_x^{\sigma-\sigma}$ (eV)
$\sigma, \pi$ Bonds							
3 pairs	-230.685 07	-230.697 01	0.8916	-0.325	-1.287	+1.464	-0.502
9 pairs <sup>a</sup>	-230.750 46	-230.762 36	0.8922	-0.324	-1.281	+1.459	-0.502
15 pairs	-230.837 87	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
Bent Bonds							
9 pairs <sup>a</sup>	-230.748 34	-230.777 52	0.9104	-0.794	-2.025	+1.941	-0.710
15 pairs	-230.835 27	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
15 pairs <sup>c</sup>	-230.834 45	-230.862 50	0.9252	-0.763	<i>b</i>	<i>b</i>	<i>b</i>

<sup>a</sup> Using SOPPCI(6) expansions to approximate SOPP wave functions to within  $\sim 10^{-5}$  h. <sup>b</sup> Not computed. <sup>c</sup> Using SOPPCI(4) expansion to approximate SOPP wave function.

$$\Psi_{C+D+E} = \Psi_C + \Psi_D + \Psi_E \quad (11)$$

so that the total VB ground state can be written as

$$\Psi^{VB} = c_k(\Psi_A + \Psi_B) + c_d(\Psi_C + \Psi_D + \Psi_E) \quad (12)$$

In the classical theory, all of the  $\pi_i$  are common to all five terms, *i.e.*, are atomic  $p_x$  orbitals, so eq 12 can be approximated as

$$\Psi^{VB} = \mathcal{A}[\Phi_{\sigma}\pi_1\pi_2\pi_3\pi_4\pi_5\pi_6\{c_k(\Theta_A + \Theta_B) + c_d(\Theta_C + \Theta_D + \Theta_E)\}] \quad (13)$$

In this representation of the wave function, the correlated electronic structure of the benzene  $\pi$  electron system can be expressed in an IP wave function that automatically describes the resonance in terms of a general spin coupling. The  $\Theta$  terms correspond to the spin functions resulting from reordering the electronic coordinates of eq 9 to put the  $\pi_i$  in the sequential order of eq 13.

The general form of the wave functions used in this study dispenses with the restriction that the bonding orbitals be segregated into separate  $\sigma$  and  $\pi$  symmetries. The wave function for the Kekulé structure A is

$$\Psi_A = \mathcal{A}[\Phi_{1s}\Phi_{CH}^A\Phi_{i=2,1}^A\Phi_{i=2,2}^A\Phi_{2-3}^A\Phi_{3=4,1}^A\Phi_{3=4,2}^A\Phi_{4-5}^A\Phi_{5=6,1}^A\Phi_{5=6,2}^A\Phi_{6-1}^A] \quad (14)$$

where  $\Phi_{1s}$  is the carbon 1s core orbital (with spin coordinates) taken from the HF calculations,  $\Phi_{CH}$  is the self-consistently derived orbitals describing the C-H bond electrons, and the remaining  $\Phi$  terms are two-electron functions describing the C-C bonds and, in general, take the form of SOPP pairs:  $\varphi_i\varphi_j(\alpha\beta - \beta\alpha)$ .  $\Phi_{i-j}$  corresponds to the orbitals describing the single bond between carbon *i* and carbon *j*, and  $\Phi_{i=j,l}$  correspond to pairs making up the double bonds of the Kekulé structures. In the  $\sigma, \pi$  bond description, the  $\Phi_{i=j,l}$  are all  $\sigma$  bonds and the  $\Phi_{i=j,2} = \pi_i\pi_j(\alpha\beta - \beta\alpha)$  are all  $\pi$  bonds between neighboring carbon atoms *i* and *j*. Alternatively, the  $\Phi_{i=j,l}$  are sets of equivalent double bent bond pairs between neighboring atoms:

$$\begin{aligned} \Phi_{i=j,1} &= \Omega_{1,i}\Omega_{1,j}(\alpha\beta - \beta\alpha) \\ \Phi_{i=j,2} &= \Omega_{2,i}\Omega_{2,j}(\alpha\beta - \beta\alpha) \end{aligned} \quad (15)$$

related by a reflection through the plane of the molecule. The alternate SOPP structure  $\Psi_B$  is generated by a 180° rotation of  $\Psi_A$ . Comparison between the two bonding models is done by using the SOPP references with equivalent pairs correlated in eq 14.

**Results.** The results obtained from the SI calculations for benzene are summarized in Table II. In the first set of calculations, the bond orbitals are segregated into orbitals of  $\sigma$  and  $\pi$  symmetries. The lowest level of SOPP correlation sustaining a resonating Kekulé description treats the six  $\pi$  electrons as three SOPP pairs. The SI calculation lowered the energy by 0.32 eV,

and the two SOPP structures having an overlap of 0.892. Our computed SI stabilization energy nearly matches a value obtained by Voter<sup>8</sup> ( $E_x = -0.33$  eV) constraining all  $\sigma$  orbitals to their HF forms. This is an indication that, within the approximation of  $\sigma-\pi$  separation, the resonance is essentially a  $\pi$  electron phenomenon independent of the  $\sigma$  electrons.

The nine-pair bent bond SOPP calculation yields an energy slightly higher than the  $\sigma, \pi$  bond calculation, by 0.06 eV, but, again, the resonance is more effective in the former, by 0.47 eV, so the final bent bond SI result is 0.41 eV superior to the  $\sigma, \pi$  bond SI result. The results of  $\sigma, \pi$  nine-pair SI calculations parallel the results of the three-pair calculations, supporting the conjecture made above regarding the independence of the  $\sigma$  and  $\pi$  electrons.

The bent bond and  $\sigma, \pi$  bond SOPP calculations correlating all 15 pairs are separated by 0.07 eV. Unfortunately, the 15-pair SI calculation was so large as to render the calculation of the Hamiltonian matrix element between the two structures computationally impractical using wave functions representing a good approximation to the full 15-pair SOPP wave function. Instead, a SOPPCI(4) wave function comprised of the 121 leading configurations in the canonical CI expansion of the bent bond SOPP wave function was used, yielding an energy within 0.022 eV of the SOPP wave function. The subsequent SI calculation finds an increased overlap and a reduced energetic stabilization with respect to the nine-pair SI calculation, but the differences are small, validating the conclusions regarding the bonding based on the nine-pair results.

**Analysis.** In this section we discuss factors neglected in the calculations and how they affect the conclusions regarding the preferred bonding description. The first factor in these calculations is the lack of d-polarization functions for the carbon atoms. In paper 2 of this series, the lack of polarization functions was seen to disproportionately impact the bent bond description. This is also seen here. Nine-pair SOPP calculations without polarization functions favor  $\sigma, \pi$  bonds by 0.057 eV. The addition of carbon d-polarization functions ( $\zeta = 0.75$ ) results in the bent bond model being favored by 0.018 eV, revealing a bias against bent bonds of 0.075 eV. However, because of these small differences, at the SOPP level of approximation the two descriptions are essentially indistinguishable.

The second factor playing a role is the non-self-consistent treatment of the resonance in our SI calculations. Voter<sup>8</sup> presented a self-consistent calculation (using the G-RVB method<sup>7b</sup>) of the  $\sigma, \pi$  SI wave function of eq 10, yielding a stabilization energy of 0.59 eV, increased from 0.33 eV using SOPP wave functions for the bonding structures. This is still 0.20 eV smaller than the SI stabilization in a non-self-consistent bent bond calculation.

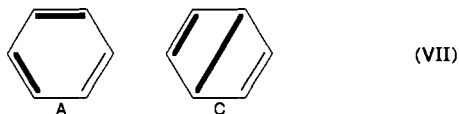
Relaxation of the SOPP restrictions within the single-structure wave functions, principally among the orbitals of each double bond, is a third factor. To estimate the differential stabilization of relaxing the SOPP restraints in the description of the double bonds in benzene, we performed model calculations on a  $C_2H_4$  molecule with the C-C distance extended to the benzene C-C distance, using the same basis set as in benzene. The calculations

applied the GVB-constrained-CI procedure (see paper 1) to the orbitals of a two-pair SOPP calculation, hence relaxing both the perfect pairing and strong orthogonality constraints on the wave function. The SOPP calculations favored the  $\sigma, \pi$  bond description by 0.24 eV. The GVB-CCI calculations for the double bond reduced this difference to 0.05 eV, indicating a bias of 0.19 eV. Adding carbon d-polarization functions ( $\zeta_d = 0.75$ ) to the basis set, the  $\sigma, \pi$  SOPP wave function is 0.18 eV lower in energy than the bent bond SOPP wave function. The subsequent GVB-CCI calculation reduced this difference to 0.05 eV, indicating a pro- $\sigma\pi$  bias in the VDZD basis of 0.12 eV. In the calculations of paper 1 in this series, the full-GVB bias was underestimated by the GVB-CCI calculations (due to the lack of self-consistency). The GVB-CCI bias for ethylene was calculated to be 0.12 eV and the GVB-SCF bias 50% larger, 0.18 eV. Applying this scaling to the current case, the effective pro- $\sigma\pi$  bias inherent in the benzene calculations due to the SOPP constraints within the double bonds is estimated to be 0.27 eV with the VDZ basis and 0.18 eV with the VDZD basis for *each* double bond.

The full self-consistent  $\pi$ -GVB calculations of Levin<sup>15</sup> gave a total energy of  $-230.709$  92 hartrees using a wave function of the form of eq 13, incorporating both the Kekulé and Dewar structures *without* any orthogonality restrictions among the  $\pi$  orbitals, but keeping the same set of orbitals for each structure. The energy obtained from that calculation is 0.68 eV lower than that from the three-pair SOPP reference energy above. This is 0.35 eV larger than the 0.32 eV of SI stabilization obtained from the SI calculation using the three-pair SOPP basis and also larger than the G-RVB stabilization of 0.59 eV with respect to SOPP.<sup>8</sup> Nonetheless, the bent bond result is still better by 0.06 eV (0.79-eV bent bond SI stabilization and 0.68-eV  $\sigma, \pi$  GVB stabilization, folding in the 0.06 eV that the bent bond SOPP description is disfavored by).

A final consideration is the issue of the importance of the Dewar bonding structures. These do not play a role in a bent bond picture but may in a  $\sigma, \pi$  bond description. As early as 1933, in a semiempirical VB calculation, Pauling had estimated that the Dewar structures were each about one-fifth as important as each of the Kekulé structures in a total SI wave function.<sup>23</sup> The magnitude of the importance of Dewar structures was later confirmed in *ab initio* GVB calculations.<sup>15,16</sup> Unfortunately, those studies did not quote results limited to the two Kekulé structures and so did not gauge the additional *energetic* importance of the Dewar structures. Toward this end, we obtained the three-pair SOPP  $\sigma, \pi$  bond Dewar structure of eq 9c. The energy of  $\Psi_C$  is  $-230.676$  02 hartrees, 0.26 eV higher than that of the three-pair Kekulé structure  $\Psi_A$ . Coherent resonance of the three Dewar structures as in eq 11 gives an energy of  $-230.691$  23 hartrees, 0.16 eV higher than that of the coherent Kekulé resonance. The mixture of all five structures in the total SI wave function of eq 12 gives no extra stabilization beyond that given by the Kekulé resonance, *i.e.*, the calculated energy was  $-230.697$  01 hartrees, unchanged from the two-structure SI wave function.

To understand this seemingly surprising result, consider the interaction between Kekulé and Dewar structures. One can think of it as a "reaction" between two bonds and four centers converting a Kekulé structure into a Dewar structure. For example, take  $\Psi_A$  of eq 9a and  $\Psi_C$  of eq 9c. In A, centers 1 and 2, and 3 and 4 are paired, while in C, 1 and 4, and 2 and 3 are paired. This four-center, four-electron reaction [see (VII)], manifested between



either Kekulé structure and any of the Dewar structures,

(23) Pauling, L.; Wheland, G. W. *J. Chem. Phys.* 1933, 1, 362.

constitutes a forbidden reaction,<sup>24</sup> *i.e.*, an interaction which is disfavored.<sup>25</sup> In paper 2, where an analogous situation existed among the four orbitals describing the C=C bond, the contribution of the subordinate spin coupling was negligible, and PP bonding coupling being totally dominant. In this case we have a bonding coupling, that given by the Kekulé structure, which is dominant, and a subordinate coupling, given by the Dewar structure, whose contribution is negligible.

The absolute limit of any  $\pi$  electron description is a full  $\pi$ -CI, as done by Hay and Shavitt,<sup>18</sup> who obtained an energy 1.04 eV lower than our three-pair SOPP. The bent bond SOPP + SI result obtains a lowering of 0.74 eV, only 0.30 eV short of this. The estimated pro- $\sigma\pi$  bias discussed above from the limitations of the basis set is 0.08 and 0.18 eV *per double bond* from the SOPP constraints. Hence, the bent bond model should be favored over the full  $\pi$ -CI, by  $\sim 0.3$  eV, *before* the extra stabilization in the bent bond model that a self-consistent treatment of the resonance would contribute is considered. This analysis indicates that the bent bond model within an IP + resonance framework is virtually certain to be better than *any*  $\pi$  electron description, much less one representable within an analogous IP + resonance framework. As with the allyl radical, this molecule is better described with bent bonds, and in this case this conclusion is unambiguous.

The calculations for the two examples considered to this point corroborate the conjecture made in the beginning regarding the relationship of  $E_x$  and the exchange kinetic energy. In the energy decompositions of Tables I–II, the calculated  $T_x$  correlates well with  $E_x$ . In general, the nuclear attraction contribution is a positive quantity, opposite to  $E_x$ , and  $V_x^{e-e}$  is either positive, as in the allyl radical, or negative, as in benzene. Taken in isolation, the benzene example might suggest that  $E_x$  correlates best with  $V_x^{e-e}$ ; taken in concert with the allyl radical example, it is clear that the kinetic energy operator is better associated with the SI exchange interaction. In each case, the exchange kinetic energy is larger than the total exchange energy, so the total exchange potential energy,  $V_x^{e-N} + V_x^{e-e}$ , is a slightly positive quantity.

#### C<sub>4</sub>H<sub>4</sub>: Square Cyclobutadiene and Resonance

**Qualitative.** The cyclobutadiene molecule is fascinating in many respects. C<sub>4</sub>H<sub>4</sub> is the smallest of the  $4n$ -electron  $\pi$  electron systems considered to be antiaromatic.<sup>26</sup> Unlike benzene, the symmetric (square) ring is unstable and the molecule distorts to a rectangular form. One study has ascribed a negative (destabilizing) resonance energy of 0.84 eV for the square structure,<sup>27</sup> though Voter calculates an  $E_x^{R-GVB}$  of 1.0 eV.<sup>8,28</sup> Molecular orbital theory fails, even in a qualitative sense, to describe the electronic structure. In a classic example of a violation of Hund's rule, MO theory predicts a triplet ground state for the square geometry, while experiment finds a rectangular singlet to be the ground state<sup>29</sup> and CI calculations find the singlet state to be more stable than the triplet at all reasonable geometries.<sup>30</sup> While valence

(24) Goddard, W. A., III. *J. Am. Chem. Soc.* 1972, 94, 793.

(25) The case of the square cyclobutadiene molecule, considered later, is a classic example of a "forbidden reaction" as the square structure is not the stable geometry. At the artificial square geometry, the resonance stabilization is computed to be rather large but does not act to stabilize the high-symmetry structure. The actual molecule distorts to a rectangular geometry, and the resonance rapidly disappears with that distortion. The prototypical forbidden reaction is H<sub>2</sub> + D<sub>2</sub>, where, if a square geometry is imposed, the "resonance" is large but disappears as the system distorts toward two diatomic molecules. The description of the relationship between the Dewar and the Kekulé structures is exactly analogous except that benzene is already distorted to the Kekulé geometry, and hence resonance with the Dewar structures is rendered ineffective and does not contribute *energetically* to the description of the molecule.

(26) Breslow, R. *Acc. Chem. Res.* 1973, 6, 393.

(27) Kollmar, H. *J. Am. Chem. Soc.* 1979, 101, 4832.

(28) Voter, A. F.; Goddard, W. A., III. *J. Am. Chem. Soc.* 1986, 108, 2830.

(29) Masamune, S.; Souto-Bachiller, F. A.; Michiguchi, T.; Bertie, J. E. *J. Am. Chem. Soc.* 1978, 100, 4889.

(30) Buencker, R. J.; Peyerimoff, S. D. *J. Chem. Phys.* 1968, 48, 354.

bond theory predicts a singlet ground state and also explains the nature of the distortion, *it has not explained why cyclobutadiene should distort and benzene should not*. It is these issues we shall address in the ensuing discussion of the electronic structure of  $C_4H_4$ .

In the MO description, one derives four molecular orbitals from the  $p_x$  orbitals of the four centers: the symmetric combination of the orbitals, of  $a_{2u}$  symmetry, a doubly degenerate level of  $e_g$  symmetry, and a  $b_{1u}$  level with a node between all neighboring atoms. The  $\pi$  electron system, with four electrons, has two electrons in the  $a_{2u}$  orbitals and the two remaining electrons are, according to Hund's rule, distributed one to each  $e_g$  orbital, and triplet coupled:

$$\Psi^{MO} = \mathcal{A}[\Phi_{\sigma} a_{2u}^2 \alpha \beta e_{gx}^1 e_{gy}^1 \alpha \alpha] \quad (16)$$

giving a total state of  ${}^3A_{2g}$  symmetry.

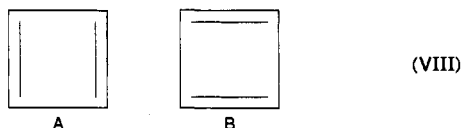
The lowest singlet has both  $e_g$  electrons in the same orbital:

$$\Psi_A^{MO} = \mathcal{A}[\Phi_{\sigma} a_{2u}^2 \alpha \beta e_{gx}^2 \alpha \beta] \quad (17)$$

but does not result in a state representable with the  $D_{4h}$  molecular point group. A minimum description for  $D_{4h}$  symmetry consists of two determinants:

$$\Psi_{A\pm B}^{MO} = \mathcal{A}[\Phi_{\sigma} a_{2u}^2 \alpha \beta (e_{gx}^2 \pm e_{gy}^2) \alpha \beta] \quad (18)$$

yielding an  ${}^1A_{1g}$  state for the symmetric and a  ${}^1B_{1g}$  state for the antisymmetric combination. Turning to the VB description, the  $\sigma, \pi$  representation of the bonding assigns one electron to the  $p_x$  orbitals  $\pi_1-\pi_4$  of each of the four centers. The natural coupling pairs orbitals on neighboring centers into singlets, giving  $\pi$  bonds. Two Kekulé-like structures [see (VIII)] are possible



whose wave functions can be written as

$$\Psi_A^{VB} = \mathcal{A}[\Phi_{\sigma} \pi_1^A \pi_2^A (\alpha\beta - \beta\alpha) \pi_3^A \pi_4^A (\alpha\beta - \beta\alpha)] \quad (19a)$$

$$\Psi_B^{VB} = \mathcal{A}[\Phi_{\sigma} \pi_2^B \pi_3^B (\alpha\beta - \beta\alpha) \pi_4^B \pi_1^B (\alpha\beta - \beta\alpha)] \quad (19b)$$

The VB ground states are the symmetric and antisymmetric combinations of these two, leading to a  ${}^1A_{1g}$  and  ${}^1B_{1g}$  states, respectively. There will also be a low-lying triplet state (see Voter and Goddard<sup>28</sup> for a more comprehensive discussion of the  $\sigma, \pi$  description of  $C_4H_4$ ).

The general form of the SOPP wave function used in this study to describe the individual bent bond structures is similar in spirit to that employed for benzene (*cf.* eq 14):

$$\Psi_A = \mathcal{A}[\Phi_{1s} \Phi_{CH}^A \Phi_{2-3}^A \Phi_{4-1}^A \Phi_{1=2,1}^A \Phi_{1=2,2}^A \Phi_{3=4,1}^A \Phi_{3=4,2}^A] \quad (20)$$

with the carbon 1s orbitals restricted to their HF forms. SI calculations are then used to generate the total wave functions:

$${}^1A_{1g}: \Psi_A + \Psi_B; \quad {}^1B_{1g}: \Psi_A - \Psi_B \quad (21)$$

and  $\sigma, \pi$  and bent bond models can be compared.

The ground state is known to be the antisymmetric  ${}^1B_{1g}$  combination of the resonance structures, but can we rationalize why this should be the case and why cyclobutadiene should be different from benzene in this respect? Voter constructs an elegant argument as to why this should be the case within the MO representation;<sup>28</sup> here we construct a qualitative argument in the spirit of the discussion above for the allyl radical to rationalize this order. Consider first the symmetric combination and, for the sake of convenience, adopt the  $\sigma, \pi$  representation of the bonding (as we shall see later, the same arguments apply to the

case of bent bonds) so that the structures are represented by the forms given in eq 19. Further, assume  $\pi_i^A = \pi_i^B$ . This is at least qualitatively correct. The symmetric  ${}^1A_{1g}$  SI wave function takes the form:

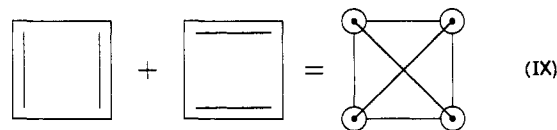
$$\begin{aligned} \Psi({}^1A_{1g}) &= \Psi^A + \Psi^B \\ &= \mathcal{A}[\Phi_{\sigma} \pi_1 \pi_2 (\alpha\beta - \beta\alpha) \pi_3 \pi_4 (\alpha\beta - \beta\alpha)] \\ &\quad + \mathcal{A}[\Phi_{\sigma} \pi_2 \pi_3 (\alpha\beta - \beta\alpha) \pi_4 \pi_1 (\alpha\beta - \beta\alpha)] \\ &= \mathcal{A}[\Phi_{\sigma} \{\pi_1 \pi_2 \pi_3 \pi_4 + \pi_2 \pi_3 \pi_4 \pi_1\} \times \\ &\quad (\alpha\beta - \beta\alpha)(\alpha\beta - \beta\alpha)] \quad (22) \end{aligned}$$

which, upon reordering of the electronic coordinates of the second spatial term to give a common order with the first term, yields

$$\Psi({}^1A_{1g}) = \mathcal{A}[\Phi_{\sigma} \pi_1 \pi_2 \pi_3 \pi_4 (-\alpha\beta\beta\alpha - \beta\alpha\alpha\beta + \alpha\alpha\beta\beta + \beta\beta\alpha\alpha)] \quad (23)$$

The physical interpretation of this is more transparent if the spatial terms are reordered to highlight the spin interactions of orbitals *across the ring* rather than of neighboring orbitals [see (IX)]:

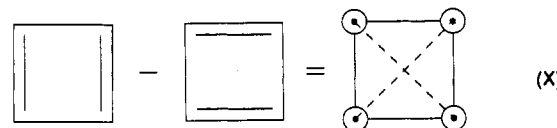
$$\Psi({}^1A_{1g}) = -\mathcal{A}[\Phi_{\sigma} \pi_1 \pi_3 \pi_2 \pi_4 (\alpha\beta\alpha\beta - \alpha\beta\beta\alpha - \beta\alpha\alpha\beta + \beta\alpha\beta\alpha)] \quad (24)$$



from which it is easily seen that  $\pi_1$  and  $\pi_3$  are singlet coupled and  $\pi_2$  and  $\pi_4$  are singlet coupled.

An analysis for the antisymmetric state [see (X)] parallel to that presented for the symmetric state in eqs 22-24 yields

$$\Psi({}^1B_{1g}) = \mathcal{A}[\Phi_{\sigma} \pi_1 \pi_3 \pi_2 \pi_4 (\alpha\beta\beta\alpha + \beta\alpha\alpha\beta + \alpha\alpha\beta\beta + \beta\beta\alpha\alpha - 2\alpha\alpha\beta\beta - 2\beta\beta\alpha\alpha)] \quad (25)$$

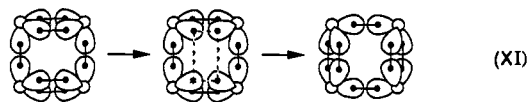


The orbitals across the ring, 1 and 3, 2 and 4, are triplet coupled, with the two triplets being coupled into an overall singlet.

The  ${}^1A_{1g}$  state of eq 24 giving pairs across the ring is patently less stable than the Kekulé structure pairing neighboring centers and hence will be an excited state. The kinetic energy will be reduced in this state, due to the extra delocalization allowed by the longer bonds. However, all four orbitals overlap in the same region of space, at the center of the molecule. This leads to strong e-e repulsions due to the Pauli exclusion principle and raises the total energy.

Consider the  ${}^1B_{1g}$  state of eq 25 instead. Triplet coupling of the long bond orbitals implies an increase in the kinetic energy, deriving from the nodes introduced into those triplet-coupled orbitals to keep them orthogonal. However, the electronic repulsion will be reduced in this state as no more than two electrons attempt to overlap the same region of space. This will be the ground state.

The same arguments apply to the bent bonded structure if one considers the hypothetical "reaction" process converting one Kekulé structure into another [see (XI)] so that the conclusions are the same regardless of the bonding representation. Interpreted in this light, the distortion of the  $C_4H_4$  molecule into the rectangular form is trivially understood; it can be thought of as being driven by the kinetic energy. The molecule will reduce



kinetic energy by increasing the separation between the triplet-coupled pairs. In much the same way that triplet  $H_2$  is unbound because of the kinetic energy and reduces the repulsive nature of the interaction by lengthening the distance between the atoms,<sup>31</sup> so, too, will the  $C_4H_4$  ring distort to separate the triplet-coupled atoms. The rectangular distortion simultaneously selects one more favorable Kekulé structure and reduces the kinetic energy pressure.

**Results.** In this section we examine more rigorously the validity of the analysis and present the results of the calculations discussed above. The results are presented in Table III. The first calculation is the single-determinant, singlet HF calculation (with no symmetry restrictions upon the orbitals), described by the wave function in eq 17. Unlike the case for benzene, this wave function lacks the full symmetry of the molecule, and an SI calculation is not redundant. The overlap is 0 (because of symmetry), but the SI stabilization amounts to a sizable 1.23 eV. Because the overlap is 0, the one-electron properties  $T_x$  and  $V_x^{e-N}$  remain unchanged and  $E_x$  is entirely attributable to changes in the  $e-e$  repulsions. Even with the SI calculation, the singlet state gives an energy higher than  $-153.59292$  hartrees, the energy of the  $^3A_2$  HF state of eq 16.

Keeping the  $\sigma-\pi$  separation for the moment, the correlation of  $\pi$  SOPP pairs,  $\Phi_{i=j,2}$ , yields an overlap of  $-0.25$  and a SI stabilization  $E_x$  ( $-0.90$  eV) reduced somewhat from the HF-derived value. The negative overlap in this structure can be understood by considering the overlap of the two Kekulé structures of eq 19, assuming that the  $\pi$  orbitals are all mutually orthogonal and the same for both structures. The overlap given by the spin coupling alone would be  $-0.50$ . Given that the orbitals do overlap and are not the same in both structures, the computed overlap will deviate somewhat from this value, but the general character of the interaction is sustained.

The correlation of additional  $\sigma$  bond pairs further demonstrates the  $\sigma-\pi$  independence. A calculation correlating all six C-C bonds generates the same SI parameters as the two-pair calculation. The six-pair SOPP calculation for the bent bond model is strongly disfavored with respect to the  $\sigma,\pi$  bond analog. The 0.59-eV difference is the most strongly pro- $\sigma\pi$  SOPP result found of all of the molecular systems considered. The calculated bent bond SI stabilization is 0.24 eV larger, but the final results still favor  $\sigma,\pi$  bonds by 0.35 eV. The overlap is much smaller than the  $\sigma,\pi$  bond value; it is still negative, but near 0.

**Analysis.** The biases against the bent bond picture discussed in the analysis of the bonding in benzene need to be almost totally effective in order to overcome the calculated deficit of 0.35 eV with respect to the  $\sigma,\pi$  bond picture. The SOPP constraints, with a bias of 0.18 eV per double bond, and the bias of  $\sim 0.1$  eV deriving from the limitations in the basis set taken together are slightly larger than the calculated difference between the calculated  $\sigma,\pi$  and bent bond energies. Hence, the two descriptions can probably be thought of as equally good descriptions of the electronic structure for this artificial molecule.

A breakdown of the SI stabilization energy  $E_x$  confirms the qualitative analysis presented earlier. Indeed, the exchange kinetic energy, in contrast to the case for other resonating molecules, shifts in a direction opposite the SI stabilization, *i.e.*, is destabilizing. This lends credence to the idea that antiaromaticity can be associated with an unfavorable delocalization of electrons, providing quantitative evidence for this point of view with use of correlated wave functions. The contrast of  $T_x$  and  $E_x$  highlights the source of the difficulty in categorizing the nature of the

resonance energy in cyclobutadiene: whether the resonance energy is destabilizing<sup>27</sup> or stabilizing.<sup>28</sup>  $E_x$ , the SI stabilization energy, is, by definition, stabilizing with respect to the single-structure calculation. The delocalization energy  $T_x$ , frequently associated with resonance, is destabilizing. Hence, the resonance is *both* destabilizing and stabilizing; the nature is dependent on the *definition of what is meant by resonance*. This confusion does not usually arise as the two definitions above normally coincide. Because of the unusual nature of this molecule, the two definitions here diverge.

### Calculated and Empirical Resonance Energies

How well do the energetics of the SI calculations correspond to empirical resonance energies? Table IV summarizes our results. Except for  $C_4H_4$ , we adopt Pauling's definition of the resonance energy.<sup>5</sup> The  $\sigma,\pi$  SI stabilization values are consistently lower than the bent bond values and even more strongly underestimate the empirical values of the resonance energies. Even self-consistent SI calculations for  $\sigma,\pi$  bonds due to Voter<sup>8</sup> obtain energies falling far short of the empirical values. For comparison, we also include the values obtained by Levin in GVB calculations.<sup>15</sup> The SI stabilization values for the bent bonds are better than the  $\sigma,\pi$  values but still are, on average, roughly half the empirical values. That the calculations do not reproduce the empirical resonance energies would appear to indicate that SI calculations, despite the fact that they represent the quantum mechanical expression of chemical resonance, are not a quantitative representation of that resonance.

Furthermore, other important factors<sup>32</sup> have been left out of the above comparisons. In particular, our computed resonance energies correspond to a "vertical" resonance that does not take account of the "compression" energy relating the geometry of an idealized nonresonating structure with the actual geometry of the molecule. For the case of benzene, this compression energy amounts to 1.6 eV.<sup>32</sup> The inclusion of this and other effects<sup>14,32</sup> further accentuates the disparity between the results of the SI calculations and the empirical resonance energies.

Nonetheless, a more careful analysis of our results reveals better parallels between the calculations and empiricism. First, evaluation of the change in the total kinetic energy with the SI calculation,  $T_x$ , finds that this quantity actually correlates rather well with the empirical resonance energy. This is also the case for  $C_4H_4$  if one adopts Kollmar's definition of the resonance energy. Second, the bent bond SI calculations do not incorporate the resonance self-consistently and therefore will underestimate the stabilization energy as two factors come into play. The final SI wave function would be lower in energy, as it is self-consistently derived, and the single structure reference will be higher in energy, as the full-GVB single structure reference will differ from the SOPP-SCF single structure reference. The calculated bent bond SI stabilization energies would reproduce the empirical values rather well if the full-GVB augmentation scales similarly to those for the  $\sigma,\pi$  bonded benzene reported by Voter.<sup>8</sup> Although it has not been our purpose in this paper to establish a quantitative scheme for reproducing resonance energies, particularly in light of the above limitations, our results clearly demonstrate that the only realistic path to achieving this goal lies within a bent bond representation of the bonding.

### Summary and Conclusions

The nature of the bonding within the IP + resonance picture has been quantitatively examined. The results of the calculations support the following conclusions.

**(1) Bent Bonds Are Better.** In the previous papers of this series, it was shown that if restrictions on the most general IP wave function are relaxed, the bent bond model emerges as the

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Table III. Analysis of SOPP-SI Wave Functions for Square Cyclobutadiene

wave function	energy (hartree)	SI energy (hartree)	$S_{II}$	$E_x$ (eV)	$T_x$ (eV)	$V_x^{e-N}$ (eV)	$V_x^{e-e}$ (eV)
$\sigma, \pi$ Bonds							
HF	-153.539 59	-153.584 85	0.0000	-1.232	+0.000	-0.000	-1.232
2 pairs	-153.620 06	-153.653 18	-0.2491	-0.901	+1.609	-5.003	+2.492
4 pairs	-153.647 07	-153.685 11	-0.2454	-1.035	+1.310	-4.728	+2.383
6 pairs	-153.672 10	-153.705 15	-0.2486	-0.899	+1.611	-5.017	+2.507
Bent Bonds							
4 pairs	-153.626 17	-153.668 96	-0.0563	-1.165	+0.701	-2.223	+0.880
6 pairs	-153.650 58	-153.692 45	-0.0560	-1.139	+0.858	-2.920	+0.923

Table IV. Comparison of Calculated SI Stabilization Energies and Empirical Values (in eV)

mole- cule	$E_{res}$ (empirical)	bent bonds		$\sigma\pi$ bonds		$E_{SI}^{SI-SCF}$	
		$E_x$	$T_x$	$E_x$	$T_x$	$-E^{SOPP}{}^a$	$E_x^{GVB}{}^b$
$C_6H_6$	-1.60	-0.79	-2.03	-0.32	-1.28	-0.59	-0.91
$C_4H_4$	+0.84 <sup>c</sup>	-1.16	+0.70	-0.90	+1.61	-0.94	
$C_3H_3$	-1.08	-0.56	-1.25	-0.42	-0.83	-0.77	-0.49

<sup>a</sup> From the G-RVB calculations of Voter (ref 8). <sup>b</sup> From the  $\pi$  GVB-SCF calculations of Levin (ref 15). <sup>c</sup> Using Kollmar's definition of resonance energy (ref 27).

preferred orbital description of the bonding. The results of this study give compelling evidence that the bent bond model is also an excellent basis with which to understand the bonding in systems where a single IP wave function is not the best means to represent the bonding, but rather the bonding is best described as the interaction of a small number of different bonding structures.

**(2) Valence Bond Resonance as Kinetic Energy.** The nature of resonance, in the valence bond sense, has been quantitatively shown, with use of explicitly correlated *ab initio* wave functions, to be intimately intertwined with the kinetic energy. Viewed from this perspective, the destabilizing nature of the resonance in cyclobutadiene is easily understood and provides a simple rationale for the physically observed rectangular distortion.

**(3) Empirical Resonance Energies May Be Calculable Quantities.** Unlike the  $\sigma, \pi$  bond model calculations, which, even if they produce good energetics, systematically fail to reproduce the features of the resonance empirically observed,<sup>8</sup> the bent bond basis may offer a vehicle by which valence bond resonance theory can be given a full quantitative expression from *ab initio* calculations. A self-consistent derivation of the SI wave functions would be necessary to accomplish this goal, but the non-self-consistent values are already very good. Thus, the reservation of Pauling to the effect that resonance is purely an empirical theory<sup>5</sup> may prove to be premature.

These results augment the classes of systems for which the bent bond model provides a simple consistent description of the electronic structure. Together with the GVB results favoring bent bonds for ethylene and acetylene presented in paper 1 of this series, all the classic examples of the  $\pi$  electron canon have been quantitatively shown to be better represented in a bent bond representation than in a  $\sigma, \pi$  bond representation.

**Acknowledgment.** This work was supported in part by the National Science Foundation MRL Program under Grant DMR-8519059 at the Laboratory for Research on the Structure of Matter, University of Pennsylvania.