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Bonding in Cyclopropane

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Abstract: A new technique is introduced for optimization of valence-bond wave functions; this consists of evaluating energy derivatives with respect to orbital coefficients and applying a steepest descent algorithm. Application to cyclopropane predicts a bonding structure of D_{3h} symmetry with three equivalent C–C bonds. The C–C bonds are localized between each two carbon atoms and are bent with orbital amplitude concentrated outside the ring. The bonding picture in cyclopropane is compared to ethylene, ethane, and diborane.

1. Introduction

Few will disagree that explanation of molecular properties (such as geometry and charge distributions) and behavior (such as molecular dissociations and reactions) in terms of orbitals has proven to be extremely fruitful. Chemists base much of their intuition about chemical systems and explanation of chemical phenomena on the idea that electrons in molecules and atoms can be described as being in independent, one-particle states called orbitals.[1] An independent particle wave function is an approximation which is extremely useful for discussing the electronic structure of atoms and molecules. An optimized independent particle wave function is one in which each orbital is the best orbital for an electron in the field of the nuclei and the averaged electron repulsion of the other electrons in the molecule.[2,3] Although powerful computers employing sophisticated computational techniques make it possible to go far beyond this independent particle approximation in the quantitative calculation of specific molecular properties (e.g., energy, geometry, electronic moments, polarizabilities), orbitals continue to be invaluable for real understanding and comparison, as opposed to just generating numbers. Even as chemists improve their ability to calculate accurate wave functions and molecular properties, there is still a fundamental need for an approach which yields a wave function that can be decomposed into simple parts that can aid understanding.

Historically, mainly because of its computational convenience, the molecular orbital or Hartree–Fock (HF) method has been the most widely used independent particle model for calculating atomic and molecular orbitals. While the HF form of the wave function has proven to be very useful in building several aspects of the intuition and understanding of chemists, it does have shortcomings. Valence-bond (VB) theory uses an alternative wave function which is more accurate than the HF function, yields unique orbitals (see below), and, using the perfect pairing approximation, retains the independent particle interpretation.[3] So for our study of the electronic structure of cyclopropane, we adopt a VB point of view.

Cyclopropane is an interesting molecule because of the significant challenge that it has provided for chemical theory. When one considers that its C–C–C internuclear angles are 60°, it has anomalously low strain energy. It is also puzzling that its C–H bond vibrational frequencies resemble olefins much more closely than alkanes. Furthermore, cyclopropane undergoes addition reactions in a similar manner to ethylene.[4] Trying to understand and explain these unusual chemical properties, in addition to describing the bonding scheme in a molecule with such acute bond angles, has occupied chemists for years.[5-7]

All sorts of theoretical treatments have been performed on cyclopropane. The form of the orbitals and the nature of the bonding have been a matter of discussion since at least 1949. In some of the earliest speculation, Walsh adopted an HF viewpoint and suggested that the principal bonding results from the overlapping of three sp^2 hybrids (one on each carbon) pointing toward the center of the ring: a three-center two-electron bond.[8] In 1965 Hoffmann[9] carried out an extended-Hückel (approximate HF) treatment on cyclopropane and found just the sorts of orbitals that Walsh predicted.

Also in 1949 but taking a VB approach, Coulson and Moffitt[10] constructed C–C bonds from s–p hybrids containing one adjustable parameter that determined their direction. By applying the variation method in an approximate way, they concluded that the bonding consisted of three equivalent single bonds. Each of their hybrids pointed 22° outward from the internuclear line forming bent bonds. This result is surprisingly similar to the prediction of the maximum overlap hypothesis which simply chooses those (minimum basis) hybrids that have the largest intrapair overlap.[11]

The first ab initio HF treatment of cyclopropane was carried out by Newton et al.[12,13] Their canonical HF orbitals provide a delocalized bonding picture consisting of a doubly occupied completely symmetrical (a_1') orbital and a degenerate e′ pair of orbitals. The symmetrical orbital is just the orbital that Walsh hypothesized years earlier. Newton et al. transformed their wave function to obtain localized HF orbitals according to the criterion of maximum self-repulsion energy[14] of Edmiston and Ruedenberg. The localized HF bonding orbitals turn out to be three equivalent bent bonds that agree quite closely with the picture of Coulson and Moffitt. The localized HF orbitals are $sp^{3.81}$ hybrids which have a calculated interorbital angle of 116° and show a concentration of orbital amplitude outside of the ring.

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[1] One could consider that electrons are in two-particle states because orbitals can be doubly occupied. We include the spin and hence consider each electron to be in a unique one-particle state (also called a spin-orbital).

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The situation just described is typical of HF predictions. The canonical orbitals give a delocalized picture of the electronic structure, and the localized (transformed HF) orbitals give a localized picture. Remember, the total HF wave function is unchanged by this transformation, so the HF method cannot provide a unique (and unequivocal) answer to questions concerning the nature of the bonding and the orbitals in molecules. The VB method, on the other hand, is well suited for such a study because its orbitals are determined solely by minimization of the energy. To date there have been some VB-type calculations on cyclopropane, but these have all used small basis sets; many have been semiempirical,[15,16] arbitrary in the way hybrids were constructed, and have imposed artificial constraints (such as orbital orthogonality) on the wave function.[10,15,16] This state of affairs creates the ideal situation for a modern self-consistent-field (SCF) VB study to be beneficial in adding to current understanding.

2. Calculational Procedure

The very same features of a perfect-pairing VB wave function that generate its improved orbital interpretation enormously increase the computational difficulty of optimizing the VB orbitals and computing the properties of that wave function. Once one goes beyond describing each electron pair as a doubly-occupied HF-type orbital $(\phi\phi)(\alpha\beta-\beta\alpha)$, one gives up the mathematical simplifications (orbital orthogonalities) that arise from the HF approximation. A VB electron pair is written as a "split pair" $(\phi_a\phi_b)(\alpha\beta-\beta\alpha)$ which represents two electrons occupying orbitals that are separately optimized, but whose spins are coupled into a singlet just as the spins of the HF pair. A full SCF optimization for a VB wave function is only possible for about eight electrons.[17,18] In order to study larger molecules, either additional simplifying restrictions must be imposed[18,19] or approximate wave function optimization schemes such as the OTTO method must be considered.[18,20–22] We present our new approach by comparison to the OTTO optimization scheme, so we first describe that method.

During the optimization of pair number 1 in a VB wave function, the most important effect of the other electron pairs enters through their electron repulsion interactions. The OTTO method assumes that the electron repulsion potential arising from a pair of electrons is not sensitive to whether that pair is described as a split pair or a doubly occupied pair. So, for the optimization of pair 1, all other pairs are replaced by their best-fit doubly occupied orbitals. All of those doubly occupied orbitals can then be orthogonalized to one another, thereby attaining considerable computational simplification in the SCF optimization step. By sequentially splitting each VB pair, the entire wave function can thus be optimized.

However, the steps just described do not optimize the overlaps between the orbitals of different VB pairs. In the OTTO procedure, those overlaps are optimized in another sequence of iterative steps.[21,22] The resulting method has been shown to give accurate VB wave functions in many examples. Despite its successes, there are situations where OTTO has difficulties. As with most SCF procedures, there is no guarantee that the energy will decrease at each step in the iterative cycle, and examples have been found where the energy increases for the last several iterations. The apparent reason for this is that the overlap optimizations partially undo or interfere with the SCF optimizations. Another important shortcoming of the OTTO procedure is that it often has much trouble converging. It is not uncommon for the procedure to oscillate or to converge so slowly as to be impractical to use. In many of these instances, a converged solution can be coaxed from the programs, but this requires much help from an experienced user.

In order to remedy some of these shortcomings, we have implemented a steepest descents minimization scheme that guarantees that the energy will go down with each step. The energy expression is written as a function of the coefficients of the basis functions in each VB orbital: $E(C_{\mu,i})$, where μ is the basis function index and i the orbital index. Steepest descents is based on the idea that the gradient of a function indicates the direction of greatest increase in the value of the function. Therefore, the gradient of the energy expression $(\partial E/\partial C_{\mu i})$ is found and the orbitals are changed in the direction opposite to this gradient. Because the gradient is a local feature, a stepwise procedure is required. Repeated calculations of the gradient and minimization along that direction are required to find the true minimum. Unlike an SCF approach, the steepest descent method requires many calculations of the energy throughout the minimization. This is an especial drawback because computation of the VB energy is costly,[20,21] but the disadvantage is outweighed by the guarantee of obtaining a lower energy at each step. The energy in a steepest descent optimization cannot oscillate as has been observed in the OTTO scheme. Steepest descents forms the starting point for optimization schemes with better convergence properties (such as the Davidon–Fletcher–Powell method or the Fletcher–Reeves method) if those are required in the future.[23]

The implementation of the steepest descents method is inspired by work of Yaffe and Goddard[24] who consider each cycle in the optimization of orbitals to be a rotation of the coefficient matrix. Instead of varying the orbitals sequentially during the optimization, one accumulates each change into a net rotation which is then applied to all the orbitals at once. In their approach, the optimum orbitals ϕ_i are expressed as $\phi_i = \sum_j \mathbf{T}_{ij}\Psi_j$, where Ψ_j are the initial guess orbitals, and $\mathbf{T}$ is the rotation matrix which optimizes the orbitals in one step. The optimization steps of OTTO or of a steepest descents method are rotations of the coefficient matrix, and, in general, these rotations do not commute. Infinitesmal rotations do commute, however, and so we have adopted the following generalization of the OTTO procedure with the aim of optimizing each VB pair in the electron repulsion potential of the other pairs, and optimizing the orbital overlaps as well. We take the specific example of a six-electron molecule; its VB wave function is written

$$\Psi = \mathcal{A}(\phi_{1a}\phi_{1b} + \phi_{1b}\phi_{1a})(\phi_{2a}\phi_{2b} + \phi_{2b}\phi_{2a})(\phi_{3a}\phi_{3b} + \phi_{3b}\phi_{3a})\alpha\beta\alpha\beta\alpha\beta \quad (1)$$

where $\mathcal{A}$ is the antisymmetrizer. Consider the optimization of pair 1. The optimization of the overlaps of the orbitals of pair 1 with those of pair i require that both those pairs be split. So we are led to consider the set of functions:

$$\Psi = \mathcal{A}(\phi_{1a}\phi_{1b} + \phi_{1b}\phi_{1a})(\phi_{2a}\phi_{2b} + \phi_{2b}\phi_{2a})\chi_3\chi_3\alpha\beta\alpha\beta\alpha\beta$$

$$\Psi = \mathcal{A}(\phi_{1a}\phi_{1b} + \phi_{1b}\phi_{1a})\chi_2\chi_2(\phi_{3a}\phi_{3b} + \phi_{3b}\phi_{3a})\alpha\beta\alpha\beta\alpha\beta \quad (2)$$

χ_i represents the best doubly occupied orbital to reproduce the charge density of the ith pair; just as in the OTTO method, these "doubly occupied sea" orbitals are taken to be the primary natural orbitals of the VB pairs.[20–22] For the optimization of pair 1, we must consider all the wave functions with pair 1 and one other pair split (the two functions of eq 2). For the complete optimization of all pairs, we must consider all the wave functions

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Table I. Cyclopropane Energies

method	energy (hartrees)	comments
HF	-117.073 503 1	
GVB	-117.240 308 3	
OTTO (converged)	-117.255 548 6	iteration no. 56
OTTO (lowest)	-117.255 552 4	iteration no. 25
steepest descents	-117.255 568 1	9 complete cycles

with two pairs split. In the simple case of six electrons, this entails only one additional function:

$$\Psi = \mathcal{A}\chi_1\chi_1(\phi_{2a}\phi_{2b} + \phi_{2b}\phi_{2a})(\phi_{3a}\phi_{3b} + \phi_{3b}\phi_{3a})\alpha\beta\alpha\beta\alpha\beta$$

Energy gradients for the coefficients of ϕ_{1a} and ϕ_{1b} are computed for each of the simplified functions with pair 1 and one other pair split and are combined to find an overall gradient for pair 1. The same procedure is followed for all the other pairs. This procedure generates multiple evaluations of each of the energy derivatives. These can be considered to be multiple rotations of the coefficient matrix; the rotations will not all be about the same axis, and the individual rotations cannot be expected to commute. Thus, the individual rotations are scaled to be sufficiently small before they are combined so that overall rotation is independent of the order of application of the individual steps. Finally the overall rotation is scaled up again and used as the gradient direction in the steepest descent minimization.

3. Results

All our cyclopropane calculations used the same optimized double-ζ plus d orbital basis set of Slater-type orbitals.[25] The exponents of a double-ζ basis were optimized using the HF energy; then a set of 3d orbitals was added to each carbon atom. The exponent of the d functions was taken from a fully optimized double-ζ plus d basis for the ethane molecule. Stevens' POLYCAL program was used to compute the integrals and perform the HF calculations.[26] All calculations used the experimental cyclopropane geometry[27] with bond lengths C–C (1.510 Å), C–H (1.089 Å), and bond angles H–C–H (115.1°) and C–C–H (117.7°).

The energy and wave function for cyclopropane were computed using the HF, GVB[19] (strongly-orthogonal VB), OTTO, and present methods. Results are summarized in Table I. As expected, relaxing the strong orthogonality constraint allows OTTO to produce a lower energy wave function than the GVB procedure. Again as expected, the steepest descent method finds a lower energy than OTTO. It is worth noticing that the lowest energy wave function found during the OTTO iterations was not at convergence (for the coefficients), but 31 iterations back! The change in the energy is not significant, but those iterations represent a substantial amount of computer time.

The performance of the present method indicates that the procedure is working by taking the energy down at each step, but it works slowly, costing 16 h of VAX station 3540 cpu time per cycle. In order to minimize the computation time, the lowest energy OTTO wave function was taken as the starting point for the steepest descent cycles. The method could probably benefit from a more sophisticated minimization procedure.[23]

VB Picture of Cyclopropane. The VB picture of cyclopropane consists of three inner shells, three equivalent C–C bonds forming the ring, plus six equivalent C–H bonds. Figures 1 and 2 show contour plots of the two orbitals which overlap to form one C–H bond. While there is no proof of the relationship, it is generally believed that the bond strength increases as the overlap of the two orbitals in a VB pair. The overlap of the two orbitals forming the C–H bond is 0.833 which indicates a very strong bond (see below). The orbital hybridization, determined by angular projection without truncation,[28] gives the average hybridization of the carbon orbital (in Figure 1) forming the C–H bond to be $sp^{1.348}$.

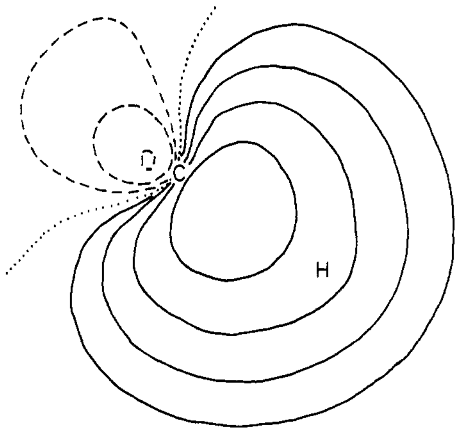

Figure 1. Cyclopropane C–H bond carbon orbital plotted in a plane perpendicular to the carbon ring. In all the plots, negative contours are dashed and the node is dotted.

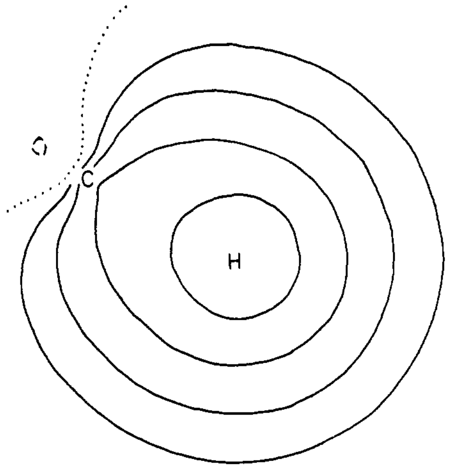

Figure 2. Cyclopropane C–H bond hydrogen orbital plotted in a plane perpendicular to the carbon ring.

Figures 3 and 4 show contour plots of the two orbitals that are paired to form one of the C–C bonds in cyclopropane (with an overlap of 0.827). The plots indicate that the C–C bond is well localized between two carbon atoms, and that the constituent orbitals do not point directly toward their bonding partner (i.e., the bond is bent). Calculation of the hybridization gives $sp^{1.706}$ with minimal d orbital participation ($d^{0.041}$) and higher angular momentum components that are vanishingly small.

Bent Bonds. As Coulson and Moffitt pointed out many years ago, the CCC angle of 60° (we call this the internuclear angle) in cyclopropane does not necessitate the same angle between the orbitals making up the C–C bonds (we call this interorbital angle the "bond angle").[10] Since then, a variety of techniques have been used to ascertain a bond angle. Coulson and Moffitt obtained 104° using simple VB hybrids formed only from s and p orbitals on one center. The original application of the maximum overlap method predicted the same result,[11] but an improved study[15] predicted 102°. The localized HF orbitals[12] point 116° from one another. Coming from a very different perspective, several authors[29-31] have chosen to analyze the total electron density and

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(25) Exponents are: for H 1s (0.946, 1.430), for C 1s (5.145, 7.658), 2s (1.315, 1.612), 2p (1.456, 3.075), 3d (2.170). Subsequent analysis showed that optimizing the d-orbital exponent changed its value from 2.170 to 2.060. This lowered the HF energy by only 0.000 25 hartree.

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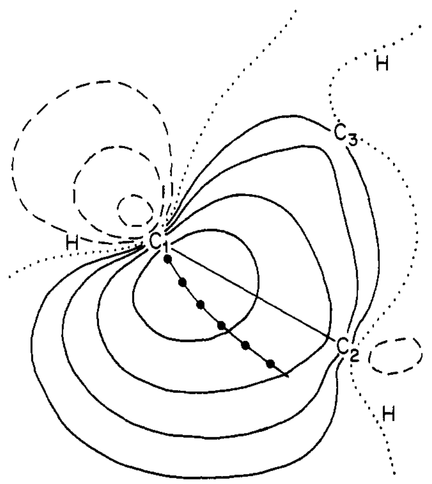

Figure 3. Carbon 1 orbital of the C_1–C_2 bond in cyclopropane plotted in the plane of the carbon ring. The bond path is shown as (●–●) compared to the internuclear line.

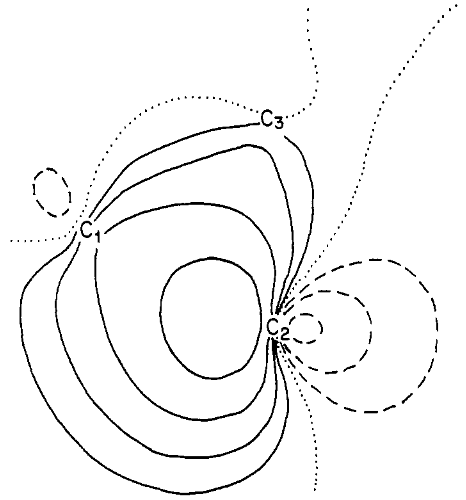

Figure 4. Carbon 2 orbital of the C_1–C_2 bond in cyclopropane plotted in the plane of the carbon ring.

define the bond as the maximum electron density path between two bonded nuclei. This approach predicts a curved bond and smaller bond angles. Depending on the basis set and the specific definitions used, the bond angle ranges from 96° (minimum basis[29]) to 79°. Because the C–H bonds and the inner shells make large contributions to the total electron density especially near the atomic nuclei, it is to be expected that analysis of the total density will lead to very different results from an analysis of the individual bonding orbitals. We prefer to base our study on the independent particle VB bond orbitals, and either to define the bond direction to be the direction at the maximum of the bond density or to take an average over the important region of the bond.

Because Figures 3 and 4 clearly show that the C–C bond is bent, it is not obvious how to define a bond angle. It is reasonable to define a bond to lie along the maximum of the orbital. Then, because the optimum VB orbitals are formed from many basis functions on many centers, each of which has different radial and angular behavior, the bond direction depends upon the distance from the center of interest. In other words, the bond is curved.[29-32] At each distance, the bond direction can be defined as the direction of the maximum orbital amplitude. If only s and p angular momentum components make significant contributions to an orbital (the case in cyclopropane), the bond direction at a given distance from the center of interest is given by the hybridization coefficients. (The s contribution is spherical, so the bond direction is simply the arctangent of the ratio of the p_x contribution to the p_y contribution.) Representative points from the radial hybridization analysis for the C–C bonds are given in Table II along with the resulting bond direction. The bond direction, according to this definition, is also plotted in Figure 3. Included in Table II is the radial distribution function ρr^2 which determines the relative importance of the orbital at each particular r. (ρ is the electron density integrated over angles.) As can be seen in Figure 3, the bond is clearly bent starting with an angle of 123° at the carbon nucleus and decreasing smoothly through the important region near the maximum of the bond orbital where the angle is 113°. The angle continues to decrease slowly at farther distances. An average bond angle could be computed by weighting with the radial distribution function. That average depends somewhat on the upper limit of integration; if the integral is extended to infinity, the average angle is 110°.

Ring Strain. It is well known that the strain energies in cyclopropane and cyclobutane are very similar even though, from a geometrical point of view, cyclopropane should have significantly more strain energy.[5,6,13] Many theoretical studies have attempted to explain this anomaly by such electronic effects as C–H bond strengthening,[10,12,33] bent bonds,[10,12,31,34] and three-center bonding in the cyclopropane ring.[12,33-36] We will analyze these questions from the viewpoint of our VB wave function which, we repeat, is determined solely by energy minimization with no imposed constraints on the orbitals. Strain in cycloalkanes is often calculated from thermochemical data by subtracting $n\Delta H^{\circ}_{\text{alk}}$ from the heat of combustion of the cycloalkane, where $\Delta H^{\circ}_{\text{alk}}$ (=157.4 kcal/mol) is the average heat of combustion per CH_2 group in noncycloalkanes and n is the number of CH_2 groups in the cycloalkane.[6] Strain energies turn out to be 27.7 kcal/mol for cyclopropane and 26.3 kcal/mol for cyclobutane.

C–H Bond Strengthening. The procedure just used for computing the strain energy assumes that the strength of C–H bonds is the same for all hydrocarbons. As has been pointed out, there is much experimental and theoretical evidence to support the idea that the C–H bond in cyclopropane is stronger than in other alkanes.[5] This C–H bond strengthening is significant because it would tend to compensate for some of the ring strain (Bayer strain) in the molecule by lowering the energy of the entire molecule.

Theoretical support for the idea of C–H bond strengthening has been sought by looking for hybridization differences between the C–H and C–C bonds of cyclopropane as compared to other alkanes. Because carbon's 2s orbital is lower in energy than its 2p's, it is presumed that larger s character in a bond means a stronger bond. Discovery of such a phenomenon would lend theoretical corroboration to the idea that the C–H bond in cyclopropane is indeed different from normal alkanes.[12] Using orthogonal VB hybrids, Coulson and Moffitt[10] found that the optimum hybrids for the C–C bonds in cyclopropane are enriched in p character, being $sp^{4.1}$ compared to Pauling's sp^3 for alkanes. p enrichment is also found in the localized HF calculations[12] which give a C–C hybridization of $sp^{3.8}$. But remember that these methods use orthogonal hybrids in addition to constraints on the composition and number of hybrids. That requires the total amount of s (or p) character on one center to remain constant, so an increase in the p character in the C–C bond necessitates an increase in s character in the C–H bonds—and hence an increase in their strength. Thus in Coulson and Moffitt's calculations, the p enrichment of the C–C bonds led to enhanced

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Table II. Compositioin of One C–C Hybrid Orbital: Percentage Composition, Radial Density, and Bond Angle as Functions of Distance from C[a]

r (au)	s	p_x	p_y	total d	ρr^2	interorbital angle,[b] deg
0.05	89.59	3.66	6.75	0.00	0.0009	123
0.20	37.70	22.09	40.18	0.02	0.019	122
0.40	33.11	24.02	42.77	0.10	0.12	121
1.00	41.10	22.35	36.06	0.49	0.54	116
1.25	41.21	23.08	35.00	0.72	0.58[c]	113
1.60	39.17	25.27	34.36	1.20	0.52	107
2.00	34.89	28.72	34.28	2.11	0.38	100

[a] The C–C bond length is 2.853 au. [b] Calculated from the relative amounts of p_x and p_y (see text). [c] This is the maximum of ρr^2 which occurs at 44% of the bond length.

Table III. Hybridizations

	cyclopropane	ethylene[a]	methane[b]	ethane[c]
C–C bond	$sp^{1.706}$	$sp^{1.370}$		$sp^{1.381}$
C–H bond	$sp^{1.348}$	$sp^{1.561}$	$sp^{1.514}$	$sp^{1.524}$

[a] Reference 39. [b] Reference 37. [c] Reference 38.

Table IV. Intrapair Overlaps

	cyclopropane	ethylene[a]	methane[b]	ethane[c]
C–C bond	0.827	0.823		0.832
C–H bond	0.833	0.830	0.831	0.829

[a] Reference 39. [b] Reference 37. [c] Reference 38.

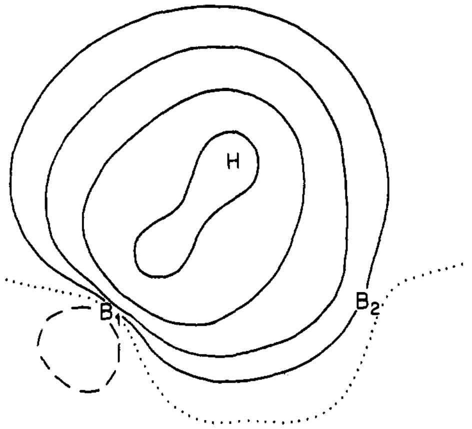

Figure 5. Diborane's B_1 orbital of the three-center two-electron bond.

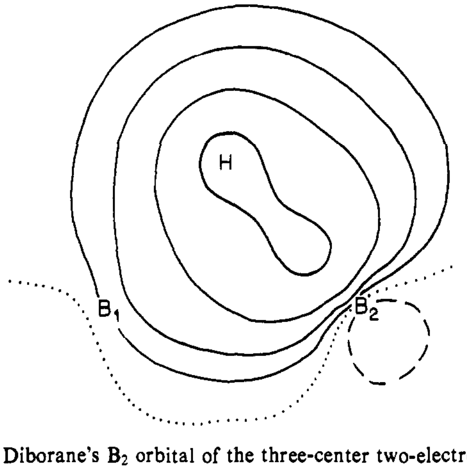

Figure 6. Diborane's B_2 orbital of the three-center two-electron bond.

s character in the C–H bonds (their hybridization is $sp^{2.3}$). These same trends have been obtained in other more recent studies as well.[15,35]

The present VB method optimizes nonorthogonal hybrids, so the hybridization of the C–C and C–H orbitals are not directly related. An increase in the p character of one hybrid does not require a change in the hybridization of any other VB orbitals.[37] Thus, insight can be gained by comparing the C–H hybridization in our nonorthogonal VB orbitals for cyclopropane to that for other alkanes. It has been observed that eliminating the orthogonality constraint between hybrid orbitals increases their s character.[37] The VB wave function satisfies the Pauli principle, so there is no "overuse" of the s orbitals in nonorthogonal VB functions. Nevertheless, hybridizations of orbitals of orthogonal-orbital wave functions cannot be compared to hybridizations of orbitals of nonorthogonal-orbital wave functions. It is the trend from one molecule to another using the same type of wave function that shows changes in the orbitals' composition. As already mentioned, the hybridizations of our VB orbitals was carried out without truncation; hybridizations of the C–H and C–C orbitals for several molecules are listed in Table III. As can be seen, the C–H bond in cyclopropane is indeed enriched in s character with respect to alkanes and alkenes as well. Further, the expected higher p character of the C–C bond is also found with a hybrid of $sp^{1.706}$, considerably more p character than either ethane[38] or ethylene.[39] Thus, even without hybrid orthogonality, the cyclopropane C–H bond is different from other alkanes.

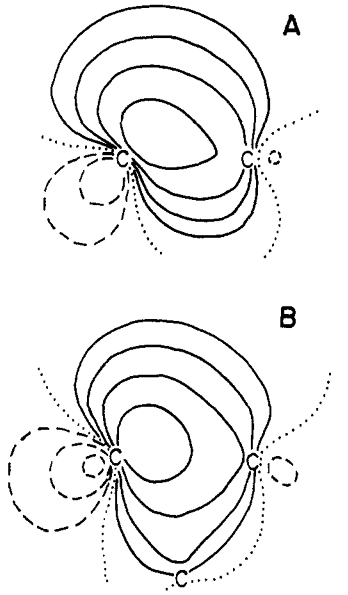

Figure 7. Comparison of ethylene's C–C banana bond orbital (A) to cyclopropane's C–C bond orbital (B).

Further corroboration for the concept of C–H bond strengthening in cyclopropane comes from a comparison of orbital overlaps. Table IV shows that the C–H bond in cyclopropane has the largest intrapair overlap of all. Although there is no rigorous relationship between intrapair overlap and bond strength, and the differences between the overlaps in these four molecules are very small, this is evidence that the C–H bond in cyclopropane is as strong and

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(37) Kirtman, B.; Palke, W. E.; Chipman, D. M. *Isr. J. Chem.* **1980**, *19*, 82.

(38) VB calculations for ethane and diborane were performed using the same set of programs as for cyclopropane. An optimized double-ζ plus d basis of Slater orbitals was used.

(39) Palke, W. E. *J. Am. Chem. Soc.* **1986**, *108*, 6543.

maybe stronger than in other alkanes. It would thereby be one factor in reducing the apparent strain energy in cyclopropane.

Nature of the C–C Bonds in Cyclopropane. From the MO viewpoint,[8,9,12,13] arguments claiming σ-aromaticity and delocalization of electrons in the plane of the cyclopropane ring[30,34] can lead one to ascribe some of cyclopropane's stability to three-center two-electron bonding among the carbon atoms. In fact, it has been suggested that the bonding in cyclopropane is similar to that of diborane, and that the three-center bonding leads to surface delocalization.[33] Further, the model of three-center bonding has been the basis for the idea of σ-bridged π orbitals used to describe bonding in molecules such as [1.1.1]propellane.[36]

It is clear from Figures 3 and 4 that the VB orbitals do not describe a three-center C–C bond in cyclopropane. The amplitude of these orbitals at the third carbon is an order of magnitude smaller than in the bonding region; C_3 seems to have little effect on the C_1–C_2 bond. It is also clear that the charge density is greater outside the ring away from the third carbon. Contrast this picture with the VB orbitals of diborane[38] shown in Figures 5 and 6. These two orbitals overlap to describe a true three-center two-electron bond with the area of high orbital amplitude extending to include the third center (the hydrogen). Thus, VB theory can and does predict three-center bonding in some situations; however, cyclopropane is not one of them. Whatever the validity of the concept of σ-delocalization, it is not a consequence of diborane-like bonding in cyclopropane.

A more appropriate description of the C–C bonding in cyclopropane is that it is similar to the C–C bonding in ethylene. Ethylene is sometimes considered to be the smallest cyclic hydrocarbon,[6] and it has been shown that, based on calculated anisotropy of electron densities, the cyclopropane C–C bond shows features of the ethylene C–C bond.[30] VB calculations on ethylene indicate that its C–C bond is composed of four equivalent hybrids forming two banana bonds,[39] one above and one below the plane of the nuclei. Figure 7 shows a comparison of the cyclopropane and ethylene C–C hybrids. They are quite similar; both bonds are bent outward from the internuclear line, ethylene more so than cyclopropane. The intrapair overlaps (Table IV) show a decrease in going from ethane to cyclopropane to ethylene which is what one would expect; as the bond is forced to point further from the internuclear line, the hybrids will not be able to point toward one another as efficiently, and the overlaps must decrease. This behavior is evidence of bond strain.