

The Nature of the Carbon-Carbon Bonds in Cyclopropane and Cyclobutane: A Comparison Based on Spin-Coupled Theory

Peter B. Karadakov,^{†‡} Joseph Gerratt,^{*‡} David L. Cooper,[§] and Mario Raimondi[‡]

Contribution from the School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, United Kingdom, Department of Chemistry, University of Liverpool, P.O. Box 147, Liverpool L69 3BX, United Kingdom, and Dipartimento di Chimica Fisica ed Elettrochimica, Università di Milano, Via Golgi 19, 20133 Milano, Italy

Received December 10, 1993. Revised Manuscript Received May 16, 1994*

Abstract: The electronic structure of the smallest cycloalkanes: cyclopropane (C₃H₆) and cyclobutane (C₄H₈) is studied by means of spin-coupled (SC) theory—the most general single-configuration approach. The comparison between the main characteristic features of the corresponding SC wave functions: orbital overlaps, orbital shapes, and correlation energies per electron pair indicates that the bonding along the carbon-carbon σ -bond frameworks in cyclopropane and cyclobutane is rather similar, which represents a convincing theoretical explanation for their surprisingly close conventional ring strain energies. These conclusions are further confirmed by the results of full-valence SC VB (valence bond) calculations and are juxtaposed with SC and SC VB results for an *n*-alkane of a similar size, propane (C₃H₈). Although the σ -electron sextet involved in the carbon-carbon bonds in cyclopropane appears to be isoconjugate to the π -electron system of benzene, its SC description is found to involve no significant resonance, and the optimal mode of coupling the spins of the six valence electrons is decidedly different from that in benzene. This undermines attempts to explain the properties of C₃H₆ by invoking the idea of σ -aromaticity.

1. Introduction

The appearance of the structural formulas of cyclopropane (C₃H₆) and cyclobutane (C₄H₈) suggests that the three-membered ring should be much more strained than the four-membered one: The C-C-C bond angles in C₃H₆ are all 60°, while in the case of C₄H₈ the corresponding figure is 88.3° (calculated from the experimental geometry of Egawa *et al.*¹), yet the conventional ring strain energies (CRSE) of cyclopropane and cyclobutane are very similar: 27.5 and 26.5 kcal/mol, respectively.^{2,3}

Bonds subject to strain are generally expected to be weaker and, consequently, longer. The lengths of the C-C bonds in cyclobutane (~1.55 Å, see ref 1) are, indeed, longer than those in *n*-alkanes (~1.53 Å), but the lengths of the C-C bonds in cyclopropane are shorter (~1.51 Å, see ref 4).

In fact, it is well-known that, in its properties, cyclopropane is quite different from any other cycloalkane which does not contain a three-membered ring. In addition to the anomalies mentioned above, cyclopropane undergoes addition reactions characteristic of carbon-carbon double bonds, and there exist certain problems with the interpretation of the magnitude of its *J*(¹³C,H) NMR coupling constant (see, *e.g.*, ref 5).

There are two principal quantum-chemical models of the bonding in cyclopropane, which have originated almost in parallel. One of these is due to Walsh,⁶ who postulated the existence of a two-electron three-center bond, resulting from the overlap of three sp² hybrid orbitals, one per carbon, pointing toward the center of the ring. The other model, suggested by Coulson and

Moffitt,⁷ explains the bonding in C₃H₆ from a valence-bond (VB) viewpoint, by assuming three bent single bonds formed from six equivalent hybrid orbitals, each directed slightly outwards of the triangle formed by the three carbons.

It is not possible to distinguish between the two models on the basis of a Hartree-Fock (HF) calculation.^{8,9} The canonical HF orbitals realize the concepts of Walsh, but a localization of the occupied orbitals (employing the invariance of the HF wave function to unitary transformations of these) leads to a description involving three equivalent bent bonds, which is in better agreement with the ideas of Coulson and Moffitt.

More general one-configuration approaches, such as the generalized VB (GVB) method,¹⁰ give clear preference to the bent-bond model. GVB calculations under strong-orthogonality (SO) and perfect-pairing (PP) constraints (see, *e.g.*, Ref 11) produce three pairs of equivalent localized orbitals of ~sp⁴ (~82% p) character bent outside the carbon ring. Recent results of Hamilton and Palke,¹² obtained without any SO constraints, also confirm the hypothesis of Coulson and Moffitt. In these calculations all C-C and C-H bonds are described by pairs of singly-occupied nonorthogonal orbitals, and the approximate hybridizations of the C-centered orbitals participating in C-C and C-H bonds turn out to be sp^{1.706} and sp^{1.348}, respectively.

One of the possible explanations for the unusual features of cyclopropane is to associate them with a new property, termed σ -aromaticity.^{5,13} In the case of the Walsh model, the two-electron three-center bond can be regarded as an aromatic 4*v* + 2 Hückel system (*v* = 0).¹³ The argument is more transparent when C₃H₆ is described by three bent bonds: The electronic sextet involved

[†] On leave from the Institute of Organic Chemistry, Bulgarian Academy of Sciences, Sofia 1040, Bulgaria.

[‡] University of Bristol.

[§] University of Liverpool.

[‡] Università di Milano.

* Abstract published in *Advance ACS Abstracts*, July 1, 1994.

(1) Egawa, T.; Fukuyama, T.; Yamamoto, S.; Takabayashi, F.; Kambara, H.; Keda, T.; Kuchitsu, K. *J. Chem. Phys.* **1987**, *86*, 6018.

(2) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic: London, 1970.

(3) Benson, S. W. *Thermochemical Kinetics*; Wiley: New York, 1976.

(4) Endo, Y.; Chang, M. C.; Hirota, E. *J. Mol. Spectrosc.* **1987**, *126*, 63.

(5) Dewar, M. J. S. *J. Am. Chem. Soc.* **1984**, *106*, 669.

(6) Walsh, A. D. *Trans. Faraday Soc.* **1949**, *45*, 179.

(7) Coulson, C. A.; Moffitt, W. E. *Phil. Mag.* **1949**, *40*, 1.

(8) Newton, M. D.; Switkes, E.; Lipscomb, W. N. *J. Chem. Phys.* **1970**, *53*, 2645.

(9) Newton, M. D. Strained organic molecules in modern theoretical chemistry. In *Modern Theoretical Chemistry, Vol. 4. Applications of Electronic Structure Theory*; Schaefer III, H. F., Ed.; Plenum Press: New York, 1977; pp 223-275.

(10) Bobrowitz, F. M.; Goddard, W. A. In *Modern Theoretical Chemistry, Vol. 3. Methods of Electronic Structure Theory*; Schaefer III, H. F., Ed.; Plenum Press: New York, 1977; p 79.

(11) Hay, P. J.; Hunt, W. J.; Goddard III, W. A. *J. Am. Chem. Soc.* **1972**, *94*, 8293.

(12) Hamilton, J. G.; Palke, W. E. *J. Am. Chem. Soc.* **1993**, *115*, 4159.

(13) Cremer, D.; Gauss, J. *J. Am. Chem. Soc.* **1986**, *108*, 7467.

makes the ring isoconjugate with benzene.⁵ The idea of σ -aromaticity is not generally accepted: for example, as it has been demonstrated recently,¹⁴ the delocalization of electrons between the orbitals corresponding to geminal C-C bonds in cyclopropane is antibonding, and thus has an opposite effect compared to π -electron delocalization in benzene.

In the present article we study cyclopropane and cyclobutane in the framework of the spin-coupled (SC) approach (see, e.g., ref 15 and references therein). The SC model offers all features necessary for the proper description of these molecules: Similar to the wave function employed by Hamilton and Palke,¹² it removes the SO constraints inherent in most GVB-type calculations. In addition to that, the SC method makes use of the *whole* spin space and not just of the perfect-pairing spin function common to other, less general, one-configuration approaches. In parallel, as a reference system, we investigate an *n*-alkane of a similar size, propane (C₃H₈).

By avoiding the *ad hoc* imposition of any orthogonality constraints on the orbitals involved in the carbon-carbon bonds in the C₃H₆ and C₄H₈ rings, the SC approach produces a clear and unbiased picture of the bonding, which offers an immediate explanation of the very close CRSE values for these systems. We confirm our conclusions, derived on the basis of the single-configuration SC wave function, by performing more advanced, full-valence VB calculations using structures constructed from SC orbitals.

The highly visual, yet quantitative vindication of Kekulé's pre-quantum-chemical concepts of resonance embodied in the SC description of benzene¹⁶⁻¹⁸ represents one of the well-known achievements of SC theory. Here we apply the same set of theoretical tools to the electronic sextet holding together the carbon framework of cyclopropane and find no evidence of significant resonance, which undermines the concept of σ -aromaticity.

2. The Spin-Coupled Model

The spin-coupled description of a system with *N* active (or valence) electrons involves the product of *N* singly-occupied orbitals $\psi_1, \psi_2, \dots, \psi_N$

$$\Psi_{SM} = \hat{A}(\Phi_{\text{core}} \Phi_{\text{val}}) = \hat{A}(\Phi_{\text{core}} \psi_1 \psi_2 \dots \psi_N \Theta_{SM}^N) \quad (1)$$

where

$$\Phi_{\text{core}} = \varphi_1^2 \varphi_2^2 \dots \varphi_n^2 \underbrace{\alpha\beta\alpha\beta \dots \alpha\beta}_{n \text{ pairs}} \quad (2)$$

accommodates the *core* (or *inactive*) electrons (their number is assumed to be $2n$). The spin function for the valence electrons Θ_{SM}^N takes the form of a linear combination of all unique *N*-electron spin eigenfunctions of \hat{S}^2 and \hat{S}_z with eigenvalues *S* and *M*

$$\Theta_{SM}^N = \sum_{k=1}^{f_S^N} C_{Sk} \Theta_{SM;k}^N = \Theta_{SM}^N C_S \quad (3)$$

where

$$f_S^N = \frac{(2S+1)N!}{\left(\frac{1}{2}N+S+1\right)! \left(\frac{1}{2}N-S\right)!} \quad (4)$$

Θ_{SM}^N and C_S denote a row vector of all spin functions and a column vector of all spin-coupling coefficients, respectively.

The core and SC orbitals are all expanded in a suitable basis set of atom-centered orbitals (AOs) $\{\chi_{p|p} = 1, 2, \dots, M\}$

$$\varphi_i = \sum_{p=1}^m c_{ip} \chi_p; \quad \psi_\mu = \sum_{p=1}^m c_{\mu p} \chi_p \quad (5)$$

The coefficients c_{ip} , $c_{\mu p}$, and C_{Sk} are calculated by variational optimization of the energy expectation value corresponding to Ψ_{SM} .

There exists a large choice of algorithms for constructing the complete set of f_S^N *N*-electron spin eigenfunctions $\Theta_{SM;k}^N$ (see ref 19). SC theory makes use mainly of those due to Kotani (K), Rumer (R), and Serber (S). Once the optimal mode of spin-coupling in one of these spin bases is known, it is straightforward to find an equivalent representation of Θ_{SM}^N in another spin basis

$$\Theta_{SM}^N = {}^K \Theta_{SM}^N {}^K C_S = {}^R \Theta_{SM}^N {}^R C_S = {}^S \Theta_{SM}^N {}^S C_S \quad (6)$$

The transformation procedure is relatively straightforward and computationally inexpensive^{20,21} and often provides indispensable aid for the interpretation of the spin-coupling pattern for the valence electrons.

In the present paper we make use of the Kotani and Rumer spin bases. The Kotani spin basis ${}^K \Theta_{SM}^N$ is constructed by successive coupling of individual electron spin functions (α or β) according to the rules for addition of angular momenta. Each spin function is uniquely defined by the series of partial resultant spins of the consecutive groups of 1, 2, ..., *N* electrons, which can be used as an extended label for the spin function

$$k \equiv (S_1, S_2, \dots, S_{N-1}) \quad (7)$$

The codes employed in order to perform the calculations for the present article²² work in the Kotani basis.

The Rumer spin bases ${}^R \Theta_{SM}^N$ is formed by the set of f_S^N linearly independent spin functions, in which the first $N - 2S$ electrons are coupled to singlet pairs, and the remaining $2S$ electrons are assigned spins α . The Rumer spin functions can be labeled by indicating the singlet pairs, *i.e.*,

$$k \equiv (\mu_1 - \mu_2, \mu_3 - \mu_4, \dots, \mu_{N-2S-1} - \mu_{N-2S}) \quad (8)$$

The representation of the spin function for the valence electrons in the Rumer spin basis often helps to establish a close correspondence between the SC wave function and the classical VB concept of resonance.

In order to ascertain the relative importance of the different terms making up Θ_{SM}^N (3) we need an expression reflecting the weight with which a single spin function $\Theta_{SM;k}^N$ participates in the spin function for the valence electrons Θ_{SM}^N , *i.e.*, its occupation number. One way of calculating this quantity is due to Chirgwin and Coulson²³ (it is assumed that Θ_{SM}^N is normalized to unity)

$$P_{Sk}^{CC} = C_{Sk} \sum_{l=1}^{f_S^N} \langle \Theta_{SM;k}^N | \Theta_{SM;l}^N \rangle C_{Sl} \quad (9)$$

(14) Inagaki, S.; Goto, N.; Yoshikawa, K. *J. Am. Chem. Soc.* **1991**, *113*, 7144.

(15) Cooper, D. L.; Gerratt, J.; Raimondi, M. *Chem. Rev.* **1991**, *91*, 929.

(16) Cooper, D. L.; Gerratt, J.; Raimondi, M. *Nature* **1986**, *323*, 699.

(17) Gerratt, J. *Chem. Br.* **1987**, *23*, 327.

(18) Cooper, D. L.; Wright, S. C.; Gerratt, J.; Raimondi, M. *J. Chem. Soc., Perkin Trans. 2* **1989**, 255.

(19) Pauncz, R. *Spin Eigenfunctions*; Plenum Press: New York, 1979.

(20) Raos, G.; Gerratt, J.; Cooper, D. L.; Raimondi, M. *Mol. Phys.* **1993**, *79*, 197.

(21) Karadakov, P. B.; Gerratt, J.; Cooper, D. L.; Raimondi, M. *Theor. Chim. Acta*, in press.

(22) Karadakov, P. B.; Gerratt, J.; Cooper, D. L.; Raimondi, M. *J. Chem. Phys.* **1992**, *97*, 7637.

(23) Chirgwin, B. H.; Coulson, C. A. *Proc. Roy. Soc. London, Ser. A* **1950**, *201*, 196.

Unfortunately, for nonorthogonal spin bases, in some cases the values of P_{Sk}^{CC} calculated by means of eq 9 can be either larger than unity or negative. Another expression for P_{Sk} , which guarantees that it always stays within the range [0, 1], has been suggested by Gallup and Norbeck²⁴

$$P_{Sk}^{GN} = c(C_{Sk})^2 / (\langle \theta_{SM}^N | \theta_{SM}^N \rangle^{-1})_{kk}$$

$$c^{-1} = \sum_{k=1}^{f_S^N} (C_{Sk})^2 / (\langle \theta_{SM}^N | \theta_{SM}^N \rangle^{-1})_{kk} \quad (10)$$

where $\langle \theta_{SM}^N | \theta_{SM}^N \rangle$ denotes the overlap matrix for the spin basis.

In the case of orthogonal spin bases (e.g., the Kotani basis) both eqs 9 and 10 reduce to a simpler expression: $KP_{Sk} = K C_{Sk}^2$.

The relation of the SC wave function (1) to the classical VB scheme becomes more apparent if we represent it as a linear combination of f_S^N structures, each of which combines the product of the N singly-occupied, nonorthogonal SC orbitals with a particular N -electron spin eigenfunction

$$\Psi_{SM} = \sum_{k=1}^{f_S^N} C_{Sk} \Psi_{SM;k} = \sum_{k=1}^{f_S^N} C_{Sk} \hat{A}(\Phi_{\text{core}} \psi_1 \psi_2 \dots \psi_N \theta_{SM;k}^N) \quad (11)$$

The appearance of eq 11 suggests one possible way of improving the SC wave function. This can be achieved by augmenting Ψ_{SM} with additional structures

$$\Psi_{SM;k}(\mu_1 \mu_2 \dots \mu_{N-1}) = \hat{A}(\Phi_{\text{core}} \psi_{\mu_1}^2 \psi_{\mu_2}^2 \dots \psi_{\mu_i}^2 \psi_{\mu_i+1} \psi_{\mu_i+2} \dots \psi_{\mu_{N-1}} \times \underbrace{\alpha\beta\alpha\beta \dots \alpha\beta}_{n+i \text{ pairs}} \theta_{SM;k}^{N-2i}) \quad (12)$$

In this notation, the *covalent* structures making up the original SC wave function can be expressed as $\Psi_{SM;k}(12\dots N)$.

Inclusion of all possible *ionic* structures in which one or more valence orbitals are doubly-occupied leads to a SC VB wave function which is almost indistinguishable from the corresponding CAS SCF wave function for an identical core-valence partitioning (a small difference arises due to the fact that the core and valence orbitals used to construct the SC VB wave function come from a preliminary SC calculation and are not optimized any further). However, it should be emphasized that in most cases the energy of the single-configuration SC wave function alone is very close to that of its CAS SCF counterpart. Further improvements may be introduced by expanding the SC VB construction with structures including virtual SC orbitals (the calculation of these and the related methodology are explained in detail in ref 25).

3. Results and Discussion

All calculations from the present article were performed at experimental geometries: For cyclopropane we used the D_{3h} geometry reported by Endo *et al.*,⁴ for cyclobutane—the D_{2d} geometry established by Egawa *et al.*,¹ and for propane—the C_{2v} geometry described by Lide.²⁶

We employed everywhere a standard double- ζ basis set of (9s5p/4s) Gaussian functions contracted to [4s2p/2s],^{27,28} with scaling factors of 1.20 and 1.15 for the hydrogen s functions, augmented with polarization functions with exponents d(C) = 0.72 and p(H) = 1.0. For convenience, we shall refer to this basis as DZP.

(24) Gallup, G. A.; Norbeck, J. M. *Chem. Phys. Lett.* **1973**, *21*, 495.

(25) Gerratt, J.; Raimondi, M. *Proc. Roy. Soc. London, Ser. A* **1980**, *371*, 525.

(26) Lide Jr., D. R. *J. Chem. Phys.* **1960**, *33*, 1514.

(27) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293.

(28) Dunning, T. H. *J. Chem. Phys.* **1970**, *53*, 2823.

Table 1. Total HF, SC, Full-Valence SC VB, and Correlation Energies [Whole (ΔE^{corr}) and per Valence Electron Pair ($\Delta E_{\text{pair}}^{\text{corr}}$)] for Cyclopropane, Cyclobutane, and Propane^a

quantity	C ₃ H ₆	C ₄ H ₈	C ₃ H ₈
$E(\text{HF})$	-117.084 46	-156.130 53	-118.292 52
$E(\text{SC})$	-117.133 93	-156.197 70	-118.322 92
$E(\text{SC VB})$	-117.14509	-156.209 27	-118.324 90
$\Delta E^{\text{corr}}(\text{SC})$	-0.049 47 (81.6)	-0.067 17 (85.3)	-0.030 40 (93.9)
$\Delta E^{\text{corr}}(\text{SC VB})$	-0.060 63	-0.078 74	-0.032 38
$\Delta E_{\text{pair}}^{\text{corr}}(\text{SC})$	-0.016 49	-0.016 79	-0.015 20
$\Delta E_{\text{pair}}^{\text{corr}}(\text{SC VB})$	-0.020 21	-0.019 68	-0.016 19

^a All energies in hartree. Values in brackets following $\Delta E^{\text{corr}}(\text{SC})$ indicate the percentage of the corresponding full-valence SC VB correlation energy included in the single-configuration SC wave function.

All preliminary HF calculations, localizations of HF orbitals, as well as the evaluation of all required integrals, were performed using the GAMESS(UK) program package.²⁹

In the case of cyclopropane the SC active space encompassing all three carbon-carbon bonds involves six symmetry-equivalent singly-occupied nonorthogonal orbitals. The number of independent spin-couplings for a singlet six-electron system is $f_0^6 = 5$. The remaining electrons occupy nine doubly-occupied orbitals. A convenient initial guess for the orbitals entering the SC wave function can be obtained by localizing the orbitals from the standard HF solution for the system using, e.g., the criterion of Foster and Boys.³⁰ Each of the three bent orbitals localized mostly in the region of the C-C bonds is then "split" in two by setting to zero all AO coefficients except those for AOs centered on one of the carbons participating in the bond. This yields initial approximations to the six SC orbitals. The remaining nine localized HF orbitals are used as an initial guess for the core part of the SC wave function. The perfect-pairing scheme containing singlet pairs over the three carbon-carbon bonds offers a suitable starting guess for the six-electron singlet spin function.

Cyclobutane contains four equivalent carbon-carbon bonds. This necessitates the use of an eight-orbital active space. The total number of spin functions we have to consider in this case is $f_0^8 = 14$. Initial guesses for the SC orbitals and for the set of spin-coupling coefficients can be obtained as described above in the case of cyclopropane. For greater computational efficiency, the four doubly-occupied localized HF orbitals which are predominantly C(1s) in character were kept fixed (or "frozen"), i.e., they were not varied any further.²² This reduces the number of core orbitals, optimized simultaneously with the active space, to eight.

The two carbon-carbon bonds in C₃H₈ can be described by means of four SC orbitals. The related number of singlet spin pairings is $f_0^4 = 2$. The calculations followed closely the routine described in the case of cyclopropane.

The HF, SC, and full-valence SC VB ground-state energies for C₃H₆, C₄H₈, and C₃H₈ are listed in Table 1. The very close values of the correlation energies per electron pair ($\Delta E_{\text{pair}}^{\text{corr}}$) for C₃H₆ and C₄H₈ recovered by means of the SC and full-valence SC VB approaches suggest that in both cases the corresponding improvements in comparison to the HF model are almost additive with respect to the carbon-carbon σ -bonds involved, which should be very similar in nature irrespectively of the different ring sizes. The correlation energies per electron pair obtained for C₃H₈ are noticeably smaller, which is especially evident in the case of the full-valence SC VB wave function. In qualitative terms, the distinctly more modest improvement which the full-valence SC VB wave function achieves over its SC counterpart for propane can be explained by the greater spatial separation between the

(29) Guest, M. F.; Sherwood, P. *GAMESS-UK User's Guide and Reference Manual, Revision B.0*, SERC Daresbury Laboratory, UK, 1992.

(30) Foster, J. M.; Boys, S. F. *Rev. Mod. Phys.* **1960**, *32*, 300.

(31) Karadakov, P. B.; Gerratt, J.; Cooper, D. L.; Raimondi, M. *J. Am. Chem. Soc.* **1993**, *115*, 6863.

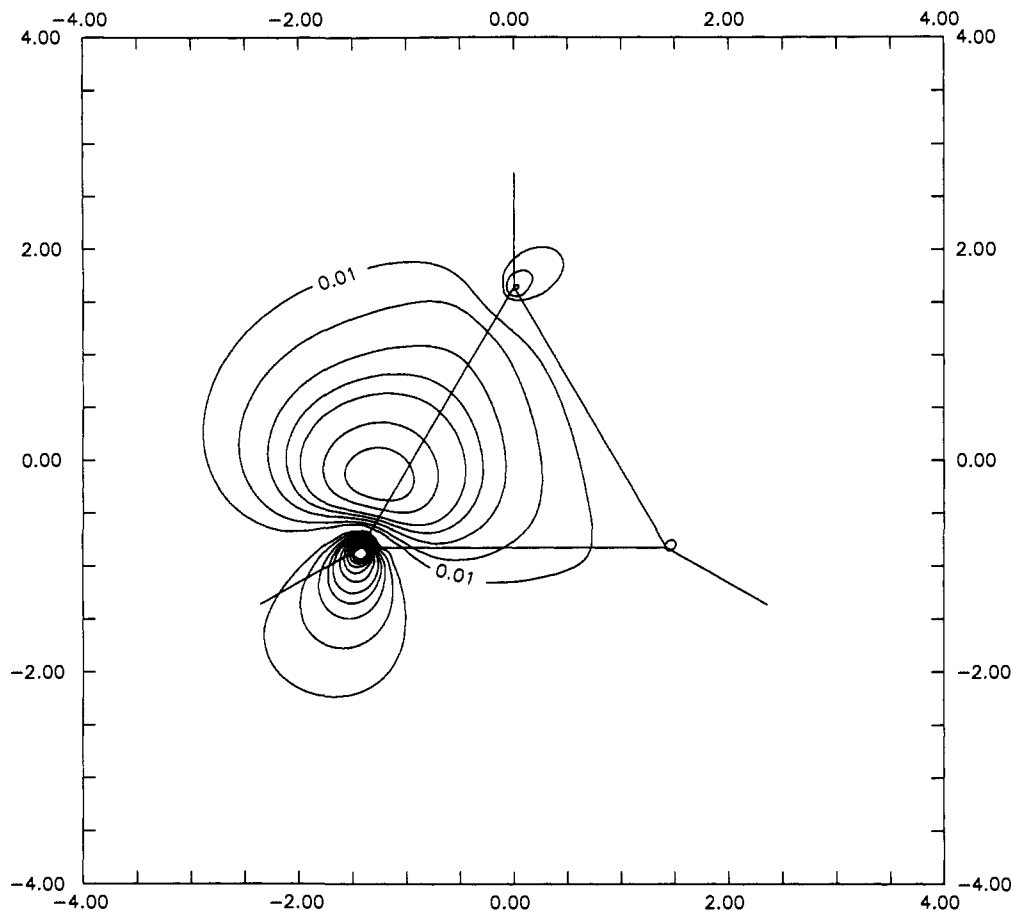


Figure 1. ψ_1 : One of the six symmetry-equivalent valence orbitals from the SC wave function for cyclopropane. Contour levels of $|\psi_1|^2$ requested at 0.01, 0.025 (0.025) 0.1, 0.15 (0.05) 0.4, 0.5 (0.2) 1.1, 1.5, 2, 5, 10, 20, 50. All distances in μ_B .

Table 2. Overlap Integrals between the Valence Orbitals from the SC Wave Function for Cyclopropane

	ψ_1	ψ_2	ψ_3	ψ_4	ψ_5	ψ_6
ψ_1	1	0.803	0.207	0.049	0.207	0.340
ψ_2		1	0.340	0.207	0.049	0.207
ψ_3			1	0.803	0.207	0.049
ψ_4				1	0.340	0.207
ψ_5					1	0.803
ψ_6						1

SC orbitals: This makes the energy difference between covalent and ionic structures (with energies defined as the respective expectation values of the total Hamiltonian for the system) larger than in the case of cyclopropane and cyclobutane. These ionic structures then mix to a smaller extent with the predominant covalent structures within the SC VB construction: The net result is a less pronounced lowering of the energy of the reference SC wave function.

One of the six symmetry-equivalent SC orbitals for C_3H_6 (ψ_1) is shown in Figure 1. The remaining five SC orbitals can be obtained from ψ_1 by applying to it operations from the point group of the molecule, D_{3h} (see Figure 4 below for a schematic representation and a numbering scheme for all six active orbitals). In shape, orbital ψ_1 is rather similar to the GVB-PP-SO orbitals obtained by Hay *et al.*¹¹ and to the GVB-PP orbitals of Hamilton and Palke.¹² The overlaps between orbitals ψ_1 - ψ_6 are listed in Table 2.

The puckered-ring equilibrium conformation of cyclobutane renders the visualization of the SC orbitals less straightforward. Therefore, although all eight SC orbitals are equivalent by symmetry, we present two contour plots: Figure 2a depicts the contours of $|\psi_1|^2$ in the plane defined by the carbon, about which it is mostly localized, and its neighboring carbons, and Figure 2b

shows the contours of $|\psi_2|^2$ in the same plane (a schematic representation and a numbering scheme for all eight active orbitals are given in Figure 5 below). All overlap integrals between orbitals ψ_1 - ψ_8 are collected in Table 3.

Due to the C_{2v} symmetry of C_3H_8 , the SC orbitals describing the two carbon-carbon bonds are equivalent in pairs. Two of the orbitals (ψ_1 and ψ_2) are shown in Figure 3, and the other two (ψ_3 and ψ_4) are trivially related to these through symmetry operations (*e.g.*, $\hat{C}_2\psi_2 = \psi_3$, $\hat{C}_2\psi_1 = \psi_4$). The overlap matrix involving ψ_1 - ψ_4 is given in Table 4.

Obviously, the tendency of the optimal nonorthogonal valence orbitals to bend out of the ring is manifested very clearly in the case of cyclopropane (see Figure 1). Although still present, it is more difficult to notice in cyclobutane (see Figure 2). In both molecules this effect improves the spatial separation of orbitals, localized mostly on the same carbon (*e.g.*, ψ_1 and ψ_6 in C_3H_6 , ψ_1 and ψ_8 in C_4H_8) and thus reduces ring strain. In contrast to the situation observed in C_3H_6 and C_4H_8 , in propane (see Figure 3) orbital ψ_2 and, correspondingly, orbital ψ_3 (which is not shown), are slightly shifted away from the C-C bond axis, toward the center of the C-C-C angle.

A closer inspection of the SC orbital ψ_1 for C_3H_6 , shown in Figure 1, reveals that in addition to pointing mainly toward ψ_2 (see Figure 4), it also exhibits a noticeable distortion in the direction of ψ_3 . Such distortions, which may be interpreted as indicating a tendency for the orbitals to participate in more than one bond each, are not observed in C_4H_8 and C_3H_8 .

In this article we do not attempt to define orbital-based bond angles and bond directions, as done by other authors (see, *e.g.*, ref 12), which is not quite straightforward in the case of basis sets involving *d*-functions. Instead, we find that inspection of the overlap matrices between the valence orbitals of the two rings

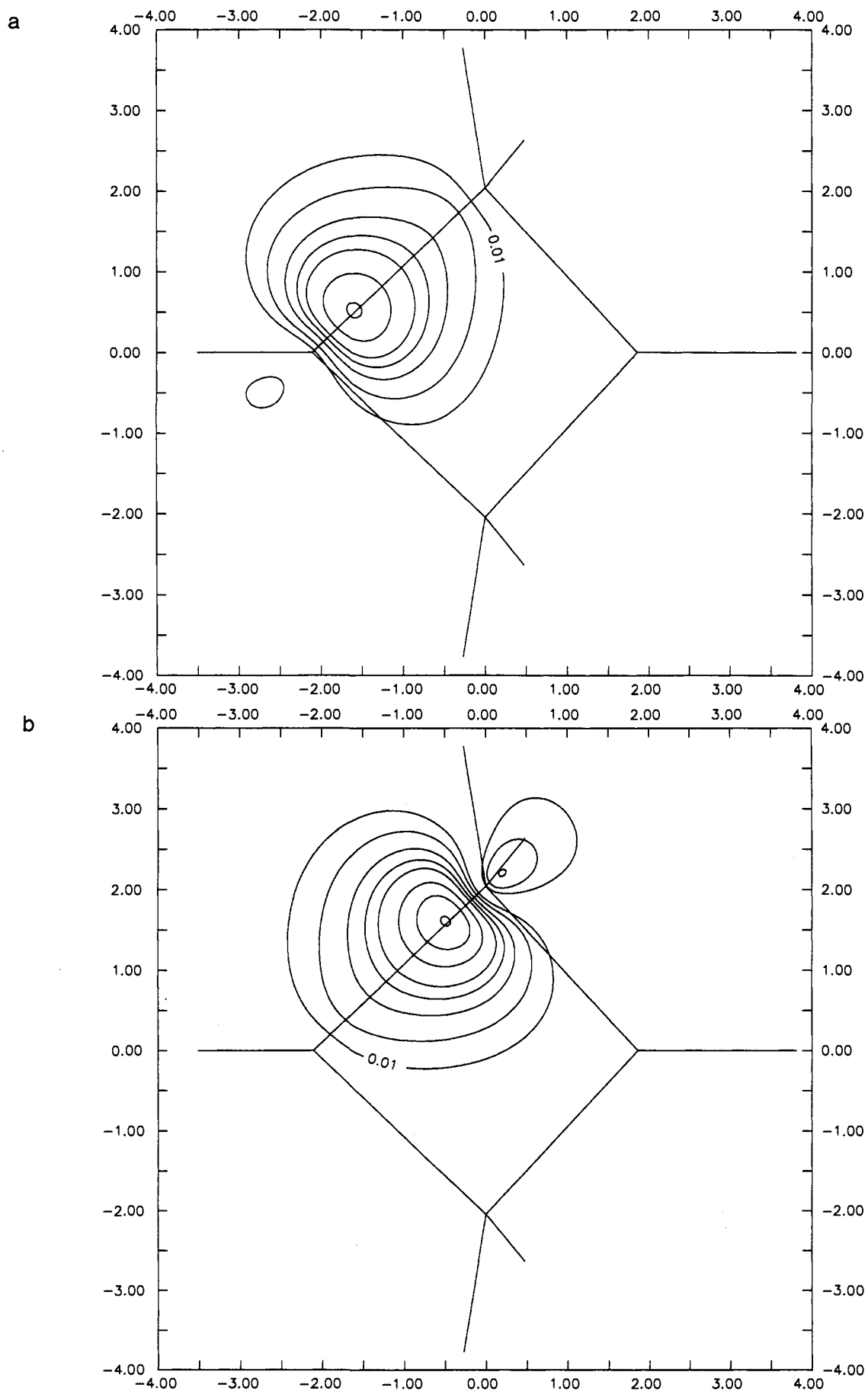


Figure 2. ψ_1 (a) and ψ_2 (b): Two of the eight symmetry-equivalent valence orbitals from the SC wave function for cyclobutane. Plot details as in Figure 1.

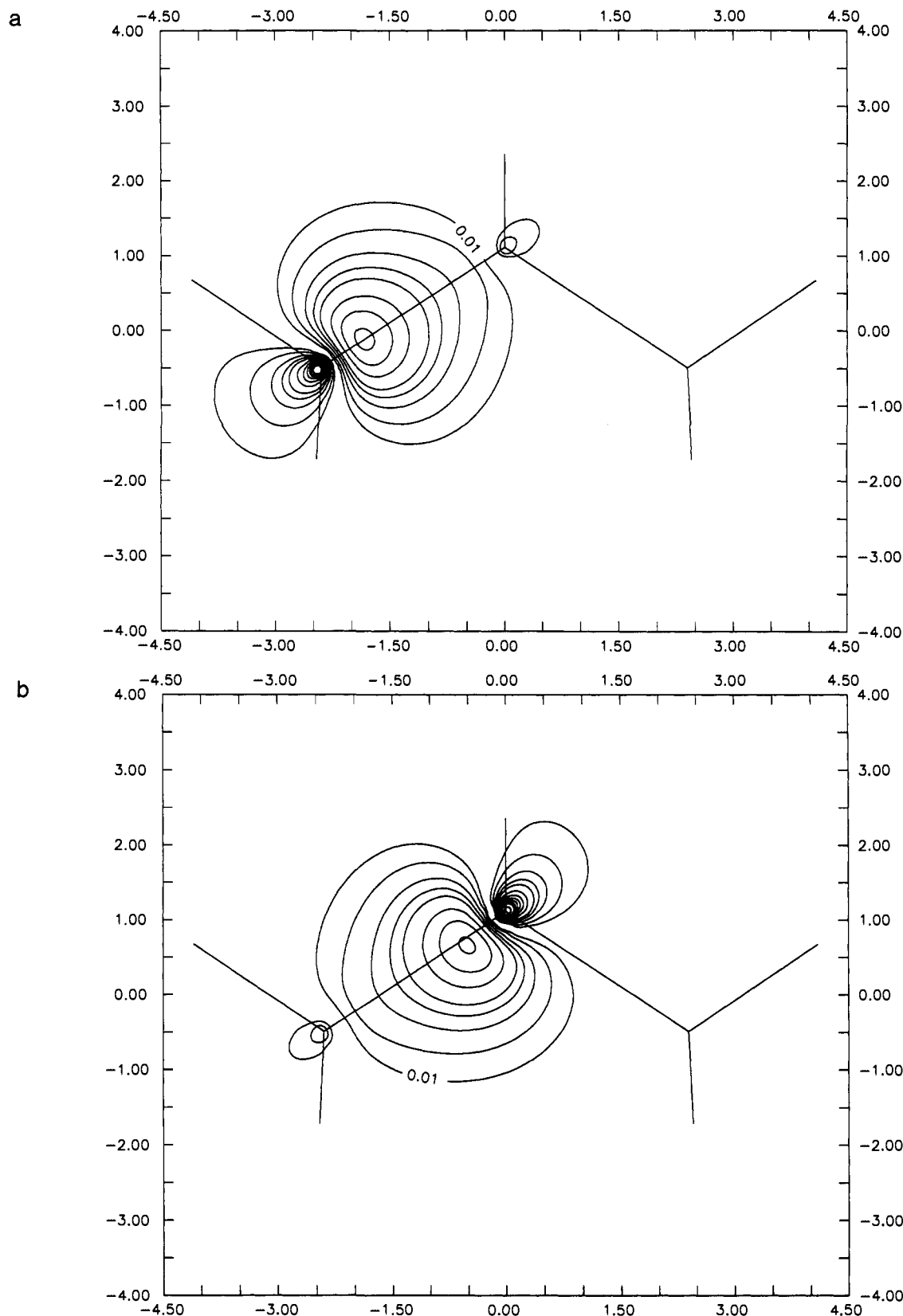


Figure 3. ψ_1 (a) and ψ_2 (b): The two symmetry-unique valence orbitals from the SC wave function for propane. Plot details as in Figure 1.

provides sufficient information for a meaningful analysis and comparison.

The most significant overlap integrals in Tables 2-4 are those between SC orbitals forming a C-C bond ($\langle \psi_1 | \psi_2 \rangle = \langle \psi_3 | \psi_4 \rangle = \langle \psi_5 | \psi_6 \rangle$ for cyclopropane, $\langle \psi_1 | \psi_2 \rangle = \langle \psi_3 | \psi_4 \rangle = \langle \psi_5 | \psi_6 \rangle = \langle \psi_7 | \psi_8 \rangle$ for cyclobutane, and $\langle \psi_1 | \psi_2 \rangle = \langle \psi_3 | \psi_4 \rangle$ for propane) and between SC orbitals attached to the same carbon ($\langle \psi_2 | \psi_3 \rangle = \langle \psi_4 | \psi_5 \rangle =$

$\langle \psi_6 | \psi_7 \rangle$ for cyclopropane, $\langle \psi_2 | \psi_3 \rangle = \langle \psi_4 | \psi_5 \rangle = \langle \psi_6 | \psi_7 \rangle = \langle \psi_8 | \psi_1 \rangle$ for cyclobutane, and $\langle \psi_2 | \psi_3 \rangle$ for propane).

The values of the overlap integrals from the first group are 0.803 (in C_3H_6), 0.798 (in C_4H_8), and 0.817 (in C_3H_8), and of those from the second group: 0.340 (in C_3H_6), 0.309 (in C_4H_8), and 0.290 (in C_3H_8). This means that the pairs of sp^x -like hybrids engaged in C-C bonds in cyclopropane and cyclobutane interact

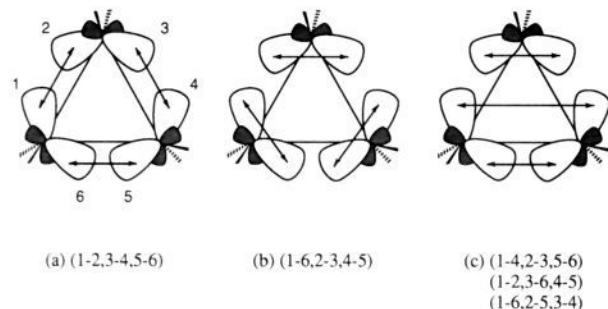


Figure 4. Schematic representation of the symmetry-unique Rumer spin-coupling patterns in cyclopropane.

in a very similar fashion, which suggests that they should form bonds of an almost equal type and strength. It should be noted that in the case of cyclopropane there is still another group of significant overlap integrals: $\langle \psi_\mu | \psi_{(\mu+2) \bmod 6} \rangle = 0.207$. This observation, in combination with the distortion of ψ_1 in C_3H_6 in the direction of ψ_5 already discussed, gives us grounds to assume that the carbon-carbon bonds in cyclopropane are strengthened additionally by interactions between the SC orbitals ψ_μ and $\psi_{(\mu+2) \bmod 6}$. Interactions of this type should be much weaker in cyclobutane: The corresponding overlap integrals ($\langle \psi_\mu | \psi_{(\mu+2) \bmod 8} \rangle$) have an appreciably lower value, namely, 0.144. The remaining nonnegligible overlap integrals in C_4H_8 , $\langle \psi_1 | \psi_6 \rangle = \langle \psi_2 | \psi_5 \rangle = \langle \psi_3 | \psi_8 \rangle = \langle \psi_4 | \psi_7 \rangle = 0.124$, are obviously related to and probably enhance the nonplanarity of the carbon framework—the analogous overlap integrals in C_3H_6 are much smaller, $\langle \psi_1 | \psi_4 \rangle = \langle \psi_2 | \psi_5 \rangle = \langle \psi_3 | \psi_6 \rangle = 0.049$.

All this agrees very well with the experimentally observed carbon-carbon bond distances in cyclopropane⁴ (~ 1.51 Å), cyclobutane¹ (~ 1.55 Å), and propane²⁶ (~ 1.53 Å).

It is interesting to juxtapose the values of the overlaps between geminal SC orbitals (*i.e.*, SC orbitals, localized mostly on the same carbon) in cyclopropane and cyclobutane to those observed in other systems in which the SC description involves bent bonds. The overlaps between geminal bent-bond SC orbitals in ethene and ethyne are 0.463 and 0.328, respectively³¹ (at experimental equilibrium geometries, within a DZ basis which differs from the DZP basis employed in the present article by the absence of polarization functions). The variation in the values of the corresponding overlap integrals in cyclopropane and cyclobutane is much smaller: They are found to be 0.340 and 0.309, respectively. As it should have been expected, $\langle \psi_2 | \psi_3 \rangle$ in C_3H_8 is smaller and equal to 0.290. The comparison between the values of the overlaps between geminal SC orbitals participating in different carbon-carbon bonds indicates that the “bending” of the orbitals in C_3H_6 leads to an overlap pattern which is definitely similar to that in C_4H_8 . This adds further support to our conclusion about the analogy of bonding over the carbon frameworks of C_3H_6 and C_4H_8 . The slightly higher geminal overlap value observed in the case of cyclopropane suggests tighter “crowding” of the orbitals and can be related to the observed small difference between the CRSEs of the two rings (see the Introduction).

In cyclopropane as well as in cyclobutane and in propane the optimal spin functions for the valence electrons Θ_{SM}^N (see eq 3) are dominated by their perfect pairing components. In the Kotani spin basis these spin coupling schemes [$5 \equiv (1/2 0 1/2 0 1/2)$] in C_3H_6 , [$14 \equiv (1/2 0 1/2 0 1/2 0 1/2)$] in C_4H_8 , and [$2 \equiv (1/2 0 1/2)$] in C_3H_8 constitute *ca.* 97.90%, *ca.* 95.76%, and *ca.* 98.99% of Θ_{00}^6 (for C_3H_6), Θ_{00}^8 (for C_4H_8), and Θ_{00}^4 (for C_3H_8), respectively.

It is easier to visualize and interpret the representations of the optimal spin functions for the valence electrons in the Rumer spin basis. The values of the corresponding spin-coupling coefficients and spin-function weights are listed in Tables 5–7, respectively. The individual Rumer spin functions entering

Table 3. Overlap Integrals between the Valence Orbitals from the SC Wave Function for Cyclobutane

	ψ_1	ψ_2	ψ_3	ψ_4	ψ_5	ψ_6	ψ_7	ψ_8
ψ_1	1	0.798	0.144	-0.022	0.081	0.124	0.144	0.309
ψ_2		1	0.309	0.144	0.124	0.081	-0.022	0.144
ψ_3			1	0.798	0.144	-0.022	0.081	0.124
ψ_4				1	0.309	0.144	0.124	0.081
ψ_5					1	0.798	0.144	-0.022
ψ_6						1	0.309	0.144
ψ_7							1	0.798
ψ_8								1

Table 4. Overlap Integrals between the Valence Orbitals from the SC Wave Function for Propane

	ψ_1	ψ_2	ψ_3	ψ_4
ψ_1	1			
ψ_2		1	0.817	-0.092
ψ_3			1	0.087
ψ_4				1

Table 5. Spin-Coupling Coefficients and Weights of the Individual Spin Eigenfunctions from the SC Wave Function for Cyclopropane (Rumer Spin Basis)

k	$(\mu_1-\mu_2, \mu_3-\mu_4, \mu_5-\mu_6)$	$R_{C_{0k}}$	$R_{P_{0k}^{CC}}$	$R_{P_{0k}^{GN}}$
1	(1-2, 3-4, 5-6)	1.150 17	1.138 01	0.962 04
2	(1-4, 2-3, 5-6)	0.112 92	-0.047 76	0.012 36
3	(1-2, 3-6, 4-5)	0.112 92	-0.047 76	0.012 36
4	(1-6, 2-3, 4-5)	0.034 55	0.005 28	0.000 87
5	(1-6, 2-5, 3-4)	0.112 92	-0.047 76	0.012 36

Table 6. Spin-Coupling Coefficients and Weights of the Individual Spin Eigenfunctions from the SC Wave Function for Cyclobutane (Rumer Spin Basis)

k	$(\mu_1-\mu_2, \mu_3-\mu_4, \mu_5-\mu_6, \mu_7-\mu_8)$	$R_{C_{0k}}$	$R_{P_{0k}^{CC}}$	$R_{P_{0k}^{GN}}$
1	(1-2,3-4,5-6,7-8)	1.212 88	1.186 90	0.934 23
2	(1-4,2-3,5-6,7-8)	0.119 90	-0.048 04	0.016 23
3	(1-2,3-6,4-5,7-8)	0.119 90	-0.048 04	0.016 23
4	(1-6,2-3,4-5,7-8)	-0.005 45	-0.000 89	0.000 03
5	(1-6,2-5,3-4,7-8)	-0.007 34	0.003 64	0.000 09
6	(1-2,3-4,5-8,6-7)	0.119 90	-0.048 04	0.016 23
7	(1-4,2-3,5-8,6-7)	-0.000 02	-0.000 00	0.000 00
8	(1-2,3-8,4-5,6-7)	-0.005 45	-0.000 89	0.000 03
9	(1-8,2-3,4-5,6-7)	-0.028 95	0.001 55	0.000 53
10	(1-8,2-5,3-4,6-7)	-0.005 45	-0.000 89	0.000 03
11	(1-2,3-8,4-7,5-6)	-0.007 34	0.003 64	0.000 09
12	(1-8,2-3,4-7,5-6)	-0.005 45	-0.000 89	0.000 03
13	(1-8,2-7,3-4,5-6)	0.119 90	-0.048 04	0.016 23
14	(1-8,2-7,3-6,4-5)	-0.000 02	-0.000 00	0.000 00

Table 7. Spin-Coupling Coefficients and Weights of the Individual Spin Eigenfunctions from the SC Wave Function for Propane (Rumer Spin Basis)

k	$(\mu_1-\mu_2, \mu_3-\mu_4)$	$R_{C_{0k}}$	$R_{P_{0k}^{CC}}$	$R_{P_{0k}^{GN}}$
1	(1-2,3-4)	1.052 914	1.047 594	0.988 021
2	(1-4,2-3)	0.115 935	-0.047 594	0.011 979

Θ_{00}^6 (for C_3H_6) and Θ_{00}^8 (for C_4H_8) are illustrated additionally by Figures 4 and 5. In all three cases the values of the spin-function weights $R_{P_{0k}^{CC}}$ calculated according to the Chirgwin-Coulson formula (9) are somewhat unphysical: The most important spin function is attributed weight larger than unity, and most of the remaining weights turn out negative. The Gallup-Norbeck weights $R_{P_{0k}^{GN}}$ (see eq 10) appear to provide a more faithful assessment of the relative importance of the individual Rumer spin-couplings within the respective total spin functions.

The set of Rumer spin functions for the carbon framework of C_3H_6 involves two symmetry-adapted spin functions and three spin functions, which are equivalent by symmetry (see Figure 4). It is not difficult to notice that the pairing in spin functions $1 \equiv (1-2, 3-4, 5-6)$ and $4 \equiv (1-6, 2-3, 4-5)$ corresponds to that in

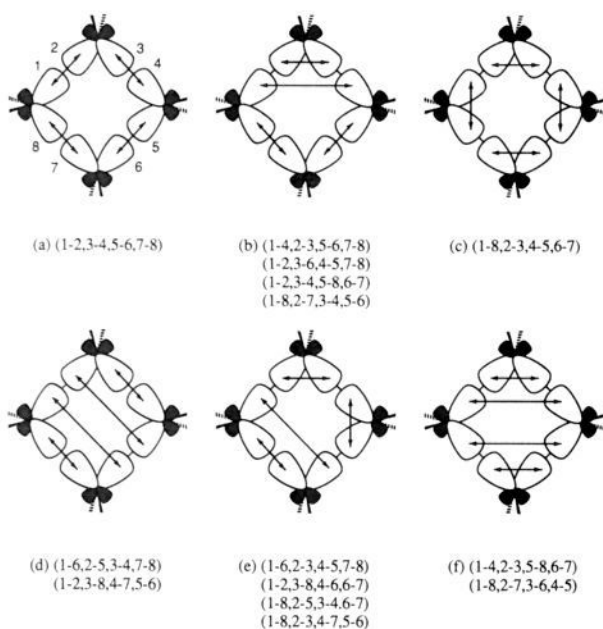


Figure 5. Schematic representation of the symmetry-unique Rumer spin-coupling patterns in cyclobutane.

the two Kekulé structures and in spin functions $2 \equiv (1-4, 2-3, 5-6)$, $3 \equiv (1-2, 3-6, 4-5)$, and $5 \equiv (1-6, 2-5, 3-4)$ —to that in the three Dewar structures from the classical VB model for benzene. The SC results for the π -system of benzene¹⁶⁻¹⁸ are well-known to be in close agreement with classical VB concepts. The six optimal SC orbitals are highly localized and, except for small distortions, closely resemble isolated $C(2p_z)$ atomic orbitals. The spin space for the π electrons includes five spin-coupling schemes, which in the Rumer basis are just those realized in the two Kekulé and three Dewar classical resonance structures. The Chirgwin-Coulson occupation numbers for the two Kekulé structures are identical, *ca.* 40.28%. Each of the three equivalent Dewar structures is found to enter the valence-space spin function with a weight of *ca.* 6.48%. Aromatic stabilization is attributed, as in classical VB theory, to resonance involving mainly the two Kekulé structures. No evidence for such a resonance is observed in the case of C_3H_6 . The Gallup-Norbeck occupation numbers for the two analogues of the Kekulé structures in benzene [see Figure 4, schemes (a) and (b)] are *ca.* 96.20% and *ca.* 0.09%, respectively (see Table 5). In fact, each of the Dewar-alike spin-couplings in Figure 4c has a higher Gallup-Norbeck occupation number (*ca.* 1.24%) than the spin-coupling in Figure 4b. Thus, from the viewpoint of SC theory, the σ -electron sextet forming the C-C bonds in cyclopropane is definitely *nonaromatic*. Its optimal spin-coupling pattern resembles those observed in other six-electron systems of D_{3h} symmetry, such as the π -electrons of borazine and boroxine, which have also been classified as nonaromatic by the SC approach.¹⁸

The 14 Rumer spin functions for C_4H_8 fall into six distinct groups (see Figure 5), which contain either a single symmetry-

adapted spin function or a set of (2 or 4) symmetry-related spin functions which transform into each other under the symmetry operations of the D_{2d} point group. The perfect-pairing scheme $1 \equiv (1-2, 3-4, 5-6, 7-8)$ is again predominant, with a Gallup-Norbeck occupation number of *ca.* 93.42% (see Table 6). Next in importance are the spin-coupling schemes from group (b) in Figure 5. Each of these has an occupation number of just *ca.* 1.62%, which indicates that classical resonance along the framework of C-C σ -bonds in C_4H_8 is negligible.

The comparison of the ${}^R P_{0k}^{GN}$ values for cyclopropane, cyclobutane, and propane (Tables 5-7) indicates that although there is no significant resonance in all three systems, the spin functions, other than the perfect-pairing one, are relatively most important in the case of C_4H_8 , and relatively least important—in the case of C_3H_8 .

4. Conclusions

SC theory furnishes a convincing explanation for the surprisingly close conventional strain energies of the smallest saturated ring hydrocarbons: cyclopropane and cyclobutane. The comparison between the main characteristic features of the corresponding SC wave functions: orbital overlaps, orbital shapes, and correlation energies per electron pair, indicates that the bonding around the carbon-carbon σ -bond frameworks in both molecules is rather similar.

The carbon atoms C_3H_6 as well as in C_4H_8 are held together by bent bonds formed by SC orbitals which closely resemble in appearance the SC orbitals observed in other systems in which the SC approach produces bent-bond descriptions: ethene and ethyne.³¹

The shorter carbon-carbon bond lengths in cyclopropane, compared to *n*-alkanes and cyclobutane, appear to be related to an obvious tendency of each of the six SC orbitals to participate, in addition to the C-C bond along which it is mostly directed, in a bonding interaction over the other C-C bond involving the same methylene group, which is expressed by a distortion in its shape and a correspondingly increased overlap integral.

Although the σ -electron sextet involved in the carbon-carbon bonds in cyclopropane is seemingly isoconjugate with the π -electron system of benzene, its SC description involves no significant resonance, and the optimal mode of coupling the spins of the six valence electrons is decidedly different from that in benzene. Thus, we find no evidence in favor of the idea of σ -aromaticity in C_3H_6 .

In cyclopropane, as well as in cyclobutane and in propane the optimal spin-coupling pattern of the electrons involved in the carbon-carbon bonds is markedly dominated by the respective perfect-pairing spin functions in which the spins of electrons occupying the pairs of orbitals forming the bonds are coupled to singlets. On the other hand, the overlap integrals between orbitals related to different bonds can be significantly nonzero. Thus, of the improvements embodied in the SC wave function ansatz, in comparison with the most commonly used GVB wave function, involving strong-orthogonality and perfect-pairing constraints, the more important one for the systems studied in this article is the lifting of the strong-orthogonality restriction.