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Theoretical Studies on 1,4,6,9-Spiro[4.4]nonatetrayl, an Organic Tetraradical

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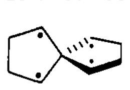
Abstract: The electronic structure of 1,4,6,9-spiro[4.4]nonatetrayl (**1**) has been investigated by using ab initio electronic structure theory. The spiroconjugative interaction of the four radical centers is evidenced by a large orbital splitting. However, spiroconjugation does not confer upon the structure the electronic properties of a biradical, contrary to qualitative MO considerations. Structure **1** possesses the six, low-lying (covalent) states that characterize a tetraradical. Spiroconjugation does strongly influence the relative energies of these six states and does lead to a small but significant stabilization of the molecule. Possible modes of ring closure and closed shell isomers of **1** are also discussed.

For some time, we have been interested in the possibility of generating and experimentally characterizing 1,4,6,9-spiro[4.4]nonatetrayl (**1**).[2] As described below, qualitative molecular orbital (MO) and strain energy considerations suggested that **1** could be especially stable relative to a prototypical tetraradical. In conjunction with our experimental efforts, we have now applied quantitative ab initio electronic structure theory to appropriate model systems for **1**. Our goal has been to evaluate both the viability of **1** as a characterizable intermediate and the validity of the qualitative MO analyses which aroused our interest in **1**.



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Qualitative MO Analysis. The Biradical Model.

A structure with four noninteracting, essentially nonbonding electrons would be expected to be highly reactive and quite difficult to characterize experimentally. In **1**, however, the four radical centers interact through the phenomenon of spiroconjugation.[3] The consequences of this effect are shown in Figure 1, in which **1** is constructed from the union of two 1,3-cyclopentanediyl (**2**) fragments. Biradical **2** contains two nearly degenerate nonbonding molecular orbitals (NBMO), designated $3b_1$ and $2a_2$ in C_{2v} symmetry.[4] By symmetry the b_1 orbitals cannot mix, and they give rise to a degenerate pair of NBMO (e) in **1** (D_{2d} symmetry). The a_2 orbitals of **2** can mix, and the result is a stabilized b_1 orbital and a destabilized a_2 orbital in **1**. While this mixing is predictable from symmetry alone, a crucial consideration is the magnitude of the spiroconjugative effect, as manifested by the b_1–a_2 orbital split. Photoelectron spectroscopic studies on spiro[4.4]nonatetraene and related structures have shown that the effects of spiroconjugation are large enough to be easily observable in the spiro[4.4]nonane ring system.[5,6] Schweig has developed an empirical correlation that allows the prediction of the magnitude of the spiroconjugative split in such structures based on the MO coefficients of the appropriate p orbitals in the noninteracting fragments.[6] If we assume coefficients of $2^{-1/2}$ for the p orbitals of the NBMO of **2**, then Schweig's formula predicts a ca. 2-eV split between the b_1 and a_2 orbitals of **1**.

The orbital diagram of Figure 1 and the electronic configuration it implies suggest that while **1** is structurally a tetraradical (two fewer bonds than allowed by the standard rules of valence),[7] electronically it is a biradical (two electrons in a degenerate pair of NBMO).[8] At the level of one-electron theory, such an electronic configuration suggests a substantial stabilization for **1** relative to a tetraradical in which the radical centers do not interact (four electrons in four NBMO). Thus, a major goal of the present work has been to determine the extent to which the $b_1{}^2\, e^2$ configuration of Figure 1 correctly describes the electronic structure of **1**.

This biradical configuration gives rise to four states: a triplet and three singlets.[8] These states are as shown in eq 1–4. Both

$$^3A_2 = \frac{1}{\sqrt{2}}\mathcal{A}[(\ldots b_1{}^2e_xe_y) - (\ldots b_1{}^2e_ye_x)]\,(\alpha\beta + \beta\alpha) \qquad (1)$$

$$^1B_1 = \frac{1}{\sqrt{2}}\mathcal{A}[(\ldots b_1{}^2e_x{}^2) - (\ldots b_1{}^2e_y{}^2)](\alpha\beta - \beta\alpha) \qquad (2)$$

$$^1A_1 = \frac{1}{\sqrt{2}}\mathcal{A}[(\ldots b_1{}^2e_x{}^2) + (\ldots b_1{}^2e_y{}^2)](\alpha\beta - \beta\alpha) \qquad (3)$$

$$^1B_2 = \frac{1}{\sqrt{2}}\mathcal{A}[(\ldots b_1{}^2e_xe_y) + (\ldots b_1{}^2e_ye_x)](\alpha\beta - \beta\alpha) \qquad (4)$$

$^1A_1$ and $^1B_2$ have zwitterionic character and are expected to be higher lying in energy. The $^3A_2$ and $^1B_1$ states are both pure biradical or covalent states, and at the level of two-electron theory, one would predict an energetic ordering of $^3A_2 < {}^1B_1$, due to the exchange repulsions in the singlet. However, one can anticipate that configuration interaction (CI) will preferentially stabilize the singlet and lead to a $^1B_1 < {}^3A_2$ energetic ordering. This prediction is based on analogy to square (D_{4h}) cyclobutadiene, for which **1** is a three-dimensional analogue. In cyclobutadiene, the electronic configuration analogous to that of Figure 1 gives rise to the same four states as in eq 1–4, with the symmetry labels augmented by a subscript g.[9] Thus, $^1A_{1g}$ and $^1B_{2g}$ are high-lying, zwitterionic states. Since the NBMO of cyclobutadiene can be confined to disjoint sets of atoms, exchange repulsions in the $^1B_{1g}$ state are minimal.[10] When CI is included in the wave function, $^1B_{1g}$ is

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[1] (a) NSF Predoctoral Fellow, 1980–1983. (b) Fellow of the Alfred P. Sloan Foundation, 1983–1985.

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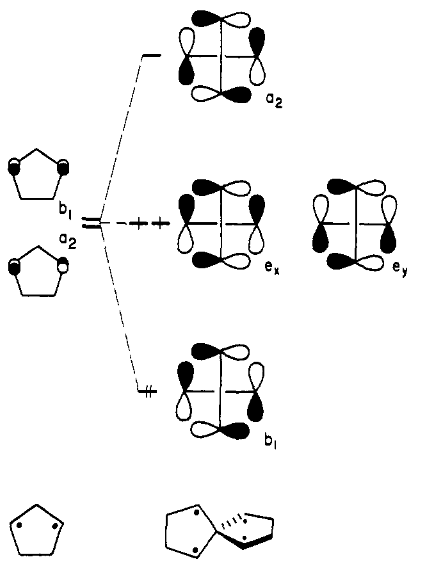


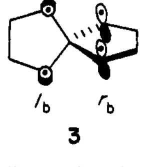
Figure 1. Orbital mixing diagram for **1**. Orbitals of **1** are pictured as Newman projections down the S_4 axis.

Figure 2. Partially localized orbitals for **4**.

preferentially stabilized and emerges as the ground state, with $^3A_{2g}$ slightly higher.[11] Clearly, by taking the appropriate linear combinations, the NBMO of Figure 1 can be made to span disjoint sets of atoms, and one would expect minimal exchange repulsions in the $^1B_1$ state of **1**. Thus, qualitative MO considerations predict a *singlet ground state* for **1** ($^1B_1$) with a low-lying $^3A_2$ state.

Qualitative Valence Bond Analysis. The Tetraradical Model

Before proceeding to our quantitative analysis of the electronic structure of **1**, we will also consider the alternative qualitative description of **1**. In this view, **1** is considered as essentially a tetraradical with little spiroconjugation. The electronic structure of such a species is most easily analyzed in terms of valence bond (VB) wave functions, in which there is one electron in the nonbonding p orbital of each of the four radical carbons. Labeling these orbitals as l_a and l_b on the left diyl and r_a and r_b on the right diyl, as in **3** leads to a singlet state (eq 5) and a triplet state (eq 6) on the left and similar wave functions $^1\Psi_r$ and $^3\Psi_r$ on the right. In the VB model the total wave function of the tetraradical is formed by products of these wave functions, leading to the combinations of eq 7.



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$$^1\Psi_l = (l_al_b + l_bl_a)(\alpha\beta - \beta\alpha) \tag{5}$$

$$^3\Psi_l = (l_al_b - l_bl_a)\begin{Bmatrix}(\alpha\alpha)\\(\alpha\beta + \beta\alpha)\\(\beta\beta)\end{Bmatrix} \tag{6}$$

$$\begin{array}{lll}\text{SS:} & ^1\Psi_l(1,2)^1\Psi_r(3,4) & \\ \text{TS} \pm \text{ST:} & ^3\Psi_l(1,2)^1\Psi_r(3,4) \pm {}^1\Psi_l(1,2)^3\Psi_r(3,4) & (7)\\ \text{TT:} & ^3\Psi_l(1,2)^3\Psi_r(3,4) & \end{array}$$

Antisymmetrization, to satisfy the Pauli principle, and consideration of the D_{2d} symmetry of the system lead to the wave functions in eq 8–12.

$$\text{SS} = {}^1A_1 = \mathcal{A}\{l_al_br_ar_b[(\alpha\beta - \beta\alpha)(\alpha\beta - \beta\alpha)]\} \tag{8}$$

$$(\text{TS} \pm \text{ST}) = {}^3E = \mathcal{A}\{l_al_br_ar_b[\alpha\alpha(\alpha\beta - \beta\alpha) \pm (\alpha\beta - \beta\alpha)\alpha\alpha]\} \tag{9}$$

$$^1\text{TT} = {}^1B_1 = \mathcal{A}\{l_al_br_ar_b[\alpha\alpha\beta\beta + \beta\beta\alpha\alpha - {}^1/_2(\alpha\beta + \beta\alpha)(\alpha\beta + \beta\alpha)]\} \tag{10}$$

$$^3\text{TT} = {}^3A_2 = \mathcal{A}\{l_al_br_ar_b[\alpha\alpha(\alpha\beta + \beta\alpha) - (\alpha\beta + \beta\alpha)\alpha\alpha]\} \tag{11}$$

$$^5\text{TT} = {}^5B_1 = \mathcal{A}\{l_al_br_ar_b[\alpha\alpha\alpha\alpha]\} \tag{12}$$

The TT cases bear some discussion here. When a pair of two-electron triplets is combined, there is a total of 3 × 3 = 9 states. However, resolving these states in terms of the total spin for the four-electron system leads to total spins of $S = 2$, 1, and 0, i.e., a quintet ($^5B_1$), a triplet ($^3A_2$), and a singlet ($^1B_1$), for a total of nine states. In the approximation that the two triplets interact only weakly, the three TT states can be described by a Heisenberg Hamiltonian (eq 13) where J is the exchange coupling

$$E_s = E_0 + JS(S + 1) \tag{13}$$

term. In the case that the orbitals of the two T states overlap, the J is expected to be positive, so that $^1B_1$ is lowest in energy. The energies of the higher spin states are then as in eq 14. In

$$E(^3A_2) = E(^1B_1) + 2J \qquad E(^5B^1) = E(^1B_1) + 6J \tag{14}$$

the case that the l and r orbitals are *orthogonal*, eq 14 still applies, but J will be negative, leading to a quintet ground state.

Assuming *no* interaction of the two 1,3-cyclopentanediyl fragments, one would expect the intrinsic 0.9 kcal/mol preference for the triplet state in this fragment[4,12] to generate the energy spectrum of eq 15.

$$E(\text{SS}) = (E(\text{TS}) + 0.9) = (E(\text{TT}) + 1.8) \tag{15}$$

Summarizing the VB description, a tetraradical is expected to have six low-lying, covalent (nonionic) states: two singlets, three triplets, and a quintet. The closeness of these six states is the signature of a tetraradical.

Computational Methods

Unless otherwise noted, all calculations were performed with a valence double-ζ (VDZ) basis set. Dunning's contraction[13] (3s,2p) of Huzinaga's (9s,5p) basis set[14] was used for carbon, and for hydrogen a comparable (4s/2s) contraction with each Gaussian exponent scaled by a factor of 1.44 was employed.[13] All C–C bond lengths were 1.52 Å, in accord with Schaefer's geometry optimization[4] of the triplet state of **2**, and all C–H bond lengths were 1.09 Å.

All ab initio calculations were performed on the model system tetramethylenemethane. Several recent studies have demonstrated that deleting the ethano bridges in 1,3-cyclopentanediyl (**2**) and related structures does not significantly alter the electronic structures of the molecules,[12,15] thus verifying the validity of this model. For most calculations a D_{2d} structure (**4**) was considered, with different sets of C–C–C angles. In **4a** the central carbon is tetrahedral, giving a structure which is unbiased with respect

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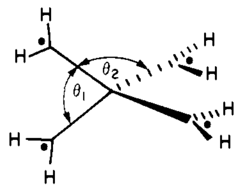

4

	θ_1	θ_2
a	109.5	109.5
b	102.0	113.3

to favoring or disfavoring the spiroconjugative effect. In **4b** $\theta_1 = 102°$, which is the value calculated by Schaefer[4] for the analogous angle in **2**. Thus, **4a** may be considered a general model for the electronic interactions we intend to study, while **4b** is perhaps a better model for the precise interactions present in structure **1**.

Results and Discussion

Spiroconjugation. As a test for the effectiveness of spiroconjugation in **1**, we determined the Hartree–Fock (HF) wave function for the $^5B_1$ state of **4**.[16] This quintet state does indeed possess MO's like those of Figure 1, and the b_1–a_2 energy gap is 2.71 eV in **4a** and 2.25 eV in **4b**. Thus, the qualitative prediction of a significant b_1–a_2 split in **1** is confirmed, and the magnitude is roughly as expected. Clearly, the smaller value of θ_1 in **4b** moves the spiroconjugatively interacting radical centers further apart and thus diminishes the orbital splitting relative to **4a**.

Electronic States of 4a. One of our major goals has been to determine the ground electronic state for a structure such as **1** and the nature of any other low-lying states. We began by allowing a complete CI for **4a** within the space of the b_1, e, and a_2 orbitals using the MO's determined in the HF calculation on $^5B_1$ and the VDZ basis set (CI–VDZ). This resulted in six low-lying states energetically ordered as $^1B_1 < {}^3A_2 < {}^3E < {}^1A_1 < {}^5B_1$. The relative energies are given in Table I, and the contributions of the various configurations to these states are given in Table II. There is a >6-eV energy gap between these six states and the next lowest state.

In order to evaluate the reliability of the CI wave functions in predicting the relative energies of these states, we extended the calculations in several ways, as summarized in Table I. Determination of the multiconfiguration self-consistent field (MCSCF) wave functions[16] (equivalent to full GVB wave functions[17]) for **4a** with the VDZ basis set for the singlet and triplet states led to only a minor decrease in energy relative to the CI wave functions. Similarly, repeating the CI calculations with the VDZ basis set augmented by a set of polarization functions (d orbitals)[18] on each carbon (CI + d) led to only a minor change in relative energies. Finally, starting with the $^1B_1$, MCSCF–VDZ wave function and allowing a full CI within the b_1 e a_2 space plus all single and double excitations from these orbitals into the virtual orbitals (POL(4/2))[16] stabilized the $^1B_1$ state by only 2.55 kcal/mol relative to the MCSCF $^1B_1$ wave function. By comparison, the corresponding POL(2/2) calculation on the $^5B_1$ state led to a 1.03 kcal/mol stabilization relative to the HF wave function.

We thus conclude that the CI-VDZ wave function using the HF $^5B_1$ orbitals provides a good description of the electronic structure of **4a**, and subsequent discussions will emphasize this level of theory. For a best estimate of the $^1B_1$–$^5B_1$ energy gap, one might assume that the stabilizations afforded $^1B_1$ by the various extensions of the CI–VDZ wave functions are additive.[19] This leads to a value of 8.5 + 1.4 (d orbitals) + 1.6 (MCSCF) + 1.5 (POL 4/2) = 13.0 kcal/mol.

Table I. Relative Energies (kcal/mol) for Various States of 4

	geometry 4a				geometry 4b
state	CI-VDZ[b]	MCSCF[c]	CI + d[d]	RCI[e]	CI-VDZ[f]
$^1B_1$ (TT)	-8.51	-10.12	-9.92	+7.61	-3.51
$^3A_2$ (TT)	-6.56	-7.31	-7.61	+5.06	-2.90
^3E (TS)	-2.44	-3.22	-2.99	+3.45	-1.11
$^1A_1$ (SS)	-2.08	-2.60	-2.71	+4.35	-0.92
$^5B_1$ (TT)	0.00[a]	0.00	0.00	0.00	0.00

[a] Total energy: -193.73288 hartrees. [b] Full four-electron CI within the b_1, e, a_2 space using the orbitals from the HF solution on the $^5B_1$ state. Total energy of the $^1B_1$ state: -193.74644 hartrees. [c] Full MCSCF solutions for each state using all configurations for four electrons distributed over the b_1, e, a_2 space. Total energy of the $^1B_1$ state: -193.74902 hartrees. [d] Same solutions as in *b* except that d functions were included on all carbons. Total energy of the $^1B_1$ state: -193.81752 hartrees. [e] Four-electron CI within the $r_+r_-l_+l_-$ space, using the partially localized orbitals of Figure 3 obtained through linear combinations of the orbitals from the HF solution for $^5B_1$. Configurations restricted to those of the $(r_+r_-)^2(l_+l_-)^2$ type. Total energy of the $^1B_1$ state: -193.72074 hartrees. [f] Same solutions as in *b* except for the geometry. Total energy of $^1B_1$: -193.73124 hartrees.

Table II. CI–VDZ Wave Functions of 4a

	configuration				
state	b_1	e_x	e_y	a_2	coeff[a]
$^1B_1$	2	0	2	0	-0.55
	2	2	0	0	0.55
	1	1	1	1	-0.47
	0	0	2	2	0.30
	0	2	0	2	-0.30
$^3A_2$	2	1	1	0	0.67
	1	0	2	1	0.46
	1	2	0	1	-0.46
	0	1	1	2	-0.36
^3E[b]	1	1	2	0	0.59
	2	0	1	1	0.56
	0	2	1	1	-0.42
	1	1	0	2	-0.40
$^1A_1$	0	2	2	0	0.51
	1	1	1	1	-0.48
	2	0	0	2	0.46
	2	2	0	0	-0.35
	2	0	2	0	-0.35
	0	2	0	2	-0.17
	0	0	2	2	-0.17
$^5B_1$	1	1	1	1	1.0

[a] Only configurations with coefficients greater than 0.05 are included. [b] The other component of ^3E is not shown. To obtain it, interchange the occupations of e_x and e_y.

We have also determined the CI wave functions for **4a** using the set of partially localized orbitals of Figure 2. Each localized orbital is confined to one "ring", i.e., a trimethylene unit which models a five-membered ring of **1**. The orbitals are designated r or l according to whether they derive from the right or left ring. The subscript describes the phase relationship between the p orbitals. The resulting wave functions, shown in Table III, allow one to confirm that the six low-lying states for **4a** do, indeed, correspond to the six covalent states discussed above (eq 8–12). For each state, each ring is in either a biradical singlet or a triplet state in the dominant configurations. The $^1B_1$ state is dominated by a (1111) configuration, and the spin eigenfunction is the coupling of two triplets to give an overall singlet.[20] Its triplet

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[16] All Hartree–Fock calculations were performed by using the MQM:GVB2P5 program: Bair, R. A.; Goddard, W. A., III, unpublished work. Bair, R. A., Ph.D. Thesis, California Institute of Technology, 1982. The CI calculations were carried out by using the MQM:CI2P5 program: Bobrowicz, F. W.; Goodgame, M. M.; Bair, R. A.; Walch, S. P.; Goddard, W. A., III, unpublished work. Bobrowicz, F. W., Ph.D. Thesis, California Institute of Technology, 1974. MCSCF calculations were carried out by using the MQM:GVB3 program: Yaffe, L.; Goodgame, M. M.; Bair, R. A.; Goddard, W. A., III, unpublished work.

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[18] The orbital exponent for the carbon polarization function was 0.75.

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Table III. CI-VDZ Wave Functions of 4a Using the Partially Localized Orbitals of Figure 2

	configuration				
state	r_+	r_-	l_+	l_-	coeff[a]
$^1B_1$	1	1	1	1[b]	0.97
	1	2	1	0	-0.18
	1	0	1	2	-0.18
$^3A_2$	1	1	1	1[c]	-0.77
	1	1	1	1[d]	0.59
	1	2	1	0	0.16
	1	0	1	2	0.16
^3E[e]	2	0	1	1	0.50
	1	1	2	0	0.50
	0	2	1	1	-0.48
	1	1	0	2	-0.48
	2	1	1	0	0.09
	1	0	2	1	-0.09
	0	1	1	2	0.08
	1	2	0	1	-0.08
$^1A_1$	0	2	2	0	0.50
	2	0	0	2	0.50
	2	0	2	0	-0.51
	0	2	0	2	-0.46
	0	1	2	1	-0.13
	2	1	0	1	-0.13
$^5B_1$	1	1	1	1	1.00

[a] Only configurations with coefficients greater than 0.05 are included. [b] Spin eigenfunction: $A\{r_+r_-l_+l_-[\alpha\alpha\beta\beta+\beta\beta\alpha\alpha - {}^1/_2(\alpha\beta + \beta\alpha)(\alpha\beta + \beta\alpha)]\}$. [c] Spin eigenfunction: $A\{r_+r_-l_+l_-\cdot[\alpha\alpha\beta\alpha - {}^1/_2(\alpha\beta + \beta\alpha)\alpha\alpha]\}$. [d] Spin eigenfunction: $A\{r_+r_-l_+l_-\cdot[\alpha\alpha\alpha\beta - {}^1/_3(\alpha\alpha\beta + \alpha\beta\alpha + \beta\alpha\alpha)\alpha]\}$. [e] The other component of ^3E is not shown. To obtain it, interchange the occupations of the left and right ring components.

counterpart is $^3A_2$, also with a (1111) spatial configuration, but possessing spin eigenfunctions representing two ring triplets coupled to an overall triplet wave function. The $^5B_1$ state is straightforward, as the (1111) configuration is required in the high spin case. The other states contain biradical singlets, as evidenced by the fact that each configuration containing a doubly occupied orbital is accompanied by an *out-of-phase* mixture[8] of the configuration with the alternative orbital of the same ring doubly occupied. For example, a $r_+^2r_-^0(l_+l_-)^2$ configuration is always paired out of phase with the analgous $r_+^0r_-^2(l_+l_-)^2$ configuration.

In the singlet manifold, after $^1B_1$ and $^1A_1$, there is a substantial energy gap to a collection of states with excitation energies in the range 6.7–11.3 eV (CI–VDZ). Inspection of these states using the localized orbitals reveals that each contains one ring in a biradical singlet state and one ring in a zwitterionic state. There is then another gap to a group of states with excitation energies from 17.8 to 19.2 eV, for which both rings have zwitterionic character. In the triplet manifold, all higher states fall in the range of 7.9–11.1 eV, since there can be no doubly zwitterionic states. The total number of higher-lying singlets is 18, while there are 12 higher-lying triplets. Combined with the six low-lying covalent states this produces the 36 states one expects from placing four electrons in four orbitals.

The results for **4a** clearly indicate that the electronic structure of **1** is essentially that of a tetraradical and not a biradical. There are six low-lying states and not two as predicted for a biradical. However, the results also demonstrate a significant interaction across the two five-membered rings, i.e., spiroconjugation. This is seen in the relative energies of the TT states, for which the noninteracting model predicts $^5B_1 < {}^3A_2 < {}^1B_1$. For **4a**, precisely the opposite energetic ordering is seen.

In order to better quantify the spiroconjugative effect, we have studied a model for **1** in which spiroconjugation is "turned off". To do so, we started with the localized orbitals of **4a** (Figure 2) and performed a CI calculation (VDZ basis). However, in the CI we forced double occupation of each ring so that each contained a fully correlated singlet or triplet biradical, but any kind of interaction between the rings was not possible. The results of this restricted CI (RCI) calculation are shown in Table I and Figure 3. There is a dramatic reversal in the order of states in the RCI results relative to the full CI. Analysis reveals that the RCI model shows excellent *quantitative* agreement with the previously discussed model (eq 13) assuming orthogonal l and r orbitals. The energetic relationships of the TT states summarized in eq 14 are completely in accord with the RCI results. Considering the $^1B_1$–$^3A_2$ gap leads to a value of −1.28 kcal/mol for J, while the $^1B_1$–$^5B_1$ gap implies a J of −1.27 kcal/mol, in stunning agreement. Also, the energy gap between the TS states (^3E) and the multiplicity-weighted average of the TT states is 0.92 kcal/mol, while that between the TS and SS ($^1A_1$) states is 0.90 kcal/mol. Again, this result is in remarkable agreement with the energy spectrum of eq 15. Thus, the RCI calculation provides an excellent model for a structure such as **1**, but with orthogonal l and r rings.

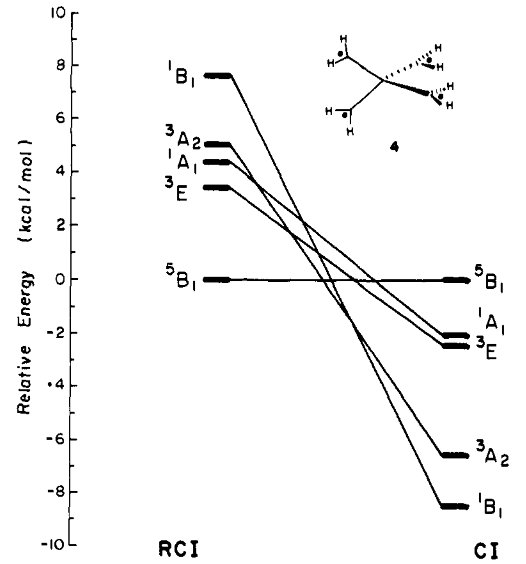

Figure 3. Relative energies of the states of **4a** from RCI and CI–VDZ calculations.

The results of Figure 3 indicate that although spiroconjugation in **4a** is not strong enough to turn the tetraradical into a biradical, it does profoundly affect the energetic ordering of the six tetraradical states. In order to rationalize the relative energies of all six states, one must invoke an interplay between two effects. These are the exchange coupling term, J, of eq 14, which is an indication of spiroconjugation, and the intrinsic, high-spin preference of the biradical components, summarized in eq 15. The energetic ordering of the TT states, $^1B_1 < {}^3A_2 < {}^5B_1$, is qualitatively understandable in terms of eq 14. Apparently, the $6J$ destabilization of the $^5B_1$ state is enough to lift this TT state above the TS and SS states. The energetic ordering $^3E < {}^1A_1$ is consistent with the expectation TS < SS.

It should be noted that although the qualitative MO model did not suggest the presence of six low-lying states for **4a**, it does satisfactorily rationalize the relative energies of these states. The basic consideration in such an analysis is the stabilization of the b_1 MO and the destabilization of the a_2 MO (Figure 1). The clear-cut prediction of a $^1B_1$ ground state followed closely by $^3A_2$ discussed above is fully confirmed by the calculations. These states are low-lying because they can fully benefit from the $b_1^2e^2$ configurations. Such configurations make up more than 60% of the $^1B_1$ wave function, compared to less than 20% for the analogous $e^2a_2^2$ configurations. In fact, throughout Table II one finds smaller CI coefficients for comparable configurations in which a_2 replaces b_1, clearly demonstrating the influence of spiroconjugation. The $^5B_1$ state is highest in energy because the $b_1{}^1e_x{}^1e_y{}^1a_2{}^1$ configuration is mandated and does not benefit from the spiroconjugative stabilization of b_1. The ^3E and $^1A_1$ states are of intermediate energy

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because each is only partially able to take advantage of the spiroconjugative effect. Each configuration that contributes to ^3E must have an odd number of electrons in the e pair of orbitals. Thus, any configuration with b_1 doubly occupied necessarily has a_2 singly occupied (Table II), which partially cancels the stabilizing effect. For the $^1A_1$ state, $b_1{}^2e^2$ configurations are possible (eq 3). However, these are less favorable, because they must have some ionic character, which is destabilizing. The reason that $^1A_1$ is a low-lying state for **1** is that there are several other configurations with A_1 symmetry that can mix with the $b_1{}^2e^2$ configuration so as to diminish the ionic nature of the state. This is not the case for $^1B_2$ (eq 4), and it thus remains high-lying.

We had previously mentioned the analogy between **1** and D_{4h} cyclobutadiene. At a comparable level of theory (CI–VDZ), the lowest-lying states for D_{4h} cyclobutadiene, along with relative energies in kcal/mol, are as follows: $^1B_{1g}$ (0), $^3A_{2g}$ (10), $^1A_{1g}$ (50), $^1B_{2g}$ (84), ^3E_u (90), and $^5B_{1g}$ (152).[21] The overall pattern is similar to that for **1**, but the energetic advantage of pairing two electrons in the lowest π MO is much greater than that of doubly occupying the b_1 MO of **1**. This is why $^1A_{1g}$ lies well below ^3E_u and why $^1B_{2g}$ is lower than ^3E_u, even though $^1B_{2g}$ is not a covalent state.

Electronic States of 4b. On going from **4a** to **4b**, in which $\theta_1 = 102°$, the magnitude of the spiroconjugative effect is diminished, as indicated by the smaller b_1–a_2 gap in the HF $^5B_1$ orbitals. By coincidence, the singlet–triplet energy gap in (0,0)-trimethylene, the fragment from which **4** is built, is the same whether $\theta_1 = 102°$ or $\theta_1 = 109.5°$.[12] Thus, the intrinsic electronic structure of the fragments is not significantly affected by this angle change. Given this result and the above analysis of **4a**, one would expect that distorting **4a** to **4b** would not alter the energetic ordering of states but would simply diminish the magnitudes of the energy separations. The results shown in Table I confirm this expectation. Thus, all of the above discussion of the electronic structure of **4a** is directly applicable to **4b**, with the only necessary change being a small weakening of the spiroconjugative effect.

Stabilization of 1. One of the major goals of the present work has been to assess the extent to which spiroconjugation in **1** stabilizes the molecule relative to a "normal" tetraradical. The choice of reference point is crucial to this determination. Given the above discussion it would seem that the RCI description provides a useful model for what a structure such as **1** would be like if there were no spiroconjugation. One could then say, for example, that $^1B_1$ is stabilized by 8.51 + 7.61 = 16.12 kcal/mol (Table I). For a reference state that models a truly typical tetraradical, it would perhaps be better to consider the spin-multiplicity-weighted average energy of the RCI states, which is 2.99 kcal/mol above the HF $^5B_1$ state. The $^1B_1$ stabilization would then be 8.51 + 2.99 = 11.50 kcal/mol.

In considering structure **1**, one should make two corrections to the above numbers. The comparisons between RCI and CI results are all based on simple CI–VDZ wave functions. We have shown that including d orbitals, using an MCSCF wave function and allowing excitations into higher orbitals (POL(4/2)) all enhance the magnitude of the spiroconjugative effect slightly. The stabilization energy could be similarly increased, but the overall effect would be relatively small. The second correction concerns the choice of the best geometry to model **1**. All of the RCI calculations were based on structure **4a**, with $\theta_1 = 109.5°$. In **4b**, with θ_1 the same as that calculated for the analogous angle in biradical **2** (102°), the spiroconjugative effect is smaller. It seems possible that in **1** θ_1 might expand significantly beyond 102°, at the expense of ring strain, so as to enhance spiroconjugation. However, it still seems likely that in **1**, θ_1 is less than 109.5°, and a stabilization energy based on structure **4a** is probably overestimated.

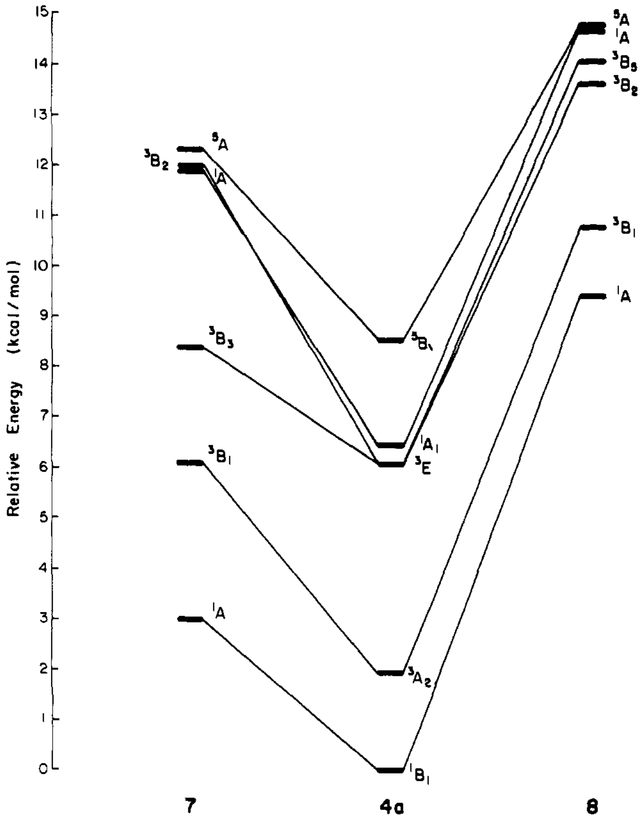
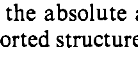


Figure 4. Relative energies of the states of **4a** and forms distorted by the second-order Jahn–Teller effect.

Geometrical Distortions. Given the analogy between **1** and square cyclobutadiene, one might expect a second-order Jahn–Teller distortion of the $^1B_1$ state, analogous to the stabilizing square-to-rectangular distortion of singlet cyclobutadiene.[11] This would push the molecule toward one of its closed shell forms, tetracyclo[4.3.0.0^{1,5}.0^{2,9}]nonane (**5**, D_2 symmetry). Structure **5** could also be called [5.3.5.3]fenestrane, and like its isomer [4.4.4.4]fenestrane (windowpane, **6**), **5** should be highly strained, with the spiro carbon distorted toward planarity.[22] In order to get some feeling for the nature of such a structure, we have completely optimized the geometry of **5** using MNDO.[23] This semiempirical method predicts $\Delta H_f°$ (**5**) = 110.5 kcal/mol and a strain energy of 139 kcal/mol. While it is very much uncertain what the absolute accuracy of MNDO is when applied to such a distorted structure, it is interesting to compare these results with a recent treatment of **6** at the same level of theory.[24] For **6**, MNDO predicts $\Delta H_f°$ = 150.6 kcal/mol, giving a strain energy of 179 kcal/mol.[24] It can be seen that **5** is predicted to be much less strained than **6**. The MNDO geometry of **5** does not contain a planar carbon, although it is highly strained. The six C–C–C angles around the spiro carbon are pairwise related by symmetry and have values of 67.3° (internal to cyclopropane), 126.8° (internal to cyclopentane), and 141.8°.



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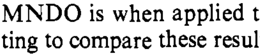

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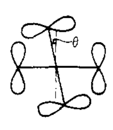
We have made two attempts using ab initio theory to determine whether **1** will undergo a stabilizing, second-order Jahn–Teller distortion. We first studied structure **7**, in which one end of **4a**



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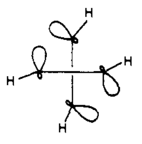

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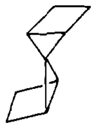

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was rotated around the S_4 axis by an angle $\theta = 10°$. The other distortion mode involved a pyramidalization at each carbon in such a way as to produce structure **8**. Such pyramidalization does distort the molecule toward **5**, but the carbon atoms are not moved any closer to one another. The pyramidalization was accomplished by moving one hydrogen at each carbon of **4a** out of plane, such that its C–H bond made at 30° angle with the original C–C–H plane. Both **7** and **8** have D_2 symmetry, which serves to remove all the degeneracies present in **4a**.

The results of the calculations on **7** and **8**, which were performed at the CI–VDZ level, are summarized in Figure 4. Both distortions are destabilizing for **4a**, and both lead to only minor perturbations of the relative energies of the six covalent states. It would thus appear that **1** cannot significantly stabilize itself by a second-order Jahn–Teller distortion.

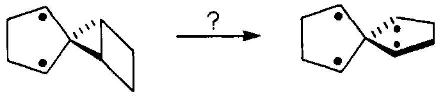
The alternative closed-shell form of **1**, 5,5′-spirobi[bicyclo-[2.1.0]pentane] (**9**, C_2 symmetry), arises by a double, disrotatory ring closure of **1**. This structure should have ca. 125 kcal/mol of strain energy, but we have recently prepared it and found it to be a stable, isolable molecule.[2] Pursuing the analogy between **1** and cyclobutadiene further, **9** corresponds to tetrahedrane. While the cyclobutadiene–tetrahedrane interconversion is forbidden by orbital symmetry, this is formally not the case for the interconversion of **1** and **9** because of the low symmetry of **9**. However, inspection of the orbitals of Figure 1 reveals that it is the e pair which on disrotation correlates with the σ-bonding orbitals of **9**. Both the b_1 and a_2 orbitals lead to σ^* interactions. Thus, the **1**–**9** interconversion is forbidden in the sense of the "natural orbital correlations",[25] and one might anticipate a barrier to the double ring closure of **1** to **9**.

Conclusions

Our calculations indicate that **1** possesses six low-lying states that correspond to the covalent states of a tetraradical. Thus, the spiroconjugative interaction predicted on the basis of qualitative MO arguments (Figure 1) is not strong enough to convert **1** into a biradical. However, the relative energies of the six tetraradical states are influenced strongly by spiroconjugation.

We believe the present results are relevant to our ongoing experimental effort to characterize **1**.[2] One of our goals is to observe **1** spectroscopically, under cryogenic, matrix-isolation conditions. The prediction of a singlet ground state rules out ESR detection of **1** (unless the $^3A_2$ state can be thermally populated), leaving IR and UV spectroscopy as the best candidates. The prediction of a significant, although relatively small, stabilization in **1** due to spiroconjugation suggests that **1** lies in a potential energy minimum. Distorting the molecule toward closed shell isomer **5** destabilizes the molecule (Figure 4), while ring closure to **9** goes against the "natural orbital correlations". Thus, one might expect potential energy barriers to closure of **1** to **5** or **9**, and **1** could well represent an absolute potential energy minimum. Given that biradical **2** is directly observable at temperatures below 40 K,[26] it seems quite possible that tetraradical **1** will also be observable.

Another goal of our experimental work has been to determine whether a structure such as **1** could be considered as a viable reactive intermediate in solution chemistry at ambient temperatures. One of the several approaches we are studying involves the ring opening of biradical **10** to give tetraradical **1**. Such a reaction would relieve over 50 kcal/mol of strain energy[22] and would turn on all of the spiroconjugative stabilization of **1**. As discussed above, there is some uncertainty as to the magnitude of the calculated stabilization energy of **1**, due to uncertainties in the choice of reference state and best geometry for **1**. As such, we do not feel that the present results allow for a clear-cut prediction concerning the viability of such a reaction. Until more complete calculations on **1**, **10**, and related structures become feasible, such questions will have to be addressed experimentally.



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Concerning the Viability of 1,4,6,9-Spiro[4.4]nonatetrayl as a Reactive Intermediate. New Biradical-to-Biradical Rearrangements

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Abstract: Direct photolysis of 7,7′-spirobi[2,3-diazabicyclo[2.2.1]hept-2-ene] (**6**) leads to loss of 1 equiv of N_2 and ring closure of the resulting biradical to 2,3-diazabicyclo[2.2.1]hept-2-ene-7,5′-spirobicyclo[2.1.0]pentane (**8**). Generation of the triplet biradical by sensitized photolysis results in a competition between ring closure to **8** and a 1,2-alkyl shift to 8,9-diazatricyclo[5.2.2.0^{2,6}]undeca-2,8-diene (**14**). While direct photolysis and thermolysis of **8** yield primarily ring closure product, sensitized photolysis leads to a series of biradical-to-biradical rearrangements that ultimately produce 2,3-divinylcyclopentene (**15**). Deuterium labeling studies indicate competing mechanistic pathways for this reaction. Rationalization of the label distribution requires one of two unprecedented processes: front-side radical attack on a C–C bond or intermediacy of 1,4,6,9-spiro[4.4]nonatetrayl (**1**), an organic tetraradical whose four radical centers are predicted to be stabilized via spiroconjugation.

There has been considerable recent interest in biradicals and related structures,[2] in part because of the important role such structures are thought to play in a variety of thermal and photochemical reactions.[3] Since biradicals are generally highly

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