

# Spin-Coupled Study of the Electronic Structure of Polyenyl Radicals $C_3H_5-C_9H_{11}$

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**Abstract:** Spin-coupled (SC) theory is applied to the description of the electronic structure of polyenyl radicals allyl ( $C_3H_5$ ),  $C_5H_7$ ,  $C_7H_9$ , and  $C_9H_{11}$ . A SC wave function treating *all* seven electrons involved in the carbon-carbon bonds in  $C_3H_5$  as *active* is found to reproduce the correct  $C_{2v}$  geometry for allyl in its ground state, as well as the proper spatial and spin symmetry of this state ( $^2A_2$ ). Although *no*  $\sigma$ - $\pi$  separation is imposed *a priori* upon the seven-electron active space, the optimized SC orbitals display this symmetry and exhibit no tendency toward bent-bond formation and/or symmetry breaking. The most important correlation effects are shown to be included in the  $\pi$  space: The energy of the  $\pi$ -only three-electron SC wave function for  $C_3H_5$  coincides with that of the corresponding "3 in 3" complete-active-space self-consistent-field (CAS SCF) wave function. The SC model for the  $\pi$  electrons in allyl confirms the utility of the *antipair* concept introduced with the SC treatment of antiaromatic systems. The SC approach is demonstrated to yield highly correlated valence-bond-style  $\pi$ -active-space wave functions of the appropriate spatial and spin symmetry ( $^2A_2$  and  $^2B_1$ ) for the subseries of polyenyl radicals, involving  $4n + 3$  and  $4n + 1$  carbon atoms, respectively. Except for allyl, the  $\pi$  electrons are accommodated in tightly localized SC orbitals, which resemble distorted  $C(2p_z)$  atomic orbitals.  $[4n + 3]$  chains (with the exception of the  $C_3H_5$ ) are best described by an *antiresonance* between equivalent Kekulé structures. The SC wave functions for the other ( $[4n + 1]$ ) series are dominated by a single symmetry-adapted Kekulé structure which is in *conventional* resonance with less important pairs of equivalent structures.

## 1. Introduction

Interest in polyenyl radicals ( $C_{2n+1}H_{2n+3}$ ), which represent classical examples of open-shell conjugated  $\pi$  systems dates from the early days of quantum chemistry.<sup>1-3</sup>

The description of the  $\pi$  electrons in a polyenyl radical within the framework of the Hückel approximation<sup>1</sup> under the assumption of an idealized geometry (either with equal or with regularly alternating shorter and longer ("double" and "single") carbon-carbon bonds) can be carried out analytically for chains of any length. This possibility makes polyenyl radicals, similarly to polyenes ( $C_{2n}H_{2n+2}$ ) and annulenes ( $C_{2n}H_{2n}$ ), one of the simplest models for studying the effects of size and different local perturbations on the electronic structure of one-dimensional extended systems (see, for example, refs 4, 5). Concepts important for modeling electron transport in polyacetylene, such as neutral solitons,<sup>6,7</sup> are closely related to the tight-binding (Hückel) description of higher polyenyl radicals.

Much of the current understanding of the conditions for the appearance of broken-symmetry spin-restricted Hartree-Fock (HF) solutions for open-shell systems and their implications derives from studies of the nature of the doublet HF wave function for the smallest representative of the  $C_{2n+1}H_{2n+3}$  series, the allyl

(2-propenyl) radical (see refs 8, 9 and references therein). Although electron spin resonance (ESR) experimental results<sup>10</sup> suggest that the molecule belongs to the  $C_{2v}$  point group, Paldus and Čížek have managed to demonstrate, first in the framework of the semiempirical Pariser-Parr-Pople approximation,<sup>8</sup> that the lowest-energy doublet HF wave function has a reduced ( $C_s$ ) symmetry leading to a higher  $\pi$  electronic density over one of the two symmetrically equivalent carbon-carbon bonds. This symmetry breaking has been found to persist at the *ab initio* level, and there is convincing evidence that it is a general feature of the doublet HF wave function for the allyl radical, rather than a computational artifact (following, for example, from the use of a limited basis set<sup>9</sup>). Moreover, the results of Paldus and Veillard<sup>9</sup> indicate that the doublet HF wave function favors a distortion of the nuclear geometry in accordance with the electronic density distribution for the broken-symmetry solution found at the  $C_{2v}$  geometry.

Using simple valence-bond (VB) arguments within the framework of the PPP approximation, Paldus and Čížek have predicted<sup>8</sup> that the restricted HF solutions for polyenyl radicals containing  $4n + 1$  carbon atoms are most likely to be doublet stable, while those for polyenyl radicals involving  $4n + 3$  carbon atoms may be doublet unstable. The results of recent *ab initio* calculations for the 1,4-pentadienyl radical<sup>11</sup> confirm these predictions.

The "symmetry dilemma" of the open-shell HF description of the allyl radical and higher members of the  $C_{4n+3}H_{4n+5}$  series can be resolved in several different ways. One possibility is to use the unrestricted HF (UHF) method, which is known to disfavor bond alternation in polyene chains.<sup>12-15</sup> However, the UHF wave

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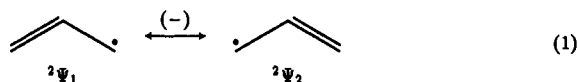
function does not represent a pure spin state, which may turn out to be an even more serious deficiency than the reduced spatial symmetry of the lowest-energy doublet HF wave function.

As has been demonstrated by Paldus and Veillard,<sup>9</sup> the symmetry breaking in the doublet HF solution for the allyl radical is in its essence a feature of the  $\pi$  electronic part of the wave function. Therefore, one can expect that a solution to the "symmetry dilemma" may be found by selectively improving the description of the  $\pi$  electrons alone. One way to achieve such an improvement is to allow, in addition to the configuration corresponding to the symmetry-adapted doublet HF wave function, other configurations in which the three  $\pi$  electrons are distributed differently in the three lowest  $\pi$  orbitals: bonding ( $\pi$ ), nonbonding ( $\pi^0$ ), and antibonding ( $\pi^*$ ). Semiempirical calculations performed by Kikuchi<sup>16</sup> have shown that inclusion of just the two monoexcited  $\pi \rightarrow \pi^*$  configurations results in a multiconfigurational self-consistent-field (MC SCF) wave function which already favors the  $C_{2v}$  geometry. The best possible description of the three  $\pi$  electrons in the allyl radical within the active space comprising the  $\pi$ ,  $\pi^0$ , and  $\pi^*$  orbitals is provided by the corresponding doublet "3 in 3" complete-active-space (CAS) SCF wave function which involves eight configurations. The first detailed study of the allyl radical based on a wave function of this type, due to Takada and Dupuis,<sup>17</sup> has indicated that it depicts correctly the most important structural characteristics of the system. Further research<sup>11,15</sup> has confirmed the utility of "2n + 1 in 2n + 1" CAS wave functions defined on an active space of 2n + 1  $\pi$  orbitals for the description of  $C_{2n+1}H_{2n+3}$  polyenyl radicals in general.

Recent calculations on the  $C_3H_5$ – $C_9H_{11}$  series<sup>18</sup> performed in the framework of the linear combination of Gaussian-type orbitals local spin density (LCGTO-LSD) formalism show very good agreement with earlier CAS SCF results.

Both CAS SCF<sup>15</sup> and density functional<sup>18</sup> calculations emphasize the subdivision of chain polyenyl radicals into a [4n + 1] and a [4n + 3] series, which have  $^2B_1$  and  $^2A_2$  ground states, respectively. The bonds connecting the central carbon atom to its neighbors are predicted to be shorter in the [4n + 3] series in comparison to those in the [4n + 1] series.

The  $\pi$  electron system of the allyl radicals is of special interest to VB theory as it is the smallest  $\pi$  system capable of resonance. Its simplest VB description considers only the "valence" (or "active")  $2p_x$  orbitals located at each of the three carbon atoms and involves two structures which can be represented as



The linear combination  $^2\Psi_1 - ^2\Psi_2$  yields a wave function of  $^2A_2$  symmetry, and  $^2\Psi_1 + ^2\Psi_2$  yields a wave function of  $^2B_1$  symmetry. As has been shown by Levin and Goddard,<sup>19</sup> the  $^2A_2$  state is lower in energy and hence the ground state of the allyl radical, within this simple VB model, is characterized by *antiresonance* between structures  $^2\Psi_1$  and  $^2\Psi_2$  (in eq 1 and further in the text we shall distinguish between resonance and antiresonance by placing a minus sign above the "left-right" arrow connecting structures in antiresonance). It is important to emphasize that both  $^2\Psi_1$  and  $^2\Psi_2$  involve one and the same orbital product and differ only in the mode of coupling the spins of the three  $\pi$  electrons.

A considerable improvement over the elementary VB description can be achieved within the framework of a much more general wave function, which still employs the easy-to-interpret single-orbital product but allows simultaneous optimization of the valence

orbitals and the related spin function. This wave function is now commonly referred to as a spin-coupled (SC)<sup>20</sup> or full-generalized VB (full-GVB)<sup>21</sup> wave function, and it was first applied to the  $\pi$  electron system of the allyl radical in ref 19. The particular wave function of this type selected by Levin and Goddard<sup>19</sup> for a qualitative discussion of the allyl radical closely parallels the simple VB picture. The important distinction is that the  $2p_x$  orbitals are substituted by molecular-orbital (MO) type expansions, which, after optimization, turn out to be well-localized about the carbon atoms and resemble distorted  $2p_x$  orbitals.

However, Levin and Goddard also obtained another solution, which is lower in energy and differs considerably from the elementary VB description. Using an analogy with later results from the SC treatment of cyclobutadiene,<sup>22</sup> this second solution may be characterized as containing an *antipair* of orbitals, semilocalized over the terminal carbon atoms. This observation is not surprising, having in mind that the lowest SC wave function for square-planar cyclobutadiene contains two such antipairs across the two diagonals of the square, and the  $\pi$  system of the allyl radical can be formally obtained from that of cyclobutadiene by abstracting one CH unit. This destroys one of the antipairs and leaves one unpaired electron. As there is evidence that antipairs appear to be a typical feature of antiaromatic systems and diradicals in general,<sup>22</sup> the corresponding wave function for the allyl radical may be more important than it was considered initially.

Another VB-type model for the  $\pi$  electron system of the allyl radical was advanced in ref 23 (see also ref 24). In this approach, the two resonance structures (eq 1) are formed using two symmetrically equivalent, but distinct, sets of  $\pi$  orbitals; that is, it employs a larger, "3 in 6" active space. The additional difficulties related to the use of a more complicated wave function of this type can be justified, if it is not possible to obtain a solution of the proper symmetry within the smaller, three-orbital active space suggested by the classical VB description. Such a necessity may arise, e.g. if the allyl radical is treated by means of a GVB wave function subject to perfect-pairing constraints,<sup>25</sup> which involves optimization of only one of the two resonance structures (eq 1). Otherwise, the energy gain resulting from the use of a spatially-projected GVB wave function,<sup>23</sup> compared to the best symmetry-adapted wave function based on a single-orbital product,<sup>19</sup> is rather modest: about 0.002 hartree.

It is both conceptually important and interesting to establish whether a wave function based on a single-orbital product is capable of producing a correct description of the allyl radical in its ground state. Although the lowest-energy full-GVB wave function for the three-orbital  $\pi$  space obtained by Levin and Goddard<sup>19</sup> is symmetry-adapted, this result cannot be considered as a complete answer to the problem. The calculations in ref 19 were carried out at a single  $C_{2v}$  geometry without core optimization (the  $\sigma$  core orbitals were taken from a previous HF calculation on the ground state of the allyl cation). Should one wish to investigate the potential surface arising from a distortion from the  $C_{2v}$  geometry, with one of the carbon-carbon bonds becoming shorter than the other, it would be necessary to have an improved, preferably variational and correlated, description of the  $\sigma$  electrons.

In the present article we study the allyl radical using SC wave functions with three and seven active electrons. The choice of the larger active space is suggested by simple VB considerations:

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It allows a correlated description of the three  $\pi$  electrons and of the four  $\sigma$  electrons involved in the carbon-carbon  $\sigma$  bonds. We do not consider active spaces intermediate in size between the three- and seven-electron ones because they have no direct chemical interpretation, although "4 in 4" and "5 in 5" active spaces have been employed in CAS SCF calculations on the allyl radical.<sup>11</sup> No further preconceptions, apart from the selection of the number of active electrons, are imposed on the wave function, and in particular, there is no *a priori* assumption of a  $\sigma$ - $\pi$  separation within the seven-electron active space. In this way, the orbitals are allowed to take any form, which may turn out to be advantageous from a variational viewpoint. For example, they are not prevented from converging to a (broken-symmetry) solution dominated by one of the two resonance structures (eq 1), where the "double" bond is described by four bent (or "banana") orbitals, similar to those recently discussed in the case of ethene (see ref 26 and references therein).

We demonstrate that the SC approach resolves completely the "symmetry dilemma" inherent in the doublet-restricted HF wave function for the allyl radical.

The other aim of the present article is to provide a quantitative, but still easily interpretable, model for the  $\pi$  electron systems of polyenyl radicals in general. The SC approach, which is known to perform very well for other conjugated systems, such as benzene,<sup>27,28</sup> naphthalene,<sup>29</sup> and five- and six-membered heterocyclic molecules,<sup>30-32</sup> represents one obvious choice of a theoretical background. We perform SC calculations for the  $\pi$  systems of polyenyl radicals with three, five, seven, and nine carbon atoms (C<sub>3</sub>H<sub>5</sub>-C<sub>9</sub>H<sub>11</sub>). The form of the optimal SC orbitals and the nature of the observed spin-coupling patterns are discussed in detail and related to SC results for other  $\pi$  systems and to classical VB resonance models. The quantitative character of the SC descriptions is corroborated by comparisons with CAS SCF calculations within identical active space selections.

## 2. Basics of the Spin-Coupled Model

Spin-coupled theory describes the *N* valence (or active) electrons in a molecule by means of the most general wave function ansatz utilizing a single product of *N* spatial orbitals  $\psi_1, \psi_2, \dots, \psi_N$ :

$$\Psi_{SM} = \hat{\mathcal{A}}(\Phi_{\text{core}}\Phi_{\text{val}}) = \hat{\mathcal{A}}(\Phi_{\text{core}}\psi_1\psi_2 \dots \psi_N\Theta_{SM}^N) \quad (2)$$

where  $\hat{\mathcal{A}}$  is the antisymmetrizer for the whole wave function and  $\Phi_{\text{core}}$  accommodates the core (or inactive) electrons. The spin function for the valence electrons  $\Theta_{SM}^N$  is allowed to have contributions from all  $f_S^N$  linearly independent *N*-electron spin eigenfunctions corresponding to the required values of the total spin *S* and its *z*-projection *M*:

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

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

In order to enable variational calculation of  $\Phi_{\text{val}}$  (see eq 2), the valence (or spin-coupled) orbitals  $\psi_1, \psi_2, \dots, \psi_N$  are approximated, as usual, by MO-type expansions in a suitable basis set of atomic

orbitals (AOs)

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

and the energy expectation value corresponding to  $\Psi_{SM}$  is optimized simultaneously with respect to the coefficients  $c_{\mu p}$  and  $C_{Sk}$ .<sup>33,34</sup> In most cases the SC orbitals are found to resemble deformed AOs or hybrid AOs, which fits in well with the classical VB concepts, but there are also notable exceptions, e.g. the *antipairs* observed in cyclobutadiene and related antiaromatic systems.<sup>22</sup>

The simplest and most convenient choice for  $\Phi_{\text{core}}$  is, in analogy with the closed-shell HF wave function, a product of the appropriate number of doubly-occupied orbitals:

$$\Phi_{\text{core}} = \varphi_1\alpha\varphi_1\beta\varphi_2\alpha\varphi_2\beta \dots \varphi_n\alpha\varphi_n\beta \quad (6)$$

where  $\varphi_1, \varphi_2, \dots, \varphi_n$  are represented, similar to eq 5, as MO-type expansions.

In many applications (see ref 35 and references therein) it is sufficient to take the orbitals appearing in  $\Phi_{\text{core}}$  from a preliminary HF, or even a CAS SCF calculation, and to keep them fixed while optimizing  $\Phi_{\text{val}}$ . A more consistent approach, especially when it is desirable to obtain a correlated description, localized within a particular region of a molecular system (e.g. a multiple bond<sup>26</sup>), or in the calculation of potential surfaces, is to optimize  $\Phi_{\text{core}}$  and  $\Phi_{\text{val}}$  simultaneously.<sup>36</sup>

The choice of the complete set of *N*-electron spin eigenfunctions  $\Theta_{SM;k}^N$  (see eq 3) is not unique: The book by Pauncz<sup>37</sup> reviews a number of algorithms for their construction. The ones most useful for the calculation and interpretation of SC wave functions are those due to Kotani, Rumer, and Serber. The interconversion between the representations of  $\Theta_{SM}^N$  in the Kotani (K), Rumer (R), and Serber (S) spin bases,

$$\Theta_{SM}^N = \sum_{k=1}^{f_S^N} C_{Sk}^K \Theta_{SM;k}^N = \sum_{k=1}^{f_S^N} C_{Sk}^S \Theta_{SM;k}^N = \sum_{k=1}^{f_S^N} C_{Sk}^R \Theta_{SM;k}^N \quad (7)$$

is computationally inexpensive.<sup>38,39</sup> It is often employed in order to highlight different aspects of the optimal spin-coupling pattern for the valence electrons. The representation of  $\Theta_{SM}^N$  in the Rumer spin basis is particularly important, because it often allows one to establish (see, for example, refs 27-29, 32, 40) a direct connection between the SC wave function and the classical VB ideas of "covalent" resonance (i.e. resonance which does not involve "movement" of charge). A particularly revealing example of this relationship is presented by the SC treatment of benzene,<sup>27</sup> which confirms and reintroduces, in a quantitative form, Kekulé's pre-quantum-chemical concepts, which had been almost completely abandoned in favor of the delocalized picture offered by MO theory.

In the present paper we make use of the Kotani and Rumer spin bases. The Kotani spin functions  $\Theta_{SM;k}^N$  are constructed by successive coupling of individual electron spins 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. This series can be

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used as an extended label for the spin function

$$k \equiv (S_1 S_2 \dots S_{N-1}) \quad (8)$$

The Rumer spin basis represents a set of  $f_S^N$  linearly independent spin functions, in which the first  $N - 2S$  electrons form singlet pairs and the remaining  $2S$  electrons are assigned spins  $\alpha$ . One convenient way of labeling the Rumer spin functions  $\Theta_{SM;k}^N$  is by listing the singlet pairs, *i.e.*

$$k \equiv (\mu_1 - \mu_2, \mu_3 - \mu_4, \dots, \mu_{N-2S-1} - \mu_{N-2S}) \quad (9)$$

The weight  $P_{Sk}$  of an individual spin function  $\Theta_{SM;k}^N$  in the spin function for the valence electrons  $\Theta_{SM}^N$  is given by

$$P_{Sk} = C_{Sk} \sum_{I=1}^{f_S^N} \langle \Theta_{SM;k}^N | \Theta_{SM;I}^N \rangle C_{SI} \quad (10)$$

where we assume that  $\Theta_{SM}^N$  is normalized to unity. This form of  $P_{Sk}$  has to be used for nonorthogonal spin bases (such as the Rumer basis) only; the expression for orthogonal spin bases (*e.g.* the Kotani basis) is much simpler:  ${}^K P_{Sk} = {}^K C_{Sk}^2$ .

While, on one hand, the SC wave function (eq 2) can be considered as an evolution of classical VB theory, it is also closely related to the "N in N" CAS SCF wave function defined within the same core-valence partitioning scheme. In general, CAS SCF theory employs  $D(N,N,S) = [(N+1)/(2S+1)](f_S^N)^2$  configuration state functions (CSFs) for a system of  $N$  active electrons in  $N$  orbitals with total spin  $S$ . Each CSF involves a product of  $N$  valence orbitals and an  $N$ -electron spin eigenfunction (core electrons, if present, are accommodated in doubly-oriented orbitals, as in eq 6); the valence orbitals are allowed variable occupancy (0, 1, or 2). All unique products of active orbitals satisfying this requirement are taken into account; the association of each one of them with a complete set of  $N$ -electron spin eigenfunctions gives rise to  $f_S^{N-2N_p}$  unique CSFs ( $N_p$  denotes the number of doubly-occupied active orbitals in the product). As a result, the "N in N" CAS SCF wave function is invariant with respect to any nonsingular transformation of the active orbitals, which can be chosen to be orthogonal.

By definition (eq 2), the SC wave function involves only  $f_S^N$  "covalent" CSFs from the "N in N" CAS SCF wave function. In contrast to the CAS SCF case, the form of the active orbitals  $\psi_1, \psi_2, \dots, \psi_N$  is unique, and as they are allowed full variational flexibility, without any orthogonality constraints within the valence space, it is determined solely by the energy minimization requirement. The optimal spin function for the valence electrons  $\Theta_{SM}^N$  realizes just one particular mode of coupling the spins of the valence electrons: In this sense, the SC wave function (eq 2) could be regarded as a *single* CSF built of singly-occupied nonorthogonal orbitals.

The correlation energies recovered by the SC approach are usually rather close to the corresponding "N in N" CAS SCF values; for example, the SC calculation of the ground ( ${}^1A_g$ ) state of benzene<sup>32</sup> with six active electrons recovers *ca.* 92% of the corresponding "6 in 6" CAS SCF correlation energy; the SC descriptions of the lowest singlet ( ${}^1A_1$ ) and triplet ( ${}^3B_2$ ) states of *o*-benzynes<sup>40</sup> with eight active electrons include *ca.* 88% and *ca.* 92% of the respective "8 in 8" CAS SCF correlation energies.

As a direct consequence, the easily interpretable VB-type picture of bonding embodied within the SC wave function has, in most cases, a rigorous quantitative justification.

### 3. Results and Discussion

The SC and CAS SCF calculations for the  $C_3H_5$ – $C_9H_{11}$  series were performed at nuclear geometries optimized using CAS SCF wave functions: For the allyl ( $C_3H_5$ ) and 1,4-pentadienyl ( $C_5H_7$ ) radicals we used the "3 in 3" and "5 in 5" CAS SCF/MIDI\* geometries reported by Szalay *et al.*,<sup>11</sup> and for  $C_7H_9$  and  $C_9H_{11}$ ,

**Table 1.** Total Energies of the Ground State of the Allyl Radical at Its Equilibrium Geometry (in hartree) Obtained with Different Wave Functions<sup>a</sup>

wave function	type of the $\pi$ orbitals	energy
doublet HF	delocalized	-116.415 09
SC(10c', 3v)	localized	-116.455 92
SC(10c', 3v)	antipair	-116.457 24
SC(10c, 3v)	antipair	-116.457 44
SC(8c', 7v)	antipair	-116.483 76
Sc(8c, 7v)	antipair	-116.484 80

<sup>a</sup> The number of core (c) and valence (v) orbitals are indicated for each SC wavefunction. Fixed core orbitals are denoted by c'.

the "7 in 7" and "9 in 9" CAS SCF/6-31G geometries obtained by Villar and Dupuis<sup>15</sup> (all these geometries belong to the  $C_{2v}$  point group).

A standard double- $\zeta$  basis set<sup>41,42</sup> of (9s5p/4s) Gaussian functions contracted to [4s2p/2s], with scaling factors of 1.20 and 1.15 for the hydrogen s functions, was employed in all calculations.

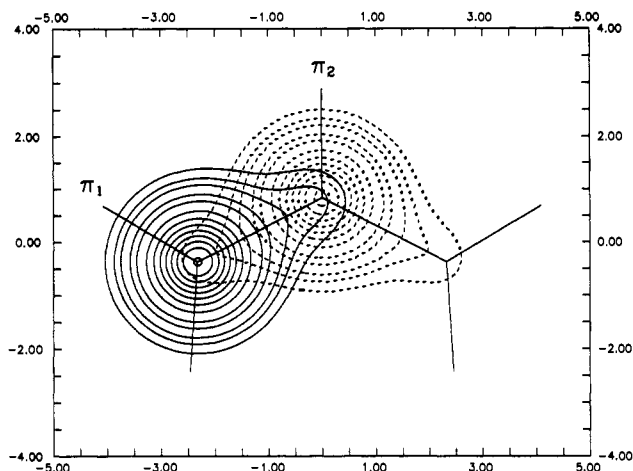
The allyl radical was studied in somewhat greater detail than  $C_5H_7$ ,  $C_7H_9$ , and  $C_9H_{11}$ : As stated in the Introduction, we applied to it SC wave functions involving three and seven active electrons. At the equilibrium geometry we carried out, in both cases, calculations with fixed core orbitals stemming from the doublet HF wave function for the system, as well as calculations in which the core and valence components of the wave function were optimized simultaneously. The selection of the HF orbitals to be left in the fixed core is quite obvious in the case of the three-electron active space: These are all orbitals of  $\sigma$  symmetry. In order to obtain a suitable set of fixed core orbitals for the larger, seven-electron active space, we localized all HF orbitals of  $\sigma$  symmetry according to the criterion of Foster and Boys<sup>43</sup> and then discarded the two orbitals localized predominantly over the carbon-carbon  $\sigma$  bonds. The four electrons in these orbitals are transferred to the active space.

The total energies of the allyl radical at its equilibrium geometry resulting from different wave functions are collected in Table 1. In the case of a three-electron active space, both when the core is kept fixed at the HF level and when it is optimized simultaneously with the valence part of the SC wave function, the solution obtained is symmetry-adapted, with  $\sigma$ - $\pi$  separation, and two of the SC orbitals form an antipair across the terminal carbon atoms (we do not show any of these orbitals, as they closely resemble the  $\pi$  SC orbitals from the seven-electron active space; see Figure 2c,d,e). A solution with localized orbitals, analogous to the one considered by Levin and Goddard<sup>19</sup> to represent best the electronic structure of the allyl radical, can be achieved by constraining<sup>36</sup> two of the three SC orbitals to be equivalent with respect to reflections in the symmetry plane which is perpendicular to the plane of the molecule. We calculated a constrained wave function of this type at a frozen core only; its energy is higher than the energy of the wave function involving an antipair (see Table 1; the corresponding orbitals are superimposed in Figure 1, and their overlaps are shown in Table 2). The solution with localized orbitals corresponds to a saddle point in the SC variational space: When the constraints are released and the optimization procedure is restarted, it departs from this solution and converges to the solution containing an antipair. The spin-coupling coefficients from the corresponding SC wave functions are shown in Table 3. As discussed in ref 19 (see also ref 22), both solutions have  ${}^2A_2$  symmetry, but the wave function involving an antipair has an additional *spin* degree of variational freedom, which explains its lower energy. It should be mentioned that Levin and Goddard<sup>19</sup> obtained the wave function with localized orbitals not by imposing symmetry constraints on the form of the valence orbitals but

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

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

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



**Figure 1.** SC orbitals  $\pi_1$  and  $\pi_2$  from the SC(10c', 3v) wave function for the allyl radical.  $\pi_3$  (not shown) is equivalent to  $\pi_1$  by symmetry. Contours of  $|\pi_1|^2$ , respectively,  $|\pi_2|^2$  are plotted in a plane 1 bohr above the plane of the molecule. Contour levels are at 0.005, 0.0075, 0.01, 0.015, and 0.02(0.01)0.1. All distances are in bohr.

**Table 2.** Overlap Integrals between the Valence Orbitals from the SC(10c', 3v) Wave Function with Localized Orbitals for the Allyl Radical

	$\pi_1$	$\pi_2$	$\pi_3$
$\pi_1$	1	0.594	0.176
$\pi_2$		1	0.594
$\pi_3$			1

**Table 3.** Spin-Coupling Coefficients and Weights of the Individual Spin Eigenfunctions from the Ground-State SC(10c', 3v) Wave Functions for the Allyl Radical (Kotani Spin Basis)<sup>a</sup>

SC orbital product	$K_{C(1/2)1}$ [1 $\equiv$ ( $1/2$ 1)]	$K_{C(1/2)2}$ [2 $\equiv$ ( $1/2$ 0)]	$K_{P(1/2)1}$	$K_{P(1/2)2}$
$\pi_{a_2}\pi'_{b_1}\pi''_{b_1}$	-0.995 64	0.093 31	0.991 29	0.008 71
$\pi_1\pi_3\pi_2$	1.000 00	0.000 00	1.000 00	0.000 00

<sup>a</sup> The antipair solution involves the SC orbital product  $\pi_{a_2}\pi'_{b_1}\pi''_{b_1}$ , and the solution with localized orbitals, the product  $\pi_1\pi_3\pi_2$  ( $\pi_{a_2}$ ,  $\pi'_{b_1}$ , and  $\pi''_{b_1}$  are very similar to the corresponding SC(8c, 7v) orbitals in Figure 2c,d,e, while orbitals  $\pi_1$ - $\pi_3$  are shown in Figure 1).

by restricting the spin function for the active electrons to its  $\Theta_{(1/2)(1/2);1}^3$  component only (assuming the orbital ordering from second row of Table 3).

In order to assess the quality of the two SC wave functions under discussion, we performed a "3 in 3" CAS SCF calculation within the same active space, keeping the core orbitals fixed at the HF level. We found that the "3 in 3" CAS SCF energy coincides to 12 significant figures with the energy of the SC wave function involving an antipair. As a consequence, in this case the lowest-energy SC wave function can be considered as one of the possible, but certainly easiest to interpret, representations of the corresponding "3 in 3" CAS SCF wave function, and the antipair of SC orbitals emerges as a meaningful attribute of the "3 in 3" active space.

The results of the SC calculations with seven active electrons carried out at the equilibrium geometry of the allyl radical do not introduce any significantly new qualitative elements in the picture obtained within the smaller, three-electron active space. Without any constraints on the form of the active orbitals, the optimization procedure converges to a SC wave function in which four of the valence orbitals are of  $\sigma$  symmetry and describe the two carbon-carbon  $\sigma$  bonds (two of the  $\sigma$  orbitals are displayed in Figure 2a,b, and the other two are trivially related to these shown by symmetry). The remaining three orbitals are of  $\pi$  symmetry, and their form (see Figure 2c,d,e; the overlap integrals between all seven orbitals are collected in Table 4) and spin-coupling

**Table 4.** Overlap Integrals between the Valence Orbitals from the SC(8c, 7v) Wave Function for the Allyl Radical

	$\sigma'_2$	$\sigma_1$	$\sigma''_2$	$\sigma_3$	$\pi_{a_2}$	$\pi'_{b_1}$	$\pi''_{b_1}$
$\sigma'_2$	1	0.851	0.298	0.107	0	0	0
$\sigma_1$		1	0.107	-0.050	0	0	0
$\sigma''_2$			1	0.851	0	0	0
$\sigma_3$				1	0	0	0
$\pi_{a_2}$					1	0	0
$\pi'_{b_1}$						1	0.725
$\pi''_{b_1}$							1

**Table 5.** Spin-Coupling Coefficients and Weights of the Individual Spin Eigenfunctions from the Ground-State SC(8v, 7v) Wave Function for the Allyl Radical (Kotani Spin Basis)<sup>a</sup>

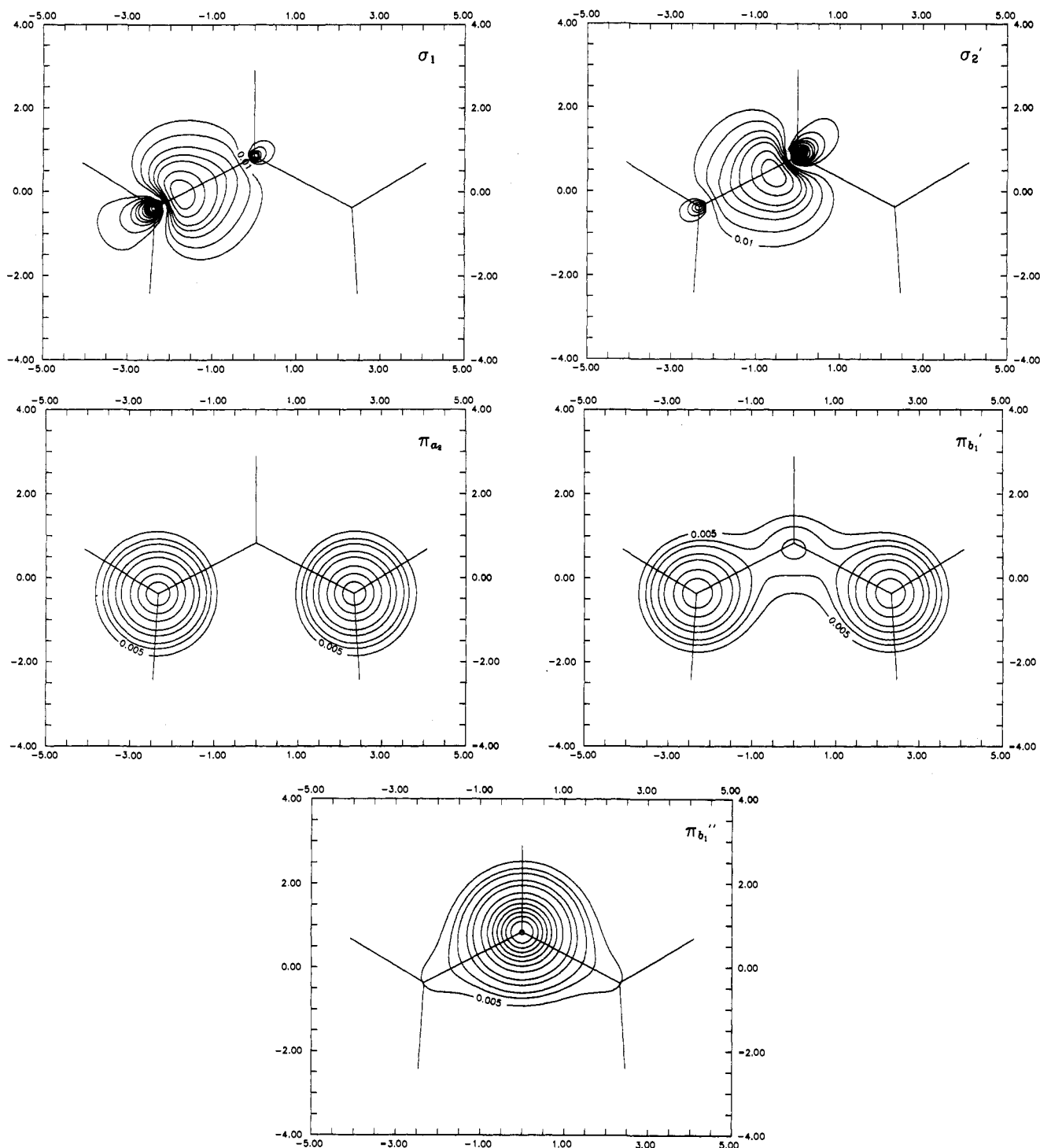
k	( $S_1S_2\dots S_6$ )	$K_{C(1/2)k}$	$K_{P(1/2)k}$
1	( $1/2^1 3/2^2 3/2^1$ )	-0.014 01	0.000 20
2	( $1/2^1 3/2^1 3/2^1$ )	-0.091 64	0.008 40
3	( $1/2^1 1/2^1 3/2^1$ )	0.064 80	0.004 20
4	( $1/2^0 1/2^1 3/2^1$ )	-0.112 24	0.012 60
5	( $1/2^1 3/2^1 1/2^1$ )	-0.098 15	0.009 63
6	( $1/2^1 1/2^1 1/2^1$ )	0.069 40	0.004 82
7	( $1/2^0 1/2^1 1/2^1$ )	-0.120 21	0.014 45
8	( $1/2^1 1/2^0 1/2^1$ )	0.105 58	0.011 15
9	( $1/2^0 1/2^0 1/2^1$ )	-0.958 75	0.919 20
10	( $1/2^1 3/2^1 1/2^0$ )	-0.049 53	0.002 45
11	( $1/2^1 1/2^1 1/2^0$ )	0.035 02	0.001 23
12	( $1/2^0 1/2^1 1/2^0$ )	-0.060 66	0.003 68
13	( $1/2^1 1/2^0 1/2^0$ )	-0.009 77	0.000 10
14	( $1/2^0 1/2^0 1/2^0$ )	0.088 90	0.007 90

<sup>a</sup> SC orbital ordering:  $\sigma'_2\sigma_1\sigma''_2\sigma_3\pi_{a_2}\pi'_{b_1}\pi''_{b_1}$ ; see Figure 2 for details.

pattern (see Table 5) are very similar to the corresponding elements of the SC wave function with three valence electrons. Our second-order optimization approach<sup>36</sup> is constructed so as to converge to local minima only, *i.e.* stationary points at which the Hessian with respect to all variational parameters is a positive definite matrix, and we do not observe any tendency toward  $\sigma$ - $\pi$  mixing and/or symmetry breaking, which are usually indicated by one or more negative eigenvalues of a Hessian corresponding to a saddle point.

However, the stability of the wave function at the equilibrium geometry does not preclude an instability of that geometry with respect to an actual distortion leading to a structure in which the lengths of the two carbon-carbon bonds become different. In order to investigate this possibility, we calculated the section of the potential surface corresponding to a shortening of one of the bonds and an elongation of the other bond by the same amount, say  $d$ ; that is, if the equilibrium bond lengths were  $R(C_1C_2) = R(C_2C_3) = R_e$ , the distorted bond lengths would be  $R(C_1C_2) = R_e - d$  and  $R(C_2C_3) = R_e + d$ . A distortion of this type corresponds to a  $C_{2v} \rightarrow C_s$  reduction of the spatial symmetry of the nuclear framework. With the exception of the two carbon-carbon bond lengths, all other geometrical parameters were kept at their equilibrium values. We employed a SC wave function with seven active electrons which allows for a correlated description of all electrons involved in the carbon-carbon bonds. As the results included in Table 1 indicate, the simultaneous optimization of the core and valence parts of the SC wave function does not influence considerably the total energies calculated at the equilibrium geometry (it should be noted that the core optimization is more important for the seven-electron active space, where the core-valence separation does not follow from spatial symmetry only). However, in order to eliminate any subjectivity in the selection of the core-valence partitioning (which might be introduced in the fixed-core scheme, *e.g.* by the choice of a particular localization procedure), during the calculation of the potential surface the core orbitals were optimized simultaneously with the valence part of the wave function.

The dependence of the SC ground-state energy of the allyl radical upon the distortion parameter  $d$  is shown in Figure 3. For



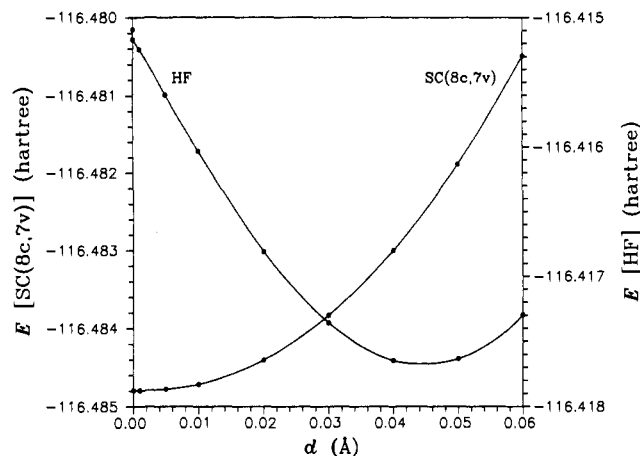
**Figure 2.** (a) SC orbital  $\sigma_1$  from the SC(8c, 7v) wave function for the allyl radical. Contours of  $|\sigma_1|^2$  are plotted in the plane of the molecule. Contour levels are at 0.01, 0.025, 0.05, 0.075, 0.1(0.05)0.4, 0.5, 0.7, and 0.9. Orbital  $\sigma_3$  (not shown) is symmetrically equivalent to  $\sigma_1$ . (b) SC orbital  $\sigma_2'$  from the SC(8c, 7v) wave function for the allyl radical. Plot details are as in a. Orbital  $\sigma_2''$  (not shown) is symmetrically equivalent to  $\sigma_2'$ . (c) SC orbital  $\pi_{a_2}$  from the SC(8c, 7v) wave function for the allyl radical. Plot details are as in Figure 1. (d) SC orbital  $\pi_{b_1}'$  from the SC(8c, 7v) wave function for the allyl radical. Plot details are as in Figure 1. (e) SC orbital  $\pi_{b_1}''$  from the SC(8c, 7v) wave function for the allyl radical. Plot details are as in Figure 1.

comparison, we have also plotted the curve corresponding to the doublet HF wave function. The SC wave function correctly predicts the  $C_{2v}$  geometry to be stable with respect to a distortion leading to a structure with different carbon-carbon bond lengths. Its behavior is markedly different from that of the doublet HF wave function, which favors the distortion (the doublet HF potential curve is discontinuous at the equilibrium geometry due to the existence of a broken-symmetry solution lower in energy than the symmetry-adapted one). This demonstrates that the SC wave function, similarly to the CAS SCF wave function, is capable of providing a proper description of the ground-state

geometry of the allyl radical, but without sacrificing the visual clarity of the model based on a single-orbital product.

The  $\sigma$ - $\pi$  separation within the active space is preserved by the variational procedure for relatively small distortions ( $d \leq 0.010$  Å). For larger distortions some symmetry breaking is observed and, in order to ensure an overall  $C_s$  symmetry of the wave function, we chose to reinstate the division of the SC orbitals into subsets of  $\sigma$  and  $\pi$  symmetry by imposing appropriate orbital constraints.<sup>36</sup>

The antipair found at the  $C_{2v}$  geometry retains its character over a considerable distortion range, and although the participating  $\pi$  valence orbitals gradually transform into localized orbitals which



**Figure 3.** SC and HF potential curves corresponding to a  $C_{2v} \rightarrow C_s$  distortion of the carbon-carbon bond lengths in the allyl radical. The separate dot above the  $d = 0$  point on the HF curve corresponds to the energy of the symmetry-adapted HF solution. For further details, see text.

resemble deformed AOs, the transition is slow and incomplete, even at the largest distortion we studied ( $d = 0.060$  Å). The stability (or "rigidity") of the antipair in the lowest doublet SC wave function for the allyl radical contrasts with the situation discovered for the lowest singlet states of the  $H_4$  ring and cyclobutadiene ( $C_4H_4$ ).<sup>22</sup> The antipairs in the corresponding wave functions emerge only at square ( $D_{4h}$ ) geometries, and even for very small  $D_{4h} \rightarrow D_{2h}$  distortions, leading to a rectangular geometry, the antipairs disappear and the SC orbitals become well-localized. On the other hand, the antipairs observed in the lowest triplet states of  $H_4$  and  $C_4H_4$  are stable, similar to the antipair in the allyl radical: The participating SC orbitals do not localize upon transition from a square to a rectangular geometry. The comparison between the ways in which the total energies of the lowest singlet and triplet states of  $H_4$  and  $C_4H_4$  and the doublet ground-state energy of the allyl radical behave upon distortion suggests that there exists a parallel between the "rigidity" of the antipair formation and the stability of the molecular geometry, at which it is observed. The antipair in the lowest doublet SC wave function for the allyl radical is the first instance of a "rigid" antipair discovered in the ground state of a molecular system.

The SC results for the allyl radical indicate clearly that the most interesting and important part of the wave function lies within the  $\pi$  space. Therefore, in our calculations for higher polyenyl radicals,  $C_5H_7$ ,  $C_7H_9$ , and  $C_9H_{11}$ , the correlated treatment is restricted to  $\pi$  electrons only. The core orbitals are borrowed from the respective doublet (symmetry-adapted) HF wave functions and are not optimized any further.

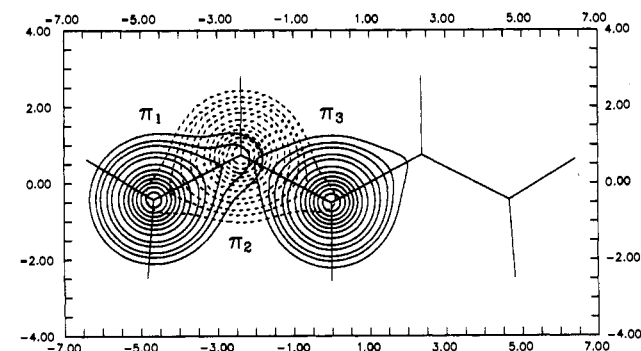
The ground-state energies of  $C_5H_7$ ,  $C_7H_9$ , and  $C_9H_{11}$  obtained with open-shell HF, SC, and CAS SCF wave functions are collected in Table 6. The percentage of the " $2n + 1$  in  $2n + 1$ " CAS SCF correlation energy recovered by the SC approach is observed to be very high in *all* cases; it is even higher than the corresponding figure for benzene (*ca.* 92%; see, for example, ref 32), whose description is regarded as one of the most spectacular achievements of SC theory.

The  $\pi$  system of the 1,4-pentadienyl radical ( $C_5H_7$ ) involves five electrons; the corresponding number of linearly independent doublet spin eigenfunctions is  $f_{1/2}^5 = 5$ . The optimized SC orbitals are well-localized and resemble distorted  $C(2p_\pi)$  AOs (see Figure 4; all overlap integrals can be found in Table 7). In such cases, it is usually the Rumer spin basis which offers the clearest picture of the spin-coupling pattern, and  $C_5H_7$  represents no exception. The corresponding spin-coupling coefficients  ${}^R C_{(1/2)k}$  and their weights  ${}^R P_{(1/2)k}$  (see Table 8) suggest a classical resonance picture, in which the three resonance structures,

**Table 6.** Total Energies (in hartree) and Percentages of the " $2n + 1$  in  $2n + 1$ " CAS SCF Correlation Energies Recovered (Values in Brackets Following the Energies) for  $C_5H_7$ ,  $C_7H_9$ , and  $C_9H_{11}$  Using Different Wave Functions

radical	wave function	energy
$C_5H_7$	doublet HF	-193.287 11 (0.0)
	SC(16c', 5v) <sup>a</sup>	-193.357 77 (97.8)
	"5 in 5" CAS SCF	-193.359 37 (100.0)
$C_7H_9$	doublet HF	-270.153 02 (0.0)
	SC(22c', 7v) <sup>b</sup>	-270.254 00 (96.2)
	SC(22c', 7v) <sup>a</sup>	-270.254 35 (96.5)
	SC(22c', 7v) <sup>c</sup>	-270.254 42 (96.6)
$C_9H_{11}$	"7 in 7" CAS SCF	-270.258 04 (100.0)
	doublet HF	-347.023 05 (0.0)
	SC(28c', 9v) <sup>a</sup>	-347.153 89 (96.5)
	"9 in 9" CAS SCF	-347.158 65 (100.0)

<sup>a</sup> Wave function with localized valence orbitals. <sup>b</sup> Wave function involving an antipair. <sup>c</sup> Broken-symmetry wave function.



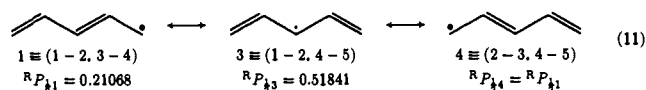
**Figure 4.** SC orbitals  $\pi_1$ - $\pi_3$  from the SC(16c', 5v) wave function for  $C_5H_7$ . Orbitals  $\pi_4$  and  $\pi_5$  (not shown) are equivalent by symmetry to  $\pi_2$  and  $\pi_1$ , respectively. Plot details are as in Figure 1.

**Table 7.** Overlap Integrals between the Valence Orbitals from the SC(16c', 5v) Wave function for  $C_5H_7$

	$\pi_1$	$\pi_2$	$\pi_3$	$\pi_4$	$\pi_5$
$\pi_1$	1	0.657	0.128	0.063	0.038
$\pi_2$		1	0.415	0.097	0.063
$\pi_3$			1	0.415	0.128
$\pi_4$				1	0.657
$\pi_5$					1

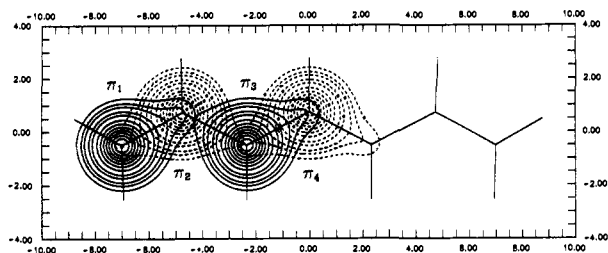
**Table 8.** Spin-Coupling Coefficients and Weights of the Individual Spin Eigenfunctions from the SC(16c', 5v) Wave Function for  $C_5H_7$  (Rumer Spin Basis, SC Orbitals Ordered Sequentially, Counting from One End of the Molecule)

$k'$	pairs in $k'$	$k''$	pairs in $k''$	${}^R C_{(1/2)k} = {}^R C_{(1/2)k''}$	${}^R P_{(1/2)k} = {}^R P_{(1/2)k''}$
1	(1-2, 3-4)	4	(2-3, 4-5)	0.294 62	0.210 68
2	(1-4, 2-3)	5	(2-5, 3-4)	-0.058 81	0.030 12
3	(1-2, 4-5)			-0.576 00	0.518 41



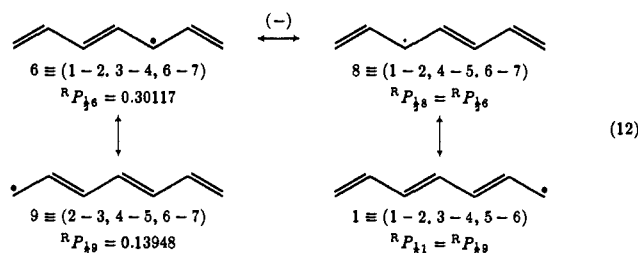
account for *ca.* 94% of the spin function. It is straightforward to demonstrate that the SC wave function has the proper  ${}^2B_1$  symmetry.

Having in mind that  $C_7H_9$  as well as  $C_3H_5$  are members of the  $[4n + 3]$  series of polyenyl radicals (see the Introduction), one would expect the SC description of  $C_7H_9$  to have common features with the SC description of the allyl radical. However, the lowest-energy SC wave function for  $C_7H_9$  with seven active electrons exhibits a symmetry breaking of a small magnitude (the dipole moment component along the chain is just 0.004 74 au). The orbital coefficients suggest that the orbitals are well-localized, in which case imposing constraints to ensure the proper spatial



**Figure 5.** SC orbitals  $\pi_1$ – $\pi_4$  from the SC(22c', 7v) wave function for  $C_7H_9$ . Orbitals  $\pi_5$ ,  $\pi_6$ , and  $\pi_7$  (not shown) are equivalent by symmetry to  $\pi_3$ ,  $\pi_2$ , and  $\pi_1$ , respectively. Plot details are as in Figure 1.

symmetry of the wave function should be expected neither to change their form too much nor to influence considerably the value of the energy. Indeed, optimization under an appropriate set of symmetry constraints yields a solution with localized orbitals which is only 0.000 07 hartree above the broken-symmetry solution. It is also possible to obtain another constrained solution involving an antipair across the carbon atoms nearest to the central carbon atom. Its energy is 0.000 35 hartree higher than that of the solution with localized orbitals. Both symmetry-adapted solutions are of  ${}^2A_2$  symmetry, and the closeness of their energies makes it difficult to decide which one provides the better model for the  $\pi$  electron system of  $C_7H_9$ . Comparing the results to those for the allyl radical (see Table 1), we notice that there the antipair solution is lower by 0.001 32 hartree than the solution with localized orbitals. This suggests that, although the SC wave function involving an antipair is lowest in energy for the first member of the  $[4n + 3]$  series, for higher members of this series the lower-energy wave function becomes the one with localized orbitals, and the switching takes place at  $C_7H_9$  ( $n = 2$ ). This situation is not without parallel in chemistry; for example, it is well-known that properties such as aromaticity and antiaromaticity are restricted to  $[4n + 2]$  and  $[4n]$  conjugated cycles of a relatively small size only, and the distinction tends to weaken and then disappear with increase of the size of the system (see, for example, ref 44). Following this line of reasoning, we prefer to describe the  $\pi$  electron system of  $C_7H_9$  in terms of the SC wave function with localized orbitals. The valence orbitals from this wave function are shown in Figure 5, and for the overlap integrals between these orbitals, see Table 9. The dimension of the complete spin space in this case is  $f_{1/2}^7 = 14$ . The spin function for the active electrons, represented in the Rumer spin basis (see Table 10), involves an antiresonance between symmetrically equivalent structures dominated by



These four structures constitute *ca.* 88% of the spin function.

It should be pointed out that the symmetry breaking observed in the SC treatment of  $C_7H_9$  is different in nature from the doublet instability of the restricted HF wave function for this system. Whereas Paldus and Čížek<sup>8</sup> associate the potential doublet instability of the restricted HF solutions for  $[4n + 3]$  polyenyl radicals, which include a single spin function, with the absence of a symmetry-adapted Kekulé structure, the SC wave function allows all independent spin couplings involving the  $\pi$  electrons. In the case of  $C_7H_9$ , within the Rumer spin basis, these spin

**Table 9.** Overlap Integrals between the (Localized) Valence Orbitals from the SC(22c', 7v) Wave Function for  $C_7H_9$

	$\pi_1$	$\pi_2$	$\pi_3$	$\pi_4$	$\pi_5$	$\pi_6$	$\pi_7$
$\pi_1$	1	0.638	0.113	0.024	-0.017	-0.004	0.000
$\pi_2$		1	0.407	0.087	-0.060	-0.029	-0.004
$\pi_3$			1	0.577	0.134	-0.060	-0.017
$\pi_4$				1	0.577	0.087	0.024
$\pi_5$					1	0.407	0.113
$\pi_6$						1	0.638
$\pi_7$							1

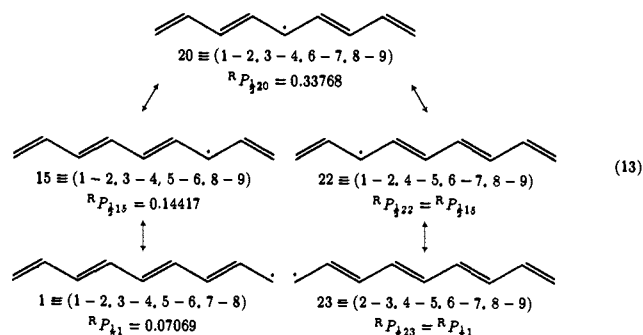
**Table 10.** Spin-Coupling Coefficients and Weights of the Individual Spin Eigenfunctions from the SC(22c', 7v) Wave Function for  $C_7H_9$  (Rumer Spin Basis, Localized SC Orbitals Ordered Sequentially, Counting from One End of the Molecule)<sup>a</sup>

$k'$	pairs in $k'$	$k''$	pairs in $k''$	$R C_{(1/2)k'} = -R C_{(1/2)k''}$	$R P_{(1/2)k'} = R P_{1/2k''}$
1	(1-2,3-4,5-6)	9	(2-3,4-5,6-7)	-0.223 53	0.139 48
2	(1-4,2-3,5-6)	12	(2-3,4-7,5-6)	0.037 04	0.015 56
3	(1-2,3-6,4-5)	10	(2-5,3-4,6-7)	0.022 98	0.011 86
4	(1-6,2-3,4-5)	13	(2-7,3-4,5-6)	-0.014 71	0.005 68
5	(1-6,2-5,3-4)	14	(2-7,3-6,4-5)	-0.003 24	-0.001 18
6	(1-2,3-4,6-7)	8	(1-2,4-5,6-7)	0.374 96	0.301 17
7	(1-4,2-3,6-7)	11	(1-2,4-7,5-6)	-0.050 24	0.027 44

<sup>a</sup> Note that  $k'$  and  $k''$  are in antiresonance.

alignments appear as seven pairs of symmetry-related spin functions (see the antiresonance picture (eq 12) and Table 10). However, even the use of all  $f_{1/2}^7 = 14$  spin functions proves insufficient to eliminate the symmetry breaking completely. As an alternative to imposing symmetry constraints on the orbitals, another way to restore spatial symmetry would be to project out the proper component from the broken-symmetry SC wave function and use the resulting two-configuration wave function. As the magnitude of the symmetry breaking is very small, we expect that this more complicated and less readily interpretable approach would bring about only an insignificant improvement of the quality of the wave function (*cf.* the discussion of the spatially-projected GVB wave function for the allyl radical in the Introduction), which renders its implementation in the present circumstances unnecessary.

$C_9H_{11}$  has nine  $\pi$  electrons; the corresponding number of linearly independent doublet spin eigenfunctions is  $f_{1/2}^9 = 42$ . Similarly to the case of  $C_7H_9$ , the SC optimization procedure converges to a symmetry-adapted ( ${}^2B_1$ ) solution with well-localized orbitals (see Figure 6 and Table 11 for the related overlap integrals). The structure of the spin function for the valence electrons is presented in Table 12 (we use again the Rumer spin basis). The prevailing resonance pattern involves five structures which, together, account for *ca.* 77% of the spin function:



The quantitative character of the SC descriptions of polyenyl radicals allows the use of features of the corresponding wave functions for a VB-type reinterpretation of certain CAS SCF<sup>15</sup> and density functional<sup>18</sup> results for these systems.

The principal component of the valence-space spin function for  $[4n + 1]$  polyenyl radicals is a Rumer spin function of a  $C_{2n}$



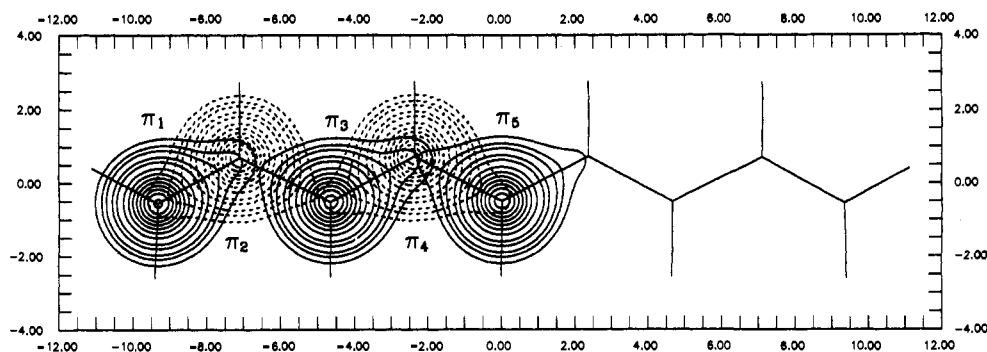


Figure 6. SC orbitals  $\pi_1$ – $\pi_5$  from the SC(28c', 9v) wave function for  $C_9H_{11}$ . Orbitals  $\pi_6$ ,  $\pi_7$ ,  $\pi_8$ , and  $\pi_9$  (not shown) are equivalent by symmetry to  $\pi_4$ ,  $\pi_3$ ,  $\pi_2$ , and  $\pi_1$ , respectively. Plot details are as in Figure 1.

Table 11. Overlap Integrals between the Valence Orbitals from the SC(28c', 9v) Wave Function for  $C_9H_{11}$

	$\pi_1$	$\pi_2$	$\pi_3$	$\pi_4$	$\pi_5$	$\pi_6$	$\pi_7$	$\pi_8$	$\pi_9$
$\pi_1$	1	0.631	0.101	0.006	-0.044	-0.003	0.000	0.001	0.000
$\pi_2$		1	0.377	0.072	-0.142	-0.028	-0.005	0.010	0.001
$\pi_3$			1	0.636	0.120	0.044	0.022	-0.005	0.000
$\pi_4$				1	0.457	0.109	0.044	-0.028	-0.003
$\pi_5$					1	0.457	0.120	-0.142	-0.044
$\pi_6$						1	0.636	0.072	0.006
$\pi_7$							1	0.377	0.101
$\pi_8$								1	0.631
$\pi_9$									1

Table 12. Spin-Coupling Coefficients and Weights of the Individual Spin Eigenfunctions from the SC(28c', 9v) Wave Function for  $C_9H_{11}$  (Rumer Spin Basis, SC Orbitals Ordered Sequentially, Counting from One End of the Molecule)

$k'$	pairs in $k'$	$k''$	pairs in $k''$	$R_{C(1/2)k'} = R_{C(1/2)k''}$	$R_{P(1/2)k'} = R_{P(1/2)k''}$
1	(1-2,3-4,5-6,7-8)	23	(2-3,4-5,6-7,8-9)	-0.135 02	0.070 69
2	(1-4,2-3,5-6,7-8)	32	(2-3,4-5,6-9,7-8)	0.025 25	0.008 58
3	(1-2,3-6,4-5,7-8)	26	(2-3,4-7,5-6,8-9)	0.023 22	0.008 70
4	(1-6,2-3,4-5,7-8)	35	(2-3,4-9,5-6,7-8)	-0.008 76	0.002 35
5	(1-6,2-5,3-4,7-8)	39	(2-3,4-9,5-8,6-7)	0.001 55	0.000 46
6	(1-2,3-4,5-8,6-7)	24	(2-5,3-4,6-7,8-9)	0.037 90	0.019 64
7	(1-4,2-3,5-8,6-7)	33	(2-5,3-4,6-9,7-8)	-0.006 90	0.002 32
8	(1-2,3-8,4-5,6-7)	27	(2-7,3-4,5-6,8-9)	-0.008 82	0.003 61
9	(1-8,2-3,4-5,6-7)	36	(2-9,3-4,5-6,7-8)	0.004 17	0.001 27
10	(1-8,2-5,3-4,6-7)	40	(2-9,3-4,5-8,6-7)	-0.000 82	0.000 26
11	(1-2,3-8,4-7,5-6)	28	(2-7,3-6,4-5,8-9)	-0.000 24	-0.000 08
12	(1-8,2-3,4-7,5-6)	37	(2-9,3-6,4-5,7-8)	-0.000 12	0.000 03
13	(1-8,2-7,3-4,5-6)	41	(2-9,3-8,4-5,6-7)	-0.000 06	-0.000 02
14	(1-8,2-7,3-6,4-5)	42	(2-9,3-8,4-7,5-6)	-0.000 03	0.000 01
15	(1-2,3-4,5-6,8-9)	22	(1-2,4-5,6-7,8-9)	0.208 18	0.144 17
16	(1-4,2-3,5-6,8-9)	31	(1-2,4-5,6-9,7-8)	-0.039 71	0.017 87
17	(1-2,3-6,4-5,8-9)	25	(1-2,4-7,5-6,8-9)	-0.038 91	0.019 70
18	(1-6,2-3,4-5,8-9)	34	(1-2,4-9,5-6,7-8)	0.012 46	0.004 56
19	(1-6,2-5,3-4,8-9)	38	(1-2,4-9,5-8,6-7)	-0.002 61	0.001 04
20	(1-2,3-4,6-7,8-9)	20	(1-2,3-4,6-7,8-9)	-0.405 22	0.337 68
21	(1-4,2-3,6-7,8-9)	29	(1-2,3-4,6-9,7-8)	0.047 19	0.025 49
30	(1-4,2-3,6-9,7-8)			-0.002 92	0.001 02

symmetry which places the unpaired electron on the central carbon atom (see eqs 11 and 13). On the other hand, the spin-coupling pattern in  $[4n + 3]$  polyenyl radicals is dominated by a pair of symmetrically equivalent Rumer spin functions in which the unpaired electron sits on either neighbor of the central carbon atom (see eq 12). The set of most important resonance structures for both types of radicals contains the unpaired electron on odd-numbered carbon atoms only (counting from one end of the chain). These observations are in very good agreement with earlier CAS SCF<sup>15</sup> and LCGTO-LSD<sup>18</sup> treatments of polyenyl radicals, according to which the spin density alternates along the carbon backbone, and the central carbon atom has either a large positive ( $[4n + 3]$  chains) or a small negative ( $[4n + 1]$  chains) spin density. The decrease of the spin density toward the ends of the molecule predicted by CAS SCF and LCGTO-LSD calculations

is paralleled by the decrease of the weights of the Rumer spin functions, in which the unpaired electron is shifted toward the ends of the chain (see eqs 11, 12, and 13).

The bond-length alternation patterns in polyenyl radicals found in refs 15 and 18 follow the distribution of  $\pi$  electron pairs in the prevailing resonance structures (eqs 11, 12, and 13), as well as the variation of overlaps between neighboring SC orbitals (see Tables 7, 9, and 11).

It could be argued that these comparisons follow immediately from the appearance of the classical Kekulé resonance structures for polyenyl chains without any need to perform SC calculations. However, in that case the observed correlations with accurate results would be only *qualitative* in nature. The close proximity of the SC total energies to their " $2n + 1$  in  $2n + 1$ " CAS SCF counterparts serves as a *quantitative* authentication of the visually appealing classical VB-style pictures embodied in the SC models for the  $\pi$  systems of  $C_5H_7-C_9H_{11}$ .

#### 4. Conclusions

In the present article we have applied SC theory to the description of the electronic structure of chain polyenyl radicals ( $C_3H_5-C_9H_{11}$ ).

Our results confirm that the SC approach accounts for the most important correlation effects in these molecules in a very physical way, combining the high visibility of the orbital description with the classical VB concepts of resonance which have always been a major tool for interpreting chemical structure and reactivity. The correlation energies included in the SC wave functions for the  $\pi$  systems of  $C_3H_5$ ,  $C_5H_7$ ,  $C_7H_9$ , and  $C_9H_{11}$  come closer to the corresponding CAS SCF values than has ever been observed in previous SC calculations for other molecules.

We have demonstrated that the SC wave function, in contrast to its open-shell HF counterpart, correctly predicts a  $C_{2v}$  geometry for the allyl radical in its ground state and reproduces the proper spatial and spin symmetry of this state ( $^2A_2$ ). The calculations indicate that the *antipairs* of SC orbitals observed previously in antiaromatic systems<sup>22</sup> reemerge as an important feature of the correlated description of the  $C_3H_5$   $\pi$  space: The energy of the "3 in 3"  $\pi$ -only CAS SCF wave functions is numerically identical to the energy of the corresponding SC wave function involving an antipair over the terminal carbon atoms. The description of the carbon-carbon bonds in the allyl radical achieved by means of a SC wave function, treating *all* electrons involved in the bonds as active, features  $\sigma$ - $\pi$  separation and does not show any tendency toward bent-bond formation and/or symmetry breaking.

A propensity toward antipair formation is observed only in the SC wave functions for the  $\pi$  systems of  $[4n + 3]$  polyenyl radicals; within the  $[4n + 1]$  series the  $\pi$  electrons are accommodated in tightly localized SC orbitals, which resemble distorted  $C(2p_\pi)$  AOs. However, while the SC wave function including an antipair is, indeed, lowest in energy for the allyl radical, it becomes slightly higher in energy than the SC wave function with localized orbitals for the next  $[4n + 1]$  radical,  $C_7H_{11}$ . This suggests that although

antipairs are an important element of the SC description of small antiaromatic cycles and radicals, results for larger systems appear to become closer to classical VB ideas and involve localized orbitals.

The SC approach yields wave functions of the proper spatial and spin symmetry for the ground states of the  $[4n + 3]$  and  $[4n + 1]$  series of polyenyl radicals:  ${}^2A_2$  and  ${}^2B_1$ , respectively. Additionally, it introduces another important distinction between the  $\pi$  systems of chains of  $4n + 3$  and  $4n + 1$  carbon atoms: The former (with the exception of the allyl radical) are best described by an *antiresonance* between equivalent Kekulé structures, while the wave functions for the latter are dominated by a single symmetry-adapted Kekulé structure which is in *conventional* resonance with less important pairs of equivalent structures.

The weights of the different Rumer pairing schemes in the  $\pi$  space spin function for polyenyl radicals can be considered to reflect the extent to which the spin of an electron in a localized

SC  $\pi$  orbital over a particular carbon atom is *unpaired* or is, alternatively, coupled to an electron pair with one of its neighbors. The analysis of these weights leads to conclusions which are in very good agreement with earlier CAS SCF<sup>15</sup> and density functional<sup>18</sup> results for spin density distributions and the carbon-carbon bond length alternation patterns in polyenyl radicals and, in fact, furnishes a VB-style reinterpretation of these results.

The highly localized nature of the SC orbitals and the well-defined resonance schemes observed in the representatives of the  $C_{2n+1}H_{2n+3}$  homologous series studied in the present article suggest that one could expect very similar results from SC calculations on higher polyenyl radicals, where one could make use of the obvious transferability of the orbitals from smaller systems to longer chains. Thus, we may conclude that the SC approach offers a consistent correlated model for the electronic structure of the  $\pi$  systems of polyenyl radicals in general, which is at the same time highly visual and easy to interpret.