

Antiferromagnetic Spin Couplings in Cyclobutadiene Chains

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The spin-coupled method, which adopts the most general single-configuration model wave function, has been used to investigate the electronic structure of dimethylenepolycyclobutadienes. A triplet “antipair” is localized on each four-membered ring: the spins of the antipairs are coupled in an antiferromagnetic fashion along the chain. Thus, for an even number of cyclobutadiene units the ground state spin multiplicity is singlet, and for an odd number of units it is triplet. The singlet and triplet states become degenerate in a long chain.

Introduction

The design of organic molecules and polymers with unusual magnetic properties has been the focus of much experimental and theoretical research (see for example ref 1). On the theoretical front, the formulation of simple qualitative rules for predicting the ground state spin multiplicity of an organic π -electron system^{2–6} has been at least as important as the increased capability to perform accurate calculations on larger and larger systems. All these rules emphasize the importance of the C atom topology in determining the magnetic properties. For example, the impossibility of coupling all the electron spins within a single Kekulé resonance structure seems to be a necessary (but not sufficient) condition for the appearance of a high-spin ground state.

Dimethylenepolycyclobutadienes (Figure 1) represent a particularly interesting class of organic π -electron systems. The monomer (DMCBD: 1,3-dimethylenecyclobutadiene, also known as 2,4-dimethylenecyclobutane-1,3-diyl) is a non-Kekulé isomer of benzene: it has been synthesized⁷ and its EPR spectrum demonstrates that it is planar with a triplet ground state, in agreement with various qualitative predictions^{2–6} and with earlier *ab initio* configuration interaction (CI) calculations by Davidson *et al.*⁸ (see refs 9–11 for subsequent calculations). These results have stimulated theoreticians to investigate the spin multiplicity of the oligomers ($n = 2, 3, 4, \dots$) and of the polymer ($n \rightarrow \infty$).^{12–15} Here there is disagreement between the qualitative predictions of “classical structure theory”⁵ ($S = 1$ for all n values, S being the principal spin quantum number), of Hückel molecular orbital theory supplemented with Hund's rule² [$S = (n + 1)/2$ for odd n , $S = n/2$ for even n], and of the more recent molecular orbital (MO) or valence bond (VB) analyses^{3–6} ($S = 1$ for odd n , $S = 0$ for even n). Semiempirical calculations on the singlet and triplet states by Pranata and Dougherty¹² and by Prasad and Radhakrishnan¹³ confirmed the latter conjecture. However, mainly on the basis of their AM1-

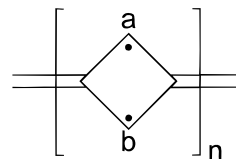


Figure 1. Structure of the dimethylenepolycyclobutadienes ($n = 1, 2, 3, \dots$).

TABLE 1: Calculated Singlet–Triplet Splittings ($E_T - E_S$, in kJ/mol) for the Monomer, Dimer, Trimer, and Tetramer: Summary of Present and Previous Results

calculation	$n = 1$	$n = 2$	$n = 3$	$n = 4$
SC (present and refs 10, 14)	−94	+18	−15	
CI (ref 8)	−99			
CI (ref 9)	−76			
PPP-CI (ref 12)	−87	+6	−8	+0.5
AM1-CI (ref 13)	−107	+12	−18	0
CASPT2 (ref 15)	−67	+10	−97	+7
AM1-CI (ref 15)	−83	+18	0 ^a	+33 ^b

^a The ground state is predicted to be a quintet. ^b The ground state is predicted to be a septet.

CI results on the higher spin states for $n = 1, 2, \dots, 9$, Dannenberg *et al.*¹⁵ have recently claimed that for sufficiently long chains one should find a *ferromagnetic* ground state with $S \propto n$. Table 1 summarizes the main theoretical results^{8–15} on the singlet–triplet splittings in DMCBD and its oligomers (up to $n = 4$). We shall return to it for further discussion in the closing section of this paper.

There is only one way to settle this controversy over the ground state spin multiplicities of the oligomers: by experiment. However, to our knowledge, so far no one has succeeded in their synthesis. In the meantime, we hope that the present theoretical study will help to clarify matters, rather than add to the general confusion. We shall argue in favor of the earlier suggestions: $S = 1$ for odd n , $S = 0$ for even n . Furthermore, our spin-coupled (SC) calculations show that the multiplicity of the ground state arises naturally from the *antiferromagnetic* coupling of triplet spins localized on each cyclobutadiene ring.

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TABLE 2: Spin-Coupled Relative Energies (in kJ/mol) for the Different Spin States of the Monomer, Dimer, and Trimer

	$S = 0$	$S = 1$	$S = 2$	$S = 3$
$n = 1$ (ref 10)	94	0		
$n = 2$ (ref 14)	0	18	152	
$n = 3$ (present work)	15	0	42	289

In the following section we present our new SC results on the different spin multiplicities of the trimer, alongside the earlier ones on the monomer and the dimer.^{10,11,14} In the closing section we compare our findings to those published by other authors^{8,9,12,13,15} and, mainly on the basis of the qualitative insight provided by the SC calculations, we extrapolate our results to the higher oligomers.

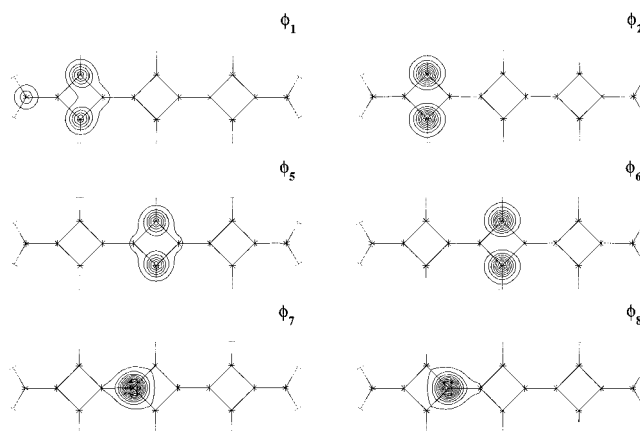
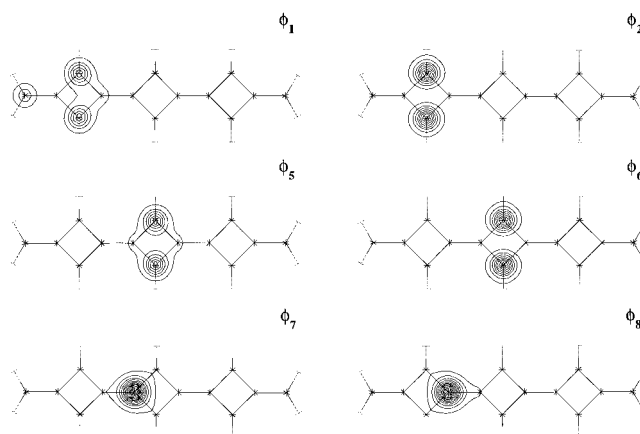
Spin-Coupled Results

The SC method^{16,17} generalizes and combines features of classical VB and of self-consistent MO theories. It adopts a correlated one-electron-per-orbital model, with simultaneous optimization of the orbital and of the spin parts of the wave function. The spin couplings are obtained by taking a linear combination of a complete set of linearly independent spin functions, for given S and M_S quantum numbers. There are no preconceptions imposed as to the form of the active orbitals (symmetry, localization, etc.), which are allowed to be *non-orthogonal*. The outcome of the orbital optimization is *unique*. Unlike other types of self-consistent wave functions, the SC wave function is not invariant to any kind of linear transformation of the active orbitals. The SC orbitals often turn out to be highly localized on the atomic centers, so that the resulting wave functions resemble closely the classical VB picture. However, the present and several other¹⁷ applications demonstrate that this is not always the case.

Let us first review our previous results on the monomer DMCBD: the reader should consult refs 10 and 11 for details on the calculation (geometry, basis set, etc.). Only the six π electrons were described by means of the correlated SC wave function; all σ electrons were kept in a frozen core of doubly occupied orbitals. Table 1 shows that the SC estimate of the singlet–triplet splitting of DMCBD is in good agreement with those reported by other authors.^{8,9,12,13,15} At the same time, these calculations led to a highly unexpected, yet simple and consistent, picture of its electronic structure. Independently of the overall spin multiplicity, four π electrons make up two ordinary C–C π bonds between the ring and the terminal CH₂ groups. This leaves two π electrons on the ring. In the triplet ground state, the corresponding orbital pair is described by the in- and out-of-phase combination of $2p_\pi$ atomic orbitals centered on carbons a and b (see Figure 1):

$$\phi^+ \simeq [2p_\pi(a) + 2p_\pi(b)], \quad \phi^- \simeq [2p_\pi(a) - 2p_\pi(b)] \quad (1)$$

Furthermore, the spins of these two electrons are almost exactly triplet-coupled;¹⁸ there is also a small delocalization of the triplet character into the external C–C π bonds, consistent with the EPR measurements. The peculiar features of such electron pairs and their recurrence in systems such as square planar cyclobutadiene and the allyl radical earned them the special name of *antipairs*.¹¹ In the excited singlet state, the last two orbitals are instead separately localized on carbons a and b . Their singlet coupling favors the formation of a direct bond between these atoms. In fact, the planar structure is not a true minimum on the singlet potential energy surface.¹⁹ It is instead a transition state for the formation of nonplanar 2,4-dimethylenecyclobutane, via the formation of a long transannular bond.

**Figure 2.** Plots of the symmetry-unique SC orbitals for the lowest singlet state of the trimer, CH₂(C₄H₂)₃CH₂.**Figure 3.** Plots of the symmetry-unique SC orbitals for the lowest triplet state of the trimer (ground state), CH₂(C₄H₂)₃CH₂.

The singlet–triplet vertical excitation energy of DMCBD can be identified with the energy needed to disrupt an antipair by recoupling its spins into a singlet. Given its relatively large value (in the range 70–90 kJ/mol: see Table 1), one can easily expect these antipairs to remain unaffected on joining two or more four-membered rings into a chain. This was demonstrated by our SC calculations on the dimer, bismethylenecyclobutadiene (BBB) (see ref 14 for details). Here there are 10 π electrons: six of them form ethylenic π bonds between the two rings and between the rings and the CH₂ groups, whereas the remaining four make up two antipairs which are localized on the rings. The SC wave functions for the different spin multiplicities ($S = 0, 1, 2$) differ only in the relative alignment of the spins of the antipairs. The singlet energy is lower than that of the triplet, which in turn is much lower than that of the quintet (see Table 2). A superexchange interaction²⁰ is responsible for the antiparallel alignment of these localized spins, which is found in the ground state. In agreement with Anderson's spin polarization mechanism,²⁰ according to which transmission of the superexchange interaction requires some opening up of the closed shell between the magnetic centers, we observed substantial triplet coupling within the electron pair that makes up the π bond between the rings.¹⁴ Notice also that the SC results indicate an important *qualitative* difference between the singlet states of the monomer and dimer: unlike DMCBD, BBB should have no tendency to distort to a nonplanar geometry by forming C–C transannular bonds.

We have now performed SC calculations on the lowest-energy singlet, triplet, quintet, and septet states of the trimer. Following ref 15, we adopted a single “idealized” geometry for all

TABLE 3: Spin Correlation Matrices $\langle \mathbf{s}_i \cdot \mathbf{s}_j \rangle$ for the Singlet and Triplet States of the Trimer (Upper and Lower Triangles, Respectively), Evaluated over the Total Wave Functions. Boldface Characters Have Been Used for the Electron Pairs in Orbitals Centered on Neighboring Carbons (See Figures 2 and 3)

	1	2	3	4	5	6	7	8	9	10
1		0.211	-0.087	-0.246	-0.087	-0.135	0.136	-0.639	0.046	0.052
2	0.211		-0.246	-0.611	-0.026	-0.041	0.067	-0.247	-0.019	0.163
3	0.072	0.125		0.211	-0.087	-0.135	0.046	0.052	0.136	-0.639
4	0.125	0.229	0.211		-0.026	-0.041	-0.019	0.163	0.067	-0.247
5	-0.127	-0.165	-0.127	-0.165		0.245	-0.479	0.095	-0.479	0.095
6	-0.192	-0.287	-0.192	-0.287	0.236		-0.448	0.128	-0.448	0.128
7	0.173	0.188	0.117	0.171	-0.480	-0.392		-0.212	0.221	-0.062
8	-0.645	-0.255	-0.063	-0.103	0.124	0.163	-0.235		-0.062	-0.028
9	0.117	0.171	0.173	0.188	-0.480	-0.392	0.234	-0.117		-0.212
10	-0.063	-0.103	-0.645	-0.255	0.124	0.163	-0.117	0.056	-0.235	

calculations: the C–C and C–H distances were fixed at 1.4254 and 1.0824 Å, respectively, and all angles at 90°, 120°, or 135°. The basis set was a standard 6-31G.²¹ If we are to use the full spin space, a full treatment of the π space goes beyond the current capabilities of the SC method. We thus reduced the number of active electrons from 14 to 10 by incorporating the two external C–C π bonds into the doubly occupied core. These two doubly occupied orbitals were fully optimized for each spin state, simultaneously with the active part of the SC wave function;^{22,23} the σ core orbitals were instead taken and used without further optimization from an open-shell RHF calculation on the quintet state [$E_{\text{RHF}}(S=2) = -535.370\,097$ au]. There are 42, 90, 75, and 35 linearly independent spin-coupling modes associated with the singlet, triplet, quintet, and septet multiplicities of the electrons in the 10 SC orbitals. We found the triplet to be the ground state, with a total energy $E_{\text{SC}}(S=1) = -535.492\,359$ au; the relative energies of the other states are given in Table 2.

Figures 2 and 3 present plots of the symmetry-unique SC orbitals for the low-energy singlet and triplet states of the trimer. From left to right, orbitals (ϕ_1, ϕ_2) , (ϕ_5, ϕ_6) , and (ϕ_3, ϕ_4) make up the three antipairs on the rings, whereas (ϕ_7, ϕ_8) and (ϕ_9, ϕ_{10}) form the two internal π bonds between adjacent rings. The shapes of these various orbitals closely resemble those already found in the monomer and dimer,^{10,11,14} and there is hardly any change on going from one spin multiplicity to another. This feature is largely shared by the orbitals of the higher-energy quintet and septet states. Hence, excitation from the ground to these low-lying excited states is mainly a matter of spin recoupling: this is closer to the VB than to the MO philosophy (see for example refs 24 and 25), even though the actual SC orbitals do not have the localized character generally associated with VB theory.

In Table 3 we have collected the expectation values of the products of the one-electron spin operators for the electrons in all orbital pairs, for the singlet and triplet states of the trimer, evaluated over the total wave functions.²⁶ These quantities contain a great deal of information about the mode of spin coupling in a molecule: $\langle \mathbf{s}_i \cdot \mathbf{s}_j \rangle$ is equal to -0.75 if electrons i and j are exactly singlet coupled, and to $+0.25$ if they are exactly triplet coupled. Elements (1,2), (3,4), and (5,6) demonstrate the almost perfect triplet coupling of the electrons in each antipair: this effect is actually more pronounced in the central antipair (orbitals ϕ_5 and ϕ_6 ; see Figures 2 and 3), for which boundary effects are less important. In the triplet ground state there is some antiparallel correlation between the spins associated with nearest-neighbor antipairs [$\langle (\mathbf{s}_1 + \mathbf{s}_2) \cdot (\mathbf{s}_5 + \mathbf{s}_6) \rangle = -0.771$]. In the excited singlet state, instead, nearest-neighbor correlations are almost absent ($\langle \mathbf{s}_i \cdot \mathbf{s}_j \rangle \approx 0$ for $i = 1, 2$ and $j = 3, 4$). Finally, matrix elements (7,8) and (9,10) show a sizeable deviation from perfect singlet coupling on the π bonds between the rings (for comparison, $\langle \mathbf{s}_i \cdot \mathbf{s}_j \rangle \approx -0.7$ for an ordinary bonded

pair in a linear polyene²⁶). As anticipated, the opening up of these ethylenic electron pairs may be explained by the superexchange mechanism for antiferromagnetic spin couplings.²⁰

Comparing the two spin states, we find similar spin correlations between all those electron pairs that are associated with adjacent carbon atoms (boldface characters in Table 3); they can instead be very different for well-separated electron pairs. In principle, the energy of each state could be approximately calculated from a Heisenberg Hamiltonian^{4,5,27}

$$E(S) = \text{constant} + \sum_{i < j=1}^N J_{ij} \langle \mathbf{s}_i \cdot \mathbf{s}_j \rangle \quad (2)$$

where N is the number of π electrons and the J_{ij} parameters depend on the sign and the strength of the exchange interaction between orbitals ϕ_i and ϕ_j . The importance of a term $J_{ij} \langle \mathbf{s}_i \cdot \mathbf{s}_j \rangle$ thus decays very rapidly with the separation between the pair (i, j) . The values of the nearest-neighbor spin correlations are thus essentially fixed by the energy minimization, whatever the overall spin state. Instead, the total spin multiplicity mainly influences the longer-range correlations through the condition

$$\langle (\sum_{i=1}^N \mathbf{s}_i)^2 \rangle = \frac{3}{4}N + \sum_{i \neq j}^N \langle \mathbf{s}_i \cdot \mathbf{s}_j \rangle = S(S+1) \quad (3)$$

Conclusions

We have used the spin-coupled method to study the electronic structure of dimethylenepolycyclobutadienes (Figure 1), containing one, two, or three four-membered rings. The SC results provide a simple and pictorial explanation for the alternation in the ground state spin multiplicity, which is either singlet or triplet depending on whether the number of units in the chain is even or odd.^{12,13} There is a triplet antipair localized on each four-membered ring: the ethylenic π bonds between the rings couple these triplet spins antiferromagnetically, by a superexchange mechanism that is qualitatively similar to that found in transition metal oxides.²⁰

Recent AM1-CI calculations on the higher oligomers by Dannenberg *et al.*¹⁵ do not agree with the present conclusions: The authors claim that for sufficiently long chains one should find a high-spin (hence ferromagnetic) ground state with $S \propto n$. For computational reasons, we are unable to perform a direct check of their results for $n \geq 4$. However, we cannot see how a ferromagnetic ground state could arise from the antiferromagnetic coupling between neighboring units. We suspect that their calculations on the higher oligomers are flawed by the lack of size-extensivity of the truncated CI expansion.^{28,29} We might add that for the shorter oligomers, in particular the trimer and the tetramer, the agreement between the semiempirical and their *ab initio* CASSCF/CASPT2 calculations¹⁵ is rather unsatisfactory (see Table 1).

In the infinite-chain limit, the singlet and triplet states will be degenerate. When $n \gg 1$, the polymer has no way of “knowing” whether n is even or odd. There will be several other low-spin states very close in energy: when N (the number of π electrons) is much greater than unity and $S \ll N/2$, the constraint of eq 3 on the spin correlations $\langle s_i s_j \rangle$ —which to a first approximation determine the energy according to eq 2—becomes irrelevant. This trend is already evident from the oligomer results in Table 1. These degeneracies destroy any long-range correlation between the electronic spins.³⁰ At short range, however, one should still observe an antiferromagnetic coupling between the triplet spins on the rings.

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