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Spin Coupling in Nonconjugated Organic Radicals

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Spin interactions in nonconjugated organic multiradical systems are analyzed using semiempirical quantum chemical computations. Implications of these results for an appraisal of the ferrocarbon model for organic ferromagnets are discussed.

Introduction

A considerable amount of theoretical and experimental studies have led to a sound understanding of the nature of spin interactions in π-electron conjugated organic diradicals and polyradicals. Early work of Coulson, Rushbrooke, and Longuet-Higgins[1] on the prediction of spin states based on a count of nonbonding molecular orbitals has been generalized by Tyutyulkov and co-workers.[2] Ovchinnikov's rule for the ground state spin of alternant systems[3] and Mataga's predictions for polycarbenes[4] have been verified by extensive computational and experimental tests.[5] Borden and Davidson[6] have discussed the spin states of conjugated radicals in terms of the disjoint nature of the nonbonding π-molecular orbitals. We have suggested simple topological rules[7] to predict the ground state spin of wide varieties of polyradicals and empirical procedures to quantify singlet−triplet energy gaps in diradicals.[8] A large number of conjugated organic diradicals and polyradicals have been studied experimentally in recent years to determine their ground state spin.[9] Through these studies, basic insight has been gained into cases of Hund's rule violation[10] and the relevance of polyradicals in the design of organic ferromagnets.[11]

Compared to the extensive research that has been carried out on conjugated radical systems, there have been relatively sparse studies on the problem of spin coupling in nonconjugated radicals, *i.e.* systems with radical sites separated by saturated carbon atoms. Nonconjugated radicals are in general more reactive than the conjugated ones, making them less amenable to experimental studies. This is possibly the main reason why less attention has been paid to nonconjugated systems. Another reason for the paucity of interest in these systems is the relatively weaker spin interactions between radical sites connected through saturated carbon atoms. However, there are indications that some of these systems may be quite interesting. For example, in the crystals of Dupeyredioxyl,[12] in which ferromagnetic transition has been demonstrated, in addition to the intermolecular magnetic interactions, the intramolecular spin coupling between the nonconjugated radical sites has been shown to be significant. There has been a number of reports of ferromagnetic materials obtained by the pyrolysis of hydrocarbons and other organic compounds.[13] Though the origin of cooperative magnetic interactions in these systems is far from clear, an understanding of spin coupling in nonconjugated systems would be useful in analyzing the properties of such materials. It is also noteworthy that several recent investigations[14] on crystals of stable nitronylnitroxide radicals have suggested the possibility of intermolecular spin interactions mediated by σ-electrons.

The prototypical system for the study of spin interaction in nonconjugated systems, namely, propane-1,3-diyl, has been the subject of several theoretical investigations. Early studies[15−17] have highlighted the relevance of considering different conformations of the spin orbitals in analyzing the spin couplings in this system; in particular, the cases of both CH_2 groups being in the C−C−C plane (0,0), one in and one orthogonal to the C−C−C plane (0,90), and both orthogonal to the C−C−C plane (90,90) were studied. Ovchinnikov proposed[18] a few years ago an interesting model for a carbon-based ferromagnetic material, which he christened as "ferrocarbon". He proposed that a phase of carbon intermediate between graphite and diamond, wherein quasi graphite layers of alternately connected sp^2 and sp^3-hybridized carbon atoms are linked at the sp^3 carbons to form a 3-D lattice, would have a ferromagnetic alignment of the spins at the sp^2 radical sites. Quantum chemical calculations carried out by Ovchinnikov on model fragments (propane-1,3-diyl and butane-1,4-diyl) with different conformations relevant to the ferrocarbon system indicated that the spins would be coupled ferromagnetically. From the point of view of spin interactions in nonconjugated systems, this model would be an interesting and important testing ground.

We have carried out quantum chemical calculations to analyze the mode of spin coupling in several nonconjugated hydrocarbon di- and multiradical systems. *Ab initio* calculations were carried out on the trimethylene systems as benchmark studies for the semiempirical calculations carried out on larger systems in the rest of the investigations. We chose the cyclohexane, decalin, bicyclo[3.3.1]nonane, and adamantane frameworks to place the radical sites to analyze the dependence of spin coupling on the relative orientation of the spin orbitals. Further examples for the study were chosen from fragments of the ferrocarbon framework. Our calculations indicated that the spin coupling strongly depends on the relative disposition of the spin-bearing orbitals. We have carried out a systematic study of this dependence using cyclohexane-1,3-diyl as the model system. The relevance of the cyclohexane-1,3,5-triyl system from an experimental point of view is analyzed using some model calculations on the potential energy pathway for 1−3 bond formation.

Computational Methods

The semiempirical calculations were carried out using the AM1 quantum chemical procedure;[19] the MOPAC93 program package was used.[20] Open shell RHF procedure has been found to provide better correlation of experimental data than the UHF method[8,21,22] and was used throughout this sudy. In general, the geometries of the radicals were fully optimized for each spin state under consideration; constraints imposed, if any, are described at the appropriate places. Energies were computed

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using the configuration interaction scheme involving all excitations within the manifold of five molecular orbitals (CI = 5) bracketing the HOMO and LUMO (test calculations using CI = 6 gave practically identical results). For the lower spin states, the OPEN(n,n) keyword was used, where n is the number of unpaired electrons in the corresponding highest spin state; the open shell condition led to a stabilization over the closed shell situation for each of the lower spin states. The ground state spin was determined on the basis of the results of these calculations. The energy gaps that we present in the paper are the differences in the energy of the various spin states of the radical with the geometry of the ground state determined above. If not explicitly stated otherwise, the energy gaps reported between any two spin states are the values obtained by subtracting the energy of the higher multiplicity spin state from the energy of the lower multiplicity one.

We would like to draw attention to the following points in support of using the AM1/CI semiempirical method for the studies reported in this paper. This procedure has been found to model spin interactions in organic polyradical systems rather well. Several earlier investigations have shown that this semiempirical method gives estimates of spin state energies in good agreement with more sophisticated computational procedures and experiments.[7,21] We have also shown that the spin densities and zero-field splitting parameters of organic diradicals are estimated very successfully by AM1/CI computations.[8,22] It was also demonstrated[22] that the elusive problem of the ground state spin of tetramethyleneethane, modeled by high-level *ab initio* computations, could be reproduced by the AM1/CI method when sufficient CI is invoked. We compare in detail the results of AM1/CI calculations on some prototypical nonconjugated radical systems with the results from *ab initio* calculations, which lends further support to our use of the semiempirical procedure for the problem presented in this paper. Primarily we have used the CASSCF procedure with 6-31G** basis set implemented in Gaussian 94.[23] Further details on these calculations are presented when the results are discussed.

For analyzing the dependence of spin coupling on the mutual orientation of spin orbitals, we have adopted the definition of a pi orbital axis vector (POAV) suggested by Haddon.[24] The POAV used here is the vector that makes equal angles with the three bond vectors around an sp^2 carbon center bearing the spin. For any pair of radical sites i, j, we choose the direction of the POAVs such that the POAVs at sites i and j make acute angles with the vectors $i \rightarrow j$ and $j \rightarrow i$ respectively. We compute the angle, θ_{ij}, between these POAVs and utilize this angle as an indicator of the mutual orientation of the spin orbitals. When the two POAVs are parallel, the θ_{ij} is taken as zero.

The computations reported in this study were carried out on SUN Sparc 10 and Silicon Graphics Power Indigo 2 (R8000) workstations.

Results and Discussion

For the purpose of testing the efficiency of semiempirical CI calculations for studying the nonconjugated radicals, we have carried out pilot calculations on the three main conformations (0,0), (0,90), and (90,90) of propane-1,3-diyl using the AM1/CI method and compared with the results of *ab initio* computations. The calculations were full optimizations except for enforcing of the specific conformations and the imposition of C_{2v} symmetry for the (0,0) and (90,90) structures and C_s symmetry for the (0,90) conformation. Since the (90,90) structures show special behavior, we consider first the other two conformations. The AM1/CI calculations showed that the triplet is preferred in the (0,0) and (0,90) conformations with the singlet−triplet gap being 2.1 and 2.8 kcal/mol respectively. *Ab initio* calculations by Doubleday *et al.*[25] using the 4-31G basis set have shown that the triplet is favored over the singlet by 0.61 and 2.04 kcal/mol respectively in the (0,0) and (0,90) conformations. We carried out CASSCF(2,4) (two electrons in four orbitals)/6-31G** calculations with full optimization of the triplet geometry in the (0,0) and (0,90) conformations. The triplet was found to be favored over the singlet (with the triplet geometry) by 0.62 and 1.88 kcal/mol respectively, in good agreement with the earlier *ab initio* results and showing the same trends as in our AM1/CI calculations. The singlet−triplet gap did not show any marked change when the energies of the fully optimized singlet geometries were used. We note that the MCSCF calculations of Ovchinnikov[18] showed very large triplet state stabilizations of the order of an electronvolt in all the conformations; we have found such large singlet−triplet gaps only in HF and CISD calculations where the singlet optimizations led to unrealistic structures with C−C−C angles of about 130°.

In the (90,90) conformer, optimization of the singlet led to 1−3 bond formation (C−C−C angle = 70.4°), and the AM1/CI singlet−triplet gap at this geometry was −73.9 kcal/mol. Since the diradical species can be obtained only at the triplet optimized geometry (C−C−C angle = 111.8°), we have evaluated the singlet−triplet gap for this structure, which turns out to be 3.3 kcal/mol. However, the *ab initio* calculations of Doubleday *et al.*[25] had indicated that the singlet is preferred in the (90,90) conformation by 4.2 kcal/mol. Since the singlet (90,90) conformation shows a tendency to form a bond, we have investigated the singlet and triplet state energies as a function of the C−C−C bond angle, using CASSCF(2,4) and AM1/CI calculations. The geometries were fully optimized in all cases except for fixing the bond angle and imposing the relevant conformation with C_{2v} symmetry. The energy surfaces had similar shapes in both calculations with the singlet energies decreasing almost linearly with the C−C−C angle and the triplet energies showing a minimum at about 112° for the AM1 and at 115° for the *ab initio* method. However, the AM1/CI shows that the triplet is energetically favored over the singlet at the minimum of the triplet surface in agreement with the data given above, but the *ab initio* calculations indicated that the singlet is energetically lower by 2.7 kcal/mol, at the C−C−C angle corresponding to the triplet minimum. Since the 6-31G** basis set provides for greater spatial extension of orbitals, we repeated these calculations using STO-3G basis set. Interestingly, the results were qualitatively similar to the results of the AM1/CI computations, showing the triplet to be stabler by *ca.* 0.4 kcal/mol over the singlet at the minimum of the triplet curve. Thus the semiempirical computation appears to be similar to a minimal basis set *ab initio* calculation and shows a preference for the higher spin state, which we attribute to the shorter expansion of the spin orbitals that leads to poorer overlaps and lower tendency for bonding interaction. The complete results of these calculations are presented in the Supporting Information.

The main focus of our study in this paper involved spin orbitals oriented toward each other at angles that are constrained by the underlying cyclohexane or related framework and thus have some resemblance to the (0,0) conformer of propane-1,3-diyl but none at all to the (90,90) conformer. To obtain a relevant appraisal of the efficacy of the AM1/CI method in relation to the *ab initio* method in describing the spin coupling within this constrained enviroment, we next compared the results of the studies on the cyclohexane-1,3,5-triyl system. The AM1/CI calculation was carried out with full optimization of the doublet and quartet states under C_{3v} symmetry constraint. The

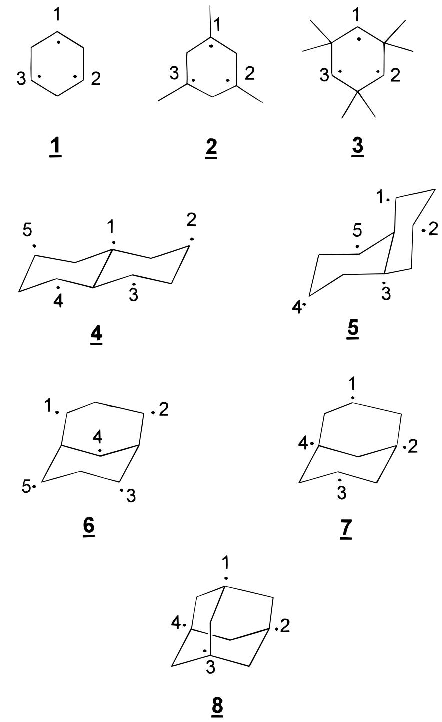

Figure 1. Nonconjugated multiradicals based on the cyclohexane, decalin, bicyclononane, and adamantane frameworks used in this study. The labeled sites are sp^2 carbons, and the unlabeled ones represent sp^3 carbons; H atoms are omitted for clarity.

quartet was found to be energetically lower by 2.2 kcal/mol, and the quartet−doublet energy gap at the quartet geometry was found to be 2.3 kcal/mol. Since the optimization of the cyclohexane system at the *ab initio* level was found to be computationally very expensive, we have used the AM1/CI optimized quartet geometry and carried out single-point calculations for the CASSCF(3,6)/6-31G** energies of the doublet and quartet states. The quartet was found to be stabler by 0.7 kcal/mol. On the basis of this result and the calculations on the propane-1,3-diyl system, we conclude that the AM1/CI method predicts correctly the ground state spin and provides a qualitative and nearly quantitative estimate of the spin state energy gaps in these nonconjugated multiradical systems; it appears to fail only in those cases that are close to bonding situations.

TABLE 1: Relative Energies of Different Spin States of Multiradicals in Figure 1[a]

structure number	spin state	relative energy (kcal/mol)	angle θ_{ij} (deg) [$i-j$]
1	quartet	0.0	37.9 [1−2]; 37.8 [1−3]
	doublet	2.3	37.8 [2−3]
2	quartet	0.0	35.2 [1−2]; 35.6 [1−3]
	doublet	2.9	34.5 [2−3]
3	quartet	0.0	27.2 [1−2]; 27.5 [1−3]
	doublet	2.4	31.4 [2−3]
4	sextet	0.0	11.3 [1−2]; 33.5 [1−5]
	quartet	1.3	13.7 [1−3]; 41.5 [1−4]
	doublet	3.0	17.5 [2−3]; 55.2 [3−4]
			27.1 [4−5]
5	sextet	0.0	27.6 [1−2]; 9.7 [1−3]
	quartet	1.9	40.1 [1−5]; 33.6 [2−3]
	doublet	3.5	46.9 [3−4]; 48.6 [3−5]
			20.8 [4−5]
6	sextet	0.0	55.6 [2−4]; 24.0 [1−2]
	quartet	3.0	55.1 [3−4]; 24.0 [3−5]
	doublet	4.2	56.0 [4−5]; 58.6 [1−4]
7	quintet	0.0	60.6 [1−2]; 61.3 [1−4]
	triplet	−2.1	60.9 [2−3]; 75.9 [2−4]
	singlet	−2.1	60.3 [3−4]
8	quintet	0.0	108.9 [1−2]; 109.9 [1−3]
	triplet	−2.6	108.8 [1−4]; 109.6 [2−3]
	singlet	−14.2	108.9 [2−4]; 110.6 [3−4]

[a] The mutual orientation of spin orbitals at the sites *i* and *j* separated by one saturated carbon atom (labeled in Figure 1) are also provided.

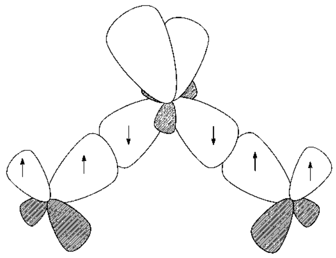

Figure 2. Schematic picture of the spin polarization in a nonconjugated diradical, involving the σ-bonds.

First we considered the set of radical systems represented in Figure 1 consisting of cyclohexane-1,3,5-triyl radicals and related systems in the decalin, bicyclo[3.3.1]nonane, and adamantane frameworks. The radicals considered in this set have pairs of radical sites separated by a saturated carbon atom with the spin orbitals sampling a variety of mutual orientations. The cyclohexane framework in particular also provides radical pairs analogous to the prototypical propane-1,3-diyl system but now in a constrained environment that is more relevant to a discussion of cases like that of ferrocarbon presented later. The AM1/CI optimized structures of these molecules (in terms of *z*-matrices) are provided in the Supporting Information. Table 1 lists the energy gaps for the relevant spin states of the different multiradical systems represented in Figure 1. The table also provides the various angles θ_{ij} between the POAV at radical sites *i* and *j* in these systems. The singlet−triplet gaps are found to be about 2.5 kcal/mol in cyclohexane-1,3,5-triyl as well as its methylated derivatives. In the pentaradicals, **4** and **5**, based on the *trans* and *cis*-decalin framework, the sextet state is the ground state and the doublet−sextet gap is found to be 3−3.5 kcal/mol. In the bicyclo[3.3.1]nonane framework, the pentaradical **6** is found to have a sextet ground state, whereas the tetraradical **7** has a singlet ground state. The tetraradical **8** based on the adamantane framework also was found to have a low-spin ground state. Due to the program limitations, we could not optimize the high-spin heptet state of the hexaradical that can be obtained by placing the radical sites at the nonbridge atoms of the adamantane framework; hence it is not included in Table 1. However, the CI calculations on the optimized singlet state of this multiradical indicated that the heptet was the ground state. Thus among the systems considered in this group, the spin couplings are found to be predominantly ferromagnetic, the only exceptions being **7** and **8**. The dominant ferromagnetic coupling of the spins at radical sites separated by one saturated carbon atom is reminiscent of the case of (0,0) conformation of propane-1,3-diyl. The basic mechanism of spin coupling could be visualized using the spin polarization involving the σ-electrons schematically depicted in Figure 2. AM1/UHF calculations (necessary to reproduce negative spin densities) on the (0,0) conformer of propane-1,3-diyl gave approximately +1.1 and −0.2 as the spin densities on the sp^2 and sp^3 carbons respectively, in support of this spin polarization picture. This model is conceptually similar to the spin polarization involving only π-electrons in conjugated polyradicals.

The exceptional behavior of **7** and **8** is interesting. The obvious difference between these systems and the rest is that only these have more than one radical site occuring on the bridge atoms. The mutual orientation of the spin orbitals at the bridge sites is quite different from the mutual orientation of other orbitals. The θ_{ij} values listed in Table 1 can be used to discuss

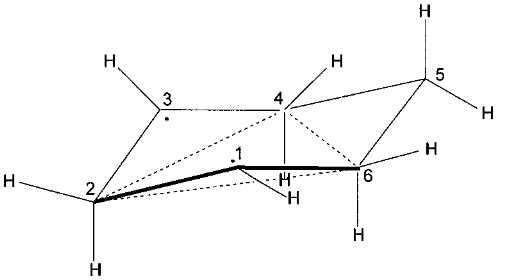

Figure 3. Schematic representation of the folding of cyclohexane-1,3-diyl used in the study of the singlet and triplet state energies as a function of spin orbital orientation.

this more quantitatively. In the ferromagnetically coupled spin systems, this angle is usually about 30−40° with a few cases of lower (10−20°) and higher (55−60°) angles. In **7** these angles are found to be about 61° with the 2−4 angle (between bridge atoms) being approximately 76°. In **8** all the angles are close to 109°. A careful observation of the optimized geometries indicates that, in the cyclohexane framework, θ_{ij} values close to or higher than 70° are associated with a decrease in the distance between the radical sites, which possibly leads to some weak overlap of the spin orbitals and bonding interaction that would result in an antiferromagnetic coupling of the spins. We analyze below, more systematically, the correlation between the nature of spin coupling and the orientation of spin orbitals.

Cyclohexane-1,3-diyl is chosen as the model system to analyze the variation of the singlet and triplet state energies as a function of the folding of the planes defined by carbon atoms 2,1,6 and 2,3,4 (see Figure 3 for the labelings). Geometries were optimized with a C_s symmetry constraint, the plane of symmetry passing through carbon atoms 2 and 5 and the four hydrogen atoms attached to them. The angle between the planes defined by carbons 2, 1, and 6 (or 2, 3, and 4 by symmetry) and the plane defined by carbons 2, 4, and 6 was varied from 180° to approximately 120° (the *z*-matrix and the definition of the dihedral angle using some dummy atoms are provided in the Supporting Information). When this angle was decreased below 120°, carbons 1 and 3 get almost bonded, and hence such points were not considered. At each fixed value of the angle, the singlet and triplet state geometries were optimized (optimized geometries are provided in the Supporting Information). Figure 4 provides a plot of the heats of formation of the singlet and triplet states as a function of θ_{13}. It is clearly seen that the triplet state is preferred when the mutual orientation angle of the POAVs is below 70° and that the singlet−triplet gap becomes the largest when this angle is about 47°. Above 70°, the singlet state is lower in energy, eventually leading to a bond. This result is in very good agreement with the observations made in Table 1. Thus, this model provides a logical background to visualize spin interactions in nonconjugated multiradicals based on the cyclohexane and related frameworks.

Next we considered four important fragments from the ferrocarbon model proposed by Ovchinnikov (Figure 5). The fragments were incised from the molecular mechanics optimized geometry of the ferrocarbon framework reported by Ovchinnikov.[18a] Each fragment along with all the atoms directly connected to it was incised from the lattice; the atoms connected to the fragment were then replaced by H atoms, and the C−H distances alone were optimized in the AM1 calculation. Thus the model multiradical systems preserve the relevant bond lengths and all bond angles and dihedrals from the ferrocarbon lattice. **9** and **10** are model systems for the basic sofa and boat units in the proposed ferrocarbon phase. **11** models a larger fragment made up of two sofas within the quasi graphite layer.

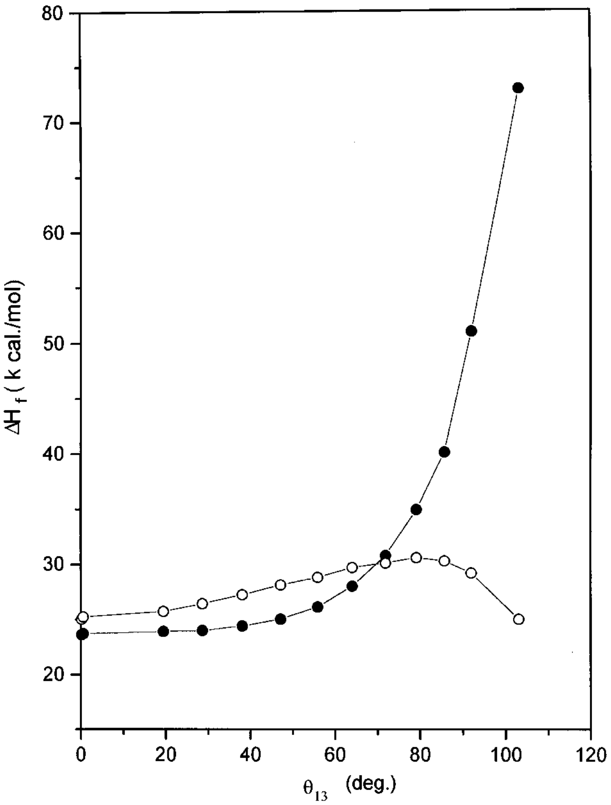

Figure 4. Plot of the AM1/CI heats of formation of the singlet (○) and triplet (●) states of cyclohexane-1,3-diyl as a function of the mutual orientation θ_{13} of the spin orbitals (see text for definition of θ_{13}). The line is only a guide to the eye.

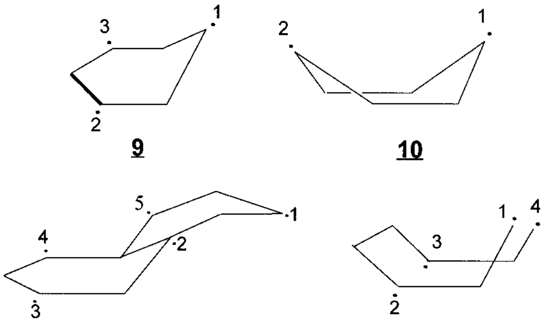

Figure 5. Nonconjugated multiradical fragments incised from the ferrocarbon framework (ref 18a). The labeled sites are sp^2 carbons, and the unlabeled ones represent sp^3 carbons; H atoms are omitted for clarity.

12 is the model fragment that represents a unit cell connecting two quasi graphite layers in the ferrocarbon phase. Table 2 provides the energies of the various spin states of each fragment as well as the relevant θ_{ij} angles. It is seen that fragments **9** and **11** show clear preference for a ferromagnetic alignment of spins, and the mutual orientations of the spin orbitals are either nearly parallel or about 55°. **10** shows antiferromagnetic coupling of the spins since the radical sites are separated by two saturated carbons and the θ_{ij} is about 123°. Extension of the spin polarization picture in Figure 2 to a 1,4-diradical would indicate antiferromagnetic coupling of the spins; butane-1,4-diyl is known to have a singlet ground state in most of its conformations.[6c] Usually this spin coupling is weak; however, in the present systems, the special conformations lead to stronger interactions. The case of **12** is interesting. The mutual orientation between orbitals at 1 and 2 (as well as 3 and 4), which are separated by one saturated carbon atom, is ap-

TABLE 2: Relative Energies of Different Spin States of Ferrocarbon Fragments in Figure 5[a]

structure number	spin state	relative energy (kcal/mol)	angle θ_{ij} (deg) [*i*−*j*]
9	quartet	0.0	57.5 [1−2]; 57.6 [1−3]
	doublet	1.7	0.2 [2−3]
10	triplet	0.0	122.6 [1−2]
	singlet	−3.4	
11	sextet	0.0	0.1 [1−2]; 57.3 [1−5]
	quartet	1.2	57.4 [2−3]; 57.3 [2−4]
	doublet	2.9	54.4 [4−5]; 57.2 [2−5] 0.1 [3−4]
12	quintet	0.0	57.4 [1−2]; 122.6 [1−4]
	triplet	−1.1	122.5 [2−3]; 57.5 [3−4]
	singlet	−7.8	

[a] The mutual orientation of the spin orbitals at sites *i* and *j* (labeled in Figure 5)are also provided.

proximately 58°. This is expected to lead to ferromagnetic coupling of spins within each of these pairs of radical sites. However these pairs are in turn separated by two saturated carbons, and the θ between 1 and 4 (as well as 2 and 3) is approximately 123°. This leads to overall strong antiferromagnetic spin interaction and a singlet ground state. This is reminiscent of the application of the rules for extended spin coupling developed by us for π-conjugated multiradicals.[7a] Thus we find that the calculated spin states of the ferrocarbon fragments are quite consistent with the analysis of the cyclohexane-1,3-diyl folding problem discussed above. Significantly, in the proposed ferrocarbon model, even though within the quasi graphite layers one may realize ferromagnetic interaction of spins, these model calculations predict an antiferromagnetic interaction between the layers. Therefore the realization of a bulk magnetic ferrocarbon is questionable on the basis of these results.

The cyclohexane skeleton is seen to be an interesting framework to install radical sites and study spin couplings to understand the problem of spin interactions in nonconjugated systems. The first set of multiradical systems we studied illustrates interesting cases of ferromagnetic and antiferromagnetic spin interactions. These systems also provide an insight into the magnetic interactions in the ferrocarbon model. From the point of view of experimental studies, we believe that the cyclohexane radical systems should prove very informative. Even though the calculated energy gap between the doublet and quartet states is only moderate, the high spin state arising from the cooperative interaction of three pairs of diradical components is found to be consistently stabler than the lower spin state. If a suitable synthetic strategy could be devised to generate **1** or its derivatives from an appropriately trisubstituted cyclohexane, the ground state spin could be determined. We believe that Kemp's triacid (1,3,5-trimethylcyclohexane-1,3,5-tricarboxylic acid) or its derivatives could prove to be interesting starting points for such studies. The triradical **3** should be particularly interesting since the permethylation should prevent any possible 1,2 hydrogen atom migrations that could take place in the case of **1** or **2**.

We have calculated the potential energy pathway to model the recombination of two of the spin sites (1 and 3) to form bicyclo[3.1.0]hexane-3-yl radical. The geometries were fully optimized at different fixed distances between C atoms 1 and 3 in both the doublet and quartet states. The energy profile is shown in Figure 6 with different energy scales for C−C distance below and above 2 Å to show clearly the situation near the quartet minimum. Interestingly, the doublet also shows a minimum at the geometry corresponding to the quartet minimum, but at a higher energy (*cf.* **1** above). There is a barrier of *ca.* 6 kcal/mol to go from this minimum to the bonded state along the doublet pathway. It is seen that there is a higher barrier of *ca.* 8 kcal/mol for the quartet triradical to go over to the doublet bicyclic system. Hence if the triradical can be generated at low temperatures, it will be protected by a moderately high barrier from immediate intramolecular recombinations.

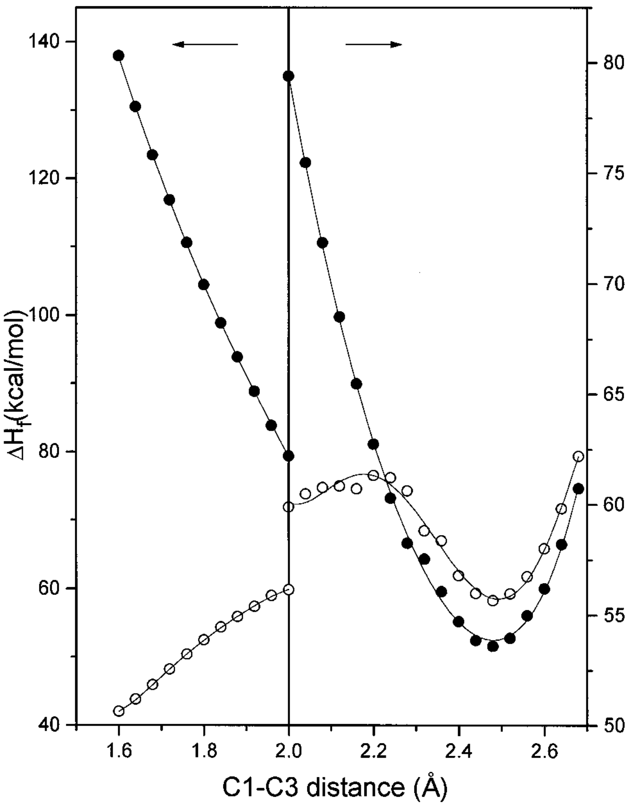

Figure 6. Plot of the AM1/CI heats of formation of the doublet (○) and quartet (●) states of cyclohexane-1,3,5-triyl as a function of the C1−C3 distance. The *y*-axis scales are different for the data points corresponding to C1−C3 distance below and above 2 Å. The line is only a guide to the eye.

Conclusion

We have studied the spin coupling in nonconjugated organic multiradical systems having different frameworks, using semiempirical quantum chemical calculations including configuration interaction. On the basis of earlier studies as well as the present comparisons with *ab inito* results, we believe that these methods are optimal procedures to carry out such analysis. The detailed analysis of the prototypical propane-1,3-diyl system has provided a fair appraisal of the efficacy of AM1/CI method to analyze the problem of spin interaction in nonconjugated systems in general. We have focused our attention primarily on multiradicals based on the cyclohexane framework for the following reasons: (i) they provide several cases of 1,3-nonconjugated radical pairs in different mutual orientations, (ii) they are relevant as model systems for an appraisal of the ferrocarbon concept proposed recently, and (iii) they are interesting prototypes for experimental studies. These studies led to a logical analysis of the ferrocarbon model for organic ferromagnets and the conclusion that strong antiferromagnetic interaction between the quasi graphitic layers may preclude the realization of ferromagnetism. Our studies have shown that the spin interaction across saturated carbon atoms is relatively weak compared to the case of π-conjugated systems. It is also observed that the mutual orientation and associated spatial separation of the spin orbitals crucially control the mode of spin interactions and can be analyzed in a logical way. We have delineated the general trends in the cyclohexane framework using model calculations on the cyclohexane-1,3-diyl system.

The results of this study may be relevant in gaining an insight into the magnetism of pyrolitic carbon materials based on molecules such as adamantane. In studies of pyrolitic carbons, many instances have been reported where ferromagnetic materials were obtained. The actual species that give rise to such magnetism are poorly understood. We propose that several random spin sites are generated during the pyrolysis of hydrocarbons and that these multiradical systems may involve several ferromagnetically coupled spins. In individual cases, if one can determine possible multiradical species that are likely to be formed, analysis similar to what we have carried out above may be utilized to investigate the spin coupling pathways and thus obtain an insight into the factors that lead to the bulk magnetic properties.

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Supporting Information Available: Comparision of the *ab initio* and AM1/CI singlet−triplet energy profiles as a function of C−C−C angle in propane-1,3-diyl. Optimized geometries of radicals **1**−**8**. Definition of the *z*-matrix used in the calculation of the cyclohexane-1,3-diyl singlet and triplet state energies as a function of the mutual orientation of spin orbitals and the optimized geometries of the various folded systems (14 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Coulson, C. A.; Rushbrooke, G. S. *Proc. Cambridge Philos. Soc.* **1940,** *36*, 193. (b) Coulson, C. A.; Longuet-Higgins, H. C. *Proc. R. Soc. London A* **1947,** *191*, 39; **1947,** *192*, 16; **1947,** *193*, 447. (c) Longuet-Higgins, H. C. *J. Chem. Phys.* **1950**, *18*, 265.

(2) (a) Tyutyulkov, N; Polansky, O. E. *Chem. Phys. Lett.* **1987**, *139*, 281. (b) Karabunarliev, S.; Tyutyulkov, N. *Theor. Chim. Acta* **1989**, *76*, 65. (c) Tyutyulkov, N.; Karabunarliev, S.; Ivanov, C. *Mol. Cryst. Liq. Cryst.* **1989**, *176*, 139.

(3) Ovchinnikov, A. A. *Theor. Chim. Acta* **1978**, *47*, 297.

(4) Mataga, N. *Theor. Chim. Acta* **1968**, *10*, 372.

(5) (a) Klein, D. J. *J. Chem. Phys.* **1982**, *77*, 3098. (b) Klein, D. J.; Nelin, C. J.; Alexander, S.; Matsen, P. A. *J. Chem. Phys.* **1982**, *77*, 3101. (c) Alexander, S. A.; Klein, D. J. *J. Am. Chem. Soc.* **1988**, *110*, 3401. (d) Koutecky, J; Dohnert, D; Wormer, P. S.; Paldus, J; Cizek, J. *J. Chem. Phys.* **1984**, *80*, 2244. (e) Lahti, P. M.; Rossi, A. R.; Berson, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 2273. (f) Sinha, B.; Albert, I. D. L.; Ramasesha, S. *Phys. Rev.* **1990**, *B42*, 9088. (g) Nasu, K. *Phys. Rev.* **1986**, *B33*, 330. (h) Teki, Y.; Takui, T.; Itoh, K.; Iwamura, H.; Kobayashi, K. *J. Am. Chem. Soc.* **1983**, *105*, 3722; **1986**, *108*, 2147.

(6) (a) Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1977**, *99*, 4587. (b) Borden. W. T.; Davidson, E. R. *Acc. Chem. Res.* **1981**, *14*, 69. (c) Borden, W. T. In *Diradicals*; Borden, W. T., Ed.; Wiley: New York, 1982; p 1.

(7) (a) Radhakrishnan, T. P. *Chem. Phys. Lett.* **1991**, *181*, 455. (b) Radhakrishnan, T. P. *Tetrahedron Lett.* **1991**, *32*, 4601; **1993**, **34**, 4399. (c) Radhakrishnan, T. P. *Chem. Phys. Lett.* **1993**, *207*, 15.

(8) Prasad, B. L. V.; Radhakrishnan, T. P. *J. Phys. Chem.* **1992**, *96*, 9232.

(9) For reviews, see : (a) Iwamura, H.; Koga, N. *Acc. Chem. Res.* **1993**, *26*, 346. (b) Radhakrishnan, T. P. In *Strongly Correlated Electron Systems in Chemistry*: *Theory and Experiment*; Ramasesha, S., Sarma, D. D., Eds.; Narosa Publishers, New Delhi, 1996; p 167.

(10) Borden, W. T.; Iwamura, H; Berson, J. A. *Acc. Chem. Res.* **1994**, *27*, 109.

(11) Rajca, A. *Chem. Rev.* **1994**, *94*, 871.

(12) (a) Chiarelli, R.; Novak, M. A.; Rassat, A.; Tholence, J. L. *Nature* **1993**, *363*, 147. (b) Chiarelli, R.; Rassat, A.; Dromzee, Y.; Jeannin, Y.; Novak, M. A.; Tholence, J. L. *Phys. Scr.* **1993**, *T49*, 706 (1993).

(13) (a) Tanaka, K.; Yoshizawa, K.; Takata, A.; Yamabe, T.; Yamauchi, J. *J. Chem. Phys.* **1991**, *94*, 6868. (b) Tanaka, K; Kobashi, M; Sanekata, H.; Takata, A.; Yamabe, T.; Mizogami, S.; Kawabata, K.; Yamauchi, J. *J. Appl. Phys.***1992**, *71*, 836. (c) Tanaka, K.; Kobashi, M.; Sanekata, H.; Takata,A.; Yamabe,T.; Mizogami, S.; Kawabata, K.; Yamauchi, J. *Mol. Cryst. Liq. Cryst.* **1992**, *218*, 223. (d) Murata, K.; Ushijima, H.; Ueda, H.; Kawaguchi, K. *J. Chem. Soc., Chem. Commun.* **1992**, 567.

(14) (a) Ueda, K.; Tsuji, M.; Suga, T.; Sugimoto, T.; Kanehisa, N.; Kai, Y.; Hosoito, N. *Chem. Phys. Lett.* **1996**, *253*, 355. (b) Nogami, T.; Tomioka, K.; Ishida, T.; Yoshikawa, H.; Yasui, M.; Iwasaki, F.; Iwamura, H.; Takeda, N.; Ishikawa, M. *Chem. Lett.* **1994**, 29. (c) Ishida, T.; Tsuboi, H.; Nogami, T.; Yoshikawa, H.; Yasui, M.; Iwasaki, F.; Iwamura, H.; Takeda, N.; Ishikawa, M. *Chem. Lett.* **1994**, 919. (d) Sugawara, T.; Matsushita, M. M.; Izuoka, A.; Wada, N.; Takeda, N.; Ishikawa, M. *J. Chem. Soc., Chem. Commun.* **1994**, 1723.

(15) Hoffmann, R. *J. Am. Chem. Soc.* **1968**, *90*, 1475.

(16) References 26−29 of ref 6c above.

(17) Dervan, P. B.; Dougherty, D. A. In *Diradicals*; Borden, W. T., Ed.; Wiley: New York, 1982; p 107.

(18) (a) Ovchinnikov, A. A.; Shamovsky, I. L. *J. Mol. Struct.*: *THEOCHEM* **1991**, *251*, 133. (b) Ovchinnikov, A. A.; Bozhenko, K. V.; Shamovsky, I. L. *J. Mol. Struct.*: *THEOCHEM* **1991**, *251*, 141.

(19) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

(20) MOPAC93, Fujitsu Inc.

(21) (a) Lahti, P. M.; Ichimura, A. S. *J. Org. Chem.* **1991**, *56*, 3030. (b) Yoshioka, N.; Lahti, P. M.; Kaneko, T.; Kuzumaki, Y.; Tsuchida, E.; Nishide, H. *J. Org. Chem.* **1994**, *59*, 4272.

(22) Prasad, B. L. V.; Radhakrishnan, T. P. *J. Mol. Struct.*: *THEOCHEM* **1996**, *361*, 175.

(23) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94, Revision 0.1*, Gaussian Inc.: Pittsburgh, PA, 1995.

(24) Haddon, R. C.; Scott, L T. *Pure Appl. Chem.* **1986**, *58*, 137.

(25) Doubleday, C., Jr.; McIver, J. W.; Page, M. *J. Am. Chem. Soc.* **1982**, *104*, 6533.