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Magnetic Interactions in Alkyl Substituted Cyclohexane Diradical Systems: A Broken Symmetry Approach

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Magnetic interactions in alkyl substituted cyclohexane diradical systems have been investigated within the framework of spin flip density functional theory. The investigations suggest a ferromagnetic interaction for both the alkyl substituted cyclohexane-1,3-diyls and cyclohexane-1,4-diyls. However, in the case of cyclohexane-1,3-diyls, the ferromagnetic interaction is much stronger than its 1,4 analogue. Interestingly, it has been observed that this interaction is reduced to almost half the value from the butyl to the decyl substituted unit relative to the lower homologues up to the propyl substituted unit in cyclohexane-1,3-diyls. On the other hand, in case of alkyl substituted cyclohexane-1,4-diyls, the ferromagnetic interaction for the higher homologues, i.e., butyl to decyl substituted units, substantially reduces to almost 5−6 times the value of its lower homologue (methyl and ethyl substituted unit). In both these cyclohexane diradical systems, beyond butyl substituted unit, a saturation effect in the magnetic coupling constant (J) value is observed. The rapid decrease followed by a saturation in the singlet−triplet gap and J as well may be explained by considering positive inductive effect of the alkyl substituent.

Introduction

A diradical is a molecule with two weakly interacting unpaired electrons centered on different sites within the molecule.[1] Apart from their high reactivity and usual occurrence as intermediates in many organic reactions, diradicals draw substantial degrees of attention owing to their many amazing and versatility features. They served as building blocks for high-spin polyradicals, molecular magnets and plastic magnetic materials.[2−5] In his review article, Rajca[3d] highlighted the spin coupling in various stable diradicals as well as polyradicals, the understanding of which is of great significance in the design of new and novel magnetic materials.[6] Diradicals play a crucial role in biological processes and served as energy-transfer intermediates in the process of photosynthesis. These systems also play a significant role in the field of photochemistry. Adam et al.[7] reported a quantitative study of the trapping of diradicals with oxygen. This oxygen trapping is very important to understand their lifetime properties, which in turn is useful in realizing the two-photon processes that involves the excitation of photochemically generated long-lived diradicals.

A lot of experimental[8−10] as well as ab initio theoretical investigations[11−14] have been performed on various diradical systems. Very recently, Rajca et al.[8] reported the synthesis and magnetic characterization of an aminyl diradical having triplet ground state. This system possesses strong ferromagnetic coupling and provides a pathway for the synthesis of high-spin aminyl polyradicals. Koivisto et al.[9] synthesized the first π-dimer of a verdazyl radical via intramolecular association of two verdazyls connected to a ferrocene moiety. In another work, Adam et al.[10] reported the photochemical generation and unusual persistence of the first hydrocarbon hexaradical containing three localized triplet diradicals connected by a ferromagnetic coupler.

Several theoretical studies have also been carried out on diradicals among which conjugated systems are the ones that gain a lot of importance. In an earlier work, Borden and Davidson[11] provide a vivid description about the spin states of some small cyclic conjugated organic diradicals containing 4π electrons. Later on, Prasad et al.[12] analyzed the nature of the coupling of spins in various conjugated diradicals and studied the effect of the π-electronic framework on spin coupling strength. They[12] also developed a model to predict the singlet−triplet energy gaps using spin densities and the number of electrons involved in coupling pathway.

Recently there has been interest in several radical systems for enhanced nonlinear optical (NLO) properties. Ohta et al.[15] reported the second hyperpolarizabilities for singlet diradicals with two phenalenyl radical rings connected by acetylene and vinylene linkers. They have employed hybrid density functional theory and provide the possibility of a novel control scheme of these response properties for phenalenyl radical systems by adjusting the diradical character and the spin multiplicity. Nakano et al.,[16] in their elegant work highlighted the huge enhancement observed in third order nonlinear properties for symmetric open-shell diradical systems. They also reported that this enhancement is related with ferromagnetic and antiferromagnetic interactions and it opens up a promising new area for designing novel third-order NLO materials. Very recently, Rinkevicius et al.[17] presented response theory based on spin-restricted Kohn−Sham formalism for computing time-dependent and time-independent nonlinear optical properties for high-spin molecules. In another recent work, spin-flip configuration interaction (SF-CI) methods with finite field scheme were employed to calculate static second-order hyperpolarizabilities of various singlet diradical systems.[18]

Although there had been a lot of studies on conjugated organic radicals, investigations on the nonconjugated systems are very few.[13,14] This may be attributed to the following two factors. First is the higher reactivity of these nonconjugated systems relative to their conjugated counterpart, which make them less

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acquiescent to experimental studies. Second is the weaker spin interaction between the radical centers that are separated by saturated carbon atoms in nonconjugated radical systems. However, Chiarelli et al.[19] reported a significant intramolecular spin interactions between the nonconjugated radical sites in Dupeyredioxyl crystals. Nonconjugated radicals are of interest in the "ferrocarbon" model for organic ferromagnets.[20] Spin interactions in some nonconjugated organic di- and multiradical systems using semiempirical quantum chemical methods have also been carried out.[13] Their results indicate a strong dependence of the spin coupling on relative disposition of spin-bearing orbitals. To highlight this dependency, cyclohexane-1,3-diyl was chosen as the model system, which is an interesting prototype for experimental studies. In another work, Datta et al.[14] performed some ab initio calculations on nine organic diradicals to find out their ground state spin multiplicities. One of the diradicals is 2,3-bis(methylene) cyclohexane-1,4-diyl with the cyclohexane framework where the unpaired electrons are located at 1 and 4 positions of cyclohexane ring system.

Although the diradical community is enriched with several high-level investigations based on their reactivity and lifetime and ground state stability (singlet or triplet), the evaluation of magnetic interaction strength is very limited.[21] In the present study, we focus our attention on how the introduction of alkyl groups on the two radical centers in cyclohexane-1,3-diyl and cyclohexane-1,4-diyl affect their magnetic interactions. To find out the strength of magnetic interactions, we have taken up spin flip density functional theory (SF-DFT) as prime investigating tool.

Computational Details

The geometry optimization for all the alkyl substituted cyclohexane diradical systems (with the diradical centers at 1,3 and 1,4 positions) have been carried out using semiempirical (AM1) methods implemented in GAMESS[22] program package at the spin polarized level. As the system size became larger with higher alkyl substituted diradicals, we confined ourselves to the semiempirical level of theory for their optimization.

Evaluation of magnetic coupling constant, J, is one of the ways to measure ferromagnetic or antiferromagnetic interactions in a system. A positive J value indicates a ferromagnetic interaction whereas systems with antiferromagnetic interaction show negative value of J. To calculate the coupling constant, J along with other parameters of interest including those of overlap integral between magnetic orbitals and diradical character, we adopted the spin flip (SF) approach.

The SF technique is a very useful and efficient way for generating the broken symmetry (BS) solution in systems with unpaired electrons. In this approach,[23,24] the spin up (e.g., α) and spin down (e.g., β) densities of a converged high-spin (HS) state are combined to yield total density and spin density matrices. The obtained spin density matrix is then modified by changing the sign of the matrix elements (the α and β spin blocks of densities are exchanged) of any one of the radical centers. Using this modified spin density matrix and the total density matrix obtained, initial guesses for both α and β densities for the BS state are generated. It is also to be noted that Krylov and co-workers[2,25,26] adopted another approach (spin flip time dependent DFT: SF-TDDFT) that is capable of treating multiconfigurational situations without invoking BS solutions. In their[2] SF-TDDFT method, a reference HS state ($M_s = 1$) is taken and the target singlet and triplet states ($M_s = 0$) are then described in terms of the reference HS state and an excitation operator which flips the spin of an electron.

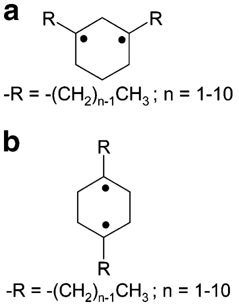

Figure 1. Schematic representation of (a) alkyl substituted cyclohexane-1,3-diyls and (b) alkyl substituted cyclohexane-1,4-diyls.

At this point it is highly instructive to mention that, of the various spin flip methods, we used the methodology adopted by Neese,[23] which is quite similar to that adopted by the group of Ågren.[24] The SF-DFT technique for generating the BS solution is implemented in the ORCA[23] suite of programs. All calculations related to magnetic interaction studies have been performed using the B3LYP[27,28] type hybrid functional with 20% HF exchange and 6-311G**[29] basis set.

Results and Discussion

A schematic representation of the alkyl ($-\mathrm{R} \equiv -(\mathrm{CH}_2)_{n-1}$-$\mathrm{CH}_3$, where $n = 1-10$) substituted cyclohexane-1,3-diyl and cyclohexane-1,4-diyl are given in Figure 1a,b, respectively. The optimized coordinates for each of these systems are given in the Supporting Information.

In general, the exchange coupling constant, J, can well be explained by the famous Heisenberg−Dirac−van Vleck Hamiltonian as

$$\hat{H}_{\mathrm{HDvV}} = -2J\hat{S}_{\mathrm{A}}\hat{S}_{\mathrm{B}} \tag{1}$$

where $\hat{S}_{\mathrm{A}}$ and $\hat{S}_{\mathrm{B}}$ are the spin operators of the two interacting sites A and B, respectively. In the BS formalism, Noodleman et al.[30,31] estimated this coupling constant after obtaining the unrestricted solutions for the determinants of high-spin (HS) ($M_{\mathrm{S}} = S_{\mathrm{A}} + S_{\mathrm{B}}$) and BS spin state ($M_{\mathrm{S}} = |S_{\mathrm{A}} - S_{\mathrm{B}}|$) as

$$J_{\mathrm{NOODLEMAN}} = -\frac{E_{\mathrm{HS}} - E_{\mathrm{BS}}}{{S_{\mathrm{max}}}^2} \tag{2}$$

where E_{HS} and E_{BS} are the energies of the HS and BS spin states, respectively. Noodleman's equation (eq 2) is valid only for the weak coupling region. To solve this problem and to generalize the above equation over the entire coupling regime, Yamaguchi et al.[32,33] obtained the following expression for J.

$$J_{\mathrm{YAMAGUCHI}} = -\frac{E_{\mathrm{HS}} - E_{\mathrm{BS}}}{\langle\hat{S}^2\rangle_{\mathrm{HS}} - \langle\hat{S}^2\rangle_{\mathrm{BS}}} \tag{3}$$

where the spin expectation values for the HS and BS determinants appear in the denominator. The Yamaguchi equation (eq 3) reduces to Noodleman's equation (eq 2) in the weak coupling limit.

In the present investigation, to evaluate the magnetic coupling constant, J, in these alkyl substituted diradical systems, we follow both the above-mentioned formalisms of Noodleman and Yamaguchi via the method of SF-DFT. Figure 2 illustrates the variation of J with the side chain length for alkyl substituted cylcohexane-1,3-diyls. A ferromagnetic (FM) interaction (positive J value) is observed for all these systems; however, the interaction gradually decreases up to the butyl unit ($n = 4$) and

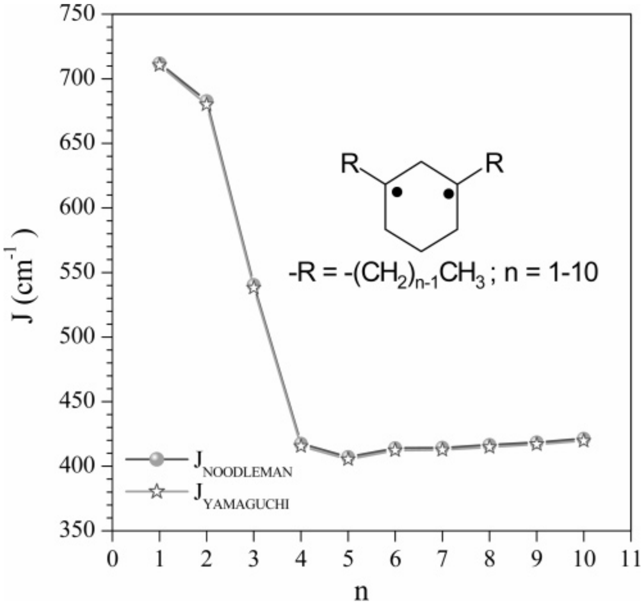

Figure 2. Variation of the magnetic coupling constant, J in both the Noodleman and Yamaguchi formalisms with increasing the side chain length of alkyl substituted cyclohexane-1,3-diyls.

then a saturation in the J value is observed up to the decyl substituted unit. Interestingly, the FM interaction reduces to almost half the value in higher alkyl substituted systems, i.e., from butyl ($n = 4$) to decyl unit ($n = 10$), compared to that of the lower homologues up to propyl unit ($n = 3$). In the case of alkyl substituted cylcohexane-1,3-diyl, both $J_{\mathrm{NOODLEMAN}}$ and $J_{\mathrm{YAMAGUCHI}}$ values are almost same. For the pristine species, i.e., cylcohexane-1,3 diyl (when $-\mathrm{R} \equiv -\mathrm{H}$), the interaction between the spins is ferromagnetic ($J_{\mathrm{NOODLEMAN}} = 414.85$ cm^{-1} and $J_{\mathrm{YAMAGUCHI}} = 407.37$ cm^{-1}) in nature, which was also reported in the literature.[3d,13] This FM coupling of the spins can easily be understood from the spin polarization picture that well describes the nature of spin interactions between the two radical sites in a diradical separated by saturated carbon atoms involving σ electron framework.[13]

Apart from the calculation of J value, several other parameters of interest, including that of the overlap integral, S_{var} ($=\langle\varphi_A|\varphi_B\rangle$), and diradical character, R_{BS}, have also been determined. In general, the BS wavefunction takes the form as shown in[34]

$$|\phi^{\mathrm{BS}}\rangle = |\varphi_A\bar{\varphi}_B| = c_{\mathrm{ion}}|^1\phi^{\mathrm{ion}}\rangle + c_{\mathrm{n}}|^1\phi^{\mathrm{n}}\rangle + c_{\mathrm{T}}|^3\phi^{\mathrm{T}}\rangle \tag{4}$$

with the coefficients

$$c_{\mathrm{ion}} = \frac{S_{\mathrm{var}}}{\sqrt{2}} \qquad c_{\mathrm{n}} = \frac{1}{\sqrt{2}} \qquad c_{\mathrm{T}} = \sqrt{1 - {c_{\mathrm{ion}}}^2 - {c_{\mathrm{n}}}^2} \tag{5}$$

The schematic representations of each of the above-mentioned components of the BS wave function, i.e., $|^1\phi^{\mathrm{ion}}\rangle$, $|^1\phi^{\mathrm{n}}\rangle$ and $|^3\phi^{\mathrm{T}}\rangle$ (right-hand side of eq 4), are represented in Figure 3a,b for cyclohexane-1,3-diyl and cyclohexane-1,4-diyl respectively. The first component $|^1\phi^{\mathrm{ion}}\rangle$ is a superposition of two orbitals where both electrons are centered on one radical site only and it may be considered as negatively charged, and the other site that is electron deficient in nature may be considered as positively charged. This term accounts for the ionic nature of the species considered. Within the BS formalism, the other two components, namely, neutral singlet, $|^1\phi^n\rangle$, and the triplet component, $|^3\phi^{\mathrm{T}}\rangle$, is pure diradical in nature having each of the two electrons located on separate sites but with opposite spins. The difference, however, lies in the fact that $|^1\phi^{\mathrm{n}}\rangle$ is antisymmetric whereas $|^3\phi^{\mathrm{T}}\rangle$ is symmetric with respect to the exchange of the electrons.

TABLE 1: Values of Different Parameters of Interest for Alkyl ($-\mathrm{R} \equiv -(\mathrm{CH_2})_{n-1}\mathrm{CH_3}$, Where $n = 1-10$) Substituted Cyclohexane-1,3-diyls

substituent (−R)	n	S_{var}	c_{ion}^2 (%)	c_{T}^2 (%)	R_{BS} (%)
methyl (−Me)	1	0.02125	0.02	49.98	99.95
ethyl (−Et)	2	0.05043	0.13	49.87	99.74
propyl (−Pr)	3	0.05443	0.15	49.85	99.70
butyl (−Bu)	4	0.05670	0.16	49.84	99.68
pentyl (−Pen)	5	0.05556	0.15	49.84	99.69
hexyl (−Hex)	6	0.05188	0.13	49.86	99.73
heptyl (−Hept)	7	0.05254	0.14	49.86	99.72
octyl (−Oct)	8	0.05352	0.14	49.86	99.71
nonyl (−Non)	9	0.05109	0.13	49.87	99.74
decyl (−Dec)	10	0.04909	0.12	49.88	99.76

TABLE 2: Values of Different Parameters of Interest for Alkyl ($-\mathrm{R} \equiv -(\mathrm{CH_2})_{n-1}\mathrm{CH_3}$, Where $n = 1-10$) Substituted Cyclohexane-1,4-diyls

substituent (−R)	n	S_{var}	c_{ion}^2 (%)	c_{T}^2 (%)	R_{BS} (%)
methyl (−Me)	1	0.06984	0.24	49.76	99.51
ethyl (−Et)	2	0.07056	0.25	49.75	99.50
propyl (−Pr)	3	0.07290	0.26	49.73	99.47
butyl (−Bu)	4	0.06614	0.22	49.78	99.56
pentyl (−Pen)	5	0.06628	0.22	49.78	99.56
hexyl (−Hex)	6	0.06586	0.22	49.78	99.57
heptyl (−Hept)	7	0.06652	0.22	49.78	99.56
octyl (−Oct)	8	0.06555	0.21	49.78	99.57
nonyl (−Non)	9	0.06679	0.22	49.78	99.55
decyl (−Dec)	10	0.06658	0.22	49.78	99.55

The diradical character, R_{BS}, is another important parameter that is defined as

$$R_{\mathrm{BS}} = 100(1 + |S_{\mathrm{var}}|)(1 - |S_{\mathrm{var}}|) \tag{6}$$

It is quite clear from eq 6 that for $S_{\mathrm{var}} = 0$, the percentage of R_{BS} becomes 100% whereas it drops down gradually to zero as the value of the overlap integral increases to one. The role of this overlap integral, S_{var}, is thus of great significance. When it approaches zero, i.e., in the limit of zero interaction, the BS state is found to be an equal mixture of both singlet and triplet states whereas in the strong coupling region, i.e., when S_{var} approaches the value of unity, the BS state represents a pure closed shell state. In an intermediate situation, the BS state is a variationally determined mixture of ionic and neutral contributions and the proportions of the individual contributions are reflected in the value of S_{var}.

The different parameters, viz., S_{var}, c_{ion}^2, c_{T}^2, and R_{BS} of alkyl substituted cyclohexane-1,3-diyls are given in Table 1. The parameters, c_{ion}^2 and c_T^2 gives the percent character of $|^1\phi^{ion}\rangle$ and $|^3\phi^T\rangle$ components respectively of the BS wave function. It is quite clear from Table 1 that as the value of the overlap integral, S_{var} increases, the diradical character, R_{BS} along with the triplet character, c_T^2 decreases with increase in the side chain length. This decrease in R_{BS} values lead to a decrease in the FM interaction and thus can well explain the nature of variation in J values obtained in Figure 2 for the alkyl substituted cyclohexane-1,3-diyls.

Similar kinds of investigations as mentioned above have also been performed for the other diradical systems, alkyl-substituted cyclohexane-1,4-diyls. The variation of J obtained from both Noodleman and Yamaguchi formalisms are plotted with the side chain length of the alkyl groups in Figure 4. Likewise, for cyclohexane-1,3-diyl, here also a ferromagnetic (FM) interaction

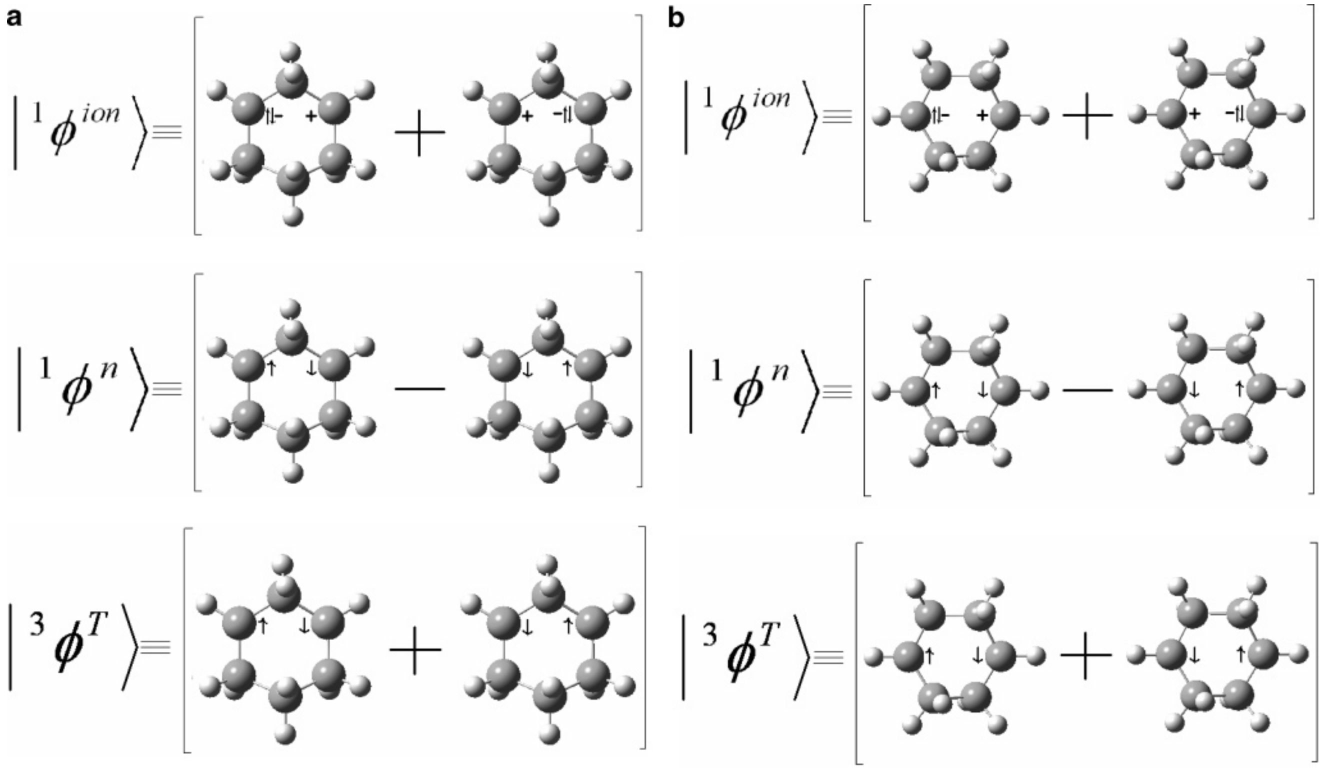

Figure 3. Schematic diagrams of $|{}^1\phi^{\mathrm{ion}}\rangle$, $|{}^1\phi^{\mathrm{n}}\rangle$ and $|{}^3\phi^{\mathrm{T}}\rangle$ components of the magnetic BS wavefunction $|\phi^{\mathrm{BS}}\rangle$ for (a) cyclohexane-1,3-diyl and (b) cyclohexane-1,4-diyl. Large spheres forming the ring represents carbon atoms and the small ones represent hydrogen atoms.

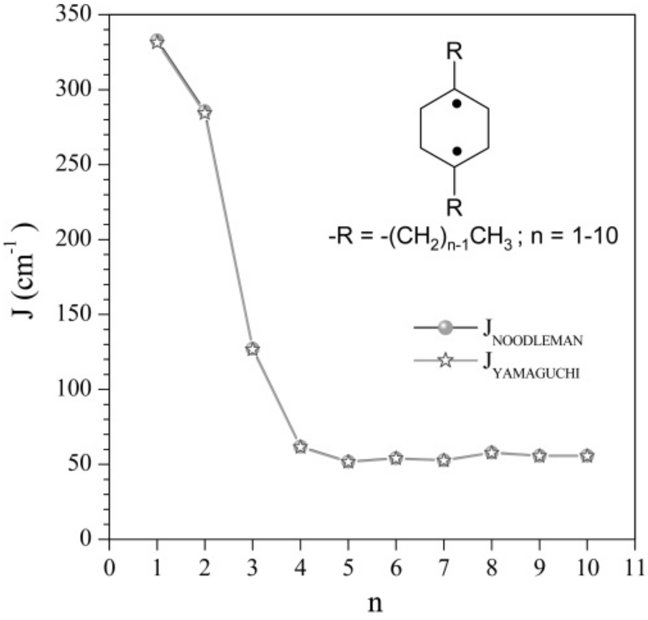

Figure 4. Variation of the magnetic coupling constant, *J* in both the Noodleman and Yamaguchi formalisms with increasing the side chain length of alkyl substituted cyclohexane-1,4-diyls.

TABLE 3: Calculated Singlet−Triplet Gaps for Alkyl ($-\mathrm{R} \equiv -(\mathrm{CH_2})_{n-1}\mathrm{CH_3}$, Where $n = 1-10$) Substituted Cyclohexane-1,3-diyls and Cyclohexane-1,4-diyls

substituent (−R)	*n*	$E_{\mathrm{S-T}}^{\mathrm{cyclohexane-1,3-diyls}}$ (kcal/mol)	$E_{\mathrm{S-T}}^{\mathrm{cyclohexane-1,4-diyls}}$ (kcal/mol)
methyl (−Me)	1	2.0362	0.9524
ethyl (−Et)	2	1.9532	0.8163
propyl (−Pr)	3	1.5450	0.3643
butyl (−Bu)	4	1.1945	0.1776
pentyl (−Pen)	5	1.1645	0.1476
hexyl (−Hex)	6	1.1830	0.1545
heptyl (−Hept)	7	1.1853	0.1499
octyl (−Oct)	8	1.1922	0.1660
nonyl (−Non)	9	1.1968	0.1591
decyl (−Dec)	10	1.2038	0.1591

is observed. The trend observed in the variation of *J* values determined by the above-mentioned formalisms are almost the same as that of cyclohexane-1,3-diyls. However, unlike cyclohexane-1,3-diyls, the ferromagnetic (FM) interaction here reduced appreciably (almost 5−6 times) for higher homologues, i.e., from butyl to decyl substituted unit, compared to that of its lower homologues (methyl and ethyl substituted unit). Beyond butyl units, the effect of side chain length on the change in magnetic coupling constant, *J*, is very small and saturation in the *J* value is observed. For the unsubstituted diradical (when $-\mathrm{R} \equiv -\mathrm{H}$), an FM interaction ($J_{\mathrm{NOODLEMAN}} = 228.37$ cm^{-1} and $J_{\mathrm{YAMAGUCHI}} = 226.70$ cm^{-1}) is observed. At this point, it is highly instructive to mention that the spin polarization picture predicts the unsubsituted cyclohexane-1,4-diyl to be antiferromagnetic (triplet instability) in nature.[13] However, experimental results[35] indicate that cyclohexane-1,4-diyl have triplet stability, i.e., ferromagnetic ground state. The experimental result is well supported by the use of SF-DFT technique in the present investigation.

Table 2 presents the variation of the parameters, i.e., S_{var}, c_{ion}^2, c_{T}^2, and R_{BS}, respectively, with side chain length of alkyl substituted cyclohexane-1,4-diyls. The values indicate that as S_{var} increases, both the diradical character, R_{BS}, and the triplet contribution, c_{T}^2, decrease.

Apart from the calculations of all these above-mentioned parameters, we have also calculated the singlet−triplet gaps for both alkyl substituted cyclohexane diradical systems, i.e., cyclohexane-1,3-diyls and cyclohexane-1,4-diyls. The energy values are determined by taking the difference of BS state and high-spin state, i.e., $E_{\mathrm{S-T}} = E_{\mathrm{BS}} - E_{\mathrm{HS}}$. The singlet−triplet gaps given in Table 3 clearly indicate the stability of the triplet state relative to the singlet for each of these diradicals. A close inspection of Table 3 also reveals the fact that as one approaches higher alkyl substituted system (large n), the singlet−triplet gap at first rapidly decreases and beyond butyl substituted unit, the energy gaps are almost similar irrespective of the length of the side chain; i.e., saturation is observed. It is well-known that alkyl groups/substituents impart positive inductive effect on a system (here on the cyclohexane ring). Usually this effect is more pronounced if the alkyl groups consisting of carbon atoms three or four. The initial rapid decrease in the singlet−triplet energy gap and J value up to $n = 4$ for both the diradical systems is mainly attributed to this inductive effect due to which the triplet state is relatively destabilized. Beyond $n = 4$, however, the inductive effect of the alkyl groups is very negligible and, as a consequence, the singlet−triplet energy gap as well as J values are almost unchanged. Interestingly, the trends observed in the singlet−triplet gaps almost exactly match with the trend observed in the J values given in Figures 2 and 4 for alkyl substituted cyclohexane-1,3-diyls and clyclohexane-1,4-diyls, respectively.

Conclusions

In summary, we have implemented the SF-DFT approach[23] to generate broken symmetry solution and to interpret the nature of magnetic interactions in alkyl substituted cyclohexane diradical systems. Ferromagnetic (FM) interactions are observed for both the alkyl substituted cyclohexane-1,3-diyls and cyclohexane-1,4-diyls. However, the FM interaction observed is much stronger in the case of 1,3-diradicals than for its 1,4 analogue. Interesting is the observation that although the FM interaction, in the case of alkyl substituted cyclohexane-1,3-diyl, is reduced to almost half the value from the butyl up to the decyl unit relative to their lower homologues up to the propyl substituted unit, the interactions for alkyl substituted cylcohexane-1,4-diyls is almost 5−6 times stronger for the lower homologues. Beyond the butyl unit, there is a negligible effect of side chain length on the magnetic interactions for both the alkyl substituted cyclohexane diradical systems and saturation is observed. The rapid change in J and its saturation beyond $n = 4$ may be attributed to positive inductive effect of the alkyl substituent.

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Supporting Information Available: Optimized coordinates of all the alkyl ($-R \equiv -(CH_2)_{n-1}CH_3$, where $n = 1-10$) substituted cyclohexane-1,3-diyls and cyclohexane-1,4-diyls. This material is available free of charge via the Internet at http://pubs.acs.org.

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