Magnetic Coupling in Oxoverdazyl-Benzene-Oxoverdazyl Diradical Systems: A DFT Study

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ABSTRACT

The intramolecular magnetic coupling constant (*J*) values of diradical-based magnet models (**S1-S5**) were studied using unrestricted density functional theory. The model systems were designed with series of oxoverdazyl radicals (**o-Ver(N)** and **o-Ver(C)**) linked through a benzene coupler. They were divided according to either connectivity of the radical (C or N) or geometrical topology (meta- and para-) of benzene coupler. Reasonable relationship was found between spin density distribution and sign of *J* value. With our results we determined ferromagnetic (positive *J* value) and antiferromagnetic (negative *J* value) interactions. *J* values were also calculated along the twisting movement by the scan of dihedral angles between the radical and the coupler. An overall trend was found as absolute value of *J* decreased over increasing torsion angles.

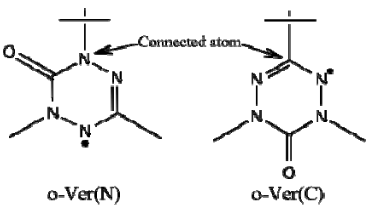
Key Words : *Magnetic Coupling Constant, diradicals, DFT*

Introduction

Organic molecule-based magnets have been under extensive studies due to their interesting possibilities regarding the development of compounds with multiple functions, for example, superconductivity,[1] ferromagnetism,[2] and optical activity.[3] Among many candidates, stable and synthetically affordable diradicals have been studied for spin sources in building blocks of crystalline lattices, as their magnetic properties can readily be tuned either by introducing a variety of couplers that link the spin sources or by adjusting their structural conformations.[4] Thus, for diradical-based magnets, estimating the intramolecular magnetic interactions is a priority task for designing and synthesizing a potential magnetic material that retains an appropriate spin-spin interaction.

A variety of stable neutral radicals have been studied as the unit of spin source in diradicals theoretically[5] and experimentally[6]. Among them, oxoverdazyl is attractive in the research area of molecular magnetism due to outstanding stabilities and simple synthetic method.[7] Interestingly, two types of oxoverdazyl (**o-Ver(C)** and **o-Ver(N)**) can be used as spin source according to their connectivity. As shown in Figure 1, the carbon atom of **o-Ver(C)** and the nitrogen atom of **o-Ver(N)** can be connected to another radical via coupler, respectively. On the other hand, for a benzene-bridged diradicals, it was well known that the geometrical topology (meta- and para-) of the benzene coupler can decide the types of magnetic interactions.

Figure 1. Two types of oxoverdazyl (**o-Ver(N)** and **o-Ver(C)**) spin source.



In this context, the aim of this study is to investigate the correlation of ferro/antiferromagnetism with the topology of a benzene coupler between two oxoverdazyl (**o-Ver(C)** and **o-Ver(N)**) radicals. It is expected that a certain rule might be found depending on the connectivity between two oxoverdazyl radicals and the benzene coupler. Moreover, we intend to examine the effect of dihedral angle on the magnetic interactions in these diradical systems.

Theory and Computational Method

In a system with two magnetic sites 1 and 2, the magnetic exchange interaction is expressed by the phenomenological Heisenberg spin Hamiltonian:

$$\hat{H} = -2J\hat{S}_1\hat{S}_2 \tag{1}$$

where $\hat{S}_1$ and $\hat{S}_2$ are the respective spin angular momentum operators and J is the magnetic exchange coupling constant, as it indicates the magnitude and type of interaction. In such a diradical system, singlet ($S = 0$) and triplet ($S = 1$) states would be eigenstates of the Heisenberg Hamiltonian. J can also be related to the energy difference between the spin eigenstates:

$$E(S = 1) - E(S = 0) = -2J \tag{2}$$

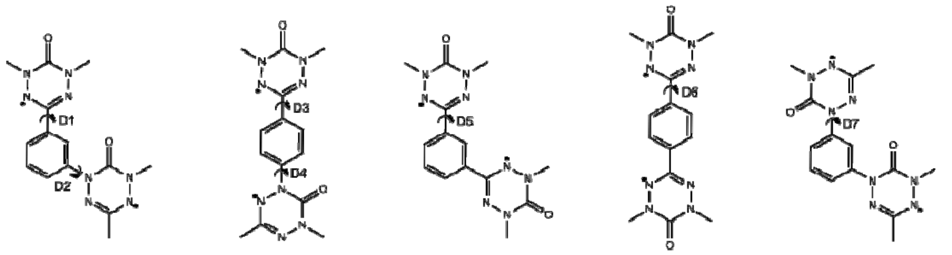
The positive sign of J represents a ferromagnetic interaction, whereas negative sign represents an antiferromagnetic interaction between the two magnetic sites. Unrestricted, pure singlet state cannot be described properly by single determinant wavefunction, and multiconfigurational methods that can describe such pure spin states are computationally expensive. Thus, Noodleman[8] and Ginsberg[9] proposed the broken symmetry formalism to describe the singlet eigenstate. Broken symmetry state is not a pure singlet spin state but is an admixture of triplet and singlet states. Yamaguchi *et al.*[10] [11] proposed the following formalism to obtain the magnetic coupling constant:

$$J = \frac{(E_{BS} - E_T)}{<S^2>_T - <S^2>_{BS}} \tag{3}$$

where E_{BS}, E_T and $<S^2>_{BS}$, $<S^2>_T$ are the energy and spin square values of the BS/triplet spin state, respectively. All calculations were done using suite of Gaussian 09 programs,[12] with unrestricted spin polarized density functional theory, UB3LYP/6-31G(d) level. Keywords "stable=opt" and "guess=mix" were used to stabilize the wave function and to obtain BS solution by generating symmetry broken initial guess. All magnetic coupling constants *J* values were calculated based on fully optimized BS state and triplet state geometries, along with frequency calculations to confirm the minima on the potential energy profiles.

Results and Discussion

Scheme 1. Model systems (**S1**-**S5**) for calculation of intramolecular magnetic interactions.



S1 o-Ver(C)-m-benzene-o-Ver(N) **S2** o-Ver(C)-p-benzene-o-Ver(N) **S3** o-Ver(C)-m-benzene-o-Ver(C) **S4** o-Ver(C)-p-benzene-o-Ver(C) **S5** o-Ver(N)-m-benzene-o-Ver(N)

For our study, five model systems denoted as **S1**-**S5** were designed (**Scheme 1**). In all systems oxoverdazyl (**o-Ver(C)** and **o-Ver(N)**) radical was used as the spin source. Benzene was used as a coupler to provide stable exchange coupling pathway via π-conjugations. **S1** and **S2** both have a **o-Ver(C)** and **o-Ver(N)** diradical pair, but these radicals are in meta- and para- position to each other, respectively. **S3** and **S4** both have two **o-Ver(C)** radicals paired, but are also different in geometrical topology. **S5** has two **o-Ver(N)** radicals paired in meta- position. Dihedral angles between each of oxoverdazyl moieties and benzene coupler are denoted as **D1**-**D7**, respectively. In order to investigate the effect of dihedral angles (**D1**−**D7**) on the magnetic interactions**,** one dihedral angle was fixed when the other was not, and *vice versa*. Methyl groups in oxoverdazyl were substituted with hydrogen to reduce computational cost.

(a) Relationships of magnetic couplings with spin density distribution.

Table 1. Calculated magnetic coupling constants (*J*/cm^{-1}) of model systems.

	S1	**S2**	**S3**	**S4**	**S5**
J value (cm^{-1})	-69.6	185.9	53.0	-92.9	64.3

The calculated magnetic coupling constants (*J* values) of the optimized model systems were listed in **Table 1**. It was predicted that **S2, S3** and **S5** show positive *J* values (ferromagnetic coupling), whereas **S1** and **S4** show negative *J* values (anti-ferromagnetic coupling). For **S3** and **S4**, the predicted types of magnetic coupling are in good agreement with those of experimental *J* values previously obtained by Gilroy *et al.*[13] By comparing the calculated *J* values between **S1** and **S2** as well as between **S3** and **S4**, these results indicate that the geometrical topology (meta- and para-) of benzene coupler can determine ferro/antiferromagnetic interactions for diradicals. On the other hand, for identically substituted diradicals (**S1** and **S3** for meta-substituted position/**S2** and **S4** for para-substituted position), it was found that the combination of radical moieties can also decide the type of magnetic coupling.

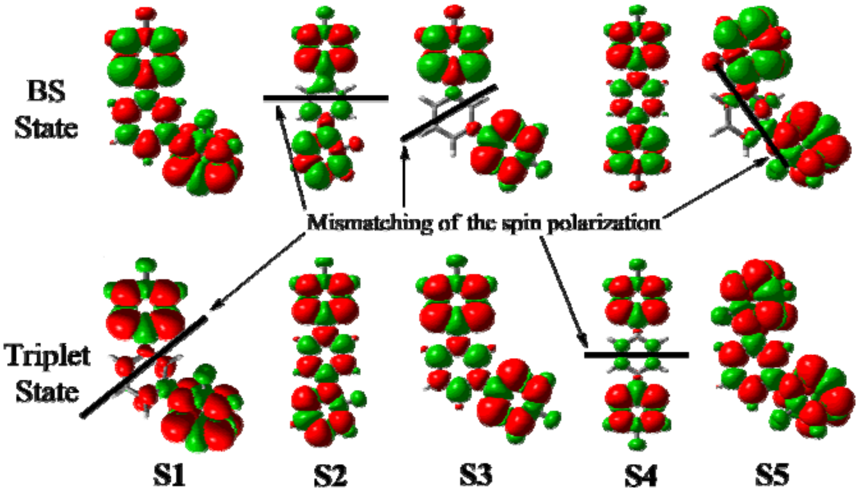


Figure 2. Spin density distribution in triplet and BS spin states of all systems. Red and Green represent positive and negative spin, respectively.

In order to explain the reason of energetically favored spin state of **S1**–**S5**, we investigated the spin density distributions depending on spin states. **Figure 2** shows the spin density distributions in triplet and

BS states of all model systems. Interestingly, it was found that a pattern showing the alternation of positive and negative spins is clearly observed for the energetically favored spin states in each of model systems. On the other hand, for energetically unfavorable spin states, such spin alternation is blocked and a mismatched line is observed. For example, in **S1** ferromagnetic coupling is favored because spin alternation is retained in the BS state.

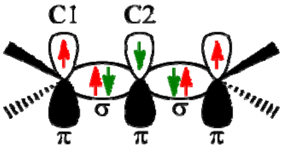


Figure 3. Schematic representation of spin polarization mechanism.

This spin alternation can be explained by the mechanism called spin polarization. As depicted in **Figure 3**, for one carbon atom denoted as **C1** in a π-conjugated system, π and σ electrons will have parallel spin alignment, since parallel spin alignment can be induced by more favorable exchange compared to anti-parallel spin alignment. For paired electrons in the same σ-orbital between two carbon atoms (**C1** and **C2**), both electrons must have opposite spin alignment due to the Pauli's exclusion principle. Thus, for the adjacent carbon atom denoted as **C2**, the π electron of **C2** will then be aligned anti-parallel to the π electron of **C1**. As a result, spin alternation will be observed, as neighboring atoms will have spin anti-parallel to each other. In this aspect, the spin alternation pattern can account for our calculated results regarding the preference for a spin state.

(b) Dihedral angle effect on magnetic coupling interactions.

Figure 4. Calculated J (cm^{-1}) values upon torsion of dihedral angles **D1-D7** (**θ_{fix}**).

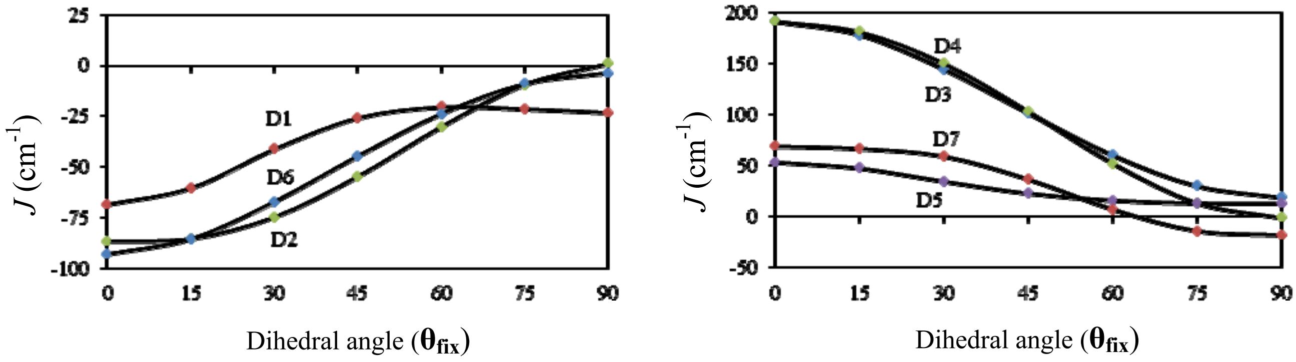


Figure 4 shows the plotted J values following the torsion of dihedral angles **D1-D7**. For **D1–D7**, J is calculated along the twisting movement by the scan of dihedral angles (**θ_{fix}**), from 0 to 90° considering increments of 15° for each diradical. All calculation results in **Figure 4** show that as dihedral angles increases, the absolute value of magnetic coupling constant (J) decreases. (See supporting information for details, **Table S1**) This trend reveals that the torsion of the spin source (oxoverdazyl radicals in this study) out of the molecular plane will weaken magnetic coupling interaction. Moreover, for **D2**, **D4** and **D7**, the spin crossovers are observed upon torsion, even though the absolute J values for the dihedral angle of 90° are very small (0.8 ~ 18.3 cm^{-1}); that is, spin state of the ground state changes when dihedral angles are near 90°.

In this study, we only considered the single molecular unit of diradicals (**S1**−**S5**). However, realistic magnetic systems should be in solid-state structure. Thus, crystallization can constrain geometry due to packing effects, which can severely modify the studied intramolecular magnetic coupling constants (J). In this respect, with the trends of dihedral angle effect found in our study, it is predicted that these diradicals (**D1**−**D7)** might exchange stronger magnetic interactions if more planarity can be forced on the diradical unit as they form lattice in solid state.

Conclusion

Organic, diradical magnets are composed of radical spin sources and coupler. Oxoverdazyl (**o-Ver(N)**, **o-Ver(C)**) radical and benzene were used as the spin source and coupler in our study, respectively. Model systems (**S1-S5**) were designed to analyze magnetic coupling interactions affected by topology of benzene, connectivity of the radical and torsion angle of the spin source. Calculated J values show that the type of magnetic coupling changes depending on meta- or para- positioned relationship between two radicals. And the combination of types of radical moieties also resulted in different spin density distributions. Between triplet and BS spin state, energetically favored spin state was determined based on the spin density distribution of each state. The favored spin state carried good alternation pattern of spins, when the other did not. This spin alternation pattern can be explained by the spin polarization mechanism applied to π-conjugated system. The torsion of spin source out of the molecular plane was found to diminish magnetic coupling interaction, and spin crossovers were found for **D2, D4** and **D7** which are near to 90°. Practical magnetic compounds in solid state will force modifications to the geometry of magnetic molecular unit. Hence, if more planarity of diradicals can be introduced in lattices, they are likely to have stronger magnetic coupling interactions. Therefore, we expect our studies would provide useful understanding in analyzing and designing better candidates for the development of future molecule-based magnets.

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Supporting Information

Table S1. Calculated absolute energies (in Atomic Units, au), $<S^2>$ values, and magnetic coupling constants (J, cm^{-1}) of all dihedral angles (**D1**-**D7**).

θ_{fix}	E_{T} (au)	$<S^2>_{\text{T}}$	E_{BS} (au)	$<S^2>_{\text{BS}}$	J (cm^{-1})	E_{T} (au)	$<S^2>_{\text{T}}$	E_{BS} (au)	$<S^2>_{\text{BS}}$	J (cm^{-1})
	D1					**D5**				
0	-974.2237627	2.044353	-974.2240734	1.049119	-68.5	-974.2356007	2.058492	-974.2353575	1.050279	52.9
15	-974.2235177	2.044025	-974.2237919	1.048761	-60.5	-974.2352535	2.057553	-974.2350376	1.050035	47.0
30	-974.2224260	2.043334	-974.2226134	1.047845	-41.3	-974.2340595	2.055411	-974.2339031	1.049534	34.1
45	-974.2203485	2.042768	-974.2204665	1.046245	-26.0	-974.2319407	2.053219	-974.2318382	1.049111	22.4
60	-974.2177388	2.042539	-974.2178327	1.044238	-20.6	-974.2293454	2.051623	-974.2292742	1.048926	15.6
75	-974.2154907	2.042571	-974.2155891	1.042559	-21.6	-974.2271594	2.050743	-974.2271010	1.048950	12.8
90	-974.2145109	2.042628	-974.2146174	1.041865	-23.4	-974.2263167	2.050475	-974.2262602	1.048997	12.4
	D2					**D6**				
0	-974.2212160	2.043525	-974.2216080	1.049407	-86.5	-974.2359309	2.048435	-974.2363480	1.063210	-92.9
15	-974.2222319	2.043601	-974.2226187	1.049382	-85.4	-974.2355574	2.048277	-974.2359414	1.062007	-85.5
30	-974.2236521	2.044068	-974.2239908	1.049201	-74.7	-974.2343182	2.048047	-974.2346208	1.059120	-67.2
45	-974.2233657	2.044971	-974.2236142	1.048818	-54.8	-974.2321025	2.048104	-974.2323044	1.055876	-44.7
60	-974.2216180	2.046252	-974.2217556	1.048436	-30.3	-974.2294261	2.048522	-974.2295342	1.053189	-23.8
75	-974.2197118	2.047527	-974.2197548	1.048264	-9.4	-974.2271701	2.049062	-974.2272113	1.051486	-9.1
90	-974.2186591	2.048235	-974.2186555	1.048290	0.8	-974.2263285	2.049314	-974.2263457	1.050909	-3.8
	D3					**D7**				
0	-974.2249314	2.052888	-974.2240532	1.042026	190.7	-974.2069283	2.043614	-974.2066146	1.038603	68.5
15	-974.2244916	2.051913	-974.2236741	1.041909	177.6	-974.2077778	2.043533	-974.2074750	1.038743	66.1
30	-974.2230736	2.049638	-974.2224126	1.041733	143.9	-974.2098435	2.043241	-974.2095746	1.038958	58.8
45	-974.2206220	2.047236	-974.2201594	1.041767	101.0	-974.2099745	2.042745	-974.2098087	1.039075	36.3
60	-974.2177212	2.045413	-974.2174482	1.042080	59.7	-974.2085423	2.042261	-974.2085108	1.039303	6.9
75	-974.2153382	2.044360	-974.2152032	1.042503	29.6	-974.2070927	2.041971	-974.2071578	1.039790	-14.3
90	-974.2144277	2.044028	-974.2143437	1.042706	18.4	-974.2065701	2.041873	-974.2066538	1.040360	-18.3
	D4									
0	-974.2249316	2.052888	-974.2240532	1.042026	190.7					
15	-974.2250633	2.052719	-974.2242330	1.042327	180.4					
30	-974.2246063	2.052100	-974.2239196	1.043236	149.4					
45	-974.2226927	2.051034	-974.2222233	1.044744	102.4					
60	-974.2200485	2.049901	-974.2198125	1.046620	51.6					
75	-974.2178495	2.049123	-974.2177907	1.048268	12.9					
90	-974.2170316	2.048870	-974.2170382	1.048926	-1.4					