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Density Functional Theory Based Study of Magnetic Interaction in Bis-Oxoverdazyl Diradicals Connected by Different Aromatic Couplers

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We design and investigate 11 different bis-oxoverdazyl diradicals connected by various aromatic couplers for their magnetic properties. The intramolecular magnetic exchange coupling constants (J) have been calculated using a broken symmetry approach in DFT framework. The J values are explained using spin polarization maps and magnetic orbitals. Isotropic hyperfine coupling constants (hfcc's) have been calculated for all the species in vacuum. The computed hfcc values also support intramolecular magnetic interactions. It has been found that some of the diradicals have ferromagnetic character while the others are antiferromagnetic in nature.

1. Introduction

A global interest has recently emerged in the field of materials science to search for new magnetic materials where a permanent magnetization and magnetic hysterisis can be achieved not through a three-dimensional magnetic ordering but as a purely one-molecule phenomenon. Diverse possibilities for the development of some novel properties such as photomagnetic behavior,[1] superconductivity,[2] spintronic property,[3] and so on make molecular magnetism an interesting field to probe theoretically. Biocompatibility of magnetic materials may lead to several prospective therapeutic applications like in the field of magnetic imaging,[4] in hyperthermic oncology,[5] etc. Stable organic radicals, which can be separated and handled in the pure state, are most suitable for the study of molecular magnetism. The search for ferromagnetic organic systems led to the invention of β-crystal phase *p*-nitrophenyl nitronyl nitroxide by Kinosita and co-workers in 1991.[6] Nitronyl nitroxide diradical with ethylene coupler has been extensively studied by Ziessel et al.,[7] which shows a very high exchange coupling constant. Nitronyl nitroxide based molecular ferromagnets with different π-conjugated couplers were comprehensively studied in DFT framework by Ali and Datta.[8,9] Verdazyl radical was first synthesized by Kuhn and Trischmann in the early 1960s;[10] nevertheless, its potential as a precursor of molecular magnets remained unnoticed for a long time.[11] To design molecular magnets, active verdazyl moiety, which is essentially resonance-stabilized hydrazyl radical, is a viable alternative to nitronyl nitroxide. Non-Kekulé bis-oxoverdazyl diradical remains in *singlet* ground state with a small amount of thermally populated *triplet*.[12] Brook et al.[13] have extensively studied its electronic properties and found strong antiferromagnetic coupling among unpaired spins. It is stable due to its chemical resistance and becomes attractive as a prospective building block for magnetic materials. Azidophenyl-substituded verdazyls have also been prepared by Serwinski et al.[14]

The extent of magnetism in molecular magnets is best represented through intramolecular magnetic exchange coupling constant and found to be dependent on the structure and spin orientation of such systems. Prior knowledge about the magnetic characteristics of designed molecular magnets is useful in the synthesis of such materials. This has been successfully proved in many cases resulting in the discovery of several ferromagnetic molecules.[15] Present theoretical study and computational technique lead us to predict magnetic properties of 11 different bis-oxoverdazyl diradicals connected with different linkage-specific aromatic ring couplers, while some of them are already synthesized.[13]

Normally, the magnetic interaction between two radical centers depends on the distance and the nature of the coupler.[8,9] Verdazyl molecule and its various derivatives have been synthesized by Gilroy et al.;[16] they have found fascinating values of magnetic exchange coupling constant for verdazyl molecules connected with a variety of organic couplers. By applying unrestricted density functional methodology, the intramolecular magnetic exchange coupling constants have been studied for a series of tetrathiafulvalene (TTF) and verdazyl diradical cations bridged with some aromatic and linear π-couplers by Polo et al.[17] Ali and Datta[8] also have investigated bis-nitronyl niroxide diradicals in DFT framework having the same couplers as used by Polo et al.[17] They have found that the magnetic interaction is mainly transmitted via π-conjugation. They have also established that the magnitude of the coupling constant depends strongly on the planarity of the molecular structure, length of the couplers, and spin polarization paths. As a logical consequence, these schemes form the background of our present work. In this work, we have considered two linkage-specific sets, set I and set II of different bis-oxoverdazyl diradical derivatives, and noticed that the magnetic exchange coupling constant enormously depends on the spin polarization path. The couplers (**i**) 2,4-furan, (**ii**) 2,4-pyrrole, (**iii**) 2,4-thiophene, (**iv**) 2,6-pyridine, and (**v**) *m*-phenylene are used in set I. On the other hand, in set II (**vi**) 2,5-furan coupler, (**vii**) 2,5-pyrrole coupler, (**viii**) 2,5-thiophene coupler, (**ix**) 2,5-pyridine coupler, (**x**) *p*-phenylene coupler, and (**xi**) no coupler are used (Figure 1). All the couplers are π-conjugated aromatic molecules.

In this work, the spin-polarized DFT methodology is used to evaluate magnetic exchange coupling constants. The broken-symmetry (BS) approach, described in the next section, has been adopted here to quantify ferromagnetic coupling constants for all the systems described above.

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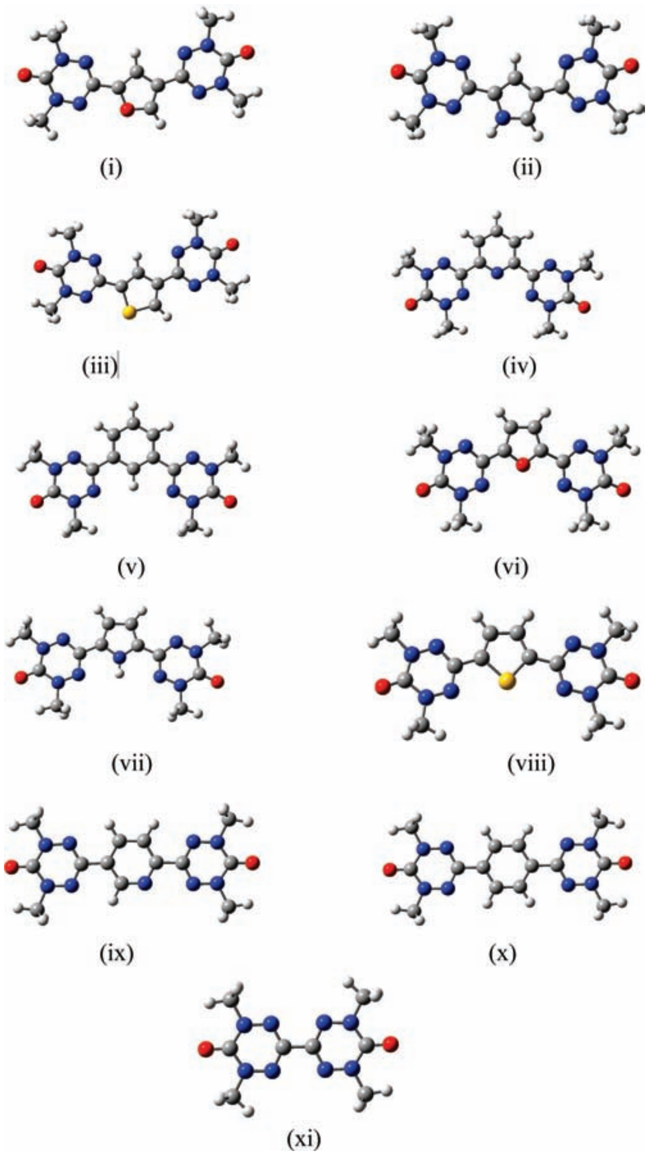

(i) (ii) (iii) (iv) (v) (vi) (vii) (viii) (ix) (x) (xi)

Figure 1. Investigated coupler-added bis-oxoverdazyl diradical sytems **i**−**xi**, where the couplers are (**i**) 2,4-furan coupler, (**ii**) 2,4-pyrrole coupler, (**iii**) 2,4-thiophene coupler, (**iv**) 2,6-pyridine coupler, (**v**) *m*-phenylene coupler, (**vi**) 2,5-furan coupler, (**vii**) 2,5-pyrrole coupler, (**viii**) 2,5-thiophene coupler, (**ix**) 2,5-pyridine coupler, (**x**) *p*-phenylene coupler, and (**xi**) no coupler. Atoms having red, blue, black, yellow, and white colors represent oxygen, nitrogen, carbon, sulfur, and hydrogen, respectively.

2. Theoretical Background

The Heisenberg spin Hamiltonian is normally used to express the magnetic exchange interaction between two magnetic sites 1 and 2

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

where J is the exchange coupling constant between two magnetic centers of a diradical and $\hat{S}_1$ and $\hat{S}_2$ are the respective spin angular momentum operators. The square of the total spin operator $\hat{S}^2$ has eigenvalue $S(S + 1)$ in units of $\hbar^2$. A ferromagnetic interaction is indicated by a positive sign of J in which a situation of parallel spin is essential, whereas the negative value indicates an antiferromagnetic interaction, where a state of antiparellel spin is favored. For a diradical with single unpaired electron on each site, J can be written as

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

The singlet state of a diradical cannot be truly represented by a single determinant (SD) wave function in the unrestricted formalism, and this leads to spin contamination in such calculations. Multiconfigurational methods are useful to describe pure spin states in an appropriate way; however, they are resource intensive and not employed in this work. Broken symmetry formalism proposed by Noodleman[18] in DFT framework is an alternative approach to evaluate J with less computational effort. The BS state is a weighted average of a singlet and a triplet state and not an eigenstate of the Hamiltonian. BS solution is often found to be spin contaminated, and using a spin projection technique a reliable estimate of magnetic exchange coupling constant can be obtained. Depending upon the extent of overlap between magnetic orbitals, different expressions for J have been given by many researchers,[18−26] using unrestricted spin-polarized BS solution for lower spin state. The expression for J given by Ginsberg,[19] Noodleman,[20] and Davidson[21] is more useful when overlap of the magnetic orbitals is very small. The expression given by Bencini and coworkers[22] and Ruiz et al.,[23] which has been further justified by Illas and co-workers[24] and Dual,[25] is applicable when the overlap is sufficiently large. Nevertheless, the expression given by Yamaguchi and co-workers[26] is a balance between above two extremes.

In this work, we have calculated the magnetic exchange coupling constant by using the elegant expression given by Yamaguchi and co-workers[26] which can be reduced to the expressions given for weak[19−21] and strong[22−25] coupling strength. The expression is

$$J = \frac{(E_{\mathrm{BS}} - E_{\mathrm{T}})}{\langle S^2\rangle_{\mathrm{T}} - \langle S^2\rangle_{\mathrm{BS}}} \tag{3}$$

where E_{BS} and E_{T} denote the energy of the broken symmetry singlet and triplet state where as $\langle S^2\rangle_{\mathrm{T}}$ and $\langle S^2\rangle_{\mathrm{BS}}$ represent average spin square values in the triplet and BS state, respectively.

Commonly used DFT exchange correlation potentials yield an overestimation of J values due to the presence of high self-interaction error (SIE). Polo et al. have concluded that the presence of SIE in commoly used functionals in DFT is related to nondynamic correlation energy.[27] Hybrid functionals perform better than pure DFT functionals in BS-UDFT calculations because the former reduce the self-interaction error (SIE) of DFT exchange functionals.[28] In a recent work, Ruiz et al.[29] have shown that B3LYP functionals in the unrestricted framework produce low SIE, and this makes the use of such functionals more suitable when spin-projected techniques are used to evaluate J. In this work the molecular geometries of all the compounds (**i**−**xi**) have been fully optimized with the UB3LYP[30] exchange correlation potential using the 6-311+G(d,p) basis set. To obtain open shell BS singlet solution, the "guess=mix" key word is used within unrestricted formalism. The BS states for all diradicals are stable. The J values for all 11 diradicals have been calculated on the optimized geometry of all the species at the UB3LYP level with 6-311+G(d,p) and 6-311++G(d,p) basis sets. All the calculations have been carried out using the GAUSSIAN 03W[31] quantum chemical package. The visualization software Hyperchem 7.5[32] and Molekel 4.0[33] have also been used.

3. Results and Discussion

Radicals of the verdazyl family are well-known for their stability and ferromagnetic characteristics, which has already

TABLE 1: UB3LYP Level Absolute Energies in au, $\langle S^2 \rangle$, and Intramolecular Magnetic Exchange Coupling Constants (J, cm^{-1}) Using 6-311+G(d,p) and 6-311++G(d,p) Basis Sets, for Bis-Oxoverdazyl Diradicals (i−xi)

diradicals		at the UB3LYP/6-311+G(d,p) level			at the UB3LYP/6-311++G(d,p) level		
		BS	triplet	J (cm^{-1})	BS	triplet	J (cm^{-1})
i	E	−1129.571 69	−1129.571 87	39	−1129.571 90	−1129.572 11	46
	$\langle S^2 \rangle$	1.044	2.051		1.042	2.050	
ii	E	−1109.721 18	−1109.721 35	37	−1109.721 38	−1109.721 45	15
	$\langle S^2 \rangle$	1.043	2.048		1.041	2.043	
iii	E	−1452.556 88	−1452.557 42	117	−1452.557 34	−1452.557 56	48
	$\langle S^2 \rangle$	1.035	2.051		1.039	2.044	
iv	E	−1147.827 54	−1147.827 73	41	−1147.827 70	−1147.827 87	37
	$\langle S^2 \rangle$	1.042	2.048		1.040	2.043	
v	E	−1131.793 27	−1131.793 60	72	−1131.793 63	−1131.793 88	54
	$\langle S^2 \rangle$	1.040	2.049		1.039	2.046	
vi	E	−1129.571 01	−1129.570 72	−64	−1129.571 10	−1129.570 85	−55
	$\langle S^2 \rangle$	1.053	2.043		1.049	2.040	
vii	E	−1109.724 06	−1109.723 79	−60	−1109.724 32	−1109.723 90	−93
	$\langle S^2 \rangle$	1.051	2.043		1.051	2.038	
viii	E	−1452.557 32	−1452.556 93	−86	−1452.557 28	−1452.557 05	−51
	$\langle S^2 \rangle$	1.054	2.044		1.045	2.039	
ix	E	−1147.831 00	−1147.830 70	−66	−1147.831 22	−1147.830 94	−62
	$\langle S^2 \rangle$	1.051	2.042		1.049	2.040	
x	E	−1131.794 40	−1131.794 10	−67	−1131.794 43	−1131.794 31	−26
	$\langle S^2 \rangle$	1.053	2.042		1.042	2.039	
xi	E	−900.671 35	−900.668 65	−579	−900.671 56	−900.668 82	−589
	$\langle S^2 \rangle$	1.010	2.033		1.010	2.031	

been theoretically and magnetically established.[24e,34] The optimized structures of the systems under investigation are planar. As a result, according to the spin polarization rule better spin polarization along the π-conjugated system stabilizes the triplet states.[35] The linker between two same or different organic radicals plays a major role in determining the sign and magnitude of the magnetic exchange coupling constant.[8,9,17] We have estimated the value of J for two sets of compounds; some of them are already known, and the others are newly designed as given in Figure 1. In each set five different linkage-specific aromatic ring couplers connect two oxoverdazyl monomers, hence forming bis-oxoverdazyl diradicals. In addition to five systems with different aromatic couplers, in set II oxoverdazyl diradical with no coupler has also been included. It is established that the unpaired spins are largely delocalized on the four nitrogen atoms of a verdazyl radical.[36] The $\langle S^2 \rangle$ and energy values for both triplet and BS states are obtained by using eq 3. Numerical values of the coupling constant for all 11 species are reported in Table 1.

Normally, the sign and magnitude of J do not largely depend on basis set. The observations made by us that the *m*-phenylene and *p*-phenylene coupled bis-oxoverdazyl diradicles are ferromagnetic and antiferromagnetic, respectively, are in good agreement with the work of Ali and Datta[8] where they have used the same couplers grafted among two nitronyl nitroxide moieties. In our computational results, the J value (Table 1) for direct coupling between two oxoverdazyl units (**xi**) leads to a very strong antiferromagnetic coupling ($J = -589$ cm^{-1}). This result is in good agreement with previous experimental studies made by Brook et al.[13] in frozen chloroform solution where they reported singlet−triplet energy separation J of -760 cm^{-1}; that is, the two radicals are strongly antiferromagnetically coupled.

For a diradical, the spin alternation rule[35] indicates that six-membered aromatic ring couplers result in antiferromagnetic coupling for *o*-phenylene and *p*-phenylene couplers, and a ferromagnetic coupling arises in the case of *m*-phenylene coupler. For five-membered heteronuclear aromatic ring couplers, 2,3 and 3,4 species are treated as *o*-couplers, the 2,5 species as *p*-couplers, and the 2,4 one as *m*-coupler because the heteroatom at 1 provides two π-electrons. The diradicals belonging to set I (*m*-coupled diradicals) yield strong ferromagnetic interaction, whereas set II diradicals (*p*-coupled diradicals) are antiferromagnetic in nature. This trend indicates triplet ground state for set I diradicals and for set II diradicals singlet ground state results. These are also the preferred ground states according to the spin alternation rule.[35] Compounds **v**, **viii**, **x**, and **xi** have been synthesized by Fox and co-workers.[12] They have found from spectral evidence that 36 and 66 nm red shift is observed for diradicals **x** and **viii** correspondingly with respect to the parent compound **xi**, indicating an increase in conjugation. It can also be noticed from their experimental studies that bis-oxoverdazyl diradical **xi** without bearing heavy substituents is planar and exists in a singlet ground state which has also been established by our investigation. In six-membered *m*-coupled diradicals **iv** and **v**, we find **v** has a larger J value (Table 1) as a consequence of increase in aromatic character in the coupler in the latter case.[8] On the other hand, decrease in aromaticity increases antiferromagnetic character (Table 1). Further, in diradical **ix** the presence of pyridyl nitrogen atom instead of phenyl C−H fragment reduces its steric hindrance compared to diradical **x**, and hence the magnitude of J increases.[17]

Spin Density Distribution. The exchange coupling constant is largely dependent on the delocalization of π-electron densities. Hund's rule based spin alternation rule,[35] for a diradical coupled with different aromatic systems, is very helpful to predict the state of magnetism. When the coupling pathway through the coupler propagates through an even number of bonds, ferromagnetism arises, but antiferromagnetism occurs in case of an odd number of bonds. The existence of apparently two different spin polarization paths, presence of heteroatom in the coupling pathway, and nonplanarity of the system make it tricky to predict the magnetic characteristics of molecular systems.[17] However, Ali and Datta demonstrate the spin density alternation in the case of such systems satisfactorily with examples of bis-nitronyl nitroxide diradicals connected by different heterocyclic aromatic couplers. At a first glance, one would think that there is a competition between the two pathways. In reality, the odd route

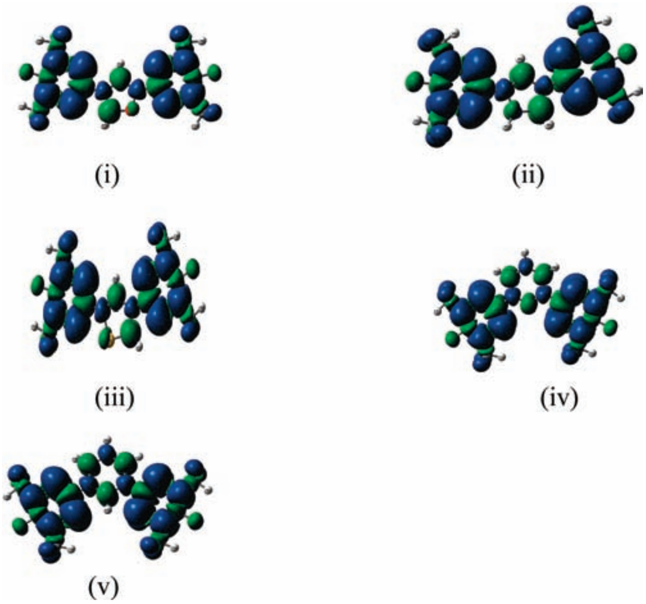

Figure 2. Spin density distribution plots for set I diradicals **i**−**v**; blue color indicates α-spin and green color indicates β-spin. Spin density distribution plots for set II diradicals **vi**−**xi** are given in the Supporting Information (Figure 2A).

SCHEME 1: General Schematic Representation of Diradicals i-xi with Different Couplers, Where There Are Two Unpaired Electrons at N_4 and N_{10} Atoms

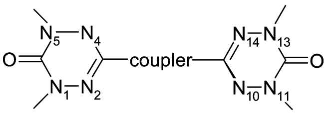

TABLE 2: Energy of SOMOs in au and Their Differences in eV at the UB3LYP Level Using the 6-311+G(d,p) Basis Set for Diradicals i−xi

diradicals	$E_S(1)$, au	$E_S(2)$, au	ΔE_{SS}, eV
i	−0.206 42	−0.204 20	0.0604
ii	−0.204 73	−0.197 05	0.2090
iii	−0.206 20	−0.204 40	0.0490
iv	−0.202 04	−0.200 44	0.0435
v	−0.204 45	−0.202 79	0.0452
vi	−0.204 96	−0.203 43	0.0416
vii	−0.205 36	−0.203 68	0.0457
viii	−0.205 07	−0.203 60	0.0400
ix	−0.209 28	−0.201 62	0.2085
x	−0.204 82	−0.203 35	0.0400
xi	−0.208 66	−0.195 51	0.3578

is supported by the even path through the heteroatom as the latter contributes two π-electrons.[8] The unpaired electron in the verdazyl radical is delocalized over four nitrogen atoms,[36] so the linker carbon atoms with two oxoverdazyl moieties suffer strong spin polarization to make the bonds stronger in nature. Moreover, the linkage position of the π-donar unit to an aromatic ring coupler determines the sign of J. As a result, five- and six-membered aromatic ring coupled para substitution as in set II and meta substitution as found in set I lead to antiferromagnetic and ferromagnetic coupling, respectively. In compound **ix** the C−H fragment is replaced by N-atom, which restores the planarity thus favoring delocalization of π-electrons.[17] The sign of J also largely depends on the number of bonds and nature of atoms in the spin polarization paths through the coupler. In our present work, in set I, diradicals with six-membered aromatic couplers are **iv** and **v** (Figure 1). There are two even (four- and six-bond) coupling pathways through the couplers for above two diradicals; as a result, the J values are positive. The set I diradicals having five-membered heteronuclear aromatic couplers are **iii**, **iv**, and **v**, where there are one even (four-bond) and one odd (five-bond) coupling pathways; nevertheless, all of them are ferromagnetic in nature. The number of bonds in the coupling pathway is even through carbon chain, though with heteroatom it is odd, with the contribution of two π-electrons by the heteroatom (the count increases by one and becomes even); the odd path also supports the spin density alternation rule.[35] As a result we get a positive J value which makes it clear that the path through carbon chain and the alternate route through heteroatom actually complement each other and spin density alternation is followed by both ways (Figure 2). The parent diradical **xi** has C_2 point group symmetry with a nodal plane passing through the linkage bond (Scheme 1) between two monoradicals, so spin distribution is subdued and as a result antiferromagnetism arises.[36] On the other hand, for the systems of set II, the J value is negative which can be easily rationalized by spin density alternation in a similar fashion. In set II diradicals, the magnitude of J values for diradicals **vi**, **vii**, and **viii** (Table 1) are larger than that of diradical **x**, which can be viewed as an extension of the spin alternation rule in the case of heteronuclear aromatic ring couplers.[8]

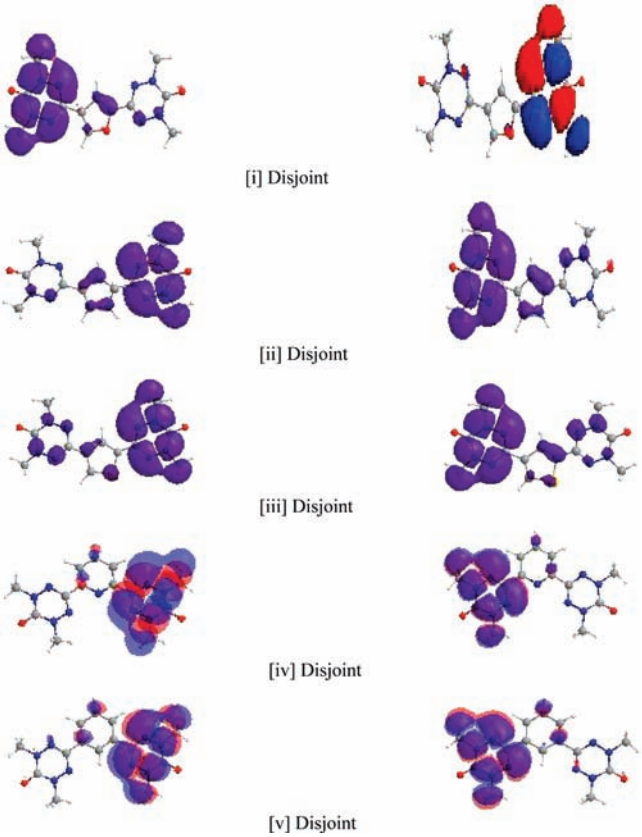

Figure 3. Triplet SOMOs for diradicals **i**−**v**, plotted at the UB3LYP level using the 6-311+G(d,p) basis set. Triplet SOMOs for diradicals **vi**−**xi** are given in the Supporting Information (Figure 3A).

Analysis of Singly Occupied Molecular Orbitals (SOMOs). Based on extended Hückel theory (ETH), that is, all valence-electron independent particle model on benzyne and diradicals, Hoffmann[37] suggested that if the energy difference between two consecutive SOMOs is less than 1.5 eV so as to maximize the electrostatic repulsion between two different degenerate orbitals, then parallel orientation of spins occurs. On the other hand, at the B3LYP level with the 6-31G(d,p) basis set, 4nπ antiaromatic

TABLE 3: Evaluated Hyperfine Coupling Constant (hfcc) in G at the UB3LYP Level Using the EPR-II Basis Set for Diradicals i−xi

diradicals	a_{N1}	a_{N2}	a_{N4}	a_{N5}	a_{N10}	a_{N11}	a_{N13}	a_{N14}
i	1.858 32	2.385 18	2.671 10	1.874 94	2.627 24	1.866 88	1.793 70	2.366 02
ii	1.825 20	2.590 19	2.413 42	1.756 96	2.356 68	1.740 92	1.962 61	2.593 18
iii	1.617 59	2.955 59	2.134 03	1.691 48	2.836 84	1.159 14	1.269 03	2.445 71
iv	1.883 13	2.450 98	2.577 99	1.805 10	2.467 30	1.808 27	1.807 89	2.541 26
v	1.875 46	2.453 33	2.503 91	1.811 05	2.459 41	1.801 40	1.807 58	2.476 63
vi	1.862 01	2.351 11	2.642 72	1.873 90	2.350 61	1.778 35	1.884 44	2.617 20
vii	1.731 90	2.259 68	2.584 98	1.889 05	2.297 39	1.737 34	1.966 81	2.591 63
viii	1.105 44	2.823 10	2.784 63	1.154 23	2.161 39	1.155 35	1.221 48	2.789 33
ix	1.854 34	2.480 57	2.455 45	1.852 64	2.451 97	1.825 53	1.810 63	2.520 09
x	1.838 63	2.499 22	2.509 99	1.828 95	2.509 99	1.828 95	1.838 63	2.499 22
xi	1.923 24	2.420 65	2.461 29	1.842 93	2.461 29	1.842 93	1.923 24	2.420 65

linear and angular polyheteroacenes have been investigated by Constantinides et al.[38] where they found that when $E_{SS} > 1.3$ eV singlet ground state results with antiparellel orientation of spins. Zhang et al.[39] using DFT calculations have shown that critical value of ΔE_{SS} is different in different cases; however, increasing values of ΔE_{SS} indicate spin pairing as evident from compounds **xi** in our present work, where we found the largest ΔE_{SS} values among the 11 diradicals, and consequently singlet ground state with antiferromagnetic character is observed. However, in set I, diradical **ii** has the highest value of ΔE_{SS} (Table 2) with a low J value. For compounds **i**, **iii**, and **v**, the ΔE_{SS} value (Table 2) decreases as the J value increases. The above observations made it clear that our calculation is in good agreement with the Hay−Thibeault−Hoffmann (HTH) formula for the singlet−triplet energy gap[40] in weakly coupled dinuclear metal complexes and as well as the work of Paul and Misra[41] where they have found gradual increase of ΔE_{SS} values with a net effect of decreased magnitudes of ferromagnetic coupling constant through the $Cr_2O_n^-$ cluster series.

The shapes of the SOMOs (Figure 3) play a major role in determining the magnetic properties of the diradicals. In this work, we have found that in set I diradicals, the SOMOs are disjoint (atoms are not common) in nature and accordingly ferromagnetic,[8] set II diradicals are antiferromagnetic, and the SOMOs are mostly nondisjoint (atoms are common).

Isotropic Hyperfine Coupling Constant (hfcc). The interaction between nuclear and electronic magnetic moment is characterized by hfcc. It depends on the spin density of the related nuclei. Due to electron correlation and basis set effects, hfcc's are difficult to calculate. Solvent also plays an effective role in evaluating the hfcc values. In our present work, hfcc's are calculated under the DFT framework by using the EPR-II basis set at the UB3LYP level in vacuum. "S" atoms are not considered in the EPR-II basis set in the quantum chemical package used for computations,[31] so we have used the 6-311+G(d, p) basis set for "S" atom.

Fox and co-workers[12] have shown that if there is an aromatic coupler (Scheme 1) between two monomers, then a red shift is observed compared to that of parent diradical **xi**, suggesting an increase in conjugation. In oxovardazyl monoradical, two sets of two equivalent nitrogen atoms (N_1−N_5 and N_2−N_4) (Scheme 1) are found. Plater et al.[42] have observed that the hfcc for $a(N_2-N_4) = 6.5$ G and $a(N_1-N_5) = 5.3$ G (depending upon the nature of substitution), which is similar to that observed by Neugebauer et al.[43,44] They have also found that larger hfcc values are obtained at N_2, N_4 and N_{10}, N_{14}, which means that the spins are localized along the N=C−N group rather than over the Me−N−CO−N−Me group (Scheme 1). Nitronyl nitroxide diradicals with different couplers[8,9] have been studied, and the hfcc values for conjugated coupler added diradicals reduce to half of the values for corresponding monoradical.

In our present work, we have computed (Table 3) hfcc values for all eight N-atoms present in each bis-oxoverdazyl diradical. We have found that the calculated gas phase hfcc values for N_2−N_4 and N_{10}-N_{14} are larger than those of N_1−N_5 and N_{11}−N_{13}, which are in good agreement with different experimental results.[43,44] However, we cannot get any perfect relationship of hfcc values with magnetic exchange coupling constant.

4. Summary

Oxoverdazyl radicals are promising groups for the development of new molecular materials with magnetic properties due to their better stability than other simpler groups. Bis-oxoverdazyl diradical **xi** is known to be one of the stable organic diradicals due to its chemical resistance but antiferromagnetic species.[12,13] In this work, we have studied intramolecular magnetic exchange coupling constants for two different linkage-specific sets of bis-oxoverdazyl diradicals with different aromatic couplers. The purpose of this investigation lies in the fact that they are straightforward to prepare and are air and moisture stable. All 11 diradicals in two different sets have been optimized at the UB3LYP level, and J values were calculated using the BS approach under the DFT framework. It is found that members of set I diradicals which are essentially *m*-coupled oxoverdazyl diradicals are ferromagnetic with high magnetic exchange coupling constant, whereas the *p*-coupled oxoverdazyl diradicals belonging to set II are antiferromagnetic. As the aromaticity of the spacer increases, the ferromagnetic character also increases and vice versa. These observations strictly follow the spin density alternation rule.[35] Here, we find that the magnetic interactions are primarily transmitted through π-electron conjugation as observed by other authors.[8,9,17] This is justified through MO analysis and spin density alternations as obvious from Figure 2. The shape of SOMOs (Figure 3) also helps to predict the magnetic characteristics of the diradicals.

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Supporting Information Available: Optimized coordinates of all 11 molecules, spin density distribution plots for set II species (Figure 2A), and triplet SOMOs for diradicals of set II (Figure 3A). This information is available free of charge via the Internet at http://pubs.acs.org.

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