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## Chapter 3

### **Magnetism in Bis-Oxoverdazyl Diradicals Coupled with Different Linkage Specific Aromatic Ring Spacers**

*In this chapter the design and investigation of 11 different bis-oxoverdazyl diradicals connected by various aromatic couplers for their magnetic properties are given. The intramolecular magnetic exchange coupling constants ( $J$ ) have been calculated using broken symmetry approach in DFT framework. The  $J$  values are explained using spin polarization maps and magnetic orbitals. Isotropic hyperfine coupling constants (hfccs) 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 these diradicals have ferromagnetic character while the others are antiferromagnetic in nature.*

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### 3.1. Introduction

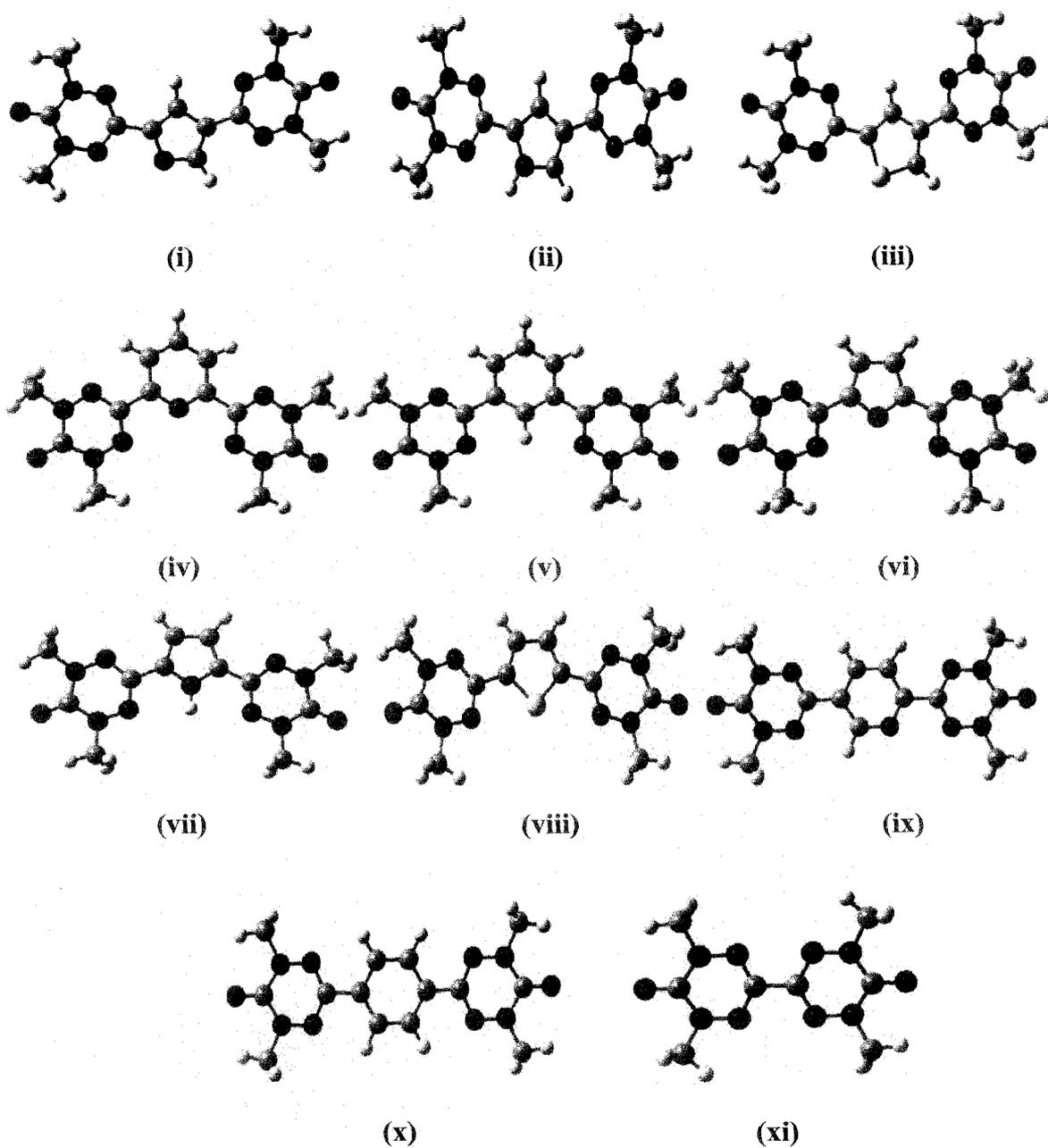
A global interest has recently been emerged in the field of materials science to search for new magnetic materials where a permanent magnetization and magnetic hysteresis can be achieved not through a three dimensional magnetic ordering but as a purely one-molecule phenomenon. Diverse possibilities for the development of some novel properties such as photo-magnetic behavior,<sup>1</sup> superconductivity,<sup>2</sup> spintronic property<sup>3</sup> 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,<sup>4</sup> in hyperthermic oncology<sup>5</sup> etc. Stable organic radicals, which can be separated and handled in pure state, are most suitable for the study of molecular magnetism. The search for ferromagnetic organic systems leads to the invention of  $\beta$ -crystal phase *p*-nitrophenyl nitronyl nitroxide by Kinosita and co-workers in 1991.<sup>6</sup> Nitronyl nitroxide diradical with ethylene coupler has been extensively studied by Ziessel et al.,<sup>7</sup> which shows a very high exchange coupling constant. Nitronyl nitroxide based molecular ferromagnets with different  $\pi$ -conjugated couplers were comprehensively studied in DFT frame work by Ali and Datta.<sup>8,9</sup> Verdazyl radical was first synthesized by Kuhn and Trischmann in early 1960s,<sup>10</sup> nevertheless, its potential as a precursor of molecular magnets remained unnoticed for long.<sup>11</sup> 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*.<sup>12</sup> Brook et al.<sup>13</sup> 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 substituted verdazyls have also been prepared by Serwinski et al.<sup>14</sup>

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.<sup>15</sup> Present theoretical study and computational technique lead us to predict magnetic properties of eleven different bis-oxoverdazyl diradicals connected with different linkage-specific aromatic ring couplers, while some of them are already synthesized.<sup>13</sup>

Normally, the magnetic interaction between two radical centers depends on the distance and the nature of the coupler<sup>8,9</sup>. Verdazyl molecule and its various derivatives have been synthesized by Gilroy et al.,<sup>16</sup> they have found fascinating values of magnetic exchange coupling constant for verdazyl molecules connected with a variety of organic couplers. 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  $\pi$ -couplers by Polo et al.<sup>17</sup> Ali and Datta<sup>8</sup> also have investigated bis-nitronyl nitroxide diradicals in DFT framework having same couplers as used by Polo et al.<sup>17</sup> They have found that the magnetic interaction is mainly transmitted via  $\pi$ -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 this very chapter. In this chapter, 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 3.1). All the couplers are  $\pi$ -conjugated aromatic molecules.

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



**Figure 3.1.** Investigated coupler added bis-oxoverdazyl diradical systems (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, and (x) *p*-phenylene coupler and (xi) no coupler. Atoms having red, blue, black, yellow and white colors represent oxygen, nitrogen, carbon, sulphur and hydrogen respectively.

### 3.2. Theoretical Background

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

$$\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2, \quad (3.1)$$

where  $J$  is the exchange coupling constant between two magnetic centers of a diradical,  $\hat{S}_1$  and  $\hat{S}_2$  are the respective spin angular momentum operators. The square of the total spin operator  $\hat{S}^2$  has eigen value  $S(S+1)$  in unit 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 antiparallel spin is favored. For a diradical with single unpaired electron on each site,  $J$  can be written as

$$E_{(S=1)} - E_{(S=0)} = -2J. \quad (3.2)$$

The singlet state of a diradical can not 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 being employed in this chapter. Broken symmetry formalism proposed by Noodleman<sup>18</sup> 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, using spin projection technique 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,<sup>18-26</sup> using unrestricted spin polarized BS solution for lower spin state. The expression for  $J$  given by Ginsberg,<sup>19</sup> Noodleman,<sup>20</sup> and Davidson<sup>21</sup> is more useful when overlap of the magnetic orbitals is very small. Expression given by Bencini and coworkers,<sup>22</sup>

Ruiz et al.,<sup>23</sup> has been further justified by Illas and coworkers<sup>24</sup> and Dual,<sup>25</sup> is applicable when the overlap is sufficiently large. Nevertheless, expression given by Yamaguchi and coworkers<sup>26</sup> is a balance between above two extremes.

In this chapter, we have calculated magnetic exchange coupling constant by using the elegant expression given by Yamaguchi and coworkers<sup>26</sup> which can be reduced to the expressions given for weak<sup>19-21</sup> and strong<sup>22-25</sup> coupling strength. The expression is

$$J = \frac{(E_{BS} - E_T)}{\langle S^2 \rangle_T - \langle S^2 \rangle_{BS}}, \quad (3.3)$$

where  $E_{BS}$  and  $E_T$  denote the energy of the broken symmetry singlet and triplet state where as  $\langle S^2 \rangle_T$  and  $\langle S^2 \rangle_{BS}$  represent average spin square values in 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 commonly used functionals in DFT is related to nondynamic correlation energy.<sup>27</sup> Hybrid functionals perform better than pure DFT functionals in BS-UDFT calculations because the former reduce the SIE of DFT exchange functionals.<sup>28</sup> In a recent work, Ruiz et al.<sup>29</sup> have shown that B3LYP functionals in the unrestricted framework produces low SIE, this makes the use of such functionals more suitable when spin projected techniques are used to evaluate  $J$ . In this chapter the molecular geometries of all the compounds (i-xi) have been fully optimized with the UB3LYP<sup>30</sup> exchange correlation potential using 6-311+G(d,p) basis set. To obtain open shell BS singlet solution “guess =mix” key word is used within unrestricted formalism. The BS states for all diradicals are stable. The  $J$  values for all eleven 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 GAUSSIAN 03W<sup>31</sup> quantum chemical package. The visualization softwares, Hyperchem 7.5<sup>32</sup> and Molekel 4.0<sup>33</sup> have also been used.

### 3.3. Results and Discussion

Radicals of verdazyl family are well known for their stability and ferromagnetic characteristics which has already been theoretically and magnetically established.<sup>24e,34</sup> The optimized structures of the systems under investigation are planar. As a result, according to spin polarization rule better spin polarization along the  $\pi$ -conjugated system stabilizes the triplet states.<sup>35</sup> The linker between two same or different organic radicals plays a major role in determining the sign and magnitude of magnetic exchange coupling constant.<sup>8,9,17</sup> 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 3.1. 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.<sup>36</sup> The  $\langle S^2 \rangle$  and energy values for both triplet and BS states are obtained by using eq (3.3). Numerical values of the coupling constant for all eleven species are reported in Table 3.1.

Normally, the sign and magnitude of  $J$  does not largely depend on basis set. The observation made by us that the *m*-phenylene and *p*-phenylene coupled bis-oxoverdazyl diradicals are ferromagnetic and antiferromagnetic respectively, are in good agreement with the work of Ali and Datta<sup>8</sup> where they have used the same couplers grafted among two nitronyl nitroxide moieties. In our computational results,  $J$  value (Table 3.1) for direct coupling between two oxoverdazyl units (xi) leads to a very strong antiferromagnetic coupling ( $J = -589 \text{ cm}^{-1}$ ). This result is in good agreement with previous experimental studies made by Brook et al.<sup>13</sup> in frozen chloroform solution where they reported singlet-triplet energy separation  $J$  of  $-760 \text{ cm}^{-1}$ , that is, the two radicals are strongly antiferromagnetically coupled.

For a diradical, spin alternation rule<sup>35</sup> indicates that six membered aromatic ring couplers result antiferromagnetic coupling for *o*-phenylene and *p*-phenylene couplers, and a ferromagnetic coupling arises in case of *m*-phenylene coupler. For five membered

**Table 3.1.** UB3LYP level absolute energies in *au*,  $\langle S^2 \rangle$  and intramolecular magnetic exchange coupling constant ( $J/\text{cm}^{-1}$ ) using 6-311+G(d,p) and 6-311++G(d,p) basis sets, for bis-oxoverdazyl diradicals (i-xi).

		At UB3LYP/6-311+G(d,p) level			At UB3LYP/6-311++G(d,p) level		
Diradicals		BS	Triplet	$J/\text{cm}^{-1}$	BS	Triplet	$J/\text{cm}^{-1}$
(i)	<i>E</i>	-1129.57169	-1129.57187	39	-1129.57190	-1129.57211	46
	$\langle S^2 \rangle$	1.044	2.051		1.042	2.050	
(ii)	<i>E</i>	-1109.72118	-1109.72135	37	-1109.72138	-1109.72145	15
	$\langle S^2 \rangle$	1.043	2.048		1.041	2.043	
(iii)	<i>E</i>	-1452.55688	-1452.55742	117	-1452.55734	-1452.55756	48
	$\langle S^2 \rangle$	1.035	2.051		1.039	2.044	
(iv)	<i>E</i>	-1147.82754	-1147.82773	41	-1147.82770	-1147.82787	37
	$\langle S^2 \rangle$	1.042	2.048		1.040	2.043	
(v)	<i>E</i>	-1131.79327	-1131.79360	72	-1131.79363	-1131.79388	54
	$\langle S^2 \rangle$	1.040	2.049		1.039	2.046	
(vi)	<i>E</i>	-1129.57101	-1129.57072	-64	-1129.57110	-1129.57085	-55
	$\langle S^2 \rangle$	1.053	2.043		1.049	2.040	
(vii)	<i>E</i>	-1109.72406	-1109.72379	-60	-1109.72432	-1109.72390	-93
	$\langle S^2 \rangle$	1.051	2.043		1.051	2.038	
(viii)	<i>E</i>	-1452.55732	-1452.55693	-86	-1452.55728	-1452.55705	-51
	$\langle S^2 \rangle$	1.054	2.044		1.045	2.039	
(ix)	<i>E</i>	-1147.83100	-1147.83070	-66	-1147.83122	-1147.83094	-62
	$\langle S^2 \rangle$	1.051	2.042		1.049	2.040	
(x)	<i>E</i>	-1131.79440	-1131.79410	-67	-1131.79443	-1131.79431	-26
	$\langle S^2 \rangle$	1.053	2.042		1.042	2.039	
(xi)	<i>E</i>	-900.67135	-900.66865	-579	-900.67156	-900.66882	-589
	$\langle S^2 \rangle$	1.010	2.033		1.010	2.031	

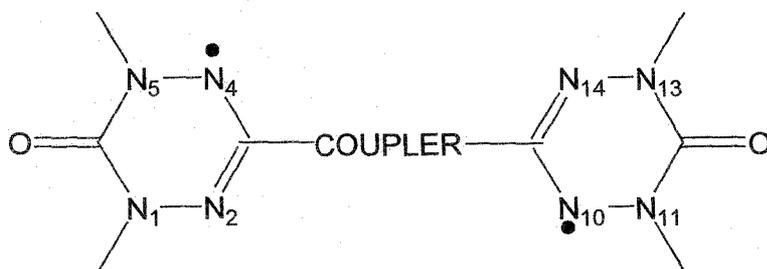
heteronuclear aromatic ring couplers 2,3 and 3,4 species are treated as *o*-couplers, the 2,5 species are *p*-coupler and the 2,4 one as *m*-couplers because the heteroatom at 1 provides two  $\pi$ -electrons. The diradicals belong to Set-I (*m*-coupled diradicals) yield strong ferromagnetic interaction 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 spin alternation rule.<sup>35</sup> Compounds (v), (viii), (x) and (xi) have been synthesized by Fox and co-workers.<sup>12</sup> They have found from spectral evidence that 36nm 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 are planar and exists in a singlet ground state which have also been established by our investigation. In six membered *m*-coupled diradicals (iv) and (v), we find (v) has larger *J* value (Table 3.1) as a consequence of increase in aromatic character in the coupler in the later case.<sup>8</sup> On the other hand, decrease in aromaticity increases antiferromagnetic character (Table 3.1). Further, in diradical (ix) the presence of pyridyl nitrogen atom instead of phenyl C-H fragment reduces its steric hindrance compared to diradical (x), hence the magnitude of *J* increases.<sup>17</sup>

### 3.3.1. Spin Density Distribution

Exchange coupling constant is largely dependent on the delocalization of  $\pi$ -electron densities. Hund's rule based spin alternation rule,<sup>35</sup> for a diradical coupled with different aromatic systems, are very helpful to predict the state of magnetism. When the coupling pathway through the coupler propagates through even number of bonds, ferromagnetism arises, but antiferromagnetism occurs in case of odd number of bonds. The existence of apparently two different spin polarization paths, presence of heteroatom in the coupling pathway and non-planarity of the system makes it tricky to predict the magnetic characteristics of molecular systems.<sup>17</sup> However, Ali and Datta demonstrate the spin density alternation in the case of such systems satisfactorily with examples of bis-

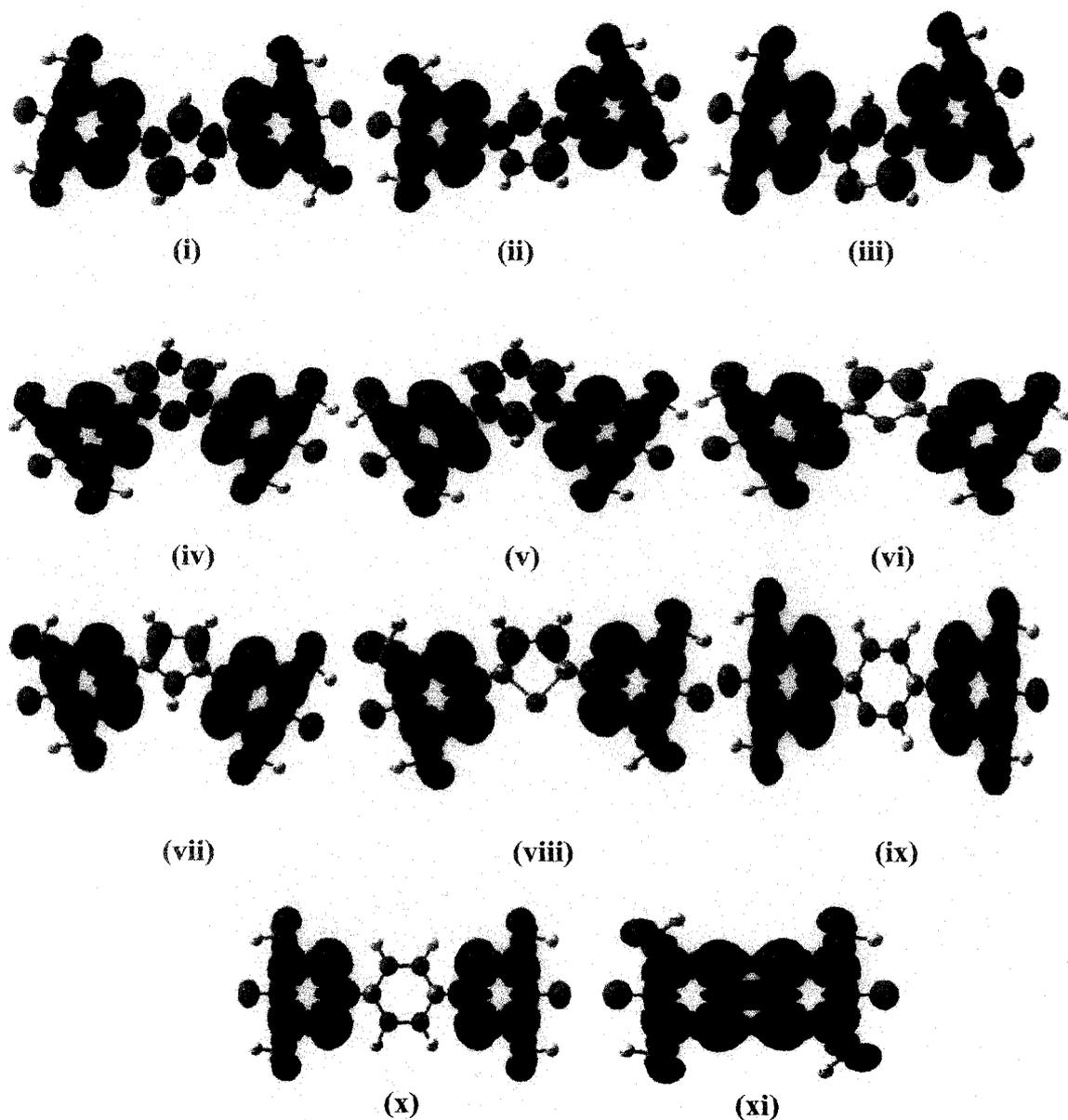
nitronyl nitroxide diradicals connected by different heterocyclic aromatic couplers. At a first glance, one would think that there is a competition between the two pathways. In

**Scheme 3.1.** General schematic representation of diradicals (i-xi) with different couplers, where there are two unpaired electrons at N<sub>4</sub> and N<sub>10</sub> atoms.



reality, the odd route is supported by the even path through the heteroatom as the latter contributes two  $\pi$ -electrons.<sup>8</sup> The unpaired electron in the verdazyl radical is delocalized over four nitrogen atoms,<sup>36</sup> 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  $\pi$ -donor 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, *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  $\pi$ -electrons.<sup>17</sup> 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 this chapter, in Set-I, the diradicals with six membered aromatic couplers are (iv) and (v) (Figure 3.1). 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 hetero atom it is odd, with the contribution of two  $\pi$ -electrons by the heteroatom (the count increases by one and becomes even), the odd path also supports the spin density alternation rule.<sup>35</sup> As a

result we get 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 the ways (Figure 3.2). The parent diradical (xi) has  $C_2$



**Figure 3.2.** Spin density distribution plots for Set-I and Set II diradicals (i–xi), blue color indicates  $\alpha$  spin and green color indicates  $\beta$  spin respectively.

point group with a nodal plane passing through the linkage bond (Scheme 3.1 and Figure 3.1) between the two monoradicals so spin distribution is subdued and as a result antiferromagnetism arises.<sup>36</sup> On the other hand, for the systems of Set -II,  $J$  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), (viii) (Table 3.1) are larger than that of diradical (x) which can be viewed as an extension of spin alternation rule in case of heteronuclear aromatic ring couplers.<sup>8</sup>

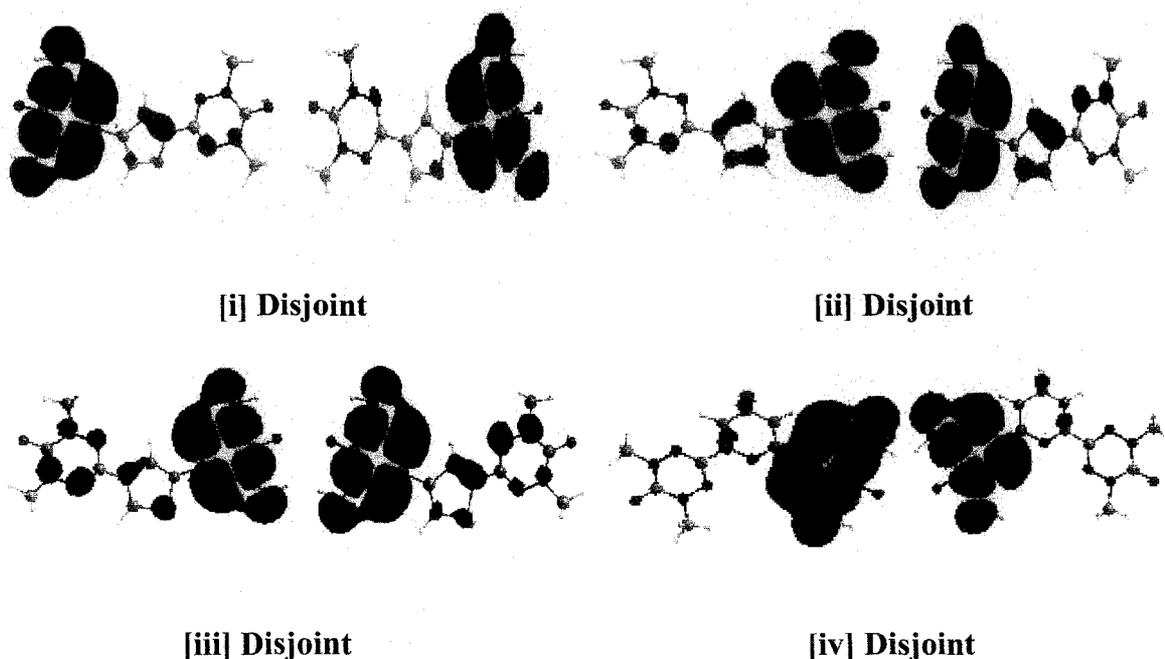
### 3.3.2. Analysis of Singly Occupied Molecular Orbitals (SOMOs)

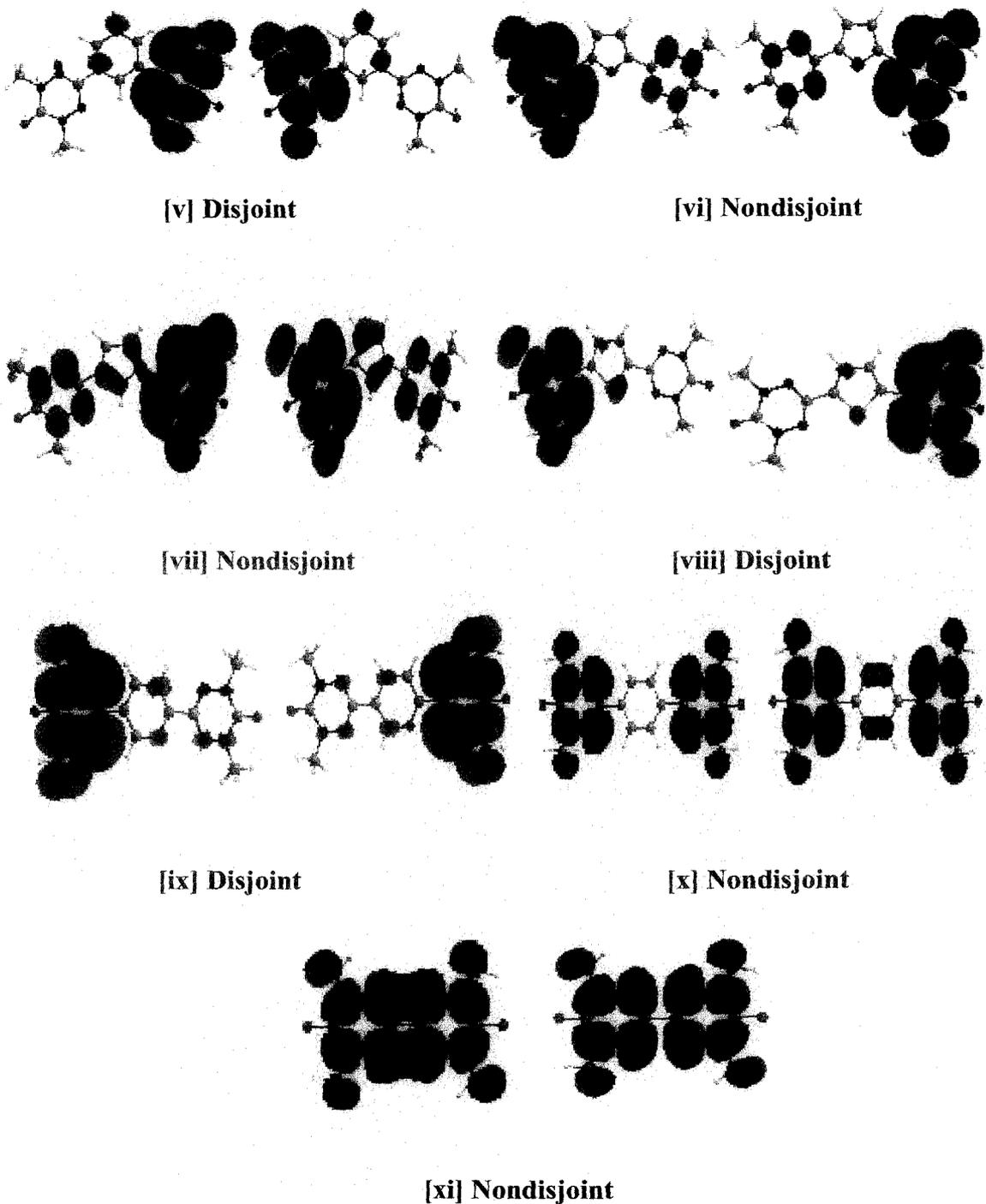
Based on extended Hückel theory (ETH), that is, all valence-electron independent particle model on benzyne and diradicals, Hoffmann<sup>37</sup> suggested that if the energy difference between two consecutive SOMOs is less than 1.5 eV so as to maximize the

**Table 3.2.** The energy of SOMOs in *au* and their differences in *eV* at UB3LYP level using 6-311+G(d, p) basis set for diradicals (i-xi).

Diradicals	$E_s(1)au$	$E_s(2)au$	$\Delta E_{ss}eV$
(i)	-0.20642	-0.20420	0.0604
(ii)	-0.20473	-0.19705	0.2090
(iii)	-0.20620	-0.20440	0.0490
(iv)	-0.20204	-0.20044	0.0435
(v)	-0.20445	-0.20279	0.0452
(vi)	-0.20496	-0.20343	0.0416
(vii)	-0.20536	-0.20368	0.0457
(viii)	-0.20507	-0.20360	0.0400
(ix)	-0.20928	-0.20162	0.2085
(x)	-0.20482	-0.20335	0.0400
(xi)	-0.20866	-0.19551	0.3578

electrostatic repulsion between two different degenerate orbitals, then parallel orientation of spins occurs. On the other hand, at B3LYP level with 6-31G(d,p) basis set,  $4n\pi$  antiaromatic linear and angular polyheteroacenes have been investigated by Constantinides et al.<sup>38</sup> where they found that when  $\Delta E_{SS} > 1.3$  eV singlet ground state results with antiparallel orientation of spins. Zhang et al.<sup>39</sup> using DFT calculations have shown that critical value of  $\Delta E_{SS}$  is different in different cases, however, increasing values of  $\Delta E_{SS}$  indicates spin pairing as evident from compounds (xi) in our present chapter, where we found largest  $\Delta E_{SS}$  values among the eleven diradicals and consequently singlet ground state with antiferromagnetic character is observed. However, in Set-I, diradical (ii) has highest value of  $\Delta E_{SS}$  (Table 3.2) with a low  $J$  value. For compounds (i), (iii) and (v) the  $\Delta E_{SS}$  value (Table 3.2) decreases as  $J$  value increases. The above observations made it clear that our calculation is in good agreement with Hay-Thibeault-Hoffmann (HTH) formula for the singlet-triplet energy gap<sup>40</sup> in weakly coupled dinuclear metal complexes and as well as the work of Paul and Misra<sup>41</sup> where they have found gradual increase of  $\Delta E_{SS}$  values with a net effect of decreased magnitudes of ferromagnetic coupling constant through the  $\text{Cr}_2\text{O}_n$  cluster series.





**Figure 3.3.** Triplet SOMOs for diradicals (i-xi), plotted at UB3LYP level using 6-311+G(d,p) basis set.

The shapes of the SOMOs (Figure 3.3) play a major role in determining the magnetic properties of the diradicals. In this chapter, we have found that in Set-I

diradicals, the SOMOs are disjoint (atoms are not common) in nature and accordingly ferromagnetic.<sup>8</sup> Set-II diradicals are antiferromagnetic, and the SOMOs are mostly nondisjoint (atoms are common).

### 3.3.3. Isotropic Hyperfine Coupling Constants (HFCCs)

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 hfccs are difficult to calculate. Solvent also plays an effective role in evaluating the hfcc values. In this chapter, hfccs are calculated under DFT framework by using EPR-II basis set at UB3LYP level in vacuum. As “S” atoms are not considered in EPR-II basis set in the quantum chemical package used for computations,<sup>31</sup> so we have used 6-311+G(d, p) basis set for “S” atom.

Fox and co-workers<sup>12</sup> have shown that if there is an aromatic coupler (Scheme 3.1) between two monomers then a red shift is observed compared to that of parent diradical ( $\xi$ ), suggesting an increase in conjugation. In oxoverdazyl monoradical, two sets of two equivalent nitrogen atoms ( $N_1-N_5$  and  $N_2-N_4$ ) (Scheme 3.1) are found. Plater et al.<sup>42</sup> have observed that hfcc for  $a(N_2-N_4) = 6.5$  G and  $a(N_1-N_5) = 5.3$  G (depending upon nature of substitution), which are nearly similar to that observed by Neugebauer et al.<sup>43,44</sup> 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 N=C-N group rather than over the Me-N-CO-N-Me group (Scheme 3.1). Nitronyl nitroxide diradical with different couplers<sup>8,9</sup> have been studied and the hfcc values for conjugated coupler added diradicals reduces to half of the values for corresponding monoradical.

In this chapter, we have computed (Table 3.3) the hfcc values for all the 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 that of  $N_1-N_5$  and  $N_{11}-N_{13}$  which are in good agreement with different experimental results.<sup>43,44</sup> However, we can not get any perfect relationship of hfcc values with magnetic exchange coupling constant.

**Table 3.3.** Evaluated hyperfine coupling constants (HFCCs) in *Gauss* at UB3LYP level using 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)	1.85832	2.38518	2.67110	1.87494	2.62724	1.86688	1.79370	2.36602
(ii)	1.82520	2.59019	2.41342	1.75696	2.35668	1.74092	1.96261	2.59318
(iii)	1.61759	2.95559	2.13403	1.69148	2.83684	1.15914	1.26903	2.44571
(iv)	1.88313	2.45098	2.57799	1.80510	2.46730	1.80827	1.80789	2.54126
(v)	1.87546	2.45333	2.50391	1.81105	2.45941	1.80140	1.80758	2.47663
(vi)	1.86201	2.35111	2.64272	1.87390	2.35061	1.77835	1.88444	2.61720
(vii)	1.73190	2.25968	2.58498	1.88905	2.29739	1.73734	1.96681	2.59163
(viii)	1.10544	2.82310	2.78463	1.15423	2.16139	1.15535	1.22148	2.78933
(ix)	1.85434	2.48057	2.45545	1.85264	2.45197	1.82553	1.81063	2.52009
(x)	1.83863	2.49922	2.50999	1.82895	2.50999	1.82895	1.83863	2.49922
(xi)	1.92324	2.42065	2.46129	1.84293	2.46129	1.84293	1.92324	2.42065

### 3.4. Conclusions

Oxoverdazyl radicals are promising groups for the development of new molecular materials with magnetic properties due to its 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.<sup>12,13</sup> In this chapter, 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 straight-forward to prepare and are air and moisture stable. All the eleven diradicals in two different sets have been optimized at UB3LYP level and  $J$  values were calculated using BS approach under 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 belong 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.<sup>35</sup> Here, we find that the magnetic interactions are primarily transmitted through  $\pi$ -electron conjugation as observed by other authors.<sup>8,9,17</sup> This is justified through MO analysis and spin density alternations as obvious from Figure 3.2. The shape of SOMOs (Figure 3.3) also helps to predict the magnetic characteristics of the diradicals.

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### 3.5. References and Notes

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