Very Strongly Ferromagnetically Coupled Diradicals from Mixed Radical Centers: Nitronyl Nitroxide Coupled to Oxoverdazyl via Polyene Spacers

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We predict extremely large and positive intramolecular magnetic exchange coupling constants (J) for coupled diradicals constructed from nitronyl nitroxide (NN) and oxoverdazyl (o-VER). These radicals have the general formula o-VER(N)−nC−NN where nC represents an olefinic spacer with $n = 0, 2, 4, 6$, and 8. Species like o-VER(C)−nC−NN have negative coupling constants. The atoms in the parentheses show the point of attachment of the coupler to the verdazyl moiety. Both the N-linked series and C-linked series have comparable stability. The triplet molecular geometries were optimized by the density functional (UB3LYP) method using the 6-311 g(d,p) basis set. This was followed by single-point UB3LYP calculations using 6-311++g(3df,3pd) basis. To calculate J, single-point broken-symmetry computations were performed on the optimized triplet geometries and using the same basis set. The N-linked diradicals coupled through conjugated polyenes are topologically different. These are found to have coupling constants of the order of 1000 cm^{-1}, whereas the C-linked diradicals show coupling constants of the order of −100 cm^{-1}. In general, for both cases, the absolute magnitude of the coupling constant decreases with the increase in the length of the spacer.

1. Introduction

In search for the organic ferromagnetic materials, diradical species have been extensively investigated during the last 3 decades.[1] The activity has been widely aimed at predicting organic molecules with expected magnetic properties so that it can provoke the actual synthesis of the materials. Intramolecular magnetic exchange coupling constants control the magnetic properties of a molecule. The nature of a molecular crystal, in turn, determines the intermolecular exchange coupling constants,[1a,d] and then can sometimes lead to a ferromagnetic material.

Synthesis and characterization of nitronyl nitroxide[2] and verdazyl[3] have already set the benchmark in the field of molecular magnetism. The stability of these species at a relatively high temperature has made them potential systems for possible application as molecular magnets. A lot of efforts have already been made by many investigators to quantify the magnetic behavior of these two important species.[4−12] Several nitronyl nitroxide (NN)-based diradicals have been experimentally investigated.[13] This is because of their exceptional stability, facile method of preparation, and ability to generate cooperative magnetic properties.[14] The first example of a pure organic ferromagnet is actually based on the β-phase of *p*-nitrophenylnitronyl nitroxide radical.[15] A large variety of imino nitroxides and nitronyl nitroxides have been investigated theoretically.[16] In a recent article, Kiovisto and Hicks have discussed verdazyl (VER)-based molecules and the methods of functionalization of such systems. They also have discussed the suitability of VER-based systems as magnetic building blocks.[17] The first point to consider in designing organic magnets with more than one radical unit connected through spacers is to gain a clear understanding of the intramolecular magnetic exchange coupling constant (J) between the radical fragments prior to their possible use as a novel building blocks in a supramolecular network.[18]

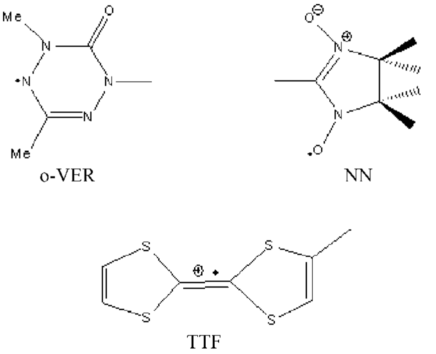

Figure 1. Structures of oxoverdazyl (o-VER), nitronyl nitroxide (NN), and tetrathiafulvalene (TTF) cation from which diradicals have been constructed.

The role of couplers in molecular magnetism is well-known.[19] It has also been noticed that the π-conjugated linear spacers, as couplers, are stronger than the aromatic ones.[7] The magnetic coupling generally arises from spin polarization and spin delocalization.[20] The magnetic interaction between two radical centers normally depends upon the nature and length of the coupler. Ali and Datta have discussed the role of different couplers in nitronyl nitroxide diradicals.[7] Most of the diradicals constructed solely from verdazyl radicals and a suitable spacer are either antiferromagnetically coupled or very weakly ferromagnetically coupled.[3d,e,10,11] The coupling constants of the diradicals constructed solely from nitronyl nitroxide radicals along with polyenic spacers also follow the same trend.[2]

Recently, Polo et al. investigated mixed diradicals constructed from tetrathiafulvalene (TTF) and verdazyl and obtained moderately high positive coupling constants (J, of the order of 167 cm^{-1}) for most of them.[21] This finding stimulated our interest in VER−NN mixed diradicals. The chemical structures of oxoverdazyl (o-VER), TTF, and NN monoradicals are shown in Figure 1.

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The objective of this work is to find molecular magnets with very high ferromagnetic exchange coupling constant. We contend that when VER and VER are magnetically coupled without spacer or with polyenic spacers, the coupling is necessarily antiferromagnetic as per the rule of spin alternation.[22] The same situation arises for NN-diradicals. For the VER and TTF combination, however, spin alternation shows the coupling to be necessarily ferromagnetic. As we show in Figure 2, this will repeat in the case of diradicals formed from VER and NN fragments. The NN fragments are known to couple more strongly than TTF, as the positive charge on the latter tends to reduce the exchange of electrons.

Using density functional treatment (DFT), we show here that diradicals made of VER and NN monoradicals connected through suitable spacers indeed have very high ferromagnetic coupling constants if the oxoverdazyl moieties are linked at the nitrogen atom adjacent to the carbonyl group of it. However, nearly all other verdazyl containing diradicals which have been studied in the context of spin coupling are linked via the substituent at the carbon atom opposite to the carbonyl group of oxoverdazyl. If we consider the C-linkage, the diradicals are found to be antiferromagnetically coupled. This paper is organized as follows: In section 2, we briefly discuss the theory involved. The results are discussed in section 3, and the concluding remarks are given therein.

2. Theoretical Background

The magnetic exchange interaction between two magnetic sites is normally expressed by the Heisenberg effective Hamiltonian

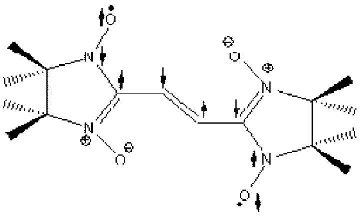
$$\hat{H} = -2J\hat{S}_1 \cdot \hat{S}_2 \tag{1}$$

A positive sign of J indicates a ferromagnetic interaction, whereas the negative sign indicates an antiferromagnetic interaction. The eigenfunctions of the Heisenberg Hamiltonian are eigenfunctions of S^2 and S_z where S is the total spin angular momentum and directly related to the energy difference between the spin eigenstates. For a diradical,

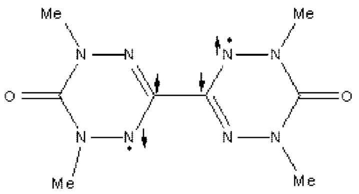
$$E(S = 1) - E(S = 0) = -2J \tag{2}$$

The magnetic exchange coupling constant can be evaluated by determining the proper singlet and triplet energy values from a multiconfigurational approach. Some MCSCF calculations have been done by Chung and Lee on bisverdazyl system.[11] However, those methods are either cumbersome (multiconfigurational) or omit correlation corrections (e.g., CAS [2, 2]). Investigations of small systems would help to calibrate the reliability of any unrestricted density functional work, but it is out of scope of the present study. On the other hand, the single determinantal wave functions give a poor representation of the ground-state singlet and, therefore, cannot give a proper accounting of this exchange.

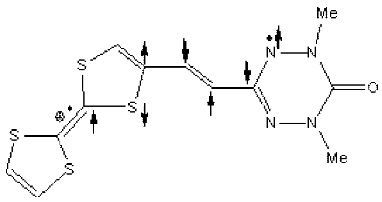
Noodleman proposed an alternative approach to reliably estimate the magnetic exchange coupling constant with less computational effort.[23a,b] In this method, the spin-polarized, unrestricted formalism and a broken-symmetry (BS) solution is needed. The BS state is not an eigenstate of $\hat{H}$. It is an equal mixture of a singlet and a triplet state. The coupling constant can be written as



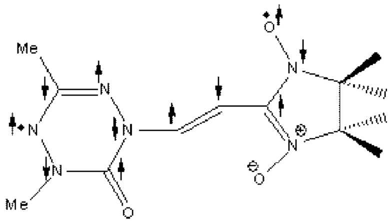
NN-2C-NN
($J_{\text{calc.}} = -350\text{cm}^{-1}$)



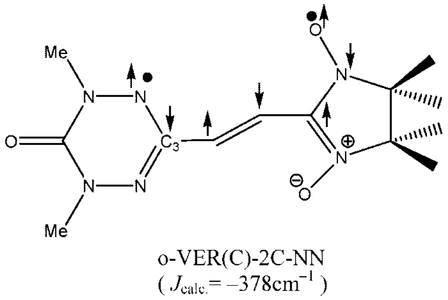
o-VER-oVER
($J_{\text{calc.}} = -600\text{cm}^{-1}$)



TTF-2C-o-VER
($J_{\text{calc.}} = 128\text{cm}^{-1}$)



o-VER(N)-2C-NN
($J_{\text{calc.}} = 1157\text{cm}^{-1}$)



o-VER(C)-2C-NN
($J_{\text{calc.}} = -378\text{cm}^{-1}$)

Figure 2. Scheme of spin alternation for various diradicals and the calculated J values. See refs 7, 10, and 21 for the first three J values. The calculated J values for the fourth and fifth are from this work.

$$J = \frac{(E_{\mathrm{BS}} - E_{\tilde{\mathrm{T}}})}{1 + S_{\mathrm{ab}}{}^2} \qquad (3)$$

where S_{ab} is the overlap integral between the two magnetically active orbitals a and b. The quantity E_{BS} is the energy of the broken-symmetry solution, and $E_{\{\tilde{\mathrm{T}}\}}$ is the energy of triplet state in the unrestricted formalism using the BS orbitals. In a single-determinantal approach, because of the much less spin contamination in the high-spin state, $E_{\{\tilde{\mathrm{T}}\}}$ can be approximated by the energy of the triplet state that is achieved from a direct computation, i.e., $E_{\{\tilde{\mathrm{T}}\}} \approx E_{\mathrm{T}}$. In contrast, the BS state is often found as spin-contaminated. Therefore, to eliminate the effect of spin contamination from the energy of the BS state, spin-projected methods have been applied. Equation 3 is valid when there is only one pair of magnetic orbitals. The following three spin-projected equations are additional results obtained from the same basic methodology and valid for different general cases:

$$J^{\mathrm{GND}} = \frac{({}^{\mathrm{DFT}}E_{\mathrm{BS}} - {}^{\mathrm{DFT}}E_{T})}{S_{\mathrm{max}}{}^2} \qquad (4)$$

$$J^{\mathrm{BR}} = \frac{({}^{\mathrm{DFT}}E_{\mathrm{BS}} - {}^{\mathrm{DFT}}E_{T})}{S_{\mathrm{max}}(S_{\mathrm{max}} + 1)} \qquad (5)$$

$$J^{\mathrm{Y}} = \frac{({}^{\mathrm{DFT}}E_{\mathrm{BS}} - {}^{\mathrm{DFT}}E_{T})}{\langle S^2\rangle_T - \langle S^2\rangle_{\mathrm{BS}}} \qquad (6)$$

Depending on the degrees of overlap between the two magnetic orbitals, these three relations differ in their applicability. Equation 4 has been developed by Ginsberg,[24] Noodleman,[23c,d] and Davidson[25] (GND) and is applied when the overlap of the magnetic orbitals is sufficiently small. Equation 5 has been proposed by Bencini and co-workers[26] and Ruiz et al.[27] Illas and co-workers[28] have justified the application of eq 5 when the overlap integral is sufficiently large, that generally happens for binuclear transition metal complexes. Equation 6, which can be reduced to eqs 4 and 5 in the weak and strong overlap limits, respectively, has been derived by Yamaguchi and co-workers.[29]

The work done by us follows the technique described in refs 10 and 21 very closely and can be said to augment the set of potentially strong coupled open-shell species discussed by Polo et al.[21] Experimental information on our chosen systems is lacking, and the present work has predictive values.

3. Results and Discussion

Borden, Davidson, and Feller[30] discussed that the ROHF calculations provide qualitatively correct molecular orbitals but in general fail to produce the correct molecular geometry. They suggested the use of the UHF methodology for a reasonably correct description of triplet (T, $S = 1$) and open-shell singlet, (S, $S = 0$) geometries. We have used spin-polarized unrestricted density functional theory (DFT), more specifically, the UB3LYP method, for both geometry optimization and single-point calculation on the five VER(N)−NN diradicals and five VER(C)−NN diradicals. The atom in the parentheses indicates the atom of attachment of the spacer with the verdazyl moiety. The diradicals with N-linkage are (i) o-VER(N)−0C−NN, (ii) o-VER(N)−2C−NN (with ethylenic spacers), (iii) o-VER(N)−4C−NN (with butadilinic spacers), (iv) o-VER(N)−6C−NN (with hexatrilinic spacers), (v) o-VER(N)−8C−NN (with octatetrilinic spacers). Similarly, the diradicals with C-linkage are (i) o-VER(C)−0C−NN, (ii) o-VER(C)−2C−NN (with ethylenic spacers), (iii) o-VER(C)−4C−NN (with butadilinic spacers), (iv) o-VER(C)−6C−NN (with hexatrilinic spacers), (v) o-VER(C)−8C−NN (with octatetrilinic spacers). For the triplet geometry optimization we have used the 6-311G(d,p) basis set. The optimized geometries for N-linked diradicals are shown in Figure 3A. The same for C-linked diradicals are given in Figure 3B. For the single-point calculations we have used the 6-311++G(3df,3pd) basis set.

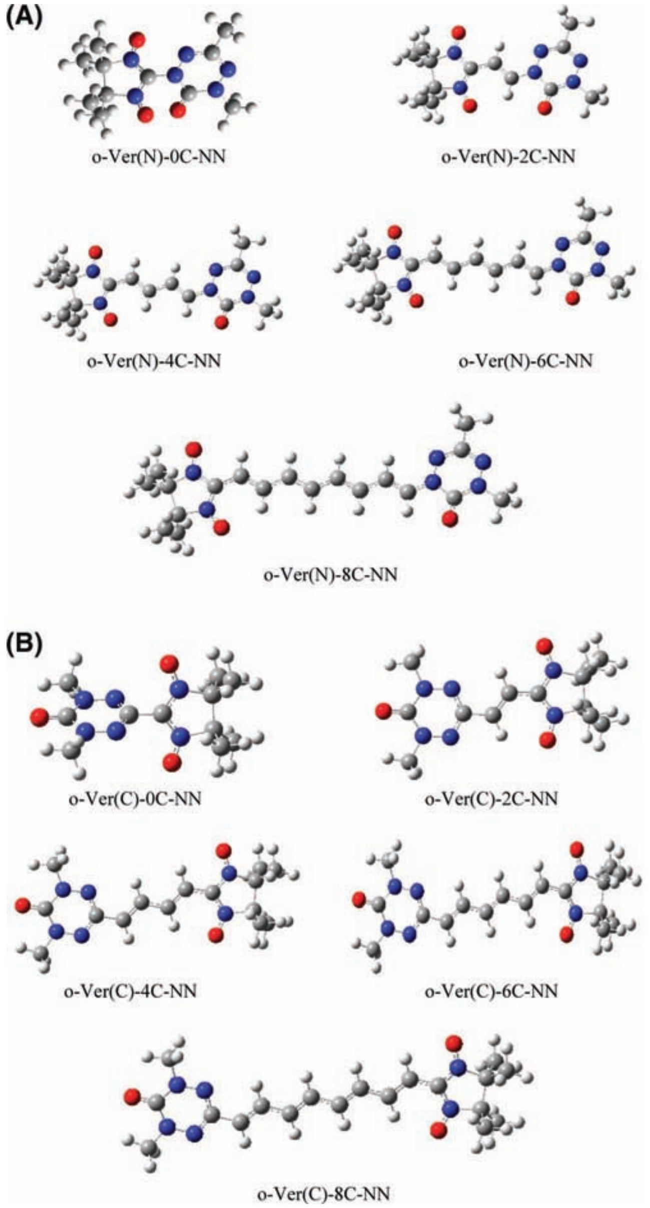


Figure 3. (A) Optimized geometries of oxoverdazyl (N-linked) nitronyl nitroxide diradicals from UB3LYP calculations with the 6-311G(d,p) basis set. (B) Optimized geometries of oxoverdazyl (C-linked) nitronyl nitroxide diradicals from UB3LYP calculations with the 6-311G(d,p) basis set.

For diradicals, the ideal BS state corresponds to $\langle S^2\rangle = 1$. Illas and co-workers found that it is always good to start with correct molecular orbitals for finding the BS solutions.[28] Hence, the symmetry breaking in the wave function in the BS calculations has been achieved by using restricted open-shell wave functions for the optimized triplet structure and then using the corresponding molecular orbitals as an initial guess. All the calculations have been performed by using the Gaussian 03 software.[31]

TABLE 1: Triplet Energy, Dihedral Angles, and $\langle S^2 \rangle$ of Oxoverdazyl(N) and Oxoverdazyl(C) Nitronyl Nitroxide Diradicals from Geometry Optimization UB3LYP Calculations Using the 6-311G(d,p) Basis Set

(a) Oxoverdazyl(N) Nitronyl Nitroxide Diradicals

system	E_T in au($\langle S^2 \rangle$)	dihedral angle (deg)[a]	
		o-VER−coupler	NN−coupler
o-VER(N)−0C−NN	−984.264865 (2.0717)	69.18	69.18
o-VER(N)−2C−NN	−1061.715849 (2.0997)	0.04	0.79
o-VER(N)−4C−NN	−1139.143579 (2.1367)	0.00	0.43
o-VER(N)−6C−NN	−1216.571011 (2.1729)	0.68	0.25
o-VER(N)−8C−NN	−1293.998648 (2.2139)	0.38	0.14

(b) Oxoverdazyl(C) Nitronyl Nitroxide Diradicals

system	E_T in au($\langle S^2 \rangle$)	dihedral angle (deg)[b]	
		o-VER−coupler	NN−coupler
o-VER(C)−0C−NN	−984.265534 (2.0670)	73.34	73.34
o-VER(C)−2C−NN	−1061.707539 (2.0767)	0.42	0.51
o-VER(C)−4C−NN	−1139.135919 (2.0912)	0.48	0.24
o-VER(C)−6C−NN	−1216.563697 (2.1033)	0.28	0.06
o-VER(C)−8C−NN	−1293.991318 (2.1150)	0.09	0.80

[a] This angle is defined with respect to the spacer plane. The dihedral angle for o-VER(N)−0C−NN is the angle between the two ring planes. [b] This angle is defined with respect to the spacer plane. The dihedral angle for o-VER(C)−0C−NN is the angle between the two ring planes.

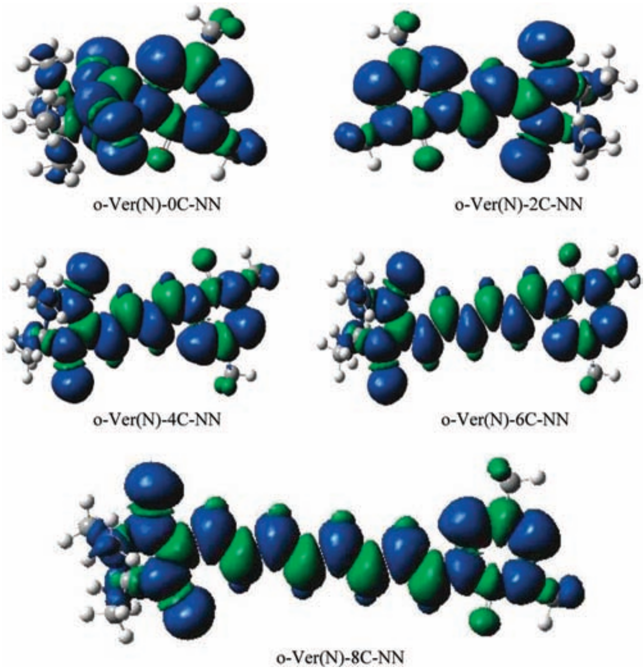


Figure 4. Spin density plot of oxoverdazyl nitronyl nitroxide triplet diradicals.

The optimized triplet energies and the dihedral angles for the N-linkage systems have been given in Table 1a. For the C-linkage systems, similar information is given in Table 1b.

The single-point UB3LYP/6-311++G(3df,3pd) energies of the triplet and broken-symmetry states for the N-linked systems are given in Table 2. The average value of the square of spin angular momentum is ideally 2.0 in the triplet state and 1.0 in the BS state. In actual calculations, however, these ideal values were only approximately obtained, showing a small amount of spin deviation. The computed ($\langle S^2 \rangle_T - \langle S^2 \rangle_{BS}$) values deviate somewhat from unity. Therefore, the coupling constants have been calculated using the Yamaguchi expression, eq 6. The calculated J^Y values are all large and positive. This shows that all the diradicals are strongly ferromagnetically coupled. The diradical which does not contain any coupler shows a much smaller J^Y, about 191 cm^{-1}. There is a noticeable jump of the ferromagnetic coupling constant with the addition of a conjugated spacer. This is attributed to a large dihedral angle (of about 69°) in the absence of a coupler (Table 1a), which is basically a stereoelectronic effect. The olefinic spacers make the diradicals almost planar. The dihedral angles are truly small in each case, less than 1°. The high degree of conjugation facilitates the migration of spin waves, and the J^Y value is of the order of 1000 cm^{-1}. The ethylenic spacer gives a J^Y of 1157 cm^{-1}. The coupling constant progressively decreases as the chain length increases. For the 8C spacer, we find a J^Y value of around 752 cm^{-1} (Table 2). In fact, the J^Y value has been known to similarly decrease in absolute magnitude for nitronyl nitroxide diradicals

TABLE 2: Magnetic Properties of Oxoverdazyl Nitronyl Nitroxide Diradicals from Single-Point UB3LYP Calculations Using the 6-311++G(3df,3pd) Basis Set[a]

system	E_T in au($\langle S^2 \rangle$)	E_{BS} in au ($\langle S^2 \rangle$)	J^Y(cm^{-1})
o-VER(N)−0C−NN	−984.354192 (2.0696)	−984.353319 (1.0681)	191.3
o-VER(N)−2C−NN	−1061.809859 (2.0955)	−1061.804393 (1.0591)	1157.5
o-VER(N)−4C−NN	−1139.244522 (2.1320)	−1139.239765 (1.0665)	980.1
o-VER(N)−6C−NN	−1216.678936 (2.1686)	−1216.674723 (1.0761)	846.3
o-VER(N)−8C−NN	−1294.113272 (2.2029)	−1294.109449 (1.0876)	752.3

[a] We have used 1 au of energy = 27.2114 and 1 eV = 8065.54 cm^{-1}. The BS calculations have been achieved by using ROHF wave functions for the optimized triplet structure and then using the corresponding molecular orbitals as an initial guess.

TABLE 3: Magnetic Properties of Oxoverdazyl C-Linkage Nitronyl Nitroxide Diradicals from Single-Point UB3LYP Calculations Using the 6-311++G(3df,3pd) Basis Set[a]

system	E_T in au($\langle S^2 \rangle$)	E_{BS} in au ($\langle S^2 \rangle$)	J^Y(cm^{-1})
o-VER(C)−0C−NN	−984.355417 (2.0656)	−984.355798 (1.0736)	−84.294
o-VER(C)−2C−NN	−1061.801518 (2.0739)	−1061.803145 (1.1294)	−378.068
o-VER(C)−4C−NN	−1139.236720 (2.0871)	−1139.237929 (1.1463)	−282.042
o-VER(C)−6C−NN	−1216.671309 (2.0986)	−1216.672274 (1.1616)	−226.033
o-VER(C)−8C−NN	−1294.105722 (2.1089)	−1294.106522 (1.1754)	−188.087

[a] The BS calculations have been achieved by using ROHF wave functions for the optimized triplet structure and then using the corresponding molecular orbitals as an initial guess. We have used 1 au of energy = 27.2114 and 1 eV = 8065.54 cm^{-1}.

TABLE 4: Ground-State Energies of Oxoverdazyl Nitronyl Nitroxide Diradicals (N−C Linked and C−C Linked, the Linkage Atom Is Given in Parentheses) from Single-Point UB3LYP Calculations Are Carried Out Using the 6-311++G(3df,3pd) Basis Set

system	E_T in au	system	estimated E_S in au
o-VER(N)−0C−NN	−984.354192	o-VER(C)−0C−NN	−984.355801
o-VER(N)−2C−NN	−1061.809859	o-VER(C)−2C−NN	−1061.803244
o-VER(N)−4C−NN	−1139.244522	o-VER(C)−4C−NN	−1139.238005
o-VER(N)−6C−NN	−1216.678936	o-VER(C)−6C−NN	−1216.672339
o-VER(N)−8C−NN	−1294.113272	o-VER(C)−8C−NN	−1294.106579

as the chain length increases.[7,32] This happens because of a decreasing strength of spin interaction between the monoradical fragments. Nevertheless, even with the 8C spacer, the calculated exchange coupling constant is very high.

The spin density plots for the triplet species are shown in Figure 4. These are manifestly in agreement with the spin alternation rule in UHF,[22] and the triplet state is undoubtedly the ground state for each species.

However, in the case of C-linkage diradicals, calculations show that all the diradicals are strongly antiferromagnetically coupled; see Table 3. This is presumably due to the presence of π^* SOMO's (singly occupied molecular orbital) nodal plane that passes through the C_3 atom of verdazyl group, as discussed by Koivisto and Hicks.[17] As a result, there is no spin delocalization on the C_3 atom. This atom carries only a small amount of negative spin density via spin polarization. However, in the case of N-linked diradicals the linker nitrogen has a large amount of spin density which results in a facile intramolecular ferromagnetic interaction.

We compared the stability of the ground states of the two types of diradicals; see Table 4. All the N-linked diradicals except VER−0C−NN shows greater stability in comparison to C-linked radicals. The discrepancy in stability for VER−0C−NN is due to the large dihedral angles as discussed before.

To conclude, we have examined 10 mixed diradicals that can be prepared from o-VER and NN. These have the general formula o-VER−nC−NN where n varies as $n = 0, 2, 4, 6, 8$. The linkages can be either through the N atom on oxoverdazyl, or through the C atom. The N-linkage species have more or less the same stability as the C-linkage ones. All N-linkage species are very strongly ferromagnetically coupled. For $n = 0$, a sharp deviation from planarity reduces the coupling constant to about 191 cm^{-1}. For the diradicals with spacers, we predict J values of the order of 1000 cm^{-1}. If these diradicals can be properly aligned in a crystal, it would be possible to have very strong ferromagnets of organic origin.

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Supporting Information Available: The optimized geometries and the log files of the optimizations as well as single-point calculations of all the diradicals. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Kahn, O. *Molecular Magnetism*; VCH: New York, 1993. (b) Goodenough, J. B. *Magnetism and the Chemical Bond*; Interscience: New York, 1963. (c) *Molecular Magnetism: From Molecular Assemblies to the Deviceus*; Coronado, E., Delhaè, P., Gatteschi, D., Miller, J. S., Eds.; NATO ASI Series E321; Kluwer Academic Publisher: Dordrecht, The Netherlands, 1996; Vol. 321. (d) Benelli, C.; Gatteschi, D. *Chem. Rev.* **2002**, *102*, 2369.

(2) (a) Awaga, K.; Maruyama, Y. *Chem. Phys. Lett.* **1989**, *158*, 556. (b) Awaga, K.; Maruyama, Y. *J. Chem. Phys.* **1989**, *91*, 2743. (c) Awaga, K.; Inabe, T.; Nagashima, U.; Maruyama, Y. *J. Chem. Soc., Chem. Commn.* **1989**, 1617. (d) Awaga, K.; Inabe, T.; Nagashima, U.; Maruyama, Y. *J. Chem. Soc., Chem. Commun.* **1990**, 520. (e) Turek, P.; Nozawa, K.; Shiomi, D.; Awaga, K.; Inabe, T.; Maruyama, Y.; Kinoshita, M. *Chem. Phys. Lett.* **1991**, *180*, 327. (f) Takahashi, M.; Turek, P.; Nakazawa, Y.; Tamura, M.; Nozawa, K.; Shiomi, D.; Ishikawa, M.; Kinoshita, M. *Phys. Rev. Lett.* **1991**, *67*, 746. (g) Tamura, M.; Nakazawa, Y.; Shiomi, D.; Nozawa, K.; Hosokoshi, Y.; Ishikawa, M.; Takahashi, M.; Kinoshita, M. *Chem. Phys. Lett.* **1991**, *186*, 401. (h) Nakazawa, Y.; Tamura, M.; Shirakawa, N.; Shiomi, D.; Takahashi, M.; Kinoshita, M.; Ishikawa, M. *Phys. Rev. B* **1992**, *46*, 8906.

(3) (a) Kuhn, R.; Trischmann, H. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 155. (b) Neugebauer, F. A.; Fischer, H. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 724. (c) Kopf, P.; Morokuma, K.; Kreilick, R. *J. Chem. Phys.* **1971**, *54*, 105. (d) Gilroy, J. B.; McKinnon, S. D. J.; Kennepohl, P.; Zsombor, M. S.; Ferguson, M. J.; Thompson, L. K.; Hicks, R. G. *J. Org. Chem.* **2007**, *72*, 8062. (e) Azuma, N.; Ishizu, K.; Mukai, K. *J. Chem. Phys.* **1974**, *61*, 2294.

(4) Castell, O.; Caballol, R.; Subra, R.; Grand, A. *J. Phys. Chem.* **1995**, *99*, 154.

(5) Barone, V.; Bencini, A.; di Matteo, A. *J. Am. Chem. Soc.* **1997**, *119*, 10831.

(6) Vyas, S.; Ali, Md. E.; Hossain, E.; Patwardhan, S.; Datta, S. N. *J. Phys. Chem. A* **2005**, *109*, 4213.

(7) Ali, Md. E.; Datta, S. N. *J. Phys. Chem. A* **2006**, *110*, 2776.

(8) Fischer, P. H. H. *Tetrahedron* **1967**, *23*, 1939.

(9) Markovsky, L. N.; Polumbrik, O. M.; Nesterenko, A. M. *Int. J. Quantum Chem.* **1979**, *16*, 891.

(10) Green, M. T.; McCormick, T. A. *Inorg. Chem.* **1999**, *38*, 3061.

(11) Chung, G.; Lee, D. *Chem. Phys. Lett.* **2001**, *350*, 339.

(12) Ciofini, I.; Daul, C. A. *Coord. Chem. Rev.* **2003**, *238*, 187.

(13) (a) Takui, T.; Sato, K.; Shiomi, D.; Ito, K.; Nishizawa, M.; Itoh, K. *Synth. Met.* **1999**, *103*, 2271. (b) Romero, F. M.; Ziessel, R.; Bonnet, M.; Pontillon, Y.; Ressouche, E.; Schweizer, J.; Delley, B.; Grand, A.; Paulsen, C. *J. Am. Chem. Soc.* **2000**, *122*, 1298. (c) Nagashima, H.; Irisawa, M.; Yoshioka, N.; Inoue, H. *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A* **2002**, *376*, 371. (d) Rajadurai, C.; Ivanova, A.; Enkelmann, V.; Baumgarten, M. *J. Org. Chem.* **2003**, *68*, 9907. (e) Wautelet, P.; Le Moigne, J.; Videva, V.; Turek, P. *J. Org. Chem.* **2003**, *68*, 8025. (f) Deumal, M.; Robb, M. A.; Novoa, J. J. *Polyhedron* **2003**, *22* (14−17), 1935.

(14) (a) Ullman, E. F.; Boocock, D. G. B. *J. Chem. Soc., Chem. Commun.* **1969**, *20*, 1161. (b) Ullman, E. F.; Osiecki, J. H.; Boocock, D. G. B.; Darcy, R. *J. Am. Chem. Soc.* **1972**, *94*, 7049.

(15) (a) Tamura, M.; Nakazawa, Y.; Shiomi, D.; Nozawa, K.; Hosokoshi, Y.; Ishikawa, M.; Takahashi, M.; Kinoshita, M. *Chem. Phys. Lett.* **1991**, *186*, 401. (b) Nakazawa, Y.; Tamura, M.; Shirakawa, N.; Shiomi, D.; Takahashi, M.; Kinoshita, M.; Ishikawa, M. *Phys. Rev. B* **1992**, *46*, 8906.

(16) (a) Shiomi, D.; Ito, K.; Nishizawa, M.; Hase, S.; Sato, K.; Takui, T.; Itoh, K. *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A* **1999**, *334*, 99. (b) Romero, F. M.; Ziessel, R.; Bonnet, M.; Pontillon, Y.; Ressouche, E.; Schweizer, J.; Delley, B.; Grand, A.; Paulsen, C. *J. Am. Chem. Soc.* **2000**, *122*, 1298. (c) Rajadurai, C.; Ivanova, A.; Enkelmann, V.; Baumgarten, M. *J. Org. Chem.* **2003**, *68*, 9907. (d) Ziessel, R.; Stroh, C.; Heise, H.; Kohler, F. H.; Turek, P.; Claiser, N.; Souhassou, M.; Lecomte, C. *J. Am. Chem. Soc.* **2004**, *126*, 12604. (e) Takui, T.; Sato, K.; Shiomi, D.; Ito, K.; Nishizawa, M.; Itoh, K. *Synth. Met.* **1999**, *103*, 2271.

(17) Koivisto, B. D.; Hicks, R. G. *Coord. Chem. Rev.* **2005**, *249*, 2612.

(18) Zoppellaro, G.; Ivanova, A.; Enkelmann, V.; Geies, A.; Baumgarten, M. *Polyhedron* **2003**, *22*, 2099.

(19) (a) Lahti, P. M.; Ichimura, A. S. *J. Org. Chem.* **1991**, *56*, 3030. (b) Ling, C.; Minato, M.; Lahti, P. M.; van Willigen, H. *J. Am. Chem. Soc.* **1992**, *114* (4), 9959. (c) Minato, M.; Lahti, P. M. *J. Am. Chem. Soc.* **1997**, *119*, 2187.

(20) Dietz, F.; Tyutyulkov, N. *Chem. Phys.* **2001**, *264*, 37.

(21) Polo, V.; Alberola, A.; Andres, J.; Anthony, J.; Pilkington, M. *Phys. Chem. Chem. Phys.* **2008**, *10*, 857.

(22) (a) Trindle, C.; Datta, S. N. *Int. J. Quantum Chem.* **1996**, *57*, 781. (b) Trindle, C.; Datta, S. N.; Mallik, B. *J. Am. Chem. Soc.* **1997**, *119*, 12947.

(23) (a) Noodleman, L. *J. Chem. Phys.* **1981**, *74*, 5737. (b) Noodleman, L.; Baerends, E. J. *J. Am. Chem. Soc.* **1984**, *106*, 2316. (c) Noodleman, L.;

Davidson, E. R. *Chem. Phys.* **1986**, *109*, 131. (d) Noodleman, L.; Peng, C. Y.; Case, D. A.; Mouesca, J.-M. *Coord. Chem. Rev.* **1995**, *144*, 199.

(24) Ginsberg, A. P. *J. Am. Chem. Soc.* **1980**, *102*, 111.

(25) Noodleman, L.; Davidson, E. R. *Chem. Phys.* **1986**, *109*, 131.

(26) (a) Bencini, A.; Totti, F.; Daul, C. A.; Doclo, K.; Fantucci, P.; Barone, V. *Inorg. Chem.* **1997**, *36*, 5022. (b) Bencini, A.; Gatteschi, D.; Totti, F.; Sanz, D. N.; McClevrty, J. A.; Ward, M. D. *J. Phys. Chem. A* **1998**, *102*, 10545.

(27) Ruiz, E.; Cano, J.; Alvarez, S.; Alemany, P. *J. Comput. Chem.* **1999**, *20*, 1391.

(28) (a) Martin, R. L.; Illas, F. *Phys. Rev. Lett.* **1997**, *79*, 1539. (b) Caballol, R.; Castell, O.; Illas, F.; Moreira, I. de P. R.; Malrieu, J. P. *J. Phys. Chem. A* **1997**, *101*, 7860. (c) Barone, V.; di Matteo, A.; Mele, F.; Moreira, I. de P. R.; Illas, F. *Chem. Phys. Lett.* **1999**, *302*, 240. (d) Illas, F.; Moreira, I. de P. R.; de Graaf, C.; Barone, V. *Theor. Chem. Acc.* **2000**, *104*, 265. (e) de Graaf, C.; Sousa, C.; Moreira, I. de P. R.; Illas, F. *J. Phys. Chem. A* **2001**, *105*, 11371. (f) Illas, F.; Moreira, I. de P. R.; Bofill, J. M.; Filatov, M. *Phys. Rev. B* **2004**, *70*, 132414.

(29) (a) Yamaguchi, K.; Takahara, Y.; Fueno, T.; Nasu, K. *Jpn. J. Appl. Phys* **1987**, *26*, L1362. (b) Yamaguchi, K.; Jensen, F.; Dorigo, A.; Houk, K. N. *Chem. Phys. Lett.* **1988**, *149*, 537. (c) Yamaguchi, K.; Takahara, Y.; Fueno, T.; Houk, K. N. *Theor. Chim. Acta* **1988**, *73*, 337.

(30) (a) Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1977**, *99*, 4587. (b) Borden, W. T.; Davidson, E. R.; Feller, D. *Tetrahedron* **1982**, *38*, 737. (c) Feller, D.; Davidson, E. R.; Borden, W. T. *Isr. J. Chem.* **1983**, *23*, 105. (d) Kato, S.; Morokuma, K.; Feller, D.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1983**, *105*, 1791.

(31) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J. J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian 03, revision C.02; Gaussian, Inc.: Pittsburgh, PA, 2004.

(32) (a) Ali, Md. E.; Datta, S. N. *J. Phys. Chem. A* **2006**, *110*, 2776. (b) Ali, Md. E.; Datta, S. N. *J. Phys. Chem. A* **2006**, *110*, 13232.

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