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Theoretical Investigation of Intramolecular Magnetic Interaction through an Ethylenic Coupler

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We show that an ethylenic coupler provides a very strong intramolecular magnetic interaction. A recently synthesized nitronyl nitroxide derivative, D-NIT2, is investigated by ab initio quantum chemical methods. The broken symmetry approach yields a coupling constant −541 K that is in good agreement with the observed value in solid state.

The research on new organic molecular magnets received a considerable amount of attention in the last few decades.[1] The exceptional stability as well as the ability to generate cooperative property made nitronyl nitroxides and imino nitroxides fascinating systems for both synthetic chemistry and theoretical sciences. The beta-phase of *p*-nitrophenyl-nitronyl nitroxide radical was the first recognized example of a pure organic magnet.[2] A large number of nitronyl nitroxide derivatives has been investigated theoretically as well as experimentally till now.[3]

Barone et al.[4] theoretically investigated bis(imino) nitroxide and concluded that most of the spin density along the O−N−C−N moiety of each monomeric unit can be attributed to the unpaired electron in the singly occupied molecular orbital. This observation indicates that a coupler that is extensively conjugated can give rise to a strong magnetic interaction between the monomeric radical centers. In fact, this has been experimentally demonstrated.[5a−d] Nevertheless, the strength of the magnetic interaction depends on the extent of mixing of the magnetically active orbitals, which decreases as the coupler size increases. Therefore, Ullman's nitroxide biradical is expected to have the largest (negative) value of the magnetic exchange coupling constant *J*. Steric effects, however, stabilize the biradical into a twisted conformation, and the measured *J* value is −448 K.[5a] This leads us to believe that the nitroxide biradical with an ethylenic coupler (D-NIT2), Figure 1, would have a larger negative *J* value. The latter was indeed observed to be −504 K in solid state.[6]

The objective of this report is to theoretically verify the proposition that a very strong intramolecular magnetic interaction can be provided by an ethylenic coupler. To our knowledge, this work represents the first ab initio investigation of the magnetic coupling between radical centers joined by an ethelynic fragment. In a future broad paper to be published, we would aim to establish that the strength of magnetic interaction decreases with the increase in size of the conjugated coupler.

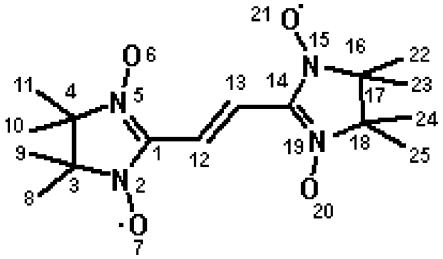

Figure 1. Diradical under investigation: D-NIT2.

A study of the interaction between two magnetic centers requires spin-polarized solutions. The unrestricted Hartree−Fock (UHF) methodology considers spin polarization, but suffers from the problem of spin contamination and an incorrect representation of the singlet state of a diradical as a single determinant.[7] The restricted (open-shell) Hartree−Fock (ROHF) theory overcomes the problem of spin contamination but does not adequately account for spin polarization, thereby requiring the study of correlation effects. Post-Hartree−Fock methods are computationally very expensive and even today cannot be efficiently performed on large systems. Therefore, we have adopted the density functional treatment (DFT), especially the B3LYP methodology, for including the correlation effects. We have also considered the broken-symmetry method within the framework of UB3LYP. This approach was proposed by Ginsberg[8] and further standardized by Noodleman[9] and explored by many other authers.[10] The exchange coupling constant for the interaction of two magnetic centers a and b, $2J_{ab}$, is defined by the Heisenberg−Dirac-van Vlek (HDVV) effective Hamiltonian $\hat{H} = -2J_{ab}\hat{S}_a\cdot\hat{S}_b$. However, a trustworthy calculation of the magnetic exchange coupling constant can be done by computing the total energy value of the maximum spin state, E_{MAX}, and that for the broken symmetry state, E_{BS}. Yamaguchi et al.[11] proposed a spin projection procedure where the dependence of $2J_{ab}$ upon the overlap is replaced by a dependence upon the spin contamination of the broken-symmetry solution, summarized by $2J_{ab} = 2(E_{BS} - E_{MAX})/(\langle S^2\rangle_{MAX} - \langle S^2\rangle_{BS})$. In the present case, the maximum spin state is triplet (T) and the broken symmetry (BS) state has the $\langle S^2\rangle$ value around 1.

The molecular geometry of the diradical has been optimized by the ROHF methodology with the 6-311G** basis set for both singlet (S) and triplet (T) states. Geometry optimization revealed an almost planar molecule that matches the reported X-ray

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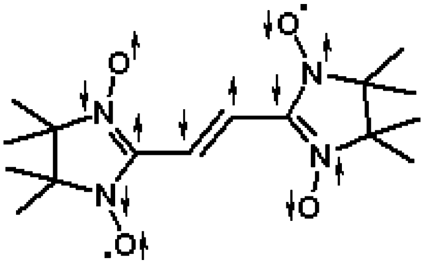

Figure 2. Scheme of spin alternation in UHF for the diradical.

TABLE 1: Results of Broken-Symmetry Density Functional Computations (UB3LYP) Performed on 6-311G Optimized Geometry**

basis set	E_{BS} in a.u. ($\langle S^2\rangle_{BS}$)	E_{MAX} in a.u. ($\langle S^2\rangle_{MAX}$)	$E_{BS} - E_T$ in K	J in K
6-31+G**	−1145.0822951 (1.1273)	−1145.0806977 (2.0620)	−505.4	−540.7
6-311+G**	−1145.3287469 (1.1286)	−1145.3271496 (2.0629)	−505.3	−540.9
6-311++G**	−1145.3289533 (1.1285)	−1145.3273567 (2.0629)	−505.1	−540.6

crystallographic geometry in ref 6. The calculated geometrical parameters are given as Supporting Information.

The broken-symmetry density functional computations (BS-DFT) are performed on the triplet optimized geometry with increasingly higher basis sets, namely, 6-31+G**, 6-311+G**, and 6-311++G**. Computed total energies for both BS and T states and the calculated *J* values are given in Table 1. We have used the Gaussian 98[12] software for our computations. Both of the states become more stable as the number of basis functions increases. The $\langle S^2\rangle$ value remained almost same for both of the states, 1.13 and 2.06, respectively. The BS state has turned out to be more stable than the T state for every basis set. The nature of the intramolecular magnetic interaction is manifestly antiferromagnetic. The energy difference remains constant at about -350 cm^{-1} (-505 K) while the basis set is increased consistently. This energy difference is apparently in exact agreement with the observed *J* value. However, there is an unequal spin contamination in the two states, and using the formula from Yamaguchi et al.,[11] we have calculated a *J* value of -541 K. This number is still in good agreement with the experimental result.

That the S state is more stable than the T state cannot be demonstrated for the present system by calculations at the UB3LYP level.[13] For instance, the UB3LYP/6-31+G** total energy for the S state turned out to be −1145.012 529 8 au, higher than those for BS and T states. It is known that the stability of the S state can be demonstrated if one carries out an explicit multiconfigurational analysis,[14] which would be prohibitively expensive for computations on the molecule under study.

In our previous work[15] on the subject, we showed that the rule of spin alternation in the UHF identifies the ground state spin without fail. The spin alternation scheme in Figure 2 is clearly in support of a singlet ground state for the diradical. Three-dimensional plots of spin isosurfaces generated at the AM1 level by the Hyperchem Professional Release 7.01 software[16] are shown in Figure 3. The spin is observed to alternate on atoms having NBOs that are orbitals not involved in the formation of σ bonds. The fact that spin alternation in the singlet state also involves the carbon atoms forming the olefinic bond is particularly significant, and manifests that there is antiferromagnetic coupling in the ground state.

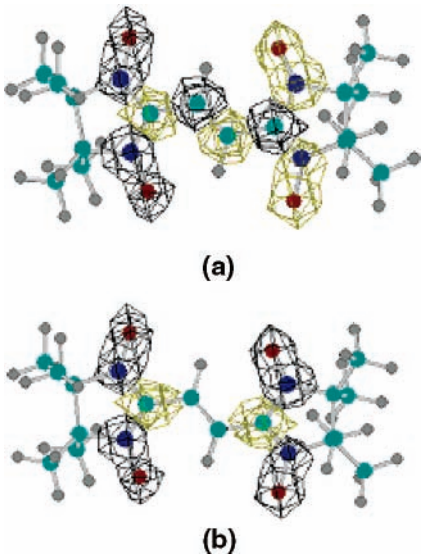

Figure 3. AM1 spin isosurfaces for the diradical in (a) singlet and (b) triplet states. The singlet state exhibits a greater spin alternation, thereby indicating an antiferromagnetic coupling between the two radical centers.

In conclusion, we have computationally derived the nature of the intramolecular magnetic interaction in a nitronyl nitroxide derivative by using large enough basis sets, and shown that the ethylenic linkage actively participates in a large, perhaps the largest, antiferromagnetic coupling between the two radical centers. The calculated intramolecular magnetic exchange coupling constant is -541 K, in good agreement with the experimental value of -504 K.

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Supporting Information Available: Optimized geometrical parameters and complete ref 12. 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) Coronado, E.; Delhaè, P.; Gatteschi, D.; Miller, J. S. *Molecular Magnetism*: *From Molecular Assemblies to the Devices*; Nato ASI Series E, Applied Sciences; Kluwer Academic Publisher: Dordrecht, The Netherlands, 1996; Vol. 321. (d) Benelli, C.; Gatteschi, D. *Chem. Rev.* **2002**, *102*, 2369.

(2) (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.

(3) (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) Wautelet, P.; Catala, L.; Bieber, A; Turek, P.; André, J.-J. *Polyhedron* **2001**, *20*, 1571. (d) Nagashima, H.; Irisawa, M.; Yoshioka, N.; Inoue, H. *Mol. Cryst. Liq. Cryst. Sci. Technol. Sect. A* **2002**, 376, 371. (e) Rajadurai, C.; Ivanova, A.; Enkelmann, V.; Baumgarten, M. *J. Org. Chem.* **2003**, *68*, 9907. (f) Wautelet, P.; Le Moigne, J.; Videva, V.; Turek, P. *J. Org. Chem.* **2003**, *68*, 8025. (g) Deumal, M.; Robb, M. A.; Novoa, J. J. *Polyhedron* **2003**, *22* (14−17), 1935.

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

(5) (a) Alies, F.; Luneau, D.; Laugier, J.; Rey, P. *J. Phys. Chem.* **1993**, *97*, 2922. (b) Caneschi, A.; Chiesi, P.; David, L.; Ferraro, F.; Gatteschi, D.; Sessoli, R. *Inorg. Chem.* **1993**, *32*, 1445. (c) Castell, O.; Caballol, R.; Subra, R.; Grand, A. *J. Phys. Chem.* **1995**, *99*, 154. (d) Matsuda, K.; Matsu, M.; Irie, M. *J. Org. Chem.* **2001**, *66*, 8799.

(6) Ziessel, R.; Stroh, C.; Heise, H.; Köhler, F. K.; Turek, P.; Claiser, N.; Souhassou, M.; Lecomte, C. *J. Am. Chem. Soc.* **2004**, *126*, 12604.

(7) (a) Ciofini, I.; Daul, C. A. *Coord. Chem. Rev.* **2003**, *238−239*, 187. (b) Calzado, C. J.; Cabrero, J.; Malrieu, J. P.; Caballol, R. *J. Chem. Phys.* **2002**, *116*, 2728. (c) Calzado, C. J.; Cabrero, J.; Malrieu, J. P.; Caballol, R. *J. Chem. Phys.* **2002**, *116*, 3985.

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

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

(10) (a) Bencini, A.; Totti, F.; Daul, C. A.; Doclo, K.; Fantucci, P.; Barone V. *Inorg. Chem.* **1997**, *36*, 5022. (b) Ruiz, E.; Alemany, P.; Alvarez, S.; Cano, J. *J. Am. Chem. Soc.* **1997**, *119*, 1297. (c) Illas, F.; Moreira, I. de P. R.; de Graaf, C.; Barone, V. *J. Phys. Chem.* **1997**, *101*, 1526. (d) Llidós, A.; Jean, Y. *Chem. Phys. Lett.* **1998**, *287*, 243. (e) Demachy, I.; Llidós, A.; Jean, Y. *Inorg. Chem.* **1999**, *38*, 5443. (f) Improta, R.; Scalmani, G.; Barone, V. *Chem. Phys. Lett.* **2001**, *336*, 349. (g) Duclusaud, H.; Borshch, S. A. *J. Am. Chem. Soc.* **2001**, *123*, 2825. (h) Petrie, S.; Stranger, R. *Inorg. Chem.* **2002**, *41*, 2341.

(11) (a) Yamaguchi, K.; Takahara, Y.; Fueno, T.; Nasu, K. *Jpn. J. Appl. Phys.* **1987**, *26*, L1362. (b) Onishi, T.; Soda, T.; Kitagawa, Y.; Takano, Y.; Daisuke, Y.; Takamizawa, S.; Yoshioka, Y. Yamaguchi, K. *Mol. Cryst. Liq. Cryst.* **2000**, *143*, 133. (c) Onishi, T.; Takano, Y.; Kitagawa, Y.; Kawakami, T.; Yoshioka, Y.; Yamaguchi, K. *Polyhedron* **2001**, *20*, 1177.

(12) Frisch, M. J.; et al. *Gaussian 98*; Gaussian, Inc.: Pittsburgh, PA, 1998. Gaussian 98 for Windows; Gaussian Inc.: Pittsburgh, 2002.

(13) Cramer, C. J.; Smith, B. A. *J. Phys. Chem.* **1996**, *100*, 9664.

(14) Nachtigall, P.; Jordan, K. D. *J. Am. Chem. Soc.* **1992**, *114*, 4743.

(15) (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.

(16) HyperChem Professional Release 7.01 for Windows; Hypercube Inc., Gainesville, 2002.