Observation of a Hysteretic Phase Transition in a Crystalline Dinitroxide Biradical That Leads to Magnetic Bistability

David A. Shultz,*[‡] Rosario M. Fico, Jr.,[‡] Paul D. Boyle,[‡] and Jeff W. Kampf[§]

Department of Chemistry
North Carolina State University
Raleigh, North Carolina 27695-8204
Department of Chemistry
University of Michigan
Ann Arbor, Michigan 48109-1055

Received June 1, 2001

Preparation and electronic structure studies of high-spin organic molecules are main research topics in modern magnetochemistry. Because of their propensities for having triplet ground-states, two types of molecules have been identified as prototypical high-spin species: *meta*-phenylene-type and trimethylenemethane-type (TMM-type) biradicals.[1−5] Bond torsions modulate exchange coupling in a variety of *meta*-phenylene-type biradicals,[6] and we have recently undertaken a magnetostructural study of the less-studied TMM-type biradicals[6−15] using a series of dinitroxides that includes **1** and **2**.[12,16] During our study of the magnetic properties of crystalline solids of this series of biradicals, we discovered that **1** undergoes a phase transition that is accompanied by hysteresis.

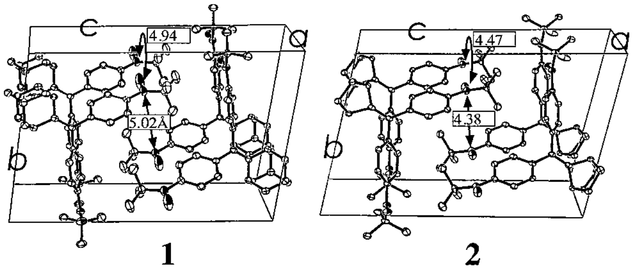
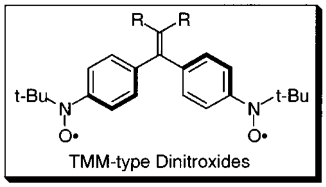


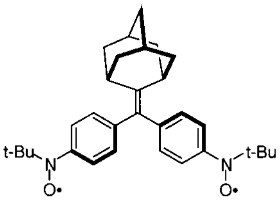
Figure 1. Packing diagrams for **1** (left) and **2** (right).

Table 1. Unit Cell and Structural Parameters for **1** and **2**

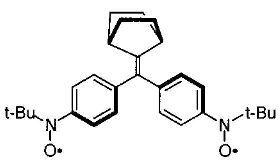
birad.	unit cell parameters	shortest intermolecular nitroxide distances	phenyl torsions[a]	nitroxide torsions[b]
1	$a = 6.2271$ Å $b = 12.170$ Å $c = 17.882$ Å $\alpha = 99.872°$ $\beta = 99.659°$ $\gamma = 95.631°$	5.02 Å (NN); 4.94 Å (NO); 6.23 Å (NN)	54.8°, 56.2° (*55.5°*)[c]	12.7°, 13.2° (*12.9°*)[c]
2	$a = 6.1933$ Å $b = 11.4950$ Å $c = 17.478$ Å $\alpha = 104.577°$ $\beta = 99.635°$ $\gamma = 94.942°$	4.38 Å (NN); 4.47 Å (NO); 5.99 Å (NN)	42.8°, 53.8° (*48.3°*)[c]	29.0°, 28.8° (*28.9°*)[c]

[a] Torsion angles between planes of phenyl rings and C═C. [b] Torsions between N−O bond vectors and phenyl ring planes. [c] Average values.





1



2

Crystal packing diagrams for **1** and **2** are very similar as shown in Figure 1: unit cell and pertinent structural parameters are given in Table 1.[17] For both biradicals, the unit cell contains two centrosymmetrically related dinitroxide molecules having phenyl ring torsions in accord with our predictions[12] as given in Table 1. The shortest NN/NO distances between molecules are given in Table 1 and Figure 1. For **1**, the shortest NO distance is 5.02 Å between two molecules related by unit translation along the *a*-axis, see Figure 1. The next shortest contact for **1** is an NN interaction between two centrosymmetrically related dinitroxide molecules in two different layers along the *a*-axis. For **2**, the corresponding intermolecular NN/NO distances between molecules are shorter, as given in Figure 1 and Table 1.

These structural elements and molecular packing allow us to predict weak intramolecular exchange coupling (χT = ca. 0.75 emu K/mol) and even weaker intermolecular coupling. The weak intramolecular coupling is consistent with moderate spin density in the phenyl rings of *tert*-butyl-phenyl nitroxides,[12,18] combined with the phenyl torsions (with respect to the C═C coupler fragment). In fact, weak intramolecular exchange was reported by Iwamura and co-workers for the dinitroxide with R = CH_3 ($J = +5.2$ cm^{-1}).[16]

Regardless of the structural similarities, the overall magnetic behaviors of **1** and **2** are quite different as shown in Figure 2.[19−27] As predicted, χT per dinitroxide is ca. 0.75 emu·K/mol at 300 K

[‡] North Carolina State University.

[§] University of Michigan.

(1) Lahti, P. M. *Magnetic Properties of Organic Materials*; Marcel Dekker: New York, 1999.

(2) Iwamura, H.; Inoue, K.; Haymizu, T. *Pure Appl. Chem.* **1996**, *68*, 243.

(3) Rajca, A. *Chem. Rev.* **1994**, *94*, 871.

(4) Dougherty, D. A. *Acc. Chem. Res.* **1991**, *24*, 88.

(5) Iwamura, H. *Pure Appl. Chem.* **1987**, *59*, 1595.

(6) Shultz, D. A. *Conformational Exchange Modulation in Trimethylenemethane (TMM)-Type Biradicals*; Lahti, P., Ed.; Marcel Dekker: New York, 1999.

(7) Shultz, D. A.; Boal, A. K.; Driscoll, D. J.; Farmer, G. T.; Hollomon, M. G.; Kitchin, J. R.; Miller, D. B.; Tew, G. N. *Mol. Cryst. Liq. Cryst.* **1997**, *305*, 303.

(8) Shultz, D. A.; Boal, A. K.; Farmer, G. T. *J. Am. Chem. Soc.* **1997**, *119*, 3846.

(9) Shultz, D. A.; Boal, A. K.; Lee, H.; Farmer, G. T. *J. Org. Chem.* **1998**, *63*, 9462.

(10) Shultz, D. A.; Bodnar, S. H.; Kumar, R. K.; Kampf, J. W. *J. Am. Chem. Soc.* **1999**, *121*, 10664.

(11) Shultz, D. A.; Lee, H.; Fico, R. M., Jr. *Tetrahedron* **1999**, *55*, 12079.

(12) Shultz, D. A.; Boal, A. K.; Lee, H.; Farmer, G. T. *J. Org. Chem.* **1999**, *64*, 4386.

(13) Shultz, D. A.; Bodnar, S. H. *Inorg. Chem.* **1999**, *38*, 591.

(14) Shultz, D. A. *Comments Inorg. Chem.* **2001**. In press.

(15) Shultz, D. A.; Bodnar, S. H.; Kumar, R. K.; Lee, H.; Kampf, J. W. *Inorg. Chem.* **2001**, *40*, 546.

(16) The dinitroxide biradical with R = CH_3 has been reported by Iwamura, et al.: Matsumoto, T.; Ishida, T.; Koga, N.; Iwamura, H. *J. Am. Chem. Soc.* **1992**, *114*, 9952.

(17) Crystallographic data for biradical **1**: red crystal; temperature (K) = 158(2); triclinic; *P*-1; $a = 6.227(2)$ Å; $b = 12.170(3)$ Å; $c = 17.882(4)$ Å; $\alpha = 99.872(5)°$; $\beta = 99.659(5)°$; $\gamma = 95.631(5)°$; $V = 1304.9(6)$ Å^3; $Z = 2$; $\mu = 0.074$ mm^{-1}; R = 0.0433; wR2 = 0.0982; GoF = 0.896 (refinement based on F^2). Crystallographic data for biradical **2**: red crystal; temperature (K) = 148; triclinic; *P*-1; $a = 6.1933(4)$ Å; $b = 11.495(1)$ Å; $c = 17.478(2)$ Å; $\alpha = 104.577(8)°$; $\beta = 99.635(8)°$; $\gamma = 94.942(8)°$; $V = 1176.5(2)$ Å^3; $Z = 2$; $\mu = 0.08$ mm^{-1}; $R_F = 0.051$; $R_w = 0.053$; GoF = 1.45 (refinement based on F_o).

(18) Aurich, H. G.; Hahn, K.; Stork, K.; Weiss, W. *Tetrahedron* **1977**, *33*, 969.

10.1021/ja011341v CCC: $20.00

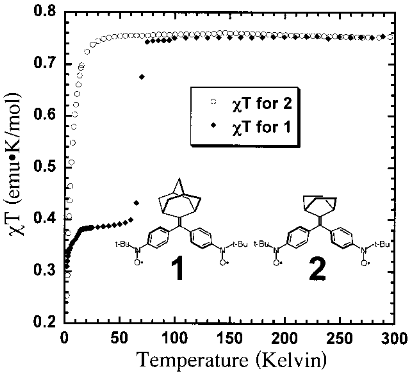


Figure 2. Plots of χT vs temperature for **1** (◆) and **2** (○).

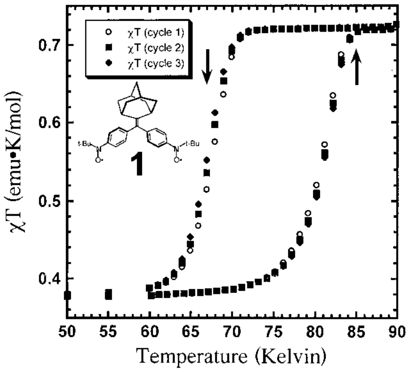
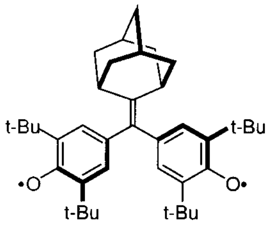


Figure 3. Hysteresis loop for **1**.

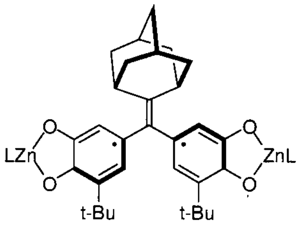
for both **1** and **2**, consistent with weakly coupled biradicals. As the temperature is lowered, χT for **2** continues to follow the trend expected for a weakly coupled biradical, but for **1** a dramatic deviation from biradical behavior is observed. Near $T = 60$ K, χT for **1** shows a precipitous decrease to 0.38 emu•K/mol. This behavior is consistent with weak intramolecular exchange coupling until $T = 60$ K, whereupon a phase transition causes a strong antiferromagnetic alignment of individual nitroxide units *between two molecules*. Moreover, this spin alignment must be characterized by an antiferromagnetic exchange parameter significantly greater than the one characterizing intramolecular exchange, $|J_{\text{intra}}|$. The most likely mechanism for this enhanced antiferromagnetic coupling is a substantial decrease in intermolecular contacts.[28] In this way, χT is consistent with *one spin* per molecule below 60 K.[29,30]

Most importantly, the χT curve for **1** shown in Figure 2 is not followed when the temperature is *increased* from 2 to 300 K, that is, hysteresis is observed.[25] An expanded view of the χT data between 50 and 90 K is shown in Figure 3. As seen in Figure 3, the temperature at which χT decreases on lowering the temperature ($T_{1/2}{\downarrow} = 67$ K) is 13 K lower than the temperature at which χT increases when increasing the temperature ($T_{1/2}{\uparrow} = 80$ K).[31] Thus, crystals of **1** exhibit a 13 K-wide hysteresis loop giving rise to magnetic bistability.

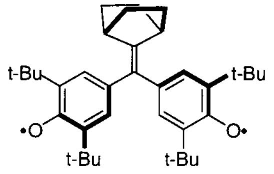
We feel that this behavior may not be an anomaly, considering related behaviors of bis(phenoxyl) **3**, and bis(semiquinone) **4**. Biradical **3** was shown to exhibit rotamer bistability with



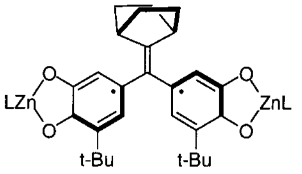
3



4



5



6

differential exchange coupling,[8] while bis(semiquinone) complex **4** shows multiple frozen solution EPR signals consistent with a rotamer distribution.[32,33] Biradicals **5** and **6** lack these behaviors.[33] Given the similarities in packing between **1** and **2** and our observations of differential bond torsions in related biradicals, it is tempting to hypothesize that aryl torsions are coupled to the phase transition in crystals of **1**. Proof of this hypothesis awaits low-temperature X-ray crystallographic analysis.

To our knowledge, this is the first report of magnetic bistability in an organic *bi*radical, and we feel that our findings further demonstrate that magnetochemistry is an excellent vehicle for studying crystal engineering.[1] Future reports will include low-temperature structural and spectroscopic studies.

Acknowledgment. This paper is dedicated to Professor Andrea Dei on the occasion of his 58th birthday. This work was funded by the National Science Foundation (CHE-9910076). D.A.S. thanks the Camille and Henry Dreyfus Foundation for a Camille Dreyfus Teacher−Scholar Award. NCSU acknowledges the National Science Foundation for the funding (Grant 9509532) to obtain the X-ray diffractometer.

Supporting Information Available: Crystallographic data and figures, EPR spectra, and Curie plots (PDF); an X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

JA011341V

---

(19) For anomalous magnetic behavior in galvinoxyl radical, see the following and refs 20−23. Mukai, K.; Nishiguchi, H.; Deguchi, Y. *J. Phys. Soc. Jpn.* **1967**, *23*, 125.

(20) Kosaki, A.; Suga, H.; Seki, S.; Mukai, K.; Deguchi, Y. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 1525.

(21) Mukai, K.; Sogabe, A. *J. Chem. Phys.* **1980**, *72*, 598.

(22) Awaga, K.; Sugano, T.; Kinoshita, M. *J. Chem. Phys.* **1986**, *85*, 2211.

(23) Chi, K.-M.; Calabrese, J. C.; Miller, J. S.; Kahn, S. I. *Mol. Crys. Liq. Crys.* **1989**, *176*, 185.

(24) For an example of a structural transition that alters the sign of the exchange coupling constant, see: Yoshioka, N.; Irisawa, M.; Aizawa, N.; Aoki, T.; Inoue, H.; Ohba, S. *Mol. Cryst. Liq. Cryst.* **1996**, *286*, 165. See also: Lanfranc de Panthou, F.; Luneau, K.; Musin, R.; Öhrström, L.; Grand, A.; Turek, P.; Rey, P. *Inorg. Chem.* **1996**, *35*, 3484.

(25) For a spectacular example of magnetic bistability in a radical crystal at room temperature, see: Fujita, W.; Awaga, K. *Science* **1999**, *286*, 261.

(26) For an example of a hysteretic phase transition in a thiazole-type radical, see: Barclay, T. M.; Cordes, A. W.; George, N. A.; Haddon, R. C.; Itkis, M. E.; Mashuta, M. S.; Oakley, R. T.; Patenaude, G. W.; Reed, R. W.; Richardson, J. F.; Zhang, H. *J. Am. Chem. Soc.* **1998**, *120*, 352.

(27) For a recent report of phase transitions in radicals, see: Sugano, T. *Polyhedron* **2001**, *20*, 1285−1289.

(28) The shortest intermolecular NO distance reported (2.36 Å) is for a di(*tert*-butylnitroxide)bipyridine molecule. The χT value for this compound is 0.085 emu•K/mol at 300 K, consistent with strong antiferromagnetic coupling: Sakane, A.; Kumada, H.; Karasawa, S.; Koga, N.; Iwamura, H. *Inorg. Chem.* **2000**, *39*, 2891.

(29) For examples of biradical dimerization in solution, see the following and ref 30: Dormann, E.; Nowak, M. J.; Williams, K. A.; Angus, J., R. O.; Wudl, F. *J. Am. Chem. Soc.* **1987**, *109*, 2594.

(30) Barclay, T. M.; Cordes, A. W.; de Laat, R. H.; Goddard, J. D.; Haddon, R. C.; Jeter, D. Y.; Mawhinney, R. C.; Oakley, R. T.; Palstra, T. T. M.; Patenaude, G. W.; Reed, R. W.; Westwood, N. P. C. *J. Am. Chem. Soc.* **1997**, *119*, 2633.

(31) $T_{1/2}$ is the temperature at which 50% phase conversion occurs, and ↓ and ↑ refer to cooling and heating cycles, respectively. Plots of χ^{-1} vs T above and below the transition give Curie constants of 0.70 emu•K/mol and 0.38 emu•K/mol, respectively, consistent with two unpaired spins per molecule at high temperature and one unpaired spin per molecule at low temperature. See Supporting Information for plots.

(32) In the solid state, **4** does not exhibit a phase transition due to the very large, ancillary ligands, L = (hydro-tris(3-cumenyl-5-methylpyrazolyl)borate.

(33) Shultz, et al., unpublished results. For examples of EPR spectra, see Supporting Information.