

Ferromagnetic Interactions in a Crystalline Nitroxide Biradical: 1,3,5,7-Tetramethyl-2,6-diazaadamantane *N,N'*-Dioxy

R. Chiarelli,^a A. Rassat*^a and P. Rey^b

^a Laboratoire de Chimie, Ecole Normale Supérieure, 24 rue Lhomond, 75231 Paris Cedex 05, France

^b Laboratoire de Chimie de Coordination, Centre d'Etudes Nucléaires, 38041 Grenoble Cedex, France

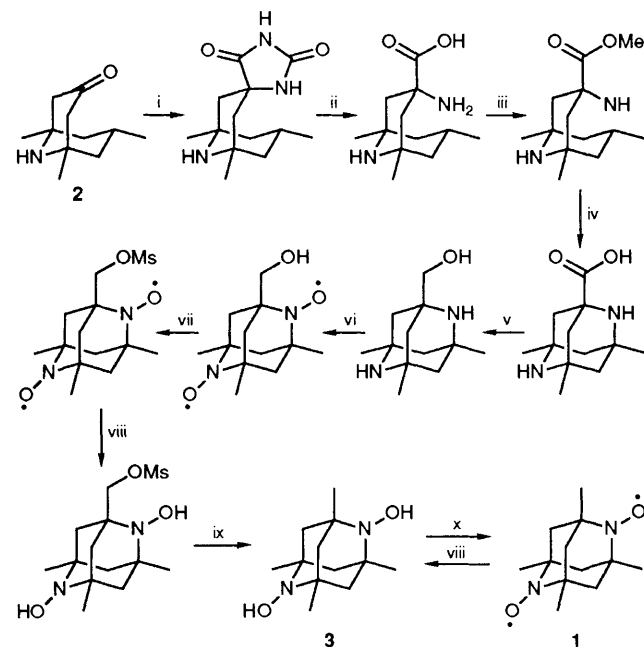
The crystalline nitroxide biradical, 1,2,5,7-tetramethyl-2,6-diazaadamantane *N,N'*-dioxy, shows ferromagnetic interactions in the solid: a positive Weiss-constant $\theta = 10$ K, a large χT increase at low temperature ($T < 20$ K) and a magnetisation curve consistent with a total spin $S = 6$.

The temperature (T) dependence of the static magnetic susceptibility (χ) of pure organic free radicals in the solid state¹ generally follows the Curie–Weiss law² with a negative Weiss constant (θ) indicating independent spins or predominant antiferromagnetic interactions in the solid. Positive Weiss constants are not common.^{1,3} They indicate ferromagnetic interactions, some of which have been characterized.⁴ We report here the magnetic properties of a nitroxide biradical showing ferromagnetic interactions in the solid.⁵

The study of bis-nitroxides derived from 2,6-diazaadamantane⁶ seemed promising for the following reasons: (i) their rigid backbone ensures orthogonal 2p nitrogen orbitals, a situation which may generate intramolecular ferromagnetic interactions,^{6,7} (ii) the packing of globular molecules with two opposite NO groups may induce structures with short intra- and inter-molecular distances between magnetic centres; such structure may lead to specific magnetic behaviour.

Biradical **1** was prepared from 1,5,7-trimethylnorpseudo-pelletierine **2**,^{6,8} in 13% yield, according to Scheme 1.

Magnetic data have been collected in the $2 \leq T \leq 300$ K temperature range at 0.5 T for a 10 mg sample of polycrystalline biradical **1**[†] using a Quantum Design MPMS



Scheme 1 Reagents: (yields): i, KCN, $(\text{NH}_4)_2\text{CO}_3$ (92%); ii, Ba(OH)₂ (96%); iii, MeOH–HCl (76%); iv, Br₂–NaOH, SO₄H₂ (76%); v, LiAlH₄–THF, (81%); vi, *m*-chloroperbenzoic acid (67%); vii, MsCl–pyridine (70%); viii, hydrazobenzene (100%); ix, LiAlH₄–THF (97%); x, *m*-chloroperbenzoic acid (68%)

[†] **1** was purified by TLC on alumina gel (eluant: diethyl ether), and recrystallised from diethyl ether prior to magnetic measurements. It has a sharp melting point (199 °C) and a correct microanalysis. No impurities could be detected by MS, or IR of **1**, or NMR of **3** (obtained by reduction). Traces of monoradical, detected on the frozen solution ESR spectra, were estimated by double integration as much less than 1%.

SQUID susceptometer. They are shown in Fig. 1 in the form χT and χ^{-1} vs. T .

From the high-temperature portion (>150 K) of the χ^{-1} vs. T curve, a Weiss constant $\theta = +10$ K was extracted. Except for the high-temperature phase of galvinoxyl,⁹ this value is, to our knowledge, the largest so far reported for an organic compound. The high-temperature value of χT (0.774 emu K mol⁻¹), is close to that expected (0.75) for two non-interacting $S = 1/2$ spins, with $g = 2$. On decreasing the temperature, χT increases continuously below 100 K, reaching (with a negative slope) 3.19 emu K mol⁻¹ (5.05 μ_B) at 2 K. Such a large low-temperature value is the sign of ferromagnetic interactions involving several spins. Independent $S = 1$ spins, resulting from intramolecular ferromagnetic coupling only, would have led to a lower and finite value of $\chi T = 1$ emu K mol⁻¹. A linear-chain model¹⁰ gives an exchange interaction $2J/k = 30.4$ K (consistent with $\theta = 10$ K).

Further support of the presence of intermolecular ferromagnetic interactions comes from the study of the magnetisation M as a function of the magnetic field H , obtained for **1** at 3 K (Fig. 2). At 50 kG (5 T), the experimental magnetisation ($M' = 9697$ emu mol⁻¹) is only 87% of the expected theoretical value for two-spin 1/2 per molecule ($M_0 = 11160$ emu mol⁻¹). Brillouin functions were calculated for different

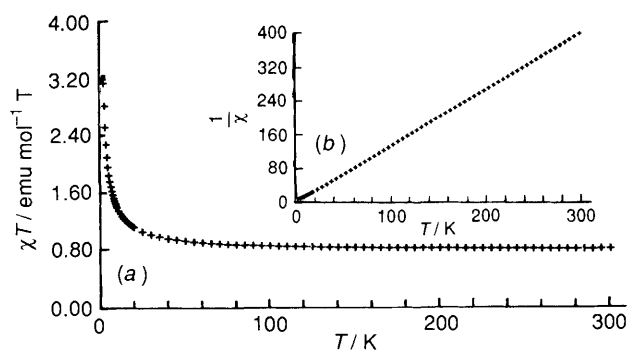


Fig. 1 Temperature dependence of the χT product (a) and of $1/\chi$ (b)

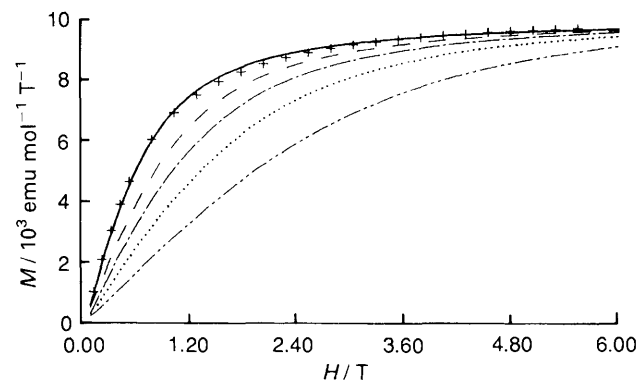


Fig. 2 Magnetisation curve at 3 K: $M = N g \mu_B S B(\eta)$, $B(\eta) =$ Brillouin function, $\eta = g \mu_B H / k T$ (see ref. 2). Experimental: + + +, theoretical: $S = 6$ —, $S = 4$ - - -, $S = 3$ - · - ·, $S = 2$ · · · ·, $S = 1$ - · - ·.

spin values assuming saturation at M' . They are reported on Fig. 2. The experimental field dependence of the magnetisation falls close to the theoretical $S = 6$ curve. The origin of the 13% discrepancy is to be determined. Impurities are certainly less than 1% and cannot account for this difference.

Received, 17th February 1992; Com. 2/008311

References

- 1 (a) A. L. Buchachenko, *Mol. Cryst. Liq. Cryst.*, 1989, **176**, 307; (b) A. Rassat, *Pure Appl. Chem.*, 1990, **62**, 223; (c) H. Iwamura, *Adv. Phys. Org. Chem.*, 1990, **26**, 179.
 - 2 R. L. Carlin, *Magnetochemistry*, Springer Verlag, Berlin, 1986.
 - 3 The following references may be added to those of ref. 1(b), (a) M. Ballester, J. Riera, C. Onrubia, *Tetrahedron Lett.*, 1976, **12**, 945, ($\theta = 0.4$ K); (b) P. R. Allemand, G. Srdanov and F. Wudl, *J. Am. Chem. Soc.*, 1990, **112**, 9391, ($\theta = 1.6$ K).
 - 4 (a) Ref. 1(c), p. 227; (b) M. Tamura, Y. Nakazawa, D. Shiomi, K. Nozawa, Y. Hosokoshi, M. Ishikawa and M. Kinoshita, *Chem. Phys. Lett.*, 1991, **186**, 401.
 - 5 A preliminary account of part of this work has been presented at the NATO Advanced Research Workshop on Magnetic Molecular Materials, Lucca, Oct. 28–Nov. 2, 1990; R. Chiarelli and A. Rassat, in *Magnetic Molecular Materials*, ed. D. Gatteschi, O. Kahn, J. S. Miller and F. Palacio, Kluwer, Dordrecht, 1991, p. 191–202.
 - 6 R. M. Dupeyre, A. Rassat and J. Ronzaud, *J. Am. Chem. Soc.*, 1974, **96**, 6559. Owing to the poor precision of the intensity measurement by ESR, the reported ferromagnetic intramolecular exchange interaction $2J/k = 170$ K was probably overestimated.
 - 7 O. Kahn, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 834.
 - 8 R. M. Dupeyre and A. Rassat, *Bull. Soc. Chim. Fr.*, 1978, 612.
 - 9 (a) K. Mukai, *Bull. Chem. Soc. Jpn.*, 1969, **42**, 40; (b) K. Awaga, T. Sugano and M. Kinoshita, *J. Chem. Phys.*, 1986, **85**, 2211.
 - 10 (a) W. Hatfield, W. E. Estes, W. E. Marsh, M. W. Pickens, L. W. ter Haar and R. R. Weller, in *Extended Linear Chain Compounds*, ed. J. S. Miller, Plenum Press, New York, London, 1983, vol. 3, p. 45; (b) J. C. Bonner and M. E. Fisher, *Phys. Rev. A*, 1964, **135**, 640.
-